



**NATIONAL
ENVIRONMENTAL
MONITORING
CONFERENCE**

2008 PROCEEDINGS

**Section 2:
Analytical Capability Needs
of the Future
Emerging Technologies
International Issues**

**Washington DC
August 10 – 16, 2008**



ELAB



NEMC

NEMC 2008 SYMPOSIUM SPONSORS



NEMC 2008 PROGRAM COMMITTEE

CONFERENCE CHAIR

Lara Autry, USEPA Office of the Science Advisor

PROGRAM CHAIR

Earl Hansen, PhD., Independent Laboratories Institute

CONFERENCE ORGANIZER

Jerry Parr, The NELAC Institute

BOARD OF TRUSTEES

Robert Benz, NSI Solutions

H. M. (Skip) Kingston, PhD., Duquesne University

Matthew Sica, Maine Center for Disease Control and Prevention

David Speis, Accutest Laboratories

Jan Young, USEPA Office of Solid Waste

SESSION CHAIRS

Lara Autry, USEPA Office of Science Advisor

Robert Benz, NSI Solutions

Richard Burrows, PhD., TestAmerica

Charles Carter, PhD., TestAmerica

Nancie Copeland, Environmental Express

David Friedman, Friedman Consulting

Diane Gregg, USEPA Region 6

Zoe Grosser, PhD., PerkinElmer

Earl Hansen, PhD., Independent Laboratories Institute

H. M. (Skip) Kingston, PhD., Duquesne University

Douglas Later, PhD., Torion Technology

Gonzalo Manchego, Duquesne University

Particia Mclsaac, TestAmerica

Marlene Moore, Advanced Systems

Stuart Nagourney, NJ Department of Environmental Protection

Nick Nigro, ECCS Nationwide Mobile Laboratories

Jerry Parr, Catalyst Information Resources

Joe Romano, Waters Corporation

Charles Sellers, USEPA Office of Solid Waste

David Speis, Accutest Laboratories

Shannon Sturgeon, USEPA Office of Solid Waste

Gary Ward, PhD., Columbia Analytical Services

Wayne Whipple, USEPA Region 5

Robert Wyeth, Columbia Analytical Services

Shen-yi Yang, USEPA Office of Solid Waste

NEMC 2008 CONFERENCE HIGHLIGHTS

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

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

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

Highlights of the week included the following keynote speakers:

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

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE PROCEEDINGS 2008

SECTION 2 TABLE OF CONTENTS

ANALYTICAL CAPABILITY NEEDS OF THE FUTURE

- | | | |
|---|--|----|
| 1 | Microbial Detection Methods for Drinking Water Regulations - Parshionikar
<i>Presentation</i> | 2 |
| 2 | The EPA's Endocrine Disruptor Screening Program (EDSP) – Timm
<i>Presentation</i> | 15 |

EMERGING TECHNOLOGIES

- | | | |
|---|---|----------|
| 3 | Automated BOD -- Moore
<i>Abstract/Paper</i>
<i>Presentation</i> | 28
35 |
| 4 | A Universal Wastewater QC Standard: A Different Approach to LCS Materials in the Wet Chemistry Lab -- Hammersla
<i>Abstract/Paper</i>
<i>Presentation</i> | 45
46 |
| 5 | Direct Analysis of High TDS Environmental Samples by ICP-MS – Wilbur and Proper
<i>Abstract/Paper</i>
<i>Presentation</i> | 51
60 |
| 6 | Portable Toroidal Ion Trap Mass Spectrometry: Taking the Instrument to the Sample - Bowerbank
<i>Abstract/Paper</i>
<i>Presentation</i> | 72
73 |
| 7 | Improving Data Quality with Automated Data Review – Fitzpatrick
<i>Abstract/Paper</i> | 89 |

INTERNATIONAL ISSUES

- | | | |
|----|--|------------|
| 8 | A Look at the Environmental Situation in China and South East Asia – Grosser and Friedman
<i>Abstract/Paper</i> | 98 |
| 9 | Challenges of Global Monitoring Programs - Eaton
<i>Abstract/Paper</i>
<i>Presentation</i> | 109
114 |
| 10 | Metal Speciation and Drug Residue Identification in Foods – A Global Perspective on Food Safety Testing – Wood
<i>Abstract/Paper</i> | 127 |
| 11 | Meeting Drinking Trace Metal Requirements in the EU and USA. Can They Be Achieved Using ICP-AES? – Brenner
<i>Abstract/Paper</i>
<i>Presentation</i> | 128
129 |

AUTHOR INDEX

2008 NEMC Proceedings

ANALYTICAL CAPABILITY NEEDS OF THE FUTURE

Microbial Detection Methods for Drinking Water Regulations

Environmental Measurement Symposium
Washington, DC
August 10-16, 2008

Sandhya Parshionkar, Ph.D.
Technical Support Center,
Office of Ground Water and Drinking Water
U.S. Environmental Protection Agency



Overview



- Office of water - Drivers and statutory requirements of regulations
- Drinking water methods
- EPA method approval process
- Method validation
- FEM guidance document on microbiology method validation
- Challenges in microbiology method development
- Future needs
- Future technologies

Office of Water Drivers



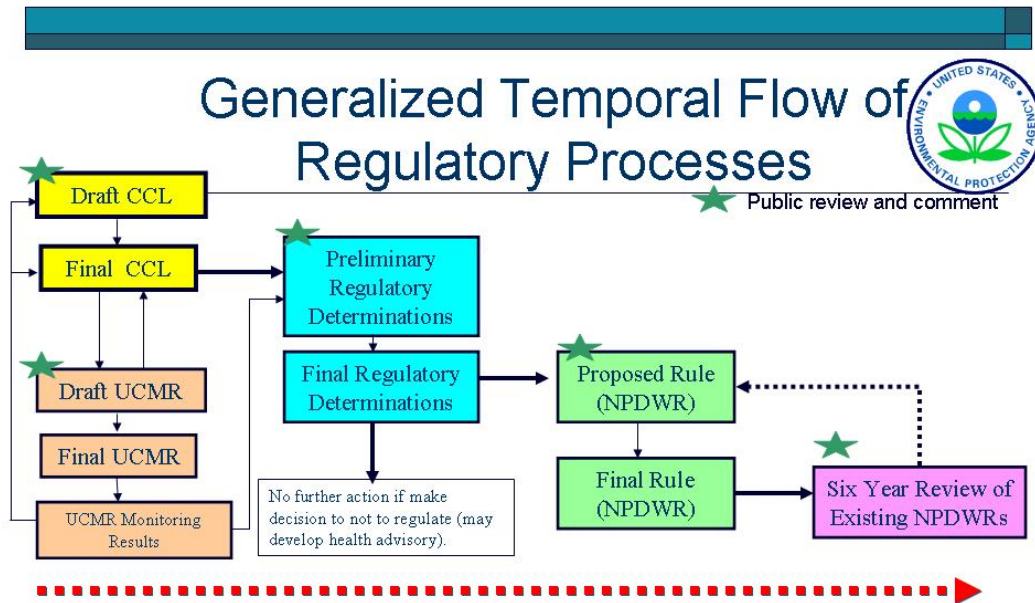
- Safe Drinking Water Act
 - EPA sets standards for drinking water quality
 - Total Coliform Rule (TCR)
 - Surface Water Treatment Rule (SWTR)
 - Long Term 2 Enhanced SWTR (LT2ESWTR)
 - Ground Water Rule (GWR)
 - Unregulated Contaminant Monitoring Rule (UCMR)

- Clean Water Act
 - Surface water quality protection

Statutory Requirements for Drinking Water Regulatory Processes



- 1) **Contaminant Candidate List (CCL)** –Develop and publish the list of contaminants known or anticipated to occur in drinking water - every 5 years.
 - 2) **Unregulated Contaminant Monitoring** (i.e., UCMR) –Establish criteria to monitor unregulated contaminants - every 5 years.
 - 3) **CCL Regulatory Determinations** – Decide whether to regulate contaminants with a national primary drinking water regulation (NPDWR)
-
- 1) **Regulation Development** - If EPA decides to regulate a contaminant, propose and finalize the Maximum Contaminant Level Goal (MCLG) and the NPDWR.
 - 2) **Six Year Review** – Once a contaminant is regulated, review and, if appropriate, revise the NPDWR every six years.



At each stage, need confidence in the type of supporting data used.

What is a method?

- Procedure used to analyze a sample to determine the identity and concentration of a specific sample component or analyte.
- Includes information on the
 - collection
 - Transport
 - storage
 - define procedures to concentrate, separate, identify and quantify components contained in samples
- Specifies quality control criteria
- Designates how to report the results of the analyses

Drinking water methods



- The agency uses methods developed by
 - EPA
 - Other government agencies
 - Universities
 - Consensus methods organizations
 - Industry

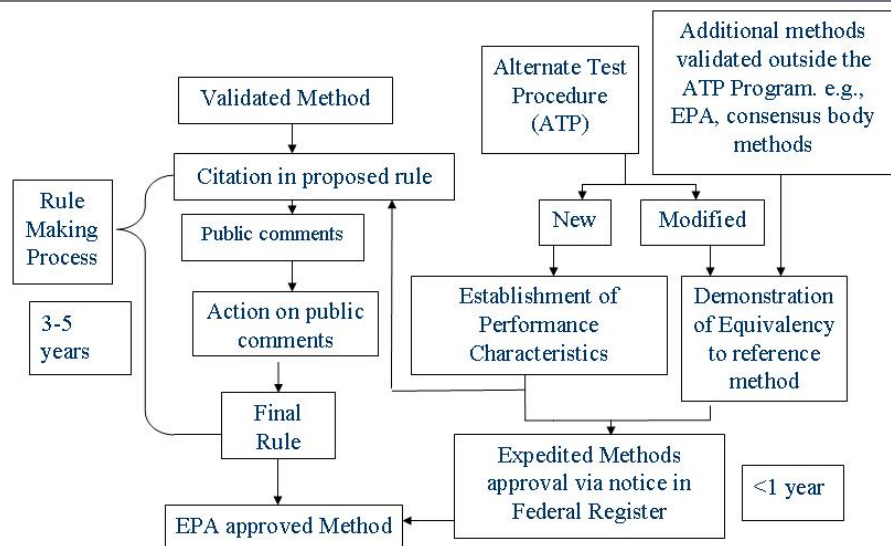
- Only EPA approved methods used for compliance monitoring

Examples of Methods used



- Rules
 - Total Coliform Rule, 1604
 - Long Term 2 Surface Water Treatment Rule, 1622/23
 - Ground Water Rule 1601, 1602
 - Unregulated Contaminant Monitoring Rule, 1605

EPA Methods Approval Process



Use of Other Methods



Methods that are published in peer reviewed journals can:

- Fill in data gaps regarding microbes
 - Occurrence in source and drinking water
 - Outbreak studies
 - Dose response studies
 - Health Effect Studies
 - Treatment criteria
 - Source tracking

- Help in calling attention to certain microbes
 - CCL (Candidate Contaminant List)
 - Rule revisions
 - Advisories

Method Validation



- A process that demonstrates the suitability of an analytical method for its intended purpose.

Agency Wide Method Validation Guidelines



- EPA Science and Policy Council established Forum on Environmental Measurements (FEM)
- FEM: A standing committee of senior managers addressing measurement and methods issues with multi-program impact
- Established Method Validation teams to develop agency wide policy to ensure validity of methods prior to their publication for general use
- Microbiological Methods validation team
 - Workgroup members
 - ORD
 - OW
 - OPPS
 - Regions

Steps in Validation



- A. Method Selection
- B. Method Optimization
- C. Development of method performance attributes
 - Specificity, sensitivity, precision, accuracy, bias, limit of detection etc.
- D. Writing the method
- E. Collaborative studies
 - Participating labs
 - Test materials
 - Development of a study plan
 - Reporting of results

A. Method Selection



- Criteria:
 - Is based on sound underlying scientific principles
 - Is applicable to routine analysis of samples
 - Can detect analyte in the concentration range of interest
 - Has sufficient specificity and sensitivity for intended use
 - Can meet specific method performance criteria
 - Has adequate QA/QC controls
 - Can be conducted at a reasonable costs
 - Addresses the level of expertise required
 - Addresses biosafety concerns

B. Method Optimization



- Identification of specific factors that can introduce variability
 - procedures, environmental conditions and reagents etc.

- Iterative testing of modifications that minimize this variability

- Will minimize problems during inter-laboratory validation

C. Development of Method Performance Characteristics



- Provides baseline numerical and descriptive specifications of the method's performance within the lab performing the tests.
 - Specificity, sensitivity, precision, repeatability, reproducibility, accuracy and bias etc.

D. Writing of the Method



- Scope and application
- Summary of method
- Equipment/Reagents
- Sample
 - Collection, preservation and storage
- Quality control
- Calibration and standardization
- Procedure
- Data analysis and calculations
- Method performance
- Safety, pollution prevention and waste management

E. Collaborative Studies



- Performed with the objective of evaluating or improving laboratory performance of the method
 - Results compared between labs or with assigned reference values
 - Assessment of the robustness of the method and readiness for widespread use
 - Provides specifications for methods performance attributes

- May have to be repeated if corrections are to be applied to the method

E. a) Participating Laboratories



- **Number of laboratories**
 - Based on statistical theory for predicting confidence intervals for parameters being tested
 - may have to use subjective judgment
 - Complexity of the method
 - Resources available
 - Balance between sound data and resource management
 - Based on tiered approach
 - 3-6 labs can be used for single matrix – multiple lab method
- **Selection of laboratories**
 - Not desirable to restrict to labs with extensive experience

E. b) Development of Study Plan



- **Study objective**
- **Study management and implementation**
- **Data reporting requirements**
- **How accuracy and completeness will be evaluated**
- **Will have to be customized as per the method**

E. c) Reporting of Results



- Results should be available for scientific peer review
 - Identify participating laboratories
 - Describe all test materials used
 - Discussion of the numerical and descriptive specifications for the performance attributes

E. d) Testing Materials



- Defined as specific analyte (microbe)/matrix/concentration combinations to which method performance parameters apply
- Should be representative of the range of matrices intended for analysis by the method
- Should originate from materials in which the analyte is distributed homogeneously.
 - Certified reference material
 - Analysis of replicate samples
 - Use of spiked materials

The FEM Microbiology Methods Validation Workgroup



- Sandhya Parshionikar

- Rich Haugland
- Margo Hunt
- Ann Grimm
- Michele Cottrill
- Andy Lincoff

- Orin Shanks
- Fred Genthner
- Stephanie Harris
- Stacy Pfaller
- Christina Sargent,
Versar

Challenges in Method Development



- Low concentrations of pathogens
 - sensitivity
- Large volumes of water needs to be tested
 - Matrix interference
- Need different processes for isolation of different classes of pathogens
- Culture methods slow, not suitable for all strains
- Molecular methods (Polymerase Chain Reaction)
 - no information on viability
 - Standardization of PCR methods
- Pathogen dose response

Future Needs



- Online monitoring/Rapid results
 - Perturbations in water quality
 - Outbreak analysis
 - Viability/infectivity
 - Quantitative
 - Genotyping/Strain identification
 - Sensitivity
- High Throughput detection
- Universal detection of all classes of pathogens
- Miniaturization of technology
 - Use in field
- Genomics/Proteomics
 - Signature of virulence

Future Technologies



- Microarrays
 - Multiple organisms/High throughput
 - Gene expression profiles
- Microfluidics
 - Concentration and separation of live bacteria
- Biosensors
 - Cantilevers



The EPA's Endocrine Disruptor Screening Program (EDSP)



National Environmental Monitoring Conference
August 13, 2008

Gary Timm
Office of Science Coordination and Policy/OPPTS
U. S. Environmental Protection Agency

1



Overview



- Statutory background and EDSTAC's recommendations
- Assay development and validation
- Selection of the first group of test chemicals
- Implementation policies and procedures
- Next steps

2



EPA's Statutory Authority



- Federal Food, Drug, and Cosmetic Act (FFDCA)
 - Requires EPA to:
 - *Develop a screening program using validated assays to identify pesticides that may have estrogenic effects in humans*
 - Authorizes EPA to include:
 - *Other endocrine effects, as designated by the EPA Administrator*
 - *Other non-pesticide chemicals that:*
 - *Have "an effect cumulative to that of a pesticide," and*
 - *To which a substantial human population may be exposed*
- Safe Drinking Water Act (SDWA) Amendments
 - Allow EPA to require testing of chemical substances found in sources of drinking water, if a substantial human population may be exposed

3



Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC)



- Chartered Oct 16, 1996
(www.epa.gov/scipoly/oscpendo)
- 39 members representing broad expertise and constituencies
- Recommendations proposed in 1998:
 - Estrogen, androgen and thyroid
 - Human and ecological effects
 - Broad universe of chemicals
 - Two-tiered approach to screening

4



Two-Tiered Approach



- Tier 1
 - In vitro and in vivo screens
 - Detect potential to interact with endocrine system
- Tier 2
 - Multi-generation studies covering a broad range of taxa
 - Provide data for hazard assessment

5



EDSTAC Criteria for Tier 1 Screens



- **Detect all known modes of action for the endocrine endpoints of concern**
 - Simple mechanistic screens do not exist for all modes of action, therefore it is necessary to include more complex multi-modal assays in Tier 1
- **Include sufficient diversity among endpoints, permitting weight-of-evidence conclusions**
 - Multiple endpoints in *in vivo* assays
 - Complementary endpoints across assays

6



EDSTAC Criteria for Screens



- Maximize sensitivity to minimize false negatives
 - *In vitro* mechanistic screens are highly sensitive
 - *In vivo* apical screens are necessary to encompass all known MOA and take metabolic activation into account
- Include a sufficient range of taxonomic groups to represent differences in endocrine system and metabolism
 - Fish included because fish and mammals differ in some hormones and metabolism

7



Tier 1 Assays Recommended by EDSTAC



- Primary recommendation:
 - Steroidogenesis (in vitro)
 - Estrogen / Androgen receptor binding and/or transcriptional activation assays (in vitro)
 - Uterotrophic
 - Hershberger
 - Pubertal female assay
 - Amphibian metamorphosis assay
 - Fish screen
- Potential alternative assays to validate:
 - Aromatase (in vitro)
 - Pubertal male assay
 - 14-Day adult male

8

EDSTAC Recommended Tier 2 Tests

Tier 2 testing is to provide a more definitive approach that will include a broad range of taxa exposed through various routes & during sensitive life-stages, so that the adverse consequences related to EAT hormonal function can be characterized with greater specificity.

Assays Recommended by EDSTAC
Mammalian 2-generation
Avian reproduction
Amphibian Growth/Reproduction
Fish lifecycle
Mysid lifecycle



Implementation of the EDSP



Priority Setting

Procedures

Assay Validation

- **Priority Setting**
 - Selecting chemicals to be screened/tested
- **Procedures**
 - Developing policy & procedures to require screening/testing of chemicals
- **Assay Validation**
 - Development & validation of assays for screening (Tier 1) & testing (Tier 2) chemicals



Priority Setting

Chemical Selection and Priority Setting



Selection of Initial List of 50-100 Chemicals for Screening

- **Methodology Described in FR Notice Issued Sept. 27, 2005**
- **Selection to be Based on Potential Human Exposure**
- **Pesticide Actives and HPVs / Pesticide Inerts**
 - 4 pathways for PAIs (food, water, residential, occupational)*
 - 4 pathways for HPV / inerts (human and eco biomonitoring, water, air)*
- **Contractor Support to Analyze Data Bases**

11



Priority Setting

Chemical Selection and Priority Setting



Preliminary Contractor Analysis

- **PAIs**
 - *approximately 1,100 total*
 - *>600 on one or more pathway lists*
 - *~80 on 3 or 4 pathway lists*
- **HPV / Inerts**
 - *approximately 650 HPV / Pesticide Inerts*
 - *<100 on one or more pathway lists*
 - *~15 on 3 or 4 pathway lists*

12



Assay Validation

Validation



- **Required** by ICCVAM Authorization Act of 2000 & by FFDCA Sec. 408p
- **Recommended** by EDSTAC
- **Endorsed** by Organisation for Economic Cooperation and Development (OECD)
- **Validation** is an assessment of the *reliability & relevance* of a test method for a particular purpose.
 - **Relevance**-- The extent to which a test method will correctly predict or measure the biological effect of interest.
 - **Reliability**-- The extent to which a test can be performed reproducibly within and among laboratories over time.

13



Assay Validation

Validation Principles OECD and ICCVAM



1. **Scientific & regulatory rationale**
2. **Relationship of endpoints to biological effect or toxicity**
3. **Formal detailed protocol**
4. **Assessment of variability**
5. **Assessment of performance with reference chemicals**
6. **Describe limitations of the assay**
7. **Data quality/use of GLPs**
8. **Availability of data & independent scientific peer review**

14



Assay Validation

The Validation Process



- **Stage 1 – Test Development**
 - Scientific literature review & preparation of Detailed Review Paper (DRP)
- **Stage 2 - Prevalidation**
 - Demonstrate relevance
 - Development of standard optimized protocol
 - Determine readiness for inter-laboratory testing
- **Stage 3 – Inter-laboratory Validation**
 - Demonstrate reliability across multiple laboratories
- **Stage 4 – Peer Review**
 - Independent scientific review of validation effort
 - Integrated Summary Reports*
 - Peer Review Record*
 - EPA response to peer review comments*
- **Stage 5 - Regulatory Acceptance**
 - Proposed Tier 1 battery & adoption

*Included in SAP review package to support discussion of proposed Tier 1 battery

15



SAP Meeting to Review EPA's Proposed Tier 1 Battery



- March 25-28, 2008
- Decision and Supporting Materials were placed on SAP website: www.epa.gov/scipoly/sap
- Integrated Summary Reports
 - Peer Review Reports
 - Response to peer reviewer's comments
 - Battery Technical Support Document
- Additional information is available on the Endocrine Disruptor Screening Program website: www.epa.gov/endo

16

Proposed Tier 1 Assays

<i>In vitro</i>
¹ Estrogen receptor (ER) binding – rat uterus
Estrogen receptor α (hER α) transcriptional activation - Human cell line (HeLa-9903)
Androgen receptor (AR) binding – rat prostate
^{1,2} Steroidogenesis – Human cell line (H295R)
² Aromatase – Human recombinant
<i>In vivo</i>
Uterotrophic (rat)
Hershberger (rat)
Pubertal female (rat)
Pubertal male (rat)
² Amphibian metamorphosis (frog)
² Fish short-term reproduction



SAP Conclusions



- The proposed set of Tier 1 assays are appropriate to begin screening for disruptors of the EAT axes. However, several assays do not represent the current state of the science, or the proposed screens do not fully address major modes of action and should be updated and extended as soon as possible. The EPA should consider this set of assays to be a work in progress. The Panel expects that the EPA will continue to develop, refine, and review the battery. New endocrine disruptors and new mechanisms of action are likely to be revealed in the future requiring that the current Tier 1 assays be modified and new ones developed and validated.



SAP Recommendations



1. **Develop assays to detect ER β**
2. **Consider dropping estrus cyclicity as an endpoint**
3. **Validate assays to detect estrogen antagonism**
4. **Validate recombinant AR binding assay**
5. **Include effects on perinatal exposure in T-1 or T-2**
6. **Standardize hormone measures**
7. **Test more chemicals, especially negatives for the pubertal assays**
8. **Add some *in vitro* thyroid assays to the battery**
9. **Include measures of thyroid hormone action in the pubertal assays**
10. **Develop new assays to cover new modes of action and different hormone systems**

19



Next Implementation Steps for Initial List



- Publish:
 - **Policy and Procedures**
 - **Final Chemical List**
 - **Battery Notice**
- OMB approves Information Collection Request
- EPA issues Test Orders
- Order recipients respond to orders
- EPA reviews responses and submitted data
 - **Functionally equivalent information**
 - **Scientifically relevant information**

20



Next Implementation Steps for Initial List (2)



- EPA notifies order recipients
- Testing and data submission
- EPA reviews data and makes Tier 2 decision
- EPA conducts review of the performance of the battery on the first list using the FIFRA SAP

21



Assay Validation

Tier 2 Assays Complete in 2010



- Mammalian 2-generation – Complete
 - **Extended one-generation test** is being developed to replace most applications of the 2-gen mammalian test.
- Avian 2-generation
- Amphibian Growth/Reproduction
- Fish 2-generation
- Mysid 2-generation

22

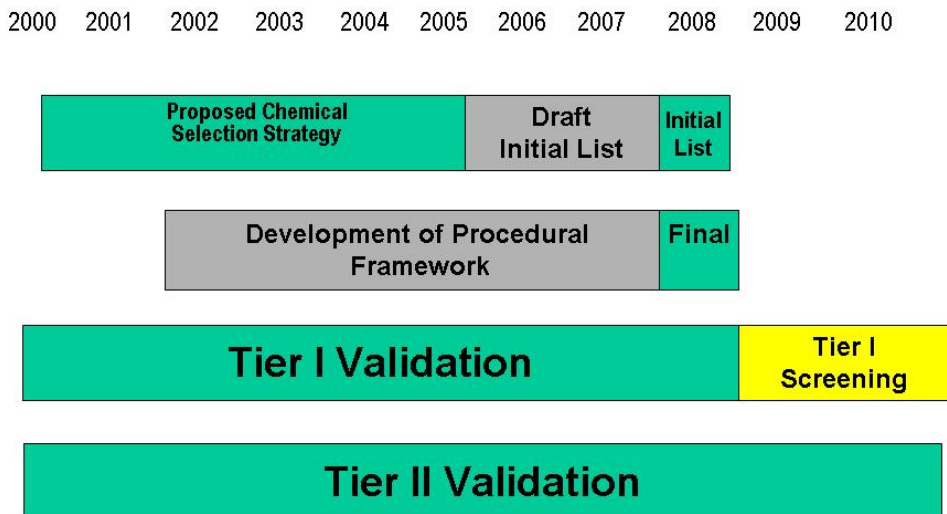


Beyond the First List

- Pesticide actives will be screened in the registration review process—a 15 year review cycle.
- Non-pesticidal chemicals and pesticidal inerts will be included on future lists
- Drinking water contaminants likely to be heavily represented on next list
- Next list will likely use exposure plus other factors for listing
 - ToxCast or other predictive methodology
 - In vitro data
- Next list will accept nominations from the public

23

EDSP Timeline



24

2008 NEMC Proceedings

EMERGING TECHNOLOGIES

Automated BOD

Stephen Moore
ManSci Inc.
600 Main St.
Tonawanda, NY 14150
866-763-2122
smoore@mansci.com

ABSTRACT

The measurement of BOD is the basic means of testing the degree of water pollution. It measures the amount of oxygen that bacteria (from sewage) take from the water to oxidize organic material. The BOD is measured on the influent and effluent of a water treatment plant to assess the effectiveness of the water treatment.

Due to budget constraints many small laboratories currently test BOD using a manual method that is both time and labor intensive. The new automated BOD method was developed to provide a time and cost saving alternative using a fully automated system. Testing of the system provided accurate and precise measurements of the dissolved oxygen of the samples in a timely fashion.

The method to be discussed is a completely automated BOD analysis system as outlined by Standard Method 5210 B 21st Edition. It will add dilution water to two thirds full. Then add seed and nitrification inhibitor as needed. The software will only calculate BOD results from samples that pass the criteria of a depletion 2.0mg/l and a final D.O. of 1mg/l. BODs and CBODs can be combined in the same run, and the appropriate seed correction factor for BOD or CBOD be used, without the need of performing two separate runs.

INTRODUCTION

The Biochemical Oxygen Demand test measures the ability of naturally occurring microorganisms to digest organic matter, usually in a 5 day incubation at 20° C, by analyzing the depletion of oxygen. This measures biodegradable organic matter, which is normally expressed as O₂ mg/L. The biochemical oxygen demand analysis is an attempt to simulate the effect a waste will have on the dissolved oxygen of a stream by a laboratory test. The BOD test gives an indication of the amount of oxygen needed to stabilize or biologically oxidize the waste. The advantage of the BOD test is that it measures only the organics which are oxidized by the bacteria. The disadvantage of this test is the 5 day time lag.

The Biochemical Oxygen Demand test provides a quantitative measure of the amount of oxygen required to maintain the growth and activities of the biological organisms responsible for the aerobic digestion of the organic in the liquid at a set temperature for a set amount of time in the dark. There is a limited amount of oxygen which will dissolve in the sample (about 9 mg/L), therefore dilutions are prepared with a buffered mineral nutrient containing water. The test does not determine the total amount of organic material present, since many compounds are not decomposed by biological and biochemical reactions in the set conditions. The BOD indicates

the concentration of biodegradable organic material. When applied to the examination of effluents, it permits calculation of the efficiency of operation of the treatment plants.

The measurement of the dissolved oxygen (DO) in the sample can be done by using an oxygen-sensitive membrane electrode, polarographic or galvanic, with an appropriate meter that meets EPA-approved method requirements. The YSI 50-series are examples of commercial meters meeting those requirements for measuring DO. The method calls for calibrating the meter using oxygen-saturated water, water-saturated air, or a Winkler titration before each use. *Standard Methods 5210 B*, and *EPA 405.1* are commonly used methods for the determination of BOD over a five day period.

The DO is measured at the beginning and recorded. After five days the DO is again determined. The BOD is then calculated on the basis of reduction of DO and the volume of the sample. The BOD₅ calculation takes into account the initial and final DO values and the percent concentration of the sample. In the BOD test you will use the difference of the two readings. Table 1 gives examples of BOD sources and ranges.

Representative Source	BOD ₅ Range (O ₂ mg/L)
Clear Creek Water	0 - 20
Polluted Creek Water and Weak Sewage	10 - 100
Strong Sewage and Industrial Waste	50 - 10,000

Table 1 Examples of BOD's from different sources.

AUTOMATED BOD

Various Levels of Automation

The PC BOD system is an automated system for measuring dissolved oxygen, calculating Biochemical Oxygen Demand (BOD) and reporting results.

The system utilizes a Man-Tech PC-BOD software and hardware including the Man-Tech AutoMax autosampler and a YSI DO meter (either a model 52 or 5100) and YSI BOD probe (Model 5905)

With this system, there are four basic levels of automation:

1. Full automation. The system will automatically add seed solution, add inhibitor solution, add dilution water, measure DO and rinse the probe.
2. Partial automation. The system will automatically add seed solution, add dilution water, measure DO and rinse the probe.
3. Partial automation. The system will automatically add dilution water, measure DO and rinse the probe.
4. Basic automation. The system will automatically measure DO and rinse the probe.

A fully automated system is illustrated in Figure 1.



Figure 1. Fully automated system for Seed, inhibitor and dilution water addition. These options are also available without the autosampler.

With the PC BOD software, you can combine BOD & CBOD samples in the same run. This eliminates the need to prepare two sets of seed solutions for two batches of samples. Prepare one seed solution, and designate half of the seed solutions to be CBOD. The software will automatically add the specified amount of inhibitor to the bottle. The same is true for CBOD samples as illustrated in Figure 2.

Rack Num	Bot Num	Sample Name	Sample ID	Sample Vol (mL)	Seed Vol (mL)	Inhib. Vol (mL)	is CBOD?	Initial DO	Final DO	BOD	Average	Flags	Comments
		Seed	artificial seed	15			Yes						
		Seed	artificial seed	15			No						

Figure 2. Specifying if a seed/sample is to be treated as a CBOD sample

During a combined run, if a sample is designated as a CBOD sample, it will only use the CBOD correction factor to calculate the result.

The software is programmed to comply with Standard Methods 18th, 20th, and 21st edition, and EPA 405.1

In reference to the Standard Methods 21st edition, the software will perform an initial addition of dilution water until the bottle is two thirds full, add seed and inhibitor (as needed), and fill the remaining to a pre-determined level. The reason for this is if seed is added directly to a sample

prior to dilution, the sample is an industrial effluent, this can be toxic to the seed and cause it to be ineffective. However, if the sample volume is above two thirds of the bottle volume, it will ignore the first dilution addition and automatically skip to the seed and inhibitor addition. The software is programmed with the allowable criteria for sample and seed DO depletion, and residual DO, as laid out by Standard Methods. The sample must have a minimum depletion of 2.0mg/L DO, and the residual DO must not be below 1.0 mg/L, as illustrated in Figure 3.

<input checked="" type="checkbox"/> Use Seed Selection Rule		
<input checked="" type="checkbox"/> Final DO less than	<input type="text" value="1.000"/>	
<input checked="" type="checkbox"/> Depletion (delta DO) less than	<input type="text" value="2.000"/>	
<input checked="" type="checkbox"/> Percentage Depletion range	<input type="text" value="1.000"/>	and <input type="text" value="100.000"/>
<hr/>		
<input checked="" type="checkbox"/> Use Sample Selection Rule		
<input checked="" type="checkbox"/> Final DO less than	<input type="text" value="1.000"/>	
<input checked="" type="checkbox"/> Depletion (delta DO) less than	<input type="text" value="2.000"/>	
<input checked="" type="checkbox"/> Ignore Depletion Rule for nonDiluted Samples		

Figure 3. BOD/CBOD rules for acceptable DO measurements

The exception to this rule is if the sample is not diluted, and the bottle is filled completely with sample, and there is less than a 2.0 mg/L DO depletion. In which case the depletion rules are ignored, shown in Figure 4.

<input checked="" type="checkbox"/> Ignore Depletion Rule for nonDiluted Samples
--

Figure 4. Depletion rule exception

For all the samples that pass these rules, an average result is calculated, and reported. From the main screen of the software, you can easily see which sample runs need to read back that day, in the section. Figure 4.

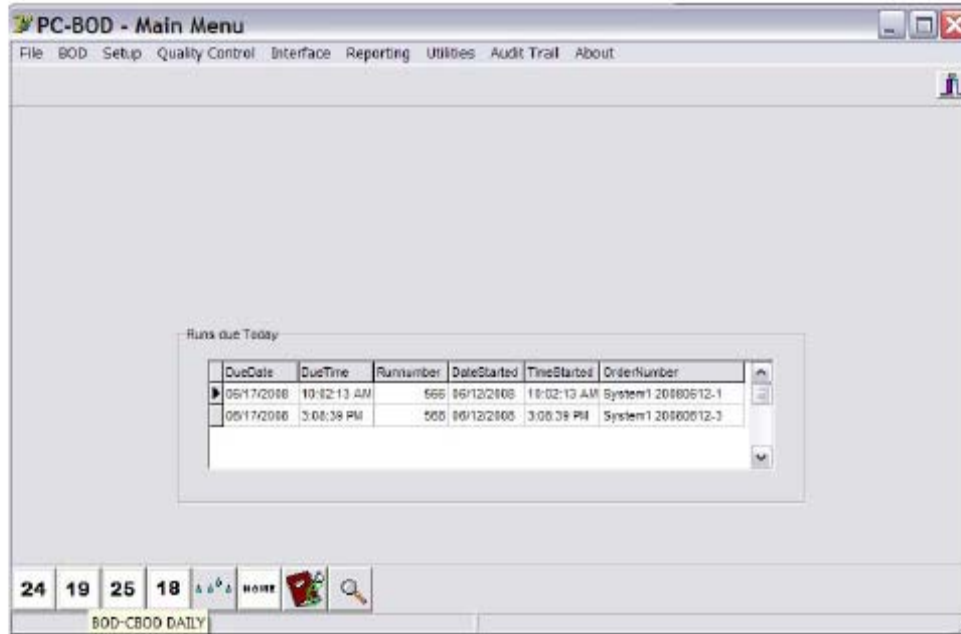


Figure 5. Main screen of software showing Runs Due Today and Autorun buttons

Also from the main screen of the software, pre-built testing templates can be linked to autorun buttons (Figure 5) to enable easy access to commonly run analysis sets (e.g. Blanks, Seeds, GGA samples). These templates can then be appended to for additional samples.

