## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Paper/Presentation/Author</th>
<th>Page #</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PLENARY SESSION</strong></td>
<td></td>
</tr>
</tbody>
</table>
| Speciation Analysis – A Necessary Shift of Paradigm in Trace Element Analysis? (presentation)  
*Michael Sperling*       | 9      |
| Top Ten Reasons We Have All Stayed in the Environmental Laboratory Business (presentation)  
*J.D. Ken Olson*        | 37     |
| Analytical Chemistry Innovations and Improvements in Environmental Quality in New Jersey: Perfect Together (presentation)  
*Stuart Nagourney*      | 44     |
| **SESSION 1: METHOD DETECTION LIMITS** |        |
| Method Detection Limits: A Data User’s Perspective  
*Rock J. Vitale, et al.* | 52     |
| Detection and Quantitation Limits – Where Do We Go From Here?  
*R. Burrows*          | 53     |
| Detection Limits – Federal Advisory Committee  
*R. Reding*          | 54     |
| New Jersey Quantitation Limits: Putting MDLs to Practical Use  
*Stuart J. Nagourney, et al.* | 55     |
| A Statistical Determination of Minimum Reporting Levels  
*Stephen D. Winslow, et al.* | 57     |
| **SESSION 2: LABORATORY ACCREDITATION** |        |
| How Accreditation Supports a Laboratory in Ensuring Data Integrity  
*Randall Querry*       | 59     |
| A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities  
*Dawn D. Thomas*      | 78     |
| Accreditation of Air Emission Testing Bodies  
*Scott Evans*         | 83     |
| LIMS and Regulatory Compliance  
*Christine Paszko and Elizabeth Turner* | 84     |
| Qualification Testing by Japan Environmental Measurement & Chemical Analysis Association (JEMCA) – Preparation of Samples, Data Analysis & Evaluation, and Feedback of Information  
*Hideo Tabata, et al.* | 93     |
| Significance of Changes in 2005 NELAC/USEPA Proficiency Testing Requirements  
*Mark J. Carter, et al.* | 94     |
| Newly Developed Biota- and Biological-related Standard Reference Materials for the Determination of Organic Contaminants  
*Dianne L. Poster, et al.* | 95     |
| **SESSION 3: INORGANIC METHODS: ELEMENTAL ANALYSIS BY ICP TECHNIQUES** |        |
| Current Status of the RCRA Inorganic Methods Program (abstract/paper)  
*Shen-Yi Yang*       | 98     |
| Current Status: RCRA Inorganic Methods Development Program (presentation)  
*Shen-Yi-Yang*       | 99     |
| Technological Advances and Optimisation in ICP-OES to Meet the Demands of Modern, Routine Elemental Laboratories (abstract/paper)  
*Paul Neal*          | 114    |
<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developing ICP-OES to Meet the Demands of Routine Laboratories</td>
<td>115</td>
</tr>
<tr>
<td>(presentation)</td>
<td></td>
</tr>
<tr>
<td>Paul Neal</td>
<td></td>
</tr>
<tr>
<td>Valuation and Comparison of ICP and ICP-MS for Environmental</td>
<td>127</td>
</tr>
<tr>
<td>Applications (abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Albert F. Vicinie and William Reinheimer</td>
<td></td>
</tr>
<tr>
<td>Transitioning to ICP/MS in an Environmental Laboratory</td>
<td>128</td>
</tr>
<tr>
<td>(presentation)</td>
<td></td>
</tr>
<tr>
<td>Albert F. Vicinie and William Reinheimer</td>
<td></td>
</tr>
<tr>
<td>Do Current EPA Methods Compromise the Productivity of Modern</td>
<td>138</td>
</tr>
<tr>
<td>Analytical Instrumentation? – Focus on ICP-MS (abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Phil Shaw and Bill Spence</td>
<td></td>
</tr>
<tr>
<td>Do Current EPA Methods Compromise the Productivity of Modern</td>
<td>139</td>
</tr>
<tr>
<td>Analytical Instrumentation? (presentation)</td>
<td></td>
</tr>
<tr>
<td>Phil Shaw</td>
<td></td>
</tr>
<tr>
<td>Comparison of Illinois EPA’s Low-Level Mercury Sample Collection</td>
<td>149</td>
</tr>
<tr>
<td>Procedures with USEPA Method 1669 (abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Michael S. Henebry</td>
<td></td>
</tr>
<tr>
<td>Comparison of Illinois EPA’s Low-Level Mercury Sample Collection</td>
<td>150</td>
</tr>
<tr>
<td>Procedures with USEPA Method 1669 (presentation)</td>
<td></td>
</tr>
<tr>
<td>Michael S. Henebry</td>
<td></td>
</tr>
<tr>
<td>SESSION 4 – BLANK</td>
<td></td>
</tr>
<tr>
<td>SESSION 5: ADVANCES IN ELECTRONIC DELIVERABLES AND INFORMATION</td>
<td></td>
</tr>
<tr>
<td>MANAGEMENT</td>
<td></td>
</tr>
<tr>
<td>SEDD – An Overview and Status Report (abstract/paper)</td>
<td>169</td>
</tr>
<tr>
<td>Anand R. Mudambi</td>
<td></td>
</tr>
<tr>
<td>Staged Electronic Data Deliverable (SEDD) – An Overview and Status</td>
<td>170</td>
</tr>
<tr>
<td>Report (presentation)</td>
<td></td>
</tr>
<tr>
<td>Anand R. Mudambi</td>
<td></td>
</tr>
<tr>
<td>The Technical Components of SEDD Stage 3 Files (abstract/paper)</td>
<td>180</td>
</tr>
<tr>
<td>Joseph Solsky</td>
<td></td>
</tr>
<tr>
<td>A Technical Overview of Staged Electronic Data Deliverable (SEDD)</td>
<td>181</td>
</tr>
<tr>
<td>(presentation)</td>
<td></td>
</tr>
<tr>
<td>Joseph Solsky</td>
<td></td>
</tr>
<tr>
<td>Automated Generation and Validation of Staged Electronic Data</td>
<td>190</td>
</tr>
<tr>
<td>Deliverable in a Commercial Laboratory (abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Jakub Rehacek, Ph.D.</td>
<td></td>
</tr>
<tr>
<td>Brewing SEDD In-House (presentation)</td>
<td>192</td>
</tr>
<tr>
<td>Jakub Rehacek, Ph.D.</td>
<td></td>
</tr>
<tr>
<td>Creating SEDD Stage 3 Deliverables: A LIMS Vendor’s Perspective</td>
<td>203</td>
</tr>
<tr>
<td>(abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Buddy Wilson</td>
<td></td>
</tr>
<tr>
<td>Creating SEDD Stage 3 Deliverables: A LIMS Vendor’s Perspective</td>
<td>204</td>
</tr>
<tr>
<td>(presentation)</td>
<td></td>
</tr>
<tr>
<td>Buddy Wilson</td>
<td></td>
</tr>
<tr>
<td>Automating the EDD Designer, Checker, and Generator Process (abstract/paper)</td>
<td>208</td>
</tr>
<tr>
<td>Paul Banfer</td>
<td></td>
</tr>
<tr>
<td>Automating the EDD Designer, Checker, and Generator Process (presentation)</td>
<td>209</td>
</tr>
<tr>
<td>Paul Banfer</td>
<td></td>
</tr>
<tr>
<td>Automated Review of SEDD Stage 3 Deliverables (abstract/paper)</td>
<td>218</td>
</tr>
<tr>
<td>Anand R. Mudambi and Alfred Mayo</td>
<td></td>
</tr>
<tr>
<td>Automated Review of SEDD Stage 3 Deliverables (presentation)</td>
<td>219</td>
</tr>
<tr>
<td>Anand R. Mudambi</td>
<td></td>
</tr>
<tr>
<td>Environmental Data from the Field to the Map, and the Impact of EDD</td>
<td>227</td>
</tr>
<tr>
<td>Formats Like SEDD (abstract/paper)</td>
<td></td>
</tr>
<tr>
<td>Dr. David W. Rich</td>
<td></td>
</tr>
<tr>
<td>Title</td>
<td>Author(s)</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Environmental Data from the Field to the Map, and the Impact of EDD Formats Like SEDD</td>
<td>Dr. David W. Rich</td>
</tr>
<tr>
<td>Remote LIMS Access from Sample Login to Result Retrieval</td>
<td>Rebekah Johnson and Christine Paszko, Ph.D.</td>
</tr>
<tr>
<td>Application of Electronic Data Verification with Data Validation to Site Characterization Projects to Maximize Efforts</td>
<td>Stephen T. Zeiner, et al</td>
</tr>
<tr>
<td>Application of Electronic Data Verification with Data Validation to Site Characterization Projects to Maximize Efforts</td>
<td>Stephen T. Zeiner, et al</td>
</tr>
<tr>
<td>Modernization of EPA's Superfund Contract Laboratory Program (CLP) through Method Customization, Electronic Data Delivery, and Client Support</td>
<td>Bruce Means</td>
</tr>
<tr>
<td>Modernization of the Superfund Contract Laboratory Program</td>
<td>Bruce Means</td>
</tr>
<tr>
<td>New Jersey Beach Monitoring Solution</td>
<td>Robert Peeples</td>
</tr>
<tr>
<td>New Jersey Beach Monitoring Solution: Lessons Learned in the NEIEN Challenge Process</td>
<td>Robert Peeples</td>
</tr>
<tr>
<td>Crossing the Digital Divide: Looking to the Future with Records Management Quality Assurance</td>
<td>Mary Thomas Sullivan</td>
</tr>
<tr>
<td>SESSION 6: ANALYSIS FOR EMERGING CHEMICALS</td>
<td></td>
</tr>
<tr>
<td>Use of Non-Standard Mass Spectrometric Techniques to Solve Analytical Problems for Emerging Contaminants</td>
<td>Richard Burrows</td>
</tr>
<tr>
<td>Use of Non-Standard Mass Spectrometric Techniques to Solve Analytical Problems for Emerging Contaminants</td>
<td>Richard Burrows</td>
</tr>
<tr>
<td>GCxGC-ECD of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides in Drinking Water</td>
<td>Jack Cochran and Frank Dorman</td>
</tr>
<tr>
<td>GCxGC-ECD of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides in Drinking Water</td>
<td>Jack Cochran and Frank Dorman</td>
</tr>
<tr>
<td>Analysis of PCB Congeners by GC-MS-MS As Compared to Aroclor Analysis</td>
<td>Pamela Hamlett and David Klein</td>
</tr>
<tr>
<td>Accelerated Solvent Extraction (ASE) as a Sample Preparation Technique for Polybrominated Diphenylethers (PDBEs) in Environmental Samples</td>
<td>Sheldon Henderson, et al</td>
</tr>
<tr>
<td>Accelerated Solvent Extraction (ASE) as a Sample Preparation Technique for Polybrominated Diphenylethers (PDBEs) in Environmental Samples</td>
<td>Sheldon Henderson, et al</td>
</tr>
<tr>
<td>RapidMS Chromatography and Tandem Mass Spectrometry for Trace Determination of Brominated Flame Retardants</td>
<td>Robert Brittian</td>
</tr>
<tr>
<td>RapidMS Chromatography and Tandem Mass Spectrometry for Trace Determination of Brominated Fire Retardants</td>
<td>Robert Brittian</td>
</tr>
</tbody>
</table>
# NEMC 2005 Proceedings

## TABLE OF CONTENTS

### SESSION 7: ANALYSIS IN PERCHLORATE ANALYSIS

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DoD Handbook for Perchlorate Sampling and Testing (abstract/paper)</td>
<td>Fred McLean and William Ingersoll</td>
<td>382</td>
</tr>
<tr>
<td>Analysis of Perchlorate by IC/MS/MS and Development of Method 6860 (abstract/paper)</td>
<td>Richard Burrows</td>
<td>384</td>
</tr>
<tr>
<td>A Discussion of Separation and MS Detection for the Determination of Perchlorate in Real World Samples (abstract/paper)</td>
<td>R. Slingsby, et al</td>
<td>385</td>
</tr>
<tr>
<td>Perchlorate in Water – A Comparison of Methods 314.0 and 332.0 (abstract/paper)</td>
<td>Scott McLean, et al</td>
<td>386</td>
</tr>
<tr>
<td>Trace Level Determination of Perchlorate in Soils and Fertilizers by Tandem Suppressed Conductivity and Mass Spectroscopy (abstract/paper)</td>
<td>Jay Gandhi</td>
<td>387</td>
</tr>
<tr>
<td>DoD Handbook for Perchlorate Sampling and Testing (abstract/paper)</td>
<td>Fred McLean and William Ingersoll</td>
<td>388</td>
</tr>
</tbody>
</table>

### SESSION 8: INNOVATIVE TECHNIQUES FOR ENVIRONMENTAL MEASUREMENTS AND MONITORING

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case Studies of Innovative Field Technologies Using a Portable GC/MS (abstract/paper)</td>
<td>Carol Thielen</td>
<td>390</td>
</tr>
<tr>
<td>Automated Thermal Desorption Methodology Improvements for Environmental Analyses (abstract/paper)</td>
<td>Andrew Tipler and Zoe Grosser</td>
<td>391</td>
</tr>
<tr>
<td>Current Passive Diffusion Sampling Devices and Their Performance with Selected Target Analytes (abstract/paper)</td>
<td>Dee O’Neill</td>
<td>394</td>
</tr>
<tr>
<td>EPA Site Program Demonstration Project Results: TEQ Screening in the Field Using Integrated Parallel Immunoassays for Dioxin/Furan TEQ and Dioxin-Like PCB TEQ (abstract/paper)</td>
<td>Robert O. Harrison</td>
<td>395</td>
</tr>
</tbody>
</table>

### SESSION 9: HOMELAND SECURITY – TRIAGE RESPONSE

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A UPLC/MS Multi-Analyte Screening Method for Deleterious Organics in Water (abstract/paper)</td>
<td>Jim Krol and Lawrence Zintek</td>
<td>397</td>
</tr>
</tbody>
</table>
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>The State Laboratory: Emergency Response and Data Integrity (abstract/paper)</td>
<td>402</td>
</tr>
<tr>
<td>Mary Abrams, et al</td>
<td></td>
</tr>
<tr>
<td>Unknown Sample Triage Using a Class III Glove Box (abstract/paper)</td>
<td>404</td>
</tr>
<tr>
<td>Phillip Adams</td>
<td></td>
</tr>
<tr>
<td>Building Environmental Laboratory Capability in Support of Emergency Response (abstract/paper)</td>
<td>405</td>
</tr>
<tr>
<td>Dana Tulis and Allan Antley</td>
<td></td>
</tr>
<tr>
<td>Low-Cost, High-Volume Air Monitoring for Homeland Security (abstract/paper)</td>
<td>406</td>
</tr>
<tr>
<td>Adam L. Hamilton</td>
<td></td>
</tr>
<tr>
<td>Validation of Sampling and Analysis Methods for Homeland Security Measurements (abstract/paper)</td>
<td>407</td>
</tr>
<tr>
<td>Larry D. Ogle, et al</td>
<td></td>
</tr>
<tr>
<td>The TIGER Biosensor: Applications in Biodefense, Epidemiology and Infectious Disease Surveillance (abstract/paper)</td>
<td>408</td>
</tr>
<tr>
<td>Steven A. Hofstadler, et al</td>
<td></td>
</tr>
<tr>
<td>Quality Control Challenges for Extremely Toxic Compounds (abstract/paper)</td>
<td>410</td>
</tr>
<tr>
<td>Larry D. Ogle, et al</td>
<td></td>
</tr>
</tbody>
</table>

### SESSION 10: MANAGING DECISION UNCERTAINTY

<table>
<thead>
<tr>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>How to Fully Integrate Available Information Resources: Maximizing Planning for Environmental Monitoring and the Real Benefits to the Planner (abstract/paper)</td>
<td>412</td>
</tr>
<tr>
<td>Ruby N. White and Jeffrey C. Worthington</td>
<td></td>
</tr>
<tr>
<td>Automation of Analytical Results for the Triad Approach (abstract/paper)</td>
<td>413</td>
</tr>
<tr>
<td>Paul Banfer</td>
<td></td>
</tr>
<tr>
<td>The South Dakota Triad Challenge (abstract/paper)</td>
<td>414</td>
</tr>
<tr>
<td>Dennis Rounds</td>
<td></td>
</tr>
<tr>
<td>Managing Decision Uncertainty on Navy Cleanup Projects (abstract/paper)</td>
<td>415</td>
</tr>
<tr>
<td>Kimberly Gates</td>
<td></td>
</tr>
<tr>
<td>Quality Assurance and Quality Control for Triad Projects (presentation)</td>
<td>416</td>
</tr>
<tr>
<td>Todd A. Kimmell and Deana M. Crumbling</td>
<td></td>
</tr>
<tr>
<td>Addressing the Misconceptions About QA/QC in Triad Projects (abstract/paper)</td>
<td>427</td>
</tr>
<tr>
<td>William M. Davis</td>
<td></td>
</tr>
<tr>
<td>Laboratory Certification for Field Analytical Methods and Triad in New Jersey: Perfect Together (abstract/paper)</td>
<td>429</td>
</tr>
<tr>
<td>Stuart Nagourney and Brian Sogorka</td>
<td></td>
</tr>
</tbody>
</table>

### SESSION 11: INORGANIC METHODS – ADVANCES IN ELEMENTAL SPECIATION

<table>
<thead>
<tr>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium(III) Oxidation in Chromite Ore Processing Residue-Enriched Soils: Theoretical Predictions and Experimental Observations (abstract/paper)</td>
<td>431</td>
</tr>
<tr>
<td>Bruce R. James and Rock J. Vitale</td>
<td></td>
</tr>
<tr>
<td>Application of Chromium (VI) Speciation Results for Remedial Alternatives Evaluation (abstract/paper)</td>
<td>432</td>
</tr>
<tr>
<td>John C. Petura</td>
<td></td>
</tr>
<tr>
<td>An Evaluation of Analyte Isolation and Analytical Finish Methods for Cr(VI) in Solids (abstract/paper)</td>
<td>434</td>
</tr>
<tr>
<td>Rock J. Vitale and Kyle R. Clay</td>
<td></td>
</tr>
<tr>
<td>When It Comes to Speciation, “To Label or Not To Label? That Is the Question” (abstract/paper)</td>
<td>436</td>
</tr>
<tr>
<td>Brian Buckley, et al</td>
<td></td>
</tr>
<tr>
<td>Bromate/Bromide Speciation by HPLC-ICP-MS (abstract/paper)</td>
<td>437</td>
</tr>
<tr>
<td>Pamela A. Perrone, et al</td>
<td></td>
</tr>
<tr>
<td>Dynamic Metal Speciated Analysis such as Cr(VI) and Alkylmercury Examined and Applied (abstract/paper)</td>
<td>438</td>
</tr>
<tr>
<td>H. M. ‘Skip’ Kingston, et al</td>
<td></td>
</tr>
</tbody>
</table>
### SESSION 12: MANAGING UNCERTAINTY

<table>
<thead>
<tr>
<th>Title</th>
<th>Author</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Managing Decision Uncertainty Resulting from Hydrogeologic Heterogeneity in Groundwater Contamination Investigations (abstract/paper)</td>
<td>Seth Pitkin</td>
<td>442</td>
</tr>
<tr>
<td>Chemical Measurements Traceability, Validation and Uncertainty (abstract/paper)</td>
<td>Martene Moore</td>
<td>444</td>
</tr>
<tr>
<td>Intrinsic Reliability — A Metric for Describing Confidence in Measurements (abstract/paper)</td>
<td>Molly Isbell and David L. Lewis</td>
<td>454</td>
</tr>
<tr>
<td>Vanishing Zero Defects (abstract/paper)</td>
<td>Dr. John Long</td>
<td>455</td>
</tr>
</tbody>
</table>

### SESSION 13: ADVANCES IN PREPARATION AND ANALYSIS OF ORGANIC COMPOUNDS

<table>
<thead>
<tr>
<th>Title</th>
<th>Author</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pursuit of Practical Particle Size Reduction and Sub-sampling for the Environmental Testing Laboratory (presentation)</td>
<td>Mark L. Bruce</td>
<td>457</td>
</tr>
<tr>
<td>An Innovative Approach to Automatic Solvent Drying and Concentration of Environmental Extracts (abstract/paper)</td>
<td>Robert Johnson</td>
<td>473</td>
</tr>
<tr>
<td>Managing Matrix Interferences in Pesticide Analysis with GC-TOFMS and GCxGC-TOFMS (abstract/paper)</td>
<td>Jack Cochran and Frank Dorman</td>
<td>477</td>
</tr>
</tbody>
</table>
Plenary Session
Speciation Analysis – A Necessary Shift of Paradigm in Trace Element Analysis?

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


Chemical analysis: An important sector of economy

A substantial amount of money is invested into analytical measurements for:

- process control and optimization,
- characterization of raw materials, intermediates and products,
- controlling the work-place and emissions to the environment and last but not least for
- monitoring the environment and the health status of its inhabitants
Chemical analysis: An important sector of economy

Chemical analysis is meant to provide information assuring:

- product quality and safety for the consumer
- process efficiency with respect to raw materials, energy and waste production
- safety for the production plant and for the workplace environment
- compliance with rules and legislation
- absence of risks for the environment and its inhabitants

Chemical analysis: Do we get the right answers?

The most often applied inorganic chemical analysis determining elements and trace elements cannot provide the necessary information, since the chemical and physical characteristics, biological activity or toxicity, mobility or bio-availability does not depend on the presence and concentrations of chemical elements but to chemical species.
Toxicity and speciation

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

Chromium: Cr(III) is considered to be essential while Cr(VI) is carcinogen

Arsenic: Inorganic As(III) compounds are carcinogen while Arsenobetaine is essential non-toxic

Tin: Inorganic tin compounds are nutrients for animals but tributyltin (TBT) is an endocrine disruptor
Chemical analysis: an information science

- Data on the presence of elements and their total concentration do not have the required information value and are therefore costly and seldom fit-for-purpose.
- The real questions to be answered are: In what chemical form do the elements occur and what is their distribution?
- **Speciation Analysis** identifying and/or measuring the quantities of one or more individual chemical species in a sample gives the answer!

---

IUPAC Definition: Speciation

- A *chemical species* is a specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.
- The *speciation* of an element is defined as the distribution of an element amongst defined chemical species of that element in a system.
- **Speciation analysis** is the activity within the framework of analytical chemistry of identifying and/or measuring the quantities of one or more individual chemical species in a sample.
IUPAC Definition: Fractionation

- In case it is not possible to determine the concentration of the different individual chemical species that sum up the total concentration of an element in a given matrix, it may be useful to identify various classes of species of an element and to determine the sum of its concentration in each class.
- Such Fractionation is defined as the process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties.

The concepts of yesterday

- Trace element determination
- Toxicity of elements
- Essentiality of elements
- Metals as environmental pollutants and workplace hazards
- Trace metals in human health and nutrition
- "Heavy metals" in the environment

These concepts do not have a sound scientific background, since discussed effects are related to the present species and not to the determined element concentrations!
The concepts for the 21st century

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

These concepts are based on a sound scientific background, since discussed effects are related to the present species!
Speciation analysis: Do we have the necessary tools?

Solid state analysis: There are some techniques available offering species related information in solid samples, such as

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

Speciation analysis: Do we have the necessary tools?

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

- Electroanalytical techniques
  - Potentiometry withIon-specific Electrodes (ISE)
  - Voltammetry
- Magnetic resonance spectroscopy
  - Nuclear magnetic resonance spectrometry (NMR)
  - Electron spin resonance spectrometry (ESR)
- Nuclear spectroscopy
  - Mössbauer spectroscopy
Speciation analysis: Hyphenated techniques

1985-1995: "The joy of coupling"

Speciation analysis: Do we have the necessary tools?

Due to developments during the last 10 years, today a rich collection of hyphenated techniques is available for speciation analysis that combine high sensitivity, element selectivity and species separation:

- using liquid chromatography
  - LC-ICP-MS (with LC-HPLC, RPLC, IEC, SEC, FPLC)
  - LC-ESI-MS
- using gas chromatography
  - GC-ICP-MS
  - GC-MIP-AES
  - GC-AFS
- using capillary electrophoresis
  - CE-ICP-MS
For the identification of species the following methods are available:

- Comparison of retention times between the unknown species and a standard
  - Confidence can be enhanced by using different separation methods
  - Availability of pure compounds limits the possibility of identification
- Application of multi-dimensional separation techniques (e.g. SEC followed by IEC and RP-HPLC)
  - Species must be sufficiently stable to survive time consuming analysis under different conditions and changing media
Multi-dimensional chromatography

**Separation of metallothioneines**

**SEC**

**IEC**

**RPIPC**

Bonding metal-biomolecule (e.g. Cd-Metallothionein)

**Separation of the MT-2 isoforms**

---

**evisa.**

For the identification of species the following methods are available:

- Comparison of retention times between the unknown species and a standard
  - Confidence can be enhanced by using different separation methods
  - Availability of pure compounds limits the possibility of identification

- Application of multi-dimensional separation techniques (e.g. SEC followed by IEC and RP-HPLC)
  - Species must be sufficiently stable to survive time consuming analysis under different conditions and changing media

- Mass spectrometry for separated compounds by using "soft" ionisation sources (ESI-MS, MALDI)
  - MS can be interfered by the presence of salts and other components at concentration levels above 10 nM
  - ESI-MS is 2-3 orders of magnitude less sensitive than ICP-MS
Improvement of accuracy

Significant improvements have been achieved in the area of quality assurance and control resulting in better accuracy and traceability:

- Application of improved techniques for sample preparation (e.g. TMAH extraction, enzymatic extraction, microwave-assisted extraction, in-situ derivatisation with tetraalkylborates, SPME), leaving the actual species intact
- Application of fast separation techniques (e.g. FPLC, CE) with directly coupled detection techniques, avoiding species transformation
- International comparison studies (e.g. BCR, IAEA)
- Application of new definitive methods (e.g. species-specific isotope dilution analysis) overcoming artifacts
- Use of certified reference materials for species

Situation: CRM’s for the speciation of Cr

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td>SRM 2108</td>
<td>Cr(III) in solution</td>
</tr>
<tr>
<td></td>
<td>SRM 2109</td>
<td>Cr(VI) in solution</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 544</td>
<td>Cr(III)/Cr(VI) in lyophilised solution</td>
</tr>
<tr>
<td></td>
<td>CRM 545</td>
<td>Cr(VI) in welding fume (loaded on filter)</td>
</tr>
<tr>
<td>DANREF</td>
<td>CEMENT 1</td>
<td>Cr(VI) in cement, low concentration</td>
</tr>
<tr>
<td></td>
<td>CEMENT 2</td>
<td>Cr(VI) in cement, high concentration</td>
</tr>
</tbody>
</table>
### Situation: CRM's for the speciation of Sn

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR</td>
<td>CRM 424</td>
<td>TBT in harbour sediment</td>
</tr>
<tr>
<td></td>
<td>CRM 462</td>
<td>Butyltin-compounds in coastal sediment</td>
</tr>
<tr>
<td></td>
<td>CRM 477</td>
<td>Butyltin-compounds in mussel tissue</td>
</tr>
<tr>
<td></td>
<td>CRM 646</td>
<td>Butyl/Phenyltin- compounds in fresh water sediment</td>
</tr>
<tr>
<td></td>
<td>CRM 710</td>
<td>DBT and TBT in oyster tissue</td>
</tr>
</tbody>
</table>

### Situation: CRM's for the speciation of Sn

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRCC</td>
<td>PACS 1</td>
<td>Butyltin-compounds in Marine sediment</td>
</tr>
<tr>
<td></td>
<td>PACS 2</td>
<td>Butyltin-compounds in Marine sediment</td>
</tr>
<tr>
<td>NMIJ</td>
<td>7301-a</td>
<td>Butyltin-compounds in Marine Sediment</td>
</tr>
</tbody>
</table>
### Situation: CRM’s for the speciation of Hg

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRCC</td>
<td>DORM 1</td>
<td>Total Hg and Methyl-Hg in fisch muscle (dogfish)</td>
</tr>
<tr>
<td></td>
<td>DORM 2</td>
<td>Total Hg and Methyl-Hg in fisch muscle (dogfish)</td>
</tr>
<tr>
<td></td>
<td>DOLT 1</td>
<td>Total Hg and Methyl-Hg in fisch liver (dogfish)</td>
</tr>
<tr>
<td></td>
<td>DOLT 2</td>
<td>Total Hg and Methyl-Hg in fisch liver (dogfish)</td>
</tr>
<tr>
<td></td>
<td>LUTS 1</td>
<td>Trace elements and Methyl-Hg in lobster tissue</td>
</tr>
<tr>
<td></td>
<td>TORT 1</td>
<td>Total Hg and Methyl-Hg in lobster tissue</td>
</tr>
<tr>
<td></td>
<td>TORT 2</td>
<td>Total Hg and Methyl-Hg in lobster tissue</td>
</tr>
<tr>
<td>NIES</td>
<td>NIES 13</td>
<td>Total Hg and Methyl-Hg in human hair</td>
</tr>
</tbody>
</table>

### Situation: CRM’s for the speciation of Hg

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td>SRM 1974 a</td>
<td>Total Hg and Methyl-Hg in mussel tissue</td>
</tr>
<tr>
<td></td>
<td>SRM 2974</td>
<td>Total Hg and Methyl-Hg in mussel tissue</td>
</tr>
<tr>
<td></td>
<td>SRM 2976</td>
<td>Total Hg and Methyl-Hg in mussel tissue</td>
</tr>
<tr>
<td></td>
<td>SRM 2977</td>
<td>Methyl-Hg in mussel tissue</td>
</tr>
<tr>
<td></td>
<td>SRM 1566b</td>
<td>Methyl-Hg in oyster tissue</td>
</tr>
<tr>
<td></td>
<td>SRM 1946</td>
<td>Methyl-Hg in fresh water fish</td>
</tr>
</tbody>
</table>
### Situation: CRM's for the speciation of Hg

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA</td>
<td>IAEA 142</td>
<td>Total Hg and Methyl-Hg in mussel homogenate</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 350</td>
<td>Total Hg and Methyl-Hg in fish homogenate (tuna)</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 140</td>
<td>Total Hg and Methyl-Hg in marine plant homogenate</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 085</td>
<td>Total Hg and Methyl-Hg in human hair, spiked</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 086</td>
<td>Total Hg in human hair</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 356</td>
<td>Methyl-Hg in contaminated marine sediment</td>
</tr>
<tr>
<td>IAEA</td>
<td>IAEA 405</td>
<td>Methyl-Hg in estuarine sediment</td>
</tr>
</tbody>
</table>

### Situation: CRM's for the speciation of Hg

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR</td>
<td>CRM 422</td>
<td>Methyl-Hg in fish muscle (cod)</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 463</td>
<td>Total Hg and Methyl-Hg in fish muscle (tuna)</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 464</td>
<td>Total Hg and Methyl-Hg in fish muscle (tuna)</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 580</td>
<td>Total Hg and Methyl-Hg in sediment</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 710</td>
<td>Methyl-Hg in oyster tissue</td>
</tr>
<tr>
<td>Immuno</td>
<td>Seronorm Whole blood</td>
<td>Trace elements and Methyl-Hg in whole blood</td>
</tr>
</tbody>
</table>
**Situation: CRM’s for the speciation of As**

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR</td>
<td>CRM 626</td>
<td>Arsenobetaine in solution</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 627</td>
<td>Organoarsenic-compounds (DMA, AsB) in tuna fish tissue</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 710</td>
<td>Arsenobetaine in oyster tissue</td>
</tr>
<tr>
<td>NIES</td>
<td>NIES 14</td>
<td>Innorganic arsenic compounds in brown algae</td>
</tr>
<tr>
<td>NIES</td>
<td>NIES 15</td>
<td>Arsenobetaine in clams</td>
</tr>
<tr>
<td>NIES</td>
<td>NIES 18</td>
<td>Arsenic species in urine</td>
</tr>
</tbody>
</table>

**Situation: CRM’s for the speciation of Pb & Se**

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Code</th>
<th>Certificate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRCC</td>
<td>CASS 3</td>
<td>Total Se and Se(IV) in coastal sea-water</td>
</tr>
<tr>
<td>BCR</td>
<td>CRM 605</td>
<td>Trimethyllead in urban dust</td>
</tr>
</tbody>
</table>
**Overview: CRM's for speciation**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Hg</th>
<th>As</th>
<th>Sn</th>
<th>Cr</th>
<th>Se</th>
<th>Pb</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air particulate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fish</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mussel, Oyster</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Serum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whole blood</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hair</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Speciation: Why is it not yet done routinely?**

**Historical reasons:**

Inorganic analysis and especially trace metal analysis has been evolved historically through the development of *atomic* spectrometry.

Unfortunately, sources for atomic spectrometry (atomizers) are meant to produce *atoms* destroying most of the information of originally present chemical species.

Most of the techniques used (AAS, AES, MS) work best with liquid samples, calling for some *sample preparation* (sample preservation, digestion etc.) destroying molecular information even in front.
Speciation: Why is it not yet done routinely?

**Methodological difficulties:**
In order to do speciation analysis, the original distribution of chemical species in the probed compartment must be either preserved within the sample or the speciation analysis must be performed in situ (on-site).

Both strategies do require more sophisticated instrumentation, higher knowledge about the chemistry and better control of the methodology than required by the total element analysis.

**Lack of species-related legislation:**
Most existing rules and legislation forces analytical laboratories to perform total element determinations.

While the European Water Framework Directive (2000/60/EC) specifies that the species of Cd, Pb, Hg, Ni as well as tributyltin have to be controlled in water, there are very few national rules and standards implemented, that regulate species related measurements.
Speciation: Existing legislation – some examples

**Hexavalent chromium:**
The amount of hexavalent chromium is regulated in some countries (e.g. Europe) for the following cases:
- Waste water
- Cement and cement products
- Leather and Bio-leather
- Automobiles and metallic parts
- Electronic equipment
- Workplace atmosphere

[Further Legislation requiring speciation analysis:]
The following rules/legislation will require speciation analysis in many cases:
- **REACH** *(Registration, Evaluation, Authorisation and Restriction of Chemicals, Europe)*
- **TSCA** *(Toxic Substances Control Act, USA)*

Or at least in some cases:
- RoHS
- WEEE
"Real world" environmental and industrial speciation issues

Drinking water:
- Enhanced characterisation of fresh water with respect to requirements for water treatment (Fe(II)/Fe(III), As(III)/As(V))
- Influence of pH, different water sources and disinfection products on remobilisation of deposited minerals from distribution system (e.g. As, Pb)
- Process control and elimination of toxic contaminants from drinking water (As(III)/As(V), Bromate)

Waste management:
- Risk assessment (mobility of pollutants, degradation and transformation, potential toxicity),
- Waste management (Cr in leather tannery waste, Se in waste water, mobility of toxic metals from solid wastes such as fly ashes,
- Optimization of remediation strategies (As, Cd, Cr, Hg and Pb in waste disposal sites, abandoned industrial production places etc.)
EVISA – the missing link

The European Virtual Institute for Speciation Analysis (EVISA)

...is meant to fill the gap between the scientific community and customers requiring species related information

...by combining the expertise of some of the most renowned research laboratories, industrial users, governmental facilities and manufacturers.

...is a service provider supporting Industry, Routine Laboratories, Government Agencies and other parties

...is promoting interdisciplinary cooperation between researchers working in different disciplines such as analytical science, toxicology, environmental chemistry, biology, nutrition science or medicine.

EVISA’s Members

Partnership has been conceived as to ensure full complementary coverage of the different aspects of speciation with respect to:

- Experience (organometallic species, valency species, metal-biomacromolecules...)
- Application area (industry, food, health, environment, research...)
- Location (35 partners from 10 countries)

EVISA is meant to be an open structure, ready to accept new partners in order to complete its area of competence
EVISA's Members

Industry
- Pharma (Pharma Nord)
- Leather (IUV)
- Electronics (TRT)
- Instruments (Anton Paar, Gerstel, JY Horiba, PSAnalytical)

Analytical services (ADERA, BRGM, ENEA, GALAB, LGC)

Research groups
- Universities (Corvinus University Budapest, TU Graz, Complutense Madrid, Münster, Pau, Plymouth, Umea, Vienna)
- Research Institutes (DVFA, Eurofins, GKSS, INERIS, Jozef Stefan Inst. Ljubljana, RIVM)

evisa's web portal: The Virtual Institute

The web portal of EVISA plays a main role for structuring the Institute itself but also for providing the tool for fulfilling its specific objectives at the operational level.

For this purpose the web site has been organized in the following way:

Entrance Hall: Public Site (www.speciation.net)
Front-desk: Login Area
First floor: Customer area
Second floor: Partners area (EXTRANET)
EVISA's WebPortal: Servicing the scientific community

The Public Section of EVISA’s WebPortal is providing the services meant to support the scientific community:

- A list of actual events related to speciation (actual status ~ 50 events)
- A directory of scientists being active in the field of speciation (actual status ~ 220, target 500)
- A database of journals related to speciation analysis (actual status ~ 40 journals, target 100)
- A news section summarising findings from recent papers/presentations and other news related to speciation
- A database on external information (~800 links)
- A section on vacant positions related to speciation
- A discussion forum for all aspects of speciation

What is EVISA offering?

- Competent consultant
- Professional analytical services
- Quality assurance-related activities
- Fit-for-purpose analytical developments
- Workshops and training courses
- Speciation related information
Who benefits from EVISA?

- Subscribers
  Make use of the services provided by EVISA
- Partners
  Share EVISA’s web portal for marketing their products
- Members
  Use EVISA’s structure for efficient cooperation
  Provide the services of “EVISA”

EVISA is supporting...

Industry...

- to meet regulatory needs
- to gain competitiveness by improving the information value of chemical analysis through species measurements
EVISA is supporting ...

Politicians and rule makers...

- to define the state-of-the-art of speciation analysis
- to access species related information in an efficient way

EVISA is supporting ...

Scientists...

- by giving easy access to valid information
- by enhancing their opportunities for interdisciplinary cooperation
- by improving their mobility and education
- by enhancing their visibility and recognition
**evisa.**

**evisa's role towards its members**

- Provide a powerful framework for efficient cooperation
  - Knowledge management
  - Provision of business tools
  - Promote contacts and exchange of knowledge
- Act as a research broker
  - Enhance the visibility of speciation by adding the global dimension
- Act as a quality label
  - Promote the establishment of methods fit-for-purpsose
  - Coordination of quality related actions
  - Enhance education and knowledge of partners by training

---

**Conclusions**

- Measurement and testing is a major cost factor
  - A cost-effective approach must provide valuable information
  - Total element analysis seldom provides the correct answers and is therefore very costly
- Speciation analysis is more complex than total element analysis and calls for more expertise
  - A number of techniques and methodologies are now available that have reached some state of maturity
  - Some standards and Certified Reference Materials are available as a starting point
  - Instrument manufacturers have entered the field supporting the analysts with products
Conclusions

- Speciated IDMS can be used for reliable quantification, verification and validation
- Speciation analysis is ready to answer questions for environmental, industrial and other fields of analytical chemistry
- Rule makers have started to consider speciation and more rules are likely to come-up soon (e.g. methylmercury in fish, arsenic species in seafood)
- A European Virtual Institute for Speciation Analysis has been founded in order to help Industry and routine laboratories to get easy access to information and knowhow collected within the research community

Many thanks for your attention!
For more information, please visit our web site at: http://www.speciation.net

Welcome to the European Virtual Institute for Speciation Analysis (EVISA)

- offering new and profitable strategies for enterprises to improve quality of industrial processes and products
- enhancing the cost/benefit ratio of analytical measurements by enhancing the information value
- making the collective knowledge of the world’s experts in speciation analysis easily accessible

EVISA is offering solutions and support for "real world" speciation issues such as:

- Effective and efficient consulting
- Professional analytical services
- Quality assurance-related activities
- Fit-for-purpose analytical developments
- Expert training activities
- Concrete web portal with discussion forum, news section, directory of scientists, calendar of events, list of vacant positions
- Comprehensive databases covering literature, reference materials, standards, standard operating procedures etc.
- Information about toxicity, bioavailability, legislation for metal and metalloid species
TOP TEN REASONS

We Have All Stayed in the Environmental Laboratory Business

10. We are all waiting to see if a Republican Administration/Congress will ever prove to us how business friendly they are by putting more money into the environmental business.
9. We are all waiting to see if a Democratic Administration/Congress will ever actually spend money on the environment to prove how *environmentally friendly* they are.

8. We are all waiting to see how long it takes for the price of a volatiles sample to go so low that the lab will have to pay the client for analyzing their sample, and report the results *before* the sample is collected?
7. We are all waiting to find a subject on which David Friedman does not have a strong opinion.

6. We all have looked for another job, but nobody would let us be President and CEO.
5. We are more attractive to the opposite sex when they see our sensitive environmental side.

4. Where else could you make these kinds of profits?
3. We are all waiting for Severn Trent to purchase our laboratories.

2. Our last career was in the oil business and it didn’t have a future.
...and finally...

The Number ONE Reason
We Have All Stayed
in the Environmental Laboratory Business:
1. A Soft Job Market
ANALYTICAL CHEMISTRY INNOVATIONS AND IMPROVEMENTS IN ENVIRONMENTAL QUALITY IN NJ: PERFECT TOGETHER

Stuart J. Nagourney
NJ Department of Env. Protection
Office of Quality Assurance
(609)-292-4945
stu.nagourney@dep.state.nj.us

ANAL. CHEM. & NJDEP MISSION STATEMENT

• Defining and publishing reasonable, clear and predictable scientifically based standards

• Achieving the Department’s goals in a manner that encourages compliance and innovation

• Assuring that the best technology is planned and applied to achieve long-term goals
SCIENCE & NJDEP’s ORGANIZATION CHART

Office of the Commissioner
  - Office of Policy, Planning, and Science
    - Land Use
    - Compliance and Enforcement
    - Environmental Regulation
      - Watershed Mgmt
      - Water
      - Air
      - Misc.
      - Hazardous Waste
      - Solid Waste
  - Site Remediation

SCIENCE & NJDEP: POLICIES & PRACTICES

- Specific procedures change with every Commissioner, but certain practices remain the same
  - Must consider views of diverse interest groups
  - Many managers have technical expertise
  - Staff always has input to policy decisions
  - Consensus sought across program lines
ANAL. CHEM. ↔ POLICY: SOIL CLEANUP STANDARDS

- Establishes parameter-specific numerical criteria that are different for residential and commercial property

- Clean-up standards must be able to be achieved by certified analytical methods

- Project-specific criteria are developed for what constitutes data sufficiency

SCIENCE ↔ POLICY: GHG’s

- NJ was the 1st state to develop a GHG Action Plan with a quantifiable goal to reduce emissions

- The plan was carefully crafted to achieve reductions in industrial, transportation, housing and other market sectors

- Goal: 3.5% reduction in 2000 baseline by 2005

- How was this numerical goal developed??
NEW JERSEY QUANTITATION LIMITS (NJQLs)

• **Definition:** Multi-lab. MDL by method & matrix (from median of data population) X 5 using data from NJ certified facilities

• The NJQL should be value that can be achieved by most labs. under normal conditions

• How to derive NJQLs? What to use them for?

NJQLs: WHERE ARE WE GOING?

• NJ has the most comprehensive lab. cert. program: >850 labs., > 12,000 parameters

• Developing a database & supporting regulations to manage NJQL data & implement uses

• Potential Uses
  – Set permit limits
  – Filter labs. eligible to do NJ analytical work
Triad

- NJs Tech. Regs. (N.J.A.C. 7:26) have always allowed for the use of real-time analytical data for at-risk remedial investigations

- Triad
  - Systematic Project Planning
  - Flexible Work Planning
  - Real Time Measurement Systems

- Triad provides less decision uncertainty
Triad NJ UPDATE

• NJ-led ITRC team has produced technical document and Internet-based training on Triad

• NJ OQA certifies labs. to perform real-time measurements

• Managers and staff trained in Triad: it is policy

• Would not have happened w/o acceptability of field analytical data

Cr(VI)

• NJ has the nation’s largest inventory of sites contaminated > 50 yrs. ago by Cr(VI)

• Clean-up strategies dependent in-part upon use of most effective available analytical technologies

• EPA withdrew non-aqueous Cr(VI) sample preparation method in early 90’s: a historic event!

• NJDEP just completed a review of Cr(VI) issues
Cr(VI) WORKGROUP
CONCLUSIONS

• Only USEPA and NJDEP certified methods will be used for future remedial activities

• Options exist for use of determinative methods, but final site decisions must pass QA or use most definitive analytical technique (Method 6800)

• Development of speciated reference materials will provide additional objective insight into performance of labs. & analytical methods

CONCLUSIONS

• Sound science (analytical chemistry) continues to drive the making of NJDEP policy

• As the science changes, policy changes as well

• Collaboration with peer organizations invaluable
  – USEPA
  – NIST
  – ITRC
Session 1

Method Detection Limits
Method Detection Limits: A Data User’s Perspective

Rock J. Vitale, David R. Blye, Ruth L. Forman, and Donald J. Lancaster
Environmental Standards, Inc., 1140 Valley Forge Road, Valley Forge, PA, 19482
Primary Author’s E-Mail: rvitale@envstd.com; Phone: 610-935-5577

ABSTRACT

Over the past several years, there has been considerable discussion in the environmental community regarding the merits of method detection limit (MDL) studies. In March 2003, US EPA withdrew its proposed rule that revised the detection and quantitation procedures for analytical methods under the Clean Water Act (CWA). This action was prompted by divergent comments about the proposed revisions and potential impact on the regulated community. In January 2005, the Agency conducted a public meeting and announced the establishment of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in CWA Programs (FACDQ).

A recent e-mail inquiry to the US EPA Office of Solid Waste (OSW) Methods Information Communication Exchange (MICE) Service concerning MDL requirements received the following response:

“Actually, the EPA OSW is now in the process of removing requirements for MDL studies in both the individual methods and chapters. Hopefully, the Fourth Edition of the manual, which should be published sometime early next year, will include these revisions. In addition, the SW-846 Methods Team is discouraging the use and application (of) the MDL determination, regardless of the sample matrix type, as defined in 40 CFR Pt 136 Appendix B, for the simple reason that it is not a true indication of the method sensitivity. The MDL calculation has been used repeatedly for a number of EPA programs and it demonstrates the potential data variability for a given sample matrix at one point in time, however, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated.”

Environmental Standards believes that the US EPA is finally openly addressing the fact that the procedure to determine MDLs as identified in 40 CFR Part 136 Appendix B is flawed. However, even with the US EPA reviewing the MDL procedures and SW-846 discouraging the use of MDLs, there are many state regulators and other offices within the US EPA that are mandating that data be reported to the MDL for compliance purposes. Environmental Standards will present issues that data users should be aware of when developing MDLs and using results that are reported to the laboratory MDLs.
Detection and Quantitation Limits – Where Do We Go From Here?

Richard Burrows, Ph.D.
Severn Trent Laboratories, 4955 Yarrow St., Arvada, CO 80002
Email: rburrows@stl-inc.com; Phone: (303) 736-0100

ABSTRACT

This paper will present a list of “consensus principles” that have received broad agreement as the desired outcomes of detection and quantitation limit procedures. We will discuss a variety of current proposals and how well they meet the goals set by the consensus principles.

1. The definition of quantitation must include both precision and bias
2. Detection limit procedures must take into account the variability and bias of method blank results
3. International definitions of LQ, LD and LC must be adopted
4. False positives and false negatives must be addressed by detection limit concepts
5. Precision, bias and qualitative identification must be addressed by the definition and concepts of quantitation
6. Detection limit procedures must include procedures for ongoing demonstration of sensitivity
Detection Limits – Federal Advisory Committee

Richard Reding, Chief
Email: reding.richard@epa.gov; Phone: 202-566-2237

ABSTRACT

We are working to establish a formal committee of about twenty individuals to provide advice to the U.S. Environmental Protection Agency on ways to improve detection and quantitation approaches in EPA's Clean Water Act programs. Our expectation is that the committee will provide advice on a common set of terms and concepts; one or more specific approaches and/or procedures for detection and quantitation; and recommendations for the interpretation and use of the numbers that result from measurements of pollutants in water. Committee members will be qualified, senior-level professionals with an emphasis on policy experience from diverse sectors, including state government; environmental professionals; regulated industry; environmental laboratories; publicly owned treatment works; and the environmental community. The establishment and makeup of this committee reflects EPA's emphasis on the need for open and inclusive approaches where stakeholders work together with EPA to develop solutions.

The committee will consider the technical and policy issues related to the calculation and use of detection and quantitation limits in Clean Water Act programs. Policy issues include consideration of how much uncertainty is acceptable to make a presence or absence decision, or a decision that a discharge limit has been exceeded. Technical issues may include topics, such as treatment of blanks and censored data, the number and types of samples, matrices, and laboratories required to develop a detection limit, and procedures for a laboratory to routinely demonstrate the capability to meet established limits. Neutral technical experts will be available to provide technical assistance to the committee. These experts would not be members of the committee nor participate in the deliberations.

We are planning to charter and operate this committee under the Federal Advisory Committee Act. We believe that this consultative process will be relatively short, e.g., five or six meetings over one year, and hope to convene this committee in June 2005. Updated information will be available at www.epa.gov/waterscience/methods/det.
New Jersey Quantitation Limits: Putting MDLs to Practical Use

Stuart J. Nagourney, Michael W. Miller, Ph.D., and Martin Hackman
New Jersey Department of Environmental Protection, Office of Quality Assurance, Trenton, New Jersey 08625
Peter Tenebruso
New Jersey Department of Environmental Protection, Office of Information Resources Management, Trenton, New Jersey, 08625
Gregory Carey
enfoTech & Consulting, Inc., 11 Princess Road, Unit A, Lawrenceville, New Jersey 08648
Primary Author's Email: snagourn@dep.state.nj.us; Phone: (609) 292-4945

ABSTRACT

The New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA) is proposing to establish a program to develop New Jersey Quantitation Limits (NJQLs) for the State. The laboratory certification program administered by the OQA offers certification for a wide variety of analytical methods that measure chemicals in the following sample matrices: drinking water, wastewater, ground and surface waters, solid hazardous wastes and air.

In order for the NJDEP to develop and enforce environmental regulations, measurement of chemical contaminants in environmental samples must be of defined and defensible quality. This includes an assessment of the laboratories’ capability to measure chemical contaminants at levels near the detection capability of the analytical method. For environmental compliance monitoring in the United States under United States Environmental Protection Agency (USEPA) regulations, the method detection limit (MDL) is defined at 40 CFR Part 136 Appendix B (July 1, 1993) as the minimum concentration of a substance that can be measured and reported with 99th-percent confidence that the analyte concentration is greater than zero. The OQA currently requires all New Jersey certified laboratories supply to the Department method detection limit (MDL) data they are currently required to generate MDLs at least annually for all analytes and methods for which they hold certification.

Since the MDL is a statistically-derived number, one cannot expect that any laboratory can quantify measurements for an environmental sample at that level. Other reasons that the MDL is not suitable as a regulatory level include the fact that the MDL varies from laboratory to laboratory, precision of measurements at the MDL are generally poor; and although the MDL provides adequate protection against false-positive results, protection against false-negatives is inadequate because samples containing contaminants at a concentration near the MDL will not always be measurable. For these and other reasons, quantitation and regulatory decision-making are not feasible at the MDL. This requires that a higher limit must be established to support and validate Department regulatory actions such as the writing of permits and the development of clean-up standards for hazardous waste sites. This higher limit has been designated by the Department as the NJQL, which is defined as the lowest concentration of a particular analyte that can be reliably determined, under routine operating conditions, within specified limits of precision and accuracy. The NJQL is an interlaboratory measure, taking into account performance variability within individual laboratories as well as within the laboratory community as a whole. The NJQL is also analyte, method and matrix-specific; for example,
cadmium and lead (the analytes) will have very different MDLs and NJQLs, and for cadmium in drinking water alone, the MDL and the NJQL may differ depending upon whether flame, graphite furnace atomic absorption spectrophotometry, inductively coupled plasma emission spectroscopy or inductively coupled plasma mass spectrometry is/are used for detection.

For any given analyte, method and matrix, the MDL is expected to vary from laboratory to laboratory because of differences in instrumentation, expertise of personnel, quality of chemical reagents and other factors. The Department plans to use the median of all results for each analyte, method and matrix, and derive a NJQL for each by taking that median of each data population and multiplying the median of that data population by a factor of 5. Since the NJQL is defined as being five times higher than the median MDL, the NJQL should be achievable by most certified laboratories in their daily operations.

Since the NJDEP certifies more than 800 laboratories for more than 10,000 test methods, the management of all of this MDL data in order to generate NJQLs is a daunting task. The NJDEP has therefore contracted with enfoTech to design a database system for this purpose. The management of MDL information from certified laboratories to the NJDEP will be accomplished by requiring each laboratory to complete a Department-supplied electronic deliverable listing all chemical test methods for which the laboratory holds certification. Additional ancillary information such as the low point on the laboratory’s calibration curve will also be requested. The database will then sort this MDL information by analyte, method and matrix and allow calculations of NJQLs.

This paper will describe the database development project and the intended use of NJQLs by the NJDEP.
A Statistical Determination of Minimum Reporting Levels

Stephen D. Winslow¹, Barry V. Pepich¹, David J. Munch², and John J. Martin³

¹Shaw Environmental, Inc., 26 West Martin Luther King Dr., Cincinnati, OH 45219; Email: winslow.stephen@epa.gov; Phone: (513) 569-7035;
²U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water, 26 West Martin Luther King Dr., Cincinnati, OH 45268; Email: munch.dave@epa.gov; Phone: (513) 569-7843
³The Cadmus Group, Inc., 57 Water Street, Watertown, MA 02472

ABSTRACT

A new statistical procedure is being evaluated for minimum quantitation levels and for verifying minimum reporting levels (MRLs) by EPA’s Office of Ground Water and Drinking Water. The lowest concentration MRL (LCMRL) is the lowest true concentration for which future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery. The procedure takes into account precision and accuracy, simultaneously applied. Four data sets of 7 samples each are processed through the entire method procedure and the data is plotted as sample concentration (y-axis) versus true concentration (x-axis). An ordinary least squares regression line is calculated and prediction interval lines (99% confidence) are drawn. At the points where the prediction intervals intersect with 50 and 150% lines of recovery, vertical lines are drawn to the x-axis, and the higher of the two values is the LCMRL. In the case of non-constant variance, a variance weighted regression is used. The LCMRL procedure is flexible because the data quality objectives (i.e., 50 to 150%) and the prediction interval confidence (99%) can be varied to suit program needs. The LCMRL determination is performed during method development only. Once an MRL is established, a simpler procedure is used for MRL lab verification. A validation of laboratory performance at or below an MRL is made using a single set of 7 samples run through the entire method procedure. If the calculated prediction interval is contained within data quality recovery limits (50 to 150%), the lab performance for that analyte is validated.
Session 2

Laboratory Accreditation
How Accreditation Supports A Laboratory in Ensuring Data Integrity

21st Annual National Environmental Monitoring Conference
Washington, DC
26 July, 2005
Randall Querry, A2LA Program Manager

Overview

- Data Integrity
- Accreditation
- Features of ISO/IEC 17025 that support data integrity initiatives
- Who’s job is it?
- Questions
Data Integrity

- Data integrity refers to the VALIDITY of data.

Data Integrity-Compromised

- Human error when data is entered
- Errors that occur when data is transmitted
- Software bugs or viruses
- Hardware malfunctions
- Environmental conditions/Natural disasters
Accreditation

- third-party attestation related to a conformity assessment body conveying formal demonstration of its competence to carry out specific conformity assessment tasks

Accreditation Bodies

- Operates to ISO/IEC 17011
- Conducts on-site assessments evaluating management systems and testing activities
- Employs the use of technical experts as assessors
- Issues Scope of Accreditation identifying applicants specific competencies
Laboratory Accreditation

- Conforms to ISO/IEC 17025 requirements
- Conforms to applicable, specific program requirements (NELAC, AOAC)
- Successful participation in relevant proficiency-testing programs

ISO/IEC 17025 and Data Integrity

- ISO/IEC 17025 specifically promotes data integrity in three primary sections:
  - 4.1.5 Organization
  - 5.4.7 Control of data
  - 4.12 Control of records
Organization requirements

• 4.1.5 states that the laboratory SHALL:
  – a) have managerial and technical personnel with the authority and resources…
  – b) have arrangements to ensure that its management and personnel are free from any undue INTERNAL and EXTERNAL commercial, financial and other pressures/influences

American Association for Laboratory Accreditation
Organization requirements

- 4.1.5 states that the laboratory SHALL:
  - g) provide adequate supervision of testing staff, including trainees, by persons familiar with the methods and procedures

Control of Data

- 5.4.7.1 Calculations and data transfers shall be subject to appropriate checks in a systematic matter
Control of Data - NELAC

- 5.4.7.1 Calculations and data transfers shall be subject checks...
- The laboratory shall establish SOPs to ensure:
  - that reported data are free from transcription and calculation errors
  - quality control measures are reviewed, and evaluated before data are reported
  - addressing manual calculations including manual integrations

Control of Data - Software Validation

- 5.4.7.2 When computers or automated equipment are used for acquisition, processing, recording, reporting...the laboratory shall ensure that:
  - a) computer software developed by the user is documented in sufficient detail and is suitably validated as being adequate for use.
Control of Data - Protecting Data

- 5.4.7.2 b) procedures are established and implemented for protecting the data, such procedures shall include, but not be limited to, integrity and confidentiality of data entry or collection, data storage, data transmission and data processing

Control of Data - Maintenance

- 5.4.7.2 c) computers and automated equipment are maintained to ensure proper functioning and are provided with the environmental and operating conditions necessary to maintain the integrity of test and calibration data
Control of Records

- ISO/IEC 17025, Section 4.12.2.3 requires that all records shall be held secure and in confidence.
- ISO/IEC 17025, Section 4.12.2.4 stipulates that the laboratory shall have procedures to protect and back-up records stored electronically and to prevent unauthorized access to or amendment of these records.

Control of Technical Records

- ISO/IEC 17025 Section 4.12.2.2 states that observations, data and calculations shall be recorded at the time they are made and shall be identifiable to the specific task.
Control of Technical Records

- Section 4.12.2.3 requires that when mistakes occur in records, each mistake shall be crossed out, not erased, made illegible or deleted, and the correct value entered along side...

Control of Technical Records

- Section 4.12.2.3 ... All such alterations to records shall be signed or initialed by the person making the correction. In the case of records stored electronically, equivalent measures shall be taken to avoid loss or change of original data...
NELAC on Data Integrity

- NELAC Chapter 5 Section 5.5.2.7 requires the following to promote data integrity:
  - data integrity training for new hires and annually
  - topics shall be documented and provided to trainees
  - topics shall include: organization’s mission, honesty, full disclosure in analytical reporting...

NELAC on Data Integrity

- Topic continued:
  - how and when to report data integrity issues
  - recordkeeping

- Training shall include a discussion of data integrity procedures, in-depth data monitoring, data integrity procedure documentation
NELAC on Data Integrity

- 5.5.7.2 also requires that training include a discussion of the consequences of infractions of the procedures
  - detailed investigation that could lead to
    - immediate termination
    - debarment
    - civil/criminal prosecution


American Association for Laboratory Accreditation

NELAC on Data Integrity

- 5.5.7.2 continues by providing examples that should be discussed as part of the training:
  - improper data manipulation
  - adjustments of instrument time clocks
  - inappropriate changes in concentration of standards

American Association for Laboratory Accreditation
ISO/IEC 17025 Principles

- Several important principles are imbedded in the requirements of the ISO standard that help assure data integrity:

Capacity

- A laboratory must have the resources, (people with the required skills and knowledge); an environment with the required facilities; equipment and instruments; procedures to ensure consistency of test processes, and quality control for the key steps in the testing processes, in order to carry out the test and produce reliable results.
Responsibility

• A laboratory shall have personnel in its organization who have the authority to execute specific functions and can demonstrate accountability for their results.

Scientific Approach

• A laboratory shall carry out its work based upon accepted scientific principles, preferably following consensus-based methods or standards.
Objectivity

• The results generated should be based upon measurable quantities and if results are subjective, they must be produced by people deemed qualified to make subjective judgements.

Impartiality

• The pursuit of reliable results through the use of accepted scientific principles is the primary and overriding influence on the persons carrying out the testing. All other influences are secondary and not permitted to take precedence.
Measurement Traceability

- The results produced are based upon on a recognized system of measurement that derives from accepted known quantities (SI system if units of measurement) or other well-characterized references.

Reproducibility

- The test method used to produce the results will produce results within an acceptable spread or range during future testing and within the constraints of using the same procedures, equipment and persons used for a prior analysis.
Transparency

- The processes within a laboratory producing objective results must be open to external as well as internal scrutiny, so that factors which may adversely affect the laboratory’s pursuit of objective results based upon scientific principles can be easily identified and resolved.

American Association for Laboratory Accreditation

Who’s job is it?

- Management
  - management’s commitment to the quality system
  - providing adequate personnel, technical oversight
  - making available proper equipment and instruments
  - training programs

American Association for Laboratory Accreditation
Who’s job is it?

- Analyst
  - Competent in quality and technical procedures

Summary

- ISO/IEC 17025 provides the framework from which to build a system that promotes the integrity of data.
- Accreditation is the attestation that a laboratory has been found to be competent in performing specific tests.
- Management and staff both share a role in data integrity.
Contact Information

Randall Query
A2LA
5301 Buckeystown Pike, Suite 350
Frederick, MD, 21704
Direct line: 301 644 3221
Main: 301 644 3248
Fax: 301 662 2974
rquery@A2LA.org
www.A2LA.org
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities

Dawn D. Thomas, ASQ CQM
Professional Service Industries, Inc.
1748 33rd St
Orlando, FL 32839
dawn.thomas@psiusa.com
407-304-5560

ABSTRACT

The original charter of the National Environmental Laboratory Accreditation Conference (NELAC), when established in the early 1990’s, 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 laboratory standard and did not specifically address other accreditation components (e.g., proficiency testing (PT), on-site assessment, and accreditation process) or requirements for sampling specific environmental matrices. In 2003, NELAC divested itself of the environmental standards development process and the Institute for National Environmental Laboratory Accreditation (INELA), a consensus based standards development organization, was formed. Within this organization, the INELA Field Activities Committee (FAC) was established to continue the standards development work for an accreditation program designed specifically for field sampling and measurement organizations (FSMO).

Objective and Goals

The primary objective of the INELA FAC is “to develop and maintain consensus accreditation standards and guidance materials for organizations engaged in environmentally related field sampling and measurement activities, consistent with regulatory and industry-specific requirements”. Its long-range focus is to replace the 2002 NELAC Field Activities Standard (Chapter 7) with an INELA stand-alone, FSMO-specific accreditation standard(s) that meets the
following goals:

- Encompasses broad scope and wide ranging applicability;
- Based on internationally recognized standards for competency (ISO/IEC 17025) and conformity assessment (ISO/IEC 17011);
- NOT prescriptive in nature, allowing for the development of FSMO-specific policies and procedures; and
- Effectively supported by sound guidance.

**Broad Scope and Applicability**

If the INELA FAC is to meet its objective of establishing performance standards for those collecting samples and conducting on-site measurements for improved environmental data quality, then the standard must be wide-ranging in scope and applicability to support existing and future state/federal environmental regulations governing field sampling and measurement activities. To this end, a primary goal of the INELA Field Activities Committee is to develop an accreditation standard (or series of standards) that will apply to organizations performing field activities for a wide variety of sampling and measurement media such as air, biological, water, soil, waste, and radiological. Due to the nuances, specific to each media, a “one size fits all” approach to standards development is not appropriate. Accordingly, the FAC has engaged field sampling and measurement “media experts” to collaborate on the development of customized, media-specific FSMO accreditation standards. The development of custom field standards for water and air are the current focus of the committee.

**ISO Foundation**

It is the consensus viewpoint of the Field Activities Committee that the common denominator, or foundation, for the custom, media-specific INELA FSMO accreditation standard(s) must be ISO/IEC 17025, *General Requirements for the Competence of Testing and Calibration Laboratories* and ISO/IEC 17011 (soon to replace ISO/IEC Guide 58), *Conformity Assessment – General Requirements for Accreditation Bodies AccrEDITING Conformity Assessment Bodies*. Using this approach to standards development, the role of the INELA FAC will be to utilize its “media experts” to determine how to best apply these generic International Standards for a particular area of accreditation (e.g., field activities – water). The INELA FAC “application” of these International Standards, for each sampling and measurement media, will include, but will not be limited to, provisions for additional requirements, exclusion of specified ISO requirements due to applicability concerns, and clarifications and interpretations of various ISO requirements. Using ISO as the foundation for custom-built FSMO accreditation standards facilitates harmonization of individual field standards specific to each sampling and measurement media.

**Non-Prescriptive Standards Development**

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. Accordingly, the committee consensus was to take a practical and realistic first step towards improved environmental data quality by establishing an
accreditation standard, based on internationally recognized standards, which are minimally prescriptive to provide a high degree of flexibility for the FSMO when implementing the standard requirements. Simply stated, applying this “less is better” approach, the FSMO will be able to craft policies and procedures, which meet the intent of the INELA standard, but are practical, functional and, most importantly, implement-able. The INELA FAC believes that if the resulting field accreditation standards cannot be effectively implemented by all parties affected, large and small, public and private, due to overly prescriptive requirements, then we, as a committee, have not successfully completed our mission for improving data quality for better decisions.

Sound Guidance

To support the “less is better” approach to standards development and to facilitate successful implementation by all FSMO impacted by the standard, the development of appropriate implementation guidance tools is a key component for realizing an improved outcome – sound and defensible data quality for better decisions. This is the long-term focus of the INELA Field Activities Committee - to “show the way” by providing the necessary guidance and support for standards implementation. Several of the many benefits associated with this INELA service to the environmental community include:

- Acceleration of the FSMO “learning curve” associated with “something new”, keeping in mind that many FSMO have not been subject to quality system/accreditation program requirements, historically;
- Improved “buy-in” by minimizing the costs associated with implementation of a new and comprehensive accreditation standard; and
- Consistency of standards interpretation and implementation.

Accomplishments

These goals for standards development, as discussed in the previous sections, have evolved over a period of two (2) years as a result of the diligent work and “outside the box” thinking of the INELA FAC. The accomplishments, which follow in this section, have contributed greatly to the refocusing of the laboratory community (regulators and those regulated) on the importance of field sampling and measurement and its role, as the “front-end” portion of the environmental data generation process.

To facilitate the development of media-specific field standards, the committee has been very active in outreach activities to engage more stakeholders – the “media experts” - in the standards development process. The INELA FAC has grown from less than ten (10) members in 2003 to more than thirty (30) participating members today. The committee has also worked to achieve balance of membership, necessary for a consensus standards development organization, with representation from government and municipal agencies; engineering and environmental consulting firms, analytical laboratories and industry. Participation in national/regional conferences and collaboration with other organizations representing specific stakeholder groups will continue to be a focus for the INELA FAC. The committee’s success in developing sound field accreditation standards depends on the continuation of these outreach activities.

Consistent with committee direction to develop “applications” of the ISO/IEC 17025 and 17011 standards, a generic (not specific to any one media) application of the ISO/IEC 17025 standard
has been completed and will be utilized by the “media experts” to guide the development of media-specific field accreditation standards. This generic application of ISO/IEC 17025 was affirmed by the INELA membership in late 2004. Additionally, the groundwork, in the form of a consensus-based conceptual model, for the application of the ISO/IEC 17011 standard was completed and presented at the INELA Accreditation Forum in Charleston, South Carolina last summer. Building on these endeavors, workgroups have been established and are tasked with producing the first Working Draft Standards for a generic application of 17011 and a media-specific (water) application of 17025 by the summer of 2005.

A great deal has been accomplished but there is more work to do.

Next Steps

To achieve its on-going objective “to develop and maintain consensus accreditation standards and guidance materials for organizations engaged in environmentally related field sampling and measurement activities, consistent with regulatory and industry specific requirements”, the INELA Field Activities Committee must effectively meet certain challenges. They are:

- To know, engage and understand the needs of all stakeholders who will be, ultimately, impacted by the standard(s).
- To know, engage and understand the needs of all potential clients, those who will adopt and implement such a standard(s).
- Finding a consensus viewpoint to the question of what makes for good quality to achieve consistent application of the ISO/IEC 17025 and 17011 standards for harmonized individual media-specific field accreditation standards.

With its new approach to standards development, the INELA FAC also has an opportunity to help chart the future path of INELA, as a standards development organization. At the 2004 INELA Summer Forum in Charleston, South Carolina, the INELA Board of Directors expressed their desire for INELA membership to seriously consider a restructuring of the NELAC laboratory standard to better meet the needs of stakeholders, existing and potential clients, and to achieve the desire growth into other areas of accreditation. There are a number of proposals for this restructuring initiative currently being considered by the INELA Board.

One of the proposals being considered has been developed by the INELA FAC, which details an approach to standard restructuring, consistent with the approach being taken for the development of media-specific field accreditation standards. This proposal has been designed to:

- Align with the INELA Strategic Plan.
- Provide a flexible framework for the development of harmonized accreditation standards in new areas such as Homeland Security.
- Positively impact a wide range of stakeholders.
- Appeal to accrediting authorities, regulators, private sector groups interested in adopting and implementing uniform standards of accreditation.
- Assure the production of scientifically valid data that can be used with a high degree of confidence by the end user.

The INELA Field Activities Committee is committed to the development of field accreditation standards using the approach detailed in this paper and strongly believes that this approach can
be effectively used for the development of new INELA standards in other areas of accreditation as well. To meet the current challenges and to adequately address the complexities of the field sampling and measurement “world”, the committee must continue to focus its energies on thinking “outside the box”, encouraging and listening to new ideas, and creating an environment where these new ideas can flourish. Your participation in the FAC activities is vital for the production of data suitable for its intended use and may have an influence on the future path of INELA as a consensus standards development organization. All are encouraged to join INELA and to get involved! More information on the efforts of the INELA FAC may be found on the INELA web site (www.inela.org).
Accreditation of Air Emission Testing Bodies

Scott Evans  
Clean Air Engineering  
500 W. Wood Street  
Palatine, Illinois  60067  
scott.evans@cleanair.com  
847-654-4569

ABSTRACT

This presentation is an update on the progress and current status of Air Emission Testing Body (AETB) accreditation. The presentation will briefly cover key requirements of the ASTM D7036 standard as well as of the draft ASTM accreditation standard currently awaiting balloting at ASTM. The presentation will also cover the current activities of the Source Testing Accreditation Council and look at proposed accreditation process models such as the AIHA model for lead laboratory accreditation.
LIMS and Regulatory Compliance

Christine Paszko, Ph.D. and Elizabeth Turner*


Primary Author’s E-Mail: CPaszko@attlab.com, Phone: (910) 673-8165

There are an increasing number of regulatory and productivity demands placed on the environmental laboratory, from NELAC, HIPPA, Sarbanes-Oxley, The Patriot Act, ELAP, CFR 21 Part 11 to name a few. This presentation will review the features in an automated Laboratory Information Management System (LIMS) from sample login through to reporting that greatly facilitate compliance.

Sample tracking functionality provides not only the capability to scan in a chain of custody form, but also provides for an internal chain of custody (the physical location of the sample within the laboratory). With the use of electronic notebooks, users can enter chain of custody information into the notebook and electronically upload that information into the LIMS thus avoiding transcription errors. Most LIMS provide CFR 21 part 11 (electronic signature) compliance. The LIMS provides instant access to the sample status and location information. During sample login, users can also select from a pull-down list (which is limited to tests that can be performed on that matrix), project, site and GIS information can be recorded. QC samples can automatically be assigned as well as custom report requirements. Once samples are signed off, a date and time stamp is applied to the sample order. Users can enter results and an Electronic Data Entry Module can be configured automatically to import data from analytical instrumentation such as an ICP, GC/MS or AA.

Any modifications to results include a complete audit trail (audit reports can also be easily printed). With integrated QA/QC, users can view trend analysis and create QC charts. In addition, users are alerted at result entry when results have exceeded pre-defined limits, which can immediately be checked. A major benefit of an automated LIMS is in reporting in both paper and electronic format to regulatory agencies often in a specified format that can be sent electronically. Permit limits can be configured in the system and triggers can be set to alert users if any limits have been exceeded for rapid response.

The Washington Aqueduct is a wholesale water utility that provides potable water to the District of Columbia Water and Sewer Authority (WASA), Arlington County, VA, and the City of Falls Church, VA. The Washington Aqueduct Laboratory serves as the contract laboratory for its wholesale customers. In January of 2004, the Washington Post reported on high lead results found in Washington, D.C. water. As the news spread throughout the region, newspapers, television stations, and radio stations delivered updates to the lead story on a daily basis causing area residents and elected officials to voice their concerns, questioning the safety of the area’s drinking water. In an attempt to understand the extent of the problem, an extensive data collection effort began involving DCWASA, Arlington County, and Falls Church. All three increased their monitoring for lead by sampling area homes, schools, and daycare centers. In addition, the large numbers of samples continue to be collected by DCWASA as lead service lines are replaced and lead profiles are studied at different locations throughout the city.

The situation demands a massive collection of data to be processed and reported with the quickest turnaround time possible. The use of a LIMS has been essential to the timely processing of samples and reporting of results to customers and regulatory agencies. The ready availability of quality control data and electronic files has been critical in responding to Freedom of Information Requests. This presentation will highlight how the Washington Aqueduct utilizes its LIMS to effectively respond to increased analytical demands and data scrutiny. It will review the features in an automated Laboratory Information Management System (LIMS) from sample login through to reporting, that greatly facilitate compliance.
Introduction
A computerized LIMS is an important tool in the growing analytical laboratory. Most laboratories begin with a paper laboratory notebook and progress to Excel for data management and Word templates for reporting. However, most quickly outgrow these tools and require a more robust, relational, and secure database. A computerized LIMS brings numerous advantages to the analytical laboratory. These advantages include the automatic generation of bar-coded labels, the ability to pre-log in samples with pre-assigned tests, limits, QC, and the ability to generate bar-coded labels and worklists in advance of the collection. The system provides the ability to rapidly log large batches of samples into the LIMS during major monitoring efforts. The ability to pre-configure tests with associated QC, and set up default methods and automatically generate bar-coded labels greatly expedites sample receipt and reduces errors associated with manual entry.

Sample Login and Tracking
Once samples are received into the laboratory, they are signed off and a computerized LIMS can record who accepted the samples and the date and time that they were received into the laboratory. In addition, it can record which analyses were assigned to those samples. Some systems also have features to record the hold times, which is the amount of time the sample, must be analyzed to obtain an accurate result. Since all of the data is in a central database, user can create a number of reports that can be automatically e-mailed to analysts. It can let them know which samples are approaching their hold times and for managers, backlog and production reports can be created that will provide information on how much work is waiting to be done, how much work was completed respectively.

Advantages of Automated Sample Tracking:
1. Pre-determined, user definable, sample number is automatically generated from a validated system, so that there is no chance of sample numbers being duplicated. Aliquots are also assigned a unique identifier.
2. Ability to scan in, link the chain of custody form, and link that to the sample order for easy retrieval by the laboratory users.
3. Selection of tests from pre-defined pull down lists that are limited by the matrix. Users are not permitted to add tests, methods or parameters on the fly to ensure that the database remains "clean". Otherwise, users could have lead, Pb, and Lead as tests that would all be recognized as different in the database.
4. Pre-defined QC can be configured for each test at login to ensure that certain QC is not forgotten to be run.

Sample Scheduling
Most LIMS offer the ability to automatically schedule sample collection in advance and even the ability to set up projects and studies. This ensures that sampling events are not missed and sample labels and worklists can be pre-printed and pre-logged into the LIMS. This allows the laboratory to prepare for the incoming workload and to prepare the sample bottles in advance.

Data Entry and Electronic Data Transfer
Users can manually enter data and if they choose to turn peer review on, the person that has entered the result cannot approve the result, a supervisor or another analyst must approve the results. The database administrator can configure the LIMS to assign LIMS access (by module and function) and LIMS permissions to specific users based on their laboratory functions. Many systems have unique features that utilize color-coding as results are entered, if they are within certain warning limits, the result is coded another color, and if they are outside warning limits the result is keyed yet another color. The effect of immediate feedback upon result entry allows analysts to double check their work and catch transcription errors prior to result validation and approval.
Another major automation enhancement includes the integration with instruments so that users do not have to re-enter instrument output files into the LIMS. The obvious advantages include: reduction of transcription errors, enhanced security, increased sample throughput and increased efficiency. However, a major advantage is the enhanced data quality. In addition, bi-directional instrument interfaces can be configured so that the LIMS sends the worklist and the order of the samples to be run to the instrument and once the samples have been analyzed, the instrument can export the data back to the LIMS in the correct format. This is especially useful with instruments, which are prolific in their output such as a tandem mass spec or an ICP.

QA/QC Functionality
A key feature of a LIMS is the ability to assign QC to samples, including: blanks, spikes, duplicates, and many other QC types. Users can also view control charts and view trends over times for various tests and at selected sites. Samples and QC standards are grouped into QC batches. It is then possible to view all the quality control related to a sample.

Resource Management
Many systems offer the functionality that will also keep track of employee training records, certification information, re-certification dates, and a description of the training. Users can also keep track of instrument calibration, maintenance, repairs, and calibration dates.

Chemical and Reagent Inventory
The ability to track reagents and chemicals in the laboratory, track lot numbers, expiration date, quantities on hand, vendor information and to create custom reports to reorder items with long lead times as in-house quantities are running low.

A few capabilities of a computerized LIMS that allow users to meet regulatory requirements:

- **Document Management** – the ability to have on-line SOPs (Standard Operating Procedures) which are linked in the LIMS and available to analysts performing the various protocols.
- **Chain of Custody within the Laboratory** – a detailed record of each location that the sample moved to and from during the analysis process, the date and time stamp, which analysts handled the samples and the storage location.
- **Electronic Signatures** – each user must log in with a unique user name and password.
- **Instrument Calibration** – instruments must be in calibration for results obtained on those instruments to be valid. A LIMS can compare the calibration date to the analysis date and if a particular instrument is past due for calibration, it can exclude the user from entering data for that instrument.
- **Employee Training Records** – analysts must pass minimum qualifications for performing analytical analysis methods. The LIMS can block users that lack the training accreditations.
- **Limit Checking** – users are alerted immediately and on-screen when results entered exceed the pre-specified limits that were previously established.

*Table 1* reflects the regulatory compliance landscape and how it impacts various data management systems. There are numerous regulatory requirements and compliance documents that define how the data in a LIMS should be accessed, maintained and protected. CFR 21 part 11 deals primarily with electronic signatures, however there are several other aspects as well, several that deal with laboratory practices and procedures. As illustrated in the table below, there is considerable overlap between the various regulatory guidelines. LIMS administrators need to keep abreast of the latest regulations to ensure that the software solutions that they have implemented in their environments are compliant.
Advantages of Automated Reporting
Another major advantage of a computerized LIMS is automated reporting. Reports can be configured to automatically be printed to a specified server, auto-faxed or auto-e-mailed in a PDF format, which cannot be modified. The LIMS allows users to configure each customer as to how they will receive their report, either via a fax, e-mail or hard copy or via the web portal, or any combination.

Washington Aqueduct LIMS
Since January 2004, the Washington Aqueduct has processed over 11,000 lead samples. The majority of these samples are for compliance with the EPA Lead and Copper Rule. The samples are for various customers with each customer having their own reporting requirements and turn-around times. The LIMS has been essential to meeting the demands of customers and the EPA.

Sample Receiving
Lead samples received by the laboratory usually belong to one of three programs: Lead and Copper samples, Lead Service Line Replacement Samples, Lead Profile Samples. Samples are received into the laboratory where they are logged into the LIMS and assigned a unique sample identification number. Turn around time requirements are then selected from a pulldown menu. Each of the lead service line replacement samples has a unique homeowner ID assigned to them by the contractor managing the collection of these samples. This ID is logged into the LIMS using the Customer Sample ID field in the LIMS (Figure 1). The lead service line replacement samples are delivered in batches to the laboratory. In addition to a chain-of-custody form for each sample, there is a bulk chain-of-custody form for the batch of samples. The bulk chain-of-custody form is scanned into the LIMS and is associated with the login batch of samples.
Sample Workload Management
One primary analyst is responsible for analyzing all the lead samples. It is their responsibility to analyze all the samples within their required turnaround times. The Lead Service Life Replacement samples have a 4-day turnaround time requirement. The Lead and Copper Samples have a 14-day turnaround requirement and the Lead Profile samples have a 21-day turnaround requirement. The analyst is able to use the Custom Report function of the LIMS to pull up a report listing samples to be analyzed and their associated due dates. This report allows the analyst to prioritize the analysis of his samples as required.

Data Entry, Validation and Approval
The results of all samples are entered into the LIMS. The EPA action levels for lead have been programmed into the LIMS so that when a result is greater than the EPA action limit, the result is flagged in red. This alerts the analyst immediately during data entry so that they can confirm that the high result is not a data entry error.

The Washington Aqueduct LIMS is configured so that all entered results must be validated by the QC Officer and then approved by the Laboratory Chief before any data can be reported to a customer. The color coded results easily alert the QC Officer and Laboratory Chief to unusual results so that the customer can be immediately notified. The QC officer is able to view the QC results for samples at the same time as the individual sample results. This facilitates the speed in which the QC Officer can validate data. In addition, the LIMS contains several user customizable fields. The Washington Aqueduct Laboratory has customized the field so that when the QC Officer does a raw data review by reviewing the lab bench sheets on certain samples, he can mark this field. During EPA inspections a query on this field easily relates to the inspectors the number of samples that have undergone a thorough raw data review in addition to a reasonableness check.

Data Reporting
Each customer and each program have unique reporting requirements. The LIMS allows the laboratory to assign reports to special projects and tests for each customer (Figure 2). Each report can be designed to include as much or as little information as each customer desires.
The reports are generated in PDF format and e-mailed to the customer. All contact information for a customer is programmed into the LIMS for automatic delivery if desired. This includes a fax number and e-mail address. There can be more than one contact per customer so that a report may be mailed to multiple parties at once. Currently, all reports are initially e-mailed to the Laboratory Chief. The Laboratory Chief reviews the PDF file and attaches a digital signature using public key infrastructure (PKI) (Figure 3). Each customer has previously been distributed a copy of the private key. The customer is then able to click on the digital signature to see a copy of the digitized signature (Figure 4). The digital signature ensures that reports cannot be modified or changed.
This feature of the Washington Aqueduct Laboratory reports was critical during an EPA data audit. There were discrepancies in some of the data reported to the EPA. The EPA was able to review all the Lead and Copper Reports that the Washington Aqueduct had created and transmitted to our customers. The digital signature and dated e-mails containing the reports provided an audit trail on the generation of reports and distribution to customers.

**Data Export**

In addition to the PDF files, the Washington Aqueduct customers require the data in Excel format so that they may be able to import the data into their own databases. Thus, the customer receives two files: an official PDF report containing a digital signature and an Excel file which the lab will not certify as official lab data. The MS Excel summary report is done as a courtesy to our customers.
The “Master Query” Window was used to easily query data in the LIMS by test, customer and collection date range (Figure 5).

The exporting feature of the LIMS allowed the Washington Aqueduct to quickly respond to Freedom of Information Request. Once the data was retrieved it could quickly be exported to Excel. The excel file was then reviewed for formatting and password protected (Figure 6).
Conclusions
The numerous features of a user-friendly LIMS are critical in allowing laboratories to quickly respond to enhanced monitoring situations, from rapid sample login through to sample tracking and final reporting.

There are several quality assurance and quality control features in a computerized LIMS that ensure a much higher data quality than in manual systems or non-relational databases. In the LIMS system used by the Washington Aqueduct, the LIMS administrator configured the various sites, sampling schedules, tests, parameters, and methods, with default methods and pre-assigned QC to ensure that the proper tests are performed on the proper samples. A key QC feature is peer review which ensures that the analyst that reviewed the sample cannot validate or approve the results for that sample, a QC officer or laboratory manager must review the results.

In addition to managing the thousands of samples analyzed annually by the laboratory, the LIMS also provides functionality that assists laboratories to meet regulatory requirements as those outlined in the beginning of this paper. A LIMS is a necessity in today's modern laboratory and critical to ensuring that high quality data is the output from all the sampling and analysis efforts that ensure a safe potable water supply.
Qualification Testing by Japan Environmental Measurement & Chemical Analysis Association (JEMCA) – Preparation of samples, Data Analysis & Evaluation, and Feedback of Information

Hideo Tabata, Mitsuo Hamaji, and Toru Matsumura

ABSTRACT

Japan Environmental Measurement & Chemical Analysis Association (JEMCA) was founded in 1973. Currently, 560 Japanese private entities engaged in environmental measurement and analysis hold membership of the association. JEMCA is a board member of UILI from 2001, and is also active as an affiliate member of ACIL from 2001.

JEMCA has been conducting qualification testing since 1999 to ensure technology improvement and to secure confidence in quality management and measurement data in laboratories. The qualification test is conducted by having the membership entities to analyze common samples distributed by JEMCA, and evaluating the measurement results statistically. So far, 26 qualification tests have been implemented using environmental media such as environmental water, effluents, soil, and environmental air, with analyzed items such as pH, COD, Nitrogen, Phosphorus, Heavy Metals, VOC and Pesticides, etc.

Application for the qualification test can be done on JEMCA website. Historical test information and statistical evaluation results can also be obtained on the website.

In this presentation, methodology used in JEMCA for sample preparation, statistical data evaluation, and feedback of technical information to membership entities is introduced.
Significance of Changes in 2005 NELAC/USEPA Proficiency Testing Requirements

Dr. Mark J. Carter, Jeff Lowry and Shawn Kassner
Environmental Resource Associates, Inc.
6000 West 54th Avenue
Arvada, CO 80002
mcarter@eraqc.com
303-431-8454

ABSTRACT

Over the past year, there have been many changes in proficiency testing requirements that laboratories must comply with to become accredited. In 1998, USEPA published a Criteria Document that established PT requirements for the potable and non-potable water analytes that the Agency included in their historical PT programs. These included organic and inorganic chemistry, microbiology, radiochemistry and whole effluent toxicity. NELAC established requirements for additional potable and non-potable water analytes in water and requirements for RCRA-Solids.

In 2004, the NELAC program was split into laboratory accreditation Standards development (INELA) and regulatory Standards adoption (NELAC). A Proficiency Testing Board, with state and EPA participation, was established to set PT policy. Working under the PT Board, a broadly-based Fields of Proficiency Testing subcommittee worked to resolve issues with the historical PT requirements and establish expanded FoPTs to better respond to laboratory accreditation needs. In November 2004, NELAC published a major revision of the PT requirements, which must be implemented June 1, 2005. For the potable and non-potable water programs, both “Accreditation” and “Experimental” tables of analytes and PT requirements were established. The significance of the two sets of tables will be discussed and the list of PT analytes will be compared to those regulated or required by major state and federal programs. As it is likely that USEPA will soon defer to these new and revised PT requirements, they will apply to laboratories in non-NELAC as well as NELAC states.

In this paper, we will explain the significant changes in sample design requirements, reporting and acceptance limits. The expected impact on laboratory PT data quality expectations and pass/fail rates will be presented. The consistency of acceptance limits with other measures of laboratory performance such as LCS limits will also be presented.
Newly Developed Biota- and Biological-related Standard Reference Materials for the Determination of Organic Contaminants

National Institute of Standards and Technology
Gaithersburg, MD  20899-8392
301-975-4166
poster@nist.gov

ABSTRACT

Since 1990, the National Institute of Standards and Technology (NIST) has issued a number of cryogenically homogenized tissue SRMs with certified and reference values assigned for organic contaminants. The cryogenically homogenized materials are powder-like with the endogenous water retained. We recently reviewed the development and availability of mussel-tissue SRMs\(^1\) and marine-related tissue SRMs\(^2\). The series of natural mussel-tissue SRMs (Organics in Mussel Tissue, *Mytilus edulis*) has been developed from mussels collected in Boston Harbor, MA. SRM 1974b is the third and current material in this series and has certified and reference values for a range of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners (1 non-*ortho*), total PCBs, chlorinated pesticides, methyl-Hg, Hg, selected trace elements, and total extractable organics. An additional mussel tissue SRM, SRM 2977, is also available. This is a freeze-dried tissue homogenate prepared from mussels collected in Guanabara Bay, Brazil\(^1\). Two cryogenically homogenized fish tissue SRMs\(^2\) have been developed from filleted adult lake trout (*Salvelinus namaycush namaycush*). SRMs 1946 (Lake Superior Fish Tissue) and 1947 (Lake Michigan Fish Tissue) are characterized for a range of PCB congeners, chlorinated pesticides, methyl-Hg, Hg, selected trace elements, fatty acids, calories, and proximates. SRM 1946 was also examined for total toxaphene and toxaphene congeners\(^3\) and SRM 1947 has been examined for selected polybrominated diphenyl ether (PBDE) congeners.

Two biologically-related SRMs are a cod liver oil SRM, SRM 1588a, and a human serum SRM, SRM 1589a. SRM 1588a is a reissue of the original cod liver oil SRM 1588 with an expanded list of PCB congeners and chlorinated pesticides having certified concentrations. The material has been examined for selected PBDE and toxaphene congeners, and total toxaphene\(^3\). Concentration values for additional PCBs, chlorinated pesticides, PBDEs, and selected fatty acids will be added to the material's Certificate of Analysis. The human serum SRM, SRM 1589a, was certified in conjunction with the Centers for Disease Control (CDC) with certified concentrations for natural levels of selected PCB congeners and chlorinated pesticides along with reference values for selected polychlorinated dibenzo-\(p\)-dioxins/dibenzofurans (PCDDs/PCDFs) congeners. Two new SRMs for serum analyses currently in development are SRMs 1957 and 1958. SRM 1957 will be characterized for natural levels of selected PCDDs, PCDFs, PCBs, PBDEs, chlorinated pesticides, toxaphene congeners, polychlorinated naphthalenes, and other halogenated compounds. SRM 1958 will be characterized for the same suite of analytes though these compounds will be added to the material. Measurements of organic contaminants in the biota- and biologically-related SRMs will be presented with an emphasis on the approach and methods used for the chemical characterization of these natural-matrix SRMs.


Session 3

Inorganic Methods: Elemental Analysis by ICP Techniques
Current Status of the RCRA Inorganic Methods Program

Shen-Yi Yang
US EPA Office of Solid Waste Economics, Methods, and Risk Analysis Division, 1200 Pennsylvania Ave., NW (5307W), Washington, DC 20460
E-mail: Yang.Shen-Yi@epamail.epa.gov

ABSTRACT

This keynote presentation will give an overview of the RCRA methods development activities for Update IV SW 846 methods (for inorganics and metals). This will include details on developments on the Methods Innovation Rule, Perchlorate monitoring, updates to SW-846 methods, new methods and method development.
Current Status: RCRA Inorganic Methods Development Program

Shen-yi Yang
U. S. Environmental Protection Agency
Office of Solid Waste – Methods Team
1200 Pennsylvania Ave., N. W. (5307W)
Washington, D.C. 20460

Topics for Discussion

- Current Issues
  - Methods Innovation Rule
  - Perchlorate analysis

- Revisions to SW-846
  - Updates IIIB and IV to Third Edition
  - Fourth Edition

- New Methods Available

- Ongoing Methods Development Projects
Current Status of the Methods Innovation Rule (MIR)

- Regulation development initiated to remove mandatory requirements to use SW-846 methods for analyses that are not method-defined parameters in the RCRA regulations
- MIR proposed on October 30, 2002 (67 FR 66251)
- Comment period closed on February 28, 2003
- OSW Methods Team completed responses to public comments

Current Status of the MIR (Cont.)

- Methods Team prepared the Final Rule and addressed all procedural issues
- Final Rule received side agreement concurrence
- Final Rule was signed by the EPA Administrator and published on June 14, 2005 (70 FR 34537)
- Promulgation of MIR eliminates the need to publish SW-846 Updates as regulation
- SW-846 functions as originally intended: as a “guidance document”
Current Status of the MIR (cont.)