Predetermined (and fully customizable) sample ID's can be used for Blanks, Seed Blanks and GGA samples (figure 6). It is also possible to customize the incubation times and bottle volume.

Bottle Size (mL)

Incubation Period (Days)

Incubation Range (+/- Hours)

Incubation Warning (Hours)

Identify labels as follows

Blanks

Seeds

BOD Standard

Seed Control

CBOD Standard

Supersaturation Limit

Figure 6. Incubation time window, and sample ID

When running the samples on day 5 for the Final DO reading, the software will perform real-time calculations, so you will see BOD results as the DO is read. If there is a run that spans over more than one rack, the software will allow you to run them in a different order as on day one. The results will populate in the template relative to the bottle position and rack number. If the seed blanks have not been completed yet, the software will calculate the BOD value with a seed correction value of 0. When the seed samples are finally run, the calculation will correct for the seed demand in the previously run samples. Anytime a run is completed, and it uses one of the predetermined sample ID's (figure 5), the software will use these values to populate several QC charts for Seed correction factor (figure 7), and GGA standards (Figure 8).

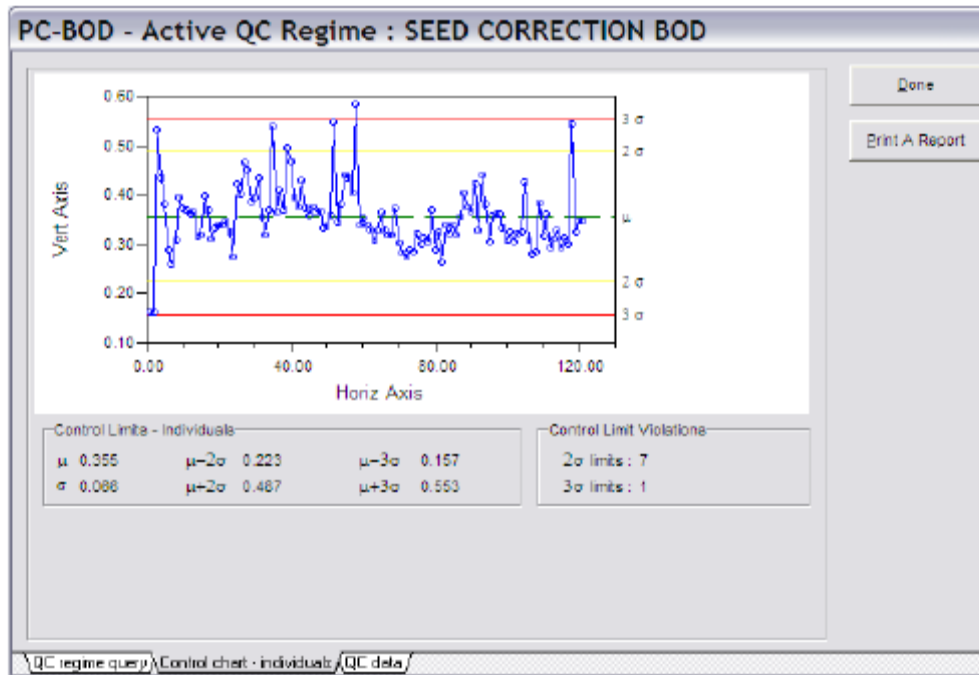


Figure 7. QC Chart for Seed correction factor

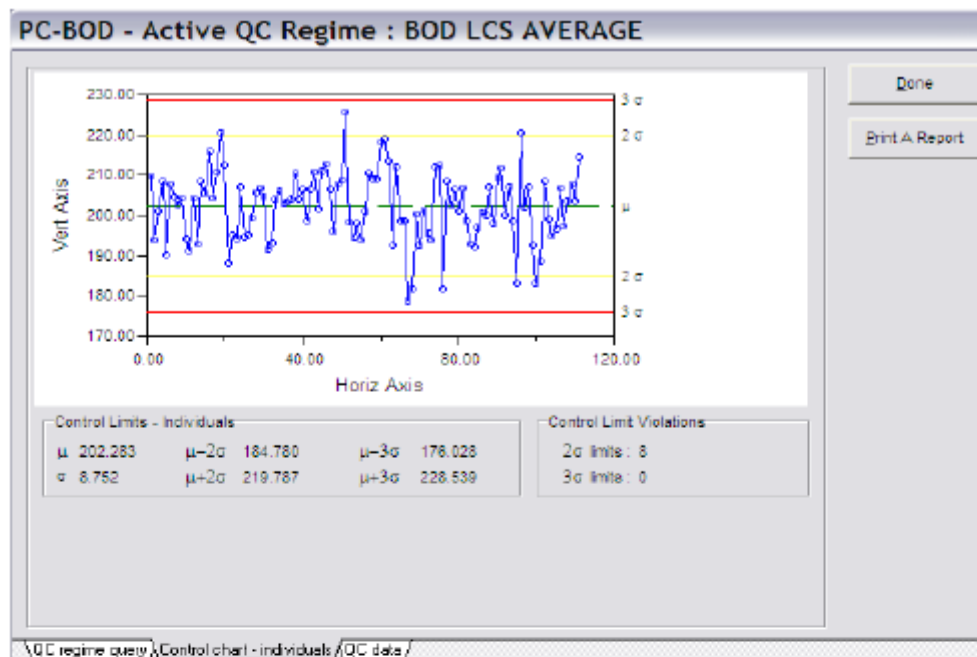


Figure 8. QC Chart for GGA samples

CONCLUSIONS

The manual BOD test is very labor intensive, and there are many areas in which transcription or operational errors can occur.

With the automated PC BOD system, the user is only required to place the samples in the bottles, and start the software. Everything else is taken care of by the system. This will reduce the intensive labor requirements, as while the system is adding all additional solutions required and taking DO readings, the technician is free to perform additional duties.

Added benefits to the automated system include identical conditions used for calibrating the DO meter and taking DO measurements. Ensuring each bottle is dealt with under the same criteria – eliminating the variation in different user techniques. Also, there are no transcription errors, since all calculations are performed by the software, and can be sent directly to a LIMS system.



Automated BOD



NEMC 2008
August 11-15, 2008
Hyatt Regency Capital Hill
Washington, DC



Distributed By
ManSci Inc.



BOD Background

What is BOD?

- A bioassay procedure that measures the dissolved oxygen consumption by bacteria from the decomposition of organic matter in water.

Why is it necessary?

- The test provides a quantitative analysis of the amount of oxygen required to maintain the growth of biological activities.



Distributed By
ManSci Inc.



Why Automate BOD?

Manual vs Automated

- The manual method is **VERY** labor intensive
 - For as little as 20 samples, each requiring 3 – 5 dilutions, you would be analyzing 60 – 100 bottles (not including you blanks, seed blanks and standards)
- Manually it is time consuming.
- There are many areas in which errors can occur
 - Transcription
 - Calculation
 - User technique



Distributed By
ManSci Inc.



How to improve the manual BOD method through automation

- Several key points were address:
- **Precision**
 - Seed, Inhibitor and dilution water addition
 - Consistent DO readings
- **Accuracy**
 - Secure calculations
- **Cost Effective**
 - Reduce labor costs
 - Ease of use
- **Automation** – which is our strength!



Distributed By
ManSci Inc.



Precision

- Slow speed peristaltic pumps are used for seed and inhibitor addition
- A high speed peristaltic pump is used for dilution water addition
 - A liquid level sensor is used to stop the pump
- Software stability settings ensure DO readings are taken when specified criteria is met



Accuracy

- Results are stored in a secure location
- Bottle data integrity maintained
- BOD correctly calculated using the relevant depletion rules





Cost Effective

- Reduce labor costs
- Ease of use

Load samples. Load Template. Start the run.



Distributed By
ManSci Inc.



• Automation



Distributed By
ManSci Inc.



Different levels of Automation

- Various levels of automation are offered.
- Fully automated
- Stand Alone (no automation)



Distributed By
ManSci Inc.



Automation Hardware

- XYZ Man-Tech AutoMax Autosampler
- YSI DO Meter (model 52 or 5100)
- YSI DO Probe (model 5905)
- Peristaltic pumps

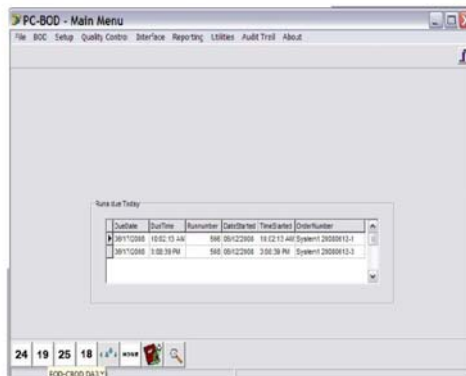


Distributed By
ManSci Inc.



PC-BOD Software

- Ease of use – Load Template, Load samples, Start.
- Autorun buttons make it easy to load frequently run samples.
- Sample runs that are due for the day 5 reading are displayed on the main screen



Software continued...

- Building a new template is also easy.

Rack	Bot	Sample	Sample	Sample	Seed	Inhib.	Is	Initial	Final	BOD			
Num	Num	Name	ID	Vol (mL)	Vol (mL)	Vol (mL)	CBOD?	DO	DO	BOD	Average	Flags	Comments
		Seed	artificial seed		15		Yes						
		Seed	artificial seed		15		No						

- The sample name & ID are added. The sample volume, seed and inhibitor volume (if required) are also entered.
- This can be accomplished by manually entering the data, or loading from a text file generated by your LIMS system.
- Is the sample to be tested for CBOD?





QC Compliance

- The software is setup to run BOD5
- The incubation time is available for alteration, if required.
- The sample ID's for sample QC is also available for customization



QC Compliance continued...

- The rules for Seed and Sample DO depletion are set up in the software.
- If required, these are available for modification.
- If the Seed or Sample fails any of the rules, it will not be used in the calculation.





QC Data

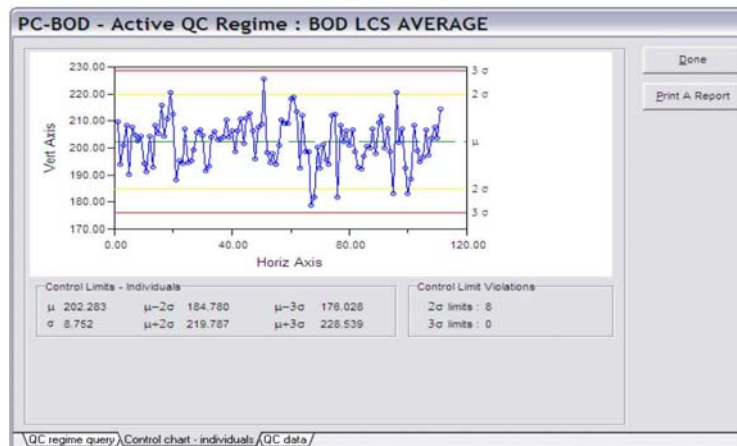
- The PC-BOD Software will keep track of all QC sample data.
- This will be used to populate a QC chart.



Distributed By
ManSci Inc.



QC Chart



Distributed By
ManSci Inc.



QC Data continued..

- For individual runs, the QC and Blank Data are displayed.
- Any samples that fail will be flagged.



QC Data continued...

PC-BOD - Post-Run BOD Analysis

System 1_000001

Rack	Bin	Sample	Free	Sample	Seed	Inhib.	Is	Initial	Final	BOD	
Num	Num	Name	Text 2	Vol (mL)	Vol (mL)	Vol (mL)	CROCI	DO	DO	Deplete BOD	Average
1	1	Blank		0.00	0.00	0.0	No	0.00	0.44	0.16	
1	2	Seed		0.00	10.00	0.0	No	0.41	0.51	2.10	
1	3	Seed		0.00	20.00	0.0	No	0.40	0.00	2.00	
1	4	Seed		0.00	25.00	0.0	No	0.62	0.09	3.53	
1	5	OGA_BOD		0.00	3.00	0.0	No	0.47	4.50	3.97	177.44
1	6	OGA_BOD		0.00	3.00	0.0	No	0.48	4.41	4.08	102.94
1	7	PC-BOD Effluent		60.00	3.00	0.0	No	0.60	0.10	2.41	9.94
1	8	PC-BOD Effluent		75.00	3.00	0.0	No	0.67	0.40	3.27	11.40
1	9	PC-BOD Effluent		90.00	3.00	0.0	No	0.65	4.68	3.97	11.83
1	10	Blank sample		0.00	0.00	0.0	No	0.64	0.65	-0.01	

Seed Correction Factor - BOD: 0.140 Seed Correction Factor - CBOD: 0.000 Blank Average Depletion: 0.160 CBOD Blank Average Depletion: 0.000

BOD Standards result -> 180.190
BOD Standards limit -> 198.000 +/- 30.500

Use Original Method

BO5 20TH SEEDED - (05007) Version 14

Exit Results Run Method

Runs to Complete

Date/Start	Time/Start	Date/Finish	Time/Finish	Order/Number	Run/Number
06/16/2007	0:43:23 AM	06/16/2007	10:01:20 AM	20070016-1	956
06/16/2007	10:10:09 AM	06/16/2007	11:08:38 AM	20070016-2	957
06/13/2008	10:26:09 AM	06/13/2008	10:37:31 AM	Stem=20000013-1	969
06/16/2008	10:37:47 AM	06/16/2008	10:38:37 AM	Stem=20000016-3	972
06/16/2008	10:32:02 AM	06/16/2008	10:33:06 AM	Stem=20000016-6	974
06/16/2008	10:38:10 AM	06/16/2008	11:50:37 AM	Stem=20000016-8	977
06/16/2008	11:49:29 AM	06/16/2008	11:53:05 AM	Stem=20000016-9	978

Done





Automated BOD Conclusions

- Reduces intensive labor requirements.
- Reduces labor costs.
- Reduces errors due to incorrect transcription, operational error.
- Increases sample integrity and data handling



Thank You

Questions?



A Universal Wastewater QC Standard: A Different Approach to LCS Materials in the Wet Chemistry Lab

Mark Hammersla
NSI Solutions
7517 Precision Drive, Ste 101
Raleigh, NC 27617
800-234-7837
mark.hammersla@nsi-es.com

ABSTRACT

Complying with SM102B3 in a multi-analyte wet chemistry laboratory setting requires burdensome, costly and error prone management of LCS reference solutions. Typical practice has been to prepare LCS materials in-house from neat chemicals or purchase multiple stock solutions from outside vendors for secondary preparation at the bench level. Both practices are error prone and labor intensive. The new Universal Wastewater QC Standard developed by NSI Solutions reduces the burden by incorporating 12 conventional pollutants analytes into a single easy to use, stable certified standard. Formulated at convenient concentrations, analytes include pH, BOD5, COD, CBOD, TOC, TSS, TS, TDS, Conductivity, n-NH3, n-NO3 and p-PO4. Presentation will describe packaging, specifications, quality control, stability, results of round robin analysis and procedures for use in the laboratory.



UNIVERSAL WASTEWATER QC STANDARD



**A Different Approach to LCS Materials
in the Municipal Wet Chemistry Lab**

**Presented By:
Mark Hammersla
NSI Solutions, Inc.**



- **Design Criteria and Product Description**
- **Manufacturing and Validation**
- **Applications**
- **Fitness For Use Validation**
- **Stability**
- **Packaging**





The Universal Wastewater Standard was developed to simplify LCS use in small wet chemistry labs.

Key Development Criteria:

- Must be really easy to use.
- Standard must contain as many compatible analytes as possible and be stable on the shelf and in use.
- Standard must be formulated at realistic analytical levels to minimize preparation steps.
- Applicable to routine analytical methods.
- Easily customized.
- Standard must have multiple uses and be applicable to broadest industry group possible.
- Formulation must be amenable to controlled scale-up.



The Universal Wastewater Standard meets our design criteria. It is a stable conventional pollutant LCS certified for 12 analytes in a proprietary aqueous buffer system.

BOD: 198 mg/L	TSS: 100 mg/L
TOC: 121 mg/L	N-NH₃: 7.50 mg/L
CBOD: 163 mg/L	N-NO₃: 3.00 mg/L
COD: 292 mg/L	p-PO₄: 2.50 mg/L
TS: 725 mg/L	Conductivity: 600 umhos
TDS: 450 mg/L	pH: 7.2 units

Contains most common NPDES analytes at levels not requiring secondary dilutions.



Manufactured and Validated to PT Standards, Sterilized and Buffered for Stability

- Analyte sources include high purity salts, 300 mg/L Glucose/Glutamic Acid (50:50) and diatomaceous earth.
- Matrix is 18 megohm water and a proprietary buffer system designed to hold pH at 7.2 while keeping total solids at about 725 mg/L.
- Sterilized after bottling to prevent GGA degradation.
- Batch homogeneity and formulation accuracy analytically validated as both total and dissolved analytes. TSS is inert to chemical analyte recoveries.
- Internal validation criteria exceed current PT requirements with direct SRM traceability for TOC, simple nutrients, pH and conductivity.



The Universal Wastewater Standard Has Wide Applicability

- Works with routine EPA methods.
- Meets SM1020B Sec. 3 requirements for daily certified independent LCS use.
- Can be used to validate PT results.
- Ideally suited as a training tool for demonstration of competence. Matrix complexity presents realistic analytical challenge.
- Useful for control charting since lot to lot concentrations are fixed.
- Can even be used for daily GGA check.



Universal Wastewater Standard Works Well in the Real World

To validate fitness for use, 9 labs were provided 4 x 1000 mL blind samples and asked to analyze using normal procedures. General guidance was provided but assigned values were withheld.

Pooled Round Robin Results, QCI-084 Lot# 090607

Analyte	True Value	Mean Recovery	% Recovery	STDEV	% RSD
TOC	121 mg/L	119 mg/L	99	1.82	1.52
COD	293 mg/L	297 mg/L	101	8.40	2.83
CBOD	163 mg/L	167 mg/L	102	3.37	2.32
BOD5	198 mg/L	202 mg/L	102	12.7	6.28
TSS	100 mg/L	95 mg/L	95	0.69	0.73
TDS	451 mg/L	472 mg/L	105	23.1	4.90
TS	732 mg/L	734 mg/L	100	7.83	1.07
Conductivity	602 umhos	610 umhos	101	11.1	1.82
N-NH3	7.50 mg/L	7.48 mg/L	100	0.058	0.78
N-NO3	3.00 mg/L	2.97 mg/L	99	0.033	1.11
p-PO4	2.50 mg/L	2.47 mg/L	99	0.062	2.51
pH	7.20 units	7.19 units	100	0.040	0.55



Formulation Characteristics and Sterilization Yields a Stable Product

QCI-084 Universal Wastewater Standard, Lot# 090607
Room temperature storage, unopened stability summary

Analyte	0-Day Mean n=9	30-Day Mean n=3	60-Day Mean n=3	120-Day Mean n=3
COD	293	291	291	294
TSS	96.6	97.4	97.1	96.3
TDS	451	452	440	442
TS	732	725	727	719
Conductivity	602	610	606	605
N-NH3	7.48	7.52	7.49	7.46
N-NO3	2.98	2.99	3.01	2.96
p-PO4	2.53	2.49	2.54	2.51
pH	7.20	7.22	7.19	7.20

All results are total analyses.



Two Package Options are Available:

- Whole volume, ready-to-use standards are provided in 4 x 1000 mL glass bottle cases.
- Also available in 20 mL concentrates for dilution to 1000 mL.



Thank You!

Mark Hammersla
NSI Solutions, Inc.

1-800-234-7837

Direct Analysis of High TDS Environmental Samples by ICP-MS

Steve Wilbur; Agilent Technologies, Bellevue WA, USA
Wim Proper; Eurofins Analytico, Barneveld, Netherlands

ABSTRACT

ICP-MS has become the preferred technique for the analysis of trace metals in environmental samples due to its multi-element capability, high sensitivity and relative freedom from interferences. However, it has always been limited to samples containing total dissolved solids (TDS) less than 0.1-0.2% (w/v), which required dilution prior to analysis for many sample types. In addition to increased reporting limits, conventional sample dilution has other disadvantages including reduced productivity, the possibility of contamination and dilution errors as well as increased waste volume. The development of a novel technique – aerosol dilution, when combined with instrument design and operational parameters to insure maximum plasma robustness, has been shown to permit the direct analysis of many samples containing TDS as high as 1% or more. This means that typical soil digests according to EPA methods 3015A, 3050B, 3051A and others can be analyzed directly without dilution. Other high TDS samples including undiluted seawaters, high TDS ground waters and TCLP leachates can also be analyzed directly. Long term stability during extended sequences of high TDS samples is significantly improved with internal standard recoveries commonly greater than 80%, even without matrix matching. This means that a wide range of sample types can be analyzed using a single non-matrix matched calibration with good results. In this work, aerosol dilution was evaluated as a replacement for conventional dilution and used to validate the Dutch regulation pertaining to contaminated soils (AS3000) with excellent results.

INTRODUCTION

The determination of trace elements in high matrix samples has always been a difficult analytical challenge. While ICP-MS has unsurpassed detection capability for trace metals, the potential for salt accumulation on the MS interface has always required that dissolved solids levels be limited. Furthermore, extremely corrosive or acidic samples can damage conventional ICP-MS interface components including the sampler and skimmer cones, requiring the use of platinum or other expensive components. Compared to ICP-OES or other non-MS-based techniques, this has been considered an inherent limitation of ICP-MS. To compensate for this limitation, samples with total dissolved solids (TDS) levels higher than 0.1-0.2%, depending on the matrix, typically require dilution before measurement by ICP-MS, relying on ICP-MS's high sensitivity to compensate for the sensitivity loss due to dilution. However, conventional sample dilution has a number of other disadvantages including reduced productivity, introduction of contaminants, dilution factor errors, and increased waste volume. As a superior alternative to conventional dilution, Agilent has developed a simple, novel modification to the sample introduction system of the Agilent 7500cx ICP-MS which can significantly improve the tolerance to high matrix samples. The Agilent High Matrix Introduction (HMI) accessory reduces sample matrix load on the plasma, making it possible to directly measure sample solutions with total dissolved solids (TDS) exceeding 1%. As a result, samples previously measurable only by ICP-OES can now be

directly measured by ICP-MS, using the 7500cx fitted with HMI. In this work, the HMI fitted to an Agilent 7500cx was used to test the system's ability to directly measure high TDS soil extracts in aquaregia and meet Dutch regulatory guidelines for reporting limits and data quality.

DIRECT ANALYSIS OF AQUAREGIA DIGESTS OF SOILS USING HMI-ICP-MS

This work was done in collaboration with the Eurofins Analytico laboratory (Analytico Milieu) in the Netherlands. In this collaboration, an Agilent 7500cx equipped with the HMI was used to generate performance data to be used for compliance with the Dutch regulation pertaining to contaminated soils (AS3000). Due to the high total dissolved solids levels and high acid concentrations of digested soils, dilution is necessary prior to analysis by ICP-MS. Analytico currently uses the Agilent Integrated Sample Introduction System (ISIS) to perform online dilutions to meet these requirements. However, the limitations of conventional dilutions prompted Analytico to evaluate the potential of HMI as a faster, simpler, less expensive replacement for conventional autodilution which would also eliminate the maintenance issues associated with a conventional autodilutor.

Instrumentation

An Agilent 7500cx with the second peripump option for high sample throughput was equipped with the HMI kit. A Burgener MiraMist (Burgener research) nebulizer was used. Instrument tune parameters including HMI settings are listed in Table 1. The plasma was optimized in ultra robust mode with 1/12 aerosol dilution. This is the maximum dilution factor that can be set with HMI and is approximately equivalent to diluting the sample x12 conventionally. All analytes except selenium were acquired in helium collision mode, thus eliminating the need for no-gas mode and the associated time required for mode switching. Selenium was acquired in hydrogen reaction mode due to the low detection limits required.

RF power (W)	1600
Carrier gas (L min ⁻¹)	0.28
HMI dilution gas (L min ⁻¹)	0.67
Aerosol dilution factor	1/12
Sample uptake rate (mL min ⁻¹)	0.17
ISTD uptake rate (ml min ⁻¹)	0.17
Total nebulizer flow (ml min ⁻¹)	0.34
Extract 1 (V)	0
Extract 2 (V)	-160
He flow (He mode)	4.0 ml min ⁻¹
KED (He mode)	2 volts
H ₂ flow (H ₂ mode)	4.0 ml min ⁻¹
KED (H ₂ mode)	2 volts

Table 1. Instrument tune conditions. Values related to HMI are shaded.

Sample Preparation

Actual soil samples received from Analytico's customers were prepared by adding 1 gram of soil to 8 ml of aquaregia prior to microwave digestion. Digested samples were then diluted to 50 ml final volume in ultra pure (18.2MΩ) water. The final acid concentration is 4% HNO₃ and 12% HCl.

Calculation of Method Detection Limits (MDLs)

Since the HMI is effectively applying a dilution, the effects on detection limits are of critical importance. While ICP-MS possesses high sensitivity, the requirement for ultra trace detection limits in high TDS samples can still be challenging. Analytico has required MDLs for most analytes (based on a 1 gram soil sample diluted to final volume of 50ml - table 2) which must be met in order for them to meet their reporting limits and satisfy Dutch regulatory requirements.

Analyte	Soil Dry wt (mg kg ⁻¹)	After 50x Dilution (µg L ⁻¹)
Cd	0.17	3.4
Cr	15	300
Cu	5	100
Ni	3	60
Pb	13	260
Zn	17	340
Hg	0.05	1
As	4	80
Ag	1	20
Se	10	200
Sb	1	20
Sn	6	120
Ba	15	300
Co	1	20
Mo	1.5	30
V	1	20
Be	0.1	2
Te	10	200
Tl	3	60

Table 2. Analytico 3-sigma required detection limits for soils

MDLs were calculated as 3-sigma of 10 replicates of a low-level (between 1 – 3 times the required MDL) spiked sand sample measured consecutively and also measured on 10 different days over a 30 day period¹ – Table 3. For all regulated elements, the calculated MDLs exceeded the Dutch regulatory requirements by at nearly an order of magnitude or better. So with the HMI operating at maximum effective dilution, the system has ample sensitivity for the application.

¹ MDLs calculated from 10 different days are informative only.

Analyte - isotope	ORS mode	MDL (1)	MDL (2)	Dutch Required MDL
Be 9	He	0.042	0.046	0.1
V 51	He	0.255	0.481	1
Cr 52	He	2.300	4.517	15
Co 59	He	0.147	0.348	1
Ni 60	He	0.770	0.922	3
Cu 63	He	0.502	1.303	5
Zn 66	He	1.704	3.104	17
As 75	He	0.549	1.079	4
Se 78	H ₂	0.832	2.041	10
Se 78	He	1.064	1.991	10
Mo 95	He	0.195	0.413	1.5
Ag 107	He	0.278	0.701	1
Cd 114	He	0.058	0.066	0.17
Sn 118	He	0.589	1.353	6
Sb 121	He	0.333	0.401	1
Te 125	He	1.217	2.112	10
Ba 135	He	3.041	6.227	15
Hg 201	He	0.014	0.025	0.05
Tl 203	He	0.285	0.546	3
Pb 208	He	1.197	2.844	13

Table 3. Calculated Method Detection Limits according to the requirements of Dutch regulation AS3000. MDL(1) = 3 σ of 10 replicates taken on the same day. MDL(2) = 3 σ of 10 replicates taken on different days¹.

Analysis of Certified Reference Materials

Two certified reference materials (BCR-144R Domestic Sewage Sludge, IRMM, Belgium and FeNeLab River Clay, FeNeLab, Netherlands) were analyzed in replicate as part of the validation procedure. The CRMs were prepared in the same manner as standard soil samples and measured on 10 different days during a 30 day time period. Table 4 shows the results of replicate (n=10) analyses of both CRMs in mg kg⁻¹. Recoveries ranged from 87 – 108%, well within the regulatory requirement of 80 - 110%.

Analyte	ORS Mode	FeNeLab River Clay			BCR144R Sewage Sludge		
		Measured (ave, n=10)	Certified	Rec. % (ave)	Measured (ave, n=10)	Certified	Rec. % (ave)
Be 9	He	1.6			0.2		
V 51	He	59.6			13.9		
Cr 52	He	191.9	187	103	88.8	90	99
Co 59	He	19.8	18.7	106	13.6	13.3	102
Ni 60	He	55.7	52.9	105	40.7	44.9	91
Cu 63	He	153.9	156	99	270.0	300	90
Zn 66	He	1031.6	970	106	825.1	919	90
As 75	He	44.7	44	102	3.2		
Se 78	H ₂	2.0			1.7		
Se 78	He	2.4			1.5		
Mo 95	He	1.3			6.9		
Ag 107	He	2.9			8.2		
Cd 114	He	8.5	8.07	105	1.7	1.84	90
Su 118	He	0.02			36.0	40.8	88
Sb 121	He	1.6			2.8	3.05	92
Te 125	He	0.3			0.1		
Ba 135	He	828.3	817	101	319.2	367	87
Hg 201	He	4.1	3.83	107	3.2	3.11	102
Tl 203	He	1.1			0.1	0.14	
Pb 208	He	297.0	274	108	94.9	96	99

Table 4. Results of replicate (n=10) analyses of two certified reference soil samples (FeNeLab and BCR144R)

Determination of precision and accuracy at high and low concentrations

In addition to analysis of replicate CRMs, both low level and high level spiked samples were analyzed in replicate (n=10; 10 different days during 30 days time period) in order to determine both accuracy and precision over a wide range of concentrations – Table 5.

Sample Analysis

In order to test the long term robustness of the HMI equipped system, a 23 hour sequence consisting of an initial calibration and 235 soil samples was analyzed. Absolute drift was measured by monitoring the recovery of the 5 internal standards (⁶Li, Ge, Rh, In, Ir) in both gas modes (He and H₂) over the course of the sequence. Normalized recoveries (relative to the method blank) are shown in figure 2. Overall downward drift over 23 hours was approximately 20%, which is easily corrected by internal standards and not sufficient to have a detrimental effect on method accuracy or sensitivity. By comparison, a similar system without HMI, running these samples directly would suffer severe loss of sensitivity (>80%) due to cone clogging before the sequence was completed.

AS3000, like most methods used for regulatory compliance, requires ongoing calibration accuracy checks. In this case continuing calibration verification (CCV) samples (1 mg/kg As, 50 µg/kg Hg, remaining elements 2 mg/kg) were analyzed after each 12 soil samples. Results are shown in figure 2. Acceptable recoveries must be within +/- 10%. 10 percent control

limits are shown in red indicating that all CCV recoveries were well within the prescribed limits for the entire sequence. This excellent calibration stability not only insures the most accurate sample results, but also eliminates time wasted in unnecessary recalibrations should a CCV fail during the sequence.

Productivity

The operation of the HMI accessory does not adversely affect productivity in any way, since the HMI conditions are constant throughout operation and do not require any additional execution or stabilization time. Therefore a given method run with HMI would take the same amount of time per sample as one run without HMI. HMI is also fully compatible with most high speed sample uptake and rinse systems, which can significantly reduce total run time. Furthermore, since HMI permits the direct analysis of undiluted samples of many types, the extra time associated with either manual or autodilution is saved. The improved stability as a result of HMI use can also minimize the need for recalibrations and sample re-runs, further reducing the average run-to-run time. In this work, the average run time for a sample in a 23 hour, 235 sample sequence of undiluted soil digestates was 5.9 minutes including acquisition in both H₂ and He modes.

Analyte	ORS Mode	Low Level Spike Conc. mg kg ⁻¹	Measured value (ave)	RSD (%)	Rec. % (ave)	High Level Spike Conc. mg kg ⁻¹	Measured Value (ave)	RSD (%)	Rec. % (ave)
Be 9	He	1	0.8	3.5	81	800	773.9	3.6	97
V 51	He	50	50.9	4.0	102	800	771.4	2.5	96
Cr 52	He	150	149.6	4.0	100	1100	1062.7	2.5	97
Co 59	He	10	10.4	4.1	104	800	766.3	2.0	96
Ni 60	He	25	25.3	5.3	101	1100	1074.1	3.1	98
Cu 63	He	40	40.0	6.2	100	1100	1058.5	2.5	96
Zn 66	He	150	151.6	4.2	101	1100	1094.3	4.7	99
As 75	He	40	39.0	5.0	97	400	395.5	2.8	99
Se 78	H ₂	100	102.7	3.7	103	1300	1336.0	2.2	103
Mo 95	He	13	12.2	5.0	93	1300	1235.3	3.3	95
Ag 107	He	8	8.3	4.6	103	40	40.8	4.2	102
Cd 114	He	1.2	1.1	7.1	94	1100	1062.8	2.9	97
Sn 118	He	40	41.7	4.0	104	1300	1262.6	3.2	97
Sb 121	He	10	9.7	5.9	97	1300	1188.0	2.4	91
Te 125	He	80	82.1	4.2	103	750	807.4	2.4	108
Ba 135	He	120	121.1	4.5	101	1100	1102.2	5.6	100
Hg 201	He	0.4	0.4	4.4	106	13	13.5	4.3	104
Tl 203	He	23	24.0	4.6	104	40	41.3	3.4	103
Pb 208	He	100	101.9	4.7	102	800	778.1	4.0	97

Table 5. Results of replicate (n=10) measurements taken on 10 non-consecutive days during a 30 day period of both low-level and high level spikes of soil samples.

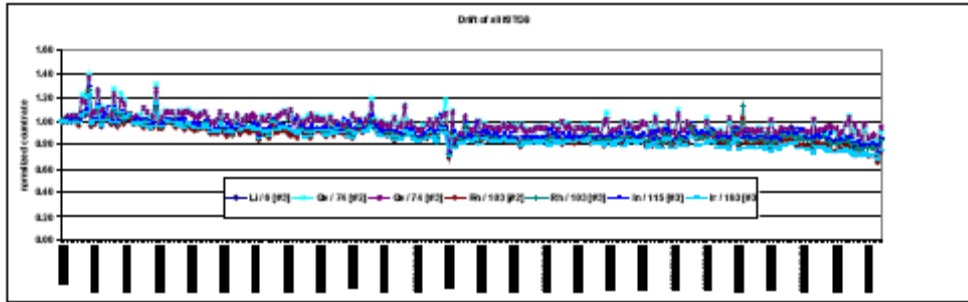


Figure 1. Normalized internal standard recovery in digested soil samples for the duration of the 23 hour sequence. Numbers next to each ISTD in the caption denote the gas mode – 2 = H₂, 3 = He.