- Updates will be put out for public comment in the Federal Register as Notice of Data Availability (NODA)
- Updates will be added to SW-846 through Federal Register notices modifying a guidance document
- No change to method-defined regulations

Perchlorate

- Perchlorate \((\text{ClO}_3^-)\): Both natural and human sources
- Serves primarily as an oxidant in the manufacture of solid propellant, missiles, and fireworks
- Other contamination sources:
  - Highway safety flares production and disposal
  - Airbag inflators
  - Nitrate-based fertilizers
- Inhibits iodine uptake by the thyroid gland and thus affects:
  - Thyroid hormone production
  - Thyroid regulation of metabolism
  - Neurological development of fetus and newborn
  - May potentially result in thyroid gland tumors
- Presently, perchlorate has been detected in more than twenty (20) States, various aquifers, crops, cow milk, beers and wine.
Perchlorate Analysis

- Current method for solids, published in 2000, has several limitations
- Biased results could hinder clean-up and monitoring efforts
- New information and analytical technologies have recently become available
- **OSW Perchlorate Task Force** initiated. Lead by OSW, members include representatives from:
  - DOD
  - Instrument vendors
  - EPA regional laboratories
  - ORD laboratories
  - Commercial laboratories
- **OSW Perchlorate Task Force Objectives:**
  - Refine current analytical method
  - Develop two new improved methods to provide better identification and quantification for perchlorate in soil, sludge, wastewater, and high salt water

---

Update IIIB of Third Edition

- Update IIIB was issued to remove references which required the use of Chapter Nine in existing method-defined parameters.
- These 11 methods will remain “incorporated by reference” in RCRA regulations.
- No other changes were made to these methods, except for correcting a typo in the method number of Method 9070A
  - **Method 1010A:** Pensky-Martens Closed-Cup Method for Determining Ignitability
  - **Method 1020B:** Small Scale Closed Cup Method for Determining Ignitability
  - **Method 1110A:** Corrosivity Toward Steel
  - **Method 1310B:** Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test
  - **Method 9010C:** Total and Amenable Cyanide: Distillation
  - **Method 9012B:** Total and Amenable Cyanide: Automated Colorimetric, with Off-line distillation
  - **Method 9040C:** pH Electrometric Measurement
  - **Method 9045D:** Soil and Waste pH
  - **Method 9060A:** Total Organic Carbon
  - **Method 9070A:** Hexane Extractables from Aqueous Matrices (Method Number Correction)
  - **Method 9095B:** Paint filter Liquids Test
Update IV of Third Edition

- Will be finalized as a NODA after MIR promulgation
- Combines Updates IVA and IVB
- 24 new methods (12 Organic & 12 Inorganic)
- 24 revised methods (16 Organic & 8 Inorganic)
- 3 OAQPS air methods added
- 44 methods deleted (1 Organic & 43 AA methods integrated into two methods, one for FLAA and one for GFAA)
- All methods in Fourth Edition format

New Inorganic Methods in Update IV

- Method 1040: Test Method for Oxidizing Solids
- Method 1050: Test Methods to Determine Substances Likely to Spontaneously Combust
- Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
- Method 6500: Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis
- Method 6800: Elemental and Speciated Isotope Dilution Mass Spectrometry
- Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry
- Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
- Method 7474: Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
- Method 9000: Determination of Water in Waste Materials by Karl Fisher Titration
- Method 9001: Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction
- Method 9058: Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection
- Method 9216: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode
Revised Inorganic Methods in Update IV

- Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
- Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils
- Method 6010C: Inductively Coupled Plasma – Atomic Emission Spectrometry
- Method 6020A: Inductively Coupled Plasma – Mass Spectrometry
- Method 7000B: Flame Atomic Absorption Spectrophotometry
- Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
- Method 9056A: Determination of Inorganic Anions by Ion Chromatography
- Method 9210A: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode

Deleted Inorganic Methods in Update IV

- 43 Individual Flame AA and Graphite Furnace AA methods integrated into two methods, Method 7000B - Flame AA and Method 7010 - GFAA
Fourth Edition of SW-846

- Designed for electronic format
- Organized in two sections:
  - Methods for laboratory analysts.
  - Systematic planning, QA/QC and sampling for both project planners and laboratory analysts.
- Major revisions to Chapter One on QA/QC
- Expansion of guidance on methods selection
- Methods to be arranged both by series and sequential method numbers

Fourth Edition of SW-846
Progress to Date

- Draft of Chapter One completed and distributed for Workgroup review.
- New draft “Style Guide” for preparation of Fourth Edition methods
  - Based on EMMC format
  - Distributed to Workgroup
  - Posted on Methods Team Web Site
- All new method submissions will be in Fourth Edition format
Fourth Edition of SW-846 Progress to Date

- All Third Edition methods currently being revised have been converted to Fourth Edition format including all Update IV methods and "New Methods"

- Original expected timeframe of having the Fourth Edition completed and ready for public comments concurrent with the promulgation of the MIR has now changed in light of the current budget situation.

Completed New and Revised Inorganic Methods for Fourth Edition

- **Method 9015**: Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection

- **Method 9013A**: Cyanide Extraction Procedure for Solids and Oils

- **Method 3200**: Mercury Species Fractionation and Quantification by Microwave Assisted Extraction, Selective Solvent Extraction and/or Solid Phase Extraction
New Method 9015

- Determines metal cyanide complexes (of iron, cobalt, silver, gold, copper, and nickel) in waters and alkaline solid extracts.
- Based on ion chromatography:
  - Anion exchange separation
  - UV spectroscopic detection
- Simple alkaline pre-extraction procedure (Method 9013) for solids
- Developed and drafted by Sharon Drop of SAIC, and Dr. Rajat Ghosh of The Retec Group, Inc.
- The inter-lab studies for quantifying both low-level (ppb) and high-level (ppm) metal cyanide complexes in waters and solid matrices were completed
- The study reports and method were reviewed by the Workgroup and revised based on their comments
- Method was posted on the OSW Methods website for public use and comments

Classification of Dissolved Cyanide Species

Increasing Binding Energy, Decreasing Dissociation Constants (-log K)

Increasing Stability

-9.2 -17.9 -19.6 -23.1 -30.2 -32.8 -35.4 -40.0 -43.6 -64.0

Free Cyanide

Weakly-complexes Cyanides

Strongly-complexes Cyanides

Analytical Definitions

Cyanides Amenable to Chlorination

Available Cyanide (EPA OA-1677)

Total Cyanide

J. Drop, R. S. Ghosh, D. Thomas, A. Battaglia, R. Ripper, *NEMC, 2009*
Revised Method 9013

- All CN species are soluble under alkaline conditions
  - Simple CN salts: \[ ACN \xrightarrow{pH \geq 11} A^+ + CN^- \]
  - Metal CN complex salts: \[ A[M(CN)]_x \xrightarrow{pH \geq 11} aA^+ + [M(CN)]_x^2- \]
  \[ M[M(CN)]_y \xrightarrow{pH \geq 11} tT^2 + b[M(CN)]_y^2- \]
  - \( A = \) alkali or alkaline earth metal
  - \( M = \) transition metal
  - \( T = \) transition metal

- Simple alkaline pre-extraction procedure (Method 9013) applicable for all determinative CN Methods: 9010, 9012, 9014
- Modification added to existing Method 9013 for pre-extraction prior to Method 9015 IC analysis of metal cyanide complexes
- Method 9013 evaluated during Method 9015 inter-lab study
  - Real-world solids spiked with Fe\(_2\)Fe(CN)\(_6\) ("Prussian Blue")
  - Solid extracts analyzed for total CN - Good recoveries obtained

New Method 3200

- Sequential extraction procedure for mercury speciation
- Separates total mercury into four different fractions:
  - Extractable inorganic mercury
  - Extractable organic mercury
  - Semi-mobile mercury
  - Non-mobile mercury

- Extracts can be analyzed by determinative methods using CVAA, ICP-MS, and HPLC-ICP-MS
- Developed and drafted by Dr. Skip Kingston at Duquesne University
- The inter-lab method validation studies were completed. Paper published:
- Study report and draft method reviewed by the Workgroup
- Method posted this July on the OSW Methods web site for public comments
Ongoing Methods Development Projects

- **Method 9058**: (Perchlorate by IC/Conductivity)
- **Method 6850**: (Perchlorate by LC/MS or LC/MS/MS)
- **Method 6860**: (Perchlorate by IC/MS or IC/MS/MS)

Method 9058 for Perchlorate

- Originally proposed in November 2000
- Current method scope and applicability:
  - 4 µg/L sensitivity for spiked reagent water samples
  - Conductivities ≤ 1000 µS/cm
  - Conductivities > 1000 µS/cm have not been tested
  - Potential for false positive and false negative results due to sample matrix interferences
    - Co-eluents
    - High total dissolved solids
  - Perchlorate identification in unfamiliar samples requires confirmation using another analytical column or another approved analytical technique such as IC/MS, LC/MS, LC/MS/MS, or ion selective electrode
    - Especially important for compliance or other regulatory purposes
**Refining Method 9058**

- **Ongoing Goals:**
  - Broaden applicability to aqueous and leachate samples having high total dissolved solids
  - Lower quantitation level to sub-ppb ClO$_4^-$
  - Improve chromatographic separation
  - Reduce false positive and negative results
  - Include an extraction procedures for solids
  - Continue refinement based on intended use:
    - Screening
    - Long-term monitoring

---

**Refining Method 9058 (Cont.)**

- **Next Steps:**
  - Perform additional extraction studies to develop the recommended sample extraction and preparation procedure
  - Determine if pre-concentration and pre-elution steps are necessary
  - Include improved chromatography equipment:
    - Separation columns – Dionex IonPac® AS16
    - Suppressor – Dionex ASRS® Ultra II
  - Consider whether or not to include a new eluant generator and/or a second confirmatory column
Method 6850 for Perchlorate

- Draft method submitted to OSW for evaluation in July 2004
- Based on high performance liquid chromatography separation and mass spectrometry detection (LC/MS)
  - Isocratic separation: K’ (Prime) Technologies, Inc. - KP-RPX250 column
  - Negative electrospray ionization
  - Detection and quantitation using m/z 83, 85 and 89
- Provides confirmation of perchlorate identification:
  - Detection of ClO^- internal standard at m/z 69
  - ^35Cl/^{37}Cl isotopic abundance ratio monitoring
- Applicability:
  - Soils, sludges, wastewaters and high salt waters
  - Also possibly applicable to other matrices (e.g., biota), but these are not being evaluated by OSW
- Final method may allow flexibility in detection pending outcome of validation study:
  - MS detection - m/z 83, 85, 89
  - MS detection – m/z 99, 101 and 107
  - MS/MS detection - m/z 83, 85, 89

Method 6850 Current Status

- Draft method revised based on comments received from the OSW Perchlorate Task Force
- Revised method forwarded for the RCRA Inorganic Workgroup for review
- 14 laboratories volunteered for participation in inter-lab validation study initiated in June 2005
- Phase I initial demonstration of proficiency (IDP) study completed
  - Analysis of perchlorate in spiked reagent waters
  - Results to be used to select final labs for participation in Phase II inter-lab study on real-world matrices
- IDP test results were shared with the OSW Perchlorate Task Force and study participants
- Phase II of method validation study is scheduled for August 2005
  - Analysis of perchlorate in spiked real-world solids and waters
Method 6860 for Perchlorate

- Draft method submitted to OSW for evaluation in January 2005
- Ion chromatography separation and mass spectrometry detection (IC/MS)
  - Isocratic separation: Choice of column under evaluation
  - Conductivity suppression of column effluent to remove salts prior to entry into MS
  - Negative electrospray ionization
  - Detection and quantitation using MS/MS at m/z 83, 85 and 89
  - MS detection also allowed using m/z 99, 101 and 107
- Provides confirmation of perchlorate identification:
  - Detection of ClO\textsuperscript{18}_2\textsuperscript{-} internal standard at m/z 89 (or 107)
  - \textsuperscript{35}Cl/\textsuperscript{37}Cl isotopic abundance ratio monitoring
- Applicability:
  - Soils, sludges, wastewaters and high salt waters
- Differences between Methods 6850 and 6860:
  - Analytical column (LC vs. IC column)
  - Mobile phase
  - Use of conductivity suppressor and detector (Method 6860 only)

Method 6860 Current Status

- The draft method is being revised based on comments received from the OSW Perchlorate Task Force
- 14 laboratories volunteered for participation in inter-lab validation study in June 2005
- Phase I initial demonstration of proficiency (IDP) study completed (conducted concurrently with Method 6850 study)
  - Analysis of perchlorate in spiked reagent waters
  - Results to be used to select final labs for participation in Phase II inter-lab study on real-world matrices
- IDP test results were shared with the OSW Perchlorate Task Force and study participants
- Phase II of method validation study is scheduled for August 2005
  - Analysis of perchlorate in spiked real-world solids and waters
Contact Addresses and Phone Numbers

- Methods Team Home Page: [www.epa.gov/SW-846](http://www.epa.gov/SW-846)

- Methods Information Communication Exchange (MICE)
  - Phone No.: (703)-676-4690
  - E-mail: mice@cpmx.saic.com

- Shen-yi Yang
  - Phone No.: (703)-308-0437
  - E-mail: yang.shen-yi@epa.gov
Technological Advances and Optimisation in ICP-OES to Meet the Demands of Modern, Routine Elemental Laboratories

Paul Neal
Thermo Electron Corporation, Mercers Row, Cambridge, UK.
E-mail: Paul.Neal@Thermo.com

ABSTRACT

ICP-OES has become the technique of choice for a large range of applications. The technique is relatively interference-free and provides analysis in the low ppb levels for most elements.

Modern laboratories require rugged, cost-effective and flexible ICP-OES solutions, which provide high throughput with low detection limits. In addition, laboratories are becoming increasingly aware of the need to provide easier set-up procedures for sample introduction, plasma optimisation and method development to maximise throughput and minimise the amount of operator time required.

To meet the expectations of the analytical community, instruments need to increase sensitivity and stability thereby driving down detection limits to even lower levels all the while increasing productivity. Recent improvements in solid-state detector arrays, optical configurations and general instrument components will allow modern ICP-OES instruments to evolve and bring the technique closer to its full potential.

Technical solutions will be presented with supporting data to show how the technological advances have and will benefit the real analysis of environmental samples.
Developing ICP-OES to Meet the Demands of Routine Laboratories

21st Annual NEMC Conference 2005

General Lab Objectives and Requirements

- Performance
  - Must meet customers analytical needs
  - Compliance with regulations/protocols
- Throughput
  - Maximum sample throughput to maximise savings
- Cost of Ownership
  - Reduced service, maintenance, gas and consumables costs
  - Maximise Uptime
  - Downtime equals increased costs and reduced revenue
Key Requirement for Environmental Labs

- **Performance**: best met with dual view ICP
  - **Axial mode**
    - Best performance in minimal matrix solutions
    - Need to meet EPA protocol requirements
    - Lowest detection limits required
  - **Toxic Elements = Low wavelength lines**
    - e.g. As 189nm, Ti 190nm, Se 196nm, Pb 220nm
  - **Radial mode**
    - Need to measure easily ionised elements
    - Na, K, Ca, Mg in ppm range
  - **Long Term Stability**
    - Lower recalibration rate
    - Improved QC success rate
    - Efficient use of available instrument time

ICP-OES – creating the ideal system

In order to overcome the following:
- Matrix tolerance, ionization effects, operating parameters
  effect on analytical performance

The ideal system should incorporate:
- Excellent matrix handling capabilities
- Robust source
- Easy user optimization
Interferences in ICP-OES

The interferences in ICP-OES break down into three categories:

- Physical
- Spectral
- Chemical

In order to understand how to overcome the interferences, we need to examine where they arise in the plasma, and the effect they have on analytical performance.

The Mechanism of Excitation within the source

The route of the sample from test tube to source
Emission Zones within the plasma

The sites of analytical performance and interference effects

Yttrium bullet test

Y ion emission
YO molecular emission
Y atom emission

Use of optimised Torch Design

- Axial Torch Design
  - TraceTech™ torch reduces plasma perturbation

  TraceTech™ Torch

  - Disturbances from air flow are reduced by enclosing the plasma over a greater distance.
How Is This Achieved - Torch Enclosure

- Air Velocity Measurements with Computational Fluid Dynamics
- Shows low air velocity in the region of the torch - good
- High velocity elsewhere - good

Optimisation of torch length - 60mm, 70mm, 100mm lengths

- Torch length vs detection limit – the longer torches provide better D.L.s than the shorter
- Effect of Ca on Na intensity – shorter torches perform better coping with ionisation effects.
Dual View Optics

Viewed axially, more light is obtained from the emission zone, providing increased sensitivity. However, it is not possible to focus only on the interference-free zones within the plasma. This configuration is more susceptible to plasma loading effects and easily ionized element interference.

Viewed radially, the optics collect light only in the areas of ion and atom emission. The cooler zones of the ICP where interferences are present, are not viewed and are therefore not a problem.

Spray Chambers modelling

- **Axial Spray Chamber Study**
  - CFD enabled axial design optimisation

  Laminar flow which is good for stability

  Velocity Isobars
Examples applied to Improving Performance

- Axial Spray Chamber Design
  - Long-necked axial cyclonic spray chamber produces laminar flow and better DLs.
  - Cyclone design gives better droplet discrimination and efficient aerosol transport

Echelle Spectrometer Components

- Entrance Slit
- Collimating Mirror
- Primary dispersing element – order
- Secondary dispersing element – wavelength
- Camera Mirror
- Detector
Detector Requirements

- Simultaneous measurement of analytical signals
- Wide spectral response
- High quantum efficiency
- Low noise characteristics
- High Dynamic range
- Fast measurement times

RACID86 Detector

- Cooled Scientific Grade imaging system
- Self contained unit with on-board Pentium processor
- Dynamic control of emission signals
- Contiguous pixel structure for high sensitivity
- Large 27um pixels with large well capacity
- Lumogen coating for extended UV sensitivity
CID Benefits

- True Random Pixel Access
  - Dynamic readout of pixel charge
  - Faster processing times
- Non-destructive readout
  - Performs multiple reads on selected pixels
  - Allows both intense and weak signals to be measured simultaneously
  - Improves dynamic Range – up to $10^8$
- Collective Read – groups of pixels summed and read non destructively or collectively
  - Improved signal to noise
- Auto - integrate algorithm combines "Fixed Time" full frame measurements with Random Access Integration
  - Improves dynamic range
  - No compromise on precision
  - Better signal to background ratio

Improved Detector Performance

- Reduced background signals
- Improved peak definition
- Improved resolution
- Wide dynamic range
- Improved signal to noise
Optimised Noise Correction

- Simultaneous background correction corrects for plasma noise
- Performance is limited by shot noise
- Detection limits optimum after 30 seconds
- Faster analysis times

Improved Performance

- Optimised design improves image quality
- Much reduced stray light
- New detector with faster readout and lower noise
- Detection limits improved by factor 2-3
Stable instrument allows to “load and leave”

- **Weekend analysis**
  - New extended autosamplers allow up to 720 samples
  - Comprehensive safety interlock protection
  - Data integrity assured with extensive QC protocols
  - Reduces costs by increasing time available for analysis without increasing working hours
  - Working weekends is possible if safe, stable instrument

---

**Performance Data - EPA 6010B**

- **Method Detection Limits**
  - Parameters
    - 1200W RF forward power
    - 0.5L/min Aux gas, 0.65L/min Neb gas, 1.7ml/min sample uptake
    - Glass cyclone and concentrator
  - River Sediment (NBS 2704) and Sewage Sludge (BCR 146) prepared according to US EPA 3050.
  - Calibration with multi-element standards from certified ICP standard solutions.
  - Initial and Continuing Calibration Verification solutions used according to EPA 6010B regulations.

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection Limit</th>
<th>Recovery</th>
<th>S/N Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>103.765</td>
<td>Room</td>
<td>4.0</td>
</tr>
<tr>
<td>As</td>
<td>169.583</td>
<td>Room</td>
<td>3.0</td>
</tr>
<tr>
<td>Bi</td>
<td>353.519</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>B</td>
<td>305.699</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Be</td>
<td>405.463</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Br</td>
<td>355.107</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Ca</td>
<td>517.955</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Ce</td>
<td>512.535</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Co</td>
<td>200.615</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Cr</td>
<td>300.679</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu</td>
<td>32.174</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe</td>
<td>107.341</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Hf</td>
<td>100.491</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>K</td>
<td>410.768</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg</td>
<td>219.129</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Mn</td>
<td>203.30</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Na</td>
<td>309.059</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>205.055</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>P</td>
<td>196.9</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Pb</td>
<td>208.917</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Sb</td>
<td>258.511</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Sr</td>
<td>60.061</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Ta</td>
<td>107.069</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Ti</td>
<td>357.959</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>U</td>
<td>223.403</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>60.7</td>
<td>Room</td>
<td>2.0</td>
</tr>
<tr>
<td>Zr</td>
<td>208.3</td>
<td>Room</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Performance Data

- **Long Term Stability**
  - Stability of 100ppb standard over 8 hours.

- **Spike Recovery**
  - A sample of Buffalo River Sediment was used for spiking to test recoveries.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference Value</th>
<th>Solution Conc. (ug/L)</th>
<th>Spike Conc. (ug/L)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>235</td>
<td>275</td>
<td>30</td>
<td>92</td>
</tr>
<tr>
<td>Ba</td>
<td>414.0</td>
<td>420.4</td>
<td>10</td>
<td>116</td>
</tr>
<tr>
<td>Cd</td>
<td>34.5</td>
<td>43.6</td>
<td>10</td>
<td>91</td>
</tr>
<tr>
<td>Ca</td>
<td>145</td>
<td>151</td>
<td>10</td>
<td>116</td>
</tr>
<tr>
<td>Cr</td>
<td>1250</td>
<td>1402</td>
<td>10</td>
<td>126</td>
</tr>
<tr>
<td>Cu</td>
<td>906</td>
<td>1003</td>
<td>10</td>
<td>116</td>
</tr>
<tr>
<td>Mn</td>
<td>5500</td>
<td>5402</td>
<td>10</td>
<td>116</td>
</tr>
<tr>
<td>Ni</td>
<td>441</td>
<td>450</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>1810</td>
<td>1806</td>
<td>10</td>
<td>97</td>
</tr>
<tr>
<td>Zn</td>
<td>37.9</td>
<td>47</td>
<td>10</td>
<td>91</td>
</tr>
<tr>
<td>V</td>
<td>955</td>
<td>1004</td>
<td>10</td>
<td>108</td>
</tr>
<tr>
<td>Cr</td>
<td>4290</td>
<td>4462</td>
<td>10</td>
<td>126</td>
</tr>
</tbody>
</table>

Concluding remarks

- There are many areas that can be improved in routine lab analysis
  - Throughput: sample handling and measurement
  - Performance to meet the needs of regulations today and tomorrow
  - Stability to improve the reliability and repeatability of measurement
- There are many tools that can be applied to understand and improve ICP-OES instrumentation
  - Computer aided design (CAD)
  - Computational fluid dynamics (CFD)
  - Finite Element Analysis (FEA)
  - Design for manufacture/assembly (DFM/DFA)
- Expect higher performance, more stable instrumentation with higher throughput in the future.
Valuation and Comparison of ICP and ICP-MS for Environmental Applications

Mr. Albert F. Vicinie, Mr. William Reinheimer
Severn Trent Laboratories, 301 Alpha Drive, RIDC Park, Pittsburgh, PA 15238
Rvicinie@stl-inc.com

ABSTRACT

STL Pittsburgh is a full service environmental laboratory that provides analytical services to both routine and specialty market segments in the determination of metals in a variety of matrices. This presentation is to review the process and challenges of evaluating and implementing new techniques, different technologies and design approaches of various manufacturers. It will also provide a review of the factors motivating laboratories to transition from ICP-AES to ICP/MS, the benefits realized resulting from the tradition and an evaluation of its effectiveness in a production environment and comparison to previous generation ICP/MS currently in use.
Transitioning to ICP/MS in an Environmental Laboratory

Mr. Bill Reinheimer - STL Pittsburgh
Mr. Albert F. Vicinie - STL Pittsburgh

“Pre-existing Condition”

- 1 TJA 61E ICP AES (radial)
  - Primarily for TCLP determinations
  - Used for Ca, Mg, Na, K

- 2 TJA Trace-ICP AES (axial)
  - Slightly different element configurations
  - Primarily for GW, WW, soils and tissues
  - Worksharing GFAA

- ~ 2,600+ billable samples/month
Why Change?

- Needed lower reporting limits
- Needed lower MDLs
- Matrix effects resulted in elevated RLs/MDLs
- Needed additional Capacity
- Replace obsolete technology
- Improve productivity
- Respond to increased Market Demand
- Elimination of inter-element spectral Interferences

Initial Challenges

- Staff while very experienced in ICP, no experience in ICP/MS
- Determining which product to choose and what options (CCT, DRC, etc)
- Data Uploads didn’t exist for this instrument
- CLP like deliverables needed created
Decision Process

- Determine what our client base DQO needs are currently
- Project what DQO needs would be in future
- Likely Matrix issues that need considered
- Productivity/Cost evaluation

DQOs

- Market segmentation
  - Ecological Risk assessments (tissues)
  - Brownsfields Programs (PA Act 2)
  - Sediment programs
  - Groundwater programs
  - Client specific program requirements
  - Product verification
  - Increased confidence in lower values
Service Considerations

- Telephone support and response
- Applications support
- Field Service Engineer experience and response time
- Remote access

“The Results”

Did we accomplish our objective?
Instrument Detection Limit Comparison (IDLs)

- Significant improvement (>50X)
  - Tl, Sb, Co, Ag, Mo
- Notable improvement (>10X)
  - Be, V, Na, Pb, As, K, Se, Cu, Ni
- Negligible difference (<3X)
  - Fe, Sr, Al, Cr, Mg, Ca, Zn

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP/MS</th>
<th>ICP</th>
<th>Element</th>
<th>ICP/MS</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL</td>
<td>0.0035</td>
<td>3.3</td>
<td>B</td>
<td>0.106</td>
<td>1.0</td>
</tr>
<tr>
<td>SB</td>
<td>0.0086</td>
<td>3.1</td>
<td>MN</td>
<td>0.0228</td>
<td>0.19</td>
</tr>
<tr>
<td>CO</td>
<td>0.0051</td>
<td>0.46</td>
<td>Ti</td>
<td>0.089</td>
<td>0.63</td>
</tr>
<tr>
<td>AG</td>
<td>0.0093</td>
<td>0.66</td>
<td>Si</td>
<td>0.078</td>
<td>0.61</td>
</tr>
<tr>
<td>MO</td>
<td>0.03</td>
<td>2.1</td>
<td>CD</td>
<td>0.046</td>
<td>0.23</td>
</tr>
<tr>
<td>BE</td>
<td>0.014</td>
<td>0.45</td>
<td>SN</td>
<td>0.053</td>
<td>0.27</td>
</tr>
<tr>
<td>V</td>
<td>0.0347</td>
<td>1.1</td>
<td>BA</td>
<td>0.178</td>
<td>0.59</td>
</tr>
<tr>
<td>NA</td>
<td>4.115</td>
<td>13.0</td>
<td>FE</td>
<td>5.016</td>
<td>12.9</td>
</tr>
<tr>
<td>PB</td>
<td>0.0468</td>
<td>1.4</td>
<td>SR</td>
<td>0.0973</td>
<td>0.22</td>
</tr>
<tr>
<td>AS</td>
<td>0.061</td>
<td>1.5</td>
<td>AL</td>
<td>10.12</td>
<td>25.3</td>
</tr>
<tr>
<td>K</td>
<td>3.67</td>
<td>67.3</td>
<td>CR</td>
<td>0.3</td>
<td>0.62</td>
</tr>
<tr>
<td>SE</td>
<td>0.18</td>
<td>2.5</td>
<td>MG</td>
<td>5.01</td>
<td>9.6</td>
</tr>
<tr>
<td>CU</td>
<td>0.113</td>
<td>1.3</td>
<td>CA</td>
<td>6.44</td>
<td>8.2</td>
</tr>
<tr>
<td>Ni</td>
<td>0.105</td>
<td>1.2</td>
<td>ZN</td>
<td>2.38</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Method Detection Limit Comparison
Method 6020 Vs Method 8010B
ug/L

<table>
<thead>
<tr>
<th>ICP/MS</th>
<th>ICP</th>
<th>ICP/MS</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCL</td>
<td>MDL</td>
<td>MCL</td>
</tr>
<tr>
<td>TL</td>
<td>0.014</td>
<td>2.300</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.033</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>MN</td>
<td>0.044</td>
<td>0.110</td>
<td></td>
</tr>
<tr>
<td>PB</td>
<td>0.044</td>
<td>1.980</td>
<td></td>
</tr>
<tr>
<td>AG</td>
<td>0.050</td>
<td>0.490</td>
<td></td>
</tr>
<tr>
<td>SR</td>
<td>0.054</td>
<td>0.170</td>
<td></td>
</tr>
<tr>
<td>SB</td>
<td>0.073</td>
<td>4.000</td>
<td></td>
</tr>
<tr>
<td>BE</td>
<td>0.096</td>
<td>0.710</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.160</td>
<td>1.300</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.120</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.130</td>
<td>1.200</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.140</td>
<td>0.760</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.190</td>
<td>2.860</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.150</td>
<td>0.480</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.300</td>
<td>3.100</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.340</td>
<td>1.330</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.380</td>
<td>22.800</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.463</td>
<td>3.430</td>
<td></td>
</tr>
</tbody>
</table>

Tissue DQO Comparison

<table>
<thead>
<tr>
<th>ANALYTE</th>
<th>6010</th>
<th>6010</th>
<th>6020</th>
<th>6020</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RLS</td>
<td>MCLs</td>
<td>RLS</td>
<td>MCLs</td>
</tr>
<tr>
<td>Silver</td>
<td>0.500</td>
<td>0.366</td>
<td>0.100</td>
<td>0.034</td>
</tr>
<tr>
<td>Aluminum</td>
<td>20.000</td>
<td>6.516</td>
<td>3.000</td>
<td>0.460</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5.000</td>
<td>0.690</td>
<td>0.100</td>
<td>0.012</td>
</tr>
<tr>
<td>Beryllium</td>
<td>4.000</td>
<td>0.154</td>
<td>0.100</td>
<td>0.007</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.500</td>
<td>0.143</td>
<td>0.100</td>
<td>0.007</td>
</tr>
<tr>
<td>Cobalt</td>
<td>5.000</td>
<td>0.120</td>
<td>0.050</td>
<td>0.003</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.000</td>
<td>0.210</td>
<td>0.200</td>
<td>0.027</td>
</tr>
<tr>
<td>Copper</td>
<td>2.000</td>
<td>0.448</td>
<td>0.300</td>
<td>0.011</td>
</tr>
<tr>
<td>Iron</td>
<td>10.000</td>
<td>1.313</td>
<td>5.000</td>
<td>0.618</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.500</td>
<td>0.011</td>
<td>0.050</td>
<td>0.008</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.000</td>
<td>0.477</td>
<td>0.100</td>
<td>0.018</td>
</tr>
<tr>
<td>Lead</td>
<td>0.300</td>
<td>0.207</td>
<td>0.100</td>
<td>0.002</td>
</tr>
<tr>
<td>Antimony</td>
<td>1.000</td>
<td>0.181</td>
<td>0.050</td>
<td>0.005</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.500</td>
<td>0.338</td>
<td>0.800</td>
<td>0.016</td>
</tr>
<tr>
<td>Tin</td>
<td>10.000</td>
<td>1.414</td>
<td>5.000</td>
<td>0.233</td>
</tr>
<tr>
<td>Thallium</td>
<td>1.000</td>
<td>0.547</td>
<td>0.100</td>
<td>0.000</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.000</td>
<td>0.272</td>
<td>0.500</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Linear Dynamic Range

- Essentially equivalent to ICP for most analytes

- No significant productivity impact of additional dilutions due to elemental concentrations

- Could be expanded further but rinse out time impacted

Linear Dynamic Range Comparison
(mg/L)

<table>
<thead>
<tr>
<th></th>
<th>ICPMS 6020</th>
<th>ICP 600</th>
<th>ICPMS 6010B</th>
<th>ICP 6010B</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>1000</td>
<td>600</td>
<td>BA</td>
<td>12.5</td>
</tr>
<tr>
<td>Mg</td>
<td>1000</td>
<td>600</td>
<td>Cu</td>
<td>12.5</td>
</tr>
<tr>
<td>K</td>
<td>400</td>
<td>400</td>
<td>SB</td>
<td>12.5</td>
</tr>
<tr>
<td>Al</td>
<td>250</td>
<td>600</td>
<td>Sr</td>
<td>12.5</td>
</tr>
<tr>
<td>Fe</td>
<td>225</td>
<td>500</td>
<td>Tl</td>
<td>12.5</td>
</tr>
<tr>
<td>Na</td>
<td>225</td>
<td>400</td>
<td>Zn</td>
<td>12.5</td>
</tr>
<tr>
<td>Si</td>
<td>150</td>
<td>50</td>
<td>Pb</td>
<td>12.5</td>
</tr>
<tr>
<td>Ni</td>
<td>12.5</td>
<td>100</td>
<td>Co</td>
<td>10</td>
</tr>
<tr>
<td>V</td>
<td>12.5</td>
<td>50</td>
<td>Cd</td>
<td>10</td>
</tr>
<tr>
<td>Sn</td>
<td>12.5</td>
<td>30</td>
<td>B</td>
<td>7.5</td>
</tr>
<tr>
<td>Ti</td>
<td>12.5</td>
<td>30</td>
<td>Be</td>
<td>7.5</td>
</tr>
<tr>
<td>Cr</td>
<td>12.5</td>
<td>20</td>
<td>As</td>
<td>4.5</td>
</tr>
<tr>
<td>Mn</td>
<td>12.5</td>
<td>20</td>
<td>Se</td>
<td>4.5</td>
</tr>
<tr>
<td>Mo</td>
<td>12.5</td>
<td>20</td>
<td>Ag</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Fe & Al Interference in soils and tissues

- Elimination of Spectral Interference on As, Pb, Se, Ti, V
- Chloride interference exists on As, V
- IECs drift as a function of Temp not observed in ICP/MS
- Greater data confidence

Interferences Fe & Al in soil (Example ICSA data on Ti)

- ICP/MS (RL= 1 ug/l)   - ICP (RL= 10ug/l)
  - Day 1  0.003 ug/l   - Day 1  11.9 ug/l
  - Day 2  0.035 ug/l   - Day 2  14.4 ug/l
  - Day 3  0.036 ug/l   - Day 3  -2.8 ug/l

- Similar effect on Pb, Cd, Se and Sb
CCT/ DRC value

- Not of significant value to routine application based on our experience
- However it does have Potential benefit in select matrices (saline etc. for As, V, Se)
- Future Potential for increased use

ICP/MS

- **Pros**
  - Improved sensitivity
  - Increased versatility
  - Reduced analysis time
  - Improved data confidence

- **Cons**
  - Cost of Operation (acids, standards, cones, detectors etc)
  - Suppression of IS w/ some matrices
  - Slightly less long-term stability
In Summary

- We are pleased with our decision and the robustness of the technology
- We anticipate more growth in this technique going forward and more transition from ICP to ICP/MS
Do Current EPA Methods Compromise the Productivity of Modern Analytical Instrumentation? – Focus on ICP-MS

Phil Shaw, Bill Spence
Thermo Electron Corporation, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, UK.
Telephone: +44 1606 548100. Fax: +44 1606 552588.
E-mail: phil.shaw@thermo.com

ABSTRACT

The EPA methods 200.8, 6020/6020a and ILM05 were either devised several years ago, or evolved from methods that were devised during the infancy of ICP-MS. As such, though many of the analytical parameters to do with data accuracy have changed to product robust measurement, many of the advances made by manufacturers in the productivity of the instrumentation have been ignored. Modern ICP-MS instrumentation is now capable of significantly better long term stability and drift free tolerance to higher matrix levels. They also have much faster sample uptake and washout times with tools for judging automatically if the wash is long enough or not. This can also be linked with automated sample dilutions based on data quality criteria leading to a re-analysis of the data without having to change from the current sample tube. These advances have dramatically reduced the cost of analysis for many laboratories around the world, but for laboratories following prescribed EPA methodologies many of these cost savings have been ignored to date as they have entailed contravening sample sequencing rules established in the Statements of Work.

This presentation will show the typical stabilities possible with modern ICP-MS which reduce the need for high frequency QC checking, even in high matrix samples. It will also describe the automation tools within modern software packages (available from several vendors) which can monitor the sample uptake and washout to improve productivity without compromising the analytical method. Data will be presented to show how these tools are proven as part of the method validation process to ensure analytical viability.

Finally, we will present data showing how modern instrumentation is capable of making intelligent decisions on measured data and then automatically diluting the sample and re-acquiring data without having to re-introduce it to the instrument, using only a fraction of the time it would take to make an off-line dilution of the sample and re-introduce it for re-analysis. Such automated dilution systems are available from several vendors now and offer dramatic improvements in productivity, cost saving and sample turn around times compared to older instrumentation. We will present data on how the dilution systems and the analytical data are validated and the cost savings that can be realised when utilising such devices.
Do Current EPA Methods Compromise the Productivity of Modern Analytical Instrumentation?
- Focus on ICP-MS

Dr Phil Shaw
Thermo Electron Corp.

Developments effecting sample throughout

- Instrument stability
- Sample uptake and wash
- Automation
  - *Uptake and wash*
  - *Dilution*

- What are the gains with these techniques
Instrument Stability – As things were

- When first developed the methods would commonly experience drift in even simple matrices.
- When the electronic drift was corrected instruments could still exhibit drift due to matrix deposition on the cones and ion optics.

Instrument stability – modern day instrumentation

- Ion optics are designed so depositions don’t effect tuning parameters
  - *Keep DC voltages static*
  - *Where material deposits, keep voltages above a few volts*
- Cone interfaces are designed to resist clogging
  - *Cones run hotter to prevent condensation on the tips*
  - *Orifice sizes and shapes reduce deposition*
So what could be the improvement?

- Currently QC sequencing requires checking every 7-10 samples?
- If modern instrumentation can maintain stability over 20, 30 or even 40 samples why can’t a laboratory take a lengthened period between QC samples “on risk”?
  - Prove the instrument’s drift characteristics under heavy matrix conditions during the method validation process
  - Allow the instrument’s QC software to automate the sample re-run process so all samples still maintain a bracketed QC
    - If the Internal Standard recovery of the QC samples is good
    - If the QC Analyte values recover then allow the bracketed samples to pass
  - If a QC fails the larger re-run batch is a commercial risk of the laboratory, not an analytical risk for the data.

Sample uptake and wash

- When originally developed the methods used older sample introduction designs with fixed rate peristaltic pumps
  - Some methods stipulate a minimum 1 minute wash
- Modern instrumentation includes
  - Small volume spray chambers
  - Zero dead-volume connections
  - Computer controlled variable pump speeds
  - Multithreaded software control of accessories
  - Automated monitoring of uptake and wash
The influence of volume

- Careful design and choice of tubing can reduce uptake times
- Similarly for washouts

This good design contravenes 200.8

The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute (Section 4.1.5). Samples should be aspirated for 30 seconds prior to the collection of data.

- And!
  - Automation can reduce times even further!

The influence of accessory control

- The uptake and washout profiles shown were done with the peristaltic pump at the analytical speed (~35 rpm)
- At the pump’s maximum speed (100 rpm), even including the stabilisation times to change speeds, uptake and wash times can be reduced to ~half of normal.
- Smart control of the autosampler also allows for the probe to go to the rinse station BEFORE the data acquisition finishes
  - Set-up timing so within a few seconds of the acquisition finishing the rinse solution reaches the nebuliser and the pump can be set to maximum
  - Can lead to <5 seconds washout for a clean sample

- SO: How do you deal with nasty samples?
The influence of automation

- During method development, all the analytes to be measured can be monitored with Time Resolved Analysis using examples of the worst matrix types.
- This will then show the WORST CASE for washout.
- The software can then be set to monitor:
  - The worst analytes
  - Up to 2x the worst time
- The software will then only move to the next sample when the "baseline test" is reached.
  - Guaranteed that worst cases are dealt with.
  - If sample is cleaner than washouts can be reduced to near zero.

Dilution

- Dilutions are required in all EPA methods whenever
  - An analyte measurement is above the analytical range of the instrument
    - Dilute appropriately to bring the analyte within the range and re-measure and report only analytes that were out of range.
  - The internal standards are suppressed (or enhanced) beyond the prescribed limits
    - Dilute by a fixed ratio and re-measure and report all analytes.

- These operations entail
  - QC checking data for failure – usually automated by LIMS or reporting software
  - Re-preparation of samples, rescheduling analysis and some form of report merging
    - Labour cost is probably ~10 minutes per failed sample.
    - Additionally failures usually add an additional day to the total time to report, reducing laboratory cycle times.
Autodilution

- Allows all samples to be reported from the batch
  - All analytes in range
  - All samples within Internal Standard limits
  - No extra labour costs
  - No report merging errors
  - Reduced sample cycle times

- The issues raised when using EPA methods are
  - Validation of dilution accuracy
  - Data flagging and collation
  - Sample sequencing for QC samples
    - Is the dilution a new sample?

ID100 – The Automation of Re-run Samples

- A precision piston pump in-line with the sample introduction
  - Linear, no user calibration
  - Accurate to >50:1 dilution without internal standards
  - Simple plumbing
  - Fast
  - No extra sample tubes required
  - Allows in-line pre-emptive dilution
### Data flagging and reporting

#### Calibration Data

<table>
<thead>
<tr>
<th>Run</th>
<th>GLI</th>
<th>Mn</th>
<th>Bi</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Other</th>
<th>7Ti</th>
<th>7Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.096</td>
<td>252.000</td>
<td>251.000</td>
<td>251.100</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
</tr>
<tr>
<td>2</td>
<td>37.096</td>
<td>240.000</td>
<td>251.000</td>
<td>251.100</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
</tr>
<tr>
<td>3</td>
<td>37.096</td>
<td>251.000</td>
<td>251.000</td>
<td>251.100</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
<td>251.000</td>
<td>253.400</td>
<td>252.000</td>
</tr>
</tbody>
</table>

#### Sample: 1

<table>
<thead>
<tr>
<th>Run</th>
<th>GLI</th>
<th>Mn</th>
<th>Bi</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Other</th>
<th>7Ti</th>
<th>7Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### User Preferences

**Presets:**
- Automatic calibration
- Manual calibration

**Calibration Type:**
- External calibration
- Internal calibration

**Dilution:**
- 1:10 dilution
- 1:1 dilution

**Sample Preparation:**
- Acid digestion
- Wet digestion

**Analysis:**
- Mass spectrometry
- ICP-MS

**Data Handling:**
- Data review
- Data correction

**Reporting:**
- Report generation
- Report export

---

**Thermo Electron Corporation**

146
Data flagging and reporting

When is a sample, another sample?

- “In-line” autodilutor means
  - Probe never leaves the autosampler tube for the original analysis and any dilutions
  - Only one sample uptake
  - Only one washout
    - Sample with no dilutions 6 minutes
    - Sample with one dilution 8 minutes
    - Sample with two dilutions 10 minutes
What are the gains?

- **Longer runs between QC samples**
  - Every ~20 samples saves 10% instrument time per batch

- **Optimising the sample introduction,**
  - Fast peri-pump speeds
  - Autosampler probe to wash during data acquisition
  - Using monitored uptake and wash
  - Ignoring the fixed EPA uptake and wash times
  - **Saves at least 45 seconds per sample for all samples**
    - Can save up to 90 seconds per sample for clean samples in a batch of dirty samples
  - **Means at least 75 minutes less instrument time for 100 samples**

- **Using an “in-line” autodilutor,**
  - Use dilutor to make calibration saves approximately 15 minutes instrument time in each analytical calibration (Blank + 4 standards)
  - Assuming 5% sample failures requiring dilution
    - Saves approximately one hour’s labour per batch of 100 samples
  - **Reduces total batch cycle time by one day**
Comparison of Illinois EPA’s Low-Level Mercury Sample Collection Procedures with USEPA Method 1669

Michael S. Henebry  
Illinois Environmental Protection Agency, 1021 North Grand Ave., East Springfield, IL 62794-9276  
E-mail: mike.henebry@epa.state.il.us

ABSTRACT

Over the past year (2003-2004), the Illinois Environmental Protection Agency (IEPA) collected samples for analysis of mercury by EPA Method 1631 from about 40 municipal and industrial wastewater facilities and from about equal numbers of stream and lake sites throughout the state. At 28 sites, samples were collected using both the “clean hands/dirty hands” (CH/DH) collection methods developed by USEPA (Method 1669) and by IEPA’s routine sample collection procedures. These comparisons were conducted because the procedures detailed in Method 1669 appeared to be problematic for routine sample collection by both the IEPA and by Illinois wastewater discharge permit holders. Procedures in Method 1669 seemed overly complex, and required at least two persons at every sampling event. The IEPA cannot afford to send more than one technician to collect routine effluent and ambient stream samples.

Mercury concentrations at most ambient sites and in most wastewater effluents were less than the Illinois statewide water quality standard (WQS) of 12 ng/L; many were in the range of 1-5 ng/L, although 454 ng/L was observed in one effluent sample. Field blanks were prepared at the time and site of each environmental sample collection, and generally showed no significant contamination. Sample collection method appeared to have no effect on the reported concentrations of mercury in environmental samples. There were no significant differences in low-level mercury concentrations in replicate samples from either wastewater effluents or from ambient stream water sites whether samples were collected by two people using CH/DH, by one person using clean technique or by one person using IEPA’s routine sample collection procedures. It was concluded that one of our routine sample collection staff using reasonable care could collect uncontaminated samples for analysis by Method 1631. Detailed sample collection procedures including photos will be presented.
Comparison of Illinois EPA’s Low-Level Mercury Sample Collection Procedures with USEPA Method 1669

Michael S. Henebry
Illinois EPA, Springfield, IL
E-mail: mike.henebry@epa.state.il.us

NEMC 2005

Acknowledgements

• Jim Miles, Alyson Grady and Stan Lowe assisted in the study design and sample collection.
• Bob Mosher, Tim Kluge, Gregg Good and Bill Ettinger assisted in the study design.
• Many other Illinois EPA field staff participated in sample collection.
Outline of Presentation

- IEPA’s collection methods for effluent and surface water samples for low-level mercury analysis
- Results of effluent and surface water samples
- Comparison of results from different collection methods
- Recommendations for sample collection

Background on Illinois Mercury Studies

- In the past, Illinois rarely found mercury in ambient surface water and effluent samples.
- IEPA had been using ICP-MS, not EPA Method 1631, for analysis of total mercury in water.
- IEPA had concerns about being able to implement the “clean hands_dirty hands” procedures in EPA Method 1669 because we usually send only one person to collect effluent and stream samples.
Changes in Mercury Monitoring

- Many new NPDES permits
  - require Method 1631
  - first time requirement for mercury testing
  - levels 400 times lower than before
  - 12 ng/L (parts per trillion) water quality standard in Illinois

Comparison of Analytical Methods

<table>
<thead>
<tr>
<th>Method Number</th>
<th>Descriptive Name</th>
<th>Reporting Level</th>
<th>Cost per Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 200.8</td>
<td>Metals in Water by ICP/MS</td>
<td>200 ppt (NEMI) 10 ppt (IEPA)</td>
<td>$18 - $30 (IEPA Lab)</td>
</tr>
<tr>
<td>EPA 1631</td>
<td>Mercury in Water Using CV-AFS</td>
<td>0.2 ppt (NEMI) 0.2 ppt (EnChem)</td>
<td>$70 - $100</td>
</tr>
</tbody>
</table>
Study Goals

- To test whether current IEPA sample collection procedures are adequate for collecting uncontaminated samples for total mercury analysis by EPA Method 1631.
- To evaluate the concentrations of total mercury in Illinois effluents and surface waters and compare them to the Illinois human health water quality standard of 12 ppt.

Site Selection - Effluents

- Some wastewater facilities were selected for their potential to have concentrations of total Hg exceeding the water quality standard of 12 ng/L.
- Other “background” facilities were not expected to have elevated concentrations of Hg in their effluents.
- Effluent samples were collected from 33 facilities distributed throughout the state.
Site Selection – Surface Waters

- We selected stream and lake sites that were part of their respective ambient water quality monitoring core networks that have been sampled over a number of years and are projected to be sampled in the future.
- We collected 52 samples from core stream (AWQMN) stations.
- We collected 32 samples from core lakes and from lakes with fish advisories for mercury.

Materials and Methods – All Sites

The analytical laboratory provided sampling kits consisting of:
- Pre-cleaned 500-mL borosilicate glass bottles that were double zip-lock bagged
- Mercury free deionized water for preparation of field blanks at each site
- Bagged, talc free vinyl gloves
IEPA Clean Hands/Dirty Hands

- The sample collection crew wore clean, unlined nylon windbreaker jackets and vinyl gloves.
- Clean Hands handled the sample bottles and the inner zip-lock bags provided by the analytical laboratory and clean parts of the sample collection apparatus.
- Dirty Hands opened coolers, handled the outer zip-lock bags, and manipulated all potentially “dirty” parts of the sample collection apparatus.

Materials and Methods – Effluents

- At least one sample of each of the first 33 facility effluents was collected by two persons using IEPA’s version of USEPA’s CH/DH technique (EPA Method 1669).
- One person using IEPA’s “routine” effluent sample collection procedure collected a second (duplicate) effluent sample during the first 19 effluent sampling events for comparison to the results from CH/DH samples.
IEPA “Routine” Effluent Sample Collection Procedures

One person:

- Performed all the tasks of both Clean Hands and Dirty Hands
- Used relatively clean sample collection apparatus
- Wore a clean, nylon windbreaker jacket and vinyl gloves
- Was aware of and was careful to avoid possible sources of sample contamination
Materials and Methods – Streams

- All AWQMN samples were collected by at least two persons using IEPA’s version of USEPA’s CH/DH procedure.
- A non-metallic, weighted-bottle sampler was used to immerse the 500-mL sample bottle directly into the top 1-foot of the center of stream flow.
Materials and Methods - Lakes

- Two persons using the IEPA’s CH/DH procedures collected all of the ambient lakes samples.
- Clean Hands collected samples from the top 1-foot of lake water by reaching over the side of the boat and immersing the Hg sample bottle until full.
Illinois Ambient Lakes Samples, Aug - Oct 2004

Field Blanks for Ambient Lakes Samples
Comparison of Stream Sample Collection Methods

Three sample collection methods were compared at 10 stream stations in central Illinois. Replicate samples at these stations were collected by:

- Two persons using IEPA’s CH/DH procedure
- By one person collecting samples using clean technique
- By the usual field staff person collecting the way that AWQMN samples are routinely collected.

Comparison of Three Collection Methods at AWQMN Stations

[Bar chart showing comparison of collection methods at AWQMN stations]
CH/DH vs. Single Clean
AWQMN Collection Method Study, Nov-Dec 2004

CH/DH vs. AWQMN Routine
Collection Method Study, Nov-Dec 2004
Summary and Conclusions

- Our results suggest strict adherence to EPA 1669 is not necessary for the collection of samples for low-level mercury analysis (EPA 1631).
- It appears that samples for low-level mercury analysis can be collected by one of our usual sample collection staff using our routine collection methods without introducing significant levels of mercury contamination.
Summary and Conclusions (Cont.)

- Concentrations of total mercury in most samples of Illinois’ facility effluents and surface waters did not exceed the human health standard of 12 ng/L.
- Concentrations of mercury in some effluent and stream samples were greater after rainfall and subsequent runoff events.

Why Did Collection Method Make No Difference in Our Results?

1) We always collected the environmental sample directly into the bottle provided by the laboratory.
2) Our sample collection staff was trained to be aware of and to avoid possible sources of sample contamination.
Recommendations for Low-Level Mercury Sample Collection

1) Make use of the sample collection kit provided by your laboratory.
2) If possible, collect samples directly into the bottles provided by your laboratory (avoid using compositors, plastic bottles or your own “clean” glass bottles).
3) Keep bottles uncapped for as short a time as possible.
4) Avoid touching the rim of the sample bottle or the inner surface of the bottle cap.

Recommendations (Cont.)

5) Be aware of and avoid possible sources of airborne contamination.
6) Periodically prepare field blanks with environmental sample collections.
7) Duplicate samples can be useful for evaluating the reliability of your sample collection methods.
Session 5

Advances in Electronic Deliverables and Information Management
SEDD – An Overview and Status Report

Anand R. Mudambi
US EPA Analytical Services Branch, 1200 Pennsylvania Ave NW, Mail Code 5102G, Washington, DC 20460
Author’s e-mail: mudambi.anand@epa.gov; Phone: 703-603-8796

ABSTRACT

SEDD (Staged Electronic Data Deliverable) is a program neutral format for the delivery of analytical data. It supports multiple users’ needs depending on the level of analytical requirements. The main advantage of SEDD is that once implemented, laboratories do not have to completely overhaul their Electronic Data Deliverable (EDD) generating systems as data requester needs become more complex, but can simply add additional elements to their current system. Using SEDD as the basis of electronic delivery of analytical data will decrease costs by reducing number of EDDs laboratories currently have to support and ease data exchange between various programs and agencies.

At the present time different levels or Stages for SEDD have been developed based on the complexity of data reporting requirements needed.

SEDD files are delivered as XML (eXtensible Markup Language) files. Sponsored by the World Wide Web Consortium (W3C), XML is license free, platform independent, final recommended standard which encapsulates structured data in text files. It is well supported by freely available third party tools.

Delivery of analytical data in the SEDD format is now a requirement in the U.S. Army Corps of Engineers’ Formerly Used Defense Sites (FUDS) program and for certain U.S. Environmental Protection Agency contracts including the new Contract Laboratory Program’s (CLP) Organic Statement of Work SOM 1.0. Interagency efforts are underway with the U.S. Air Force, U.S. Navy, and the Department of Energy to promote the use of SEDD.

Laboratories and LIMS vendors are gearing up to provide SEDD files as required in the upcoming contracts. Laboratories have already submitted compliant SEDD files as part of the new CLP Organic Solicitation. U.S. EPA is providing tools to assist laboratories in both creating and checking SEDD files prior to submission. Private parties are also evaluating SEDD as a basis for uniform delivery of analytical data.

I prefer to give an oral presentation.
STAGED ELECTRONIC
DATA DELIVERABLE (SEDD) - AN OVERVIEW AND
STATUS REPORT

Dr. Anand R. Mudambi
Environmental Protection
Agency (USEPA)

National Environmental Monitoring Conference
Washington DC
July 26, 2005

Federal Agency Need for
Data in Electronic Format

- Collection of Large Amounts of Data Required to Make Various Environmental Decisions, Including:
  - Cleanup Remedies
  - Site Remediation End Points
- Ease of Transmission, Receipt, Evaluation, Storage, and Retrieval
- Efficient and Cost-Effective
Problems with Current Electronic Data

- Most data is received in proprietary formats (e.g., documents in Word or WordPerfect, spreadsheets in Excel or Lotus).
- The business model for proprietary formats is PLANNED OBSOLESCENCE with little or no backward compatibility.
- Thus, most data generated in these formats today will not be accessible 5-10 years from now.

The Need for Open Data Standards

- Eases data exchange between parties.
- Allows all vendors/parties to compete on a level playing field.
- Prevents individual monopolies locking a large market share into their proprietary formats.
- Evolves to meet future needs.
- Provides incentives for market forces to ensure backward compatibility.
Open Data Standard Examples

- HTML - Hypertext Markup Language (Used for the Web Pages on the Internet)
- XML - eXtensible Markup Language (Becoming the Standard for Data Exchange)
- GAML - General Analytical Markup Language

XML – A Self Defining Data Format

- XML - eXtensible Markup Language
- Final Recommended Standard by the World Wide Web Consortium
- Each Piece of Data in XML Has a Tag (or Is Tagged) so the Data Set Electronic Data Deliverable (EDD) Is Self-Defined
- Under SEDD, the EDD From the Laboratory Is Transmitted as an XML Document Based on a Document Type Definition (DTD)
The Problem – Too Many EDDs

- Laboratories Produce More than 300 Different EDDs
- Most EDDs to Date Are Customer-Specific
- Most EDDs Are Proprietary
- No Stand-Alone, Self-Defining EDD Present - a Must in Case of Another National Emergency
- No EDD Present That Meets Diverse Customer Needs for Detailed Analytical Chemistry Reporting

The Solution - SEDD

- Staged Approach Allows for Meeting Diverse Reporting Requirements
- Eases Data Exchange between Various Parties
- Analytical Data Delivered in XML Format (Non-Proprietary)
- XML is Designed for Input into Various Databases
Common SEDD Misconceptions

SEDD Is NOT:
• A Database
• A Flat File
• A Parser

So What is SEDD?

• **SEDD is a hierarchal file created by a Laboratory Information Management System (LIMS) or any other database.**
• **A SEDD file contains information regarding the chemical analysis of sample(s).**
• **Information (analytical results) from a SEDD file can be reviewed and then input into customer databases using parsing routines.**
• **Parsing routines need to be written ONLY once for each database type.**
Advantages of Using SEDD

- **For Laboratories** - Reduce the Number of EDDs That They Support
- **For Data Requesters** - Develop Common Automated Data Review Tools to Check EDDs
- **For Data Storage** - EDDs Stored in Non-Proprietary Format

Cost Savings Using SEDD

- Laboratories are already delivering SEDD files for input into electronic review software.
- Preliminary results show a 30 to 50% cost savings when compared to the same level of manual review.
SEDD Status

- Working on Pilots with Laboratories since 2002
- Laboratories (Including At Least One Major Network) and Two LIMS Vendors Are Already Delivering Compliant SEDD Stage 2 Files
- SEDD Files Being Input and Checked by Automated Data Review Software

SEDD Implementation

- US Army Corps of Engineers (USACE) Formerly Used Defense Sites (FUDS) Policy Requirement - June 2004
- US EPA Region 10 Emergency Response - November 2004
- All EPA Regions Emergency Response - 2005
- US EPA Contract Laboratory Program (CLP) – Summer 2005
- USACE District Contracts – Summer 2005
SEDD Outreach

- Working with US Department of Energy (DOE) Sites
- Working with US Navy
- Working with States
- Working with the Private Sector

What’s New with SEDD!

- SEDD is being considered as an American Society for Testing and Materials (ASTM) standard for LIMS-to-LIMS data transfer.
- SEDD is being embraced by the industry as it becomes a contract requirement.
- SEDD Stage 4 is being developed with input from instrument manufacturers.
SEDD Implementation Support

- For Laboratories, SEDD Tool Provided by US EPA to Create SEDD Files
  - SEDD Files Can Also Be Created Using Vendor Support or by In-House Systems
- For Contractors Working on Federal Projects, SEDD Parser and Automated Data Review (ADR) Software Is Available

SEDD Implementation Support (con’t.)

- For Federal Agencies, contract language for implementing SEDD is available.
- For all parties interested in implementing SEDD, two courses are being offered at NEMC on Thurs July 28
  - Morning – Technical Implementation of SEDD
  - Afternoon – SEDD Files: Automating the Parsing and Review of Analytical Data
SEDD Implementation Support on the Web

- A Web Page for SEDD Implementers
- A List of Laboratories and Vendors Who Support SEDD (YOUR NAME HERE?)
- A SEDD Q & A Web Page
- A 10 Step Process for SEDD/ADR Implementation

Contact Information

- For more information regarding SEDD Implementation, please contact:
  - Anand Mudambi, Phone: 703-603-8796, email: mudambi.anand@epa.gov
  - Joe Solsky, Phone: 402-697-2573, email: joseph.f.solsky@usace.army.mil
  - The SEDD Web Page, located at: www.epa.gov/superfund/programs/clp/sedd.htm
The Technical Components of SEDD Stage 3 Files

Joseph Solsky  
U.S. Army Corps of Engineers (CENWO-HX-C), 12565 W Center Rd, Omaha, NE 68144  
E-Mail: Joseph.F.Solsky@usace.army.mil; Phone: 402-697-2573

ABSTRACT

No one single electronic data deliverable format would be able to meet the needs of the multiple data users due to the various levels of data complexity and reporting as required by those users. As a consequence, SEDD accommodates the reporting of data in 'Stages', with each stage building on the next using XML technology. Currently, three stages or unique electronic data deliverable formats have been defined for SEDD. Stage 1 contains the minimum number of analytical data elements to report 'Results Only' data to the end user. Stage 2 builds on Stage 1 and adds method (Stage 2a) and instrument (Stage 2b) Quality Control (QC) data. Stage 3 builds on Stage 2 and adds additional measurement data to allow for the independent recalculation of the reported results.

SEDD delivers data in the form of an XML document. A common structure has been developed that will allow for the reporting of all types of data. SEDD allows for the complete linking of all samples to their associated QC samples, the complete linking of all samples to their associated continuing and initial calibration data, and the complete linking of all reported results to the specific analysis that was used to derive that specific result. It is these linkages that allow for the complete and independent recalculation of all reported results within a SEDD Stage 3 file. This independent recalculation is performed by starting with an integrated area count for a typical organic chromatographic method or by starting with a background corrected spectral intensity measurement for a typical inorganic spectroscopic method.

A SEDD Stage 3 file captures and reports all of the data needed to independently recalculate all final results by capturing this data in the manner in which it was generated. By capturing the data in this manner, the data can be reported and reviewed against the requirements of many different programs. For initial calibrations, average calibration/response factors, linear regressions, quadratic regressions, and other techniques can all be used. These calibration strategies can be applied on a per peak basis or applied when peaks are summed together. Various weighting factors can also be used when regressions are performed. In addition, either 'external standard' or 'internal standard' procedures can be used for any analyte using any method. This same type of flexibility that is used for the reporting of initial calibrations is used throughout the sample preparation and analysis process.

(2) I prefer to give an oral presentation.
A TECHNICAL OVERVIEW OF
STAGED ELECTRONIC
DATA DELIVERABLE (SEDD)

Joseph Solsky
US Army Corps of Engineers (USACE)
July 26, 2005

The Problem With Today’s EDDs

- Laboratories Produce More than 300 Different Electronic Data Deliverables (EDDs).
- Most EDDs to Date Are Customer-Specific.
- Most EDDs Are Proprietary.
- No Stand-Alone, Self-Defining EDD Present - a Must in Case of Another National Emergency.
The Solution - SEDD

- SEDD - Staged Electronic Data Deliverable
- Staged Approach Allows for Meeting Diverse Reporting Requirements
- Eases Data Exchange Between Various Parties
- Analytical Data Delivered in eXtensible Markup Language (XML) Format (Non-Proprietary)
- XML Is Designed for Input into Various Databases

XML – A Self Defining Data Format

- XML - eXtensible Mark-up Language
- Final Recommended Standard by the World Wide Web Consortium
- Each Piece of Data in XML Has a Tag (or Is Tagged) so the Data Set (EDD) is Self-Defined
- Under SEDD, the EDD from the Laboratory Is Transmitted as an XML Document Based on a DTD or Schema
What is SEDD?

- Uses a common syntax to describe diverse laboratory activities and report analytical data electronically.
- Allows users to link analytical data to underlying laboratory activities and processes to provide full traceability.
- Provides a means for reporting complex analytical relationships.

The Stages of SEDD

- **Stage 1** - Contains the minimum number of analytical data elements required to transmit results-only data.
- **Stage 2** - Data content builds on Stage 1 by adding method (Stage 2a) and instrument (Stage 2b) Quality Control (QC) data.
- **Stage 3** - Data content builds on Stage 2 by adding additional measurement data to allow for independent recalculation of the reported results [e.g., Contract Laboratory Program (CLP)].
Stage 3 SEDD Files

- A SEDD Stage 3 file contains enough data to allow for the independent recalculation of the reported results.
- Raw instrument data would generally not be used. Corrected instrument data, such as peak areas or corrected intensity readings, would normally be captured.
- This file contains all of the linkages to relate all calibration data and other data to each reported result.
- This file contains information to associate all standards used to their original vendors and lot numbers.

The Future – SEDD Stage 4

- A Stage 4 file uses the same structure as Stage 3 but includes all instrument raw data files that were generated during the analysis of the sample. Other supporting files could also be included.
- These instrument raw data files are stored in a nonproprietary XML format.
- Significant advantages can be realized when data is delivered at this level.
Example XML File

<ReportedResult>
  <AnalyteName>Benzene</AnalyteName>
  <CASRegistryNumber>71-43-2</CASRegistryNumber>
  <Result>24.2</Result>
  <ResultUnits>ug/L</ResultUnits>
</ReportedResult>

Example XML File (as viewed in XML Notepad)
What Are DTDs?

- Would specify what parts of the SEDD structure (nodes) are required.
- Would specify what data elements are required for each node.
- Three stages have now been defined. Data can be delivered based on the amount and complexity of the data required by the user. Generic DTDs are developed for Stage 2a, 2b and 3.
- Schemas can also be used in place of DTDs.

The Valid Value Issue

- SEDD Draft Version 5.1 includes a set of valid values.
- Whenever possible, all valid values were tied to an existing standard or recognized database of values. When valid values are reported, they are reported with the appropriate source identified.
- All critical data, such as analyte and method IDs, can be identified using lab, client, and referenced values.
SEDD Stage 1 Structure

SEDD Stage 2a Structure
Contact Information

• Contact information for SEDD:
  Anand Mudambi
  Phone: 703-603-8796
  EMail: mudambi.anand@epa.gov

• Contact information for SEDD:
  Joseph Solsky
  Phone: 402-697-2573
  EMail: joseph.f.solsky@usace.army.mil

• CLP SEDD Web Page:
  www.epa.gov/superfund/programs/clp/sedd.htm
Automated Generation and Validation of Staged Electronic Data Deliverable in a Commercial Laboratory

Jakub Rehacek, Ph.D.
PEL Laboratories, Inc., 4420 Pendola Pt. Rd., Tampa, FL 33619
email: lof@pelab.com, phone: 813-247-2805

ABSTRACT

SEDD is an emerging electronic data deliverable offering program-neutral, non-proprietary format for electronic data exchange. PEL Laboratories, Inc., has participated in the Staged Electronic Data Deliverable (SEDD) Pilot study under GEITA T.O. 041, and has successfully delivered all stages of the SEDD.

PEL has developed an in-house data management system (PEL DMS) that automates all aspects of our analytical services. The projects are tracked from the bid stage through bottle kit assembly, sample receiving, prep, and analytical stages to final data reporting in hardcopy and EDD. The system interfaces directly with email and PEL's data driven web site in real time. All reviews and releases are done digitally, narratives are automatically generated from the data and analyst feedback, most logbooks and lab notebooks are electronic. A complete Level-IV CLP package is automatically assembled and generated by the PEL DMS. There are several hundred QC and data validation checks performed on each test/method at each review/release level.

Both Windows and Internet-based front-end user interfaces were developed to facilitate automated and streamlined EDD deliverables. The graphical user interface (GUI) allows Project Managers to generate SEDD as one of the EDD "flavors" we routinely provide to our clients. The SEDD is generated automatically in conjunction with hardcopy reports directly from our LIMS. Our Lab currently provides over 100 custom EDD formats. The SEDD would greatly simplify our EDD reporting as a single electronic deliverable.

Our Data System has the capability to generate both SEDD and customer specified EDD at the same time in order to ease the transition into the SEDD based deliverables. All necessary information comes from the same data store so we can guarantee that the SEDD, custom EDD, and hardcopy will all have identical values. We can also generate SEDD deliverables for projects that have already been processed through the Lab and were reported in a different EDD format.

SEDD Data Review and Validation Tool
One of the modules in our Client Web Portal is an online data review and validation tool capable of reviewing and validating SEDD deliverables. Our clients can upload the SEDD XML file via custom web page and match it with Project specific QC criteria (Project Profile). PEL Data Validation/Review tool significantly reduces the time and cost for a validator to review results delivered in SEDD format. This tool makes it possible to generate reports quickly via our website, including a Summary of all QC exceptions with their associated prep and analytical runs, an Executive Summary report showing all values detected above the Method Detection Limit, or above custom Contaminant Levels. A comprehensive Laboratory Review Checklist (LRC) that quickly summarizes all variances is also available. Analytical runs are cross-
referenced to prep batches and to calibrations. For the SEDD Stage 3, clients have option of independent recalculation of reported results from raw data. The reported results can be reviewed from many angles; all pertinent information is just few clicks away.

(2) I prefer to give an oral presentation
Brewing SEDD In-House
Automated generation and validation of Staged Electronic Data Deliverable in a commercial laboratory

Jakub Rehacek, Ph.D., PEL Laboratories, Inc.

Who are we?

- PEL Laboratories, Inc. is a small laboratory (50 people)
- Specializing in high end analytical and data management services
- Providing full service capabilities in Inorganic, Organic, and Wet Chemistry Analyses
- Highly automated
Overview

- Laboratory Background Info
- SEDD Creation Prerequisites
- SEDD Generation
- SEDD Review and Validation

Why is SEDD good for a Lab?

- PEL provides EDDs in over 100 different EDD “flavors” to its clients
  - Parser maintenance issues
  - Data exchange difficult – multiple contractors on the same project
- SEDD
  - single common data format
  - “pass-thru” review and validation by contractor
Laboratory Background

- Data Acquisition
- LIMS
- QC
- Reports + EDDs
- Web Portal
- Web Services

Data Acquisition

- Advanced stages of the SEDD deliverable call for high levels of detail in the reporting of analytical results.
- Success in automated SEDD generation starts at the bench.
- The data acquisition software must have the capability of providing complete access to the raw data underlying the acquisition of analytical results.
- PEL uses a suite of highly customized data acquisition software with automated transfer to LIMS.
LIMS

The success of automated SEDD generation actually starts long before the samples arrive at the laboratory

- Project “Profile” built during the bid phase
  - QC and analytical requirements as well as HC and EDD format are “locked” in
- Real-time tracking and interaction with the Web Portal
  - Automated QC review at each stage of lab processing
  - “McDonald’s” screen real-time project status
- All parameters required for SEDD are collected along the way and stored in LIMS

Quality Control

- Automated batteries of Quality Control Checks at various stages of sample package generation
  - “Assembly-line,” step-by-step, computer driven sample prep
  - Barcode verifications of samples and spike solutions
  - Reasons for manual integrations must be explained
  - Sample Narratives are generated automatically
- Capture raw instrument data down to the chromatograms/spectrograms.
  - All the data is kept in the system
  - Cross-linked with clean-up/prep info and with calibration runs

Essential ingredients for generation of the SEDD files.
Reports EDD + Hard Copy

- Project Managers generate SEDD at the push of a button
  - The SEDD is generated automatically in conjunction with hard copy reports directly from our LIMS.
- SEDD is validated as a part of the final package QC/data validation check sequence.
- We routinely generate both SEDD and customer-specified EDD at the same time in order to ease the transition into the SEDD-based deliverables.
- All information comes from the same source (LIMS) so that we can guarantee that the SEDD, custom EDD, and hardcopy will have identical values.
- We can re-generate SEDD deliverables for historical projects that have already been processed through the Lab, but reported in a different format.

Web Portal

Complete on-line data management system directly interfaced with LIMS

- Real-time Project Status/Package Tracking
- Preliminary results available online immediately after release
- Data Review and Validation
- Screening Criteria/Action Levels
- Chain-of-Custody Documents online
- Immediate Access to Test Results
  - "Executive Report"
  - QC and calibration data is also available
- Hardcopy Reports available online
- Billing Information
  - Historical billing information is maintained
  - Automated project financial summaries to assist with the Sarbanes-Oxley Act disclosure
  - Final invoices may be downloaded in PDF format
- Auto-Email Notification/Reports
- EDD's are available online at the same time the work order is finalized
Web Services

The next step in Client-Laboratory interaction

- A web service is a web site to be used by computer programs instead of by humans.
- Each web service is a small application accessible through the Internet.
- Web services use XML for transferring information.
- The SEDD deliverable is uniquely qualified for use as a data transfer medium between web services.
- Simple Excel spreadsheet transparently links to a laboratory web service to retrieve relevant analytical results for further processing.

Automated Generation of SEDD

Available Tools

- SEDD Tool – EPA’s data converter
- Commercial LIMS
- Off-the-shelf tools (MS SQL Server, .NET)
EPA SEDD Tool

- The SEDD Tool's primary task is to convert local database data into an Extensible Markup Language (XML)-compliant file for delivery to other remote data systems.
- The SEDD Tool addresses the U.S. Environmental Protection Agency's need to receive analytical data electronically from its contracting laboratories.

Commercial LIMS

- Several commercial LIMS software vendors have incorporated the SEDD generation into their products.
- Laboratories have to work with the vendor to ensure that their SEDD generators are kept up to date with the latest changes in the SEDD format.
Off-the-shelf tools

- The SEDD is an XML document. It can be created fairly easily with the use of generic programming tools.
- PEL chose the Microsoft product line because it links up with the business productivity software used in the lab.
  - The **MS SQL Server** database platform provides a robust back-end foundation for data storage and manipulation.
  - The **Visual Studio.NET** suite provides tools for development of data retrieval engines and user interfaces.
  - **Microsoft Office** applications are the ultimate consumers of the final data products as they provide a familiar interface for users.

- All modern database and programming platforms have embraced the XML, and provide a multitude of tools to generate, manipulate, and consume the XML.

Prerequisites for Automated SEDD generation

- **All the fields must be available in LIMS**
  - Correct and streamlined back-end database structure.
  - All the data elements required by SEDD must be present in the database.
  - The correct linkages must be set.
  - Required data are collected along the way as the samples are processed through the laboratory.
  - The data acquisition is an integral part of the process, and can be streamlined. For example:
    - the sample bottle id’s are stored in the system
    - the pre-weight information is also readily available for relevant calculations.
    - pH and sample temperatures recorded

- **Relationships established**
  - The SEDD file format stores the analytical results information as well as information about the relationship of the result to associated quality control samples and instrument calibration. These relationships must be established in the underlying data structures for error-free automated EDD generation.
SEDD Generation Process

- **Query LIMS – SQL**
  - The SEDD creation is a matter of querying the data store to retrieve the desired Work Order results and associated QC information.
  - The amount of information and complexity of relationships between the SEDD nodes increases with each level of SEDD (1, 2a, 2b, 3).
  - We have built a modular query and retrieval engine that brings in all relevant information based on the SEDD level being produced.

- **XML export routine in .NET**
  - **Visual Studio.NET** provides a feature-rich environment for the creation of XML documents.
  - Entire XML document is generated and fully formed according to the Document Type Definition (DTD) template.
  - The System.XML namespace provides all classes necessary for creating, processing, and validation of XML files.

Validation/Review Tool

- **PEL’s Data Validation/Review tool** is an on-line service that assists a project chemist or independent validator with review of our chemistry.
  - Data review/Validation
  - QC Reports
Validate Review Chemistry

- The SEDD contains all necessary relationships between the results and QC samples
  - validated against the DTD, and then parsed
  - analytical runs are cross-referenced to prep batches and to calibrations
  - reported results can be reviewed from many angles
- The SEDD Stage 3 allows clients to recalculate the results from the raw on-column values independently from our data processing software and LIMS.

QC Review Reports

- Our Review tool makes it possible to generate reports quickly via our website. The reports include an Executive Summary report showing all values detected above the Method Detection Limit, and a comprehensive Laboratory Review Checklist (LRC) that quickly summarizes any exceptions. A detailed QC flagging report can also be created to assist with validation flag applications in our clients' data systems.
- Our system can also export EDDs in multiple formats to facilitate transition from legacy data systems. Clients can upload the SEDD data file and export in ERPMS, ERIS, or any other format that PEL currently supports. PEL Laboratories, Inc., is currently working with other companies to facilitate automated communication in order to provide push-button validation of laboratory results.
Questions

Contact info:

Jakub Rehacek, Ph.D.
VP Information Systems
PEL Laboratories, Inc.
jrehacek@pelab.com
813-247-2805
www.pelab.com
Creating SEDD Stage 3 Deliverables: A LIMS Vendor’s Perspective

Buddy Wilson
Promium
22522 29th Dr SE, Suite 205
Bothell, WA 98021
Primary Author E-Mail: buddy@promium.com
Phone: 425.286.9200

ABSTRACT

The SEDD (Staged Electronic Data Deliverable) specification provides a common structure and data element dictionary to report a wide variety of data to multiple customers. The SEDD specification is program-neutral and allows for reporting of data in a single deliverable format that contains results ranging from simple sample concentrations (Stage 1) all the way to a CLP (Contract Laboratory Program) type data package (Stage 3). Because of the potential and flexibility of the SEDD format, Promium has actively worked with the EPA and Army Corps of Engineers to support the use of the format by laboratories with Promium’s Laboratory Information Management (LIM) system when they perform testing for projects that must be reported to those agencies.

Promium already supports the SEDD format by providing native generation capability for Stage 2a and 2b deliverables within Element DataSystem, its out-of-the-box LIMS for Environmental Testing Laboratories. During 2004, the SEDD format gained further acceptance among federal agencies and was written into the SOM 1.0 Organics CLP Contract. Keeping with its commitment to support this well-designed deliverable, Promium included the most complex form of the SEDD, Stage 3, within its LIMS application during the last half of 2004 and assisted one of its client laboratories in generation and the new CLP Forms and Exhibit H SEDD deliverable for the Performance Evaluation sample submission requirement of the new CLP contract. The process of writing support for this stage of the deliverable presented a different set of issues than previous development efforts. In particular, the company found itself re-designing some aspects of its existing LIMS application to better support the structure and data elements required for a Stage 3 SEDD. The end result was a more comprehensive LIM system for Environmental Testing Labs with a native ability to generate SEDD Stage 3 deliverables for CLP laboratories or for non-CLP laboratories wishing to provide electronic deliverables in this very comprehensive format.

<I prefer to give an oral presentation>
Creating SEDD Stage 3 Deliverables: A LIMS Vendor’s Perspective

Buddy Wilson
26 July 2005

About Promium

- Software vendor specializing in LIM systems for public and private environmental laboratories
- Systems currently used in over 100 environmental laboratory facilities
- Operating in EPA Regional Labs 5, 6, 8, 9 and Army Corps of Engineers MRD Lab
- Base LIM system includes a standard EDD library with over 35 common EDD formats including SEDD 2a, 2b and 3 (CLP Exhibit H).
Fun with SEDD:
The 2004 EPA CLP SOM01.0 PE

- First time electronic deliverables were required with CLP Contract RFP PE sample submission
- Samples were shipped to labs December 6th and (originally) due January 3rd
- EPA provided an on-line SEDD checking tool
- Promium had previously participated in several projects requiring SEDD Stage 2a and 2b with its clients
- SEDD Stage 3 (Exhibit H) required 74 new fields and 5 new tables added to existing LIMS structure (96 tables)
- New CLP forms presented a few challenges but were relatively quite similar to previous forms
- Some labs tried to do the SEDD manually

Capturing CLP Package and SEDD Data into the LIMS

Diagram showing the flow of data from various processes to the primary LIMS database.
Fun with SEDD:
The 2004 EPA CLP SOM01.0 PE

- More challenging than we thought it was going to be
- Staggered dual-column PEST and ARO were particularly difficult to deal with
- Several conflicts between forms and SEDD regarding sig figs and decimals
- On-line SEDD checking tool was very helpful
- Not something you would want to do manually...

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Data Elements</th>
<th>Data Elements Filled</th>
<th>File Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aroclors</td>
<td>41693</td>
<td>12755 (30.6%)</td>
<td>1.81 MB</td>
</tr>
<tr>
<td>Pesticides</td>
<td>96565</td>
<td>28829 (30.0%)</td>
<td>4.19 MB</td>
</tr>
<tr>
<td>BNAs</td>
<td>151648</td>
<td>44919 (29.6%)</td>
<td>6.55 MB</td>
</tr>
<tr>
<td>VOA Low</td>
<td>170140</td>
<td>49148 (28.6%)</td>
<td>7.37 MB</td>
</tr>
<tr>
<td>VOA Trace</td>
<td>85394</td>
<td>24760 (29.8%)</td>
<td>3.70 MB</td>
</tr>
<tr>
<td>Total</td>
<td>545460</td>
<td>160546 (29.4%)</td>
<td>23.62 MB</td>
</tr>
</tbody>
</table>
Contact Information

• Buddy Wilson, Promium
  Phone: 425-286-9200
  EMail: bwilson@promium.com
Automating the EDD Designer, Checker, and Generator Process

Paul Banfer  
Vice President / Product Technology EISC  
EISC, 6767 W. Tropicana Ave, Las Vegas, NV 89103  
Primary Author's E-Mail: eisc@eisc.net; Phone: 702-248-1021

ABSTRACT

The EDD Designer, Checker, and Generator process provides a 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.

All in all, the most significant result of the industries diverse deliverables has pushed the focus to data deliverables rather than analytical data.

To combat this industry shift many laboratories, engineering firms, and agencies have focused their attention to automate the EDD process through the EDD Designer, Checker, and Generator Process.

This presentation will focus on example automation models consisting of:

1) Commercial Laboratories that have many different EDD formats to produce  
2) Analytical Laboratories for Water Utilities – meeting the 50 state requirements  
3) Automation of Commercial Laboratory to Data Validation  
4) An Engineering Firm or Agency model for Data Validation  
5) XML, SEDD, Superfund, and Stage 4  
6) XML and the States  
7) Chaining information sources to present the combined results to the decision maker  
8) Chaining instrument data sources to present combined data to the decision maker

(2) I prefer to give an oral presentation.
Automating the EDD Designer, Checker, and Generator Process

Washington, D.C.
July 2005

Overview

- **Management challenge**
  - Increased diversity in client deliverables offers management challenges for today’s lab
    - Data Quality
    - Data Integrity
    - Growth
    - Productivity
    - All effect...Revenue!

- **Meeting the challenge**
  - Industry focus on EDD process automation
    - The EDD Designer, Checker and Generator

- **Challenge Met**
  - EISC’s experience and approach across variety of analytical industries
Mission Statement

To create a b2b connectivity system so that you and your client can operate as one!

The Commercial Laboratory Story

Back in the late 80’s Mr. EDD was born.

Mr. EDD soon became so popular that everyone wanted one!

Over the years, Mr. EDD became a national analytical icon. Everyone wanted to personalize Mr. EDD!
The EDD Designer, Checker, and Generator Process

The Commercial Laboratory Story

Some labs tried to refrain from personalizing Mr. EDD ...

But eventually they started to lose out!

To stay up with the mass market demand, all kinds of personalized Mr. EDD’s became available. Labs worked hard!

New personalized Mr. EDD products became available at a breakneck pace!
The EDD Designer, Checker, and Generator Process

Flash forward to 2005!

Diversity of client deliverables

- CLP
- CLP-Like
- AFCEE
- Sub-Package
- State Reports
- EDD Format 1
- EDD Format 2
- EDD Format 3
- EDD Format 4
- EDD Format 5
- EDD Format 6

The EDD Designer, Checker, and Generator Process

- Commercial Laboratories that perform Federal and State work have issues with EDD’s:
  - Excessive variety of EDD formats (up to 300 for some labs)
  - Requires IT development staff to create an EDD Format Generator
  - Diverts key resources from future growth
    - Lab IT focused on EDD’s, not systems development
  - EDD generator not a “good fit” for lab’s production process
  - Review...a big issue
  - Non-billable work
The EDD Designer, Checker, and Generator Process

EISC’s approach...

Allows a non-IT employee to design EDD’s through templates

The EDD Designer, Checker, and Generator Process

Creates Valid Value tables to be dynamically produced with automatic reconciliation
The EDD Designer, Checker, and Generator Process

Makes the EDD Generation part of the deliverable production process

The EDD Designer, Checker, and Generator Process

Perform edits on a global or single field level. Edits are tracked and written to an SOP.

NEMC 2005 EISC
The EDD Designer, Checker, and Generator Process

SOP’s are used as instructions to generate the next EDD or a communication tool to enhance the template.

The EDD Designer, Checker, and Generator Process

The EDD Role: Different Scenarios

- Engineering Firm
- Commercial Lab
- Data Validation Firm
- Army Corp
The EDD Designer, Checker, and Generator Process

The EDD Role: Different Scenarios

B2B Scenario: Expanding laboratory capability

Sub-Contracted Specialty Lab:
- Radiation
- Dioxins
- Air
- Biological

Commercial Lab:
- SVOCs
- VOCs
- Metals

Decision Maker

The Future

Lab Data
Consequences
Actions

Commercial Lab Generates EDD

Decision Maker
**The EDD Designer, Checker, and Generator Process**

**The EDD Role: Different Scenarios**

- Lab Data - Calculated Results
- Consequences
- Actions
- Raw Data

**The Future**

- Commercial Lab Generates EDD of Standard Data
- Commercial Lab Generates EDD of Converted Raw Data Separated From Other Clients

**Decision Maker Makes Decisions**

**Decision Maker Defensibility of All Decisions**

---

**Conclusion**

**Motivation for the Lab to Produce Quality EDD’s**

A lab's client will never go to a competitor (not even for price), when:

- Deliverables (report and electronic) are perfect
- Turnaround time is swift

This is a solid business strategy to build a consistent revenue base of return clients (a.k.a. Residual Revenue)!

**Happy clients make a happy lab!**

**Have a great Day!**
Automated Review of SEDD Stage 3 Deliverables

Anand R. Mudambi
US EPA
1200 Pennsylvania Ave., Mail Code 5102G
Washington DC 20460
E-Mail: mudambi.anand@epa.gov Phone: 703-603-8796

Alfred Mayo
CSC,
15000 Conference Center Dr.,
Chantilly, VA, 20151
E-Mail: amayo@csc.com Phone: 703-818-4299

ABSTRACT

CSC has developed the EXES (Electronic data eXchange and Evaluation System) software for the USEPA Analytical Services Branch to review SEDD (Staged Electronic Data Deliverable) XML files up through SEDD Stage 3. EXES is designed primarily to review files submitted under the USEPA Contract Laboratory Program (CLP). However, the software has been designed to allow review of data submitted for other programs and methods or for modified CLP analyses. EXES can be used as a stand-alone system or linked to a database system. Over 4000 separate tests can be performed on a data deliverable and the results reported to the data user. The software can recalculate all values derived from the raw (quant report) data along with inspecting each required data element for presence, validity, and correctness. EXES can inspect data directly against a lookup table or by iteration (e.g., no more than x values may exceed a requirement). It also checks analysis sequence. The software provides pre-inspection capability to laboratories to allow problems to be corrected prior to submission.

I prefer to give an oral presentation.
Automated Review of SEDD Stage 3 Deliverables:

EPA’s Electronic data eXchange and Evaluation System

Presented by:
Dr. Anand Mudambi,
USEPA

What is EXES?

- A system developed by CSC for the USEPA Analytical Services Branch (ASB) to evaluate analytical data technical and contractual quality.
- Performs Contract Compliance Screening based on the technical requirements of the appropriate Statement of Work (SOW).
- Performs technical data qualification based on the National Functional Guidelines.
Contract Laboratory Program

- Used by USEPA to evaluate samples from Superfund sites.
- In FY04 alone over 126,000 analyses were process through the CLP program.
- High sample volume requires automated review of electronic data deliverables.
- New CLP SOWs require Electronic Data Deliverables (EDD) in SEDD Stage 3.
- EXES can evaluate EDDs from all three stages of SEDD.

Review of SEDD Stage 3 Files - Process

- Labs generate SEDD Stage 3 Files and upload them to the SMO Server via EXES website.
- Files are then evaluated by EXES for the different Test Types.
- EPA also provides CLP labs (with SOM01.1 Contracts) with a Self Inspection Tool.
Self-Inspection

- EXES is available on-line to allow CLP laboratories and their software vendors to inspect data prior to submission.
- This approach will allow CLP laboratories to correct all deficiencies found prior to delivery to USEPA.
- Ensures delivery of a complete and technically compliant data to USEPA.
- Does not guarantee that the SEDD files will be compliant with all SOM01.1 requirements.

Test Types

- Presence, Validity, Correctness.
- Completeness.
- Sequence and Frequency.
- Batching.
- Recalculation.
Presence, Validity, Correctness

- Are required data elements present and populated?
- Is data element content valid (date, numeric, character) and are Valid Values used?
- Are the correct Valid Values used?
- Are date sequences logical?

Completeness

- Are all requested samples, analyses, and analyte results present?
- Are all required dilutions, re-analyses, or re-preparations present?
Sequence and Frequency

- Are specified analytical sequences followed?
- Do QC occur at required frequencies?
- Do no more than “x” values fail to meet specified windows?

Batching

- SEDD has 11 batch types, SOW SOM01.1 specifies the use of seven of these.
- All samples must link to their required batches.
- No sample can link to a non-existent batch.
- Batches must contain required QC.
Calculation

- **Calculates all calibration results from the instrument response.**
- **Recalculates all final reported results from the instrument response and the recalculated calibration results.**
- **Recalculates all spikes and additions (Internal Standards, Surrogates, MS/MSD) from standard concentrations, amounts added, and sample volumes/masses.**

Flexibility

- **Designed to accommodate Modified Analysis Requests.**
  - **Modified Quantitation Limits.**
  - **Modified Analyte lists.**
  - **Modified matrices and methods.**
- **Designed to accommodate Non-CLP data so long as SEDD specifications are met.**
Custom Reports

- Provides electronic database ready reports via e-mail summarizing data assessment results.
- All reports are stored at a central database for future references by users.
- Reports can be customized to accommodate each users specific reporting and technical needs.
- Saves cost and time by expediting transfer of data to end users database and eliminating manual processing of hardcopy reports.

Stand-Alone Version

- A stand-alone version of EXES is being planned.
- Features:
  - Users may store results to their own databases.
  - Users may customize checks to meet their program needs.
  - Users may customize analyte lists, reporting limits, and data qualification flags.
Contact Information

- Anand Mudambi
  - mudambi.anand@epa.gov
  - Phone: 703/603-8796
Environmental Data from the Field to the Map, and the Impact of EDD Formats Like SEDD

Dr. David W. Rich
President
Geotech Computer Systems, Inc., Englewood, CO

ABSTRACT

Introduction

The amount of data being gathered at environmental sites is growing at ever increasing rates. Action levels are becoming more stringent, leading to more exceedences, and the expectations for using the data is also growing rapidly. Most people recognize the need for efficient tools for managing laboratory and field data, and affordable software is now readily available to more efficiently manage data. Advances in electronic data deliverable formats such as SEDD (Staged Electronic Data Deliverable) may remove some obstacles to data exchange, improving efficiency and improving data integrity. Cost savings of 50% or more can be documented resulting from better data management, and these savings can result in a high return on investment for software purchases, staff training, and data conversion. This talk follows the data through such a system from the field to the final uses of the data, and addresses a number of data interchange issues.

Gathering Data

Management of groundwater and related data starts in the field, taking physical samples to send to the lab, and gathering field data. The field data is imported into the database, and then associated with the analytical data when it arrives from the laboratory. The data management system should help with all phases of this process.

Data Interchange Issues

Efficiently moving data between project participants is a challenging and often time-consuming issue. New data formats like SEDD have the promise of simplifying data transfer by providing a standardized interface between data providers and consumers. This should contribute to data management efficiency and data integrity. As with most things, however, there are some challenges to overcome, some inherent in the process, and some dependent on the implementation of the interchange.

Quality Control, Storage and Retrieval

There are many different aspects of quality control that apply to managing environmental data, many of which can be made more efficient through effective use of data management software, and by implementing efficient transfer of EDDs. The software should help with simple statistical tests such as outlier and charge balance calculations. For more rigorous checking, the software
should check holding times, spike recoveries, QC sample frequencies, and other more traditional “validation” activities before the validator makes the final determination of suitability for use. Once the data has undergone the appropriate level of review, it is stored in a central repository, usually in a normalized relational data model. The user interface of the data management system should provide selection and display tools that provide a good level of flexibility, while still being easy to use.

Reports and Graphs

In the past the primary deliverable for project data has been tabular reports. These displays remain important, and software features such as flexible and automated formatting of results, and automatic comparison to target levels, can make this process much more efficient. With the data stored in a comprehensive data management system, other displays such as time-sequence graphs, also with comparison to limits, are easy to generate, and can tell quite a bit about the site, providing a greater return on the investment in sampling and analysis.

Display Using GIS

The spatial component of contaminant distribution can be a critical factor in understanding site issues. The spatial component is very difficult to visualize from tables and graphs, but often can be easily understood with one or more maps. Tight integration between the data management system and GIS displays is the key to efficiently generating good maps, and ensuring that the quality of the data is not degraded in the process. Graphically rich displays such as callouts (data tables on the map), graphs on the map, and Stiff water quality diagrams can aid greatly in understanding site conditions and making project decisions.

*****

Author Biographical Sketch

Dr. David W. Rich has a PhD in geology and over 30 years experience solving earth science computing problems. He is President of Geotech Computer Systems, where he directs their technical and business development efforts, and is the author of Relational Management and Display of Site Environmental Data from CRC Press.

Contact Information:

Dr. Dave Rich
President, Geotech Computer Systems, Inc.
6535 S. Dayton Street, Suite 2100
Englewood, CO 80111
Phone: 303-740-1999 Fax: 303-740-1990
Email: drdave@geotech.com
Web page: www.geotech.com
Environmental Data From the Field to the Map, and the Impact of EDD Formats Like SEDD

Dr. David W. Rich
drdave@geotech.com

Washington, DC July 25-29, 2005

Presentation Outline

- Introduction
- Gathering Field and Lab Data
- Transferring Data
- Quality Control
- Storage and Retrieval
- Reports and Graphs
- Display using GIS
- Return on Investment
- Conclusion
Introduction

- Environmental projects are inherently complex
- Expectations for data management are growing rapidly
- Budget pressures require you to do more with less
- Tools to do this are affordable and have a high return on investment
- We will walk through examples of using this technology for environmental projects
Gathering Data - Planning the event

Gathering Data - Field data
### Example Format - SEDD

<table>
<thead>
<tr>
<th>Field Data</th>
<th>SEDD</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site IDName</td>
<td>Sample</td>
<td>The Site IDName is used to link related data to the Site.</td>
</tr>
<tr>
<td>SiteName</td>
<td>Sample</td>
<td>The Site Name is typically used for identification purposes.</td>
</tr>
<tr>
<td>Sample IDName</td>
<td>Sample</td>
<td>The Sample IDName is used for tracking and identification.</td>
</tr>
<tr>
<td>Sample OCID</td>
<td>Sample</td>
<td>The OCID is used for unique identification within a project.</td>
</tr>
<tr>
<td>Description</td>
<td>Sample</td>
<td>The Description is used to provide additional information about the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
<tr>
<td>Sample Quantity</td>
<td>Sample</td>
<td>The Sample Quantity is used to indicate the amount of sample collected.</td>
</tr>
<tr>
<td>Sample Status</td>
<td>Sample</td>
<td>The Sample Status indicates the status of the sample.</td>
</tr>
<tr>
<td>Sample LocID</td>
<td>Sample</td>
<td>The LocID is used to identify the location of the sample.</td>
</tr>
<tr>
<td>Sample Type</td>
<td>Sample</td>
<td>The Sample Type is used to classify the type of sample.</td>
</tr>
</tbody>
</table>
Quality Control - Consistency checking

Quality Control - Verification and validation
Storage and Retrieval - Selection and display

Display options determine how your results are displayed

Example options:
- Regulatory limits for comparison
- Values and flags
- Unit conversion
- Date display
- Calculated parameters
- Handling of non-detects
- Significant figures
Water and Product Level Observations

<table>
<thead>
<tr>
<th>Sample Date</th>
<th>Depth to Water</th>
<th>Corrected Depth to Water</th>
<th>Corrected Water Elevation</th>
<th>LNAPL Thickness</th>
<th>Groundwater Elevation</th>
<th>BenZene</th>
<th>Depth to LNAPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/29/2005</td>
<td>7.75</td>
<td>0.34</td>
<td>739.14</td>
<td>24.05</td>
<td>709.90</td>
<td>7.0</td>
<td>2.3</td>
</tr>
<tr>
<td>9/6/2005</td>
<td>5.25</td>
<td>2.25</td>
<td>717.16</td>
<td>28.15</td>
<td>705.70</td>
<td>2.8</td>
<td>4.8</td>
</tr>
<tr>
<td>10/14/2005</td>
<td>26.51</td>
<td>16.24</td>
<td>740.12</td>
<td>25.05</td>
<td>716.20</td>
<td>5.5</td>
<td>2.7</td>
</tr>
<tr>
<td>5/6/2005</td>
<td>30.95</td>
<td>22.60</td>
<td>720.30</td>
<td>23.25</td>
<td>706.70</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>9/14/2005</td>
<td>34.05</td>
<td>24.78</td>
<td>716.16</td>
<td>20.05</td>
<td>701.60</td>
<td>10.4</td>
<td>3.8</td>
</tr>
<tr>
<td>12/14/1999</td>
<td>34.10</td>
<td>21.80</td>
<td>720.26</td>
<td>25.45</td>
<td>707.70</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>5/14/2000</td>
<td>17.05</td>
<td>13.80</td>
<td>739.70</td>
<td>14.35</td>
<td>719.00</td>
<td>10.6</td>
<td>4.6</td>
</tr>
<tr>
<td>9/15/1999</td>
<td>25.35</td>
<td>17.51</td>
<td>720.54</td>
<td>25.05</td>
<td>719.90</td>
<td>9.6</td>
<td>3.3</td>
</tr>
<tr>
<td>9/18/1999</td>
<td>39.25</td>
<td>28.10</td>
<td>727.00</td>
<td>24.26</td>
<td>707.90</td>
<td>6.7</td>
<td>4.0</td>
</tr>
<tr>
<td>11/18/1999</td>
<td>29.05</td>
<td>18.70</td>
<td>723.02</td>
<td>24.05</td>
<td>708.90</td>
<td>4.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

This groundwater graph shows water levels and NAPL thickness along with a dissolved constituent (benzene). It shows marked seasonality in the data.
Put data from the database on GIS maps – First use the database to select data for display.