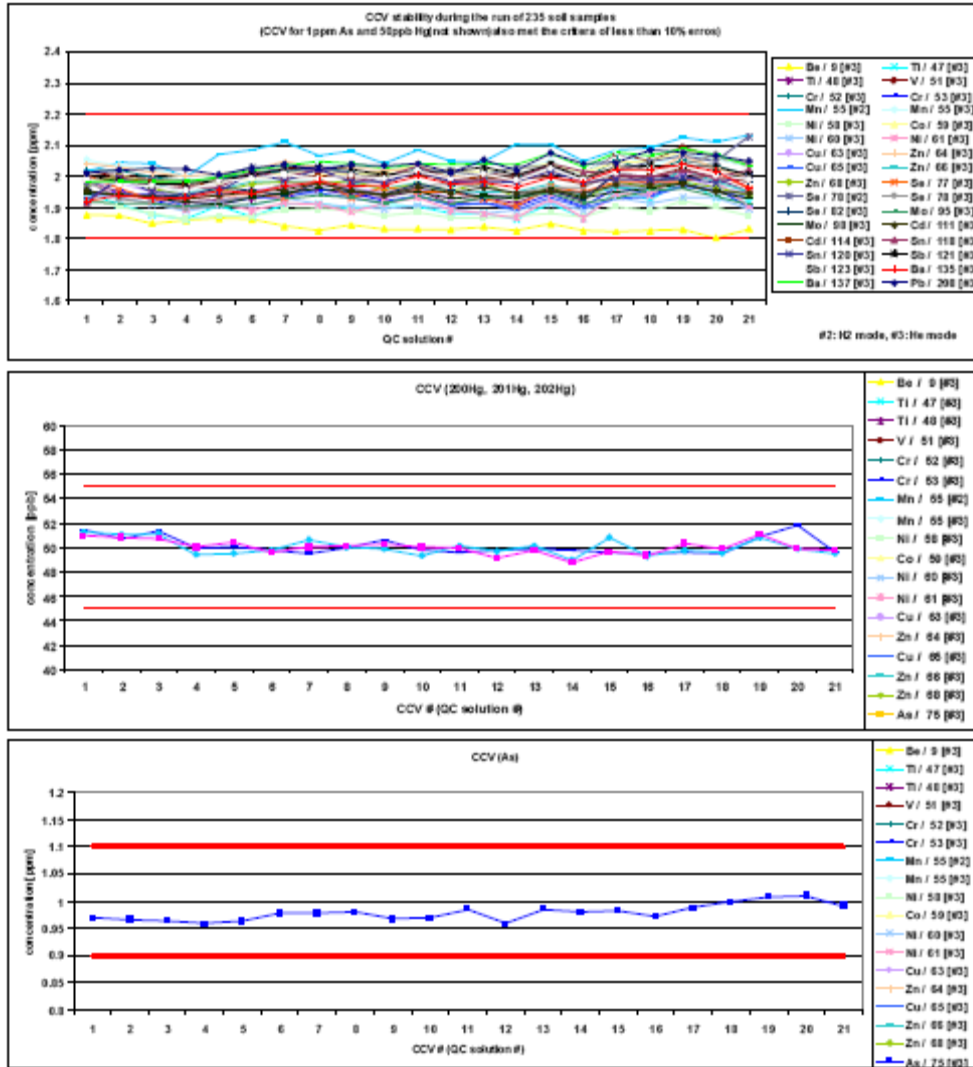


Figure 2. Continuing Calibration Verification (CCV) recoveries (n=21) for all analyte elements over the 235 sample sequence of soils and sludges. Analytes at 2 mg/kg are shown on top, Hg, at 50µg/kg – middle, As at 1 mg/kg - bottom. Method required control limits (90 – 110%) are shown in red.

CONCLUSIONS

Based on Analytico's evaluation, when compared with conventional autodilution for high TDS, high acid digests of soil and sludge samples, Agilent's HMI interface provided a number of significant advantages.

- Speed – HMI does not require liquid dilution of sample and stabilization of diluted sample. It also permits the use of Agilent's pre-emptive rinse function which allows rinsing of the sample tubing to begin before acquisition has finished.
- Low maintenance – no tubing to replace, no moving parts to maintain
- Simple – no critical timing issues or plumbing common to continuous flow autodilutors
- Flexibility – since hardware changes or reconfigurations are not required after installation of HMI, the system can be switched between conventional mode and HMI mode on the fly.

These advantages have allowed Analytico to use a single 7500cx ICP-MS fitted with HMI to replace several instruments required for the analysis of these sample types including conventional ICP-MS, ICP-OES and a dedicated mercury analyzer.

ACKNOWLEDGEMENTS

Wim Proper
Eurofins Analytico
Barneveld, Netherlands

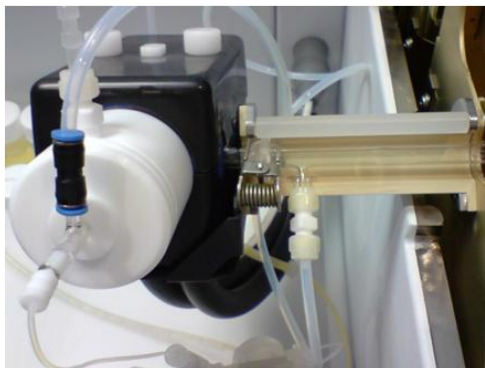
Noriyuki Yamada
Agilent Technologies
Hachioji, Japan

REFERENCES

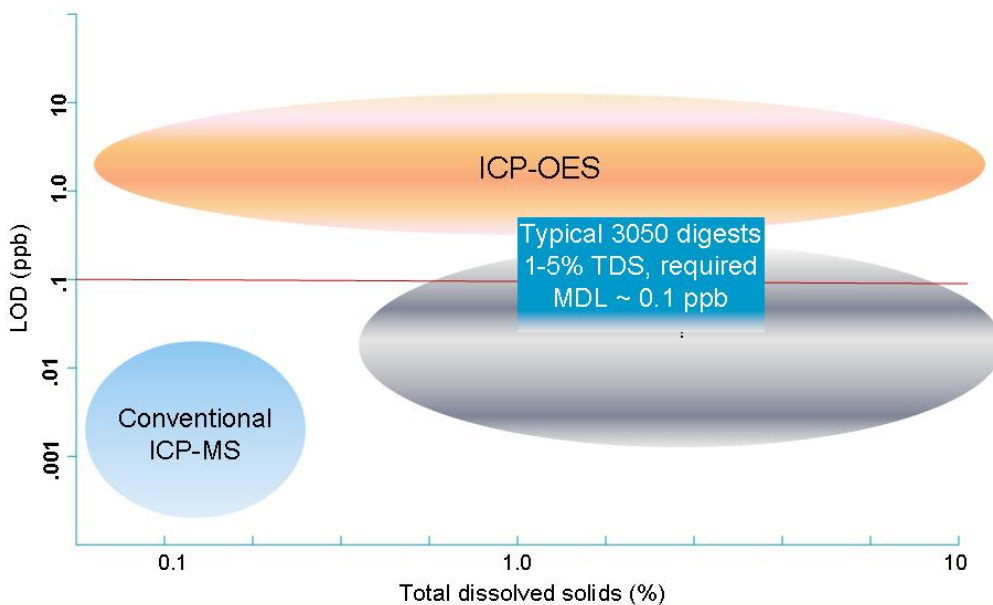
1. Agilent Technologies, 2008. *Direct Analysis of Undiluted Soil Digests Using the Agilent High Matrix Introduction Accessory with the 7500cx ICP-MS*. Agilent Technologies application note 5989-7929EN
2. Agilent Technologies, 2008. *Performance Characteristics of the Agilent High Matrix Sample Introduction (HMI) Accessory for the 7500 Series ICP-MS*. Agilent Technologies application note 5989-7737EN

Direct Analysis of High TDS Environmental Samples by ICP-MS

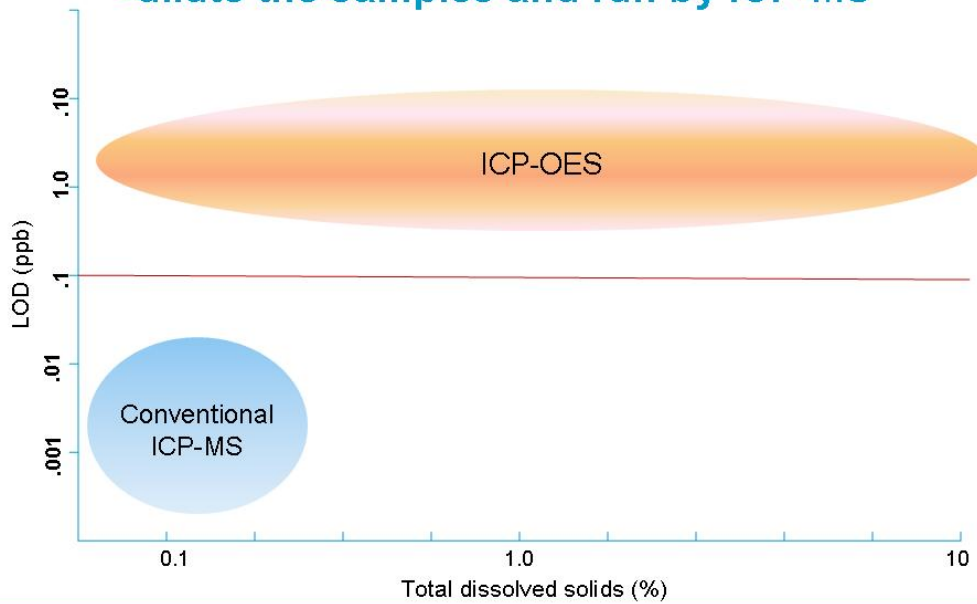
The Agilent High Matrix Introduction Accessory for the 7500 ORS Series ICP-MS



The gap between ICP-MS and ICP-OES



The current solution -dilute the samples and run by ICP-MS



3

Agilent Technologies

Disadvantages to conventional dilution

Autodilution is expensive

Manual dilution takes time – possibility of errors

Additional source of contamination

Increased waste volume

4

Agilent Technologies

So Why Use ICP-MS?

Simply

Much better detection limits (ppt or sub ppt) even after dilution

Fewer, simpler interferences – mostly eliminated using CRC technology → Higher confidence in data quality

One technique is simpler than 2 (or 3)

Single sample prep

Reduced QA/QC

Simplified reporting

But...

High TDS samples (> 0.1 - 0.2%) require dilution

5

 Agilent Technologies

Limitations of ICP-MS to high salts

- ✓ High salt samples can result in salt buildup on the cones and interface components resulting in loss of sensitivity and drift.
- ✓ High salts cause suppression of sample response in the plasma
 - **Ionization suppression** especially from easily ionizable elements (EIEs)
 - Ionization is not necessary in ICP-OES

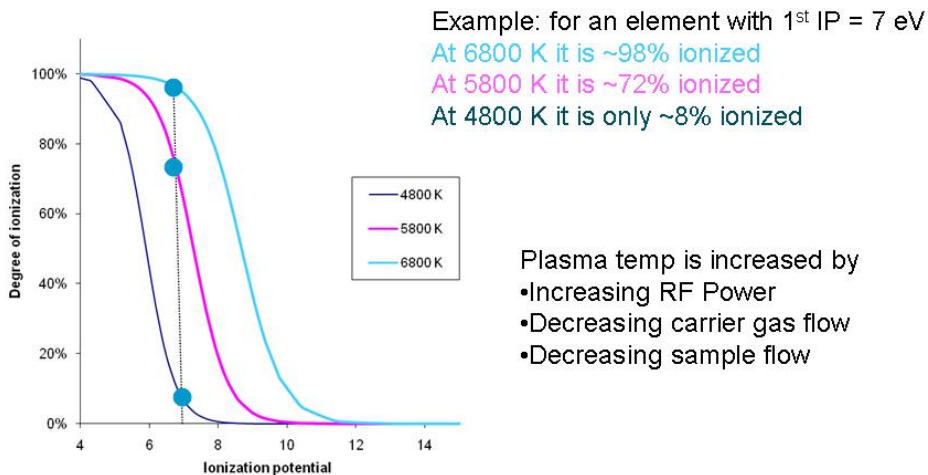


6

 Agilent Technologies

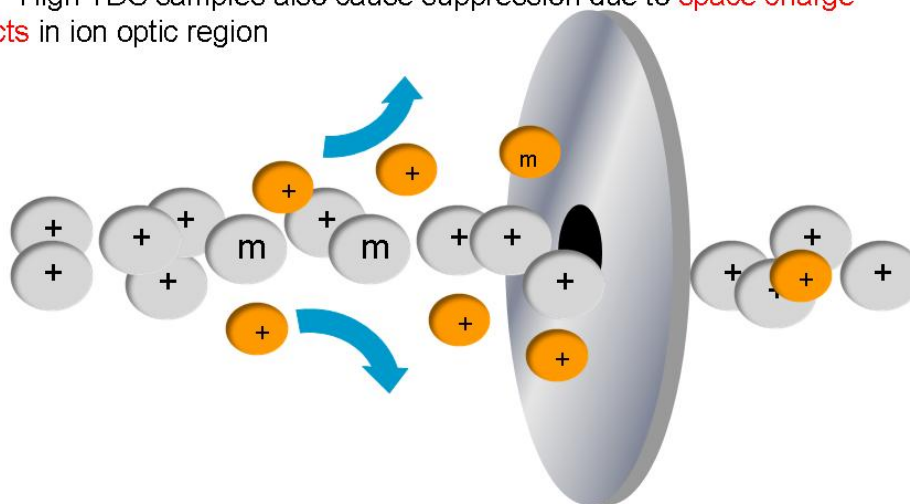
Limitations of ICP-MS to high salts

- ✓ Ionization is also suppressed by reduction in **plasma temperature**



Limitations of ICP-MS to high salts

- ✓ High TDS samples also cause suppression due to **space charge effects** in ion optic region



Low mass ions are suppressed by high mass ions

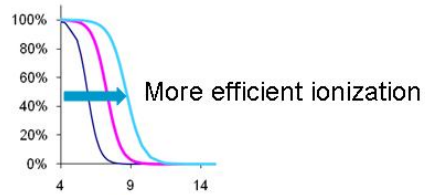


Summary – Overcoming the limitations of ICP-MS to high TDS samples

Matrix effects can be reduced by:

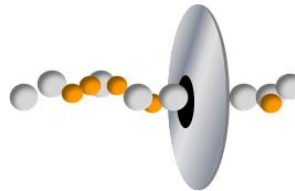
1. Increasing plasma temperature

- Higher power
- Lower carrier gas flow
- Lower sample flow



2. Reducing matrix load

- Lower sample flow
- Sample dilution
 - But conventional dilution does not reduce the solvent (dilute acid or other) which is also a major component of the matrix
 - Other disadvantages to dilution (contamination, time, errors, waste)



9

A Simpler, More Efficient Alternative to Conventional Dilution

→ Aerosol Dilution

1. Decrease sample flow and carrier gas flow to nebulizer

- Reduces total sample and reduces nebulizer/spraychamber efficiency

2. Make up the flow with a dilution gas added between the spraychamber and torch

- Maintain correct carrier gas flow to torch
- Reduce total amount of water or other solvent going to plasma

Results in hotter, more robust plasma with much lower oxides

Cannot introduce contamination

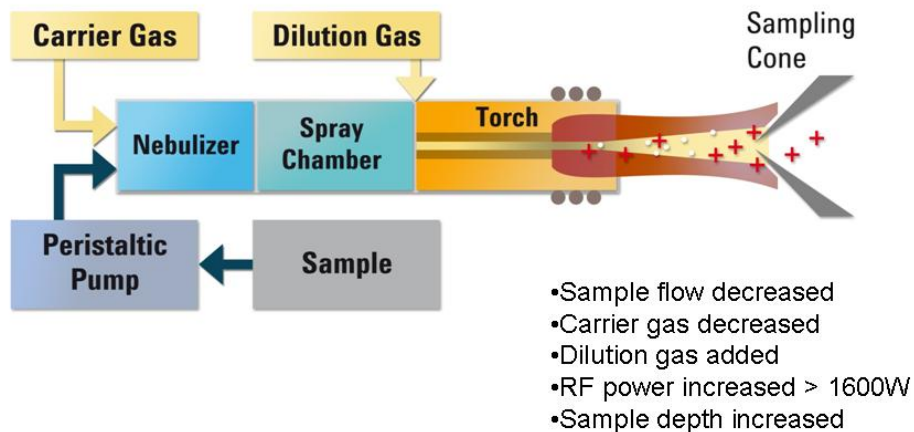
Error free (optimized using sophisticated software algorithms)

Virtually instantaneous

10

The Agilent High Matrix Interface (HMI)

Maximizes Plasma Robustness
Minimizes Matrix Load via "Aerosol Dilution"

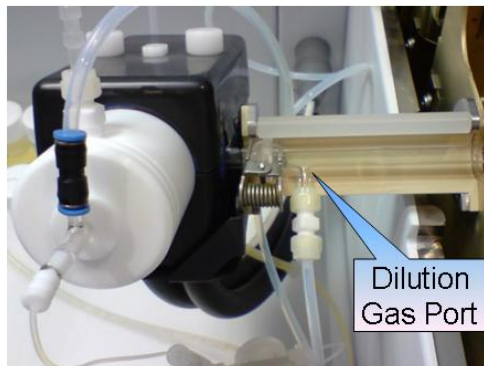


11

Simple Hardware – Sophisticated Software

Once the hardware is installed, HMI can be switched on or off via the software.

- No need to remove it or make any hardware adjustments to operate in non-HMI mode
- When the dilution gas is switched off – system operates in "normal" mode



12

Measuring “Plasma Robustness” when using HMI

Typically measured by examining the ability of the plasma to break down or prevent the formation of Metal Oxides such as Cerium Oxide

Measure CeO^+/Ce^+ ratio – lower is better

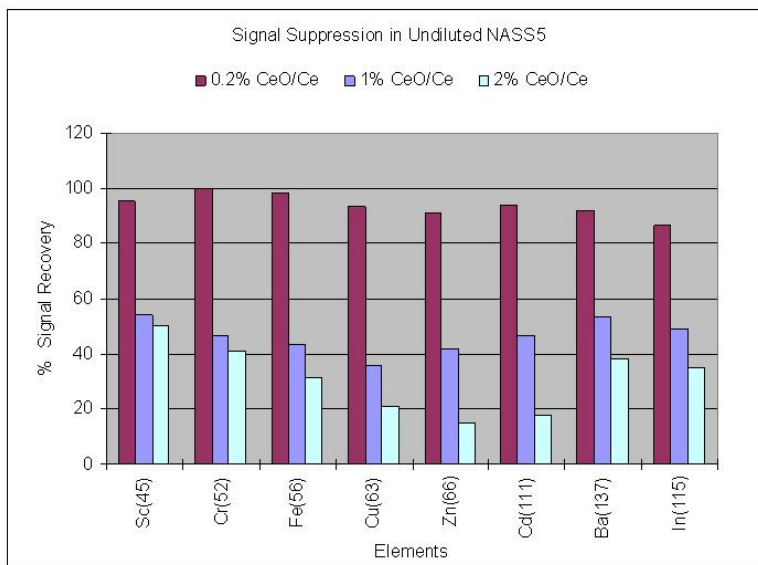
Typical values are 1-3% depending on instrument design and tune conditions

HMI can deliver 0.2% CeO or better

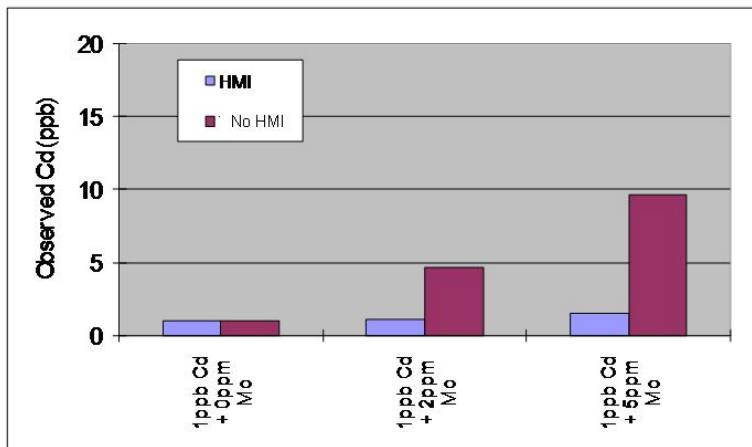
Samples containing 1% TDS or higher can be directly introduced into the ICP-MS without dilution



Signal Suppression as a Function of Cerium Oxide Ratio in Undiluted Seawater



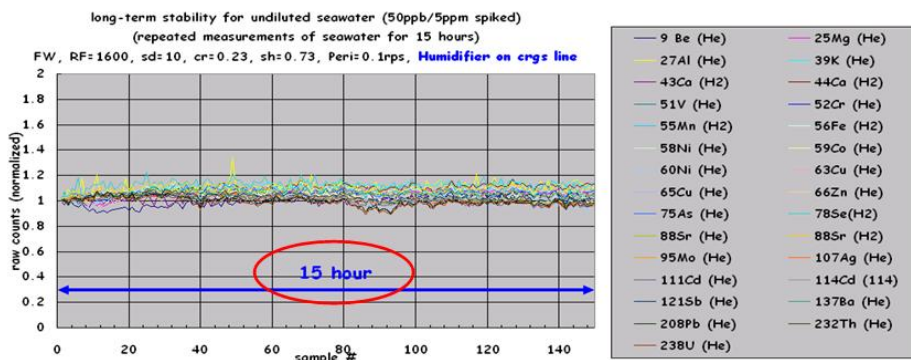
Robust Plasma → Low Oxides → Lower Interferences



Effects of interference from MoO on a 1 ppb Cd spike at increasing Mo concentrations (0 ppm, 2 ppm, 5 ppm) shown for both typical configuration (1% oxides) and HMI equipped 7500cx (0.2% oxides)



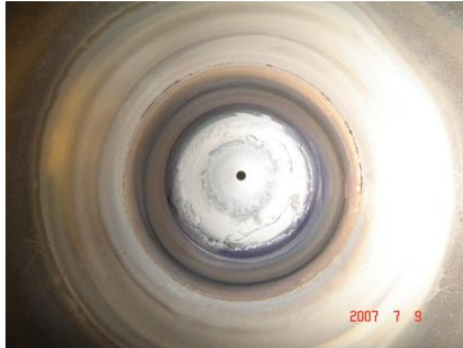
150 Sample Sequence of Undiluted Spiked NASS 5 Seawater – Long-term Stability



No drift in 15 hours!



After neat seawater analysis with HMI – No blockage of either Sampler or Skimmer



Sampler



Skimmer

Instrument Detection Limits (IDLs) in Maximum Robustness Mode with HMI

Based on 10 replicates of 1% nitric acid blank

- Ultra robust conditions
- Maximum aerosol dilution

IDLs are significantly better in high TDS samples using HMI than using conventional dilution

- More precise
- Less contamination

Element	<i>m/z</i>	int. time (sec)	ORS Mode	ISTD	IDL (ppb) (3-sigma)
V	51	0.3	He	Sc	0.064
Cr	52	1	He	Y	0.030
Mn	55	0.3	He	Y	0.069
Fe	56	0.3	H ₂	Y	0.021
Ni	60	3	He	Ge	0.012
Co	59	1	He	Ge	0.003
Cu	63	6	He	In	0.025
Zn	66	3	He	In	0.084
As	75	3	He	Y	0.030
Se	78	9	H ₂	Ge	0.035
Mo	98	0.3	He	Tb	0.015
Ag	107	1	He	In	0.007
Cd	111	3	He	In	0.015
Pb	208	1	He	Bi	0.005
U	238	1	He	In	0.001

TCLP Method Detection Limits (MDLs) with and without HMI*

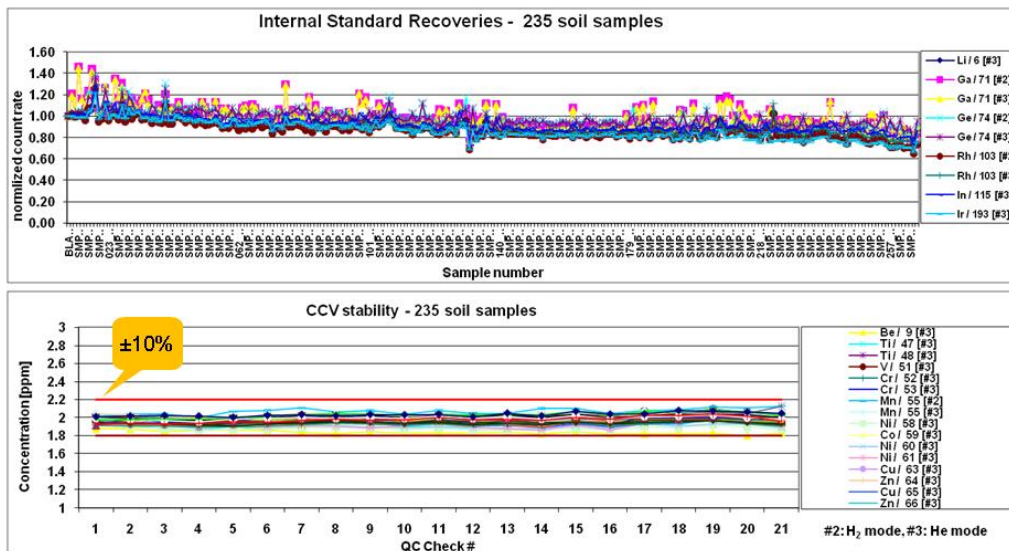
3 sigma MDLs in mg/kg for same spiked samples run conventionally with 1/10 dilution and directly with HMI

Analyte	HMI MDL mg/kg	w/o HMI MDL (1/10 dil.) mg/kg
Al / 27	4.1	5.8
Sb / 121	0.026	0.031
As / 75	0.03	0.15
Ba / 137	0.053	0.17
Be / 9	0.021	0.018
B / 11	0.33	1.3
Cd / 111	0.029	0.031
Ca / 40	5.7	8.4
Cr / 52	0.031	0.13
Co / 59	0.0064	0.0034
Cu / 63	0.078	0.14
Fe / 56	1.7	4.6
Pb / 208	0.055	0.03
Mg / 24	1.3	1.9
Mn / 55	0.037	0.11
Mo / 95	0.036	0.058
Ni / 60	0.024	0.036
K / 39	3.8	6.5
Se / 78	0.13	0.044
Ag / 107	0.005	0.0071
Na / 23	1.8	15
Sr / 88	0.051	0.066
Tl / 205	0.026	0.015
Sn / 118	0.105	0.24
Ti / 47	0.17	0.12
V / 51	0.041	0.096
Zn / 66	0.84	0.64

*Courtesy TestAmerica, Savannah



Internal Standard and Calibration Stability in 23 Hour Sequence of Undiluted Soil Digests



Results of replicate (n=10) analyses of two certified reference soil samples (FeNeLab and BCR144R*)

Both run as undiluted digests in He mode

Excellent recovery of certified values for all elements

Element	ORS Mode	FeNeLab River Clay			BCR144R Sewage Sludge		
		Measured ⁽¹⁾ (ave n=10)	Certified	Rec. % (ave)	Measured ⁽¹⁾ (ave n=10)	Certified	Rec. % (ave)
Be 9	He	1.6			0.2		
V 51	He	59.6			13.9		
Cr 52	He	191.9	187	103	88.8	90	99
Co 59	He	19.8	18.7	106	13.6	13.3	102
Ni 60	He	55.7	52.9	105	40.7	44.9	91
Cu 63	He	153.9	156	99	270.0	300	90
Zn 66	He	1031.6	970	106	825.1	919	90
As 75	He	44.7	44	102	3.2		
Se 78	H ₂	2.0			1.7		
Se 78	He	2.4			1.5		
Mo 95	He	1.3			6.9		
Ag 107	He	2.9			8.2		
Cd 114	He	8.5	8.07	105	1.7	1.84	90
Sn 118	He	0.02			36.0	40.8	88
Sb 121	He	1.6			2.8	3.05	92
Te 125	He	0.3			0.1		
Ba 135	He	828.3	817	101	319.2	367	87
Hg 201	He	4.1	3.83	107	3.2	3.11	102
Tl 203	He	1.1			0.1	0.14	
Pb 208	He	297.0	274	108	94.9	96	99

*BCR-144R Domestic Sewage Sludge, IRMM, Belgium and FeNeLab River Clay, FeNeLab, Netherlands
(1) Units in mg kg⁻¹

21



Target Applications for HMI ICP-MS

High TDS Samples requiring high sensitivity, few interferences

- Soil digests (undiluted)
- High TDS ground waters
- TCLP leachates
- Geological digestions and fusions
- RoHS samples
- High purity metals
- Neat seawater
- HPLC-ICPMS applications requiring high salt buffers

22



Summary

HMI

1. *Significantly* improves matrix tolerance of the ICP-MS
2. Minimizes or eliminates the need for matrix matching for most sample types
3. Improves limits of detection in high matrix samples when compared to conventional dilution
4. Improves long term stability in high matrix samples
5. Improves the accuracy of internal standard correction
6. Reduces interferences due to metal oxides
7. Reduces system cleaning and maintenance
8. Allows ICP-MS to directly analyze many samples prepared for ICP-OES

Thank You

Portable Toroidal Ion Trap Mass Spectrometry: Taking the Instrument to the Sample

Christopher Bowerbank
Torion Technologies
2400 North 180 West
Pleasant Grove, UT 84062
801-830-6083
chris.bowerbank@torion.com

ABSTRACT

A hand portable gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS) has been used for the rapid detection and positive identification of toxic industrial chemicals (TICs) and hazardous chemicals in both laboratory and field settings. Novel applications of this GC-TMS system include explosive and forensic compound on-site identification and near-real time environmental contaminant identification in site remediation scenarios. The GC is a resistively-heated, low thermal mass assembly that provides high-speed temperature programming (up to 120°C/min). The miniaturized toroidal design of the TMS ion trapping region provides analysis of a similar number of ions compared to traditional benchtop cylindrical ion trap configurations. The TMS has a mass range of ~50-500 Daltons with unit mass resolution or better across the mass range. A peak deconvolution algorithm is used to accurately deconvolve and identify substantially co-eluting compounds. Compound fragmentation patterns generated by the TMS typically contain major fragment ions which match closely with standard reference libraries such as NIST. A customizable compound library is resident on the TMS and is user-definable for creation of compound libraries specific to the user's needs.



Portable Toroidal Ion Trap Mass Spectrometry: Taking the Instrument to the Sample

Christopher R. Bowerbank, Douglas W. Later,
Edgar D. Lee, Jacolin A. Murray, Milton L. Lee

NEMC 2008
Washington D.C.

© 2007 TORION TECHNOLOGIES, INC.



Presentation Outline

- GC-TMS
- CUSTODION SPME sampling
- SPME/GC/TMS Applications
- TMS fragmentation vs. NIST
- Peak Deconvolution

© 2007 TORION TECHNOLOGIES, INC.



Trends in Analytical Procedures

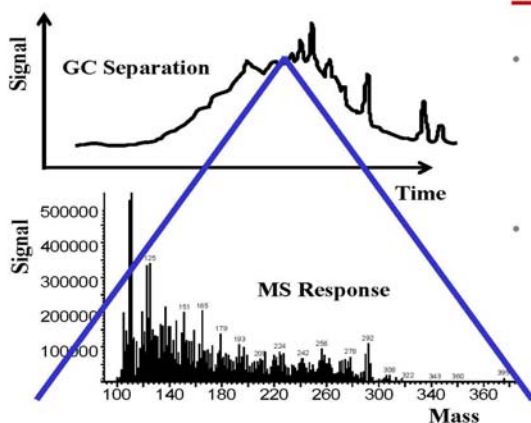
Prominent analyses trends common to all fields:

- *Faster analysis methods*
- *Increased sensitivity*
- *Increased measurement selectivity*
- *Increased productivity*
- *Reduce cost per sample*

© 2007 TORION TECHNOLOGIES, INC.



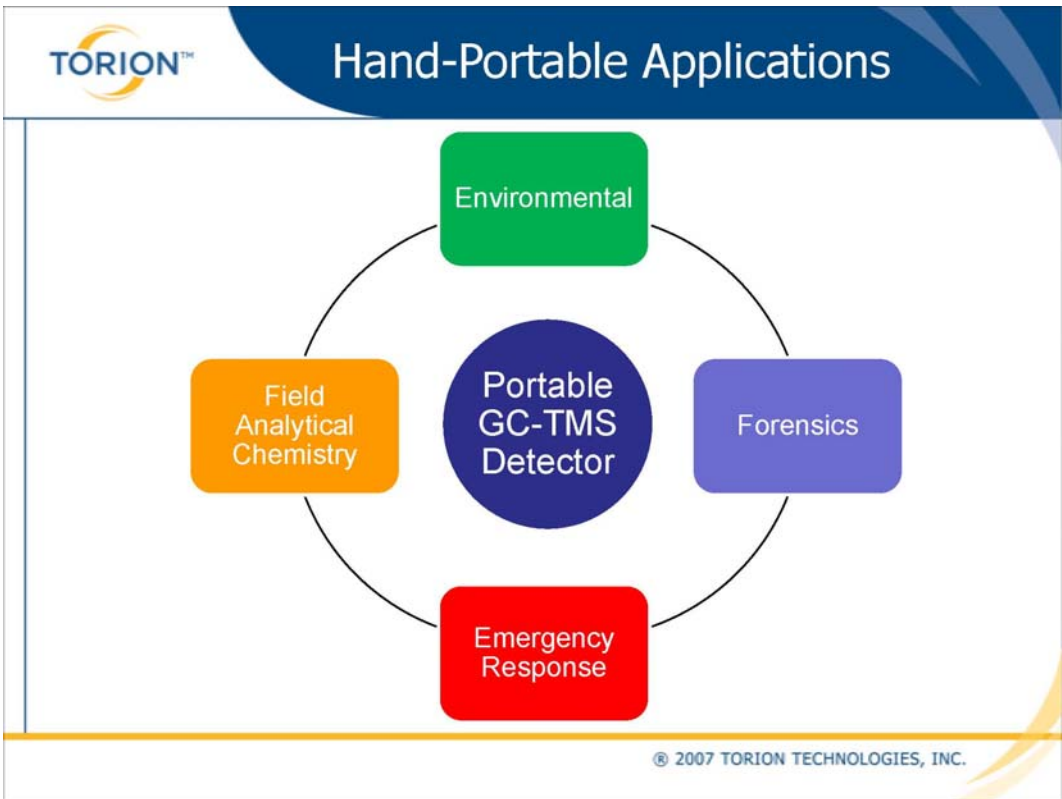
Industry Shift to Faster Analysis



Time Compression Means

- *Dramatic increases in*
 - false positives/negatives
 - sample reanalysis rates
 - sample preparation
- *Dramatic reductions in*
 - precision and accuracy
 - sensitivity
 - robustness

© 2007 TORION TECHNOLOGIES, INC.





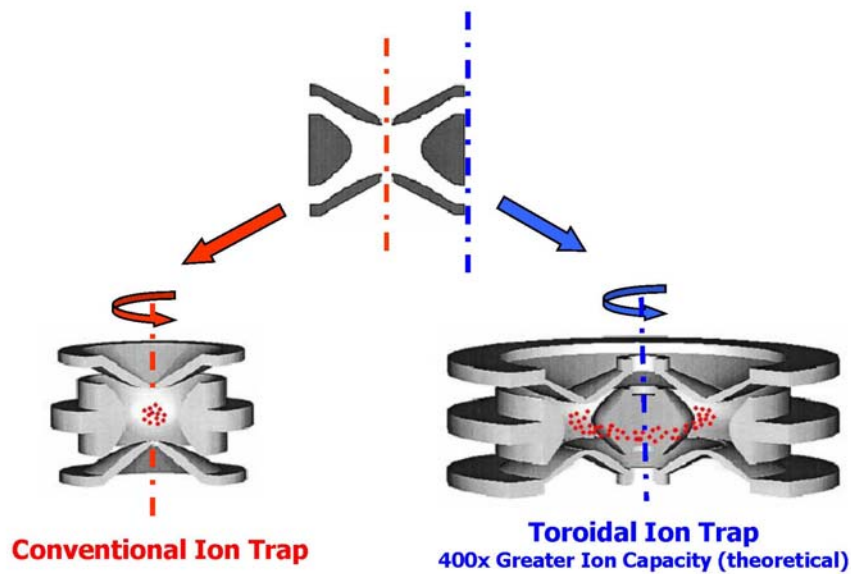
Ion Trap is Ideal for Portability

- *Simple, rugged detector design*
- *Less stringent vacuum requirements than other types of MS detectors*
- *Low power consumption (max 80W)*
- *High duty cycle → High sensitivity*
- *Toroidal ion trap configuration ideal for miniaturization*

© 2007 TORION TECHNOLOGIES, INC.



Innovation in Ion Trap MS

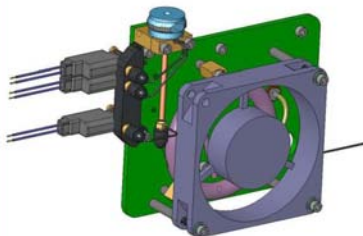


© 2007 TORION TECHNOLOGIES, INC.



Sample Separation

Low Thermal Mass GC System



- **Column:** MTX-5 (5 m x 0.1 mm x 0.4 μ m)
- **Mobile Phase:** Helium
- **Head Pressure:** 25 psig
- **Column Max Flow:** 0.7 scc/min @ 20°C
- **Split-splitless Injection:** Split ratio 20
- **Program:** 40°C (hold 10 s) to 270°C (hold 10 s) @ 120°C/min
- **GC-TMS run time:** <5 min (including cooling & data analysis)

© 2007 TORION TECHNOLOGIES, INC.



The GUARDION-7™

Portable—Fast—Reliable—Easy

Specifications



- **Dimensions:** 47 cm x 36 cm x 18 cm
- **Weight:** <13 kg or 28 lbs (including batteries)
- **Peak Power:** ~ 80 W
- **Sample Introduction:** SPME
- **GC:** RTX-5, 5 m x 0.1 mm x 0.4 μ m
- **TMS:** Toroidal Ion Trap
- **Mass Range:** 45 to 500 Daltons
- **Resolution:** < Unit mass
- **Vacuum:** Turbo molecular and roughing pumps
- **~50 Analysis:** battery power
- **~100 Analyses:** cartridge He gas supply

© 2007 TORION TECHNOLOGIES, INC.



Accessories Lifetime Test Results



Batteries

24V, 7.5 Ah Lithium sulfur dioxide (LiSO_2)
GC-TMS run time of 5 minutes
30 to 50 analyses per set of 2 batteries*
Can also run on DC (110V) line power

Helium UHP Gas Cylinder

90cc stainless steel cylinder at 2500 psi
25 psi GC column head pressure
50 to ~100 analyses*
Can be attached to laboratory gas supply



*depending on whether the GUARDION-7 is turned off between analyses

© 2007 TORION TECHNOLOGIES, INC.



Why SPME?

- Solvent-free
- Reusable
- Simple to use
- Faster than other extraction techniques
- Low cost per sample

© 2007 TORION TECHNOLOGIES, INC.



SPME

- Semi-quantitative
 - Quantitative when the matrix and sampling is the same as the standards/QCs
- Applicable to air, liquid, and solid samples
- Utilized in many fields including environmental, medical, culinary, and forensics
- Organic-phase coated fused silica fiber
- Fiber is attached to a microsyringe

© 2007 TORION TECHNOLOGIES, INC.



SPME sampling

Headspace

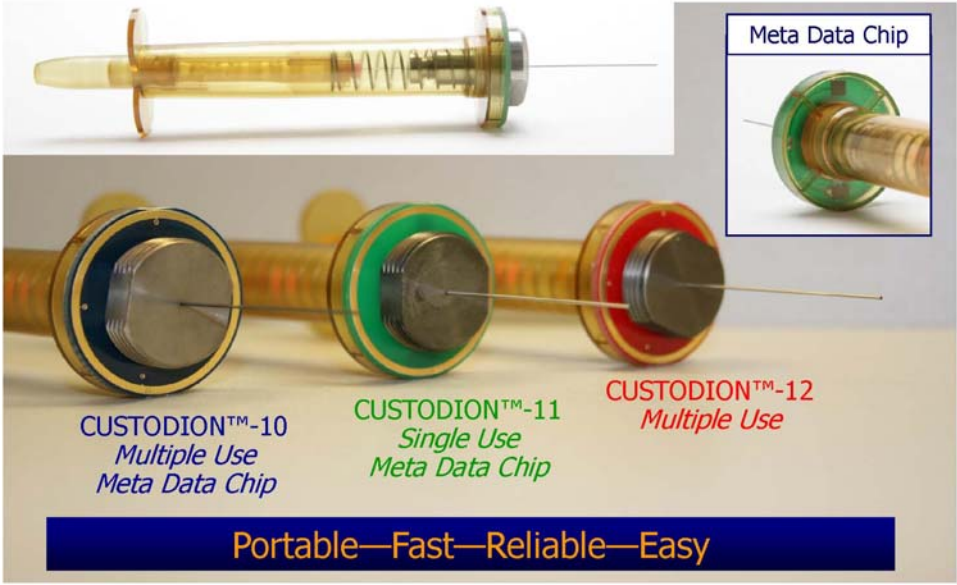
- Fiber is exposed directly above the surface of the sample
- Used to analyze volatile compounds

Direct

- Used to analyze compounds that are non-volatile
- Fiber is submerged into the sample (liquid or dissolved solids)

© 2007 TORION TECHNOLOGIES, INC.

TORION™ CUSTODION™ Syringes



The image displays three Custodion syringes with different colored caps: blue (C-10), green (C-11), and red (C-12). An inset shows a close-up of the Meta Data Chip on the syringe cap. The syringes are labeled with their respective models and uses.

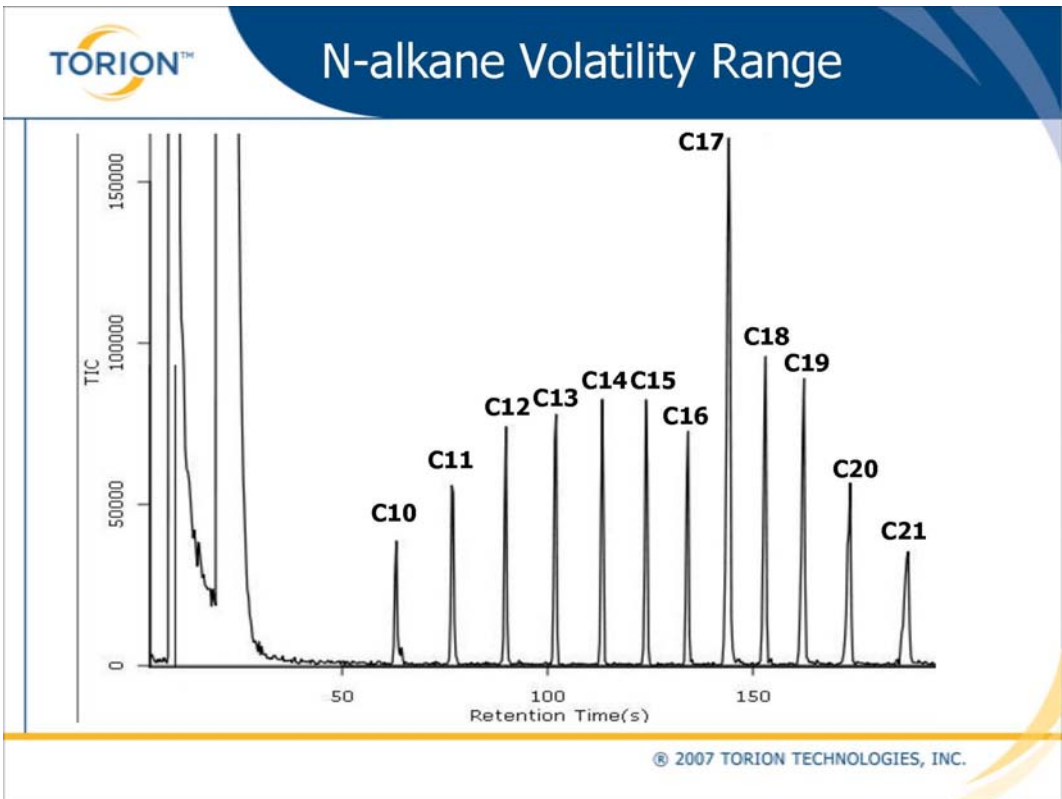
CUSTODION™-10
Multiple Use
Meta Data Chip

CUSTODION™-11
Single Use
Meta Data Chip

CUSTODION™-12
Multiple Use

Portable—Fast—Reliable—Easy

© 2007 TORION TECHNOLOGIES, INC.





TMS Compound Library

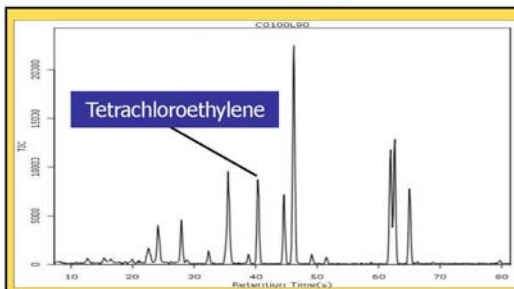
EPA 624 VOC and SVOC Mix

- Benzene
- Bromodichloromethane
- Bromoform
- Carbon tetrachloride
- Chlorobenzene
- 2-chloroethyl vinyl ether
- Chloroform
- Dibromochloromethane
- 1,2-dichlorobenzene
- 1,3-dichlorobenzene
- 1,4-dichlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethane
- 1,1-dichloroethene
- *trans*-1,2-dichloroethene
- 1,2-dichloropropane
- *cis*-1,3-dichloropropene
- *trans*-1,3-dichloropropene
- Ethylbenzene
- Methylene chloride
- 1,1,2,2-tetrachloroethane
- Tetrachloroethene
- Toluene
- 1,1,1-trichloroethane
- 1,1,2-trichloroethane
- Trichloroethene

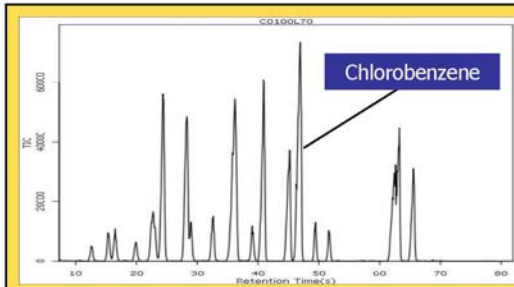
© 2007 TORION TECHNOLOGIES, INC.



EPA 624 VOC Mix

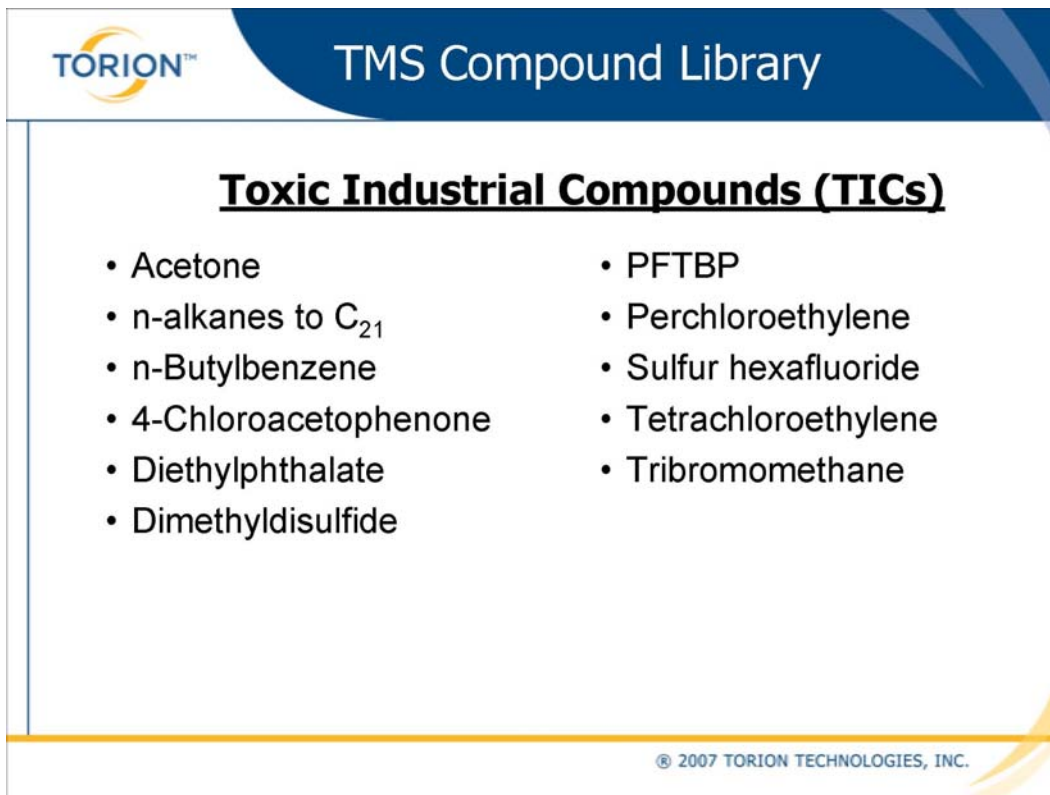
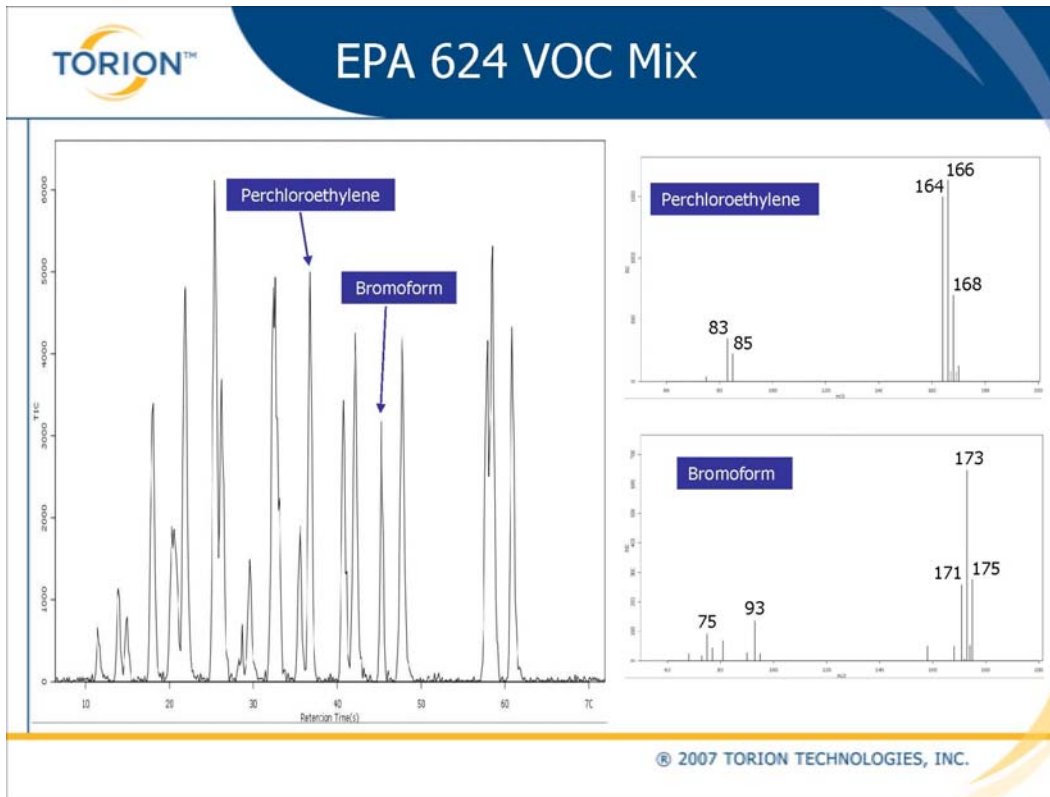


EPA 624
Headspace
75 ppb in water



EPA 624
Direct sampling
20 ppm in water

© 2007 TORION TECHNOLOGIES, INC.





TMS Compound Library

PAH's

- Naphthalene
- Acenaphthylene
- Fluorene
- Phenanthrene
- Anthracene

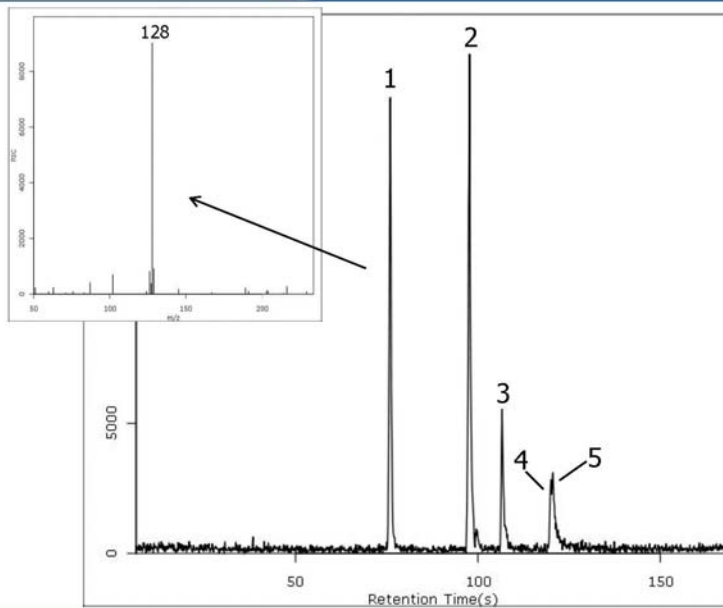
Acid/Base VOCs

- Bis(2-chloroethyl) ether
- 2-chlorophenol
- Diethylphthalate
- Dimethylphthalate
- Diphenylamine
- 1-Methyl-2,4-dinitrobenzene
- Nitrobenzene
- 2-Nitrophenol
- 4-Nitrophenol
- 3-Nitrotoluene

© 2007 TORION TECHNOLOGIES, INC.

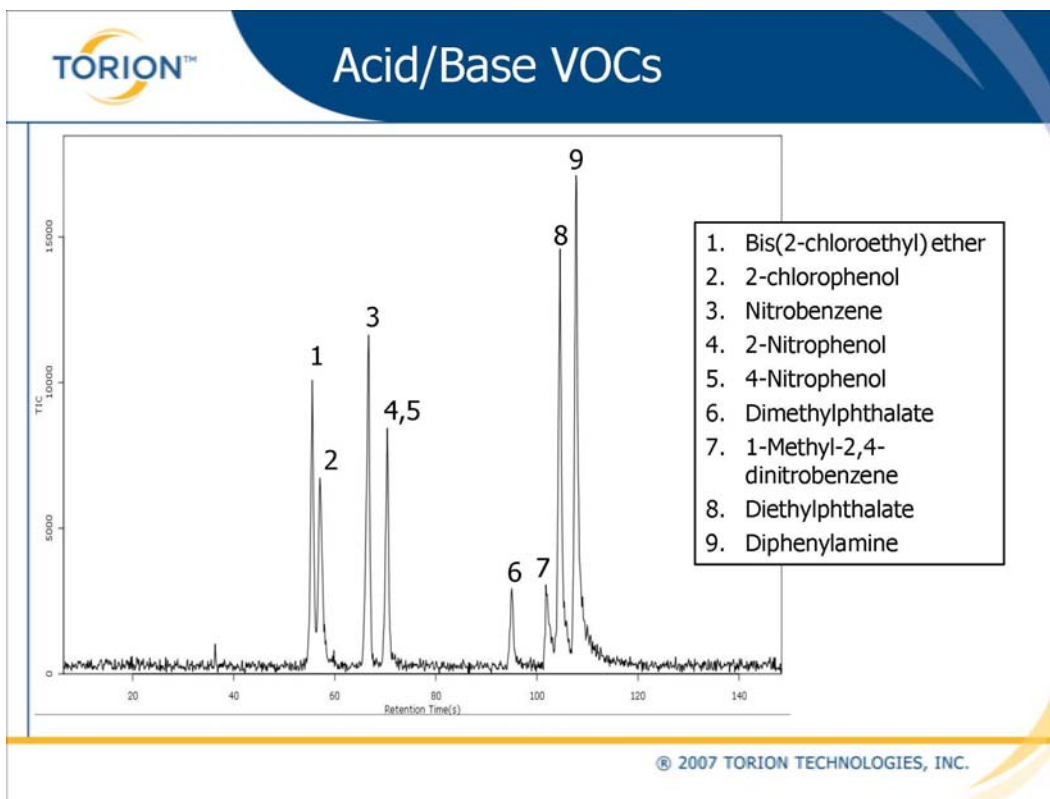


Polycyclic Aromatic Hydrocarbons



1. Naphthalene
2. Acenaphthylene
3. Fluorene
4. Phenanthrene
5. Anthracene

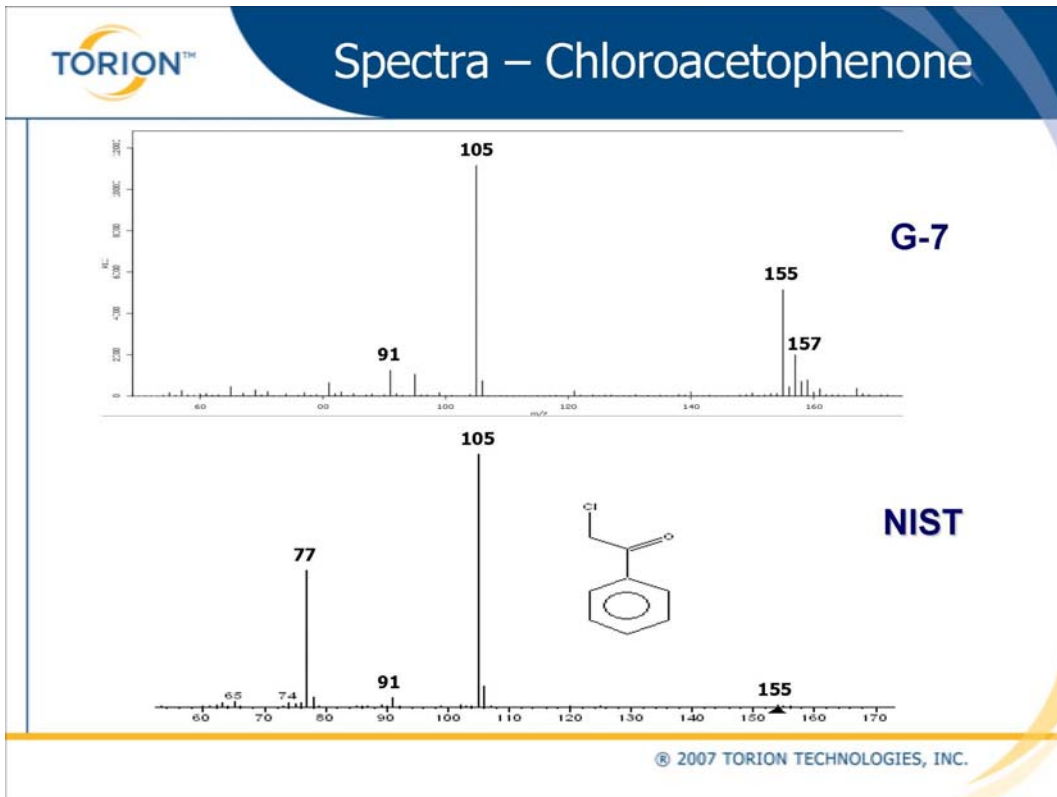
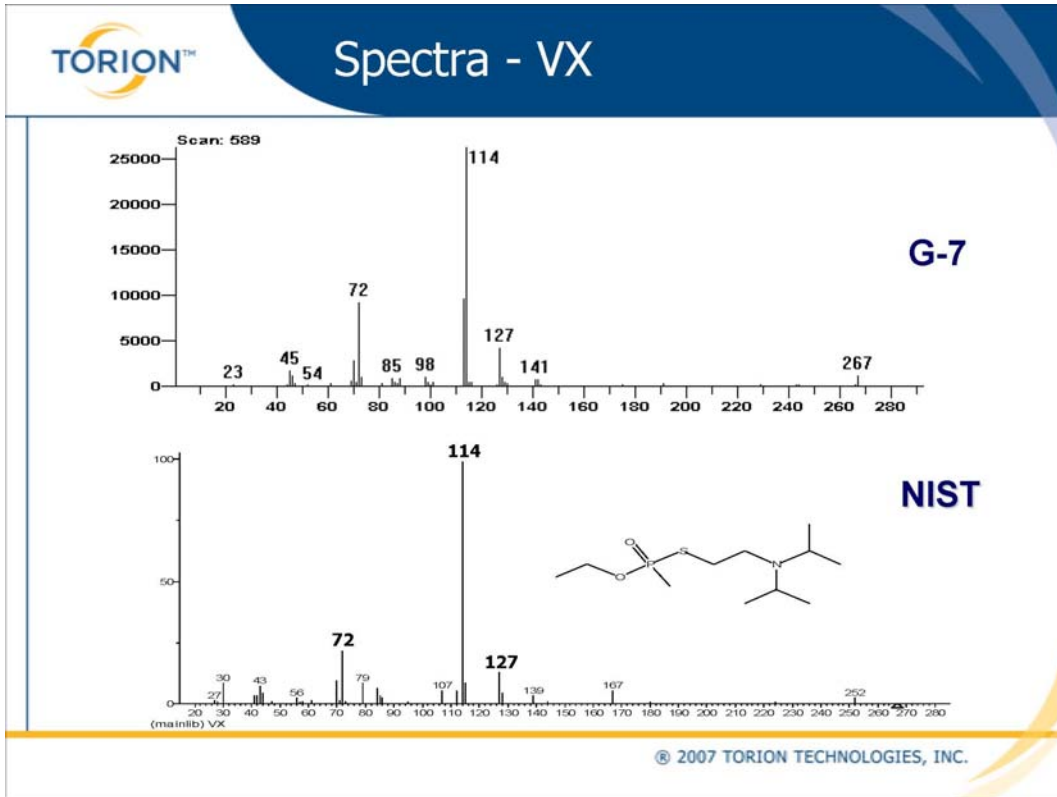
© 2007 TORION TECHNOLOGIES, INC.

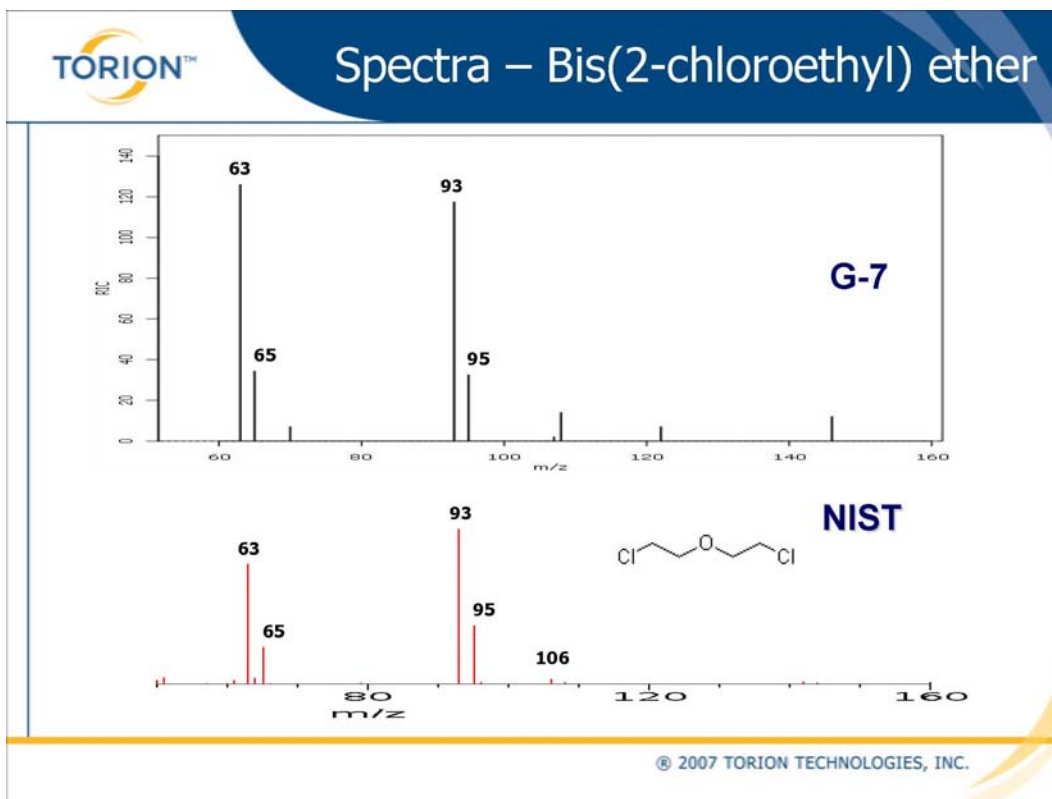


TORION™ Chemical Warfare Agents

<u>CWA</u>	<u>CWA Simulants</u>
VX	• Pinacolyl Alcohol (G-agent)
GA	• Triethylphosphate (G-agent)
GB	• Dimethylmethylphosphonate (G-agent)
GD	• Diisopropylmethylphosphonate (G-agent)
GF	• Dibutylsulfide (H-agent)
HD	• Methylsalicylate (H-agent)
	• Bis-4-chlorobutylether (H-agent)
	• Malathion (VX)
	• Tributyl Phosphate (VX)
	• Bis-(2-ethylhexyl)-phosphite (VX)

© 2007 TORION TECHNOLOGIES, INC.





TORION™ **GUARDION-7™**

June 22 – 25, 2007

Instrument	Runs	Blanks	Identified	Percent
C03	6	7	29/31	93.6%
C04	6	7	30/30	100%
C06	6	6	29/31	93.6%
C07	8	7	43/43	100%
C08	6	6	29/30	96.7%
C11	7	7	22/23	96.6%
C13	6	6	34/34	100%
C14	6	7	28/32	87.5%
			Average:	96.1%

Runs were a combination of 2-mix and 6-mix standards

© 2007 TORION TECHNOLOGIES, INC.



Library Matching

- Ion extraction and library matching widely used for compound identification/confirmation
- Works well for:
 - Pure standards
 - Clean samples
- The majority of real world samples are not simple, pure, or single component

© 2007 TORION TECHNOLOGIES, INC.



Potential Interferences

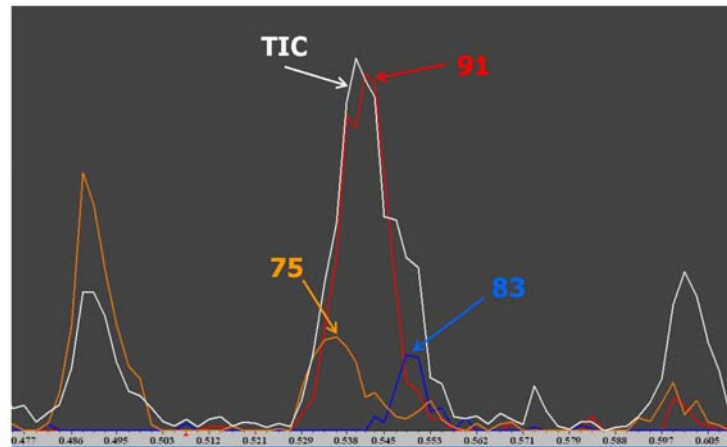
- | | |
|-------------------------|------------------------------------|
| • Artillery Grease | • Jet Fuel/exhaust/vapor |
| • Betadine | • Kerosene |
| • Bleach | • M56 Fog Oil with Graphite |
| • Brake Fluid | • M76 Smoke |
| • Cardboard, Burning | • Menthol Based Supplies |
| • Decon Soln No.2 (DS2) | • Motor Oil |
| • De-Icing Fluid | • Perchloroethylene |
| • Diesel Exhaust | • Polyethylene Glycol (coolant) |
| • Engine Exhaust | • Propellants |
| • Explosives | • Skin Disinfectants |
| • Floor Wax | • Transmission Fluid (Vapor) |
| • Glues and Adhesives | • Waste Products (garbage, sewage) |
| • Insect Repellent | |

© 2007 TORION TECHNOLOGIES, INC.



Deconvolution Benefits

- Original mass spectral data effectively resolved into components
- Extract accurate individual mass spectra for each analyte
- Accurately distribute the signal from masses shared by several components



© 2007 TORION TECHNOLOGIES, INC.



Thank You for Participating Today



TORION TECHNOLOGIES INC.
Solid Science— Creative Ideas— Innovative Products

© 2007 TORION TECHNOLOGIES, INC.

IMPROVING DATA QUALITY WITH AUTOMATED DATA REVIEW

Timothy Fitzpatrick

Laboratory Data Consultants
10647 Old Black Canyon Hwy
Dewey, AZ 86237
619-818-6898
tfitzpatrick@lab-data.com

INTRODUCTION

This paper outlines the integration of Automated Data Review (ADR) into high profile and major Quality Assurance programs. This paper will highlight the features of the ADR software and how the software has improved data quality and streamlined the data review process.

PRODUCT BACKGROUND AND PROCESS OVERVIEW

The ADR software tool was initiated by the US Army Corps of Engineers in 1999 and since utilized nationally under Army Corps, Navy, Superfund, DTSC, Caltrans, Florida DEP, and EPA projects. The software was developed by Laboratory Data Consultants, Inc. under contract to the Army Corps of Engineers, Sacramento District.

The software program uses an electronic data deliverable (EDD) format (ADR A1, A2, A3 text files) based upon data elements originally documented in the Implementation Guide for the Department of Energy Environmental Management Electronic Data Deliverable Master Specification (DEEMS).

Customized modules perform automated data review and provide the user with discrete data qualification based on the EPA functional guidelines for data validation. The data, now appended with a qualifier tag, can then be uploaded to a master database for overall project use. This greatly assists in determining the usability of the data with respect to project-specific QAPP criteria, not merely the contract lab's internal limits.

The EDD format includes QA/QC batch links and routine accuracy and precision parameters such as surrogate, matrix spike, and laboratory control sample recoveries. In addition, initial and continuing calibration and GC/MS tuning data can be delivered in this format, assuming that the lab has the ability to capture these data electronically. Development of the EDD integrated these data elements required by end users with consideration for the current data deliverable capabilities of commercial laboratories.

Once the EDD is prepared, the ADR Contract Compliance Screener (CCS) module verifies the completeness and compliance with the EDD format requirements as contained within the project library. This step is performed by the laboratory prior to sending the EDD to the end user, i.e., consultant, regulator, etc who will be performing that actual data review and applying any

qualifiers. The ADR process is designed so that the laboratory checks every EDD before shipping, thereby minimizing re-issues and errors prior to performing the project level data review.

During CCS, the software references a project-specific library built from data in the project QAPP to verify that all required data are populated and that all populated fields have the proper formatting. Any deficiencies in the EDD are detailed in an outlier report. Access to the EDD file in table format allows for quick and easy correction of errors. Any error that cannot be fixed by the lab is detailed in an error log. The lab then sends the CCS-checked EDD along with the error log to the end user (i.e., consultant, regulator, project chemist, etc.) who initiates the electronic data review process.