Add to the GIS as XY data

Define display parameters
Time sequence graphs on the map

Return on Investment

<table>
<thead>
<tr>
<th>Cost Items</th>
<th>Example</th>
<th>Your company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Software</td>
<td>$4,000</td>
<td></td>
</tr>
<tr>
<td>Support (3 years)</td>
<td>2,400</td>
<td></td>
</tr>
<tr>
<td><strong>Total cost</strong></td>
<td><strong>$6,400</strong></td>
<td></td>
</tr>
<tr>
<td>Cost savings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data loading – save 50% of 4 days per year at $80 per hour, for 3 years</td>
<td>$3,840</td>
<td></td>
</tr>
<tr>
<td>Analysis – save 50% of 4 days per year at $80 per hour, for 3 years</td>
<td>$3,840</td>
<td></td>
</tr>
<tr>
<td>Reporting – save 50% of 4 days per year at $80 per hour, for 3 years</td>
<td>$3,840</td>
<td></td>
</tr>
<tr>
<td><strong>Total savings</strong></td>
<td><strong>$11,520</strong></td>
<td></td>
</tr>
<tr>
<td>Payback – $11,520 – 6,400</td>
<td>1.8:1</td>
<td></td>
</tr>
<tr>
<td>Plus intangibles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Work quality</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Client satisfaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Staff morale</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

- Environmental projects are inherently complex
- Efficient data management can reduce cost and improve quality
- Implementing a centralized data management system makes sense for most environmental projects
- Tools to do this are affordable and have a high return on investment
- Is it time to retire your spreadsheet?

Finally - answers to your environmental data management questions!

The Definitive Text

Now available from Lewis Publishers / CRC Press
Cat. #: L1591  ISBN: 1566705916

Relational Management and Display of Site Environmental Data provides you with the skills needed to effectively implement and operate an environmental data management system. The concepts covered can be applied to any system, from stand-alone through client-server to Web-based. This text/reference book combines the fundamentals of data management and display with the author's many years of experience to help you create your own data management system or more intelligently select and use a commercial solution.

www.geotech.com
Enviro Data®
Relational Management of Site Environmental Data

Enviro Spāse®
Display and Analysis of Site Environmental Data

Coming soon - Planning and Tracking for Enviro Data

Geotech
Computer Systems, Inc.
www.geotech.com
Remote LIMS Access from Sample Login to Result Retrieval

Rebekah Johnson and Christine Paszko, Ph.D.
Accelerated Technology Laboratories, Inc., 496 Holly Grove School Road, West End, NC 27376
Primary Author's E-Mail: rjohnson@atlab.com; Phone: 910-673-8165

ABSTRACT

In today’s complex and dynamic business environment, laboratories are focused on maximizing customer lifetime value, providing those customers with real-time access to data and controlling the cost of service. To survive in this environment, laboratories must offer remote Laboratory Information Management System (LIMS) access solutions to their customers. This presentation will describe a remote access system that will allow remote sample login functionality and result retrieval.

Request Point™ is a web based system that provides remote LIMS access for sample login. Request Point™ allows customers of a laboratory to submit order requests over the Internet. Instantly, the laboratory is notified of the request and the laboratories’ LIMS can be configured to log in the order. The system also allows customers to review the status of their orders submitted online from login to results. With this power of remote login, the order process is streamlined for laboratories and their customers.

Result Point™ is a system for remote LIMS access for result retrieval. This system allows the customer, who has a valid username and password, to login and view the status of their samples from pending entry to pending approval, as the samples travel through the analysis process. The power of Result Point™ is realized through the access of real-time results. When results are entered into the LIMS, customers will instantly be able to view their results. Not only will customers be able to view results, they will be able to generate reports. Reporting functions currently provided in the LIMS are extended to the customer by offering complete analytical reports with customized letterhead, if desired. With the power of remote results retrieval, laboratories can offer instant results and satisfaction to their customers.

Reducing overhead and maximizing the customers experience with a contract analytical laboratory are some of the advantages resulting from remote LIMS access. These systems allow users to extend the power of the LIMS from the laboratory to their customers.

(2) I prefer to give an oral presentation.
Application of Electronic Data Verification with Data Validation to Site Characterization Projects to Maximize Efforts

Stephen T. Zeiner, CEAC, CPC, Ruth L. Forman, CEAC, and David R. Blye, CEAC
Environmental Standards, Inc.  1140 Valley Forge Road, Valley Forge, PA  19482-0810
Primary Author's E-mail: Szeiner@EnvStd.com  Phone: 610-935-5577

ABSTRACT

Data validation has traditionally been used to determine the usability of the reported analytical results for site characterization and site remediation. In the recent past, data validation was required to be performed on 100% of the data for federal and state-led project sites and litigious sites. There is a growing trend to use electronic data verification (EDV) to assess data usability. Although it is time-efficient and cost-effective to utilize the automated EDV process to evaluate project data, relying on EDV alone can result in increased costs based upon decisions made using incorrect or incomplete information. Utilizing data validation and EDV has proven to be a very powerful combination in understanding site characterization data.

Electronic data verification is an automated process by which the quality assurance/quality control (QA/QC) results supplied in an electronic data deliverable is utilized to assess the usability impact of select QA/QC information and to subsequently apply applicable data qualification codes to the associated investigative sample results. EDV generally evaluates only a subset of the QA/QC that is evaluated during the data validation process. EDV assumes that the reported analytical results and associated QA/QC results are correct as reported by the laboratory. EDV is quicker and less expensive than data validation because EDV is an automated process.

Data validation, which must be performed by an experienced chemist, is a process by which the data package deliverable is reviewed relative to the following areas: correctness of the reported analytical results; completeness of the hardcopy data package deliverables to substantiate the reported analytical results; compliance with the associated analytical method and/or site-specific project requirements; and usability of the analytical results. Data validation examines all aspects of the data from sample receipt through data reporting, inclusive of the raw data for investigative samples, QA/QC samples, and calibrations. Data validation does not make any assumptions relative to the correctness of the information provided in the hard copy data package deliverable. Data validation requires more time and is more expensive than EDV due to the extensive labor involved.

This presentation will briefly describe the items reviewed during the data validation and EDV processes. In addition, this paper will present case studies involving large environmental investigations that utilized a combination of EDV and data validation to assess data usability. These case studies will provide examples of “issues” identified in EDV that were not issues when data validation was performed and, conversely, “issues” that were not identified in EDV and were issues when data validation was performed. These case studies will provide a demonstration of how data validation and EDV work together to improve the understanding of the site characterization data.

I prefer to give an oral presentation.
Application of Electronic Data Verification With Data Validation to Site Characterization Projects to Maximize Efforts

Stephen T. Zeiner, CEAC, CPC; Ruth L. Forman, CEAC; and David R. Blye, CEAC

Electronic Data Verification

- Electronic Data Verification (EDV) is:
  - A program add-on to a data base
  - An automated process
  - Evaluates results based on programmed logic using data from an EDD
Typical EDV Components

- Typical QA/QC elements evaluated:
  - Holding Times;
  - Percent Solids:
  - Method/Field/Trip blank results;
  - Matrix spike/matrix spike duplicate results;
  - Laboratory/Field duplicate results;
  - Surrogate compound recoveries; and
  - Laboratory control sample results.

EDV Advantages

- Automated process
- Error reduction
- Speed of assessment
- Lower overall cost
EDV Disadvantages

- Evaluates a limited set of QC data
- Set up cost for smaller projects
- Modification costs for project specifics
- Assumes reported data in the EDD are correct

What Is Data Validation?

- Typical data validation includes a review of a hardcopy data package for:
  - Correctness (qualitative ID and quantitation) of reported data;
  - Completeness of deliverable;
  - Method compliance; and
  - Usability of the results.
Data Validation Components

- Data validation includes all of the EDV elements.
- Additional elements:
  - Sample receipt information;
  - Initial and continuing calibrations;
  - Internal standard results;
  - Instrument check results;
  - Instrument blank results; and
  - Evaluation of raw data.

Data Validation Advantages

- Complete evaluation of all results
- Data base not required
- No size restriction on project
- Raw data review for interferences
Data Validation Disadvantages

- Time consuming
- Requires expert knowledge
- Higher cost than EDV
- Potential for human error

Case Study 1 - Background

- Characterize soil and monitor groundwater and surface water
- Perchlorate and 1,4-dioxane drivers
- Four laboratories
- QAPP
  - Defined Data Quality Objectives
  - Reporting/Method Guidance
Case Study 1 - Process

- Analytical data in a single data base
- EDV performed on all results
- 10% of soil underwent data validation
- Majority of aqueous underwent data validation

Case Study 1 - Results

- All EDV qualifications were reflected in the data validation reports
- Data validation identified several issues that were not covered under EDV
  - Improper quantitation
  - False positives
  - Incorrect sampling and analysis dates
  - Calibration Issues
  - Chromatographic interferences
Case Study 1 - Summary

- Data validation was able to identify and correct systematic issues such as:
  - Reporting errors
  - Quantitation and initial calibration issues
- Laboratories were able to adjust processes to improve data reliability
- EDV and data validation addressed a budget issue without breaking the bank

Case Study 2 - Background

- Characterize large sediment site
- Analyte list is short but PCB driver
- Five laboratories splitting analytical load
- QAPP includes:
  - Data quality objectives
  - SOPs for preparation and analysis
Case Study 2 - Process

- Field and analytical data in a single data base
- EDV performed on all results
- First year: each group has PCB audit sample
- Remaining years: 6% of PCB data
- Random selection of two delivery groups for other analytes
- Total of 20% of data underwent validation

Case Study 2 - Results

- All EDV qualifications were reflected in the data validation reports
- First year: data validation identified several issues that were not covered under EDV
  - Reporting errors
  - Method compliance issues
- Remaining years, data validation did not identify issues outside of EDV qualifications
Case Study 2 - Summary

- First year, data validation was able to identify and correct systematic issues
- Remaining years EDV and data validation identified same issues
- EDV and data validation were used to increase the confidence in entire data set

Case Study 3 - Background

- Characterize numerous small sites
- One laboratory
- Large range of analytes including:
  - Metals/mercury
  - Volatile organic compounds
  - GRO/DRO/RRO
  - Cl/\text{SO}_4
- No QAPP
Case Study 3 - Process

- Analytical data in a single data base
- EDV performed on all results
- About 20% of samples underwent data validation
- Utilized laboratory limits for data evaluation in EDV and data validation

Case Study 3 - Results

- First couple of years laboratory had issues with EDD and EDV was not possible
- Laboratory erratically updated limits
- Data validation identified several issues that were not covered under EDV
  - Hard copy did not match EDD
  - Large disparity between total and dissolved metals
  - Elevated temperatures upon receipt
Case Study 3 - Summary

- Inability to produce an EDD eliminated the cost savings of the central DMS and prevented EDV for the first couple of years
- Data reporting issues further reduced the efficacy of the DMS and EDV
- Laboratory was able to fix the issues

Case Study 4 - Background

- Characterize and Remediate many sites
- Large number of analytes
- Seven laboratories providing analyses
- Sites tied to a single central document
- QAPP includes:
  - Data quality objectives
  - Analytical method guidelines
  - Reporting requirements
Case Study 4 - Process

- Field and analytical data in a single database
- EDV performed on all results
- Random selection of 10% of total samples collected underwent data validation

Case Study 4 - Results

- All EDV qualifications were reflected in the data validation reports
- Data validation identified several issues that were not covered under EDV
  - Chromatographic interferences
  - ICP response suppression
  - Reporting errors
  - Method compliance issues
  - Sample receipt issues
Case Study 4 - Summary

- Data validation was able to identify and correct systematic issues such as:
  - Reporting errors
- Data validation was able to identify matrix issues such as
  - Chromatographic interferences
  - ICP response suppression
- EDV and data validation were used to increase the confidence in entire data set

Conclusion

- Laboratory performance is critical to success
- EDV and data validation can be used to improve laboratory performance and data quality over time.
- The combination of EDV and data validation enhance the advantages of both while minimizing the disadvantages.
Setting the Standards for Innovative Environmental Solutions
Modernization of EPA’s Superfund Contract Laboratory Program (CLP) through Method Customization, Electronic Data Delivery, and Client Support

Bruce Means  
US EPA  
1200 Pennsylvania Ave., Mail Code 5102G  
Washington DC 20460  
E-Mail: means.bruce@epa.gov  
Phone: 703-603-8815

ABSTRACT

Since its inception in the 1980s, Superfund’s Contract Laboratory Program (CLP) has provided EPA’s regional Superfund community analytical data of known, documented, and court defensible data. Originally designed to offer analytical support for the more “routine” site projects, the CLP has now evolved into a complete turn-key, full customer support mechanism, offering: Ability to log field sample information using CLP’s Field Operations and Records Management System (FORMS II Lite); sample scheduling with contemporary Organic and Inorganic Environmental Testing Laboratories via the Sample Management Office (SMO); flexibility in requesting analyses for specific analytes, reporting levels, and quality assurance requirements; data delivery through Staged Electronic Data Deliverable format (SEDD), data assessment using the CLP Data Assessment Tools (DAT), and invoice processing through use of our Web Based Invoicing System (WIS). The “new” CLP was purposely re-designed to provide maximum flexibility, while providing the highest level of legal defensibility. The combination of these services has proven to be better, faster, and more cost effective for HQ EPA and its customers.

I prefer to give an oral presentation.
Modernization of the Superfund Contract Laboratory Program

NEMC 2005
Bruce Means
US EPA
Analytical Services Branch

What is the CLP?

- National network of EPA personnel, commercial labs, and support contractors.
- Superfund Program’s preferred mechanism for providing routine analytical services.
- CLP is managed by the Superfund’s Analytical Services Branch (ASB).
CLP History and Growth

- Over the last 24 years, the CLP has provided data of known and documented quality for over 1,000,000 samples for EPA data users.
- The CLP has grown from about 30,000 samples in FY 97 to over 85,000 samples for FY 2004.
- FY 2005 projections: 100,000 samples, 150,000 analyses.

CLP Supports All SF Activities (FY 04)

![Pie chart showing distribution of CLP activities in FY 04]

- ER/Removal: 4%
- Site Assessment: 11%
- Post Listing: 36%
- Post-ROD: 21%
- Other: 28%
The CLP Today

- Quick access to laboratories available to accept samples 365 days of the year.
- 48 or 72-hour preliminary analyses, on request.
- 7, 14 and 21-day turnaround options.
- As of 2002, all CLP contracts offer a flexibility clause.
- Electronic tools used to automate the flow of data from the field to the final data recipient.
- Strong QA program

CLP Quality Assurance

- Annual Data & Tape Audits.
- Annual Lab On-Site Audits.
- Performance Evaluation Sample (PES) Development and Scoring:
  - Quarterly Blind
  - Site-Specific
- Limited Method Development.
The New CLP Process

- Field personnel coordinate sample shipment to CLP labs through Superfund’s Sample Management Office contractor (SMO).

- SMO assigns a lab(s) to each site project based upon scope of project, lab capacity, and the labs prior performance ranking.

Measuring Lab Performance

- SMO monitors 100% of generated data:
  - Timeliness;
  - Completeness;
  - Adherence to the SOW;
  - Accuracy.

- ~3500 separate data checks are made for each group of laboratory data.
Rewarding Good Performance

- Laboratory performance results are then weighted and considered with their prices to come up with a final ranking.

- Lab rankings are performed on a monthly basis.

- Top performers are considered first in assigning new work.

Support for Regional Data Review and Validation

- Performance monitoring results delivered to the data user within 24-48 hours of receipt of data from the lab.

- Results are used for Regional data validation.

- On request, SMO provides specialized computer aided data review of data formatted to meet user needs.
Analytical Data Management – the Big Picture

CLP Electronic Tools

- Field Operations Records Management System (FORMS) II Lite
- Data Assessment Tool (DAT)
- Web Contract Compliance Screening
- Web Invoicing System (WIS)
FORMS II Lite

A flexible, stand-alone, Windows-based software that automates documentation for CLP and non-CLP samples.
FORMS II Lite Advantages

- Generates tags, bottle labels, Traffic Reports, and chain-of-custody records.
- Facilitates electronic transfer of sample information to other databases (XML).
- Saves up to 10-15 minutes of work per sample (~ $1M/year)
Data Assessment Tool (DAT)

- Assesses >3,500 contract compliance and QC parameters within 24 to 48 hours of receipt.
- Provides customized electronic deliverables for direct input into client databases.
- >$17 million in savings.

Web-Based Contract Compliance Screening

- Web-based tool designed to check deliverables prior to submission.
- Ensures accurate and complete data packages.
- Significantly reduces errors in final data deliverables.
- Greatly facilitates on-time payment.
Web-Based Invoicing System

- Allows CLP contractors to electronically bill EPA for work performed.
- Billing is done in safe and secure environment.
- Invoices built on information already present in EPA Databases.

WIS - Advantages

- Eliminates paper invoices
- Eases monitoring of invoices needing payment
- Eliminates re-keying of invoice data
- Reduced the number of disallowed invoices by 96%.
The New Organic Contracts

- Awards: Summer 2005
- Statement of Work (SOM 1.1) details methods consistent with SW 846.
- Requires use of the Staged Electronic Data Deliverable (SEDD Stage 3).
- Contact: Anand Mudambi
  - 703-603-8796
  - Mudambi.anand@epa.gov

CLP Inorganic Contracts

- Current SOW ILM05.3 incorporates ICP-AES and ICP-MS analytical services.
- A new SOW is under development.
- Also to require SEDD Stage 3.
- Contact: John Nebelsick
  - 402-697-2572
  - nebelsick.john@epa.gov
Staged Electronic Data Deliverable (SEDD)

- New electronic data deliverable format developed jointly with USACE.
- Open, non-proprietary.
- Uses XML to transmit the data.
- New EPA RAC and START contracts also require SEDD.

SEDD Benefits

- Will reduce industry-wide EDD confusion.
- Will improve compatibility and versatility in electronic data reporting, review, handling, and archiving.
- Pilots suggest data review time and cost savings of 30-50%.
- Interagency effort: EPA, USACE, Air Force, Navy, others working to implement.
Other National Non-Routine Analytical Services

- Air analysis by TO-14, TO-15
- Dioxin by High Resolution GC/MS.
- PCB congeners (all 209) via analytical protocol developed from OW Method 1668A.

CLP Contact Information

Bruce Means
Chief, Analytical Services Branch (MC 5102G)
Technology and Innovation and Field Services Division
USEPA Office of Superfund Remediation and Technology Innovation

Phone: 703-603-8815
E-Mail: means.bruce@epa.gov
New Jersey Beach Monitoring Solution

Robert Peeples, PE
BMS Project Manager
Earth 911

ABSTRACT

Developed for the State of New Jersey, this monitoring solution package is a fully paperless Electronic Data Delivery (EDD) system from beach sampling field data to EPA reporting. Our work with New Jersey and four other states on the 2003 NEIEN Challenge Grant taught us that in order to send quality data to EPA, data quality must remain in control starting from the shoreline. Handheld and tablet computers were used to demonstrate a wireless web system for field data entry, and web-based forms for laboratory results posting and risk-based decisions. The system automatically updates both the New Jersey Web site (www.NJBeaches.org) and the Earth 911 Web site (www.Earth911.org) and retains the information necessary to send reports to the EPA activity tracking database (PrAWN) and the EPA water quality database (StoRet) through the state exchange node or Earth 911’s virtual state node, which we have registered with the Central Data eXchange (CDX). This year we added handheld XML-based entry systems to act as a temporary solution when wireless communications are not available or cost-effective. The system is automatically updated on return to the office by synchronizing the handheld database across the Internet. New Jersey is offering this system free of charge to anyone who may wish to implement it in their state. Earth 911 is also available to help with the implementation of this new EDD system.
New Jersey Beach Monitoring Solution: Lessons Learned in the NEIEN Challenge Process

Robert S Peeples, PE
Earth 911

NEIEN Challenge Baseline

- NEIEN – National Environmental Information Exchange Network
- The original process had local health authorities rolling up data to the State via disparate and separate spreadsheets, database tables, and paper records.
- The State reformatted critical elements of the records so they could be merged into a single spreadsheet.
- Spreadsheets were used to build annual reports for EPA to meet public notification reporting requirements of the BEACH Act of 2000.
- Virtually all other related information, including monitoring results, was lost to file cabinets and disk drives.
Raising the Bar

- EPA decided to add monitoring data reporting requirements to the BEACH program.
- EPA’s oldest database, StoRet, was to be used for reporting monitoring data.
- StoRet required substantial modification in order to accept modern data transfer techniques.
- The NEIEN was in development as a method of automating reporting through a Central Data eXchange (CDX).
The Obvious Solution?

- Control the data flow from generation to reporting in a single, coherent data management system.
Questions?

Contact Information

• Bob Peeples
  – Telephone Number: 480-889-2650
  – E-Mail: bpeeples@earth911.org
  – www.earth911.org
Supplemental Slides
BMS Beach Results Web-page Generator

County: All
Start date of Week: 
End date of Week: 
Date Notes: Today is Monday, June 27, 2005.

Beach Notes: Located in Atlantic City - Illinois
Station in Atlantic City : Bacteria levels in monitoring exceed State standards

Aerial Notes: 

Save Changes  Cancel
Crossing the Digital Divide: Looking to the Future through Quality Assurance of Records Management

Mary Thomas Sullivan, MLS, CRM, CQIA
Associated Records and Information Services, P.O. Box 937, Caddo Mills, TX 75135
Email: aris@associatedrecords.com Phone: 903-527-2156

ABSTRACT

Documents that are not filed correctly run the risk of not being retrieved. This principle applies to electronic files as well as paper files. This presentation will

- Go beyond offering a surface view of the various aspects of records management as it pertains to industry, laboratory and homeland security.
- Show ways information may be saved and migrated as software and hardware technologies advance.
- Present future methods of saving electronic information.
- Review methods of preventing loss of information due to a disaster as well as preventing the loss.
- Include scenarios to illustrate information included in the presentation.
- Enable the attendee to learn how knowledge management will increase the viability and credibility of the organization as a whole.

We are pioneers standing on the new frontiers of quality. Quality defines the information gained from processes in the organization and ensures the management of such information through the quality assurance of records management. Quality assurance of information is a strong defense for the country. As we cross this new frontier let us ensure the high standards of quality are maintained at all levels of research and policy implementation.

Join others at this presentation to learn the benefits of good records management and the problems associated with poor records management. Learn where disaster begins when quality assurance is left out of records management.

I prefer to give an oral presentation.
The 21st Annual National Environmental Monitoring Conference

WASHINGTON, D.C.

Protecting People and the Environment Through Environmental Monitoring

JULY 25-29, 2005

CROSSING THE DIGITAL DIVIDE:

LOOKING TO THE FUTURE WITH RECORDS MANAGEMENT QUALITY ASSURANCE
ITEMS OF CONCERN

- Management of Files
- Management of Indexing
- Management of Computerized Documents
- Management of Email
- Management of Information

MANAGEMENT OF FILES

- File Naming
- File Indexing
- File Arrangement
- Protection of Information
MANAGEMENT OF FILES

- Consequences of Poor Management of Files:
  - Increase in costs
  - Loss of Credibility
  - Higher Audit Fees
  - Slower Disaster Recovery

MANAGEMENT OF INDEXING

- Purpose of Retention Plan
- Indexing = Ease of Retrieval
- Metadata – Controlled Vocabulary
- Content Management
- Knowledge Management
MANAGEMENT OF COMPUTERIZED DOCUMENTS

- Naming Responsibilities
- Uniform Filing
- Saving of Document
- Backup of Files

MANAGEMENT OF EMAIL

- Guidelines
- Vulnerability of Information
- 90 Day Policy
- Training – Print out records need to be maintained as part of records management procedures
MANAGEMENT OF INFORMATION

Security:
- Common Sense Application
- Vital Records
- Continuity of Operations
- Security of Information

MANAGEMENT OF INFORMATION

- Information Responsibilities:
  - Accuracy on part of creator of document
  - Accuracy on filing method and retrieval of document
MANAGEMENT OF INFORMATION

- Training:
- Naming responsibilities
- Ethical responsibility
- Business continuity practices
- Storage responsibilities

MANAGEMENT OF INFORMATION

- ISO 15489:
  - Clause 4: “Integrate records management into business systems and processes”
  - Crucial in meeting goals through best practice in managing information assets
MANAGEMENT OF INFORMATION

• Sarbanes Oxley:
• Refers to Risk Management
• Not a Document Management regulation – have a “domino” effect on document management

MEASUREMENT OF INFORMATION

• Tape Measure / Ruler / Yardstick
• Databases – Production Charts
  – Software Applications:
    • Access
    • Excel
• Quality Management Tools
  – Relationship to Records Management
MANAGEMENT OF DIGITAL INFORMATION

- Migration of Information
- Software
- Hardware
- Non-electronic methods:
  - Microfilm
  - Imaging

MANAGEMENT OF IMAGING INFORMATION

- Information = Selective Process
- Indexing = Ease of Retrieval
- Image:
  - For documentation
  - For convenience
  - Not to save space
FUTURE OF INFORMATION

• Portal = an opening / Business Portal = an electronic opening to a private Internet cache of information / sometimes found as an Extranet.

• Problems with portals: finding the right software company to support the operation / allowing only specific individuals access to the portal.

FUTURE OF INFORMATION

• Benefits of portals: cuts down on communication costs / cuts down on travel.

• Future of portals: Pratt & Whitney sees a federated portal coming where an aircraft mechanic at American Airlines can access information from Pratt & Whitney on a part for the plane and Boeing for a delivery date on a new model.
FUTURE OF INFORMATION

• Data Mining – similar to Portals, similar to an Internet search. A term is entered and various companies reply with answers.

• Data Warehouses – the Internet site for storage of information, releasing earthbound servers from saving unlimited amounts of information.

FUTURE OF INFORMATION

• New Employment Positions:
  – KO – Knowledge Officer
  – Army leads the way with an AKO (Army Knowledge Online) – useful in the field – allows all Army personnel to know where everyone is located at an exact moment.

  – CIO – Chief Information Officer
Mary T. Sullivan, MLS, CRM, CQIA
Associated Records and Information Services
Phone: 214-675-9598
FAX: 903-527-0326
aris@associatedrecords.com
www.associatedrecords.com
Session 6

Analysis for Emerging Chemicals
Use of Non-Standard Mass Spectrometric Techniques to Solve Analytical Problems for Emerging Contaminants

Richard Burrows
Severn Trent Laboratories
4955 Yarrow St.
Arvada, CO 80002
(303) 736-0100
rburrows@stl-inc.com

ABSTRACT

Analysis of low levels of some emerging contaminants in complex matrices can be challenging, and in some cases requires the use of more advanced mass spectrometric techniques to assure sufficiently low quantitation limits and freedom from matrix interference.
This presentation provides some examples, including:

- N-Nitrosodimethylamine by GC/Chemical ionization MS/MS
- Explosives by LC/MS/MS
- PBDEs
- PFOA

Limitations of the standard methods along with performance details of the new methods will be presented.
Use of non-standard Mass Spectrometric Techniques to Solve Analytical Problems for Emerging Contaminants

Richard Burrows
Severn Trent Laboratories

National Environmental Monitoring Conference
July 2005

The Mass Spec Toolbox

- HPLC/MS, HPLC/MS/MS
- IC/MS, IC/MS/MS
- GC/MS, GC/MS/MS
- High resolution MS
- Time of Flight MS
  - Electrospray ionization
  - Atmospheric Pressure Chemical Ionization
  - Chemical Ionization
  - High Resolution Mass Spectrometry
Electron Impact GC/MS

Advantages
- Powerful separation
- Structural information from fragmentation
- Affordable instrumentation
- Universal detector (if the analyte gets to the MS)

Disadvantages
- Most organic compounds will not go through a gas chromatograph
- Some compounds fragment too much
- No selectivity

Desirable method characteristics

- Linearity - predictable instrument response
- Precision - reproducibility of results
- Accuracy - proximity of results to true value
- Sensitivity - low concentration reliably detected
- Selectivity - ability to differentiate compound of interest from interferences
- Robustness - ability of method to work properly in a variety of types of samples
Phenoxy Acid Herbicides

- Existing Method
  - 8151A, GC/ECD
- Limitations
  - Insufficient selectivity, difficult sample prep leads to poor precision and accuracy
- Solution
  - LC/MS/MS

Herbicides 1 ppb on column
Energetic compounds

- Standard method is 8330 HPLC/UV
  - Insufficient
    - Sensitivity
    - Selectivity
    - Robustness
- Solution
  - LC/MS
  - Extraction – similar to 8330 – 2g sonicated in acetonitrile for soil, SPE of 1L water eluted with acetonitrile to 5 mL final volume.

Energetic Compounds

- Analysis
  - LC- 250 mm C18 column, mobile phase 0.01M ammonium acetate in water and methanol mixture
  - MS- APCI negative ion polarity – single stage MS detection of characteristic mass
  - 3 isotopic labeled internal standards and one surrogate used for QC compounds
  - Calibration – 10 to 300 ug/L instrument concentration
### Detection limits, LC/MS vs. LC/UV

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LC/UV MDL</th>
<th>LC/MS MDL</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5-Trinitrobenzene</td>
<td>0.037</td>
<td>0.015</td>
<td>2</td>
</tr>
<tr>
<td>1,3-Dinitrobenzene</td>
<td>0.065</td>
<td>0.008</td>
<td>8</td>
</tr>
<tr>
<td>2,4,6-Trinitrotoluene</td>
<td>0.047</td>
<td>0.015</td>
<td>3</td>
</tr>
<tr>
<td>2,4-Dinitrotoluene</td>
<td>0.068</td>
<td>0.013</td>
<td>5</td>
</tr>
<tr>
<td>2,6-Dinitrotoluene</td>
<td>0.075</td>
<td>0.013</td>
<td>6</td>
</tr>
<tr>
<td>2-Amino-4,6-dinitrotoluene</td>
<td>0.058</td>
<td>0.012</td>
<td>5</td>
</tr>
<tr>
<td>2-Nitrotoluene</td>
<td>0.065</td>
<td>0.022</td>
<td>3</td>
</tr>
<tr>
<td>3-Nitrotoluene</td>
<td>0.034</td>
<td>0.016</td>
<td>2</td>
</tr>
<tr>
<td>4-Amino-2,6-dinitrotoluene</td>
<td>0.028</td>
<td>0.015</td>
<td>2</td>
</tr>
<tr>
<td>4-Nitrotoluene</td>
<td>0.042</td>
<td>0.014</td>
<td>3</td>
</tr>
<tr>
<td>HMX</td>
<td>0.068</td>
<td>0.015</td>
<td>4</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.096</td>
<td>0.020</td>
<td>5</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>0.374</td>
<td>0.039</td>
<td>10</td>
</tr>
<tr>
<td>PETN</td>
<td>0.529</td>
<td>0.016</td>
<td>33</td>
</tr>
<tr>
<td>RDX</td>
<td>0.098</td>
<td>0.006</td>
<td>18</td>
</tr>
<tr>
<td>Tetryl</td>
<td>0.084</td>
<td>0.010</td>
<td>9</td>
</tr>
</tbody>
</table>

### 10 μg/L RDX

![LC/MS and HPLC/UV graphs showing RDX detection](image-url)
Explosives low std Compounds 9-16

Explosives low std Compounds 17-20
RDX control chart

Quality Control Chart

Statistical Calculations

- N: 27
- Mean: 145.9
- Std. Dev.: 0.3818

Calculated Limits

- UCL: 150.7
- LCL: 79.8
- RPO: 0

Rejected data points are charted

Picric Acid

- Existing Method
  - HPLC/UV
- Limitations of Existing Method
  - Insufficient selectivity and sensitivity
- Solution
  - LC/MS/MS
Picric acid 10ppb on column

Perfluorooctanoic acid, PFOA

- Used in the manufacture of fluoropolymers – non-stick cookware, water and stain resistant finishes, fire resistant finishes

- Persistent in the environment

- Related compounds, Perfluorooctyl sulfonate (PFOS) and perfluorooctanesulfonic acid (PFOSA) can be analyzed using the same method
Limitations of existing method
- There is no existing method
- Not a good compound for GC
- No strong chromophore

Solution
- LC/MS/MS

Extraction
- Aqueous – SPE extraction using C18 cartridge
- Solids - 10g sonicated with methanol

LC – 250 mm C18 column, aqueous formic acid and methanol mobile phase

MS – ESI negative ion MS/MS detection

C13 labeled PFOA used as an internal standard and PFNA (closely related cmpd) used for a surrogate

Calibration - 1 to 50 ug/L instrument concentration
PFOA 1 ppb on column
50 ppt in sample

1 µg/L

14:16:13

pf35c1061 Sm (Mn, 2x2)

F1

1.41

412.8 > 218.7

1.28e3

1.31

2.07 2.23

1.42

595

11

1.00 2.00

Time

1 µg/L

14:16:13

pf35c1061 Sm (Mn, 2x2)

F1

1.41

414.8 > 369.7

6.03e4

6126

Area

1.00 2.00

Time

SEVERN TRENT STL

LC/MS/MS

SEVERN TRENT STL
PFOA ICAL

PFOA low std
Existing method
- 8270C GC/MS, 8070A GC/NPD

Limitations
- Insufficient sensitivity, selectivity

Solution
- GC/ Chemical Ionization MS/MS
- High Resolution MS

- GC/CI/MS/MS positive ion analysis
  - CI gas – ammonia

- Extraction – CLLE of 1L water with CH₂Cl₂, concentration to 1.0 ml final volume

- 624 type capillary column with helium carrier gas

- Cryogenic cool on-column injection

- NDMA-d6 used for an isotope dilution standard

- Concentration – 1.0 to 100 ug/L instrument concentration
More than just Dioxins!

- Target analytes are fragmented in the ion source of a triple-sector instrument
- Ion fragments are selected by energy-dependent trajectory in first electrostatic field (ESA1)
- Exact mass fragments selected by mass-dependent trajectory in magnetic field (Magnet)
- Residual interferences filtered and removed in ESA2
- Exact mass fragments are detected at the photomultiplier with sensitivity at low femtogram levels (on column)
Why High Resolution Analysis is Better

- A target analyte’s **exact mass is highly characteristic** of its identity
- Mass resolution measures the ability of the instrument to **isolate and detect a particular exact mass**
- Triple sector instruments operate at **mass resolution of ~10,000** (high) vs ~100 (low) for quadrupole instruments.
- High Res analyses are nominally **100 times better at filtering interferences** than conventional Low Res analysis.
- High Res analyses offer **improved sensitivity, selectivity, and robustness**.
NDMA Low Calibration Standard (1 ng/L)

NDMA
Exact Mass - 74.0480

d$_6$-NDMA
Exact Mass - 80.0857

Brominated flame retardants

- Existing method
  - None, GC/MS and GC/ECD are possibilities
- Limitations of standard methods
  - Insufficient sensitivity and selectivity
- Solution
  - High Resolution GC/MS
Brominated Flame Retardant
Low Standard (20 pg/L)

BDE-99
Exact Mass - 563.6216

BDE-99
Exact Mass - 565.6196

$^{13}\text{C}_{12}$ - BDE-99
Exact Mass - 575.6619

$^{13}\text{C}_{12}$ - BDE-99
Exact Mass - 577.6598

Calibration Curve for Low Level Organics by HRMS

- NDMA
- 1,4-Dioxane
- 1,2,3-Trichloropropane
**Limitations of Exotic Mass Spectrometry**

- **LC/MS**
  - Need good separation of ionization suppression can be a problem
  - No library searching
  - Difficult if there are many compounds in the method
  - Soft ionization – MS/MS very desirable to avoid interferences
  - MS/MS is expensive

---

**Conclusions**

- Electron impact GC/MS works for many analytes, but not for everything
- LC/MS, LC/MS/MS, LC/MS/MS and CI-GC/MS/MS and High Resolution MS can provide definitive data
- MS/MS is very desirable when soft ionization techniques are used
- Ionization suppression is a concern in LC/MS, and isotopically labeled internal standards are the best solution
- When a lab claims a low detection limit, check the signal to noise!
SEVERN TRENT

STL

Good

SEVERN TRENT

STL

Not so good
Conclusions

- Electron impact GC/MS works for many analytes, but not for everything
- LC/MS, LC/MS/MS, LC/MS/MS, CI-GC/MS/MS and High Resolution MS can provide definitive data
- MS/MS is very desirable when soft ionization techniques are used
- Ionization suppression is a concern in LC/MS, and isotopically labeled internal standards are the best solution
- When a lab claims a low detection limit, check the signal to noise

Acknowledgments
Mark Dymerski  Steve Cowling
STL Denver

Eric Redman  Pamela Schemmer
STL Sacramento

Further Information
Richard Burrows  (303)736-0100  rburrows@stl-inc.com
GCxGC-ECD of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides in Drinking Water

Jack Cochran*
LECO Corporation
815 Pilot Road, Suite C
Las Vegas NV 89119
702-614-1143 x230
jack_cochran@leco.com

Frank Dorman
Restek Corporation
110 Benner Circle
Bellefonte, PA 16823
* presenting author

ABSTRACT

Comprehensive two-dimensional GC (GCxGC) is a powerful technique where two independent separations are employed in one analysis for the entire injected sample. In a typical GCxGC setup, a thermal modulator separates press-fitted serial columns of differing phases. One separation is performed on the first column (usually a “boiling point” type), and its effluent is continually focused and “injected” onto the second column (most often a polar or selective phase), where another separation occurs. By keeping the second column short, a series of high-speed chromatograms are generated, and the first column separation is preserved. Separation results can be plotted as a retention plane (column 1 time x column 2 time), also known as a contour plot, or a surface plot, which is a 3-dimensional representation of x (column 1 retention time), y (column 2 retention time), and z (intensity of peaks).

GCxGC produces chromatographic peaks that range from 50 to 500 ms wide. Only a few detectors are available that have the necessary acquisition rates to define peaks this narrow. For example, when mass spectrometry is used, only time-of-flight (TOF) that can record hundreds of spectra per second will work. Of the other detectors used for GCxGC, the flame ionization detector (FID) and electron capture detector (ECD) are most represented in the scientific literature.

The potential of GCxGC-ECD is extremely attractive for environmental analysis since many environmental contaminants are halogenated, including polychlorinated biphenyls (PCBs), chlorinated dioxins and furans, brominated flame retardants, chlorination disinfection byproducts, chlorinated solvents, and pesticides. The sensitivity of the ECD towards halogenated compounds, and its selectivity against those that do not contain halogens, are well known, but both, sensitivity and selectivity, can be enhanced through GCxGC.

A new, commercially available GCxGC-ECD system with a quad-jet, dual-stage modulator was used to demonstrate the potential of the system for the analysis of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides (the compounds in US EPA Method 551.1) in drinking water. Separations, instrumental detection limits, and quantification will be discussed.
GCxGC-ECD of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides in Drinking Water

Jack Cochran
LECO Corporation, Las Vegas, NV
Frank Dorman
Restek Corporation, Bellefonte, PA

Outline

- Current EPA 551.1 methodology
- GC-TOFMS analysis of standards
  - 551 GC conditions for retention time mapping
- Introduction to GCxGC-ECD
- Preliminary results using GCxGC-ECD
  - Chromatography of standards
  - Analysis of Las Vegas drinking water
US EPA Method 551.1

- For chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides in drinking water
- Pentane or MTBE shake extraction
- GC-ECD analysis
  - 30 m x 0.25 mm x 1.0 μm DB-1
  - 30 m x 0.25 mm x 1.0 μm Rtx-1301
- Method detection limits range from ~2 to 200 ppt depending on analyte

GC Conditions for TOFMS

- 30 m x 0.25 mm x 1.0 μm Rtx-1 (Restek)
  - He carrier, 0.7 mL/min constant flow
- Split injection of standard
  - 1 μL, 250°C, split ratio 40:1
- Oven program (according to Method 551.1)
  - 15°C, 2°/min, 50° (10 min)
  - 10°/min, 225° (15 min)
  - 10°/min, 260° (30 min)

Run time = 93.5 min
TOFMS Conditions
LECO Pegasus III

- Source temperature: 225°C
- Electron ionization: 70 eV
- Stored mass range: 35 to 450 u
- Acquisition rate: 2 spectra/sec

LECO Pegasus III GC-TOFMS

- Make ions
- Pulse them down a flight tube
- Arrival at detector is by time-of-flight
  - Low mass = faster
  - High mass = slower
- Detect ions
<table>
<thead>
<tr>
<th>Compound</th>
<th>RT_{FIA}</th>
<th>RT_{TOF}</th>
<th>Compound</th>
<th>RT_{FIA}</th>
<th>RT_{TOF}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>8.4</td>
<td>8.6</td>
<td>Decachlorobiphenyl</td>
<td>39.5</td>
<td>38.4</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>9.3</td>
<td>9.5</td>
<td>Hexachlorocyclopentadiene</td>
<td>43.9</td>
<td>42.8</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>11.0</td>
<td>11.8</td>
<td>Trifluoromethane</td>
<td>49.0</td>
<td>46.9</td>
</tr>
<tr>
<td>Trichloroacetonitrile</td>
<td>12.0</td>
<td>12.2</td>
<td>Simazine</td>
<td>50.1</td>
<td>47.2</td>
</tr>
<tr>
<td>Dichloroacetamide</td>
<td>13.5</td>
<td>13.8</td>
<td>Ammonia</td>
<td>56.4</td>
<td>47.4</td>
</tr>
<tr>
<td>Bromochloromethane</td>
<td>13.7</td>
<td>13.9</td>
<td>Hexachlorobenzene</td>
<td>51.1</td>
<td>47.9</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>13.9</td>
<td>14.1</td>
<td>gamma-Hexachlorocyclohexane</td>
<td>51.7</td>
<td>48.3</td>
</tr>
<tr>
<td>1,1-Dichloropropane</td>
<td>15.0</td>
<td>15.7</td>
<td>Methoxybromide</td>
<td>54.0</td>
<td>49.9</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>18.0</td>
<td>18.6</td>
<td>Atliclor</td>
<td>55.7</td>
<td>51.2</td>
</tr>
<tr>
<td>Chloroparvin</td>
<td>20.5</td>
<td>20.5</td>
<td>Bromide</td>
<td>55.9</td>
<td>51.2</td>
</tr>
<tr>
<td>Chlorodibromomethane</td>
<td>21.0</td>
<td>21.1</td>
<td>Cyanazine</td>
<td>57.0</td>
<td>52.0</td>
</tr>
<tr>
<td>Bromochloracetetonitrile</td>
<td>21.3</td>
<td>21.3</td>
<td>Hepthalur</td>
<td>57.2</td>
<td>52.1</td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>22.0</td>
<td>22.0</td>
<td>Metolachlor</td>
<td>59.1</td>
<td>53.4</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>24.8</td>
<td>24.6</td>
<td>Heptachloroepoxide</td>
<td>62.5</td>
<td>56.7</td>
</tr>
<tr>
<td>1,1,1-Trichloro-2-propanone</td>
<td>27.9</td>
<td>27.7</td>
<td>Endrin</td>
<td>68.0</td>
<td>63.2</td>
</tr>
<tr>
<td>Bromoform</td>
<td>31.0</td>
<td>30.7</td>
<td>Endrin aldehyde</td>
<td>69.3</td>
<td>64.0</td>
</tr>
<tr>
<td>Dichloroacetetonitrile</td>
<td>31.5</td>
<td>31.2</td>
<td>Endrin ketone</td>
<td>75.7</td>
<td>68.4</td>
</tr>
<tr>
<td>1,2,3-Trichloropropane</td>
<td>32.8</td>
<td>32.4</td>
<td>Methoxybromide</td>
<td>77.0</td>
<td>69.5</td>
</tr>
<tr>
<td>1,2,4-Trichloro-3-propanone</td>
<td>38.3</td>
<td>37.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**GC-TOFMS Chromatogram**

![Chromatogram Image](image-url)
GC-TOFMS Chromatogram

Bromacil/Alachlor and Cyanazine/Heptachlor

Coeolute at 30 but resolved at 25 cm/sec helium

29 Bromacil
30 Alachlor
31 Cyanazine
32 Heptachlor
GC-TOFMS Chromatogram

Spectral Deconvolution of Alachlor from Bromacil
Typical GCxGC Setup

- Primary column (1st dimension)
  - Longer, wider bore, thicker film
  - Non-polar
- Modulator
  - Thermal in nature
  - Focuses effluent from primary column
  - "Injects" this effluent onto secondary column
- Secondary column (2nd dimension)
  - Very short, narrow bore, thinner film
  - Polar or selective

GCxGC Schematic

```
From Injector

Modulator

1st Dimension

To Detector

2nd Dimension

Two independent separation mechanisms
```
GCxGC-ECD

- Agilent 6890N GC
  - ECD
  - FID
- LECO thermal modulator
  - Quad-jet
  - Dual-stage
- LECO ChromaTOF software
  - Instrument control and data processing fully integrated

Modulator and Secondary Oven
**GCxGC Columns**

- 30 m x 0.25 mm x 1.0 \( \mu \)m Rtx-1 (Restek)
  - 100% dimethyl polysiloxane
- 1 m x 0.18 mm x 0.10 \( \mu \)m Rtx-35 (Restek)
  - 35% diphenyl – 65% dimethyl polysiloxane
- Constant flow He at 1.0 mL/min
- Split injection
  - 1 \( \mu \)L at 250°C, 10:1 ratio
GCxGC-ECD Conditions

- Primary oven
  - 30°C (4 min), 2°C/min, 50°C (10 min)
  - 10°C/min, 225°C (15 min)
  - 10°C/min, 260°C (30 min)
- Modulator
  - Temperature offset: 30°C
  - Modulation time: 3 sec
- Secondary oven
  - 5°C offset from primary oven
- Detector
  - ECD, 325°C, N₂ makeup gas at 150 ml/min, 50 Hz

Run time = 90 min
Calibration and Quantification with GCxGC-ECD

- Analyze standards and sample
  - Internal standard
    » p-Bromofluorobenzene
- Find peaks and combine slices for peak areas
  - Automatic through software
- Use retention time for identification
- Quantify 551 method analytes against prepared calibration curves
Calibration Curve – Trichloroacetonitrile

Disinfection Byproduct

2 to 2000 pg/μL

Calibration Curve – Trichloroethene

Chlorinated Solvent

2 to 2000 pg/μL
Calibration Curve – Heptachlor epoxide

Halogenated Pesticide

2 to 2000 pg/μL

GCxGC-ECD Screening Results for Las Vegas Drinking Water

- Pentane extraction
- Only disinfection byproduct and chlorinated solvent results shown here
- Trihalomethane results are similar to previous determinations with SPME GC-TOFMS

<table>
<thead>
<tr>
<th>Compound</th>
<th>ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>17</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>0.26</td>
</tr>
<tr>
<td>Carbon tetrafluoride</td>
<td>0.21</td>
</tr>
<tr>
<td>Trichloroacetonitrile</td>
<td>0.11</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>0.09</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>0.14</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>0.25</td>
</tr>
<tr>
<td>1,1-Dichloropropane</td>
<td>1.3</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>ND</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td>ND</td>
</tr>
<tr>
<td>Chlorodibromomethane</td>
<td>0.63</td>
</tr>
<tr>
<td>Bromochloroacetonitrile</td>
<td>9.1</td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>ND</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>0.16</td>
</tr>
<tr>
<td>1,1,1-Trichloro-2-propane</td>
<td>1.4</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2.2</td>
</tr>
<tr>
<td>Dibromoacetonitrile</td>
<td>0.77</td>
</tr>
<tr>
<td>1,2,3-Trichloropropene</td>
<td>0.15</td>
</tr>
<tr>
<td>1,2-Dibromo-3-chloropropane</td>
<td>0.29</td>
</tr>
</tbody>
</table>
Conclusions

- GCxGC-ECD offers selectivity not available with conventional, one-dimensional GC-ECD
  - Always two retention times for each compound
  - Separation of compounds from each other and from matrix interferences

- Calibration and quantification was demonstrated for 551 compounds

Acknowledgment

The LECO thermal modulator was built by LE CO under license from Zoex Corporation.
Analysis of PCB Congeners by GC-MS-MS As Compared to Aroclor Analysis

Ms. Pamela Hamlett* and David Klein, Ph.D.
Texas Parks & Wildlife
Environmental Contaminants Lab
505 Staples Road
San Marcos, TX 78666
512-353-3486
pamela.hamlett@tpwd.state.tx.us
* presenting author

ABSTRACT

The analysis of legacy pollutant PCBs continues to be of interest. Many organizations have historical data that was compiled as Aroclor fractions or even “Total” Aroclors. We have been working on a novel method to revise this “semi-quantitative” approach. Analytical chemistry works well when specific compounds are measured. When data is multiplied by some “factor” and a “selected” number of analytes are used to represent a larger group, the quantitative analysis becomes less and less accurate. By employing the readily available technique of tandem mass spectrometry we have found a good method to obtain reliable data with acceptable sensitivity.
Accelerated Solvent Extraction (ASE) as a Sample Preparation Technique for Polybrominated Diphenylethers (PBDEs) in Environmental Samples

Sheldon Henderson*, Richard Carlson and Bruce Richter
Dionex Corporation
1515 W. 2200 S., Suite A
Salt Lake City, Utah 84119
801-972-9292
sheldon.henderson@dionex.com
* presenting author

ABSTRACT

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

There has been increasing concern from scientists and public health officials about polybrominated diphenylethers (PBDEs). PBDEs are part of a class of brominated flame retardants used in the manufacturing of textiles, furniture, polymeric parts in consumer electronics, polyurethane foams, and other polymeric materials. These compounds have been shown to enter the biosystem and have been found in drinking water, animal tissues and human breast milk. They have been found in all animal tissues examined including samples taken from Arctic regions. Their concentration in the environment is increasing annually, and as a result of this increase and concern over possible health effects, their production and use have been banned or soon will be banned in both North America and Europe.