The ADR software is initiated by the data user (i.e., project chemist, prime contractor, etc.) to review analytical data based upon project-specific criteria. Upon execution of the program, data is qualified using standard EPA functional guideline data flags and exported in a format compatible with the master database. Command buttons generate reports such as a rejected data table, method blank contamination, surrogate outliers, etc. Forms and view screens also provide on-line review of data qualifiers. ADR.NET has a much larger selection of available reports than its predecessors.

PROJECT LIBRARIES (eQAPPs)

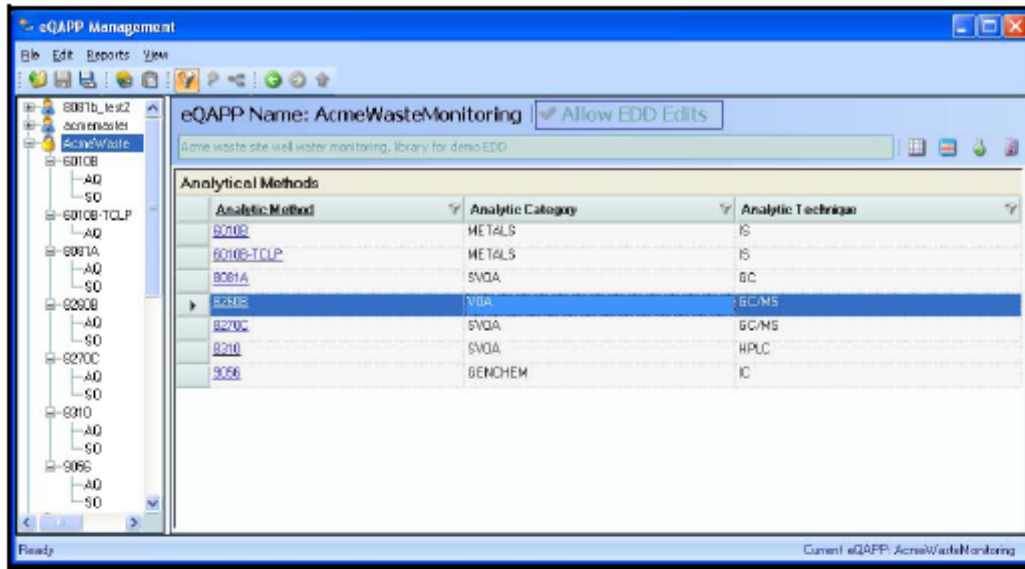
The project library is an electronic representation of the information contained in the project QAPP. This can refer to method QC limits, i.e., MS/MSD, surrogate recovery, etc., field QC, project-specific target analyte lists, project-specific spiking mixes, contract required detection limits (CRDLs), holding times, etc.

It is the end user/project chemist's responsibility to prepare the project library ahead of time and distribute a copy of the library to the laboratory with sufficient lead time before the laboratory begins to receive samples from the project. This is the critical step in the ADR process. The earlier that the lab can be made aware of any project-specific requirements such as special detection limits or target analyte lists, the smoother the process will be for all.

Improvements/modifications in ADR.NET

- New user interface makes building and populating libraries more user-friendly
- Expanded eQAPP features that allow more user flexibility and customization (i.e, user defined matrix IDs, QC Types, and data review qualifiers, grouping analytes within a method, method QC requirements, and others)
- Improved copy and paste capability?
- Server based eQAPPs with full security implementation
- ADR.Net allows user defined valid values for MatrixID and QCType

Figure 1: Project Library (eQAPP) Management Screen



CONTRACT COMPLIANCE SCREENING (CCS)

The first step in using ADR is running the Contract Compliance Screening (CCS) of the EDD(s). This step is performed by the lab prior to delivery of the EDD in order to minimize the number of errors and re-issues from the lab. Data qualifiers are not applied in CCS. The following checks are performed during the CCS process:

- Mandatory Required Fields
- Conditional Required Fields
- Data Types (numerics and dates)
- Field Length
- Logical date checks (collection not later than analysis, etc)
- Valid Values required by ADR and valid values specific to project requirements (methods and analytes)
- QC Batching is correct
- Missing QC samples
- Reporting Completeness with respect to project requirements for target analytes and QC analytes (spikes)
- Reporting limits
- Duplicate Records
- A1/A3 consistency
- If doing Region II then CCS checks U238 against Total U for waters and Th234 against Total U for soils and sediments

Any errors discovered during CCS are viewable in both summary and detailed report formats and tabular format. Tabular format view allows the lab to isolate and fix the errors expediently. Once all errors have been identified and addressed by the lab, the checked EDD is delivered to the consultant/project chemist for data review.

Batching reports are also available from the CCS menu. Batching associations in ADR include:

- Prep Batch: MB, LCS, samples
- Method Batch: MS, sample dup/MSD, samples
- Analysis batch: CCV, ICV, samples

Improvements/modifications in ADR.NET

- Warning log in addition to Error Log
- CCS is done automatically
- Ability to handle different EDD types besides the ADR format, such as ERPIMS and SEDD, striving toward the goal of any EDD in, any EDD out
- Multi-EDD batch processing

Figure 2: CCS Screen

Line	ProjectNumber	ProjectName	ClientSampleID	Collected	MatrixID
1	1001.312	ACME Waste Mon	MBLK100899		AQ
2	1001.312	ACME Waste Mon	MLCS100899		AQ
3	1001.312	ACME Waste Mon	RW-01	10/06/2001 0:00:0	AQ
4	1001.312	ACME Waste Mon	RW-01MS	10/06/2001 0:00:0	AQ

Load Time: 0:2:24

Welcome

Figure 3: Error Log Tabular Format Screen

Contract Compliance Screener
 Edit View Reports Tools Admin Help
 AcmeWasteMonitoring

AW309546
 Sample Analysis
 Calibration
 Analytical Result
 Error Log

AW309546: Error Log (6 of 6)

Line #	Table	Field	Value	Error #	Message	Comments
333	Calibration	ClientAnalyteID	LDC-0454	105	LDC-0454 is not a valid before	
340	Calibration	ClientAnalyteID	LDC-0454	105	LDC-0454 is not a valid before	
1205	Analytical Results	AnalyteType	SPK	28	This AnalyteType is incorrect F	
1390	Analytical Results	RelativePercentDi	18.57922497	105	Value exceeds maximum allo	
1391	Analytical Results	RelativePercentDi	22.22222222	105	Value exceeds maximum allo	
1392	Analytical Results	RelativePercentDi	105.6023773	105	Value exceeds maximum allo	

Load Time: 0:32.716

Figure 4: Error Log

Error Log for Edd net7 Checked Against AcmeWasteMonitoring

EDD Error Log

Lab Reporting Batch ID: net7
 eQAPP: AcmeWasteMonitoring
 Laboratory: LDC

Table	Line #	Column	Value	Error #	Description
Sample Analysis	3	Temperature	NULL	2	Temperature is required for Client Samples and Client QC for Method * and Matrix: 'AQ'.
Sample Analysis	3	LabAnalysisRefMethodID	NULL	103	LabAnalysisRefMethodID is a required field.
Sample Analysis	4	Temperature	NULL	2	Temperature is required for Client Samples and Client QC for Method * and Matrix: 'AQ'.
Sample Analysis	4	LabAnalysisRefMethodID	NULL	103	LabAnalysisRefMethodID is a required field.
Analytical Results	5			102	Orphan row.
Analytical Results	6			102	Orphan row.
Analytical Results	7			102	Orphan row.
Analytical Results	8			102	Orphan row.
Analytical Results	9			102	Orphan row.
Analytical Results	10			102	Orphan row.

DATA REVIEW MODULE

After receiving the checked EDD from the lab, the consultant/project chemist then runs the data review. The user is prompted to assign field QC after selecting data review from the menu. Data review proceeds automatically from this point. At the conclusion of the review process, the chemist can review and choose to override any qualifications based on professional judgment. Any manual changes are documented in a history file with the reason for the change, the person who made the change and the date and time the change was made.

A number of summary and detailed reports are available in ADR.NET (see figures 7 and 8 for some examples). The other end product is the qualified data. Once the data is qualified, the user selects the desired format for the data to be exported in and the process is completed.

Improvements/modifications in ADR.NET

- Data review is done automatically
- User is prompted to assign field QC when data review is selected from the menu
- Multi-EDD batch processing
- Professional Judgment
- List of new parameters that can be reviewed now, e.g., Int Stds, etc
- Improved editing of data review qualifiers that update changes on a QC batch basis
- Future expanded data review capability to consider additional information in SEDD (i.e. GC/MS internal standards, second column verification, metals calibration standards such as ICB and CCB, recalculation of results from raw data, and others)
- Internet deployment with automatic upgrades and bug fixes

Figure 5: Assign Field QC before Data Review

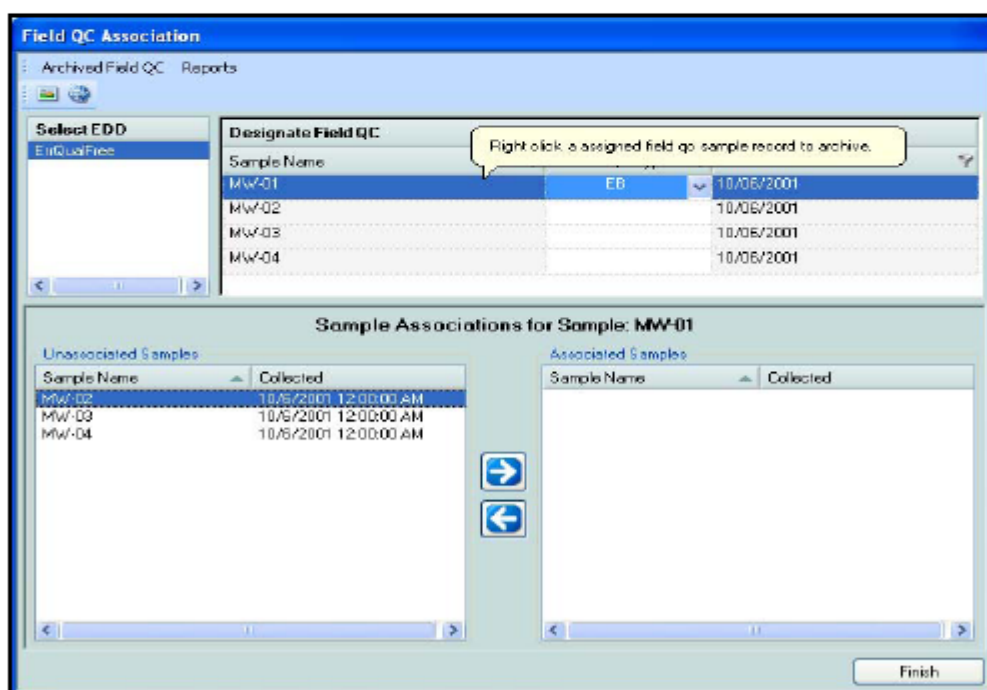


Figure 6: Data Review Main Screen

The screenshot shows the 'Data Review' application window. The main area displays a table of analytes for sample MW-01, collected on 10/6/2001 at 12:00:00 AM. The table includes columns for Analyte Label (CAS), Analyte Name, Result, Modified Result, Units, Lab Qualities, and Detection Limit. Below this table is a section for 'Associated Quality Control' showing 'Matrix Spike results for Method Batch: FMB10039W' with columns for Analyte Label (CAS), Analyte Name, MS Percent Recovery, MSD Percent Recovery, and RPD.

Analyte Label (CAS)	Analyte Name	Result	Modified Result	Units	Lab Qualities	Detection Limit
5103-74-2	GAMMA-CHLORDAZIE	0.05		UG/L	U	0.05
76-44-8	HEPTACHLOR	0.05		UG/L	U	0.05
1024-57-3	HEPTACHLOR EPOXIDE	0.05		UG/L	U	0.05
72-43-5	METHOXYCHLOR	0.05	05	UG/L	J	0.1
8001-35-2	TD-WAPHENE	0.0		UG/L	U	1.0
319-85-7	BETA-BHC	0.05		UG/L	U	0.05
319-85-8	DELTA-BHC	0.05		UG/L	U	0.05
60-57-1	DIELDRIN	0.10		UG/L	U	0.05
959-99-9	ENDOSULFAN I	0.05		UG/L	U	0.05
33213-85-9	ENDOSULFAN II	0.10		UG/L	U	0.05

Analyte Label (CAS)	Analyte Name	MS Percent Recovery	MSD Percent Recovery	RPD
300-00-2	ALDRIN	71	75	5
60-57-1	DIELDRIN	75	85	13
72-30-8	ENDRIN	71	88	21
58-89-9	GAMMA-BHC	85	81	5
76-44-8	HEPTACHLOR	77	81	5

Figure 7: Example Summary Qualifier Report

The screenshot shows a 'Data Qualifier Summary' report. It includes a header with 'Lab Reporting Batch ID: ErrQualFree', 'Laboratory: LDC', 'EDD Filename: ErrQualFreeA3.txt, ErrQualFreeA2.txt, ErrQualFreeA1.txt', and 'eGAPP Name: AcmeWasteMonitoring'. Below this is a table for 'Method Category: GENCHEM' and 'Method: 9056'. The report is divided into sections for four samples (MW-01, MW-02, MW-03, MW-04), each with a table of analyte results including Lab Result, MDL, RL, Units, Lab Qual, Data Review Qual, and Reason Code.

Analyte	Lab Result	MDL	RL	Units	Lab Qual	Data Review Qual	Reason Code
CHLORIDE	0.2	0.1	0.20	MG/L		J	Lcc

Analyte	Lab Result	MDL	RL	Units	Lab Qual	Data Review Qual	Reason Code
CHLORIDE	810	1	2	MG/L		J	Lcc

Analyte	Lab Result	MDL	RL	Units	Lab Qual	Data Review Qual	Reason Code
CHLORIDE	490	1	2	MG/L		J	Lcc

Analyte	Lab Result	MDL	RL	Units	Lab Qual	Data Review Qual	Reason Code
CHLORIDE	170	1	2	MG/L		J	Lcc

Figure 8: Example Detailed Qualifier

Matrix Spike/Matrix Spike Duplicate Outlier Report							
Lab Reporting Batch ID: AW089546				Laboratory: LDC			
EDD Filename: AW089546A3.txt, AW089546A2.txt, AW089546A1.txt				eQAPP Name: AcuteWasteMonitoring			
Method: 8056							
Matrix: AQ							
QC Sample ID (Associated Samples)	Compound	MS %R	MSD %R	%R (Units)	RPD (Units)	Affected Compounds	Flag
MW01 B3 MW01 MW02 MW02 MW04	BETANOL	13	-	10.00-110.00	-	BETANOL	J (Off-Scale) R (All non-detect)
Method: 80100							
Matrix: AQ							
QC Sample ID (Associated Samples)	Compound	MS %R	MSD %R	%R (Units)	RPD (Units)	Affected Compounds	Flag
MW01 B3 MW01 MW02 MW02 MW04	MW01AM03B	58	-	10.00-110.00	-	MW01AM03B	J (Off-Scale) R (All non-detect)
Method: 8310							
Matrix: AQ							
QC Sample ID (Associated Samples)	Compound	MS %R	MSD %R	%R (Units)	RPD (Units)	Affected Compounds	Flag
MW01 B3 MW01	ACENAPHTHENE	-	48	50.00-110.00	20 (25.00)	ACENAPHTHENE	
	ARTHRACENE	-	-	50.00-110.00	30 (25.00)	ARTHRACENE	
	FLUORANTHENE	-	-	50.00-110.00	87 (25.00)	FLUORANTHENE	
	FLUORIDE	-	48	50.00-110.00	50 (25.00)	FLUORIDE	J (Off-Scale) U (All non-detect)

CONCLUSION

In conclusion, the ADR software was developed as a tool to support technical staff in the evaluation of analytical chemistry data using an expedited and cost effective automated process. The software was not intended to replace a chemist and requires use by an experienced chemist to layer on professional judgment and review areas of the data package not encompassed by the ADR review. ADR.NET has incorporated several new features to further enhance the abilities of the original ADR application.

2008 NEMC Proceedings

INTERNATIONAL ISSUES

A Look at the Environmental Situation in China and South East Asia

Zoe Grosser; Perkin Elmer Analytical Sciences, 710 Bridgeport Ave., Shelton, CT 06484; 203-402-5320; zoe.grosser@perkinelmer.com

David Friedman; Friedman Consulting, LLC, 10817 Rippon Lodge Drive, Fairfax, VA 22032; 703-389-3821; friedmanconsulting@cox.net

ABSTRACT

The nations of the Pacific Rim have increasingly become concerned about environmental issues due to a number of factors. Some of these include: climate change and its impact on these countries with their large coastlines, low lying regions, and sensitive ecosystems; the increasing awareness of how pollutants impacting their ecosystem result from migration through the atmosphere from neighboring countries; water pollution that because of its affecting on the food that they grow/catch is having a significant impact on worldwide food sales; pollution caused contamination of herbal based medicinal products and its negative impact on their production and sale; and the tremendous impact pollution is having on the health and well being of the population of some of these countries. This paper will be presented in two parts. The first presentation will review and discuss environmental monitoring in China and the second in Korea, Singapore, Malaysia, Thailand and Australia. For each country, the authors will discuss the growing importance of environmental issues, the overall state/health of the environment, and will highlight the environmental testing situation in the country.

INTRODUCTION

The nations of the Pacific Rim have increasingly become concerned about environmental issues due to a number of factors. Some of these include: climate change and the impact rising ocean levels may have given their large coastlines and low lying areas; the increasing awareness of how pollutants impacting their ecosystems have been impacted by pollutants coming to them through atmospheric transport; water pollution that because it has resulted in contamination of the food they grow and catch is having a significant impact on worldwide food sales; pollution caused contamination of herbal based medicinal products and its negative impact on their production and sale; and the tremendous impact pollution is having on the health and well being of the population of some of these countries. In China, for example, pollution of surface waters has had a tremendous negative impact on the quality of water used for drinking and irrigation. While not all of these countries are experiencing all of these problems, all are impacted by, at least, several of the above issues. The presentation will be in two parts. The first part will focus on China and the second on Korea, Singapore, Malaysia, Thailand and Australia.

In our talks today, we will give a brief overview of the environmental situation in each of the countries. Our focus will be to try and give you a sense of the trends taking place and, where we can, discuss the impact the changes will have on environmental monitoring in each country. Having recently just visited the region and meeting with scientists from commercial, academic and government laboratories involved in monitoring, we can assure you that improving and expanding their monitoring capabilities and programs are of great interest in all the countries.

CHINA

China is the most populated countries in the world having more than 1.3 billion people living in a land area slightly smaller than the United States. The country has undergone tremendous industrial growth over the past decade and suffers from many environmental problems. These include: air pollution (greenhouse gases, sulfur dioxide particulates) from reliance on coal which produces acid rain; water shortages, particularly in the north; water pollution from untreated wastes; deforestation; the estimated loss of one-fifth of agricultural land since 1949 to soil erosion and economic development; desertification; and trade in endangered species.

The northern part of China suffers from terrible drought conditions. This is critical since they are trying to feed 20% of the world's population on 7% of the land. The Gobi Desert seems to be spreading and to what extent global climate change is increasing the severity of the sand storms is unknown. The problem is so severe that they are trying to reclaim desert by using water from the Yalu River, massive irrigation projects and planting of millions of trees. Water levels in the reservoirs which supply Beijing, are falling and a \$56 billion water diversion project to move water from the South to the North is underway. This 50+ year project will require the construction of 160 miles of tunnels through mountains. One of the many problems with using southern water to provide drinking and irrigation water to the North is that the southern rivers are polluted. They will have to be cleaned up before they can be used. For example, the Han River at Wuhan is so polluted that people are banned from even boating on it. Fish are dying and it has been reported that even contact with the water is dangerous. (7C)

From personal observation, I can tell you that the air is terrible and the surface waters heavily polluted to the point of posing an acute health hazard to the people who drink water, irrigate their crops, or eat the fish from these rivers and lakes. As anyone who has read the paper or seen the news on television knows air pollution is such problem that the government is having to take drastic steps just to try and get the air in Beijing clean enough so as not to threaten the Olympics. They plan to stop all construction in and around the city, ban half of the vehicular traffic, turn off power plants, and even force factories in and around Beijing to stop production.

Looking at a few reported statistics (6C), it is obvious that China has major problems in all environmental areas, but that a great deal of progress has been made. For example:

Indicator	2000	2005
Waste Water Discharge (100 million tons.)	415	525
Proportion of Industrial Waste Water Meeting Discharge Standard (%)	77	91
Waste water treatment facilities	64453	69231
Industrial air emissions (non-power generation)(100m cu. m.)	56032	113749
Emission of Industrial Dust (10K tons)	1092	911
Industrial solid waste generated (10K tons)	81608	134449
Hazardous industrial solid wastes utilized (%)	46	56
Households with access to sanitation lavatory (%)	44.8	55.3
Sulfur dioxide emissions (10K tons)	1995	2549
Forest area (10K hectares)	15894	17491
Wetland (10K hectares)	3849 (2003)	3849

The government reports that 116 million people currently breathe air that the government considers dangerous to health and that 400,000 people die from pollution every year. (7C) Contributing to this problem is the fact that China uses a great deal of high-sulfur coal to generate power and few power plants practice sulfur dioxide removal.

Recognizing that their environmental problems have reached a crisis, at the Chinese Communist Party Congress held last October, the leadership of China identified that sustainable development and protecting the environment will be a major focus of the country's new 5 year plan. As the chairman of the Party stated in his report to the assembled leadership, "Improve energy, resources, ecological and environmental conservation and enhance China's capacity for sustainable development. Adhering to the basic state policy of conserving resources and the environment is vital to the immediate interests of the people and the survival and development of the Chinese nation. We must give prominence to building a resource-conserving, environment-friendly society in our strategy for industrialization and modernization and get every organization and family to act accordingly. We will improve laws and policies to promote energy, resources, ecological and environmental conservation, and speed up the formation of systems and mechanisms for sustainable development. We will implement the responsibility system for conserving energy and reducing emissions. We will develop and extend advanced and appropriate technologies for conserving, substituting and recycling energy and resources and for controlling pollution, develop clean and renewable energy sources, protect land and water resources and set up a scientific, rational system for using energy and resources more efficiently. We will develop environmental conservation industries. We will increase spending on energy and environmental conservation with the focus on intensifying prevention and control of water, air and soil pollution and improving the living environment for both urban and rural residents. We will improve water conservancy, forestry and grasslands, intensify efforts to bring desertification under control and prevent the spread of stony deserts, and promote restoration of the ecosystems. We will enhance our capacity to respond to climate change and make new contributions to protecting the global climate." It has been estimated that the cost for China to clean up its environment will decrease economic growth by about 8%.(7C)

The government has begun to take steps to implement this program. These include the establishment of a new ministry, the State Environmental Protection Administration (SEPA). This will raise the environmental protection organization to full ministry status in the government in order to give it more weight. According to Wang Yuqing, former environmental ministry deputy director, "the elevation will enable the agency to join every important meeting of the State Council, and ensure environmental protection efforts are better integrated into the decision-making process. The new ministry will also have more staff and greater financial support." James Zimmerman, chairman of the American Chamber of Commerce in China, said: "SEPA's elevation to ministry level reflects the government's commitment to sustainable development and environmental protection. It's progression from a lower-level bureau, under the Ministry of Construction to a ministry within just 10 years is a reflection of the change in thinking and heightened awareness of the need to better manage growth."(3C)

However, SEPA will not have direct authority over local anti-pollution agencies. Local governments will keep control of the budgets and staffing of the local regulatory enforcement officials who are charged with enforcing the permits and pollution standards. According to the China Post, "rapid industrialization over the past three decades has battered China's air, water, and land, sparking social unrest and dragging on economic growth. SEPA officials have openly lamented that central government directives are ignored by growth-hungry local officials." (4C)

During a recent visit to China, we were encouraged by the number of scientists that attended the monitoring seminars and the expanded resources that they seem to be receiving. For example, meeting with staff of the new Waste Research Institute, David found them in a large, research center that had only recently been completed and in the process of installing large numbers of modern, instruments procured from Western companies. The government established this institute to provide scientific support to SEPA in the areas of solid and hazardous waste management. It was interesting to see that China recently adopted the TCLP for their waste management program, although the test is used differently than we use it in the US.

In their new five year plan, SEPA listed a number of steps related to environmental monitoring that will be taken during the 2007 – 2010 period. These include:

- Efforts will be made to ensure that automatic air quality monitoring stations are installed in each prefecture-level city, and baseline monitoring stations will be established in rural areas. In addition, acid deposition, sand, and dust monitoring will be conducted.
- A national surface water monitoring system will be established which will focus on real-time monitoring to detect pollution accidents and trans-boundary movement of pollutants.
- Conduct routine monitoring of surface water, drinking water sources, solid waste, soil ecology, noise, and coastal sea water. Establish a nation radiation monitoring network to identify releases from nuclear facilities.
- Procure environmental emergency response monitoring vehicles (mobile laboratories) for use in emergencies and accidents. Equip county monitoring stations with necessary laboratory equipment (goal is to reach 90% in East China, 80% in Central China, 60% in West China).
- Put in place the necessary infrastructure to support the environmental protection program which includes developing the needed research and engineering centers, monitoring laboratories, reference standards, and national environmental information system. (5C)

The China National Accreditation Service is the national accreditation body authorized by both China's State Bureau of Technical Supervision (CSBTS) and by law. It was established in 2002 and is responsible for the accreditation of laboratories throughout China. Currently its web site (www.cnas.org.cn) lists 406 laboratories accredited for environmental monitoring. Most seem to be government or in-house laboratories of private companies or municipal water facilities.

AUSTRALIA

While Australia is only slightly smaller geographically than the United States it has a much fewer people. Its population is only 20 million and most of the people live in a few coastal cities. Much of the country is relatively desolate and has poor agricultural productivity. In flying across the width of the country, I was personally amazed by the desolateness. Compounding the problem, for a number of years now, the country has been suffering from lack of rainfall and drought is a problem. Other significant environmental problems facing the country include: soil erosion from overgrazing, industrial development, urbanization, poor farming practices; rising soil salinity due to the use of poor quality water for irrigation; desertification; clearing of land for agricultural purposes which threatens the natural habitat of

many unique animal and plant species; limited natural fresh water, and destruction to the Great Barrier Reef off the northeast coast. (3A).

Responsibility for protecting the environment in Australia is split between the federal government (the Department of the Environment, Water, Heritage and the Arts which was previously called the Department of the Environment and Water resources)(DEWHA) and the states. The states and territories appear to have a larger role, more responsibility, and more independence in environmental matters relative to the federal government that we have in the United States. It reminds me of the Canadian model. It seems that DEWHA functions on a mega level being responsible for issues such as biodiversity, sustainable development of large river basins, providing resources to state governments for land preservation. It works with various stakeholders including the states and territories, industry, and public groups to develop guidelines and agreements. The federal government does not appear to be doing much water quality monitoring. According to a National Land and Water Resources Audit of water monitoring in Australia, the state and territorial agencies conduct about 70% of the water quality monitoring, local governments about 19%, and federal agencies, industry, community groups and others the remaining 11%. The report further went on to state that "with such a wide range of organizations providing data, incompatibilities can occur, sometimes making it difficult to interpret and compare results." While guidelines have been developed for conducting scientifically valid water monitoring programs, such guidelines do not appear to be mandatory.

The environment ministry periodically issues reports describing the state of the Australian environment and their activities. In 2007, they reported that the government implemented major initiatives to deal with climate change, water resource management, and environmental impact assessment. One area that was highlighted in the 2007 report was the need for better quality baseline information to assess changes in the environment over time. The report indicates that government plans to develop improved monitoring methods and tools and conduct increased monitoring. (5A)

Turning now to the issue of air quality. In 1998, the National Environment Protection Measure for Ambient Air Quality went into effect. The measure requires the various states and territories to monitor air quality for six pollutants. These are: carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide, PM 10 and PM 2.5. The law gives the federal government responsibility for those regions that are under federal jurisdiction and have populations above 25,000. Currently there are no such regions so the monitoring is conducted by the six states and territories and each issues its own annual reports on air quality. Air quality is a problem in many parts of the country. For example, in New South Wales which includes the cities of Canberra and Sydney, the air quality was generally compliant with the standards for carbon monoxide, nitrogen dioxide, sulfur dioxide but problem levels were found for particulate matter and ozone. Part of the problem is that Australia has been suffering drought conditions for a number of years and brush fires, dust storms have all been contributing to the problem in addition to emissions from motor vehicles, industry, and heating. In speaking with a resident of Perth, which is located in Western Australia, I learned that Western Australia has been suffering from drought conditions for the past 5 years.

Australia has many laboratories engaged in environmental testing and monitoring. These include: commercial, government, quasi-government, and academia. In 1991, the National Association of Testing Authorities (the Australian laboratory accreditation body) began to see a strong increase in requests for registration of laboratories involved in environmental testing.

These accreditations are for areas such as soil and water testing, air monitoring and the analysis of stack gas emissions. Currently, 371 organizations are listed as being accredited for one or more types of environmental testing. In a manner a bit reminiscent of our own DOE National Laboratories, Australia has its Commonwealth Scientific and Industrial Research Organization. This is an independent organization but, but it is not only chartered by the government, but members of the government serve on its Board. It provides scientific services (including environmental monitoring and assessment services) to government and industry. It is the largest employer of scientists in Australia having a staff of over 6,500 people in 57 locations and, to some extent, competes with private sector testing organizations. (4A)

KOREA

South Korea is about the size of the state of Indiana and has a population of 48 million people. It is considered to be one of the Asian Tigers and has undergone a tremendous industrialization and growth of its economy. Major environmental issues facing Korea include: air pollution in large cities, acid rain, water pollution from the discharge of sewage and industrial effluents, and drift net fishing. (1K)

Korea's environmental program began in 1980 with the establishment of the Environment Administration (EA) and six regional environmental monitoring offices. Even then they recognized the importance of recycling by establishing the Korea Recovery and Reutilization Corporation. (2K) Over the years, the EA's responsibilities increased, its importance increased, and it became the Ministry of Environment. In addition, a National Institute of Environmental research was established which is responsible for research in areas such as: environmental assessment, recycling and reuse of wastes, assessment of health risk from pollutants, drinking water and indoor air pollution, cap and trade systems, and environmental measurement standards. (3K)

With the increased income and standard of living of its people, there has been an increased demand for improving environmental quality and protecting the environment. (4K). As a result, in the past two years, over 28 new or revised environmental laws were enacted addressing issues as diverse as water pollution, persistent organic pollutants, climate change, and noise pollution. Reflecting this increased call for improvement, the past 5 years has seen investment in environmental protection increase at an annual average of over 7% and the budget for the Ministry increased by over 4%. Highlighting the importance of water, water supply, water quality, and sewage services received the bulk of the increases and saw an average annual increase of over 29%. Recently, the allocations for air quality, nature conservation and environmental health have been reported to be receiving increased attention.

Each year the Ministry publishes its Green Korea report (now called ECOREA) presenting a picture on the state of the Korean environment and its activities. (5K) In determining water, air, and soil quality they rely on a variety of monitoring studies. Air in the major cities is monitored for sulfur dioxide, PM 10, acid rain, ozone, and nitrogen dioxide. Surface water is monitored for BOD, pH, suspended solids, dissolved oxygen and coliform bacteria. Ground water quality was monitored at 2462 sites and they reported that the water was analyzed for general bacteria, Ph, NO3-N, chloride and trichloroethane. To identify soil contamination due to improper waste disposal, a nationwide series of soil monitoring stations which began in 1987 with 250 stations and now encompasses 4500 stations has been established. The soil is tested for cadmium,

copper, arsenic, mercury, lead, chromium (6), zinc, nickel, fluoride, organophosphate, PCB, cyanide, BTEX, TPH, TCE, and PCE.

A relatively small number of laboratories have been accredited by the Korea Laboratory Accreditation Scheme (the national accreditation body) for conducting chemical tests of air, water, waste, or soil. Many of them are either captive industrial laboratories or government bodies of one level or another (i.e., city, federal, national research institute). (6K)

MALAYSIA

Malaysia is slightly larger than our state of New Mexico (127 K square miles) but with a population of 27 million people. Increasing urban migration has resulted in more than half of the population now living in urban areas. Since the issuance of the Environmental Quality Act of 1974, Malaysia has developed a significant environmental monitoring program. In 1983 the Department of Environment was established and has grown to a staff of more than 1500 employees located in over 40 offices across the country. Each year the Malaysian Department of the Environment publishes a report on the status of the environment based on the country's extensive monitoring program.

Monitoring is conducted of the air, noise, rivers, ground and near shore marine waters. In 2006, the air was being monitored through a network of 51 automated ambient air monitoring stations located in residential, urban and industrial areas which is supplemented by manual air quality monitoring stations at an additional 19 sites. Based on the monitoring data, the DOE reported that, from 2005 to 2006, the overall air quality in Malaysia deteriorated slightly. Since 2006, the number of air monitoring sites has continued to increase. (3M)

The DOE initiated its river water quality monitoring program in 1978 in order to establish baselines and detect changes in river water quality. The monitoring has since been expanded to identify sources of pollution. In 2006, the monitoring network encompassed a total of 1,064 water quality monitoring stations covering 146 river basins. The Department employs a Water Quality Index (WQI) to evaluate the status of river water quality which consists of parameters such as Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand, Ammoniacal Nitrogen, Suspended Solids, and pH. In 2006, based on the WQI, 58% of the rivers were found to be clean, 34% slightly polluted, and 8% of unacceptable quality.

Recognizing the importance of ground water as a source of drinking water, in 1997 the DOE expanded its environmental monitoring program to include a National Groundwater Monitoring Programme. By 2006, a network of 88 monitoring wells had been established. The sites were selected to include sites subject to impact from agricultural, urban/suburban communities, industrial sources, landfills, mining, aquaculture, and others.

In its National Policy on the Environment that was updated in October 2007, the Government of Malaysia committed itself to expanding its environmental quality monitoring programme in order to strengthen its environmental enforcement program and to enable the Department to generate comprehensive annual environmental status reports.

The DOE monitoring program is conducted under a contract with a private company Alam Sekitar Malaysia Sdn Bhd (ASMA). ASMA was incorporated in 1993, and in 1995 received a 20-year concession to provide air and water quality monitoring for the DOE. Its concession includes:

- The establishment and implementation of a comprehensive national environmental monitoring programme;
- The collection, processing, interpretation, analysis and dissemination of environmental data;
- The establishment and management of National Environmental Data Center;
- The provision of primary source of environmental database for the country.

In addition to ASMA, Malaysia has other commercial companies providing commercial environmental monitoring services. These include: Chemsain Konsultant, Permulab (water/air), Asia Pacific Environmental Consultants (water/air), DHI Water and Environmental (water).

SINGAPORE

Singapore is very small country. It is a City-State consisting of one city which is about 3.5X the size of the District of Columbia but with a much larger population. It has a population of about 3.5 million people. Singapore is located on the southern end of the Malaysian peninsula and across the Singapore Strait from Indonesia. It is a beautiful place with a great deal of lush vegetation.

Environmental problems include: industrial pollution; limited supplies of natural fresh water; limited land availability presents waste disposal problems; and seasonal smoke/haze resulting from forest fires and agricultural land clearing in Indonesia. (1S) Due to its large coastline (193 km) and critical role that ocean shipping plays in the economy of Singapore, oil spill and maritime pollution are also major concerns and focuses of the government. The Maritime and Port Authority of Singapore (MPA) is responsible for marine environment protection from sea-based activities.

The Ministry of the Environment and Water Resources (MEWR) started as the Ministry of the Environment in 1972 and in 2004, the current name took effect to reflect the ministry's expanded role in managing water as a strategic national resource.

Rainwater is collected in reservoirs and about half of Singapore is being utilized as catchments for rainwater collection. The government plans to increase the catchment area to include about two-thirds of the island. To add to the water supply, desalinated water and water reclamation are employed.

Singapore maintains its ambient air quality through stringent emission standards, promoting energy efficiency, and using energy sources such as natural gas that emit less pollutants. As a result, the ambient concentrations of most major air pollutants (sulphur dioxide, nitrogen oxides, carbon monoxide, ozone, particulate matter below 10 microns) have stayed within US Environmental Protection Agency (USEPA) Ambient Air Standards. Singapore has managed to

achieve the PSI (Pollutant Standards Index) in the “Good” range for at least 85% of the days in the year from 2003 to 2006.

An emerging pollutant of concern is particulate matter smaller than 2.5 microns in size (PM_{2.5}), which has been linked to respiratory effects such as bronchitis and asthma. Singapore, like many other urban cities, cannot meet the USEPA standard for PM_{2.5}. As diesel vehicles account for about half of the PM_{2.5} present in ambient air, stricter emission standards have been adopted for new diesel vehicles to reduce this problem. In addition to this, we can all strive to keep our air clean for as long as possible by conserving electricity and taking public transport. (2S)

Currently about 45% of the country’s solid waste is incinerated while 4% is landfilled. The remaining 51% is recycled. The country has only one landfill. What to do, in the future, with solid wastes is an issue since building landfills is not easy given the scarcity of land.

I can’t say much about environmental monitoring Singapore. According to their environmental plan for the next 5 years, they plan to push industry to conduct more emissions monitoring. The focus seems to be on air emissions. Singapore conducts monitoring of persistent organic pollutants (POPs) as part of their obligations under the Stockholm Convention. They monitor for aldrin, endrin, chlordane, dieldrin, DDT, heptachlor, toxaphene, hexachlorobenzene, dioxins, and furans in their inland waters. They annually check for dioxins and furans in the municipal solid waste incinerator emissions. Toxic industrial and biohazard incinerators, which are privately owned, are required to conduct annual monitoring. Since 1999, the ministry conducts annual monitoring for dioxins and furans in ambient air and has never detected same.

THAILAND

Thailand is a bit more than twice the size of Wyoming (198 K square miles) with a population of 65 million people. About 40% of the country’s land area consists of agricultural land. In response to the impact pollution was having on the country’s economy, Thailand began its environmental protection program in 1975 with the enactment of its first environmental protection law “Enhancement and Conservation of National Environmental Quality”. At the time, the government also established the National Environmental Board. This law was amended several times and in 1992 was reformulated to cover environmental tasks of local, national and international levels, and by 2003 responsibility for environmental protection was transferred to the new Ministry of Natural Resources and Environment.

In 2000, Thailand launched a project to report the progress and achievements that the country had made in implementing the Agenda 21 Agreement (2T) which Thailand and over 180 other countries have adopted. At the time, they found that the country did not have the necessary data to meet the requirements of the UN’s Commission on Sustainable Development. As a result, Thailand has initiated a program to develop a system of environmental indicators and monitoring to determine the state of its environment.

Major environmental problems facing the country include: air pollution from vehicle emissions in major cities; water pollution from organic and factory wastes; increasing demands for potable water coupled with drought conditions and increasing levels of pollution in watershed rivers, wildlife populations threatened by illegal hunting, and loss of agricultural land due to improper

land management and deforestation. Due to the political changes that have been taking place in the country, it has been reported that enforcement of environmental regulations has been a serious problem.

For the past several years, the Thai Office of Natural Resources and Environmental Policy and Planning (ONEP) issues its State of the Environment Report. The 2005 report is the latest that has been published and highlights significant environmental issues facing the country in 2005. These include: disasters from tsunamis, drought, hazardous substances and waste, protecting their Tha Chin Watershed global climate change, and open burning. As you can see, these are qualitatively different types of monitoring and impact assessment methodology problems than those facing us here in the United States. For example, a tsunami hit the Southern part of the country in December 2004 and affected almost 60,000 people in 407 villages and severely damaged the coastal environment. This included damage to coral reefs, loss of mangrove forests, damage to beaches and coastal areas, damage to drinking water wells and infrastructure, and problems with solid wastes and wastewater.

In 1975, Thailand instituted a program that requires any new facility that might have a significant impact on the environment is required to conduct an environmental impact assessment prior to construction. The Ministry of Natural Resources and Environment reviews these impact assessments. How the environmental performance of the project can and will be monitored is an integral component of the assessment. Assessments are prepared by consulting firms which must be registered with and licensed by the Ministry. Many of the consultants perform environmental monitoring as part of their services. Currently there are 51 registered consulting firms. As near as I can tell, the monitoring requirements of these assessments and of the facility's ongoing operations are minimal.

Thailand has a number of environmental monitoring laboratories. These include government, captive laboratories belonging to the private sector, and commercial service laboratories. Currently there are 31 environmental testing laboratories accredited according to ISO 17025 by the Thai Industrial Standards Institute which is part of the Ministry of Industry (4T). Several members of the US testing community have commercial testing laboratories in Thailand.

REFERENCES

- (1C) The World Factbook, CIA
- (2C) Report by Premier Hu Jintao to 17th Congress of Chinese Communist Party, October 2007
- (3C) China Daily March 13, 2008.
- (4C) China Post, March 14, 2008
- (5C) The National Eleventh Five-year Plan for Environmental Protection (2006 – 2010), SEPA, March 5, 2008
- (6C) China Environmental Statistical Yearbook 2006,
- (7C) China from the Inside, May 11, 2008 WETA (www.PSS.org)

- (1A) Quality Monitoring Guidelines, Section 1.1, Joint Primary Industries Ministerial Council and Natural Resources Management Ministerial Council, October 2000.
- (2A) 2007 Annual Report, Department of Environment, Water, Heritage and the Arts.
- (3A) The World Factbook, CIA
- (4A) National Association of Testing Authorities (www.nata.asn.au)

- (5A) Department of the Environment and Water Resources Annual Report 2006 – 2007
(www.environment.gov.au/about/publications/annual-report/06-07)
- (1K) The World Factbook, CIA
- (2K) Ministry of Environment (www.eng.me.go.kr)
- (3K) National Institute of Environmental research (www.eng.nier.go.kr)
- (4K) Green Report 2006
- (5K) ECOREA 2007
- (6K) Korea Laboratory Accreditation Scheme (www.kolas.go.kr)
- (1M) Malaysian National Policy on Environment, Oct 2006
- (2M) Malaysian Department on the Environment 2006 Environmental Quality Report
- (3M) Alam Sekitar Malaysia Sdn Bhd (2008)
- (1S) CIA World Factbook, 2007
- (2S) Singapore Department of Environment and Water Resources (<http://app.mewr.gov.sg>)
- (3S) Singapore Green Plan (2006)
- (4S) Singapore Stockholm Convention Implementation Plan 2007
(www.pops.int/documents/implementation/nips/submissions/singapore.pdf)
- (1T) Thailand Office of Natural Resources and Environmental Policy and Planning site
(www.onep.go.th)
- (2T) Rio Declaration on Environment and Development, United Nations 1992
- (3T) The World Factbook, US CIA 2007
- (4T) Thai Industrial Standards Institute (www.tisi.go.th)

Challenges of Global Monitoring Programs

Andrew Eaton
MWH Laboratories
750 Royal Oaks Drive #100
Monrovia, CA 91016
626-386-1125
andrew.d.eaton@us.mwhglobal.com

ABSTRACT

With the onset of "globalization" in the environmental testing business a whole new set of challenges is presented to the testing laboratory. Issues range from the relatively simple (language barriers) to logistical (which couriers can provide timely delivery) to the important aspect of assessing data usability when samples are not received in a timely manner or with improper preservation or at room temperature. Over the last 3 years we have performed numerous investigations of the impact of these sources of uncertainty. Results of those studies suggest that a) EPA preservation requirements are in some cases overly conservative; b) refrigeration is the most effective preservation for many organic constituents c) depending on a client's monitoring triggers, increasing the sensitivity of analytical methods can sometimes compensate for potential sample degradation, but may require significant data qualification. Educating global clients on uncertainty in analytical monitoring programs is an even greater challenge.

INTRODUCTION

Water quality monitoring around the world is performed to meet a variety of needs. These include required monitoring for regulatory compliance, such as EPA, FDA, WHO, or EU, process control and treatment optimization, or response to potential emerging contaminants. By far the most common reason for monitoring is in response to regulatory demands.

Standards for water quality vary globally. In the United States monitoring standards are generally based on the Environmental Protection Agency's (EPA) Safe Drinking Water Act (SDWA) requirements. EPA currently regulates over 80 constituents in potable water, encompassing inorganics, organics, and microbials. EPA also mandates specific test methods for analysis.

In other parts of the world, water quality monitoring is based on World Health Organization (WHO) guidelines, which overlap to a certain extent with EPA standards, but often have differences in acceptable concentrations and also have a number of constituents that are different from the EPA list. Additionally WHO does not mandate any specific methodologies for testing, but instead relies on quality systems (ISO17025) as a basis for data quality.

The European Union (EU) has also provided guidelines for water quality monitoring. A key element of the EU monitoring requirements is the restriction of individual pesticide concentrations to 0.1 ug/L (ppb), which is subject to both significant analytical and sampling challenges.

NEMC 2008

BACKGROUND

In the past few years we have been involved in several global water quality monitoring programs that have presented unique challenges in order to maintain any degree of integrity to analytical results. Issues have included language barriers, logistics associated with transport issues (both directions), developing analytical methods to consistently meet client requirements for sensitivity and accuracy, and maintaining sample integrity (or at least being able to assign uncertainty to the resulting values). Straddling the fence between performance-based approaches and the rigorous requirements of EPA mandated methods has presented both unique opportunities and unique challenges which will be discussed, along with solutions and remaining issues.

Language Barriers

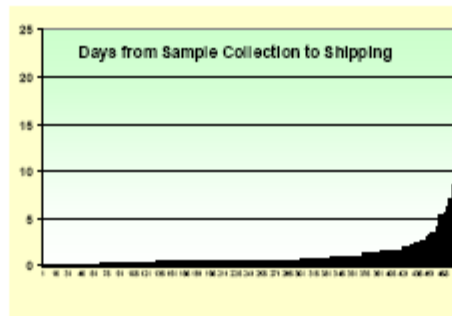
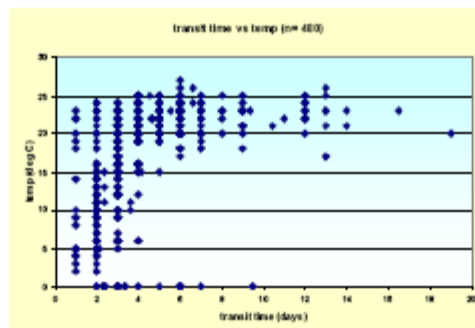
There are actually two types of language issues that can impact data usability. One is not unique to global programs and that is the translation of the language of chemists to samplers. This is usually most effectively accomplished by using the active voice and supplementing this with photos. The second issue is addressed in part by again using clear and simple instructions and also by translating instructions into multiple languages (which is made simpler when the instructions are simple). In our case during the course of several monitoring programs we ended up translating customized sampling instructions into both Spanish and Japanese.

Logistics

There are issues for both outbound and inbound shipments that we do not see in domestic monitoring programs.

On the outbound side, one must first determine whether a particular carrier (e.g. DHL or FedEx) actually services a particular area. As an example, we recently needed to send sample kits to Syria. Neither DHL nor FedEx would service Syria directly from the US for sample kits (although they would deliver documents), so in order to get kits delivered it was necessary to ship to a partner in Europe who in turn forwarded the kits on to Syria (using DHL). Second, many countries have restrictions on "dangerous goods" beyond the DOT and IATA restrictions, which limits the ability to use standard EPA preservation techniques such as acids. This necessitates either arranging for onsite preservation (if a sampling site has local access to the necessary acids) or changing the preservation and determining the impact. Third, many countries have specific formats for commercial invoices that are not necessarily consistent with what laboratories who ship domestically are used to using. The bottom line is that one needs to develop an entirely new skill and knowledge set to deal with these issues.

On the inbound side, the biggest challenges are: first, being sure that the samplers understand the need to properly package samples to try to maintain temperatures in transit; second to educate both the samplers and the couriers on the importance of timeliness (figure 1 and figure 2).

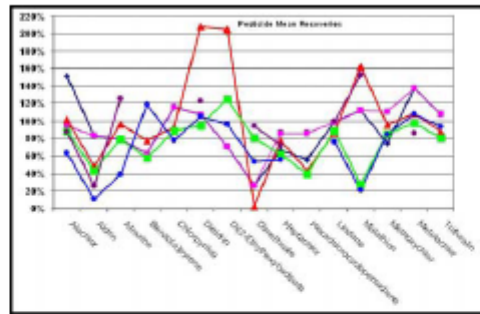
Figure 1: Typical Days from Sample Collection to Shipment**Figure 2: Typical Transit to Laboratory and Receipt Temperature**

Third, it is critical to ensure that paperwork is completed that facilitates rapid customs clearance in the US. With the FDA bioterrorism regulations, many water samples shipped from abroad end up being held up in customs unless the facility shipping the sample is already “registered” with the FDA. Registration is not something that is usually an environmental lab issue and also not something where the environmental lab can act on behalf of the sampler, so it requires a lot of upfront coordination (or conversely a lot of expense and education with customs brokers). Ultimately the reality is that a significant number of samples may be received either a) past hold time or b) over temperature or c) both, requiring an understanding of the impact of these deviations on the data usability.

Analytical Methods Development Issues

One of the biggest challenges for global monitoring programs is developing and validating appropriate methods. With the EU requirement for 0.1 ppb individual pesticides, which many other countries have adopted (similar to the fact that while there are 13 NELAP AAs, there are far more states who will accept NELAP accreditation as an indicator), it is necessary to demonstrate that analytical methods have sufficient sensitivity to meet this requirement even if samples have been subject to degradation. Most of the EPA 500 series (and SW846 8000) methods have not been tested routinely to these levels. In 2006 Carter et al presented a paper at this conference demonstrating some of the variability among global labs when measurements were made at concentrations near the EU limits (figure 3).

Figure 3: Average recoveries for different spiking levels among multiple labs (adapted from Carter et al, 2006)



A second analytical methods issue involves developing and validating new methods for parameters that may be monitoring under WHO or EU guidelines but not EPA guidance. This can be a significant task, depending largely on preservation and holding time issues.

A third issue deals with the desire to reduce sample size from the typical large volumes used in many EPA methods. Reducing sample size greatly simplifies transport both in terms of cost (by reducing weight) and in maintaining sample integrity (it is much easier to keep small bottles cold than large bottles). In some cases this means merely doing minor method modifications (most of which are even permitted within the methods) but in other cases it requires developing entirely new methods.

The final analytical methods issue has to do with evaluating the sensitivity of samples to degradation when not preserved according to EPA protocols (Eaton et al, 2007). This is critical in terms of being able to advise clients as to the validity of their data in such programs. This also often entails looking at alternative preservation methodologies (figure 4 and Table 1).

Figure 4. Alternative preservation schemes for epichlorohydrin (from Eaton et al, 2007).

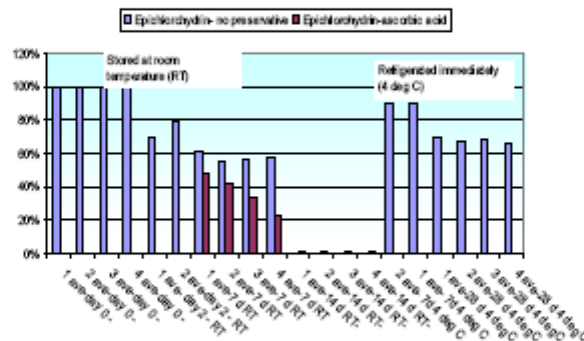


Table 1: Comparison of stability of different pesticides analyzed by EPA method 525 with and without acidification in multiple matrices (Eaton et al, 2007)

Preservative	Sulfite Only								Sulfite followed by HCl							
	1-7 D	2-7 D	3-7 D	4-7 D	1-14 D	2-14 D	3-14 D	4-14 D	1-7 D	2-7 D	3-7 D	4-7 D	1-14 D	2-14 D	3-14 D	4-14 D
Storage Conditions	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT
4-4-DOO	100%	97%	100%	98%	104%	100%	101%	92%	102%	103%	102%	104%	102%	102%	102%	102%
4-4-DOE	95%	94%	95%	77%	90%	99%	95%	97%	102%	103%	94%	95%	95%	98%	98%	95%
4-4-DOF	95%	91%	92%	93%	79%	99%	94%	99%	101%	104%	95%	95%	94%	98%	98%	97%
Alachlor	100%	95%	104%	103%	103%	103%	105%	103%	105%	107%	105%	107%	107%	106%	102%	100%
Azinphos	97%	100%	128%	106%	106%	104%	109%	89%	99%	76%	98%	107%	102%	98%	100%	100%
azithiazuron	100%	104%	100%	95%	98%	102%	97%	98%	104%	106%	101%	101%	104%	108%	110%	109%
Bifenthrin	95%	98%	104%	94%	98%	101%	101%	104%	94%	93%	97%	96%	96%	92%	95%	98%
Bifenthrin (racemic)	97%	93%	98%	92%	97%	98%	100%	97%	99%	98%	97%	97%	97%	97%	97%	97%
Chlorpyrifos (Quinon)	23%	99%	99%	98%	97%	97%	99%	97%	97%	98%	99%	99%	99%	99%	99%	99%
Diazinon	73%	94%	99%	96%	95%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%
Diazinon (racemic)	84%	95%	100%	96%	98%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%
Diflufenican	100%	110%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Dinoseb	71%	78%	68%	70%	72%	62%	70%	68%	102%	98%	99%	97%	98%	98%	98%	98%
Endosulfan	95%	88%	101%	98%	105%	110%	113%	94%	97%	97%	97%	97%	97%	97%	97%	97%
fenitrothion	100%	104%	98%	98%	100%	100%	97%	96%	102%	100%	102%	102%	104%	104%	104%	104%
fenprophos	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
fenprophos (racemic)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
fenprophos (racemic)	95%	95%	97%	95%	94%	94%	94%	95%	94%	95%	95%	95%	95%	95%	95%	94%
fenprophos (racemic)	83%	87%	96%	96%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%	99%
fenprophos (racemic)	100%	100%	101%	98%	99%	101%	99%	104%	101%	102%	102%	102%	102%	102%	102%	102%
fenprophos (racemic)	92%	85%	90%	91%	87%	88%	90%	87%	99%	101%	97%	97%	94%	94%	94%	97%
fenprophos (racemic)	100%	100%	104%	100%	103%	101%	102%	106%	104%	108%	108%	107%	107%	107%	107%	107%
fenprophos (racemic)	100%	100%	100%	98%	105%	99%	107%	107%	102%	98%	98%	102%	99%	98%	94%	95%
fenprophos (racemic)	94%	87%	95%	95%	99%	101%	95%	95%	98%	101%	95%	102%	94%	94%	93%	95%
fenprophos (racemic)	99%	97%	98%	94%	99%	97%	101%	92%	101%	101%	101%	101%	101%	101%	101%	101%
fenprophos (racemic)	96%	98%	100%	96%	104%	104%	112%	107%	99%	94%	97%	96%	99%	97%	97%	96%
fenprophos (racemic)	97%	99%	104%	100%	100%	100%	114%	111%	97%	97%	97%	97%	97%	97%	97%	97%
fenprophos (racemic)	100%	100%	98%	98%	97%	104%	99%	98%	101%	104%	104%	104%	104%	104%	104%	104%
fenprophos (racemic)	100%	97%	98%	97%	99%	90%	98%	74%	107%	102%	98%	100%	98%	98%	98%	98%
Cyfluthrin	97%	95%	101%	96%	99%	97%	105%	105%	96%	95%	96%	96%	96%	96%	96%	96%

Our experience has been that laboratories that are not US based often do not do the same rigorous evaluation of preservation issues that are done in many of the newer EPA methods, so adopting a method from European based labs (that deal with EU and WHO lists and the 0.1 ppb reporting limit) may often provide a framework for a method, but often does not truly address sample stability issues. As an example we are aware of one monitoring program conducted by a UK based government lab for some 50+ pesticides that uses a single thiosulfate preserved pH neutral bottle for several different fractions that in the US may require 4 or 5 different preservatives.

CONCLUSIONS

A careful evaluation of all of the factors that make up a global monitoring program is critical for assessing data usability. Experience over the last 4 years demonstrates that while some parameters are essentially useless in making “compliance decisions” due to the difficulty associated with obtaining valid samples, there are many other parameters where with proper care in the laboratory and sufficient attention to establishing proper preservation schemes one can obtain reproducible and robust data sets to evaluate water quality across the globe.

REFERENCES

1. Carter, M., Laferty, J., Huff C, and J Lowry. 2006. Report on a Multi-Analyte, Multi-Method Detection Limit Study Presentation to NEMC. August 2006.
2. Eaton, A, Geddes, L., and A. Haghani. 2007. Assessing the Stability of Pesticides and VOCs Under Various Preservation Conditions Presentation at NEMC August 2007.

Challenges of Global Monitoring Programs

Andrew Eaton
MWH Laboratories



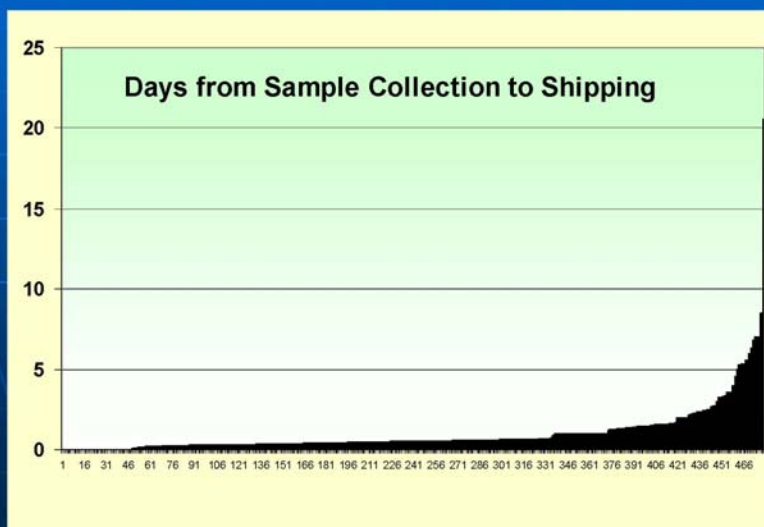
Global Monitoring Presents Unique Challenges We Don't Normally Face

- MWH is a global firm, but that doesn't make it any easier
- We can't rely on "overnite" transport
- We can't always use prescriptive methods
- We can't rely on clear communication
- It needs a true client partnership to be a success, but it can be successful

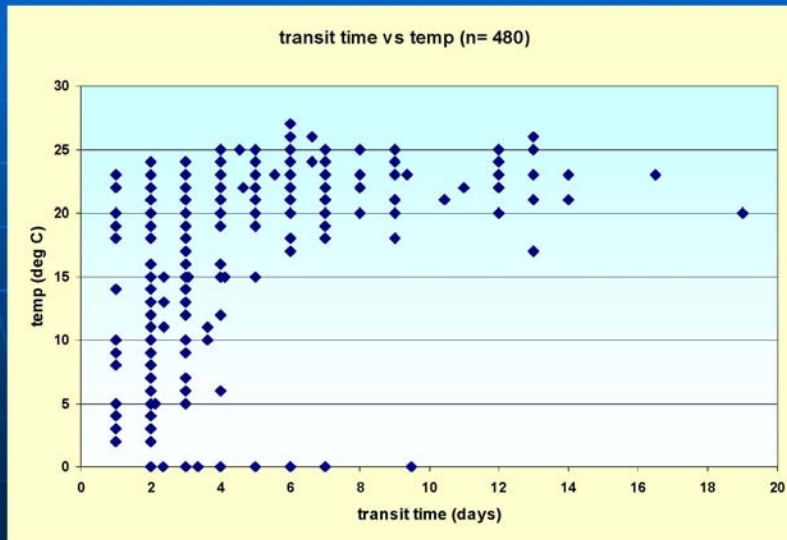
Overnite Chilled Transport?

- Remote locations
 - “Up the Amazon”
- What do couriers guarantee for service?
 - HIGHLY location dependent
- Do the samplers understand the needs?
 - You’re not always talking to the right person
- September 11 Effect
 - FDA Registration and Bioterrorism
 - Customs hold-ups
- Most coolers only hold temp for a few days

Sometimes it’s a Training Issue- Remind Them to Sample Quickly!



You Can't Rely on Time or Temperature in a "flat" World



Can We Use EPA Methods?

- Not always the same analytes
- Other nations are more performance based
 - But don't always have a quality system built in
- Reporting limits may be different
- Can't rely on sample integrity

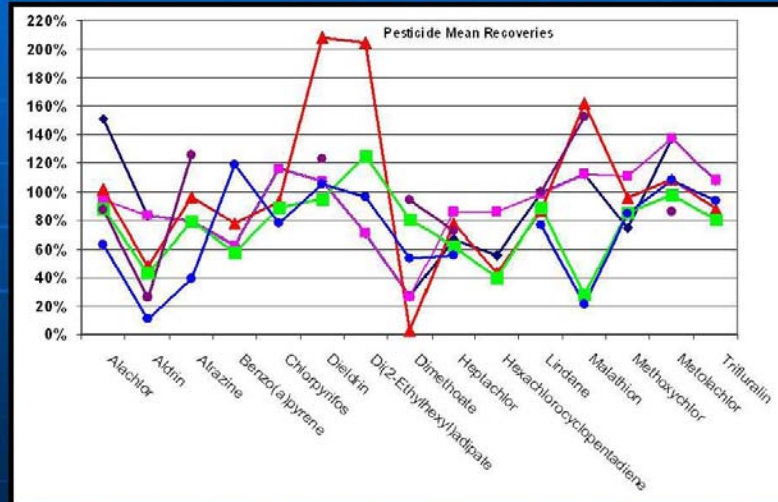
Differences in Global Monitoring Programs

Program	# of "Regulated" Analytes	Required MRL Level	Action Level
USEPA	Large (80+)	High	High
WHO	Medium (40+)	Varies	High
Company 1	Large	Low (EU based)	Medium to Low (WHO and EU)
Company 2	Large	Medium (Company based)	Medium (WHO and Company)

Global Preservation, Method and Holding Time Issues

Program	Preservation Specs?	Holding Time Specs?	Method Specs?
USEPA	Regulated	Regulated	Regulated
WHO	Performance Based	Performance Based	Performance Based
Company 1	Performance Based	Performance Based	Some
Company 2	Performance Based	Performance Based	Some

Not All Labs are Created Equal in a Flat World



From Carter et al (2006)

Communications Challenges

- Historic monitoring in sites has not necessarily entailed complete quality systems
 - 2 liters in one bottle vs. 18 liters in 50 bottles
- Language gaps
- Terminology gaps
- Communication issues are not JUST with samplers, but also with couriers

How to Improve Compliance in a Multi-lingual World

- Simple instructions
- Lots of Photos
 - A picture is worth 1000 words
- Translations
 - Spanish
 - Japanese
- Work with couriers to facilitate clearance
 - DHL and FedEx each have their own arrangements

Simple Instructions Use the KISS Principle.

STEP 1 - RECEIPT OF SAMPLE KITS

- Plant inspects each kit when received for completeness against the description of contents listed on the following pages.
- Gel packs supplied with each kit are taken out and placed flat in a freezer at least 48 hours prior to sampling. They are then placed back into the kit along with collected samples for return to the testing lab.

Photos of Exactly How to Pack a Cooler

Layout and packing/re-packing of cooler Kit for MWH Labs

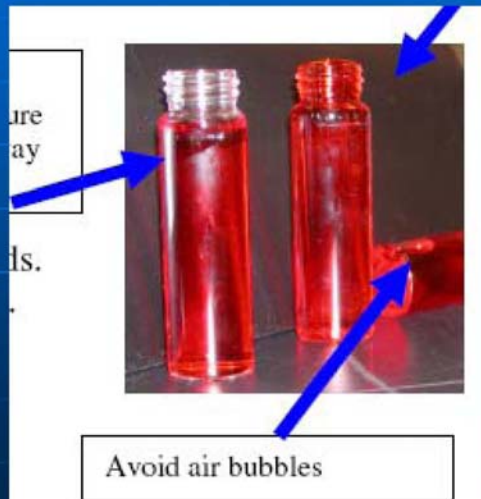
Step 1 - frozen gel packs on bottom Step 2-cover with bubble wrap Step 3 - Put bottles back in foam inserts

Step 4- frozen gel packs on top Step 5 - cover with bubble wrap step 6 - cover with foam

Step 7: put in chain of custody

Avoiding Headspace

A picture is much more effective than text.



Having The Ability To Keep Track Of Kits Enroute Helps To Minimize Problems

Group	Division	Plant	Type	Address	City	SDG	DHL Tracking	Shipping	Shipped	Sampled	Received	Loaded							
Latin America	South Latin Division	Guerrero, Salta		Av. Chile y Ruta 9, Ciudad de Salta	Salta, Argentina	156306	78833845971	Track DHL Shipment to Lab	08/04/05	8/4/2005	8/8/2005	8/8/2005							
								Kingstown, Saint Vincent	153943	78833842046	Track DHL Shipment to Lab	08/04/05	8/4/2005	8/8/2005	8/8/2005				
								Kingstown, Saint Vincent	153943	78833842342	Track DHL Shipment to Lab	08/04/05	8/4/2005	8/8/2005	8/8/2005				
								Basseterre, Saint Kitts And Nevis	154704	78833842604	Track DHL Shipment to Lab	08/16/05	8/15/2005	8/17/2005	8/17/2005				
								Junin, Peru	156905	78833842204	Track DHL Shipment to Lab	09/13/05		9/20/2005	9/20/2005				
								San Lorenzo, Paraguay	154420	78833841734	Track DHL Shipment to Lab	08/09/05	8/8/2005	8/13/2005	8/13/2005				
								Barranquilla, Colombia	153939	78833841152	Track DHL Shipment to Lab	08/05/05	8/1/2005	8/8/2005	8/8/2005				
								Coquimbo Rut. Chile	152166	78833840824	Track DHL Shipment to Lab	07/12/05	7/11/2005	7/16/2005	7/16/2005				

But this does require follow up – real labor...

Customs Clearance Can Add Another Series of Challenges

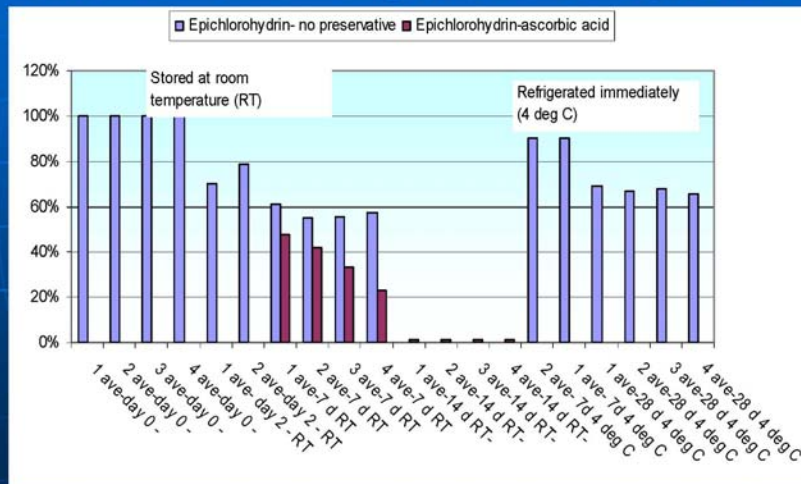
- Time to deliver
- Condition upon receipt
- Needs a lot of "backup" and "cannibalizing"



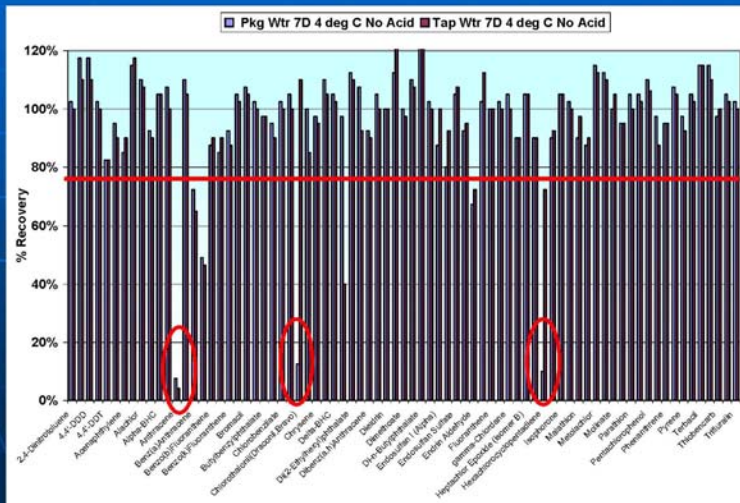
You Must Prove The Ability to Meet Specs on an Ongoing Basis

- Lowered Calibration Range
- Inclusion of MRL Checks in EACH run
- Verify the impact of preservation and storage
- Know when/how to flag data
- Resampling is NOT usually an option

Special Preservation and Hold Time Studies are Required to Optimize



Pesticides-Chilled, No Acid Better, but Not Perfect Data Must be Qualified



The More Analytes, the More Complicated the Options

Preservative	Sulfite Only								Sulfite followed by HCl							
	1-7 D RT	2-7 D RT	3-7 D RT	4-7 D RT	1-14 D RT	2-14 D RT	3-14 D RT	4-14 D RT	1-7 D RT	2-7 D RT	3-7 D RT	4-7 D RT	1-14 D RT	2-14 D RT	3-14 D RT	4-14 D RT
4,4'-DDD	100%	101%	100%	89%	104%	105%	103%	52%	103%	107%	109%	104%	101%	102%	107%	101%
4,4'-DDE	98%	94%	91%	77%	98%	99%	85%	37%	102%	103%	104%	93%	95%	96%	96%	88%
4,4'-DDT	95%	91%	89%	78%	73%	99%	84%	35%	101%	104%	105%	99%	94%	96%	96%	93%
Alachlor	100%	99%	104%	102%	102%	100%	106%	108%	108%	107%	105%	102%	100%	99%	102%	100%
Aldrin	97%	100%	125%	106%	106%	104%	130%	85%	99%	78%	86%	107%	102%	88%	98%	105%
alpha-Chlordane	105%	104%	102%	98%	95%	103%	97%	58%	104%	105%	107%	101%	104%	106%	110%	105%
Atrazine	95%	96%	104%	93%	98%	101%	107%	104%	84%	83%	87%	88%	85%	82%	82%	58%
Benzol(a)pyrene	76%	53%	98%	52%	80%	25%	106%	33%	95%	48%	64%	71%	73%	37%	67%	51%
Chlorpyrifos (ursban)	23%	99%	98%	95%	8%	93%	97%	77%	101%	93%	101%	105%	93%	78%	93%	98%
Di-(2-Ethylhexyl)adipate	7%	24%	0%	0%	8%	106%	0%	0%	92%	86%	93%	85%	70%	66%	71%	70%
Di-(2-Ethylhexyl)phthalate	24%	82%	16%	0%	85%	85%	23%	7%	95%	100%	106%	85%	83%	93%	87%	83%
Dieldrin	109%	110%	107%	110%	109%	113%	116%	97%	103%	110%	118%	110%	106%	111%	111%	112%
Dimethoate	71%	76%	85%	70%	73%	92%	70%	85%	102%	93%	93%	87%	48%	85%	74%	74%
Endrin	99%	88%	101%	98%	105%	110%	113%	94%	72%	57%	57%	64%	45%	30%	33%	32%
gamma-Chlordane	105%	104%	98%	93%	100%	108%	97%	52%	107%	109%	109%	103%	102%	104%	103%	102%
Heptachlor	18%	16%	14%	13%	3%	3%	1%	3%	14%	14%	14%	13%	8%	8%	7%	7%
Hepachlor Epoxide isomer B	107%	107%	107%	109%	101%	105%	106%	91%	108%	107%	110%	108%	105%	105%	108%	109%
Hexachlorobenzene	95%	95%	97%	99%	94%	94%	94%	86%	94%	93%	95%	98%	93%	91%	91%	94%
Hexachlorocyclopentadiene	52%	12%	0%	0%	35%	3%	0%	0%	94%	95%	99%	103%	80%	83%	79%	89%
Lindane	102%	99%	101%	98%	99%	101%	96%	104%	105%	102%	103%	107%	98%	96%	97%	99%
Methoxychlor	92%	85%	90%	91%	87%	86%	90%	63%	96%	101%	97%	97%	93%	94%	94%	97%
Metolachlor	101%	102%	104%	105%	103%	101%	110%	116%	104%	108%	106%	110%	100%	99%	102%	104%
Moinate	101%	100%	102%	99%	105%	99%	107%	107%	100%	94%	86%	102%	99%	76%	84%	95%
Naphthalene	94%	87%	0%	0%	99%	101%	0%	0%	98%	101%	93%	100%	94%	94%	93%	96%
Pendimethalin	99%	97%	98%	94%	95%	97%	101%	82%	106%	107%	105%	105%	101%	99%	100%	100%
Simazine	96%	98%	107%	92%	105%	104%	112%	107%	85%	84%	87%	85%	85%	61%	61%	56%
Terbuthylazine	123%	128%	134%	122%	102%	106%	114%	112%	91%	91%	90%	92%	91%	91%	89%	85%
trans-Nonachlor	102%	101%	99%	88%	97%	104%	98%	44%	105%	104%	109%	102%	102%	101%	104%	100%
Trifluralin	102%	97%	98%	92%	95%	90%	96%	74%	102%	100%	96%	105%	96%	96%	94%	99%
Cyanazine	97%	90%	101%	98%	95%	97%	106%	105%	28%	15%	18%	24%	12%	9%	11%	12%

What Have We Typically Seen Around the World in Municipal and Potential Potable Well Sources?