Traditional methods such as Soxhlet have been used to extract samples containing PBDEs. These methods require long periods of time (16 hours) and large volumes of solvent (300 mL). ASE can perform these extractions in short periods of time and with small amounts of solvent. This presentation will discuss the use of ASE for the extraction of several environmental matrices for PBDEs including sediments, fish tissue and human breast milk. Comparisons to traditional methods of extraction will be presented.
Accelerated Solvent Extraction (ASE) as a Sample Preparation Technique Polybrominated Diphenylethers in Environmental Samples

S. Henderson, R. Carlson and B. Richter
Dionex Corporation, Salt Lake City, Utah

This Is the Toxic Substance You Can’t Avoid; Chemical Residue from Flame Retardants Is Nearly Everywhere

“Created by chemical companies to make hard plastic and polyurethane foam less flammable, polybrominated diphenylethers or PBDEs, are added to computers, TVs, furniture cushions, upholstery textiles, carpet backings, mattresses, cars, buses, aircraft and construction materials.”

“The flame retardants have been detected in virtually every person and animal tested, even newborns and fetuses, around the world, including Australia, Arctic Canada and Svalbard, Norway, near the North Pole. Amounts in people and wildlife are doubling in North America every four to six years, a pace unmatched for any contaminant in at least 50 years.”

Los Angeles Times, June 20, 2004
**Introduction**

- Polybrominated diphenyl ethers (PBDEs) were developed in the early 1970s
- PBDEs are manufactured as flame retardants for consumer products
- Discovered in European waterways in the 1980s
- Production and use banned by European Union
- Ban to take place in California in 2006
- Toxicity has yet to be determined
  - Evidence suggests it may compromise endocrine or hepatic functions

**EPA Proposed Rule**

- Tetra-, penta-, hexa-, hepta-, octa-, and nonabromodiphenyl ether
- Manufacturers and importers have to inform EPA at least 90 days before commencing the manufacture or import of any one or more of these compounds on or after January 1, 2005 for any use
- Released December 6, 2004
Background

♦ Penta-, octa-, and deca-BDE are most commonly produced
♦ Found in consumer products
  – Clothing, furniture, plastics
  – Up to 28% by weight in seat cushions
♦ Disposed in landfills
♦ Find their way into biosystem
♦ Accumulation in biosystem is on the rise
♦ Flame retardants do prevent fire-related deaths

Analytical Techniques

♦ GC/ECD
  – High-molecular-weight compounds require special high-temperature columns
  – Electron capture detector may require second column confirmation
♦ GC/MSD or GC/HRMS
  – High-molecular-weight compounds require special columns
  – Long run times (approximately 1 h)
♦ High-temperature column
  – 380 °C temperature limit
  – Separates 20 PBDE congeners, including DBDE 209
Sample Preparation Techniques for Solids

- Methods for extracting polybrominated diphenyl ethers
  - Sonication
  - Soxhlet
  - Shake or soak
  - Accelerated Solvent Extraction (ASE®, PLE, or PFE)
  - Silica gel cleanup may be necessary for environmental samples
    » SW 846 8290 procedure

What Is ASE®?

- ASE is a technique for extracting solid and semisolid samples with liquid solvents
- ASE uses increased temperature and pressure with common solvents to increase the efficiency of the extraction process
- ASE can be used to replace Soxhlet, sonication, boiling, wrist-shaker, and other extraction methods (U.S. EPA Method 3545A)
Why ASE® for PBDEs

- Provide fast extraction of high-molecular-weight organic compounds
- Minimal solvent consumption when compared to traditional techniques
- Provides automation
- Minimal solvent handling and exposure
- Closed system protects DBDE from UV breakdown

ASE® Schematic

- Load Cell
- Fill with Solvent Time (min) 0.5–1
- Heat and Pressurize 5
- Static Extraction 5 Cycle
- Flush with Fresh Solvent 0.5
- Purge with Nitrogen 1–2
- Extract Ready Total (min) 12–18

Pump
Solvent
Oven
Extraction Cell
Static Valve
Collection Vial
Nitrogen
Purge Valve
ASE® 200

- Automated extraction of 24 sample cells
- Sample cell sizes of 1-, 5-, 11-, 22-, and 33-mL internal volume
- Typical extraction times of 15 min per sample
- Extraction solvent volumes of 10–50 mL

A Faster, More Efficient Way of Sample Preparation

Matrices Investigated Using ASE® for PBDE Determination

- Sediments
- Fish tissues
- Polymers
- Human breast milk
PBDE from Sediments

- Samples were dried prior to extraction
- ASE® 200 conditions
  - Solvent: Methylene chloride
  - 100 °C 2–5 min static cycles
  - 60% flush 60-s purge
- Solvent exchanged to hexane
- Cleanup
  - GPC and silica gel

Analysis of PDBE from Sediments

- Analysis by CG/ELCD
  - 60-m DB-5 column
  - High-temperature program
- Confirmation by GC/MS
  - Full scan electron ionization
  - Quantitation
    » Summation of three major ions (BDE 47, 99, 100)
Summary of PBDE from Sediments

- Fast extractions using ASE®: 18 min per sample
- Detection limit of 0.5 μg/Kg
- BDE 47 detected in 22% of samples
- Bottom feeding fish (catfish) had a PBDE profile similar to river sediment

PBDE Extraction from Fish Tissues

- Sample prep
  - Fillets were removed from fish
  - Fish samples lyophilized
- ASE® 200 conditions
  - Solvent: methylene chloride
  - 100 °C 2–5 min static cycles
  - 60% flush and 60-s purge
- Cleanup
  - Size-exclusion chromatography
  - Silica gel cleanup
  - Solvent exchange to hexane
Analysis of Fish Tissue

- Analysis performed by GC/ECD
  - GC/MSD for confirmation
- GC conditions
  - 90 °C for 2 min, 4 °C/min to 320 °C hold 10 min
- BDE 47 was found in 89% of fish samples at or above a detection limit of 5 µg/kg

Summary of Fish Tissue Analysis

- ASE® extractions reduce solvent consumption when compared to traditional techniques
- ASE provided fast extractions: 18 min per sample
- BDE 47 was found in 89% of fish samples at or above a detection limit of 5 µg/kg
- Study focused on tetra-, penta-, and hexa-BDE
PBDE from Polymer

- Grind pellets to powder
- Add sample to thimble then place in stainless steel cell
- ASE® conditions
  - Solvent: Isopropanol or THF
  - 80 °C, two 10-min cycles
  - 70% flush 60-s purge
- HPLC/UV or GC-MS

Cryo-Grinding of Polymer Pellets

Spex-Certiprep 6750 Freezer Mill
Cryo-Grinding of Polymer Pellets

Grinding greatly enhances surface area and extraction efficiency

Essential for fast, quantitative extraction

Analysis of Polymer for PBDE

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compound</th>
<th>ASE® Recovery (% of Soxhlet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Polybromodiphenylether</td>
<td>81.3</td>
</tr>
<tr>
<td>SB</td>
<td>Polybromodiphenylether</td>
<td>76.3</td>
</tr>
<tr>
<td>SB</td>
<td>Polymbrominated Biphenyl</td>
<td>76.2</td>
</tr>
</tbody>
</table>
PBDE from Polymers Epoxy Resin

- **ASE® conditions**
  - Solvent: Toluene
  - 120 °C, two 5-min cycles
  - 100% flush 60-s purge
- **GC-MS analysis**

---

**PentaBDEs in Polymers**

**ASE® Comparison with Soxhlet**

<table>
<thead>
<tr>
<th></th>
<th>BDE 100</th>
<th>BDE 99</th>
<th>BDE 85</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soxhlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. (W%)</td>
<td>0.21</td>
<td>0.87</td>
<td>0.04</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>7.58</td>
<td>4.74</td>
<td>7.75</td>
</tr>
<tr>
<td><strong>ASE</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. (W%)</td>
<td>0.20</td>
<td>0.94</td>
<td>0.05</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>2.76</td>
<td>6.73</td>
<td>3.04</td>
</tr>
<tr>
<td>% Soxhlet</td>
<td>95.2</td>
<td>108</td>
<td>125</td>
</tr>
</tbody>
</table>
Summary of Polymer Extraction

- Recovery of PBDE is similar to Soxhlet
- Reduced solvent consumption
  - 30 mL versus 70 mL
- Faster extraction time
  - 25 min versus 3 h or more

PBDE from Human Breast Milk

- Samples are freeze dried
  - 3.50 g mixed with Ottawa sand in a 22-mL ASE® cell with filters
- ASE conditions
  - Solvent: hexane, methylene chloride, methanol 5:2:1
  - 80 °C 3–5 min extraction cycles
  - 60% flush and 240-s purge
- Concentration by evaporation
- Extract cleanup
  - Silica gel and GPC
Analysis of Human Breast Milk

<table>
<thead>
<tr>
<th>Human Breast Milk Sample</th>
<th>BDE 77</th>
<th>BDE 153</th>
<th>BDE 209</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Recovery as a % of Spike</td>
<td>79.9</td>
<td>76.8</td>
<td>85.7</td>
</tr>
</tbody>
</table>

Summary Human Breast Milk Extraction GC/HRMS

- AOAC method is liquid–liquid
  - Sep funnels will clog
- Comparison of liquid milk and dried milk samples
  - No difference when extracted by ASE®
- ASE extraction
  - 25 min
  - 30 mL of solvent
  - UV protection is important
    » Use amber collection vials
Conclusion

- Sample preparation
  - ASE® is a fast and effective tool for extraction of PBDE
  - ASE provides automation for sample preparation
- Analysis
  - GC/MS (1000 amu)
  - GC/ECD
  - Requires high-temperature column

References

Acknowledgements

- Dr. Jian Wen, Dr. Arthur Holden, and Margaret Sharp from California EPA, Berkeley, CA
- Mark Olson, Underwriters Laboratories, Northbrook, IL
RapidMS Chromatography and Tandem Mass Spectrometry for Trace Determination of Brominated Flame Retardants

Robert Brittian
Varian, Inc.
2700 Mitchell Drive
Walnut Creek, CA 94598
925-942-4857
Presented by: Ed George, ed.george@varianinc.com

ABSTRACT

Polybrominated diphenyl ethers (PDBEs) have been widely used since the 1960s as flame retardants in a variety of products such as clothing, furniture, carpets, electronic components, and plastics. At every stage, from production, to use, to disposal or recycling, PDBEs are released into the air, water, and soil. These compounds will bioaccumulate in fatty tissues and are known to have endocrine disrupting effects, particularly affecting thyroid function. Production of some commercial mixes of PDBEs has halted, but worldwide production of these reported in 1999 was 67,000 metric tons.

A sensitive and selective method for the detection of PDBEs in environmental and food samples will be described. It involves the use of a column known as Rapid-MS combined with tandem mass spectrometry. Rapid-MS vacuum chromatography accomplishes efficient transfer of even the heaviest deca-BDE into the mass spectrometer while maintaining excellent chromatographic resolution in a very short run time. Traditional Selected Ion Monitoring (SIM) methods are very sensitive, but lack the ability to separate the target compounds from complex matrices. Tandem ion trap mass spectrometry ensures that complex matrix interferences are eliminated providing accurate quantitation at sub-pg detection limits.
RapidMS Chromatography and Tandem Mass Spectrometry for Trace Determination of Brominated Fire Retardants

Robert D. Brittain
Varian, Inc.

21st Annual National Environmental Monitoring Conference
Washington, DC
July 25 – 29, 2005

Presentation Outline

- PBDEs as Persistent Organic Pollutants
  - Polychlorinated Biphenyls
  - Polychlorinated Dioxins
  - Many congeners: mono- to deca-BDE

- The Chromatographic Challenge
  - High Molecular Weights (> 950u)
  - Thermal Instability

- Vacuum Chromatography for better separations
- Sensitivity/Selectivity with MS/MS Detection
- Calibration and Detection Limits
- Sample Analyses
What are PBDEs?

- Polybrominated Diphenylethers
- Structurally Similar to Polychlorinated Biphenyls
  - 209 Congeners
  - Similar Nomenclature
- Chemically stable – persistent organic pollutants (POPs)

2,2',4,4',6 – Pentabromodiphenylether (PBDE-100)

Some Uses of PBDEs

- Fire retardants, especially inside homes, vehicles
- “Penta” BDE used largely in polyurethane foam for furniture cushions, mattresses, etc.
- “Deca” BDE in carpet backing, fabric treatments
- Other uses in plastics, electronic components, will be regulated in Europe with upcoming RoHS

Global consumption 67,000 metric tons in 1999

Environmental Concerns

- PBDEs are released to environment via many pathways from production through to disposal
- Bioaccumulation known to be increasing since 1970s, doubling about every five years
- Hydroxylated metabolites are endocrine disruptors – known to affect thyroid function
- Toxicity & carcinogenicity not yet established although studies are under way

Chromatographic Challenge

- PBDEs are heavy compounds
  - Deca-BDE molecular ion cluster begins at m/z 950
- Difficult to get heavy components through standard-bore GC columns
- Subject to thermal degradation so high injector or column temperatures will destroy heavier species
**Rapid-MS™: Key Characteristics for Determination of PBDEs**

- Lower elution temperature for heavy PBDEs
- Fast analysis with 10m x 0.53 mm capillary column
- Positive inlet pressure is used with standard injection techniques and flow / pressure regulation
- High sample capacity due to 0.53 mm column and thicker film
- Peak shape and resolution are maintained

**Rapid-MS™- Columns**

- Implement vacuum separation by applying a restriction at the injection side of the system

![Restriction Diagram]
Linear gas velocity: Rapid-MS™ vs conventional GC

Optimum velocity increases more for larger-bore columns

0.53 mm ID Atmospheric Outlet

0.53 mm ID Vacuum Outlet

0.53 mm
$U_{opt} : 20 \rightarrow 190 \text{ cm/s}$
10 times faster

0.25 mm
$U_{opt} : 40 \rightarrow 120 \text{ cm/s}$
3 times faster

Varian 4000 GC/MS System
Separation via RapidMS Column

Isolated Molecular Ion Cluster for Deca-BDE (BDE-209)

Shown in Centroid mode (Above) and Profile mode (Below)
**MS/MS on Brominated Clusters**

- BDE spectra are composed of \( M^+ \) and \( (M-Br_2)^+ \) clusters
- Isolate entire cluster as MS/MS precursors
- Collision-assisted dissociation (CAD) to product cluster (loss of 2 Br atoms)
  - Use multiple resonant frequencies to achieve dissociation of entire cluster
  - He is collision partner
- Approach is highly selective and very sensitive

---

**External Ionization – 4000 GC/MS**

- 2 μL pressure-pulsed, splitless injections (8400 AutoSampler)
- Siltek-coated, fritted liner, 1177 Injector @ 260°C
- Rapid MS Column CP-Sil8 (10m x 0.53mm ID x 0.25df)
  - 80°C (hold 1.5min) // 250°C @ 12°C/min // 300°C @ 25°C/min // Hold 5.33 min (Total Run Time 23.00 min)
- MS/MS
  - **External Ionization Configuration** – 2.5 ml/min He damping
  - Temperatures: Transfer Line 280°C/Source 225°C/Ion Trap 100°C
  - Electron Ionization – 70eV – **Pulsed ON only during ionization**
  - Multiplier 10^5 gain + 300V
  - AGC Target 5000
  - Filament Delay 9.00 min
  - MS/MS Time-Programmed for each BDE component
  - I.S. Perylene-d12 acquired in SIS (263-265u)
### Calibration Levels (pg/μL)

<table>
<thead>
<tr>
<th>Calibration Level</th>
<th>Deca-BDE pg/μL</th>
<th>All Others BDEs pg/μL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>500</td>
<td>250</td>
</tr>
<tr>
<td>9</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>10</td>
<td>2000</td>
<td>1000</td>
</tr>
</tbody>
</table>

### Representative Calibration Plots

- **Penta-BDE Response was Linear**
  - Range 1 – 1000 pg/μL

- **Deca-BDE Response was Quadratic**
  - Range 2 – 2000 pg/μL
### Calibration Data 1 – 1000 pg/μL (Deca-BDE from 2 – 2000 pg/μL)

<table>
<thead>
<tr>
<th>Compound</th>
<th>#Br</th>
<th>Corr. Coef.</th>
<th>%RSD</th>
<th>Type Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-17</td>
<td>3</td>
<td>0.9986</td>
<td>8.77</td>
<td>Linear</td>
</tr>
<tr>
<td>BDE-47</td>
<td>4</td>
<td>0.9997</td>
<td>7.31</td>
<td>Linear</td>
</tr>
<tr>
<td>BDE-66</td>
<td>4</td>
<td>0.9994</td>
<td>8.79</td>
<td>Linear</td>
</tr>
<tr>
<td>BDE-100</td>
<td>5</td>
<td>0.9994</td>
<td>6.27</td>
<td>Linear</td>
</tr>
<tr>
<td>BDE-153</td>
<td>6</td>
<td>0.9986</td>
<td>16.15</td>
<td>Quadratic</td>
</tr>
<tr>
<td>BDE-183</td>
<td>7</td>
<td>0.9980</td>
<td>15.47</td>
<td>Quadratic</td>
</tr>
<tr>
<td>BDE-209</td>
<td>10</td>
<td>0.9993</td>
<td>42.81</td>
<td>Quadratic</td>
</tr>
</tbody>
</table>

### Method Detection Limits

<table>
<thead>
<tr>
<th>Compound</th>
<th>MDL (pg/μL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-17</td>
<td>0.309</td>
</tr>
<tr>
<td>BDE-47</td>
<td>0.225</td>
</tr>
<tr>
<td>BDE-66</td>
<td>0.165</td>
</tr>
<tr>
<td>BDE-100</td>
<td>0.207</td>
</tr>
<tr>
<td>BDE-153</td>
<td>0.233</td>
</tr>
<tr>
<td>BDE-183</td>
<td>0.263</td>
</tr>
<tr>
<td>BDE-209</td>
<td>0.764</td>
</tr>
</tbody>
</table>

Based on 10 replicates @ 2 pg/μL

\[ \text{MDL} = \sigma \times \text{(Student’s t(99% conf.))} \]
House Dust Samples

- Dust removed from vacuum cleaner bags
  - Two different houses
    - First had hardwood floors, second was carpeted
  - Sonicate 1 g dust in 10 ml hexane 5 min
  - Filter
- Add perylene-d12 Internal Standard @ 500 pg/μl
- Run samples in El/MS/MS
- Run second dust sample in full scan (50 – 1000u) and high-mass scan range (240 – 980u)
### EI/MS/MS Results for PBDEs

<table>
<thead>
<tr>
<th>Component</th>
<th>House Dust #1 ng/g(dust)</th>
<th>House Dust #2 ng/g(dust)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-17 (Tri)</td>
<td>Not Found</td>
<td>30</td>
</tr>
<tr>
<td>BDE-47 (Tetra)</td>
<td>1961</td>
<td>4326</td>
</tr>
<tr>
<td>BDE-66 (Tetra)</td>
<td>157</td>
<td>117</td>
</tr>
<tr>
<td>BDE-100 (Penta)</td>
<td>616</td>
<td>1318</td>
</tr>
<tr>
<td>BDE-153 (Hexa)</td>
<td>315</td>
<td>1052</td>
</tr>
<tr>
<td>BDE-183 (Hepta)</td>
<td>Not Found</td>
<td>46</td>
</tr>
<tr>
<td>BDE-209 (Deca)</td>
<td>473</td>
<td>206</td>
</tr>
</tbody>
</table>

**Hardwood Floors**

**Carpeted**

---

### Spectra and Sensitivity – House Dust Sample

Penta-BDE peak in full-scan, high-mass scan, and MS/MS
Selectivity Enhancement with MS/MS – House Dust Sample

- Full-Scan, High-mass, MS/MS Chromatograms
- Same Retention Time as Previous Slide

Fish Tissue Sample

- Wild sturgeon extract received from nearby lab
- Run earlier on magnetic sector instrument
- Exact volume not available. Estimated that 10.8g concentrated to ~50μL
- Volume too low to estimate correct IS addition, so quantitation based on external standard calibration
- Quality of external standard curves comparable to those for internal standard
Wild Sturgeon Extract

Duplicate Wild Sturgeon Sample Chromatogram

Original Wild Sturgeon Chromatogram

Wild Sturgeon Results (pg/g Fish Tissue)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic Sector</th>
<th>4000 MS Ion Trap - #1</th>
<th>4000 MS Ion Trap - #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-17</td>
<td>30</td>
<td>57</td>
<td>36</td>
</tr>
<tr>
<td>BDE-47</td>
<td>3950</td>
<td>3919</td>
<td>3893</td>
</tr>
<tr>
<td>BDE-66</td>
<td>45</td>
<td>n.d.*</td>
<td>47</td>
</tr>
<tr>
<td>BDE-100</td>
<td>651</td>
<td>881</td>
<td>912</td>
</tr>
<tr>
<td>BDE-153</td>
<td>75</td>
<td>46</td>
<td>89</td>
</tr>
<tr>
<td>BDE-183</td>
<td>22</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>BDE-209</td>
<td>0</td>
<td>118</td>
<td>108</td>
</tr>
<tr>
<td>Total BDEs</td>
<td>6688**</td>
<td>5035</td>
<td>5103</td>
</tr>
</tbody>
</table>

* - Interference by neighboring tetra-BDE
** - More congeners calibrated for sector instrument
2 µL pressure-pulsed, splitless injections (8400 AutoSampler)
1177 Injector @ 250°C
Rapid MS Column CP-Sil8 (10m x 0.53mm ID x 0.25df)
80°C (hold 1.5min) // 250°C @ 12°C/min // 300°C @ 25°C/min // Hold 6.33 min (Total Run Time 24.00 min) Flow Rate = 2 ml/min
MS/MS
Internal Ionization Configuration
Temperatures: Transfer Line 280°C/Ion Trap 210°C/Manifold 60°C
Multiplier 10^5 gain + 300V
AGC Target 5000
Filament Delay 8.00 min
MS/MS Time-Programmed for each BDE component
I.S. Decabromobiphenyl (DBB)
Internal Ionization: BDE-209 20pg/μL

Note lower response for BDE-209 isomer in internal mode

Internal Ionization: Calibration

- BDE-209 shown at left
- Calibration Range: 2 to 100 pg/μL (4-200 BDE-209)
- Most curves quadratic
- RSDs 17% to 45%
- Corr. Coeff 0.998 or greater
**Internal Ionization: 8 reps @ 5pg/μL**

**BDE-209 @ 10 pg/μL**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ave</th>
<th>RSD (%)</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-28</td>
<td>4.869</td>
<td>4.8</td>
<td>0.703</td>
</tr>
<tr>
<td>BDE-47</td>
<td>4.972</td>
<td>3.8</td>
<td>0.560</td>
</tr>
<tr>
<td>BDE-66</td>
<td>4.804</td>
<td>5.7</td>
<td>0.816</td>
</tr>
<tr>
<td>BDE-77</td>
<td>4.814</td>
<td>4.8</td>
<td>0.692</td>
</tr>
<tr>
<td>BDE-100</td>
<td>4.837</td>
<td>5.2</td>
<td>0.749</td>
</tr>
<tr>
<td>BDE-99</td>
<td>4.714</td>
<td>9.2</td>
<td>1.305</td>
</tr>
<tr>
<td>BDE-85</td>
<td>4.036</td>
<td>12.2</td>
<td>1.479</td>
</tr>
<tr>
<td>BDE-154</td>
<td>4.821</td>
<td>6.3</td>
<td>0.915</td>
</tr>
<tr>
<td>BDE-153</td>
<td>4.015</td>
<td>9.0</td>
<td>1.079</td>
</tr>
<tr>
<td>BDE-138</td>
<td>3.526</td>
<td>12.4</td>
<td>1.309</td>
</tr>
<tr>
<td>BDE-209</td>
<td>9.803</td>
<td>17.8</td>
<td>5.218</td>
</tr>
</tbody>
</table>

**Conclusions**

- Concepts reduced to practice in PBDE analysis:
  - Vacuum chromatography practical for Deca-BDE
  - EI/MS/MS with $10^3$ practical quantitation range
  - PBDEs can be determined in real samples with minimal cleanup
- Internal vs External Ionization
  - External more sensitive, less noise
  - Better RSDs and Linearity in external for most compounds
- Future project: Develop MRM for all congeners
Session 7

Analysis in Perchlorate Analysis
DoD Handbook for Perchlorate Sampling and Testing

Mr. Fred McLean* and Mr. William Ingersoll
U.S Navy Laboratory Quality & Accreditation Office
1661 Redbank Road
Goose Creek, SC 29445
Phone: (843) 764-7337       Fax: (843) 764-7360
mcleanfs@navsea.navy.mil
* presenting author

ABSTRACT

The Department of Defense (DoD) Environmental Data Quality Workgroup (EDQW) is working towards a unified approach for all Components in the area of perchlorate sampling and testing. This has lead to the development of the Handbook for Perchlorate Sampling and Testing.

The Handbook provides instruction on planning and execution for perchlorate data generation. A critical part of the process is proper project scoping and development of Conceptual Site Models. Identification of exposure pathways can determine the extent of sampling and testing required. The handbook gives guidance on development of project quality objectives, sample design, collection, and selection of analytical services. New technologies for the analysis of perchlorate are discussed. The pros and cons of different analytical methods from EPA are explained.

The goal of the Handbook is to inform Components of the available options for sampling and testing for perchlorate. With the proper information, a Component can make decisions that provides the required data quality.
Method 6850 - Determination of Perchlorate Using High Performance Liquid Chromatography/Mass Spectrometry (LC/MS)

Robert P. Di Rienzo*
DataChem Laboratories, Inc.
960 West LeVoy Drive
Salt Lake City, UT 84123
(801) 266-7700
dirienzo@datachem.com

Kham Lin
K'(Prime) Technologies, Inc.

USEPA OSW
Inorganics Method Development
* presenting author

ABSTRACT

A new method for the detection and confirmation of perchlorate utilizes liquid chromatography to separate perchlorate from interferences and mass spectrometry to confirm and quantify. DataChem Laboratories, Inc. in conjunction with K'(Prime) Technologies, Inc. has developed this new liquid chromatography mass spectrometry method for the detection and confirmation of perchlorate in drinking water, ground water, saline water, soil and biota samples. The USEPA is currently evaluating method SW846 Method 6850, with an inter-laboratory validation study.

Method 6850 for the determination of perchlorate uses a newly developed, commercially available, liquid chromatography column developed by K'(Prime) Technologies, Inc. By using this column in an Agilent 1100 LC/MSD system, the technique separates perchlorate from known interferences in difficult matrices and can detect perchlorate in matrices that are unacceptable for analysis by drinking water methods.

Mass spectrometry is used to monitor perchlorate at mass 83, which is achieved by the partial fragmentation of perchlorate to remove an oxygen atom. Confirmation of perchlorate is obtained not only by retention time and mass but by the isotopic ratio of mass 83 and 85 and an internal standard of Oxygen-18 labeled perchlorate.

Method 6850 can easily quantify perchlorate at 0.2 ppb in environmental sample matrices, uses simple determinative techniques available to current LC/MS technologies and does not require systematic pretreatment of samples prior to analysis. 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.

Inadequacies of EPA drinking water concerning matrix interference, high dissolved solids and conductivity are eliminated and confirmation of perchlorate is accomplished with method 6850.
Analysis of Perchlorate by IC/MS/MS and Development of Method 6860

Richard Burrows
Severn Trent Laboratories
4955 Yarrow St.
Arvada, CO 80002
(303) 736-0100
rburrows@stl-inc.com

ABSTRACT

This paper will describe the development and performance of an IC/MS/MS method for analysis of perchlorate. We will cover instrumental conditions and critical QA parameters to ensure that the method is performing effectively. The current status of SW-846 method 6860 will be presented.
A Discussion of Separation and MS Detection for the Determination of Perchlorate in Real World Samples

R. Slingsby*1, C. Saini1, C. Pohl1 and H. El Aribi2
1 Dionex Corporation, 445 Lakeside Dr., Sunnyvale CA 94088
2 MDS Sciex, 71 Four Valley Drive, Concord, Ontario L4k 4V8, Canada
408-481-4542
Rosanne.Slingsby@Dionex.com
* presenting author

ABSTRACT

In the last several years, IC-MS and IC-MS/MS technologies have been developed and successfully applied to the determination of perchlorate in drinking water and various food types. Results from the analyses of many real world samples have been the topic of great national and international interest. As these technologies are applied to more complex sample matrices including well water, waste water, various agricultural crops and finished food products, the demands for robust and adaptable methodologies are increasing. In a sense the “toolbox” available to the analyst must become larger and more powerful as interest in more complex sample types increases.

Ion exchange resins have been used successfully for a number of years to selectively retain perchlorate in relation to common matrix ions including chloride, carbonate and sulfate. The IonPac® AS16 resin has an ion exchange latex agglomerated to a highly cross linked, aromatic substrate resin particle. This phase selectively retains polarizable anions including perchlorate while also providing excellent peak shape in aqueous eluents. As the perchlorate analysis using this column was applied to well water, aromatic sulfonate contaminants were found to interfere with the elution of perchlorate on the AS16 ion exchange phase. New synthesis technology was recently developed that provides novel selectivity for perchlorate and the aromatic sulfonates. The IonPac AS20 stationary phase is based on the new Hyperbranched Condensation Graft Technology, which combines the excellent peak shape benefits of Dionex latex technology with the selectivity benefits of graft technology. The AS20 anion exchange polymer is built with an aliphatic backbone and therefore, provides an orthogonal selectivity to the AS16 column. These 2 columns expand the analyst’s “toolbox” by providing complementary separation information even for very complex sample types.

Multiple reaction monitoring (MRM) is the standard technique for quantitative LC-MS/MS analysis. In general, the LODs/LOQs, precision, and accuracy achieved with this technique are difficult to match. In this paper, we will discuss the chemistry of the separations, the coupling to MS and MS/MS detection using on-line matrix diversion and an isotope-enriched perchlorate internal standard. The analytical statistics (including the 37Cl/35Cl ratios) obtained for drinking water, waste water, soil extracts and several food samples will be presented.
Perchlorate in Water – A Comparison of Methods 314.0 and 332.0

Scott McLean*, James F. Occhialini, Arin Jones and James Todaro
Alpha Analytical Labs, Eight Walkup Dr., Westborough, MA 01581
(508)898-9220
scott@alphalab.com
* presenting author

ABSTRACT

Perchlorate is a natural and man-made chemical that has been used as an oxidizer in rocket fuel, munitions and fireworks since the 1950s. It is known to disrupt thyroid function by inhibiting iodine uptake, thereby inhibiting the production of key thyroid hormones. It is very soluble in water and therefore highly mobile. Perchlorate has been detected in drinking water supply wells in several MA communities. In 2004, a drinking water MCL of 1 ppb was proposed by MADEP, consistent with the MCL proposed by EPA in 2002. While the CADHS set a notification limit of 6 ppb, NAS recently concluded that a level roughly equivalent to 20 ppb might be more appropriate. The current accepted method for low level analysis, EPA 314.0, utilizes an Ion Chromatograph fitted with a conductivity detector and a suppressor to reduce interference from background contaminants; however this method encounters problems in the presence of elevated sample conductivity. An alternative method, EPA 332.0, has been developed to address these problems. Method 332.0 utilizes an IC fitted with an MS or MS/MS. The MS technology allows for the detection of perchlorate to sub ppb concentrations even in the presence of high concentrations of interferents. In this paper the authors present method qualification data as well as real world sample data from both methods. Comparison of real world data from samples with high conductivity will demonstrate the capability of Method 332.0 to accurately and precisely quantitate perchlorate at or below the current draft MCLs.
Trace Level Determination of Perchlorate in Soils and Fertilizers by Tandem Suppressed Conductivity and Mass Spectroscopy

Jay Gandhi, Sr. Development Chemist,
Metrohm-Peak, Inc.
12521 Gulf Freeway,
Houston, TX – 77034
Ph: 281-484-5000    Fax: 281-484-5001
jay@mp-ic.com

ABSTRACT

Perchlorate salts are being used as rocket propellants, in fireworks and in electroplating industry. Currently, perchlorate is being monitored under USEPA Unregulated Contaminant Monitoring Rule (UCMR-1) at 4.0 parts per billion (USEPA method 314.0). Recently, it is believed by the scientific community that perchlorate hinders the iodine absorption ability of the thyroid gland posing higher health risk for the public. Perchlorate contaminated fertilizers and naturally occurring perchlorate in “Chilean Fertilizers” can leach perchlorate into the soils, ground water, surface water and irrigational waters, which in turn contaminate crops of vegetables and fruits. It is critical to identify and quantify levels of perchlorate contamination in soils, fertilizers and waters. This presentation demonstrates use of conventional ion chromatography conductivity detection and mass spectrometer in tandem. Benefits of mass spectrometer will be discussed.
DoD Handbook for Perchlorate Sampling and Testing

Mr. Fred McLean* and Mr. William Ingersoll
U.S Navy Laboratory Quality & Accreditation Office
1661 Redbank Road
Goose Creek, SC 29445
Phone: (843) 764-7337 Fax: (843) 764-7360
mcleanfs@navsea.navy.mil
* presenting author

ABSTRACT

The Department of Defense (DoD) Environmental Data Quality Workgroup (EDQW) is working towards a unified approach for all Components in the area of perchlorate sampling and testing. This has lead to the development of the Handbook for Perchlorate Sampling and Testing.

The Handbook provides instruction on planning and execution for perchlorate data generation. A critical part of the process is proper project scoping and development of Conceptual Site Models. Identification of exposure pathways can determine the extent of sampling and testing required. The handbook gives guidance on development of project quality objectives, sample design, collection, and selection of analytical services. New technologies for the analysis of perchlorate are discussed. The pros and cons of different analytical methods from EPA are explained.

The goal of the Handbook is to inform Components of the available options for sampling and testing for perchlorate. With the proper information, a Component can make decisions that provides the required data quality.
Session 8

Innovative Techniques for Environmental Measurements and Monitoring
Case Studies of Innovative Field Technologies Using a Portable GC/MS

ABSTRACT

The first case study was a project directed by the US Army Corp of Engineers using a man-portable GC/MS to expedite site investigation of a contaminated airfield. The GC/MS was used to characterize both the vertical and horizontal extent of the contamination and the data were used to determine the appropriate placement of monitoring wells. The power of using an on-site GCMS was further demonstrated when an unexpected contaminant was discovered in addition to the expected contaminants. By using this on-site technique, the project saved 36% of the expended cost.

The second case study was a project to pinpoint the source of chlorinated solvent contamination around a landfill. The solvents were leaching out into a nearby stream and contaminating the water.

The third study used the portable GCMS in a vapor intrusion application. A city health department alerted the state Department of Environmental Protection (DEP) to a home where they suspected the resident was illegally disposing of solvents. This was based on their preliminary analysis of the area surrounding the home using colorimetric indicator tubes. The GCMS was deployed by the DEP to determine what chemicals were actually present in the home and surrounding area.
Automated Thermal Desorption Methodology Improvements for Environmental Analyses

Andrew Tipler and Zoe Grosser
Zoe.Grosser@perkinelmer.com  Phone: 203-402-5320

ABSTRACT

The uses of thermal desorption–GC systems in environmental applications are well established. A popular application is for industrial hygiene monitoring where volatile organics are trapped on a tube in the breathing range of workers. It is desorbed and chromatographed to characterize the amount and type of potential hazardous material exposure. Ozone precursor analysis to evaluate outdoor air in noncompliance areas for volatile organics is an exacting analysis requiring collection and analysis within an hour. This allows the modeling of changes in organic concentrations over the course of time to better understand the source and impact of troublesome compounds on the production of ground-level ozone. A third environmental application is the measure of a wide variety of volatile compounds in air that may be toxic. Air toxics are more important as air regulations become more comprehensive and the additional chemicals require assessment. There may also be implications for homeland security.

Although systems have been available for these types of analysis for several years they continue to improve. Recent advances have added additional throughput capability and data integrity testing to improve environmental analyses. Sample integrity can be assessed by adding the internal standard prior to collecting the sample. Testing the tube impedance can indicate the quality of data generated in the current desorption and ensure the integrity of the tube for future use. Other improvements in gas flow control, dry purging, and sample recollection improve laboratory productivity. Manifolds are used instead of valves, demonstrating better cleanliness in support of the trend to use mass spectrometry. This talk will discuss some of these improvements and the implications for existing and future environmental analyses.

I prefer to give an oral presentation.
Tree Coring for Ground-Water Contaminant Tracking and As An Optimization Tool for Monitoring-Well Placement

Don A. Vroblesky¹, Clifton C. Casey², and Gregory J. Harvey³
¹U.S. Geological Survey, Columbia, 720 Gracern Road, Suite 129, Columbia, South Carolina 29210
²Southern Division Naval Facilities Engineering Command, Charleston, South Carolina
³U.S. Air Force Aeronautical System Center, Wright Patterson Air Force Base, Ohio
Primary Author’s E-Mail: vroblesk@usgs.gov; phone 803-750-6115

ABSTRACT

Trichloroethene (TCE) was detected in cores of trees growing above TCE-contaminated ground water in a variety of environments, including the foothills of the Rocky Mountains, a golf course in Texas, pine forests in South Carolina, and a cypress swamp in South Carolina. The data show that tree coring can be used to locate TCE-contaminated ground water and, in some cases, map the lateral extent. In addition, tree coring can be a useful reconnaissance tool for optimizing well placement. For example, Solid Waste Management Unit 17, Naval Weapons Station Charleston, South Carolina, is in a forested area between two tidally influenced surface-water bodies. The dominant tree species is loblolly pine. Three exploratory monitoring wells at the site showed the presence of chlorinated-solvent contaminated ground water. Tidal influences on the water table made it difficult to predict the probable transport direction of the contamination, and therefore, difficult to place additional wells to map the plume. As a tool to provide a preliminary assessment of the extent of contamination and as an aid in well placement, 63 trees were cored at the site and analyzed using photoionization detection gas chromatography to determine the TCE, PCE, and cis-1,2-dichloroethene (cDCE) content of the head space in sealed serum vials that contained the cores. Most of the cores were collected on a single day. The tree coring showed the presence of two apparently separate plumes of subsurface contamination. One plume was predominantly composed of TCE and the other was predominantly composed of PCE. The tree-coring results were used to direct a subsurface investigation using membrane interface probes, which involved collecting ground-water samples. Contaminant concentrations from the ground-water samples showed good correspondence with the TCE, PCE, and cDCE concentrations in the tree cores. This investigation demonstrates that tree coring can be a fast and inexpensive reconnaissance tool to locate and map volatile organic compounds in contaminated ground water and to optimize placement of monitoring wells.

Prefer oral presentation
Ambient Air Toxics in the Houston-Galveston Area with High and Low TRI Emissions – Monitoring in Three Areas Using Passive Sampling Devices (PSDs)

Thomas H. Stock, Maria T. Morandi, and Masoud Afshar
University of Texas School of Public Health, POB 20186, Houston, TX 77225

Kuenja C. Chung
U.S. Environmental Protection Agency, Region 6, 1445 Ross Avenue, Dallas, TX 75202

ABSTRACT

In order to evaluate and compare the spatial variation of ambient air toxics concentrations in urban areas with high or low density of Toxics Release Inventory (TRI) facilities, a series of passive air monitoring measurements were conducted in each of the selected residential areas in the Houston-Galveston area. The purpose of this task was to perform intensive spatial monitoring in the areas surrounding three existing air monitoring stations, i.e., in a high-density TRI area with high mobile source influence, a high-density TRI area with low mobile influence, and a low-density TRI area.

As the high-density TRI area with high mobile source influence, an area including a source-oriented ambient air-monitoring site in the Houston Ship Channel area (Clinton site) was selected. As the high-density TRI area with less mobile source influence, an area including a source-oriented residential ambient air-monitoring site in Deer Park, (Deer Park site) was selected. And, as the low-density TRI area, an area including a receptor-oriented (residential) ambient air monitoring site in north Houston, (Aldine site) was selected.

72-hour samples of volatile organic compounds (VOCs) were collected using the 3M 3500 Organic Vapor Monitors (OVMs). Samples were collected six times with the planned sampling frequency of every 24 days, over approximately 4 month. During each of six sampling events, ambient samples were collected outside ten residences in each of the three areas, within a 2-mile radius of the central site, and simultaneously at the state-operated air monitoring site and at the centroid of the census tract in which the monitoring site was located, which totals 36 sampling sites. Field blank and field duplicate samples were also collected for quality assurance and quality control. All OVM samples were extracted and analyzed for 31 target compounds by gas chromatography/mass spectrometry (GC/MS).

For the major target VOCs, which include BTEX, MTBE, and chlorinated VOCs, the results are compared for the concentration distributions at all houses, the centroid and the central monitoring station for each of the three study areas. Concentrations distributions are also compared among the three study areas.
Current Passive Diffusion Sampling Devices and Their Performance with Selected Target Analytes

Dee O’Neill
Columbia Analytical Services, 1317 S. 13th Avenue, Kelso, WA 98626, USA, doneill@caslab.com, Telephone: (360) 577-7222, Fax: (360) 501-3395

ABSTRACT

For several years now Passive Diffusion Sampler (PDS) technology has been applied to many sites to improve the information gained during monitoring and to reduce the cost of sampling. Wide acceptance of these samplers has been gained for hydrophobic Volatile Organic Compounds (VOCs) using the polyethylene bag technique with hundreds of studies demonstrating their effectiveness since 1998. While this material is extremely useful for these specific target analytes, there is a need to identify additional materials that would enable similar performance for hydrophilic organics, semivolatile organics and inorganic target analytes as well. Additional studies using new materials have been underway and progress can be reported on several additional options.

These include:

- Polyethylene Diffusion Bag Sampler (PDBS)
- Nylon-Screen Diffusion Sampler (NSDS)
- Rigid Porous Polyethylene Samplers (RPPS)
- Dialysis Membrane Diffusion Sampler (DMDS)
- Polyethylene Vapor Diffusion Sampler (PVDS)
- Semi-Permeable Membrane Device (SPMD)

Along with USGS, efforts to develop passive diffusion samplers for common long term monitoring inorganic and organic parameters include both laboratory and field demonstration studies. Recent data will be presented to demonstrate the performance and feasibility of these materials in prototype sampler designs.
EPA SITE PROGRAM DEMONSTRATION PROJECT RESULTS:
TEQ SCREENING IN THE FIELD USING INTEGRATED PARALLEL
IMMUNOASSAYS FOR DIOXIN/FURAN TEQ AND DIOXIN-LIKE PCB TEQ

Robert O. Harrison
CAPE Technologies, South Portland ME 04106 (email: cape-tech@ceemaine.org; ph: 207-741-2995)

The realtime analytical component of EPA's Triad approach to site assessment and remediation is supported on the organic side by commercial immunoassay kits accepted within the SW-846 Compendium of Solid Waste Methods. Most solid waste immunoassay work to date has involved analytes such as total PCB, total petroleum hydrocarbons, and PAH. Kits for these analytes were approved during the early 1990s in the newly created 4000 series of methods and have seen routine field use since then. More recently, Method 4025 for dioxin/furan TEQ, based on a commercially available kit, was approved in 2001 by EPA's Office of Solid Waste and Emergency Response (OSWER). Because of this acceptance, Method 4025 is now often considered an important first step in site assessment or an essential time saving tool during remediation.

Because of the history of other 4000 series immunoassays and the obvious potential benefit of such a method for field dioxin/furan screening, the EPA Superfund Innovative Technology Evaluation (SITE) Program conducted a field demonstration project in 2004 for Method 4025 and related technologies. In addition to demonstrating the kit on which Method 4025 is based, CAPE Technologies added a second immunoassay kit for measurement of TEQ from dioxin-like PCBs. This PCB TEQ kit is expected to be validated in the near future for use in SW-846 Method 4026 for TEQ from dioxin-like PCBs.

Due to the extremely wide range of source materials, sample types, and TEQ levels, the sample processing of the original Method 4025 was not used. Instead, an adaptation of the Smith-Stalling cleanup method was used for the rapid batchwise cleanup of extracts made by shaking solid samples in acetone/hexane. This method, described before at this conference as Method 4025m (modified Method 4025), allows for easy capture of two discrete fractions, one for dioxins and furans, and the other for dioxin-like PCBs. In the SITE demonstration project, these fractions were analyzed separately using their respective immunoassay kits. The resulting TEQ_{diox} and TEQ_{PCB} values were first evaluated separately, then again after adding the two component TEQ values together to get a total TEQ value.

During the demonstration project, 209 soil and sediment samples were analyzed by both CAPE Technologies immunoassay methods as well as by Methods 1613B and 1668A. Comparisons were made in sample throughput, cost, ease of use, and waste generation, as well as in various analytical performance measurements, such as decision making at pre-selected target levels. The summary of the final report stated that, "These data suggest the CAPE Technologies kits could be an effective screening tool for determining sample results above and below 20 pg/g TEQ and even more effective as a screen for samples above and below 50 pg/g TEQ, particularly considering that both the cost ($59,234 vs. $398,029) and the time (3 weeks vs. 8 months) to analyze the 209 demonstration samples were significantly less than those of the reference laboratory." Specifics of the report will be described in more detail. Suggestions about implementation of this technology for routine use will also be presented.
Session 9

Homeland Security – Triage Response
A UPLC/MS Multi-Analyte Screening Method for Deleterious Organics in Water

Jim Krol¹, and Lawrence Zintek²

¹) Jim Krol, Sr. Applications Chemist, Waters Corporation, 34 Maple St, Milford, Massachusetts, 01757, Office 508/482-2131, Email Jim_Krol@Waters.com

²) Larry Zintek, Sr. Chemist, EPA Region 5 Laboratory, 536 Clark St, Chicago, IL, 60605 Office 312/886-2925, Email: Zintek.Lawrence@EPA.gov

ABSTRACT

The determination of deleterious organics in drinking water, or soil extract, 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 question is raised…what organics are present in this water? Whether it is drinking water, surface water, soil leachates, or wastewater, where does a chemist begin to answer this question? Time is critical.

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). Recently, UPLC technology, Ultra Performance Liquid Chromatography, a revolutionary advance in chromatographic science, became available offering enhanced resolution and faster analysis times.

Thus, a “universal” reversed phase gradient providing high resolution analyte separation coupled with the specificity of mass spectrometry allows for the “screening” for multi-analytes in less than 15 minutes.

This method incorporates the use of ESP libraries that can be used with single quadrupole MS instruments in the field, or the same method with MS/MS to quantification and confirmation in the laboratory. Time of Flight MS is becoming practical and offers exact mass determination to the 4th decimal place. This high specificity is the future of identifying unknown analytes.

This presentation will discuss the development of a single, multi-analyte screening strategy for several deleterious pesticides and herbicides in drinking water using UPLC/ 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 UPLC/MS strategy into a validated screening method template.

Dan Kroll, Karl King
Hach Homeland Security Technologies, 5600 Lindbergh Drive, Loveland Colorado 80539
DKROLL@hach.com 970-663-1377 ext 2637

ABSTRACT

Drinking water is one of the nation’s key infrastructure assets that have been deemed vulnerable to deliberate terrorist attacks. While the threat to reservoir systems and water sources is deemed to be minimal, the vulnerability of the drinking water distribution systems to accidental or deliberate contamination due to a backflow event is becoming a well-recognized possibility. The myriad possible points of incursion into a distribution system and the ease of mounting a backflow event, combined with the fact that little or no quality monitoring occurs after water has left the treatment plant, makes the danger of such an attack acute. This was clearly stated in a GAO report to Congress that listed the vulnerability of the distribution system to attack as the largest security risk to water supplies.

Prior to this there has not been a system capable of detecting such an event and alerting the system’s managers so that effects of an attack or accident can be contained. The general scientific consensus is that no practical, available, or cost-effective real-time technology exists to detect and mitigate intentional attacks or accidental incursions in drinking water distribution systems.

A system designed to address the problem of distribution system monitoring is described here. The developed system employs an array of common analytical instrumentation, such as pH and chlorine monitors, coupled with advanced interpretive algorithms to provide detection/identification-response networks that are capable of enhancing system security, as has been advocated by several Federal research initiatives. Through the use of laboratory testing, pilot scale testing on pipe loops, and real world beta site deployment the system has been shown to be effective in detecting a wide diversity of possible threats. The system has been challenged with, and found effective against, a variety of agents including TIMs (toxic industrial materials), TICs (toxic industrial compounds), chemical warfare agents, and biological warfare materials. Other possible more obscure classes of threat agents such as street drugs, homemade toxins and commercial preparations have also been tested. In addition, the system has been shown to recognize common accidental intrusions such as antifreeze and sewage.

The response of these various agents is not only adequate to detect the presence of a contaminant, but the unique profile of the responses allow for some degree of identification. Through the use of a searchable library of agent profiles the system is capable of providing not only an alarm but also an identification of the likely cause. The profiles of over 80 of the most likely threat agents and many common contaminants have been compiled.

A proprietary baseline estimator dramatically and immediately reduces false warnings from regular fluctuations in operational parameters upon start-up. As time since deployment
increases the number of false positives is rapidly reduced to near zero by the system’s programmed ability to learn what is normal for a given operation.

The rapid detection and identification of breaches of security in the water distribution system is crucial in initiating appropriate corrective action. The ability of the described system to detect incursion on a real time basis and give indications as to the cause could dramatically reduce the impact of any such scenario. As the vulnerability of the distribution system becomes more widely recognized, the deployment of a system such as the one described will be an invaluable tool in maintaining the integrity of the nation’s drinking water supply.
Near Real-Time VOC Monitoring of Public Drinking Water Systems in Response to Water Security Concerns

Carol Thielen

ABSTRACT

Because of the growing concern of terrorist activity directed at this country’s infrastructure, the USEPA, the American Water Works Association (AWWA) and numerous municipal water systems have recognized the need to monitor public drinking water distribution systems to detect unknown chemicals which may be intentionally or unintentionally introduced into the water. Within this monitoring system, the detection and identification of VOCs are of the highest concern.

This presentation describes a VOC monitoring system currently installed in a public drinking water system that has been operational for the last 2 years. This monitoring system uses an unattended in-situ, purge and trap GC to monitor VOCs in the influent water to the water treatment system. The GC makes measurements every 30 minutes producing detection limits in the parts per trillion range. This equipment provided the city with a means of early notification when a surge of MTBE and other unknown contaminants were detected in the influent water. The system was initially installed for water security purposes and has demonstrated it’s efficacy within the first year of installation.

In addition, this presentation also describes a more sophisticated unattended monitoring system which incorporates many sensors and probes for a variety of water quality indicators in addition to VOCs. This system will automatically compile the real time data, use an inference engine to make adjustments for seasonal variations and alert operators when any of the monitored parameters are outside of the predetermined range.
An Automation of Analytical Data Perspective for Homeland Security

Paul Banfer
Vice President / Product Technology EISC
EISC, 6767 W. Tropicana Ave, Las Vegas, NV 89103
Primary Author's E-Mail: eisc@eisc.net; Phone: 702-248-1021

ABSTRACT

The automation of analytical data for Homeland Security requires a dynamic, flexible, and manageable process that can be quickly distributed to multiple locations and provide rapid, efficient, and consistent analytical data of the highest quality and integrity from many sources to the expert decision makers.

To establish these processes we must first define the scope:

A) Potential Threats
B) Emergency Response – Immediate, 8 hours, 24 hours, 48 hours, 72 hours
C) Contamination Sources, Hazards, Transfer Mechanisms, and Solutions
D) Analytical Laboratory capabilities
E) Analytical Methods to perform
F) Preparation for occurrence

The potential problems:

A) Training Issues
B) Laboratory Capability
C) Logistics
D) Mobility
E) Distribution
F) Consistency of data deliverables

Potential Solutions:

A) Training
B) Distribution of software for data deliverables
C) Software that is mobile, flexible, manageable, and fast
D) Automation of Quality Assurance
E) Consistency of deliverables
F) 100% automation of Method and Standard Operating Procedure verification, Data Validation, and Deliverable Review
G) Communication of Results from Business to Business, IMS to IMS
H) Combining information to be represented as one
I) Communication of Results to decision makers
J) Potential Models – Chemical, Biological, Water resources
The State Laboratory: Emergency Response and Data Integrity

Mary Abrams, PhD, Norman Crouch, PhD, George Mills, and Michael D. Wichman, PhD
Association of Public Health Laboratories (APHL)
2025 M Street, NW; Suite 550
Washington, DC 20036
Email: mwichman@uhl.uiowa.edu

SESSION DESCRIPTION

This session will describe state laboratory infrastructure and the essential role state laboratories play in responding to emergencies. The discussion will emphasize the respective roles of CDC, EPA, and NELAC in ensuring integrity of state laboratory data generated during emergency responses. The discussion will show how state laboratory certification/accreditation programs view EPA's oversight role as key to ensuring data integrity.

OBJECTIVES

- To describe how state laboratories serve as a unifying element for many state programs, including those directly related to preparedness for emergency actions requiring analytical support
- To stress the importance of including state laboratories as a key element in development of an integrated all-hazards emergency response plan.
- To highlight the role of state laboratories in terrorism preparedness and response.

ABSTRACT

This session will examine/describe how state laboratories serve as a major underpinning of an integrated, all-hazards approach for an effective emergency response. This includes responding not only to terrorist events, but also to other events that threaten public health, such as natural disasters (e.g., earthquakes and hurricanes), environmental exposures (e.g., spills and industrial accidents), accidental leaks, discharges, or explosions.

In emergencies, state laboratories must provide data that require the highest level of integration between the laboratory and one or more essential partners. Partners can include state/local health departments, local/state/federal law enforcement, local HazMat and Civil Support Teams, EPA, CDC, and other private or governmental laboratories. Reliable data required by these partners, to make critical decisions regarding public health and safety, can only be obtained through high quality laboratory analyses. It is critical that the quality/reliability of state laboratory data be documented by an established accreditation/certification process.

State laboratories involved with analysis of drinking water and other environmental matrices are often accredited according to National Environmental Laboratory Accreditation Conference (NELAC) standards, certified by the EPA Drinking Water program, or accredited by state-specific accreditation programs. State laboratories involved in analysis of clinical specimens are
required to meet regulatory standards of the Clinical Laboratory Improvement Act (CLIA) and are under CDC oversight as part of the national Laboratory Response Network (LRN). Many state laboratories are involved in more than one of these programs. There continues to be a pressing need for EPA to expand its accreditation/certification role to include all of its environmental programs, not just drinking water, so that laboratory data integrity can be ensured in all areas of importance to emergency preparedness and response.

Making critical, rapid decisions necessary in the face of credible terrorist threats, or a multitude of other events that may threaten public health, requires accurate, timely laboratory data that are carefully controlled for quality. While tremendous progress has been made in this regard for the analysis of clinical specimens for both biological and chemical terrorist agents, there remains much to be accomplished to assure quality laboratory data in the analysis of environmental samples and to achieve full integration of state laboratory capability and emergency response. Remaining unaddressed gaps include issues regarding environmental sampling/analysis, food sampling in chemical terrorism events, and appropriate training of first responders and law enforcement in the uses/limitations of field-testing devices. This session will describe the need for credible state laboratory data in response to all-hazards. For this purpose, credible laboratory data will be defined as those based on defensible laboratory procedures with appropriate QA and QC compliant with national standards such as NELAC, or federal standardized methods such as those developed by CDC or EPA as part of a national laboratory infrastructure that includes the LRN and the Food Emergency Response Network (FERN).
Unknown Sample Triage Using a Class III Glove Box

Phillip Adams
Scientific Laboratory Division, 700 Camino de Salud NE, Albuquerque, NM 87106
E-mail: phillip.adams@state.nm.us; Phone: 505-841-2510

ABSTRACT

Over recent years, there has been an increased need at Public Health laboratories and other testing facilities to have a system in place for handling and analyzing unknown samples in a safe and effective manner. These unknown samples often fall into the FBI’s ‘suspicious package’ category, especially if any evidence of a threat is present. This presentation will outline the necessary steps for unknown sample triage of potentially hazardous materials using a class III glove box. This containment system offers possibly the best available protection to the analyst for both chemical and biological hazards, and ensures sample integrity during analysis.

The main focus of this presentation will be on the screening for hazardous chemicals inside the glove box. The hazards covered will include radiologicals, explosives, corrosives, volatiles, and chemical terrorism agents. Subsequent testing for biological agents will be done outside the glove box in a Biosafety Level III laboratory. The tests will follow the EPA’s triage screening protocols that are currently in draft format, and which should be finalized later this year.

The intention of the presentation will be to give the audience an idea of how the EPA’s draft triage screening protocols may be implemented in practice, using a class III glove box as the all-hazard containment equipment. The presentation will also address peripheral issues such as correct personal protective equipment, training, chain of custody forms, secure sample storage, and elements that should be included when writing work instructions for people conducting the screening.
Building Environmental Laboratory Capability in Support of Emergency Response

Dana Tulis (tulis.dana@epa.gov 703-603-8722)
Allan Antley (antley.allan@epa.gov 706 355-8506)
US Environmental Protection Agency

ABSTRACT

Last year, Agency representatives presented a session regarding plans to address laboratory needs in the event of a terrorist incident. In the event of an actual or suspected terrorist incident, comprehensive laboratory resources will need to be called upon to allow the nation to deal with any situation. Over the past year, the Department of Homeland Security, the Centers for Disease Control, and the Environmental Protection Agency led an effort to draft a Memorandum of Understanding to formalize a federal Integrated Consortium of Laboratory Networks (ICLN) capable of sample analyses for chemical, biological and radiological contaminants of concern in clinical, food, plant, and environmental media.

The President’s National Homeland Security Strategy calls upon EPA to be the primary agency responsible for environmental sampling and analyses in response to a terrorist incident. In response to this strategy, and in concert with the Agency’s role in the ICLN, an environmental laboratory response network program (eLRN) is in the formative stages in the Office of Emergency Management.

EPA possesses limited capabilities and capacities to analyze environmental samples for chemical, biological, and nuclear materials associated with Weapons of Mass Destruction (WMD). The eLRN is exploring approaches to address this limitation. The Agency’s primary analytical capability is oriented toward routine analysis of industrial chemicals, pesticides and conventional pollutants. The first phase of the eLRN will be to formalize network relationships using these pollutants as the model. EPA intends to fully integrate state environmental laboratory counterparts into the eLRN similar to the integration utilized in the other networks.

The structure of the ICLN and the associated networks will be discussed as well as the structure, approach, and status of the eLRN.

The eLRN approach will continue the follow the precepts below:

- to the extent possible make use of the nation’s current laboratory resources
- address the problem in the most cost-effective manner
- develop a solution as quickly as possible
Low-Cost, High-Volume Air Monitoring for Homeland Security

Adam L. Hamilton, P.E.
Signature Science, LLC
8329 North MoPac Expressway
Austin, TX 78759
Primary Author's E-Mail: ahamilton@signaturescience.com
Phone: 512-533-2001

ABSTRACT

Regional sampling for chemical and biological threats often depends on stationary point samplers that are expensive and provide limited spatial coverage. Augmenting existing point sampling networks with lightweight, inexpensive mobile samplers provides a cost-effective option that enhances the spatial coverage. Suitable mobile platforms include public vehicles (such as buses and trains that operate on predefined routes), public service fleets (police, sheriff, EMS, etc.), and perhaps private fleets (utility, service, etc.). In some cases, even small unmanned aerial vehicles (UAVs) may be used.

A low-cost, high-volume chemical/biological sampler has been developed and tested. This new sampler is:

- Inexpensive;
- Expendable;
- Lightweight (<100 grams);
- Simple to use;
- Capable of collecting trace amounts of material; and
- Operates without electrical power.

The design was a collaborative effort between environmental engineers, aerospace engineers, and manufacturing experts. The result is the Aeroret®. The Aeroret contains filter media for capturing biological materials, as well as a carbon-based sorbent for capturing chemical threat agents (and/or their signatures) present in the form of trace organic chemical vapors. The sampler uses an airfoil shape to enhance flow through the system and to provide the differential pressure to drive air across the filter (for aerosol collection) and the sorbent bed (for vapor collection). The electret filter material has a permanent electrostatic charge and high filtration efficiency for the capture of particulate and aerosols with particle diameters between 0.3 and 10 µm. The inner portion of the filter has a “W” configuration, which provides a means of separating particles by size, driving the larger particles into the center of the W shape and capturing the smaller particles in the airfoil portion of the filter. The outer portion of the filter forms two airfoils. Computational Fluid Dynamics (CFD) modeling indicates the collection rate is equivalent to about 200 liters per minute when the sampler is moving at 35 knots.

The sampler was tested in wind tunnel challenges with various air loadings of fine and ultra fine particle standard dusts with traceability to NIST. Collection efficiencies of the 0.7-10 µm particle size dust standard were greater than or equal to 80%. Simple and efficient installation, handling, and analytical finishes have also been developed to support the sampler.
Validation of Sampling and Analysis Methods for Homeland Security Measurements

Larry D. Ogle, David L. Lewis, Molly Isbell, and Kennedy Gauger
Signature Science, LLC
8329 North MoPac Expressway
Austin, TX 78759
Primary Author's E-Mail: logle@signaturescience.com
Phone: 512-533-2004

ABSTRACT

As new samplers and sensors are developed for Homeland Security monitoring for CBRN, explosives, and toxic industrial chemicals, it is of vital importance that these devices be validated under realistic scenarios. Validation should include tests to verify response according to the manufacturer's specifications and to show that performance satisfies the needs of the end-user. Ideally, the response of these units will be demonstrated against the actual target agents, compounds, or biological threats. Complicating factors in validating the devices are the facilities and permits required to handle and test extremely toxic CBRN materials. In many cases, less toxic surrogates are used to validate device performance.

Device validation should be designed to show that they will display advertised sensitivity and will exhibit a minimum of interferences or false positives. For most devices, operation has been "validated" in a laboratory environment, but there may be a significant "gap" between performance demonstrated during product testing and performance when operated by the end-user in a field detection situation. This paper addresses these performance gaps and describes details for design and implementation of a field validation/verification program for new and improved samplers and sensors. In addition, traditional EPA validation steps have focused on determining precision, accuracy, and sensitivity of the measurement process. For CBRN field instrumentation, rather than obtaining accurate quantitative measurements, the focus of the validation process may be directed toward answering the question of presence or absence at a specific concentration with changing environmental interferences.

A successful field validation program begins with a comprehensive and well-designed test plan. The test plan should include a statistically valid test design; specify the range of test materials (e.g., target compounds) and conditions; detail release conditions and test materials, including the potential for interferences; describe the Ground Truth method to be used for comparing performance; and include a Health and Safety plan. The Health and Safety Plan must address test material toxicity, personal protective equipment (PPE), and potential ambient concentrations. As appropriate, release levels should be modeled and exclusion zones established to restrict access to hazardous areas during testing. Following the test, the data should be compiled and a final report developed that incorporates a statistical evaluation of all data with conclusions based on measurement data.
The TIGER Biosensor: Applications in Biodefense, Epidemiology and Infectious Disease Surveillance

Steven A. Hofstadler, Kumar L. Hari and David J. Ecker
The Ibis Division of Isis Pharmaceuticals
1891 Rutherford Rd
Carlsbad, CA, 92008
Primary Author's E-Mail: shofstad@isisph.com
Phone: 760-603-2599

ABSTRACT

The TIGER (Triangulation Identification for Genetic Evaluation of Risk) biosensor provides a novel and universal strategy for the detection and characterization of microorganisms associated with a potential biological warfare attack or a natural outbreak of an emerging infectious disease. The process uses mass spectrometry, signal processing, and base composition analysis of PCR amplification products from biologically conserved regions of microbial genomes to simultaneously identify the organisms present in a sample without the need for culture. The sample can be derived from air filtration devices, clinical samples, or other sources. Core to this approach are “intelligent PCR primers” that target broadly conserved regions of microbial genomes that flank variable regions. This strategy distinguishes TIGER from other detection/identification strategies in that TIGER requires no prior knowledge about an organism in order to identify it in a sample. The approach requires that high-performance mass measurements be made on PCR products in the 80 – 140 bp size range in a high-throughput, robust modality. The base compositions from multiple primer pairs are used to “triangulate” the identity of the organisms present in the sample. Use of species-specific primers allows rapid strain-typing of the organism. The concept is equally applicable to bacteria and viruses and could be further applied to fungi and protozoa. Moreover, the use of biologically essential gene targets to obtain microbe signatures enables the high-probability detection of both natural and bioengineered agents.

The TIGER system has been rigorously validated for use in biodefense applications, including surveillance for biological weapons agents in environmental samples, and tested against a broad range of biological samples in military troop health settings. For applications in air surveillance, the detection of numerous biothreats, surrogates, and near neighbors is demonstrated by spiking air filtrate with spores, vegetative cells, virion, or gDNA from threat organisms. Excellent performance is demonstrated even in the presence of a significant “clutter” of background organisms. Preliminary results will be presented on testing normal drinking water for the presence of biological threat agents. In an emerging infectious disease surveillance modality, an example will be shown in which the SARS virus was characterized and readily distinguished from all other organisms, including other strains of SARS. Further, in a collaborative effort with Naval health officers, we have examined cultures and direct throat swabs obtained from military personnel suspected to be suffering from Group A Streptococcus (GAS) infections. Samples were first analyzed using a panel of survey primers that readily identified the infectious agent as Streptococcus pyogenes, clearly distinguishable from all other organisms, including other streptococci and staphylococci. Subsequent TIGER analysis with Streptococcus-specific primers rapidly yielded emm-type strain resolution for each sample, which was later
corroborated with conventional MLST analyses. This study demonstrated that TIGER can be used to detect and identify infectious agents directly from throat swabs. In the present configuration, hundreds of samples can be analyzed within 12 hours allowing near real-time evaluation of patient samples and will make possible more rapid and appropriate treatment of patients in an ongoing epidemic. The use of “drill down” primers allows closely related strain variants to be distinguished and accurately identified. This is of particular importance when distinguishing biological weapons agents from near-neighbor surrogates, or when tracking the spread of particularly virulent strains of disease-causing organisms.
Quality Control Challenges for Extremely Toxic Compounds

Larry D. Ogle, David L. Lewis, Kennedy Gauger, and Molly Isbell
Signature Science, LLC
8329 North MoPac Expressway
Austin, TX 78759
Primary Author's E-Mail: logle@signaturescience.com
Phone: 512-533-2004

ABSTRACT

Continuous monitoring for chemical and biological agent attacks has become of vital interest to our national Homeland Security initiatives. Monitoring systems (such as those used in the Biowatch program) placed in large urban areas across the country will generate a huge amount of data, with most if not all, being negative for the CW or BW agents of interest. However, a positive result, and the decisions that must be made in response to this result, can have an enormous impact on the affected location and on our nation. Therefore, the Quality Assurance and Quality Control program associated with these monitoring programs must vigorously assess the performance of the continuous monitoring systems to fully characterize and understand that performance.

Minimizing the number of false positive results from these measurement programs is of great interest, since the decision to evacuate or quarantine a large population area based on a faulty measurement could have a grave negative impact on the population and on the monitoring program. Of equal or greater importance is the determination of the program false negative rate (e.g., how often would we NOT see the target when it was actually present). Common QA practices such as field spikes and blind media spikes are impractical since the targets of interest are extremely toxic and their handling and shipping are restricted. However, false negative rates can be assessed through the use of surrogates provided the laboratory routinely monitors for the surrogate compounds. In addition, the performance of the monitoring systems with the actual targets can be routinely assessed in controlled laboratory experiments at surety facilities designed to handle the agents.

This paper will discuss the approaches to assessing the continuous monitoring systems performance via QA/QC samples employing control samples spiked with surrogate compounds. In addition, the numbers of blanks, spikes, and other controls necessary to establish high confidence levels will be discussed. Challenges associated with monitoring system evaluation using the actual targets will be discussed as it is considered to be very important to assess collection efficiencies, desorption efficiencies, analytical variability, etc., with these agents.
Session 10

Managing Decision Uncertainty
How to Fully Integrate Available Information Resources: Maximizing Planning for Environmental Monitoring and the Real Benefits to the Planner

Ruby N. White  
EPA ECO Associate and Analyst  
White.Ruby@epa.gov  
202-566-1427

Jeffrey C. Worthington  
Director of Quality  
Worthington.Jeffrey@epa.gov  
202-566-0995

Policy and Program Development Staff  
Office of Planning, Resources, and Outreach  
U.S. EPA Office of Environmental Information  
1200 Pennsylvania Ave, NW  2812T  
Washington, DC  20460

ABSTRACT

Scientists, analysts, engineers, and managers know that planning environmental monitoring or increasing understanding of current environment status requires ready access to available information resources. Public sector planners, including those conducting technical monitoring as well as communities, use Web tools offered by EPA and others to construct targeted information searches. Understanding how these tools work as well as the information provided is critical to their efficient use in planning, and ultimately, the success of associated technical activities. Availability of all these tools, along with associated tutorials that offer varying degrees of assistance, may not be known to planners and the public.

This technical presentation provides:

- a detailed analysis of information resource tools available to planners,
- a standard approach for structuring access to best benefit users,
- a method for users to compare information available to their planning objectives, and
- a feedback mechanism to ensure continued improvement in integrating the tools into environmental planning.
Automation of Analytical Results for the Triad Approach

Paul Banfer
Vice President / Product Technology EISC
EISC, 6767 W. Tropicana Ave
Las Vegas, NV 89103
Primary Author's E-Mail: eisc@eisc.net
Phone: 702-248-1021

ABSTRACT

The analytical industry now provides an array of Scientific Data Management Software products that can work with or without a Laboratory Information Management System (LIMS). These software products focus on the analytical quality assurance, quality control, and data deliverable production within an analytical department (Volatiles, Semi-Volatiles, Pesticides/PCBs, Metals, and General Chemistry). Therefore, these systems can be used quite extensively with the Triad Approach because they can be used in a Mobile Lab, an ASP, or contracted along with a laboratory analyst and instrument to meet specific needs of the project, quality assurance, and regulatory requirements.

One of the key elements of the Triad Approach is the real-time measurement for real-time decision making. To facilitate real-time decision making, analytical data need to be of sound quality and Data Management tools used in the field should be able support rapid transfer of data to all the interested parties.

These systems can also work with Laboratory Information Management Systems or other Data Management Systems to pass information back and forth as if the process was one streamlined system.

This presentation will focus on the automation of Analytical Results to the Decision Makers through analytical software:

1) Mobility
2) Flexibility
3) Manageability
4) Capability
5) Communication of analytical data
6) Monitoring and analytical process, procedures, and data
7) Defensibility
The South Dakota Triad Challenge

Dennis Rounds  
South Dakota Petroleum Release Compensation Fund  
445 East Capitol Avenue, Suite 200  
Pierre, SD  57501  
E-Mail: dennis.rounds@state.sd.us  
Phone: 605-773-3769

ABSTRACT

In the fall of 2004, the South Dakota Petroleum Release Compensation Fund (PRCF) initiated a study to determine the cost and effectiveness of using the Triad approach at relatively small petroleum release sites. The results of the study suggest that the Triad approach will work well managing data uncertainty at small sites and may be preferential to other more conventional methods of site characterization.

The South Dakota PRCF is a state agency and is the financial assurance mechanism for regulated UST owners. Five sites were chosen for the study which included three active gas stations, one closed gas station and a railroad fueling site. The EPA provided the PRCF with a $50,000 grant to assist with the study. All locations were considered "legacy" sites because the petroleum releases had been discovered some time ago, yet none of the sites were effectively moving toward regulatory closure. Some of the sites had been in the assessment process for over a decade with no remediation to date. The known tanks at the closed gas station had been removed over 10 years ago, but no assessment had been conducted. The goal of the study was to apply the principals of the Triad in order to rapidly characterize the sites, develop accurate conceptual site models, establish clear cleanup goals and move the languishing sites toward regulatory closure as rapidly as possible. The principals of the Triad were used in the management of the project sites. In accord with the graded approach endorsed by Triad, planning and site work were tailored to fit the relatively small nature of the petroleum release sites. The PRCF contracted with Columbia Technologies to conduct the field analyses and Mid-continent laboratories to perform collaborative analyses as necessary using quality assured laboratory methods. A team was assembled for each site which included personnel from the PRCF, the SD Dept. of Environment and Natural Resources, the owner or his agent, the environmental consultant and personnel from Columbia Technologies. Systematic planning was conducted with the use of an experienced Triad mentor to establish clear objectives for each site. Direct push and direct sensing technologies were used in the field to gather site data and conduct the rapid, real-time measurement aspect of the Triad approach. All team members remained on site until uncertainty was minimized and data gaps were filled. Decisions regarding the depth and location of borings and the type and number of collaborative lab samples were made by the team on site, relying on the real-time measurements. The team did not move to the next site until all members were satisfied that data uncertainty had been minimized to an acceptable level. Columbia Technology's "Smart Data Solutions" was used to convey field collected data to a secure internet website where it was posted as it was collected. The site model was updated several times per day using 3-D graphic images to aid the team in reducing uncertainty and filling data gaps. All 5 sites were successfully characterized within a single three-week period. All sites now have clear objectives for remediation and site closure.
Managing Decision Uncertainty on Navy Cleanup Projects

Kimberly Gates, P.E.

ABSTRACT

Almost all (important) environmental decision problems involve some level of uncertainty either in its data or measurements, the values assigned to parameters describing future work on the site or even about the environment in which we operate. "Uncertainty" refers to our imperfect and inexact knowledge of the world. We can use certain management approaches to quantify and "tame" uncertainty on cleanup projects.

The Triad approach seeks to manage uncertainty throughout the cleanup process. The three key elements of the Triad approach that achieve successful uncertainty management are: systematic planning, dynamic work strategies, and real-time measurements. The first stages of the Triad approach determine whether the type, quantity, and quality of environmental data needed to support a decision has been achieved. This presentation will introduce environmental professionals to this approach for managing decision uncertainty using case studies from two Navy sites to demonstrate the success of the Triad approach. The Navy will continue support the utilization of Triad approach for managing decision uncertainty for cleanup projects from initiation of the Triad team until the land is available for reuse.
Acknowledgments

The Triad is an EPA initiative, with active federal involvement by representatives of:

- The U.S. Army Corps of Engineers
- The U.S. Navy
- The U.S. Air Force
- The ITRC and state representatives
- DOE’s Argonne National Laboratory

My Co-author, Deana Crumling, represents EPA’s Technology Innovation and Field Services Division, part of the Superfund Program (old TIO)
Introduction

- Our presentation is intended to present Quality Assurance and Quality Control (QA/QC) needs for Triad-based programs
- First, I'll present a brief summary of what Triad is all about
- Then I'll discuss QA/QC concepts and show how they relate to Triad
- I'll then discuss specific Triad QC components
- And conclude with the main Triad-QA/QC message we want you to go away with, which can be characterized by one word:

  "FOCUSED"

EPA’s Triad Initiative

- **Systematic Planning**
  (facilitated by Conceptual Site Models - CSMs)
- **Dynamic Work Strategies**
  (leading to more and more accurate CSMs)
- **Real-Time Measurement Systems**

For site characterization and remediation projects
What is the Goal of the Triad Initiative?

- Encourage the environmental community into understanding that there is a critical need to adopt 2nd-generation practices
- Adopt modern characterization, remediation and monitoring technologies and strategies to improve CSM accuracy and cleanup efficiency
- Implement change in related areas, such as procurement, project planning, regulation development/implementation, and QA/QC

The Triad IS about...

- Facilitating communications with stakeholders initially and throughout the project
- Cultivating professional competence and multidisciplinary teams (“allied environmental professionals”)
- Constructing accurate CSMs (as a primary Triad product) to support cost-effective decisions
  - Done in real-time to cut lifecycle costs
  - Controlling for sampling variables and focusing QA/QC to manage data uncertainties specific to project decisions
- Actively managing decision uncertainty using efficient and cost-effective tools and strategies
What is the “Keystone” Concept for Triad?

- The “Keystone” principle that links all other Triad concepts is **Management of decision uncertainty**

- Is gathering new data necessary to manage decision uncertainty? Ask yourself: Will new data or information change the decision?

- When data relevant to the decision-making process needs to be gathered then:
  - Need to target specific data needed
  - Collect and manage that data with the goal of minimizing decision uncertainty

Where Does Uncertainty Lie?

- **Lack of clarity here**

- **Reuse Plans, Goals, Outcomes**

- **CSM**

- **Impact**

- **...means lack of clarity here**

- **...which means no foundation for agreement here**

- **Determine**

- **Approaches to:**
  - Assessment
  - Investigation
  - Cleanup Design, Implementation
  - Closeout, Long Term Operations and Maintenance

- **Decisions:**
  - Exposure risk?
  - Cleanup goals
  - Data (type, quality)
  - Tolerable uncertainty

- **Tools for:**
  - Sampling, Analysis, Interpretation
  - Cleanup/Remediation
  - Containment
  - Cleanup
  - Controls
  - Monitoring, Maintenance
The Data Quality Chain

All links in the **Data Quality Chain** must be intact for **Decision Quality** to be supported!


---

Collaborative Data Sets Play an Important Role in the Triad

How Do We Combine These Concepts Into a Cost-Effective QA/QC Program for Triad?

- Systematic Project Planning provides the foundation for
  - Ensuring quality at all levels
  - Fostering effective management of decision uncertainty

- Dynamic Work Strategies means
  - Changing or modifying measurement systems as conditions warrant AND
  - Changing or modifying QC protocols as conditions warrant

- So Triad projects should include
  - Initial planning sessions geared towards management of decision uncertainty
  - Subsequent planning sessions that consider changing or modifying measurement systems and QC protocols as warranted

QA/QC is Focused Under Triad...

- QC in the Triad sense involves controlling factors that could introduce uncertainty into the data quality chain

- QC under Triad includes control of field and lab methods:
  - Equipment is working properly
  - Field and laboratory operators are performing appropriately
  - Geotechnical techniques are properly preformed
  - Samples are collected and processed using the proper procedures and with the proper sample support
  - Software and computer programs are appropriate and properly applied
What Specifically Do We Mean By Use of the Term “Focused?”

- Initially focused on QC NEEDED to determine method performance, and to document data quality
- Then refocused as the CSM is modified with new data to target specific data elements that are relevant to the decision-making process
- BECAUSE the level, frequency or type of data needed may change over time, the level of QC activity can also be changed over time – to focus on specific elements that impact decision uncertainty
- Ultimately, QC under Triad is focused on parameters that are relevant to the decision-making process

Now Lets Look at Some Examples of Focused QC...

- As objectives move from producing data for risk assessment to hot spot identification, QC may be relaxed
- If data collection switches from supporting a remedial action to site closure documentation, QC may become more stringent
- If the real-time method is producing non-detect results, more frequent use of laboratory methods may also be considered as part of a collaborative data set. Additional options can include steps to confirm that that field non-detects are not false negatives and include:
  - Increase the frequency of low-level spikes
  - Perform more frequent low-level calibrations
  - Increase field and laboratory quality control samples
And Some More Examples of Focused QC…

- After initial determination that real-time methods are producing accurate results, less frequent use of lab methods may be considered as part of a collaborative data set
- Sample matrix characteristics might change unexpectedly (e.g., due to higher moisture content, increased organic carbon content) and warrant closer monitoring of method performance
- Focus back-end data review (verification/validation) on data that will drive decision making
- After initial data verification/validation shows that systems are in control, reduce the frequency of these activities

Triad QC Includes the Need For Some Traditional QA/QC Elements

- A “culture of quality” among all team members, especially the field team – because especially with real-time measurement systems, the first line of defense is in the field
- A QAPP that documents methods to be employed and QA/QC to be performed
- Well-defined performance goals and metrics such as criteria for data precision, accuracy, representativeness, comparability and other traditional data quality indicators (articulated in the QAPP)
- Use of and adherence to Standard Operating Procedures for ensuring consistency and data reliability (also articulated in the QAPP)
- A knowledgeable technical team member with responsibility for project QA/QC (often called a Quality Assurance Officer)
But Triad QC Includes Some Elements That Are Unique to Triad or Different in Scope...

- A QAPP that that is dynamic and that can be modified and focused (often in the field) as the project proceeds

- Methods Evaluation Studies (Demonstration of Method Applicability)
  - To establish a quantitative relationship between field-deployed methods vs. laboratory methods with site-specific media
  - To identify specific parameters that must be carefully monitored, such as moisture content of soils and sediments

- Provisions for “Customized QC” for the performance of laboratory methods - in the spirit of PBMS
  - Is the type of stringent QA/QC called for by standards setting organizations always necessary?
  - A cold hard look, for example, at calibration regimes, internal standards, surrogate analyses, and laboratory QC samples

And Other Elements That Are Unique to Triad or Different in Scope...

- **Data Evaluation** – Data verification and validation is a critical component of QA/QC programs. Key questions are:
  - How can data evaluation be performed real-time?
  - What level of data evaluation is really necessary?
  - Can evaluation steps be done in a less time-critical fashion?

- **Logistical Considerations** – Time is often critical when field activities are underway and decisions need to be made in real-time. For example:
  - If laboratory data are needed as a point of comparison, there may be a lag between availability of real-time and lab results
  - Establishing communication protocols between field teams, database managers and decision makers can also be critical
  - Readiness reviews and “dry-runs” can be an important QA component of a Triad program to ensure that logistical considerations have been sufficiently addressed
Conclusions

- Triad is a coordinated effort to integrate proven strategies into a framework that improves the cost-effectiveness of and confidence in project outcomes.
- Triad is all about managing decision uncertainty.
- QA/QC for Triad projects is different from conventional cleanup programs.
- While the goal is the same – To generate data of known quality whose quality characteristics are documented, verifiable and technically defensible.
- QA/QC for Triad is focused then adapted and refocused as a project proceeds in response to changing project needs or site conditions.
- Focused QA/QC inherently means using limited QA/QC resources so as to maximize decision certainty.
- Put your QA/QC money where it will do the most good – data sets important for decision making, and QC necessary to document data quality.

For More Information

- EPA’s Triad resource center may be accessed at [http://www.triadcentral.org/](http://www.triadcentral.org/)
- **Dan Powell**
  
  U.S. EPA  
  Office of Superfund Remediation and Technology Innovation  
  U.S. Environmental Protection Agency  
  Phone – (703) 603-7196, Fax (703) 603-9135  
  Email - powell.dan@epa.gov
- **Todd Kimmell**
  
  Argonne National Laboratory  
  Environmental Assessment Division  
  Phone - (202) 488-2483, Fax - (202) 488-2413  
  Email – tkimmell@anl.gov
A Bit About Myself and Argonne’s Triad Experiences

- Todd Kimmell - Former EPA employee and an “Argonnite” since 1993
  - Environmental Scientist and Policy Analyst
  - Worked for EPA in OSW’s Methods Program in “the early days” (TCLP)
  - A RCRA “weenie” specializing in the DOE and DOD “special waste” issues, including conventional munitions and chemical warfare agents
  - Heavily involved post-HSWA in EPA’s RCRA Corrective Action Program
  - QAO for two large Army RIIs with conventional and CWA munitions issues
  - Input to EPA’s Triad initiative, specifically with respect to QA/QC

- Argonne’s Environmental Assessment Division (Chicago and DC)
  - Involved in many site characterization/remediation programs over the years
  - Developed a precursor to Triad called Adaptive Sampling and Analysis Program (ASAP)
  - Involved in many facets of DOD’s munitions and range management initiatives
  - Assisting EPA in developing the web-based Triad Resource Center
  - Assisting several federal and private organizations in implementing Triad
Addressing the Misconceptions About QA/QC in Triad Projects

William M. Davis
Tri-Corders Environmental, Inc.
McLean, VA

ABSTRACT

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

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

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

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

This paper will discuss the implementation of QA/QC procedures during a recent Triad investigation that used semi-quantitative data (MIP) and both on site quantitative (EPA Method 8265) and off-site quantitative (EPA Method 8260b) data to address uncertainty in the CSM.
Laboratory Certification for Field Analytical Methods and Triad in New Jersey: Perfect Together

Stuart Nagourney and Brian Sogorka
New Jersey Dept. of Environmental Protection
401 East State St.
Trenton, NJ 08625
E-Mail: Stu.nagourney@dep.state.nj.us
Phone: 609-292-4945

ABSTRACT

New Jersey has more than 10,000 contaminated sites, many of them brownfields 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.

NJDEP is exploring mechanisms to convince its staff and management that field analytical measurements can be relied upon to build accurate conceptual site models and reduce project decision uncertainty while saving time and money. NJDEP is exploring ways to break traditional beliefs that data generated by certified permanently-sited laboratories are definitive, despite the very low density of such data points. Two NJDEP units, one responsible for laboratory certification, and the other for management of site cleanups, are collaborating to improve the confidence in and acceptability of field analytical data by management and staff within the NJDEP. This talk will provide an update on NJDEP’s experiences and lessons-learned developing an accreditation program for service providers of field-generated data, as well as technical and institutional barriers.
Session 11

Inorganic Methods – Advances in Elemental Speciation
Chromium(III) Oxidation in Chromite Ore Processing Residue-Enriched Soils: Theoretical Predictions and Experimental Observations

Bruce R. James and Rock J. Vitale

1Soil Chemistry Program, Natural Resource Sciences
University of Maryland, College Park, MD 20742
Email: bj5@umail.umd.edu; Phone: 301-405-8573

2Environmental Standards, Inc., Valley Forge, PA 19482-0810

ABSTRACT

The oxidation of Cr(III) to Cr(VI) in field-moist soils can theoretically occur using Mn(III,IV)(hydr)oxides as the oxidant. Uncertainties surrounding whether or not this redox reaction may occur in chromite ore processing residue (COPR)-enriched soils have complicated decision-making on the analysis, remediation, and regulation of these alkaline soils containing both Cr(III) and Cr(VI). Thermodynamic predictions show that pH and Eh are soil master variables affecting the speciation, solubility, and reactivity of Cr(III) and Mn(III,IV)(hydr)oxides. The hexaquo Cr$^{3+}$ cation is the most reactive form of Cr(III) with negatively-charged Mn(III,IV)(hydr)oxides; and insoluble forms of Cr(III) in paracrystalline hydroxides, crystalline oxides, and organic complexes are much less reactive or are not oxidizable at all. In alkaline (pH 8-13), aerobic COPR-enriched soils; Cr(III) has been shown to be inert toward oxidation to Cr(VI), and Cr(VI) has also been shown to be inert toward reduction under unremediated field conditions.

During the hot, alkaline extraction used to dissolve sparingly-soluble and soluble forms of Cr(VI) from COPR-enriched soils (USEPA SW-846 Method 3060A); residual chromite, Cr$_2$O$_3$, and other COPR-borne forms of Cr(III) are not prone to oxidation, especially with Mg$^{2+}$ added as a suppressant. In COPR soils in which remediation-by-reduction methods have been used to convert Cr(VI) to Cr(III), questions have been raised as to whether such newly-reduced, precipitated Cr(III) may re-oxidize in the future by O$_2$ or Mn(III,IV). Laboratory and field studies have failed to show that such a re-oxidation reaction occurs, presumably due to the recalcitrant nature of insoluble complexes of Cr(III) with OH$^-$ or the oxidized forms of the reducing agents used for remediation.

A knowledge of the redox soil chemistry of Cr is essential for predicting accurately the extent to which a given form and concentration of Cr(III) might oxidize in a COPR-enriched soil. Thermodynamic predictions, kinetic experiments, and site-specific observations and field trials provide evidence that COPR-borne forms of Cr(III) are not expected to oxidize to Cr(VI) under alkaline, aerobic field conditions.
Application of Chromium (VI) Speciation Results for Remedial Alternatives Evaluation

John C. Petura, P.E. DEE, QEP
Applied Environmental Mgt, Inc.
16 Chester County Commons
Malvern, PA 19355
Email: jpetura@aem-inc.com
Phone: 610-251-0450

ABSTRACT

Although speciating quantitatively hexavalent chromium [Cr(VI)] in industrial wastes has been routine practice in the electroplating industry since the late 1960s, reliable quantification of Cr(VI) in solid matrices (e.g., soils, hazardous wastes) has been achieved only since the early 1990s. This was accomplished through research and development focused on the characterization and treatment of Cr(VI)-bearing soils, particularly those enriched with chromite ore processing residue (COPR). A major landmark in quantifying Cr(VI) in solid matrices was promulgation of SW-846 Methods 3060A/7196A (Alkaline Digestion Followed by Colorimetric Determination for Analysis of Cr(VI) in Solid Matrices) in 1997. Acceptance of these methods essentially “superceded” prior conventional practice for quantitative speciation of Cr(VI) in solid matrices. The approach to speciation embodied in these commercial laboratory methods requires the use of ancillary parameters to determine the oxidizing or reducing state of a sample. Comparative analysis of samples containing COPR using SW-846 Method 6800 (Elemental and Speciated Isotope Dilution Mass Spectrometry) yielded essentially identical results to those obtained by Methods 3060A/7196A. However, Method 6800 has been used by only a limited number of researchers and is not yet available commercially. Notwithstanding, a regulatory agency has proposed Method 6800 for Cr(VI) analysis as part of a tiered decision hierarchy related to Cr(VI) data use that would reject Cr(VI) data obtained using Methods 3060A/7196A for site characterization and remedial actions.

The data and knowledge gained comparing various extraction and analysis methodologies for Cr(VI) quantitation have been applied both to characterize the extent of Cr(VI) contamination at multiple sites suspected to have COPR, and were subsequently applied to determine whether Cr(VI)-bearing soils, particularly those enriched with COPR, could be treated to meet soil Cr(VI) cleanup levels under regulatory consideration.

Applying the significant differences in mobility and toxicology between soluble Cr(VI) and stable insoluble Cr(III), the results from characterizing thousands of solid matrix (e.g., COPR, soils, debris, various other fill materials) samples and extensive treatability efforts have been derived from basic laboratory research, field pilot studies of remediation technologies, and full-scale ex situ treatment system implementation. A major focus of treatability testing was to determine if elevated Cr(VI) could be irreversibly reduced to contemplated soil cleanup criteria levels (~20 mg/kg to ~200 mg/kg), depending upon site-specific risk assessment results obtained from scenarios ranging from residential to industrial/commercial property use.