- Positive total coliform is more common than we would like, even for municipal supplies
- DBPs (inorganic and organic) are a global issue
- Metals are sometimes high, but usually turbidity related (duh!)
- Some local Pesticide issues, but not major
- Few volatile issues
- Little data so far on "emerging contaminants"

Conclusion

- Even in a "flat" world, there are a lot of challenges for environmental monitoring.
- A performance based approach solves some of the problems, but not all.
- There is a lot of valuable data to be gained from global studies.
- Water quality "Gaia-cide" does not seem imminent.

Contact Information

- Andrew D. Eaton
andrew.d.eaton@mwhglobal.com

Metal Speciation and Drug Residue Identification in Foods - A Global Perspective on Food Safety Testing

Curtis Wood
ERA
6000 W. 54th Ave.
Arvada, CO 80002
800-372-0122
cwood@ercqc.com

ABSTRACT

The food borne outbreaks of E.coli and salmonella poisoning that occurred in 2007 highlighted for the general public the importance of food safety monitoring. However, the need for stricter, more comprehensive and complete testing reaches far beyond what the public may appreciate. In 2007, importation accounted for 80% of the nation's seafood, 45% of its fresh fruit and 17% of its fresh vegetables. This increasing level of food importation has placed a strain on foreign suppliers. Relative to large domestic producers, many importers have insufficient modernization; insufficient investment capital and inadequate education of food and agricultural producer responsibilities. Although there have been significant improvements in all these areas in recent years, challenges still exist.

Improved controls and quality testing of food products document that chemical and microbiological risks to public health have been reduced over the past five years. Furthermore, contamination of soil, water and food has also diminished over this period; however, additional improvements are necessary, especially for foods of animal origin. What may come as a surprise to many is that the FDA inspects only 1% of the food it regulates in the US and the USDA only 16% of what it is responsible for (US government statistics). With such a significant (and growing) amount of foreign food importation coupled with insufficient inspection, it is clear that food quality and safety testing globally is on the brink of a rapid and significant evolution.

This paper presents a global account of food quality and safety testing requirements in the context of the large/popular regional farming and ranching segments for major exporting countries. Specifically it reviews the latest analytical testing trends associated with food quality and safety testing and highlights the major challenges associated with testing as it relates to instrumentation, method development and the availability of traceable reference standards for calibration and competency testing.

Meeting Drinking Trace Metal Requirements in the EU And USA. Can They Be Achieved Using ICP-AES?

Isaac Brenner
Environmental Analytical Services
9 Dishon Street
Jerusalem, Israel 96956
brenner@cc.huji.ac.il

ABSTRACT

The application of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is now widely applied for routine analysis of waters and wastes in environmental monitoring programs. However, regulation concentration limits of several toxic elements in drinking water have recently been reduced resulting in a serious challenge for axially viewed (AX) ICP-AES (1). In order to meet new US MCL requirements, USEPA published a new procedure (EPA 200.5) (2) detailing compliant analysis of drinking water using an AX-ICP-AES. The IDLs in this method are lower than those prescribed in 200.7 and in the Standard Methods. In particular, the reporting limit (RL) of 10 ppb and an IDL of 2 ppb for As has resulted in the withdrawal of 200.7 for compliant analysis. Because USEPA stipulates the use of pneumatic sample introduction, USN (3,4) or other desolvation devices or an integrated hydride generation system (MSIS) (5,6) cannot be used to improve aerosol production efficiency.

A systematic examination of published vendor IDLs surprisingly reveals that commercially available spectrometers fail to meet performance IDLs listed in EPA 200.5 (2) and EU protocols (7). All IDLs quoted in this evaluation were obtained using commercial charge transfer instruments – a dual view segmented CCD, a dual view CID, CCDs installed on a vertical Rowland Circle - Paschen Runge configuration and a semi-sequential radially viewed (RAD) - ICP-AES. All data are in the public domain and were available at the time of the evaluation – but may be improved with technological development. Current available data indicate that with exception of one instrument, the others fail to fully meet EPA 200.5 IDLs. Moreover, because EU requirements are much more stringent than those stipulated by EPA 200.5, drinking water according to EU stipulations can only be monitored using ICP-MS. This will cause a switch in the approach to complaint trace metal drinking water analysis.

Compliant Analysis of Water and Liquid and Solid Wastes by ICP-AES. Standard Methods, USEPA 200.7, 200.5 and SW 846 6010C

I.B. Brenner
Brenner Scientific
 9 Dishon Street, Malkha,
 Jerusalem, 96956, Israel
 Tel 972-2-6797-255, mobile 972-54-
 424-403, FAX 972-2-6797-145,
 e-mail BRENNER@cc.huji.ac.il



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

1

APPLICATION OF ICP-AES IN WASTE DISPOSAL

I.B. Brenner
Environmental Analytical
Laboratory, BGU
 Address for correspondence:
 Dishon Street, Malkha,
 Jerusalem, Israel, 96956
 E mail: Brenner@cc.huji.ac.il



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

2



08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

3



08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

4

INTRODUCTION

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

5

Outline of Short Course

- ❖ Introduction
- ❖ Overview of ISO 17025
- ❖ Sample collection
- ❖ Sample preparation
- ❖ Instrumentation
- ❖ Overview of EPA Methods
 - ❖ 200.5, 200.7, 6010, SM
 - ❖ Optimization
 - ❖ Spectroscopic and nonspectroscopic interferences
- ❖ Quality Control
- ❖ IDLs, MDLs, LDRs,
- ❖ Performance Data
- ❖ QA/QC, ICVs, CCVs, recoveries
- ❖ PT, uncertainty
- ❖ Conclusions

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

6

Need to defend legitimate analysis



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

7

Why Accreditation?

- Data validation to ensure lab methods meet analytical specifications
- Understand method advantages vs. disadvantages
- Documentation to ensure consistent application of method within defined scopes, for QA, regulatory and contractual purposes
- Laboratory benefits - enhances expertise, improves efficiencies
- Client benefits - Creates trust in results
- Regulation benefits
 - ✓ Trustworthy information to protect public health and environment
- Builds trust in the lab, organization

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

8

Must be able to “defend” results

- Practicing analytical chemists must demonstrate quality and fitness for purpose.
- To meet this challenge, a rigorous QA/QC system should be deployed.



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

9

Challenges for ISO 17025

- *Will ISO/IEC 17025 have a sweeping influence in commercial and national environmental laboratories?*
- Why do we need ISO 17025?
- *Are compliant lab routines with their built-in QA/QCs adequate ?*
- How can 17025 be incorporated into these SOPs and vice-versa?

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

10

ISO 17025-2005 Accreditation – Requirements

- Management requirements
- Regulator Requirements
- *Trained and competent staff - Competence of Testing and Calibration Laboratories*

- Technical and analytical requirements - GLP
- Scope specification
- Complaint sampling
- Verified method of measurement
- Traceable calibration standards

- Maintains QA/QC system and documentation

- Satisfactory participation in Proficiency Testing (PT) program
- Measurement uncertainty

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

11

Requirement of a compliant lab procedure

- Possess all analytical QA/QC requirements specified by ISO 17025 – built into the analytical SOP
- The selected procedure should be compliant, well defined and recognized
- Simplifies assessment of data quality (uncertainty) *and also the audit*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

12

Importance of selecting ICP SOPs

- Environmental labs must make large changes in existing noncompliant methods and irregular management procedures
- High cost of obtaining and maintaining ISO 17025 accreditation
- Therefore labs must be sure that plasma-based SOPs meet QA/QC requirements of ISO 17025-2005

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

13

Scope of Measurement

- Competence
- Purpose of measurement
- List of elements to be measured
- Methods to be used – sample preparation, instrumental methodology
- Critical performance and QA/QC parameters
- Compliance with regulatory requirements

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

14

ISO-17025, Sec 5.4.1, 5.4.5 - Method Validation Scrutiny of fitness of purpose



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

15

Accreditation 17025 - Validation

Purpose: *quantitative check and verification of analytical process, documentaton and calculations*

Strengths: *Validates data quality defensibility and compliance; has been used to detect fraud*

- Lab must demonstrate to expert technical assessors that it *meets all relevant criteria contained in ISO/IEC 17025*
- Method validation is an essential part of good measurement practice and a requirement of ISO 17025
- Lab must demonstrate *its competence to perform analytical tasks detailed in the scope of its SOP*
- *Analytical data must be fit for purpose (conform to EAP SOP QA/QC criteria)*
- Documented experimental evidence that method conforms to well-defined *figures of merit*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

16

Plasma-based geoenvironmental analysis - challenges

- Very low concentrations of toxic and diagnostic elements - require subppb – ppt LODs
- Trace elements occur in complex forms – colloids, metal organic compounds
- Volatile species
- Biological materials
- Sampling and preservation
- Validity

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

17

TRACE ELEMENT WATER ANALYSIS USING ICP-AES

- Determination of transition metals in ppb range
- Multi-element capability
- Minimum spectral interferences due to overlap and optical imperfections
- High plasma robustness to minimize EIE and Ca interference effects
- Versatile sample introduction systems
- Capability of analyzing saline waters
- Speed of analysis and ease of operation

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

18

Challenges of ICP-AES

- Lowering of regulation limits of toxic elements in drinking water
- RV-ICP-AES fails to meet new concentrations
 - ✓ 200.7 will be withdrawn – at the moment for As, in the future
- Improvement of IDLs by 5-10 using USN ineffective due EIE interference effects
- USEPA published new SOP (EPA 200.5) for analysis of drinking water using AX-ICP-AES.
- Are enhanced AX-ICP-AES IDLs (x 5-20) sufficient ?

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

19

Main tasks of water research and survey programs using ICP-AES

- Ground water monitoring
- Monitoring of waste disposal sites and dispersion halos
- Analysis of industrial and domestic sludges
- Trace element variations in soils - total and extractable – metal fractionation and speciation

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

20

Samples and sample collection

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

21

Sample types

- ***Surface and subsurface water***
- ***Sea and estuarine waters***
- ***Industrial and domestic effluents***
- ***Sludges***
- ***Colloidal and suspended fractions***
- ***Soils and Sediments***
- ***Biological samples - vegetation***
- ***Soils***

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

22

Water sample collection

- **Sampling strategy – seasonal, geographic, morphological (drainage patterns), point sources**
- **Preservation – holding time, field/lab pretreatment**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

23

SAMPLE COLLECTION

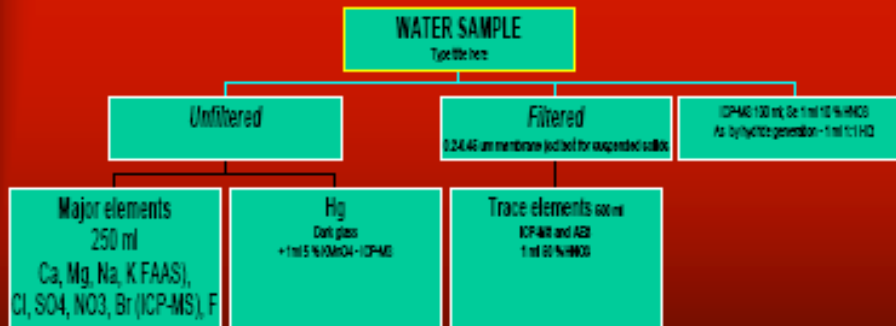
- *Water samples collected in acid cleaned polyethylene bottles (soaked in 10 % nitric acid for 24 hours)*
- *Bottles rinsed with ultrapure deionized water (Millipore Q grade)*
- *Samples filtered through a 0.25-0.45 μm filter- remove suspended material - "dissolved fraction"*
- *Prompt acidification with several ml of ultrapure nitric acid - preservation during transport and storage.*
- *Water samples collected for determination of major anions, As, Se and Hg, and speciation*
- *Collection of > 0.45 mm residues*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

24

Flow chart for sampling and analysis of water



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

25

Plasma-based compliant procedures for analysis of surface, ground, and drinking water, liquid, solid and semi-solid wastes, sludge, and sediments.

Sample preparation protocols allow for determination of dissolved, particulate and total concentrations

ICP-MS

EPA 200.8
SW846-6020 B,
EPA CLP ILM05.2D
DOD
Standard Methods
ASTM
ISO 17294
AOAC

ICP-AES

ISO 11885
EPA 200.7
EPA SW 846 - 6010
B and C
Standard Methods
ASTM
AOAC

EPA-CLP

N30
Eurachem – ISO
EPA 200.5

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

26

For Additional Information

- 200.7
- www.lib.ucdavis.edu/govdoc/EPA/200_7.pdf
- www.esb.enr.state.nc.us/lab/qa/epamethods/200_7.pdf

- 6010
- www.epa.gov/epaoswer/hazwaste/test/up4a.htm

- CLP SOW
- www.epa.gov/superfund/programs/clp/ilm5.htm

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

27

Terminology

- **MAY** – Action, activity, or procedural step neither **REQUIRED** nor prohibited.
- **MAY not** – Action, activity, or procedural step - prohibited.
- **MUST** – Compulsory action, activity, or procedural step
- **SHALL** – Compulsory action, activity or procedural step
- **SHOULD** – Action, activity, or procedural step - suggested but not **REQUIRED**.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

28

Mode of occurrence of trace elements in water

- *Dissolved* – ions , organo-metallic complexes. Analytes are determined in water filtered < 0.45 μm
- *Suspended* – Colloidal and particulates in form of Fe-Mn oxy-hydroxides, silicates, sulfides, absorbed on clay, silica and organic particles
- Total recoverable acid extractable
- Metal-organic species.
 - ✓ Metals have high affinity for humic acids, organo-clay and oxides coated with organic matter

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

29

Sample Preparation

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

30

Digestion procedures

- *Sample treatment and acid decomposition differ in extraction efficiency*
- *In all cases the procedure employed must be stated*
- *Procedures are based on end-user needs*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

31

Contamination

- *Apparatus, sample containers*
- *Dust*
- *Clean laboratory work area*
- *Surface desorption, leaching, adsorption*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

32

Reagents

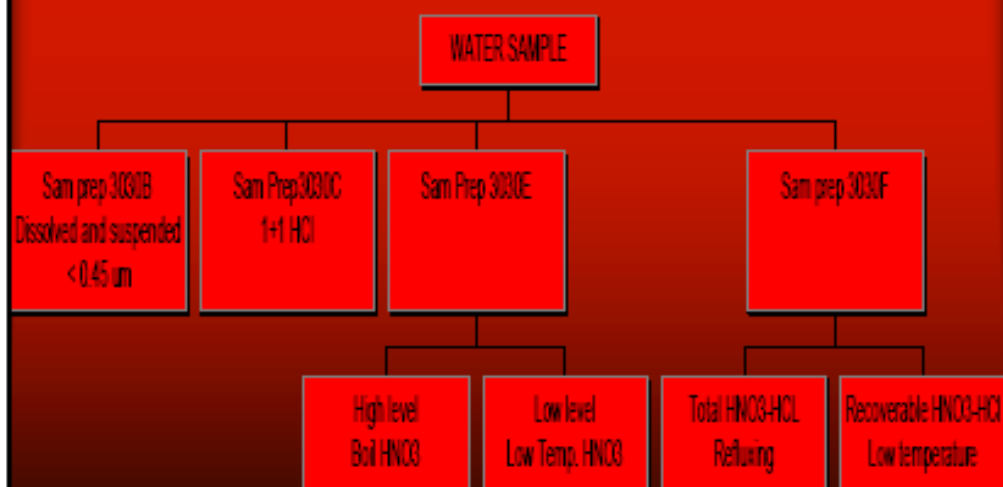
- Hydrochloric acid (1+1, 1+4, 1+20)
- Nitric acid (1+1, 1+2, 1+5, 1+9)
- Conc. ammonium hydroxide,
- Tartaric acid
- Hydrogen peroxide (50, 30 %)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

33

Block diagram for sample preparation schemes for the analysis of waters and wastes by ICP-AES



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

34



Sample preparation

Standard Methods

- SM 3030B - < 0.45 um – dissolved elements
- 3030C - 5 ml HCl + 5 ml HCl 15 min, 100°C
- 3030E - 3 ml HNO₃. Hot plate , not boiling, evaporate
- 3030F Nitric -hydrochloric acid digestion
 - ✓ Two procedures - total HNO₃/HCl (refluxing) and recoverable HNO₃/HCl (relatively lower temperature)
- 3030G - HNO₃ boil then HNO₃+H₂SO₄
- 3030H – HNO₃+HClO₄
- 3030I – HNO₃+HClO₄+HF
- 3030K - microwave

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

36

Dissolved and suspended metals according to SM 3030B

- *Determination of dissolved trace elements in waters after membrane filtration using a 0.4-0.45 μm filter*
- *Filtrates acidified in field or brought to lab in acid washed Nalgene bottle (500 ml), refrigerated at 4°C, filtered and acidified.*
- *Suspended solids retained on filters can be digested and analyzed.*

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

37

Dissolved and suspended metals SM 3030B Filtration procedure

- **Filtration performed using Nalgene filter assembly and positive pressure with Ar or nitrogen.**
- *Before using assembly and filter, determine level of contamination with metal-free deionized water.*
- *If metal contaminants are identified, flush with 1N HNO_3 , rinse with deionized water.*
- **Use first 50-100 ml to rinse filtration apparatus to avoid contamination and discard this portion.**
- **After filtration acidify to pH 2 with conc. HNO_3 (usually 1 ml/1000 ml is normally adequate.**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

38

Dissolved and suspended metals***SM 3030B******Analysis of suspended fraction***

- **Transfer membrane filter containing insoluble material to 150 ml acid washed beaker**
- **Add 4 ml conc. HNO₃ and heat gently**
- **Continue as described in SM 3030F**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

39

***Acid extractable metals using 1+1
HCl (SM 3030C)***

- *Extraction of lightly absorbed elements on particulate materials.*
- **100 ml sample into 250 ml acid washed beaker**
- **5 ml 1+1 HCl. Cover with watch glass and heat 15 min on steam bath.**
- **Filter through membrane filter**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

40

Sample volumes – 3030D

- *Not < 5 ml especially when particulates present.*
- *When elevated analyte concentrations occur, dilute after digestion.*
- *For low concentrations and low-salt solutions - concentrate by evaporation.*
 - ✓ *Conducted in acid washed PTFE vessels in contamination free hood*
- *For samples that are concentrated, determine metal recovery to evaluate matrix effects*
 - ✓ *Spike using separate aliquots with with CPI*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

41

SM 3030E

- *HNO₃ extraction for samples that contain suspended solids and easily oxidized matter*
- *Two routines*
 - ✓ *High-level metal concentrations (slow boil with HNO₃)*
 - ✓ *Low-level contents (low temperature heating with 2 N HNO₃)*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

42

Low-level 3030E concentrations (< 100 µg/l)
Clean up

- Soak new polypropylene tubes and caps overnight in 2 N HNO₃
- Triple rinse with deionized water
- Store cleaned tubes with DI water until use or in acid washed plastic bags before use
- Pipette tubes SHOULD also be cleaned - evaluate before use.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

43

Low-level 3030E concentrations (< 100 µg/l)
Procedure

- 10 ml sample into precleaned tube with acid-washed macro pipet
- 0.5 ml conc. HNO₃ to all samples, blanks standards and QC samples
- Heat tubes in block heater at 105°C
- Digest samples for at least 2 h.
 - ✓ Do not boil
- Add more conc. HNO₃ until digestion is complete (clear solution)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

44

High-level 3030E concentrations

- 100 ml well-mixed sample to beaker
- Add 5 ml concentrated HNO_3 in hood.
- Bring to *slow boil* and evaporate on a hot plate to about 10-20 ml, before precipitation occurs. *Do not allow sample to dry during evaporation*
- Continue heating, adding conc. HNO_3 until digestion is complete (light-colored, clear solution)
- Wash down beaker and watch glass and filter if necessary
- Transfer filtrate to 100 ml volumetric flask

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

45

Nitric -hydrochloric acid digestion SM 3030F

Two procedures - total HNO_3/HCl (refluxing) and recoverable HNO_3/HCl (relatively lower temperature).

- HCl enhances solubility of Ag and other chemically resistant solid fractions.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

46

3030F Recoverable HNO_3/HCl *Less rigorous digestion*

- Transfer 100 ml sample to flask or beaker.
- 2 ml 1+1 HNO_3 and 10 ml 1+1 HCl and cover with ribbed watch glass
- Heat on *steam bath or hot plate* until volume is reduced to 25 ml - *do not boil!*
- Cool and filter to remove particulates or centrifuge, or let settle overnight.
- Transfer quantitatively to 100 ml volumetric flask

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

47

3030F Total HCl/HNO_3 *HCl enhances solubility of Ag*

- 100 ml sample to Erlenmeyer flask or beaker
- 3 ml conc. HNO_3 and cover with ribbed watch glass.
- Heat on hot plate and evaporate to < 5 ml.
- *Do not boil and do not allow evaporation to dryness*
- Cool and rinse walls of beaker and watch glass and return to hot plate.
- Increase temperature for reflux action, adding more acid until digestion is complete (light in color)
- Cool, 10 ml 1+1 HCl + 15 ml DI water
- Heat for 15 min. to dissolve precipitates or residue.
- Cool, wash beaker and watch glass if used with DI water. Mix thoroughly.
- Filter to remove insoluble material that could clog nebulizer
- Transfer filtrate to 100 ml volumetric flask or centrifuge or allow solution to settle overnight

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

48



EPA Methodology (1)

- Establishes 'recommended' conditions, instrument parameters, method validation and QC, sample preparation, sampling
- EPA Methodology for ICP-OES includes:
 - ✓ 200.7 (rev 4.4 current, 5.0 proposed)
 - ✓ SW 846 6010 (rev B current, rev C proposed) CLP ILMO SOW (rev 5.3 approved March 2004, ILM 6.0)
- 'current' version depends on regulators, auditors, individual permits, state and local regulations

08-Aug-07 Joe Brenner, Compliant Analysis of Waters and Wastes 50

EPA Methodology (2)

- EPA method criteria can be stringent or performance based – I.E., can be modified providing performances are met
- Several LODs of 200.7 do not meet drinking water requirements
- Current revision of method ILMO lists Contract Required Quantitation Limits (CRQL). These can be extrapolated to CRDLs.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

51

EPA Methodology (3)

- Regulatory methods are trending more toward performance based methodology using EPA Methods as 'guidance documents'.
- Method 200.7 page iii
 - ✓ *Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met.*
- Method 200.7 section 9.1.2
 - ✓ *'In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences...'*
- Method 6010 section 1.5
 - ✓ *'The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.'*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

52

Definition of Terms - 1

- Optimum concentration range:** A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. Range varies with the sensitivity of the instrument and the operating conditions employed.
- Sensitivity:** (a) *Atomic Absorption:* The concentration in milligrams of metal per liter that produces an absorption of 1%; (b) *Inductively Coupled Plasma (ICP):* The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.
- Instrument detection limit (IDL):** The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.
- Method detection limit (MDL):** The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDL is determined from analysis of a sample in a given matrix containing the analyte which has been processed through the preparative procedure.
- Interference check sample (ICS):** A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.
- Linear dynamic range:** The concentration range over which the analytical curve remains linear.
- Method blank:** A volume of reagent water processed through each sample preparation procedure.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

53

Definition of Terms - 2

- **Initial calibration verification (ICV) standard:** A certified or independently prepared solution used to verify accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength and at each mass used in the analysis.
- **Continuing calibration verification (CCV):** Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.
- **Calibration standards:** A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve)
- **Calibration blank:** A volume of reagent water acidified with the same amounts of acids as the standards and samples.
- **Laboratory control standard:** A volume of reagent water spiked with known concentrations of analytes carried through preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.
- **Method of standard addition (MSA):** The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard.
- **Sample holding time:** Time allowed between sample collection and sample analysis when designated preservation and storage techniques are employed.
- **Check Standard:** Solution containing known concentration of analyte derived from externally prepared test materials. Check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

54

Definition of Terms - 3

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (*Method 3005*).

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45- μm filter (*Method 3005*).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45- μm filter (*Method 3005*).

Total metals: The concentration of metals determined in a sample following digestion by *Methods 3010, 3015, 3020, 3050, 3051, or 3052*.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

55



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

56

**METHOD 200.7 TRACE ELEMENTS IN WATER,
SOLIDS, AND BIOSOLIDS BY INDUCTIVELY
COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRY**

**Revision 5.0, August 1998, Draft 1
U.S. Environmental Protection Agency,
Office of Water,
Office of Science and Technology,
Engineering and Analysis Division (4303),
401 M Street SW, Washington, D.C. 20460**

Will be withdrawn !

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

57

Samples – EPA 200.7

- **Biosolids** – A solid, semisolid, or liquid residue (sludge) generated during treatment of domestic sewage in treatment works.
- **Solid sample** – a soil, sediment or sludge
- **Total Solids** – Residue left after evaporation of liquid sample and subsequent drying at 103 – 105°C

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

58

Water and wastes biosolids (municipal sewage sludge), and solid samples

- Dissolved - analytes in aqueous samples after filtration and acid preservation. To reduce potential interferences, dissolved solids SHOULD be **<0.2% (w/v)**
 - ✓ Aqueous samples MAY be analyzed directly without acid digestion if sample has been preserved with acid and has turbidity of <1 NTU at time of analysis.
- **Partial extraction** – organic and inorganic bound
- **Total extraction** - total recoverable analytes - digestion/extraction is **REQUIRED** when elements are not in solution (e.g., biosolids, soil, sludge, sediment, and aqueous samples containing particulate and suspended solids)
 - ✓ Aqueous samples containing total suspended solids >1% (w/v) - solid sample

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

59

EPA 200.7 Determination of dissolved elements

- Sample **MUST** be filtered through a 0.45 µm membrane filter at time of collection or as soon thereafter as **practically POSSIBLE**
- Only plastic apparatus SHOULD be used when B and silica are determined
- Acidify filtrate with (1+1) HNO₃ to pH <2 immediately following filtration

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

60

Dissolved analytes in ground, drinking and surface waters

- ✓ Pipet aliquot (≥ 20 mL) of **filtered**, acid preserved sample into a 50 mL polypropylene centrifuge tube.
- ✓ Add (1+1) HNO_3 to adjust acid concentration to about 1% (v/v) HNO_3
 - ✓ e.g., 0.4 mL (1+1) HNO_3 to 20 mL sample
 - ✓ Cap tube and mix analyze
- ✓ **Allowance for sample dilution SHOULD be made in calculations**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

61

"Direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU

- Treat **unfiltered, acid preserved sample** aliquot using the sample preparation procedure described in Section 11.1 (**Aqueous samples**) while making allowance for sample dilution in the data calculation
- For determination of **total recoverable analytes** in all other aqueous samples or for preconcentrating drinking water samples prior to analysis, follow the procedure given in Sections 11.2.2 through 11.2.7.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

62

EPA 200.7 Determination of **total recoverable elements** in aqueous samples

- **UNFILTERED** samples acidified with (1+1) HNO₃ to pH <2 (normally, 3 mL (1+1) acid/liter sample)
- Preservation MAY be made at time of collection
- *However, to avoid hazards of strong acids in field, transport restrictions, and contamination, it is recommended that samples be returned within 2 weeks !!!! of collection and acid preserved in lab*
- Following acidification, sample SHOULD be mixed, held for 16 h, then verified pH <2 prior to withdrawing aliquot for processing or "direct analysis."
- If, pH is > 2 (high alkalinity), more acid **MUST** be added, and sample held for 16 h+ until pH <2

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

63

Determination of total recoverable analytes in **aqueous sludge samples containing total suspended solids < 1% (w/v).**

- 100 mL of well-mixed sample + 3 mL of conc HNO₃
- Heat and evaporate to 5 mL
 - ✓ *If sample contains large amounts of dissolved solids, adjust volume upwards to prevent sample from going to dryness*
- Add 3 mL of conc HNO₃ and reflux until sample is completely digested or no further changes in appearance occur, adding additional aliquots of acid if necessary to prevent sample going to dryness
- Evaporate to 3 mL, again adjusting upwards if necessary.
- Add 10 mL of reagent water and 4 mL of (1+1) HCl and reflux for 15 min.
- Cool and dilute to 100 mL with reagent water
- Remaining solid material SHOULD be allowed to settle, or aliquot of final volume MAY be centrifuged.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

64

**Total recoverable analytes in aqueous samples >1
NTU turbidity**
Sections 11.2.2-11.2.7

- Reflux 100 mL well mixed, acid preserved sample with **2 mL (1+1) HNO₃ and 1.0 mL (1+1) HCl**. Reduce volume to about 20 mL by gentle heating at 85°. **DO NOT BOIL**. Avoid vigorous boiling to prevent loss of HCl-H₂O azeotrope
 - ✓ When necessary, smaller volumes MAY be used.
- NOTE: If sample contains >1 % undissolved solids but <1 g acidified aliquot SHOULD be evaporated to near 10 mL and extracted using acid-mixture procedure described in Sections 11.3.3-11.3.6. (4 mL of (1+1) HNO₃ and 10 mL of (1+4) HCl).
- Undissolved material - settle overnight or centrifuge
- Note: If after centrifuging or standing overnight, sample contains suspended solids sample MAY be filtered to remove particles to prevent nebulizer clogging
- Stability - analyze as soon as POSSIBLE

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

65

Solid samples

- No preservation prior to analysis other than storage at 4°C.
- There is no established holding time limitation for solid samples.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

66

TOTAL RECOVERABLE ANALYTES in SOLID SAMPLES - *sample drying*

- Mix sample thoroughly and dry sample to constant weight at 60°C. (60°C to prevent loss of Hg and other volatile metallic compounds, to facilitate sieving)
- For samples with < 35% moisture, 20 g portion sufficient. For samples moisture > 35%, 50-100 g is REQUIRED.
- Sieve dried sample using 5-mesh polypropylene sieve and grind in mortar and pestle (clean between samples)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

67

Determination of total recoverable analytes in sludge samples containing total suspended solids > 1% (w/v).