This paper addresses the application of Cr(VI) speciation data collected for site characterization and delineation, and evaluation of treatment alternatives and achievement of Cr(VI) soil cleanup
criteria via *ex situ* or *in situ* site remediation activities. The data and results are examined in terms of scientific validity, process performance achievement, and treatment methodology limitations/obstacles to successful transformation of Cr(VI) to an immobile and essentially non-toxic Cr(III)-bearing solid matrix that allows sites containing COPR-enriched soils to be remediated and restored to beneficial community use. The proposed use SW-846 Method 6800 and its implications on (a) site characterization and delineation, (b) "clean closure" where remediation activities have met the designated Cr(VI) soil cleanup criteria, and (c) these same issues associated with other metals-contaminated sites nationwide, will also be addressed.
An Evaluation of Analyte Isolation and Analytical Finish Methods for Cr(VI) in Solids

Rock J. Vitale, CEAC, CPC; Kyle R. Clay
Environmental Standards, Inc.,
1140 Valley forge Road
Valley Forge, PA 19482-0810
E-Mail: rvitale@envstd.com
Phone:(610) 935-5577

ABSTRACT

Chromium exists predominantly in two stable forms (valence states): Cr(VI) and Cr(III). In environmental samples, there is a fundamental need to differentiate between the two valence states because Cr(III) is not considered to be toxic to humans, whereas Cr(VI) is considered an inhalation carcinogen. The analysis for total chromium is relatively straightforward; however, the successful analysis for Cr(VI) in complex soils/solid matrices can be more complex.

In solid materials, there are always two steps to the quantification of Cr(VI): The extraction or isolation of the hexavalent chromium species and the analysis of the digestate for Cr(VI). The development and ultimate promulgation of SW-846 alkaline digestion procedure (Method 3060A) provided the critical means to reliably extract Cr(VI) in a solid material sample while preserving the native valence state of chromium in its environmental setting. A variety of analytical finish methods are available to quantify the Cr(VI) in solution. The colorimetric procedure, SW-846 Method 7196A, is the most common for Method 3060A digestates because of its wide availability and low cost. Somewhat less widely used is SW-846 Method 7199 which utilizes an ion chromatograph (IC) with separation of Cr(VI) on an anion exchange separator column. SW-846 Method 6800 - Elemental and Speciated Isotope Dilution Mass Spectrometry- was promulgated in 1998 and can be used to speciate chromium as well as other metals of environmental concern (e.g., As, Hg) in solid matrices. Method 6800, however, is not yet available at commercial laboratories and the unit cost [currently much higher than 7196A or 7199] for commercial utilization remains to be determined. In New Jersey, regulators previously mandated the use of an alkaline digestion procedure (NJDEP-modified Method 3060) coupled with a colorimetric analytical finish (NJDEP-Modified Method 7196A) on New Jersey chromite ore processing residue (COPR) Sites. NJDEP-modified Methods 3060/7196A specify essentially identical chemistry and laboratory procedures as SW-846 Methods 3060A/7196A.

Regardless of the analytical finish method performed, extensive research has conclusively demonstrated that in the analysis for Cr(VI), soils or waste samples rich in reducing agents (e.g., organic matter, sulfides, ferrous iron) cannot support chromium in the hexavalent state. Low matrix spike recoveries (<75%) are actually expected in these matrices, not because of bias, but because Cr(VI) cannot exist. Thus, the evaluation of Cr(VI) matrix spike recoveries when assessing method performance or potential bias requires a non-traditional approach. Specifically, it is inappropriate to automatically deduce poor method performance or result bias for Cr(VI) matrix spike recoveries outside the traditional acceptance range (e.g. 75%-125% recovery).

Despite definitive research results and peer-reviewed publications, a regulatory agency has recently suggested policy changes that would render Cr(VI) results via Methods 3060A/7196A (or
NJDEP-modified Method 3060/7196A) unacceptable for samples associated with matrix spike recoveries <75% or >125%. The proposed change would reject data associated with matrix spikes <75% or >125%, essentially mandating the use of Methods 3060A/6800 for the analysis of Cr(VI).

A sizeable database of Cr(VI) analytical results for soils and sediment samples by the various analytical finish methods has been developed through remedial investigation of more than 35 COPR sites in New Jersey. The database includes an abundance of matrix spike recovery data by the various methods. This paper provides a comparison of the results generated by the various methods and a discussion of matrix spike recovery as it relates to the efficacy of these methods.
When It Comes to Speciation, “To Label or Not To Label? That Is the Question”

Brian Buckley, Willie Johnson, Qiang Tu, Eric Fisher and Riumin Xie
Environmental and Occupational Health Sciences Institute
Rutgers University
170 Freilighuysen Road
Piscataway NJ 08854
bbuckley@eohsi.rutgers.edu

ABSTRACT

EPA method 6800 allows the analyst to monitor changes in the chemical species during sample; transport, storage, processing and even analysis. Using stable isotopes allows multiple spiking solutions to be added to the sample, each labeling a different chemical species. It would appear that this method should allow everyone to perform speciation analysis without fear of introducing bias to the analysis. With this capability, one might wonder what are the limitations to the method? The first is that it requires mass spectrometric measurement of each of the chemical species. Second is that it is not applicable to analytes with only one isotope (monoisotopic) and third is that it can be very expensive to perform. There is an alternative to method 6800, using recovery percentages. For those who use optically based detection techniques this alternative is a viable option. For the more frugal analyst it may present an alternative worth exploring and for someone looking at either As or Mn, it is the only way to check for interconversion. Its drawback is that it does not allow the analyst to observe species cycling if it occurs. This presentation will focus on the use of recovery percentages to monitor for species interconversion and its application to As and Hg speciation.
Bromate/Bromide Speciation by HPLC-ICP-MS

Pamela A. Perrone Ph.D., Wilhad M. Reuter, Ph.D., Kenneth R. Neubauer, Ph.D., Zoe A. Grosser, Ph.D.
PerkinElmer Life and Analytical Sciences
710 Bridgeport Avenue
Shelton CT 06484 USA
Zoe.Grosser@perkinelmer.com
Phone: 203-402-5320

ABSTRACT

Water for public consumption must be purified prior to distribution. A number of processes are used for water purification, including treatment with ozone to kill bacteria. While this method is effective, ozonolysis can also convert bromide (a natural component of many waters) into bromate (BrO₃⁻), a carcinogen. Therefore, the need exists to measure bromate in drinking waters, which means that it must be measured separately from other forms of bromine. Current methods for measuring bromate and bromide involve separating the bromine-containing components by ion chromatography and using ICP-MS as a detector monitoring bromine at m/z 79; this is the protocol stated in EPA method 321.8.

This work focuses on bromide/bromate speciation by ion chromatography using Dynamic Reaction Cell (DRC) ICP-MS as the detector. A faster chromatographic method is developed than presented in the current version of method 321.8, more closely matching the capability of the detector. Stability and repeatability of the bromate signals over several days are demonstrated. Possible interferences and the detection limit achievable will be discussed.
Dynamic Metal Speciated Analysis such as Cr(VI) and Alkylmercury Examined and Applied

H. M. ‘SKIP’ KINGSTON, MIZANUR RAHMAN, THEO TOWNS, DENGWEI HUO, YUSHENG LU, RANDY CAIN, JOHN KERN, ROBERT POWELL
Department of Chemistry and Biochemistry, and Center for Environmental Research and Education
Duquesne University, Pittsburgh, PA 15282-1503
Kingston@duq.edu, 412-396-5564

ABSTRACT

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 and the measurement steps. 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 preparation and certification of standard reference materials and for accurate speciated measurements. Other countries such as the European Community through EVISA have reached these conclusions and have supported only isotopically traceable solutions are effective diagnostic tools. Speciated isotope dilution mass spectrometry (SIDMS), which addresses the correction for such degradations or conversions and its use in validation will be demonstrated and discussed (1, 2). It has been demonstrated to accurately determine the species concentrations at both the time of spiking and measurement. The method also has the ability to perform diagnostic analysis isolating specific procedural protocol steps in specific matrices enable their evaluation for species shifting potential. SIDMS has the potential to be used as a diagnostic tool to validate other methods and to evaluate 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).

As examples, SIDMS has been applied to monitoring the fate of Cr(III) and Cr(VI) in processing samples using EPA method pair 3060A/7196A, which has been used for the quantification of Cr(VI) in solid samples. Method 3060A includes extracting Cr(VI) from samples in an alkaline solution, filtering the extracts and neutralizing the filtrates. Method 7196A is a colorimetric detection method, using diphenylcarbazide to complex with Cr(VI) which forms a purple product that is usually measured at pH 2. IC and HPLC ICP-MS were used as detection methods in this study (4).

The results of this study showed that classical methods may not be able to detect alteration of the species from difficult matrix samples, and that neutralization and measurement steps can contribute to transformation of species. In specific and difficult matrices, Cr(III) could be oxidized to Cr(VI); and, during neutralization, Cr(VI) could be reduced to Cr(III). The degree of the species’ conversions is highly dependent on the sample matrix and the instrument’s operating condition. When using EPA method 7196A to quantify Cr(VI) in some soil extracts, low recoveries were observed. SIDMS, however, obtained 100% recoveries despite the reducing matrices. SIDMS has successfully identified and corrected these conversions,
demonstrating that SIDMS is a more appropriate method in speciation analysis and that it is also a diagnostic tool for other speciation methods. Applications in coal fly ash have been studied extensively and are widely applicable across the nation. The study in this matrix will show that Cr(III) is oxidized to Cr(VI) in coal combustion processes and that it then is stable in the environment and is released as run-off from fly ash sites (5). Road aggregate materials that leach Cr(VI) and sediments where the Cr(VI) is deposited are examples of methods specific matrix conversions (11).

Mercury has recently become the focus of debate on transformations between methylmercury and inorganic mercury during the measurement process (6). SIDMS is a method that can be generalized for many poly isotopic species that have the potential to be transformed from species to species during the evaluation process such as Cr, Hg, Se, Sn and other species where multiple isotopes (in species relevant forms) provide the necessary resources to make these measurements. Standards may also be produced with isotopically enriched species that may be evaluated prior to use if processes alter the species forms (7, 8).

Field environmental examples are presented to demonstrate the effectiveness of SIDMS for Cr in the coal fired power industry. SIDMS has been standardized and approved as a new EPA method “6800” (9, 10). This new EPA method is intended to assist with some of the uncertainty in speciated environmental measurements. The general method is described and applications to both Cr species and Hg species will be discussed.


• Oliver Fordham, Jr., “SW-846 Method 6800: Elemental and Speciated Isotope Dilution MS” Environmental Testing and Analysis, March/April 1999.

Session 12

Managing Uncertainty
Managing Decision Uncertainty Resulting from Hydrogeologic Heterogeneity in Groundwater Contamination Investigations

Seth Pitkin
Senior Hydrogeologist
Stone Environmental, Inc
spitkin@stone-env.com

ABSTRACT

The Triad Approach focuses on managing uncertainty in decision-making relative to management of the site. Decision uncertainty stems primarily from two types of uncertainty associated with the data: sampling uncertainty and analytical (or measurement uncertainty). Analytical uncertainty is well understood and is controlled at low levels. Sampling uncertainty arises from the heterogeneity inherent in natural hydrogeological systems. Examples include the spatial structure of: hydraulic conductivity controlling groundwater flow; capillary pressure controlling non aqueous phase liquid movement; and the very weak nature of hydrodynamic dispersion in directions normal to the primary groundwater flow direction, resulting in very steep concentration gradients.

Conventional techniques used to investigate groundwater contamination, such as monitoring wells result in depth-integrated, flow weighted average concentrations and large spacings between samples that result in a high level of uncertainty in the conceptual site model and hence in decision making. A primary means of reducing sampling uncertainty is through the use of tools and techniques that provide many more data points at a more appropriate scale than conventional methods.

The Waterloo Profiler is a direct push groundwater sampling tool that has been modified to allow for the collection multiple data sets that are used collaboratively to test and revise the conceptual site model. The modified Waterloo Profiler provides discrete groundwater samples at virtually any vertical spacing while developing a continuous log of the Index of Hydraulic Conductivity as well as hydraulic head distributions and specific conductance, pH, oxidation/reduction potential and dissolved oxygen of groundwater.

A Triad investigation team incorporated source zone data collection in the vadose zone using a passive soil gas survey, membrane interface probe explorations and conventional soil coring and onsite analyses along with the integrated data sets provided by the Waterloo Profiler below the water table to revise a conceptual site model through a three week investigation. The uncertainty that had been hindering use of the site for over a decade was reduced as a result of the investigation and the stakeholders were able to move forward.

~~~

Seth Pitkin is a Senior Hydrogeologist and Leader of the Investigation and Remediation Group at Stone Environmental in Montpelier, Vermont. He received a B.S. in Geology from the Evergreen State College in 1984 and a M.Sc. from the Department of Earth Sciences at the University of Waterloo in 1994. Mr. Pitkin was involved with the development of the Waterloo Profiler at the University of Waterloo and over the ensuing years has adapted, expanded and
improved the profiler. He has over 19 years of experience in the investigation of groundwater contamination, predominantly chlorinated solvent plumes in porous media and twelve years of intensive experience in Triad-type site investigations.
Chemical Measurements Traceability, Validation and Uncertainty

Marlene Moore  
Advanced Systems, Inc.  
PO Box 8032  
Newark, DE 19711  
Phone - (302) 368 1211  
Fax - (720) 293 2706  
email - mmoore@advancedsys.com

ABSTRACT

In environmental testing one of the data quality indicators required is comparability. The predominant process to ensure comparability has been based on performing the same method and demonstrating the same quality control performance limits. The international community is establishing a uniform process for ensuring chemical measurements achieve comparability by a defined process for traceability. This process involves the need for method validation and the expression of the estimated uncertainty.

To achieve comparability of results, a link is needed for all the individual measurement results to some common, stable reference or measurement standard. Results are compared through their relationship to that reference. The linking of results to a reference is termed “traceability.” The definition of traceability as found in the International Vocabulary of Basic and General terms in Metrology (VIM) is the: “property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.”

In an increasingly regulated environment attempting to move to a performance approach rather than a method based process, laboratories are under pressure to demonstrate that their use of measurement method is indeed both appropriate and sufficient. This can be achieved through the use of the appropriate reference standards. Many of the physical quantities used in routine chemical measurement are supported by extensive and effective calibration and traceability systems, making the traceability for these quantities straightforward. The values of chemical quantities involved are typically drawn from a wide range of reference materials and data with varying sources and unknown origins. The selection is often based on the statement on the certificate that it is “NIST traceable” with little regard or knowledge how this is established and without any stated uncertainty.

Chemical measurements require confirmation of identity and amount of the element, compound or mixture. Further, it is not uncommon for the measurement of the element, compound or mixture in complex matrices, to include chemical results that arise from the measurement of operationally defined parameters, for example “Toxicity Characteristic Leaching Procedure [TCLP] or Oil and Grease) (sometimes called “empirical” measurements or method defined parameters). In such circumstances, it is not always so straightforward to identify the requirements for traceability, or to demonstrate that the traceability in place is adequate, since the current process is to perform the method without modification. The problem is when the matrix being measured or options are found in these methods require method modification to
achieve performance. The result is confusion as to what is allowed and not allowed when method modifications are made by the testing organization.

This talk presents the key elements in achieving traceability including the process for method validation and estimating the uncertainty in order to ensure the comparability, identity and amount of the environmental chemical measurements used for making the decision.

References:

International Vocabulary of Basic and General Terms in Metrology. ISO, Geneva, 1993

Traceability in Chemical Measurement A guide to achieving comparable results in chemical measurement, Eurochem/Citac, 2003


ILAC Guidelines for the Competence of Reference Material Producers, ILAC G12, 2000

National Environmental Laboratory Accreditation Conference Standard, USEPA, 2003
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities  
By Dawn D. Thomas, ASQ CQM

The original charter of the National Environmental Laboratory Accreditation Conference (NELAC), when established in the early 1990’s, 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 laboratory standard and did not specifically address other accreditation components (e.g., proficiency testing (PT), on-site assessment, and accreditation process) or requirements for sampling specific environmental matrices. In 2003, NELAC divested itself of the environmental standards development process and the Institute for National Environmental Laboratory Accreditation (INELA), a consensus based standards development organization, was formed. Within this organization, the INELA Field Activities Committee (FAC) was established to continue the standards development work for an accreditation program designed specifically for field sampling and measurement organizations (FSMO).

Objective and Goals

The primary objective of the INELA FAC is “to develop and maintain consensus accreditation standards and guidance materials for organizations engaged in environmentally related field sampling and measurement activities, consistent with regulatory and industry-specific requirements”. Its long-range focus is to replace the 2002 NELAC Field Activities Standard (Chapter 7) with an INELA stand-alone, FSMO-specific accreditation standard(s) that meets the following goals:

- Encompasses broad scope and wide ranging applicability;
- Based on internationally recognized standards for competency (ISO/IEC 17025) and conformity assessment (ISO/IEC 17011);
- NOT prescriptive in nature, allowing for the development of FSMO-specific policies and procedures; and
- Effectively supported by sound guidance.
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities

By Dawn D. Thomas, ASQ CQM

Broad Scope and Applicability

If the INELA FAC is to meet its objective of establishing performance standards for those collecting samples and conducting on-site measurements for improved environmental data quality, then the standard must be wide-ranging in scope and applicability to support existing and future state/federal environmental regulations governing field sampling and measurement activities. To this end, a primary goal of the INELA Field Activities Committee is to develop an accreditation standard (or series of standards) that will apply to organizations performing field activities for a wide variety of sampling and measurement media such as air, biological, water, soil, waste, and radiological. Due to the nuances, specific to each media, a “one size fits all” approach to standards development is not appropriate. Accordingly, the FAC has engaged field sampling and measurement “media experts” to collaborate on the development of customized, media-specific FSMO accreditation standards. The development of custom field standards for water and air are the current focus of the committee.

ISO Foundation

It is the consensus viewpoint of the Field Activities Committee that the common denominator, or foundation, for the custom, media-specific INELA FSMO accreditation standard(s) must be ISO/IEC 17025, General Requirements for the Competence of Testing and Calibration Laboratories and ISO/IEC 17011 (soon to replace ISO/IEC Guide 58), Conformity Assessment—General Requirements for Accreditation Bodies Accrediting Conformity Assessment Bodies. Using this approach to standards development, the role of the INELA FAC will be to utilize its “media experts” to determine how to best apply these generic International Standards for a particular area of accreditation (e.g., field activities – water). The INELA FAC “application” of these International Standards, for each sampling and measurement media, will include, but will not be limited to, provisions for additional requirements, exclusion of specified ISO requirements due to applicability concerns, and clarifications and interpretations of various ISO requirements. Using ISO as the foundation for custom-built FSMO accreditation standards facilitates harmonization of individual field standards specific to each sampling and measurement media.

Non-Prescriptive Standards Development

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. Accordingly, the committee consensus was to take a practical and realistic first step towards improved environmental data quality by establishing an accreditation standard, based on internationally recognized standards, which are minimally prescriptive to provide a high degree of flexibility for the FSMO when implementing the standard requirements. Simply stated, applying this “less is better” approach, the FSMO will be able to craft policies and procedures, which meet the intent of the INELA standard, but are practical, functional and, most importantly, implementable. The INELA FAC believes that if the resulting field accreditation standards cannot be effectively implemented by all parties

March 11, 2005
Page 2 of 5
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities

By Dawn D. Thomas, ASQ CQM

affected, large and small, public and private, due to overly prescriptive requirements. Then we, as a committee, have not successfully completed our mission for improving data quality for better decisions.

Sound Guidance

To support the “less is better” approach to standards development and to facilitate successful implementation by all FSMO impacted by the standard, the development of appropriate implementation guidance tools is a key component for realizing an improved outcome – sound and defensible data quality for better decisions. This is the long-term focus of the INELA Field Activities Committee - to “show the way” by providing the necessary guidance and support for standards implementation. Several of the many benefits associated with this INELA service to the environmental community include:

- Acceleration of the FS MO “learning curve” associated with “something new”, keeping in mind that many FS MO have not been subject to quality system/accreditation program requirements, historically;
- Improved “buy-in” by minimizing the costs associated with implementation of a new and comprehensive accreditation standard; and
- Consistency of standards interpretation and implementation.

Accomplishments

These goals for standards development, as discussed in the previous sections, have evolved over a period of two (2) years as a result of the diligent work and “outside the box” thinking of the INELA FAC. The accomplishments, which follow in this section, have contributed greatly to the refocusing of the laboratory community (regulators and those regulated) on the importance of field sampling and measurement and its role, as the “front-end” portion of the environmental data generation process.

To facilitate the development of media-specific field standards, the committee has been very active in outreach activities to engage more stakeholders – the “media experts” - in the standards development process. The INELA FAC has grown from less then ten (10) members in 2003 to more than thirty (30) participating members today. The committee has also worked to achieve balance of membership, necessary for a consensus standards development organization, with representation from government and municipal agencies, engineering and environmental consulting firms, analytical laboratories and industry. Participation in national/regional conferences and collaboration with other organizations representing specific stakeholder groups will continue to be a focus for the INELA FAC. The committee’s success in developing sound field accreditation standards depends on the continuation of these outreach activities.

Consistent with committee direction to develop “applications” of the ISO/IEC 17025 and 17011 standards, a generic (not specific to any one media) application of the ISO/IEC 17025 standard has been completed and will be utilized by the “media experts” to guide the development of media-specific field accreditation standards. This generic application of ISO/IEC 17025 was

March 11, 2005
Page 3 of 5
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities

By Dawn D. Thomas, ASQ CQM

affirmed by the INELA membership in late 2004. Additionally, the groundwork, in the form of a consensus-based conceptual model, for the application of the ISO/IEC 17011 standard was completed and presented at the INELA Accreditation Forum in Charleston, South Carolina last summer. Building on these endeavors, workgroups have been established and are tasked with producing the first Working Draft Standards for a generic application of 17011 and a media-specific (water) application of 17025 by the summer of 2005.

A great deal has been accomplished but there is more work to do.

Next Steps

To achieve its on-going objective “to develop and maintain consensus accreditation standards and guidance materials for organizations engaged in environmentally related field sampling and measurement activities, consistent with regulatory and industry specific requirements”, the INELA Field Activities Committee must effectively meet certain challenges. They are:

- To know, engage and understand the needs of all stakeholders who will be, ultimately, impacted by the standard(s).
- To know, engage and understand the needs of all potential clients, those who will adopt and implement such a standard(s).
- Finding a consensus viewpoint to the question of what makes for good quality to achieve consistent application of the ISO/IEC 17025 and 17011 standards for harmonized individual media-specific field accreditation standards.

With its new approach to standards development, the INELA FAC also has an opportunity to help chart the future path of INELA, as a standards development organization. At the 2004 INELA Summer Forum in Charleston, South Carolina, the INELA Board of Directors expressed their desire for INELA membership to seriously consider a restructuring of the NELAC laboratory standard to better meet the needs of stakeholders, existing and potential clients, and to achieve the desire growth into other areas of accreditation. There are a number of proposals for this restructuring initiative currently being considered by the INELA Board.

One of the proposals being considered has been developed by the INELA FAC, which details an approach to standard restructuring, consistent with the approach being taken for the development of media-specific field accreditation standards. This proposal has been designed to:

- Align with the INELA Strategic Plan.
- Provide a flexible framework for the development of harmonized accreditation standards in new areas such as Homeland Security.
- Positively impact a wide range of stakeholders.
- Appeal to accrediting authorities, regulators, private sector groups interested in adopting and implementing uniform standards of accreditation.
- Assure the production of scientifically valid data that can be used with a high degree of confidence by the end user.

March 11, 2005
A Harmonized National Accreditation Standard: The Next Step for INELA Field Activities

By Dawn D. Thomas, ASQ CQM

The INELA Field Activities Committee is committed to the development of field accreditation standards using the approach detailed in this paper and strongly believes that this approach can be effectively used for the development of new INELA standards in other areas of accreditation as well. To meet the current challenges and to adequately address the complexities of the field sampling and measurement “world”, the committee must continue to focus its energies on thinking “outside the box”, encouraging and listening to new ideas, and creating an environment where these new ideas can flourish. Your participation in the FAC activities is vital for the production of data suitable for its intended use and may have an influence on the future path of INELA as a consensus standards development organization. All are encouraged to join INELA and to get involved! More information on the efforts of the INELA FAC may be found on the INELA web site (www.inela.org).

© Authored by Dawn D. Thomas, ASQ CQM, 2005. Thomas is a corporate Quality Assurance Manager for Professional Service Industries, Inc., a national engineering consulting firm, in Orlando, Florida and is certified by the American Society for Quality (ASQ) as a Quality Manager (CQM). She is the current Chairperson of the INELA Field Activities Committee and is a member of the INELA Board of Directors.
ABSTRACT

Traditional approaches to environmental laboratory subsampling usually result in inaccurate analytical measurement results. Correct subsampling that includes multiple increment sampling helps control sampling error. A material preparation and subsampling strategy that takes into account compositional and distribution heterogeneity of the sample matrix and environmental analytes can be developed to minimize analytical measurement uncertainty.

BIO

Bill Ingersoll is a Chemist with the Naval Sea Systems Command, Programs Field Office (SEA 04XQ/LABS) located in Charleston, South Carolina. Mr. Ingersoll has worked as a chemist in environmental sampling and analysis for 15 years. His work for NAVSEA includes technical and scientific assistance for Navy laboratory and engineering personnel, and environmental laboratory assessment to support the Navy IR QA program. Bill is a member of the DoD joint Environmental Data Quality Work Group (EDQW), Institute for National Environmental Laboratory Accreditation (INELA) and serves on the Proficiency Testing Board of the National Environmental laboratory Accreditation Conference (NELAC).

BACKGROUND

Scientifically valid environmental decisions require quality data. Data quality can be defined as the ability of data to provide information that meets the data-users requirements. Generation of quality data for environmental decision-makers and data-users is the goal of environmental laboratories. For laboratories to achieve quality data, the data must be accurate. Minimizing analytical measurement uncertainty and bias helps ensure that accurate data are generated in the environmental laboratory.

General particulate sampling theory developed by Pierre Gy attributes sampling error to:

- Large-scale errors (trends and cycles),
- Materialization errors\(^1\) (material preparation, delimitation, and extraction errors), and
- Small-scale errors (fundamental error, and grouping and segregation error).

Materialization error, and fundamental error and grouping and segregation error affect laboratory uncertainty and bias. Generally, the laboratory components of analytical measurement can be broken down into material preparation and subsampling, and chemical preparation and instrumental analysis. Material preparation and subsampling are frequently the overlooked components in the equation for determining and controlling laboratory analytical measurement uncertainty. Traditionally, resources are concentrated on more and more sophisticated instrumental techniques while subsampling is relegated to entry-level personnel with minimal training. Sophisticated instrumental analyses combined with incorrect subsampling

\(^1\) Both primary field sampling and secondary laboratory subsampling affect materialization error. However, the laboratory usually cannot control field-sampling effects on materialization error.
techniques results in inaccurate data. Correct subsampling requires as sophisticated a strategy as instrumental analysis to control analytical measurement uncertainty and bias. Choosing the correct subsampling approach minimizes uncertainty and bias and improves data quality.

Subsampling bias and uncertainty result from heterogeneity of the sampled material. Fluids such as gases and liquids are collections of large numbers of randomly distributed molecules. Single-phase aqueous samples therefore do not present a significant challenge to collecting representative samples. However, soils, sediments, and solid wastes are usually heterogeneous collections of compositionally and distributionally variable arrangements of particles. Heterogeneity (compositional and distributional) of soils makes representative sampling and subsampling a significant challenge. Compositional heterogeneity results when particles with different sizes, shapes, densities, and chemical properties have different environmental analyte concentrations. Distributional heterogeneity results when analytes tend to clump and stratify within the sample material.

SUBSAMPLING STRATEGIES

The strategy for selecting a laboratory subsample from a field sample requires an approach that ensures representativeness. Traditional subsampling techniques such as selecting a single 1-gram increment “off the top” of the sample container is usually non-representative. To achieve representative subsampling, every particle must have equal probability of selection. That includes the entire sample container subsampled from top to bottom. Laboratory techniques including drying, mixing, and grinding, and multiple increment subsampling can be used to ensure that representative subsamples are selected. Multiple increment subsampling is the technique where many small portions of the sample are selected from the entire sample material to make up the subsample. Materialization error in the laboratory can be controlled by correctly delimiting and extracting increments without cross-contamination or losses. The choice of the material preparation and subsampling techniques depends upon the sample matrix, the type of sample preparation and analysis performed, the environmental analyte(s), and the measurement quality objectives for a specific project. No technique or suite of techniques is correct for all matrices and analytes. For example, samples tested for volatiles cannot be dried, mixed or milled.

VOLATILES

For correct sampling of volatile organic compounds the sample must not be exposed to air or elevated temperature. Traditionally, the collection of solid matrices for volatile analyses resulted in significant negative bias from volatilization during the sampling processes. Research indicates that losses of as much as 3-orders of magnitude between replicates result from incorrect volatiles sampling.

Correct sampling requires minimizing exposure of the sampled material to ambient air or elevated temperature. Traditional sampling techniques disturbed the soil structure integrity. The material disturbance increases the surface area exposed to air resulting in volatilization, and the disturbance promotes degradation by oxidation and microbial activity of the volatile organic compounds. Method 5035 was developed to reduce VOC losses attributable to volatilization and degradation during traditional sample collection, handling, and preparation techniques. This approach provides a closed-system for collection in vials that minimizes disturbing soil structure. EnCore® study data demonstrates that sampling variability is negligible when field
cores are sealed in closed-system vials. Variability of analytical measurements for replicates decreased from 3-orders of magnitude to a relative standard deviation at the 95% confidence level (RSD$_{95\%}$) of ~ 20%. The 20% can be attributed to the instrumental analysis variability independent of matrix interference.

**SEMIVOLATILES**

For correct subsampling of semivolatile organic compounds the sample must be homogenized before subsampling. This can be accomplished by mixing the sample material before multiple increment sampling. Mixing breaks up grouping and segregation of the sample matrix and analytes, and disperse the analytes randomly throughout the sample prior to subsampling. Although exposing sample material to air during the subsampling process does not significantly volatilize semivolatile organic compounds (SVOCs), wet samples cannot be dried at elevated temperature (above ambient temperature). The problem of material preparation and subsampling of wet samples can be overcome by drying the sample with anhydrous sodium sulfate. Mixing anhydrous sodium sulfate with the sample until the material is free-flowing helps in homogenization.

In a study conducted by Analytics Environmental Laboratory LLC of New Hampshire, soil samples were subsampled for PCB testing. Aroclor 1260 concentrations for the different samples ranged from 500 ppb to 15,000 ppb. Without mixing the soil samples, the RSD$_{95\%}$ was 240%. However, when to samples were homogenized by hand mixing, the RSD$_{95\%}$ was reduced to 30%. The 30% can be attributed to the chemical preparation and instrumental analysis variability, and the subsampling contribution to analytical measurement uncertainty was negligible.

**SOLID PARTICLES**

For correct subsampling of solid particles the sample must be homogenized and particles size must be reduced before subsampling. The compositional heterogeneity increases with the increase in particle size. To decrease compositional (and distributional) heterogeneity particle size must be reduced. This can be accomplished by milling or grinding the sample. Particle size reduction minimizes fundamental error that is caused by compositional heterogeneity. The compositional heterogeneity increases with the increase in particle size. To decrease compositional (and distributional) heterogeneity particle size must be reduced or the analytical subsample size increased. Analyzing a larger subsample can also help minimize fundamental error. However, larger subsamples may not be practical because of matrix interferences affecting chemical preparation and instrumental analysis.

Metallic lead fragments and explosive residue are examples of solid environmental analytes that may range from dust size to gravel size particles. In a USACE-CRREL study for explosive residue subsampling, the analytical measurement variability was minimized by particle size reduction. When the soil sample was not ground prior to subsampling, the RSD$_{95\%}$ was 600% for TNT. However, when the sample was ground in a milling machine, the RSD$_{95\%}$ was reduced to 12%. The 12% can be attributed to the chemical preparation and instrumental analysis variability, and the subsampling contribution to analytical measurement uncertainty was negligible. Increasing the subsample mass from 2 grams to 50 grams (without particle size reduction) only reduced the RSD$_{95\%}$ to 300%.
Intrinsic Reliability — A Metric for Describing Confidence in Measurements

Molly Isbell, David L. Lewis
Signature Science LLC, 8329 North MoPac Expressway, Austin TX 78759
Primary Author’s E-Mail: misbell@signaturescience.com; Phone: 512-533-2020

ABSTRACT

A critical need for any environmental sampling program is to describe the reliability of measurement results. For traditional environmental sampling and monitoring programs where the focus is on quantitative measurements of chemicals in the environment, measurement reliability metrics (e.g., precision, quantitative accuracy, detection limits) are typically well established. However, due to a fundamental difference in objectives, these metrics are not always directly applicable in the context of monitoring for threat agents. In a program designed to detect threat agents in the environment, it is necessary to know the likelihood that a positive detection is a false alarm. The concept of Predictive Value addresses the need to address such questions and is widely accepted in the clinical testing context, where positive predictive value (PPV) describes the probability that a patient actually has a disease, given a positive test result. In the context of threat-agent detection, PPV describes the likelihood that an agent is present, given a positive test result.

Calculation of predictive value requires knowledge of false-positive and false-negative rates, which can be determined through positive and negative control samples and through proficiency tests and validation testing. However, predictive value also requires information about the a-priori likelihood of the threat agent in the environment, which is often very uncertain.

Predictive value equations can be expressed such that they are separable into one component that describes the a-priori likelihood that the target is present and one that describes the reliability of the measurement process. Because the two components can be separated, it is possible to compute a statistic (Intrinsic Reliability) based only on the reliability of the measurement process, which can be determined experimentally and does not depend on a-priori information. This Intrinsic Reliability statistic therefore describes the value of a reported detection in determining the likelihood that the threat agent is actually present.

I prefer to give an oral presentation.
Vanishing Zero Defects

Dr. John Long
GFS Chemicals, Inc 3041 Home Rd, Powell, OH 43065
ejlong@gfschemicals.com; phone 740-881-5501 x 144

ABSTRACT

Resourceful environmental monitoring has to be a consequence of realistic policy protocols that, in turn, are developed from sound scientific information. Beyond the conclusions that can be drawn from toxicological data, many other factors can play important roles in determining both advisory and legislative guidelines. These include uncertainty factors, which may give special consideration to test regimens, extrapolation of data from animal to human conditions, or accountability to certain subpopulations, for example. However, one particularly important factor has been changing with time and needs to be made a priority by the scientific community: the growing distance between the sensitivity of toxicological studies (typically parts per million of target substrate) and the thresholds of analytical instrumentation used to measure the substrate (frequently parts per trillion). This “detection limit creep” and the divergence of the data trails have made it increasingly difficult to relate some environmental conditions to an accurate (or unbiased) assessment of probable risk. The greater the gap between the respective data thresholds, the greater the opportunity for manipulation based on political or personal motivations, and subsequent abuse of scientific methods. The example of perchlorate in the environment is instructive: eminent toxicologists have gone on record indicating that exposure in the general U.S population to perchlorate at levels equivalent to 0.2 parts per million should be considered safe, while other voices have demanded that the public be protected to one part per billion. The EPA’s February, 2005 determination that 0.7 microgram per kg of body weight represents a safe dose for human ingestion of perchlorate. This presentation takes a deeper look at all the factors at work in the controversial and very political process that led to this decision.

I prefer to give an oral presentation.
Session 13

Advances in Preparation and Analysis of Organic Compounds
Pursuit of Practical Particle Size Reduction and Sub-sampling for the Environmental Testing Laboratory

Mark L. Bruce Ph.D.

Severn Trent Laboratories, Inc.
North Canton, OH
mbruce@stl-inc.com

Why Sub-sample?

• Impossible to put the entire test area or quantity through the measurement process
  – Field sub-sample
  – Analysis process sub-sample
  – Instrumental sub-sample
Why Sub-sample?

- Fractionate sample to assess transport pathway
  - Sieve for small particle content
    - air borne
    - Adhesion to skin
  - Phase separation
    - Non-aqueous phase liquids
    - Settled solids
  - Dissection

---

EPA Guidance Document

- *Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples.*
- EPA/600/R-03/027
- November 2003
- 134 pages
- Non-volatile analytes only
Representative Sub-sample

- Laboratory sub-sample
  - Tug-o-war match

statisticians  ------ analyst ----- waste, cost & labor minimizers

Representative Subsample

- How do we keep everybody happy?
- Particle size reduction
- Mixing
  - Smaller sample
    - Represents bigger sample
    - Better precision
    - Accuracy
      - same analytes
      - same concentrations
Precision Improvement

Rav High Metal Content Soil

- %RSD best with grinder, improved with chopper

The Ideal

- Place sample jar as received from the field into a magic homogenizer
- Run for a few minutes
- Then any 0.5 to 30 g aliquot accurately represents the whole
  - i.e. dig-a-spot technique works
Status Report

How To Do Particle Size Reduction?

- Form suitable to grind, crush or chop
  - Dry sample
    - Room temperature
    - Oven
  - Wet sample
    - Slurry grinding or chopping
  - Freeze sample
    - Dry ice
What does homogenization and sub-sampling mean?

- Stir and dig multiple spots
- Air dry, grind, stir & dig
- Sieve, cone & quarter, line & scoop
- Air dry, chop, sieve, shake, dig
Sieve, cone & quarter, line & scoop
Sieve, cone & quarter, line & scoop

Air dry, chop, sieve, shake, dig

- Large capacity air drying
- Approx. 500 1 kg samples
Air dry, chop, sieve, shake, dig

3 Cup Chopper

Sieve (1 mm)
Application to Organic Analytes

- Low vapor pressure organics
  - Explosives
  - PCBs
  - Air drying usually acceptable
- Semi-volatile organics
  - PAHs
  - Substituted phenols
  - Chlorinated aromatics
  - Amines
  - Phthalates

Accuracy Concerns

- SVOC recovery relative to LCS
  - general loss of low boiling compounds
  - large losses of specific compounds
Accuracy Concerns

- Lost analytes (negative bias)
  - Thermal degradation
    - heating due to friction
    - less stable analytes
      - hexachlorocyclopentadiene
      - organophosphorus pesticides
      - endrin & DDT
  - Volatilization losses
    - air drying
    - grind / chop process

How to Homogenize a Clay Mud Ball?

- Flashback to Supercritical Fluid Extraction
  - CO₂
  - Agilent (Hewlett Packard)
  - Dennis Gere
  - Mix CO₂ snow and wet sample in a blender
Mud Ball >> Mixable Powder

Dry Ice Chopping Results

- SVOC recovery relative to LCS
  - improved recovery of low boiling compounds
  - reduced recovery of high boiling compounds

% of LCS Recovery

Increasing retention time
“Magic Mill”

- Matrix Spike, single spot on wet clay
- 1.5 minutes homogenization time
- Temperature: 20°C >> ~40°C
  - friction
- Moderate air exposure
  - similar to chopper

“Magic Mill SVOC Results”

- Average %RSD: 16%
  - Good precision for dig-a-spot sub-sampling
- Analyte recovery
  - Low boiling analytes
    - > air dried
    - < dry ice chopped
  - High boiling analytes
    - Low recovery like dry ice chopped
- Contamination
  - Benzoic acid and bis-2-ethyl hexyl phthalate
    - Plastic parts in chopper and magic mill
“Magic Mill Results”

- SVOC recovery relative to LCS

Conclusions - Pursuit of Practical

- Practical now
  - Air drying of samples up to 1 kg
  - Sieving dried samples up to 1 kg for metals, PCBs
  - Chopping dried samples up to 200 g for metals, PCBs
Conclusions - Pursuit of Practical

• Potentially practical
  – Chopping dried samples up to 1 kg for metals, PCBs
  – Grinding dried samples up to 1 kg for metals, PCBs
  – Sub-sampling by cone & quarter, line & scoop

Conclusions - Pursuit of Practical

• Still in pursuit
  – Chopping, grinding, milling of samples with semi-volatile analytes

• Holy Grail
  – Universal homogenization technique in the original sample container
Parting Thought

“It takes work to bring order to a cloud of dust. Applications are being accepted now.”

Voyager 2 false color image of Saturn
August 1981.

Sandstorm in China, April 2001, ESA

Acknowledgments

Frank Calovini, Becki Strait, Tom Hula,
Darren Miller, Frank Gallegos,
Pat O’Meara, Karen Counts,
Larry Williams, Al DiPofi,
Katy Tucker, John Donat

Samir Mansy, Paul Zorko,
John Jent

STL
An Innovative Approach to Automatic Solvent Drying and Concentration of Environmental Extracts

Robert Johnson  
Horizon Technology, Inc., 45 Northwestern Drive, Salem, NH 03079  
603-893-3663  
rsjohnson@horizontechinc.com

ABSTRACT

Two steps that have a major impact on the recoveries for both liquid-liquid (LLE) and solid phase (SPE) extraction techniques are drying and concentrating the extract prior to GC analysis. Residual water must be removed to prevent the extract from separating into multiple phases and back extraction of water soluble analytes. The extract must also be concentrated to improve detection limits by selectively evaporating the extraction solvent, without inducing loss of the more volatile components. Drying extracts has historically been accomplished manually with sodium sulfate. Currently, properly optimized hydrophobic membranes are available that can provide automated removal of residual water. Further, this step can be incorporated into equipment that selectively evaporates the extraction solvent to completely automate sample drying and concentration for GC analysis. The use of such equipment for environmental applications will be discussed. Emphasis will be placed on analyte recovery, carryover, and sample throughput.
Using Headspace Trapping Technology for Measuring Environmental Volatile Organic Compounds (VOCs) by Method EPA8260B

H.Grecesk*, A.Tipler, and L. Marotta
PerkinElmer LAS,
710 Bridgeport Avenue
Shelton, CT 06484
Heidi.Griffith@perkinelmer.com
* presenting author

ABSTRACT

Environmental methods, such as 8260B have traditionally been complex and time-consuming to perform. New regulations often add target analytes and lower the concentration levels of interest. In addition, productivity pressures force laboratories to look for more efficient ways to generate quality data. Therefore, successful environmental labs have moved to become automated, fast, and precise.

A large number of EPA methods have required a purge and trap methodology to extract volatile compounds from environmental matrices. Most labs find purge and trap instruments difficult to use, and high in maintenance. However, because of the trace detection levels required in EPA methods it has been difficult to find an alternative extraction method to this system, until now.

New headspace trap technology gives operators the benefits of traditional headspace and now adds a trap option to meet the needs of lower detection 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 system uses a unique dry purge technology to remove the water vapor and uses overlapping thermostating, to produce maximum throughput. Using heating instead of purging to extract the volatile components makes the gas chromatographic run time the time limiting factor, rather than the introduction system.

EPA 8260B results will be presented using the headspace trap equipment connected to a GC/MS. Instrument calibration, repeatability, linearity, response factors, and minimum detection limits will be demonstrated. Fuel oxygenates analysis with the trap system will also be shown. As well as, other results using a salting technique to reach low ppb (parts per billion) detection limits for tough compounds.
How to Improve Detection Limits, Reduce Maintenance Time and Minimize Breakdown for Pesticide Analysis and Other EPA Method 8270 Analytes using Enhanced Large Volume Injection

Lee Marotta*, Andy Tipler, and Heidi Griffith
PerkinElmer LAS
710 Bridgeport Avenue
Shelton, CT 06484
203-402-1878
lee.marotta@perkinelmer.com
* presenting author

ABSTRACT

The ability to improve detection limits in environmental analyses is quite advantageous. There are several techniques employed to optimize the analysis of pesticides with Mass Spectrometry (MS) and/or Electron Capture (ECD) detection.

To attain our goals, the parameters employed are Enhanced Large Volume Injection (injector isolation and backflush modes) and simultaneous Full Scan and Single Ion Monitoring.

With Enhanced Large Volume Injection, the analyst has the ability to inject large volumes of sample into the Gas Chromatograph. During the solvent purge time, the injector is completely isolated from the analytical column thereby preventing solvent from reaching the column and detectors. This enables the use of less sample and less extraction solvent while maintaining and exceeding the necessary detection limits.

In addition, isolating the injector, allows for the use of chlorinated solvents with Electron Capture detection. Isolating the injector after the injection has been made, enables the baking and maintaining of the injector port during the analysis.

With a program injector, the analytes of interest (in this case pesticides), experience controlled evaporation minimizing thermal breakdown inherent in classical flash injections.

Two advantages will be discussed -- the ability to increase sensitivity at least 25x, and the ability to enhance integration improving precision.
Improved Sensitivity and Analysis Time for Semivolatile Organic Compounds Using GC-TOFMS: Can this Analysis really be Performed in less than 10-Minutes?

Frank L. Dorman*1, Jack W. Cochran2, Gary B. Stidsen1, Chris M. English1, and Michael S. Wittrig1
1 Restek Corporation
110 Benner Circle
Bellefonte, PA 16823

2 LECO Corporation
815 Pilot Rd. Suite C
Las Vegas, NV 89119.
* presenting author

ABSTRACT

The analysis of the semivolatile organic compounds, like those found in USEPA method 8270D, places significant demands on the gas chromatographic column and analytical instrument. Concentrations of target and non-target components may range from low nanograms to milligrams, and the target compound list includes reactive acid and base compounds. Additionally, laboratories constantly try to improve detection limits and analysis time in an effort to differentiate their services while maintaining high sample throughput. In order to significantly improve upon the current state-of-the-art it is necessary to optimize the dimensions of the GC column, and also investigate MS systems that have the ability to accurately characterize the narrow peaks that are obtained in using more rapid GC separations.

This presentation will demonstrate a method improvement that addresses the above concerns. First a split injection is utilized to decrease the amount of material injected onto the column. Second, a narrow i.d. and short length GC column is used to achieve a faster run time, under more efficient separation conditions. Finally, TOFMS is used to achieve accurate peak characterization, over a wider range of calibration standard concentrations. Results of this method will be discussed and compared to the data obtained from a commercial laboratory for a series of sample extracts analyzed by conventional methodology.
Managing Matrix Interferences in Pesticide Analysis with GC-TOFMS and GCxGC-TOFMS

Jack Cochran*
LECO Corporation
815 Pilot Road, Suite C
Las Vegas NV 89119
702-614-1143 x230
jack_cochran@leco.com

Frank Dorman
Restek Corporation
110 Benner Circle
Bellefonte, PA 16823
* presenting author

ABSTRACT

Often the main challenges in the analysis of pesticides are to qualitatively and quantitatively determine a pesticide in the presence of sometimes-overwhelming matrix components. Numerous methods are employed to deal with matrix interferences, including off-line cleanup approaches such as solid phase extraction, and/or selected ion recording (SIR) when performing gas chromatography-mass spectrometry (GC-MS). SIR, while valuable for excluding matrix and increasing sensitivity, comes at the expense of a loss of information (versus full mass range acquisition), and may not be that helpful for avoiding interference for pesticides that have mainly low m/z ions in their mass spectra.

Time-of-flight mass spectrometry (TOFMS) offers benefits for pesticide analysis by GC that quadrupole MS systems do not have. Using TOFMS, a full mass spectrum is acquired, with low pg detection of many pesticides. Acquisition speed (up to hundreds of spectra/sec) and spectral continuity (due to the almost instantaneous mass analysis) permit automated peak find and spectral deconvolution algorithms to be included in the data processing software, enhancing pesticide location in complex samples.

A relatively new way to solve separation of matrix components and pesticides is to use comprehensive two-dimensional GC (GCxGC). GCxGC is a way to increase peak capacity by applying two independent separations to a sample in one analysis.

This paper will compare results for the analysis of pesticides in complex matrices using GC-TOFMS and GCxGC-TOFMS.