- Reflux 1 g dried, sieved and ground sample + 10 mL of (1+1) HNO₃ for 10 min
- Remove sample from hot plate and allow to cool.
- Add 5 mL of conc HNO₃ and reflux for 30 min. Repeat this last step
- Add 2 mL of reagent water and 3 mL of 30% H₂O₂. Place beaker on hot plate and heat until a gentle effervescence
- Add additional 1 mL H₂O₂ until no effervescence is observed, but no more than a total of 10 mL
- Add 2 mL conc HCl and 10 mL of reagent water and reflux for 15 min
- Remaining solid material SHOULD be allowed to settle, or aliquot of final sample volume MAY be centrifuged.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

68

TOTAL RECOVERABLE ANALYTES in SOLID SAMPLES

- Reflux 1.0 g sample with 4 mL (1+1) HNO₃ and 10 mL of (1+4) HCl at 95°C on hot plate or block digester
- Vigorous boiling MUST be avoided to prevent loss of HCl-H₂O azeotrope.
- Allow extract solution to *stand overnight to separate insoluble material or centrifuge*
 - ✓ *If after centrifuging or standing overnight, solution contains suspended solids that would clog nebulizer, filter prior to analysis – beware contamination*
- **Analyses SHOULD be performed as soon as possible**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

69

EPA 200.7 - summary sample preparation

- **Dissolved Analytes** in FILTERED aqueous sample or in drinking water where turbidity is <1 NTU, add HNO₃
- **Total Recoverable Analytes** in UNFILTERED aqueous sample or "DIRECT ANALYSIS" for total recoverable elements in drinking water where turbidity is <1 NTU, add HNO₃
- **Total Recoverable Analysis of Solid or Aqueous Sample Containing Undissolved Material (> 1 NTU)** - gentle refluxing with 2 mL (1+1) HNO₃ and 1.0 mL (1+1) HCl.
- **Total Recoverable Analysis of Aqueous Sample Containing Undissolved Material (> 1 %, <1 g)** reflux with 4 mL of (1+1) HNO₃ and 10 mL of (1+4) HCl).
- **Total Recoverable Analysis of Solid Sample.** Reflux sample with 4 mL (1+1) HNO₃ and 10 mL of (1+4) HCl
- **Total recoverable analysis of aqueous sludge containing <1% total suspended solids, solubilized by successive refluxing with HNO₃ and HCl.**
- **Total recoverable analysis of a sludge containing total suspended solids > 1% (w/v) solubilized by refluxing with HNO₃, organic materials oxidized with H₂O₂, further solubilized by refluxing with HCl.**
 - ✓ centrifuged or settle overnight

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

70



08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 71

***US-EPA Office of Solid Waste
publication SW-846***

***“Test Methods for Evaluating Solid
Waste”***

***26 elements by ICP-MS, ICP-OES,
FAAS, GFAAS, (CVAAS)***

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 72

Methods for Evaluating Solid Waste (SW-846)

- **Collection and testing waste samples**
- *SW-846 includes QC, sampling plan development and implementation*
- **Analysis of inorganic and organic constituents, estimation of physical properties and appraisal of waste**
- **Basis for development of laboratory SOPs**
- **Trouble shooting**
- **Statistical evaluation of data**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

73

SW 846 Digestion procedures

- **3050A**
 - ✓ Acid digestion of waters for total recoverable or dissolved metals
- **3015A**
 - ✓ Acid leaching of aqueous samples and extracts
- **3050B**
 - ✓ Strong acid digestion of sediments, sludge and soil. Dissolves elements that are “environmentally available”
- **3051A**
 - ✓ Acid leaching of sediments, sludge, soil and oil
- **3052**
 - ✓ Acid digestion of siliceous and organically based matrices

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

74

**METHOD 3005A - ACID DIGESTION OF WATERS
FOR TOTAL RECOVERABLE OR DISSOLVED
METALS**

- **Acid digestion for surface and ground water samples for ICP-AES and MS**
- **Al, Mg, Sb, Mn, As, Mo, Ba, Ni, Be, K, Cd, Se, Ca, Ag, Cr, Na, Co, Tl, Co, V, Fe, Zn, Pb**
- **Total dissolved metals**
 - ✓ **Filter sample at time of collection, acidify filtrate with nitric acid**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

75

**METHOD 3005A - OF WATERS FOR TOTAL
RECOVERABLE OR DISSOLVED METALS SUMMARY**

- **Dissolved metals** - sample is filtered through 0.2-0.45- μm filter at time of collection.
 - ✓ filtrate acidified at time of collection with nitric acid.
 - ✓ *Some metal complexes may not dissociate*
- **Total recoverable metals** - sample is acidified at time of collection with nitric acid.
 - ✓ At time of analysis sample is heated with HNO_3 and reduced in volume
 - ✓ Digestate is filtered and diluted to volume

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

76

ACID DIGESTION of SEDIMENTS, SLUDGES and SOILS - METHOD 3050B

○ Scope

✓ Strong acid digestion - dissolves elements that are "environmentally available."

○ *Immobile elements* in silicate structures are not dissolved (total digestion - Method 3052).

○ Al, Mg, As, Sb, Mn, Be, Ba, Mo, Cd, Ni, Cr, K, Co, Ca, Ag, Fe, Na, Pb, Tl, V, Se, Zn

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

77

ACID DIGESTION of SEDIMENTS, SLUDGES and SOILS METHOD 3050B - SUMMARY

○ 1-2 g (wet wt) or 1 g (dry wt) sample digested with repeated additions of nitric acid and hydrogen peroxide

○ ICP-MS analysis - digestate reduced in volume, diluted to 100 mL.

○ HCl added to increase metal solubility

○ Digestate filtered and filter paper and residues rinsed

○ Residues analyzed by HF-HNO₃

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

78

SW 846 - Microwave assisted procedures
Soil, sediment, sludge, fly-ash, wastewater etc.

○ **US-EPA 3015 Update II**

- ✓ Microwave-assisted acid digestion of aqueous samples and extracts

○ **US-EPA 3051 Update II**

- ✓ Microwave-assisted acid digestion of sediments, sludges, soils and oils

○ **US-EPA 3052 Update III**

- ✓ Microwave-assisted acid digestion of siliceous and organic matrices

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

79

Benefits of closed vessel digestion systems

- Higher temperature and pressure than open vessel digestion
- High recovery due to sealed vessels
- No loss of acid strength
- Reduced reagents – lower blanks
- Volatile retention
- Multi samples/run
- *Pressure and temperature sensors and connections*
- *Vessels convert from fully sealed to self-venting*
- Meets USEPA SW-846 Methods 3015, 3051, 3052 and NPDES

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

80

**METHOD 3015 - MICROWAVE ASSISTED ACID
DIGESTION OF AQUEOUS SAMPLES AND
EXTRACTS - SCOPE AND APPLICATION**

○ Acid digestion of aqueous samples

✓ Mobility of analytes in wastes that
contain suspended solids

**○ Al, Pb, Sb, Mg, As, Mn, Ba, Mo, Be,
Ni, Cd, K, Ca, Se, Cr, Ag, Co, Na, Cu,
Tl, Fe, V, Zn**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

81

**METHOD 3015 - MICROWAVE ASSISTED ACID
DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS
SUMMARY**

**○ 45 mL aqueous sample digested in 5 mL
conc. nitric acid in a fluorocarbon (PFA or
TFM) vessel for 20 min using MW**

**○ Sample cooled, filtered, centrifuged or
allowed to settle**

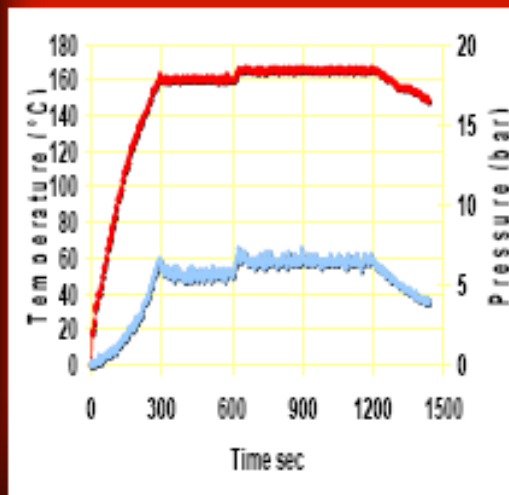
*Samples that contain organics, such as TCLP
extracts, will result in higher vessel pressures
which could cause venting and loss of analytes
and/or sample*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

82

US EPA 3015



- Sample 45 mL
- 2.5 mL HNO₃ 65% and 2.5 mL HCl (37%) for FAAS and ICP)
- 5 mL HNO₃ 65% only for FLAA, GFAA, ICP and ICP-MS
- Digestion 20 min
- Temperature should reach 160°C in 10 min and remain between 165-170°C for additional 10 min
- Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Na, V, Zn

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

83

METHOD 3051 - MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

○ SCOPE

- ✓ Microwave assisted acid digestion of sludges, sediments, soils, and oils
- ✓ Rapid multielement acid leach digestion for evaluation of site cleanup, TCLP testing of waste

○ ICP-AES and MS

- ✓ Al, Cd, Fe, Mo, Na, Sb, Ca, Pb, Ni, Sr, As, Cr, Mg, K, Tl, B, Co, Mn, Se, V, Ba, Cu, Hg, Ag, Zn, Be

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

84

METHOD 3051 - MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS - SUMMARY

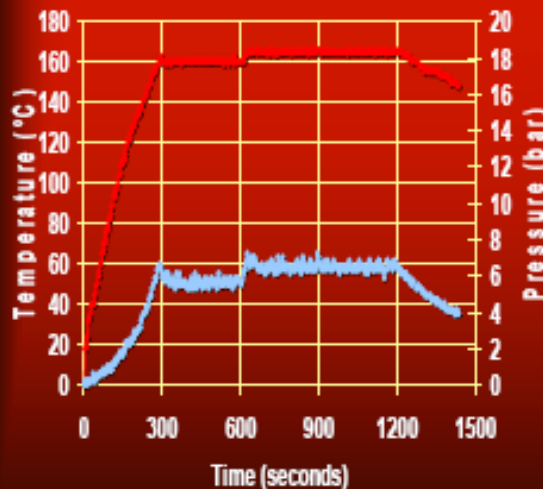
- 0.5 g digested in 10 mL conc. nitric acid for 10 min using MW in fluorocarbon (PFA or TFM) microwave vessel
- Filtered, centrifuged, or allowed to settle, diluted to volume and analyzed by appropriate SW-846 method
- Residues analyzed by HF-HNO₃ mixture

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

85

US EPA 3051- II



- 0.5 g + 10 mL HNO₃ 65%
- Acid leaching method
- Digestion time 10 minutes
- Temperature to reach 175°C within 5.5 minutes and to remain between 170-180°C for the balance of 10 min
- Al, Sb, As, B, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sr, V, Zn

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

86

**METHOD 3051 - MICROWAVE ASSISTED ACID
DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS
- INTERFERENCES**

- **Reactive/volatile materials MAY create high pressures and cause vessel venting with sample loss**
- **Complete decomposition of carbonates or C- based samples - vessel venting if sample size > 0.25 g when used in 120 mL vessels with a pressure relief device that has upper limit of 7.5 ± 0.7 atm (110 ± 10 psi)**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

87

METHOD 3052 - SCOPE

- ***Total decomposition for geological studies, mass balances, SRMS***
- ***Rapid multi-element, MW-assisted acid digestion for strategic decisions***

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

88

US EPA method 3052- III

- Microwave assisted acid digestion of siliceous and organically based matrices
- *“Temperature profile specified to permit specific reactions. Dictates that $180^{\circ} \pm 5^{\circ}\text{C}$ will be attained in < 5.5 min., persisting for $180^{\circ} \pm 5^{\circ}\text{C}$ for 9.5 min. for completion of specific reactions...”*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

89

METHOD 3052 - MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND CARBONACEOUS MATRICES

- **SCOPE** - total decomposition of siliceous, organic and complex matrices.
- Ash, biological tissues, oils, contaminated soils, sediments, sludges
- Al, Cd, Fe, Mo, Na, Sb, Ca, Pb, Ni, Sr, As, Cr, Mg, K, Ti, B, Co, Hg, Ag, Zn, Be

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

90

US EPA 3052 - III

Temperature

✓ Reach 180°C in 5 min and remain between 175-185°C for 10 min

- 0.5-1 g
- 9 ml HNO₃ + 3 ml HF, addition of HCl for higher recovery of Ag, Ba, Sb, Fe, Al, H₂O₂ for organic samples

Microwave hardware requirement

- Temperature control
- Kitchen-type units not permitted
- Optional facility for evaporation

Pressure vessel requirement

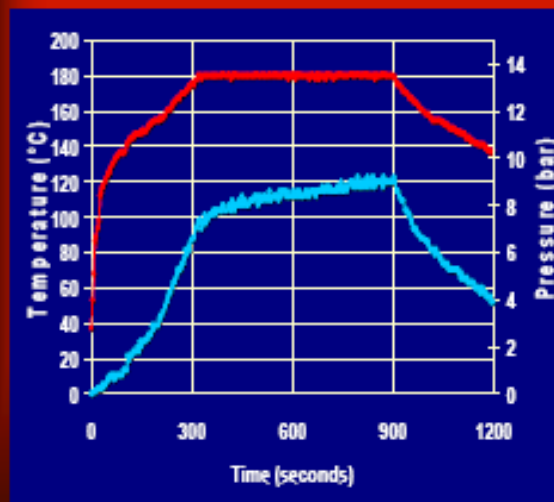
- Made of PFA or TFM
- 50 mL volume or higher, 30 bar pressure or higher

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

91

US EPA 3052



- EPA-approved method for "Total microwave sample preparation"
- Soil, sludge, sediment, fly-ash and oil-contaminated soil
- Complete sample decomposition ?
- Validated for Al, Sb, As, B, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sr, Tl, V, Zn
- FL-AAS, CV-AAS, ICP-OES and ICP-MS

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

92

Analysis of NIST Buffalo River Sediment using EPA 3052-III

- Experimental Conditions
- Sample – 0.5 g
- Temperature feedback
- 9 ml HNO₃, 3 ml HF
- Vessel MDR 600
- Tem 800°C

Analyst P.J. Walter, Duquesne University

Ele	Anal	SD	Cert	SD	Tech
Cd	3.5	1.2	3.45	0.22	ICP-MS
Cr	132.9	1.3	135	5	ICP-MS
Cu	98	4.2	98.6	5	FAAS
Ni	43.6	3.9	44.1	3.0	ICP-MS, ETV-AAS
Pb	154.5	9.2	161	17	FAAS
Zn	441.9	0.8	438	12	FAAS

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

93

Comparison of sample preparation procedures

EPA 200.7	Procedure	Other methods
Dissolved analytes in filtered sample	Filtration < 0.45 um 1:1 HNO ₃ 2 ml/100ml	SM 3030B
Total recoverable analysis of aqueous sample ("direct analysis") < 1 NTU	Unfiltered and acidification with HNO ₃	
Total recoverable analytes in aqueous samples >1 NTU turbidity	Gentle HNO ₃ -HCl reflux (2 mL (1+1) HNO ₃ and 1.0 mL (1+1) HCl)	3030F Nitric - hydrochloric acid digestion.
Total recoverable analysis of aqueous samples >1% total suspended solids	Reflux with 4 mL of (1+1) HNO ₃ and 10 mL of (1+4) HCl	Two procedures
Total recoverable analysis of a sludge sample containing total suspended solids > 1% (w/v) (< 1g)	Reflux with 4 mL (1+1) HNO ₃ and 10 mL of (1+4) HCl at 95°C	
Total recoverable analysis of aqueous sludge containing <1% total suspended solids	Successive refluxing with HNO ₃ and HCl	
Total recoverable analysis of a sludge containing total suspended solids > 1% (w/v)	Refluxing with HNO ₃ , organic materials oxidized with H ₂ O ₂ , further solubilized by refluxing with HCl	

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

94

US EPA method 3052 vessel cleaning procedure

- TFM vessels in 1:1 sub-boiled HCl overnight at 80° - 120°C
- Rinse with double distilled H₂O
- Store in 1:1 sub-boiled HNO₃ overnight at 80 -125°C
- Rinse with then store in double distilled H₂O
- Dry in particle and fume-free environment

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

95

- In EPA methods no HClO₄, HF, H₂SO₄
- In SM – no H₂O₂
- In SM HCl only extractions
- In SM MW poorly defined

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

96

INSTRUMENTATION

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

97

Equipment ICP-AES

- Fully computer controlled
- Background-correction
- RF generator compliant with FCC regulations.
- Argon gas supply– high purity (99.99%).
- Variable speed peristaltic pump to deliver standards and samples to nebulizer.
- Optional mass flow controllers to regulate argon flow rates especially aerosol carrier

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

98

Axial Viewed Plasma



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

99

Vista CCD Simultaneous ICP Spectrometer

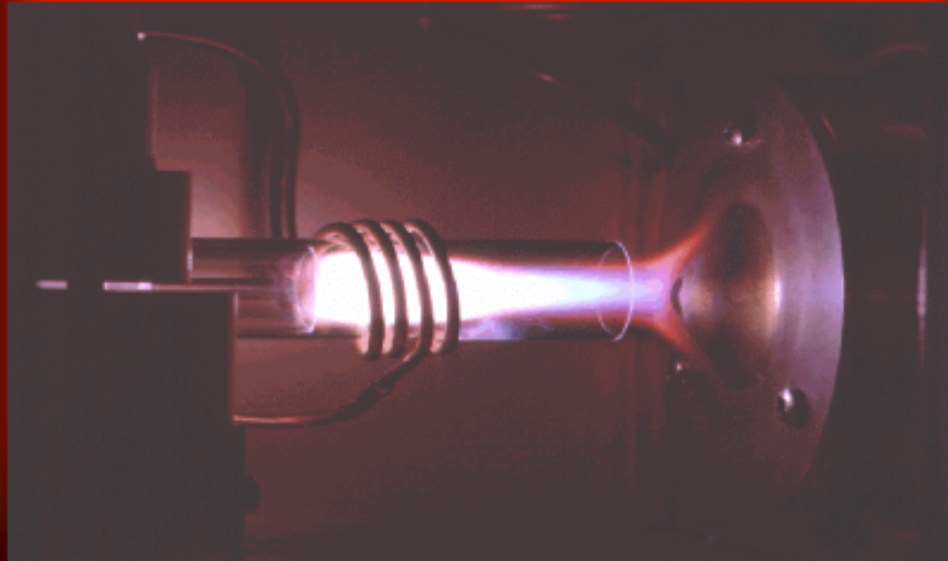
- Echelle 0.4 m spectrometer, thermostatted to 35°C
- 94.74 lines/mm grating used in 19 to 88 orders
- 7-9 pm resolution in UV
- CaF₂ prism cross-disperser for order sorting
- Ar or N₂ purge allows low UV detection (167 nm)
- Axial viewing with end-on Ar shear gas
- Computer controlled vertical and horizontal positioning of plasma

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

100

Cooled Cone Interface



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

101

Axial Viewed Plasma Torch Box

○ Cooled cone interface – minimizes interferences from molecular



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

102

Vista CCD Axial ICP Cooled Cone Interface (CCI)

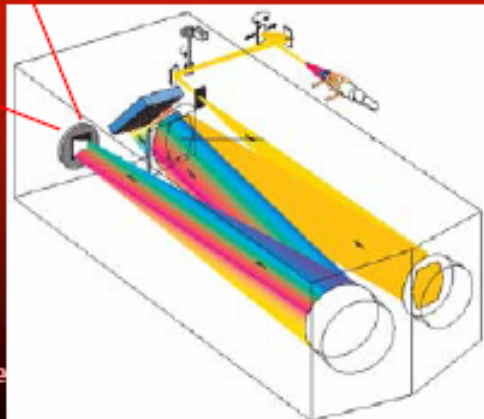
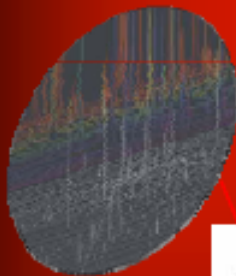
- End-on gas removes cool plasma fringe where EIE atomization and ionization interferences prevail
- Interferences similar to Radially Viewed ICPS
- No need for dual view systems and dual analysis
- Plasma tolerates 5% dissolved solids [compared with 0.5% for dual view systems]

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

103

Vista-PRO Chip Image



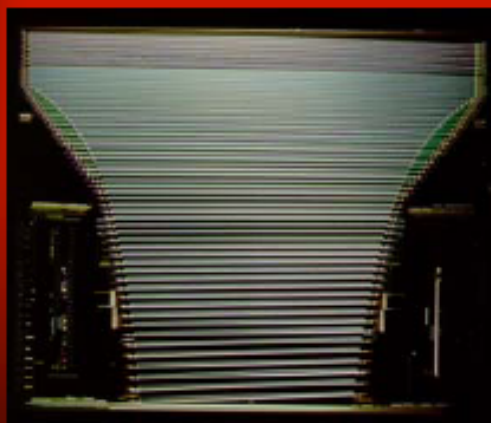
08-Aug-07

Joe Bren

Wastes

104

The Vista Chip Custom CCD Detector



- Full wavelength coverage
- Individually addressed arrays
- Individual pixel anti-blooming protection
- Adaptive Integration
- Use alternate wavelengths to extend linear dynamic range and confirm results
- Trace and high matrix elements determined simultaneously

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

105

Vista CCD - Resolution

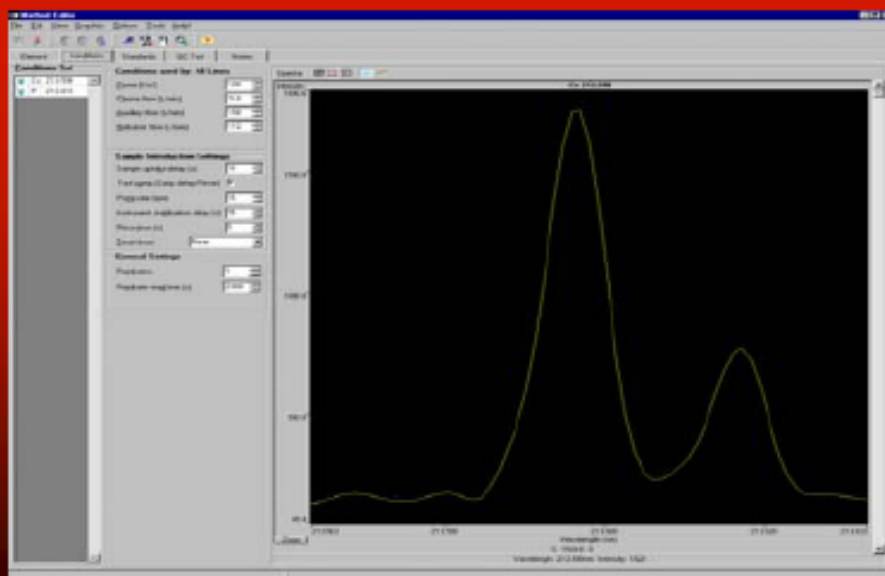
Element	Wavelength	Resolution, nm
As	188.979	0.007
Be	234.861	0.008
B	249.773	0.008
Ca	396.847	0.011
Li	670.784	0.024
K	769.896	0.045

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

106

Resolution- Cu and P



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

107

Vista CCD Simultaneous ICP - CCD detector

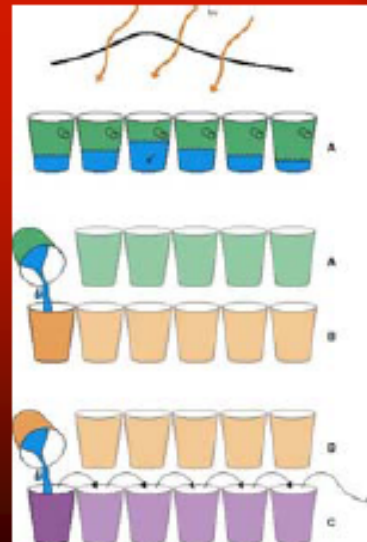
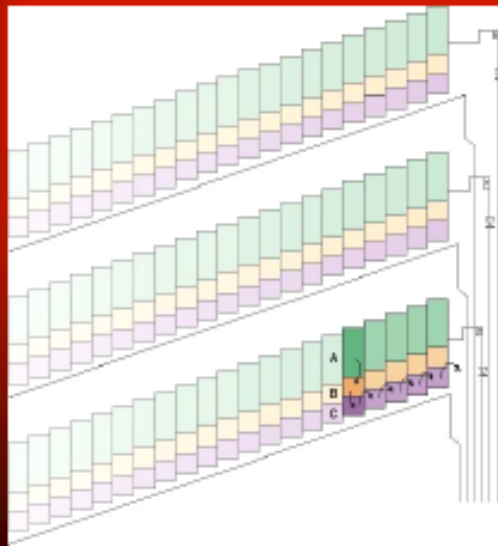
- Custom CCD detector designed for ICP-AES
- 70,000 pixels for wide wavelength selection
- *Pixels arranged to exactly match two-dimensional echelle image (I-MAP technology)*
- *Duplex readout circuitry halves readout time*
- Processing electronics 40 times faster
 - ✓ 1 Megahertz pixel processing speed
- *Vista Chip Peltier cooled to - 35°C for low noise*
- Processing electronics off-chip for high QE

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

108

CCD - How Does it Work?



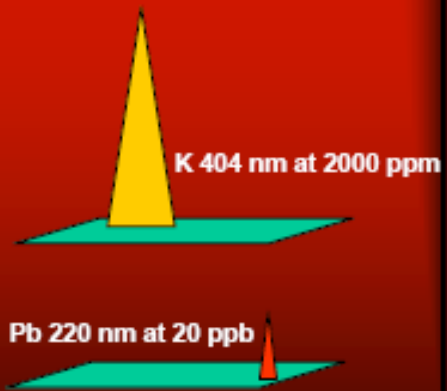
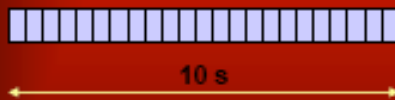
08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

109

Smart Signal Processing

Adaptive Integration



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

110

Advantages of VISTA CCD spectrometer

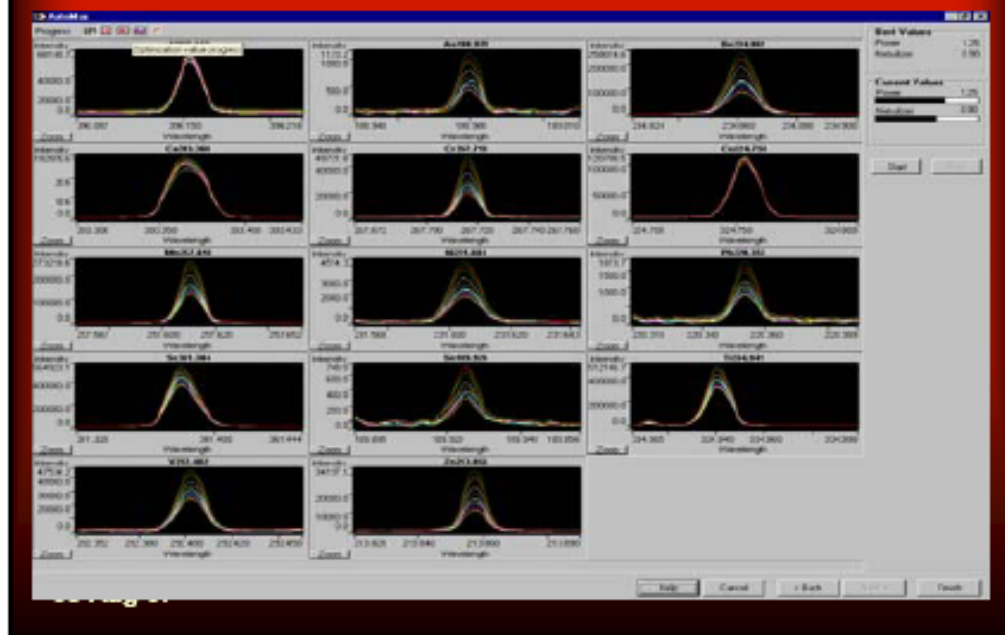
- Simultaneous determination of numerous elements, many spectral lines of the same element
- Selection according to energy, interferences and sensitivity
- Internal validation of analytical results
- ppb ILDS, wide dynamic range of several orders of magnitude
- Average spectral band pass of 0.01 nm in UV-VIS region
- Simultaneous spectral background correction in proximity of spectral lines on one or both sides of spectral lines.
- Mathematical treatment of background and spectral line coincidences under computer control - FACT.
- Flushed with Ar - spectral lines in UV region (167-190 nm range)
- Visual examination of spectral profiles for determining background positions, spectral line interferences, washout time, optimization of ICP conditions

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

111

Multielement capability. More than one line of the same element



Manipulation of multielement data using CCDs – many samples- many elements

- Identification of spectral interferences
- EIE effects - utilization of lines of same element with different energy potentials – higher the energy, higher the interference
- Extending concentration ranges – over range
- Compensation of background using different techniques – IECs, FACT, etc.
- Data with high % RSDs
- MgII/Mg ratios
- Automatic queries using analytical criteria
- End result – inter spectral line compatibility. Trouble shooting for disorders based on poor results
- Unusual blank data

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

113

Need for software to handle multiple wavelengths of the same element

- ❖ Time consuming to manually evaluate lines
- ❖ Compare wavelengths – set threshold – if 2 of 3 lines agree within X % - calculate mean and mean %RSDs
- ❖ If none of the results agree then flag the lines for spectral review
- ❖ Semiquantative analysis
- ❖ Other routines can be introduced – blank screening, IDL, MDLs, etc.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

114

Sample introduction system

- Meinhard type concentric nebulizer, Micromist - GE
- Small conical rapid wash-out spray chamber
- Argon humidifier for high salt concentrations
- Ultrasonic nebulizer for 10-fold enhancement of LODs
- High salt nebulizers for saline samples

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

115

TYPE OF NEBULIZERS



Sample

Cross Flow Nebulizer

Uptake 1 ml/min



Parallel Path nebulizer:

Burgener Micro Mist nebulizer:

Uptake 0.3-0.7 ml/min

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

116

ICP Optimization

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 117

Plasma solution

- Used for determining optimum position (X and Y) of plasma
- As, Pb, Se, Tl in 20 mL (1+1) HNO₃ and (1+1) HCl and diluting to 500 mL

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 118

Operating conditions for aqueous solutions

Forward power	1100-1200 watts
Viewing height	15-16 mm
Argon coolant flow	15-19 L/min.
argon aerosol flow	0.6-1 L/min.
Sample pumping rate	1-1.8 mL/min
Preflush time .	60 s
Measurement time	1 s per wavelength peak for sequential instruments 10 s per sample for simultaneous instruments

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

119

Plasma optimization

- After establishing nebulizer gas flow rate, determine solution uptake rate of nebulizer in mL/min. by aspirating known volume of calibration blank for at least 3 min.
- Divide spent volume by aspiration time (in min) and record uptake rate
- Set peristaltic pump to a stable uptake flow rate
- Align horizontally the plasma and/or optical profile spectrometer
- Use selected instrument conditions and aspirate **PLASMA SOLUTION** (10 µg/mL As, Pb, Se and Tl)
- Collect intensity data at wavelength peak for each analyte at 1 mm intervals from 14-18 mm above top of work coil
- This region of plasma is referred to as **analytical zone**
- Repeat using calibration blank. Determine net signal /blank intensity ratio for each analyte for each viewing height
- Choose viewing height or depth that provides largest SBR ratio for least sensitive element of the four analytes
- If more than one position provides same ratio, select position that provides highest net intensity or accept a compromise position for all four analytes.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

120

ICP Expert Software

- **Method Development / Optimization**
- **Interference / Background Correction**
- **Inter Element Corrections**
- **Background Correction**
- **Automated Quality Control Parameters**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

121

Instrumental Quality Control

Use of Cu/Mn and MgII/Mg

- **Optimum operating conditions** Check Cu and Mn signals, Cu/Mn and MgII/Mg I ratios and tune ICP operating conditions to obtain optimum values.
- **Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting argon aerosol flow)** recommended to achieve repeatable ICFs and to optimize plasma operating conditions

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

122

Use of Cu/Mn intensity ratio

- **Cu/Mn intensity ratio at 324.754 nm and 257.610 nm**
- **Cu/Mn intensity ratio (by adjusting argon aerosol flow) recommended to achieve repeatable ICFs (Ref 17) and to optimize plasma operating conditions**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

123

MULTIELEMENT OPTIMIZATION EMISSION INTENSITY RATIO METHOD

HELD CONSTANT

- POWER
- OBSERVATION HEIGHT
- OUTER Ar FLOW
- INTERMEDIATE Ar FLOW

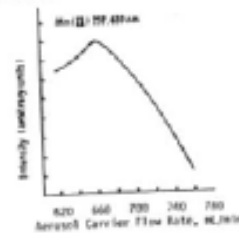
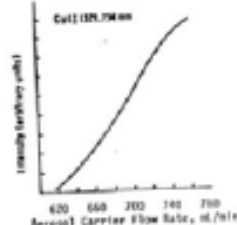
VARIED FOR OPTIMIZATION

- INNER (AEROSOL CARRIER) FLOW

EMISSION INTENSITY RATIO

Cu (I) 324.754 nm
Mn (II) 257.610 nm

EXCITATION POT. 3.8 eV
EXCITATION POT. 12.2 eV

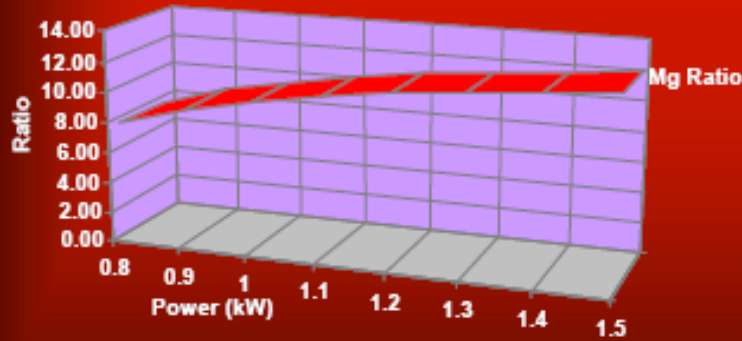


08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

124

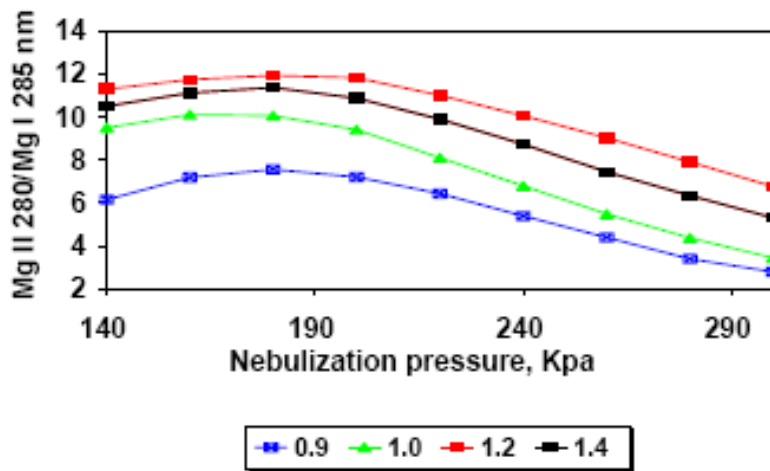
Robust 40 MHz plasma



- MgII 280.270/Mg I at 285.213nm
- >10 indicates highly robust plasma

Joe Brenner, Compliant Analysis of Waters and Wastes

Variation of Mg II 280/Mg I 285 as a function of nebulization and power



08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

126

Spectral line selection

- See wavelengths tables in procedures
- Other wavelengths MAY be substituted if they can provide needed sensitivity and are corrected for spectral interference.
- Instrument and operating conditions **MUST** be capable of providing data of acceptable quality
- Follow instructions provided by instrument manufacturer unless other conditions provide similar or better performance

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

127

Background and spectral corrections

- **Background correction**
 - ✓ 1 or 2 points - free selection
 - ✓ Automatic Fitted Gaussian
- **Multivariant Curve-fitting Techniques)**
 - ✓ Spectral line interference corrections using on-line deconvolution for resolution of complex spectra - up to 3 models

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

128

Manipulation of multielement data using CCDs – many samples- many elements

- Identification of spectral interferences
- EIE effects - utilization of lines of same element with different energy potentials – higher the energy, higher the interference
- Extending concentration ranges – over range
- Compensation of background using different techniques – IECs, Multivariant, etc.
- Data with high % RSDs
- MgII/Mg ratios
- Automatic queries using analytical criteria
- End result – inter spectral line compatibility. Trouble shooting for disorders based on poor results
- Unusual blank data

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

129


Need for software to handle multiple wavelengths of the same element

- ❖ Time consuming to manually evaluate lines
- ❖ Compare wavelengths – set threshold – if 2 of 3 lines agree within X % - calculate mean and mean %RSDs
- ❖ If none of the results agree then flag the lines for spectral review
- ❖ Semiquantative analysis
- ❖ Other routines can be introduced – blank screening, IDL, MDLs, etc.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

130



08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* **131**

**METHOD 200.7 TRACE ELEMENTS IN WATER,
SOLIDS, AND BIOSOLIDS BY INDUCTIVELY
COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRY**

**Revision 5.0, August 1998, Draft 1
U.S. Environmental Protection Agency,
Office of Water,
Office of Science and Technology,
Engineering and Analysis Division (4303),
401 M Street SW, Washington, D.C. 20460**

Will be withdrawn !

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* **132**

Approved elements in EPA 200.7

- Ag, Al, Sb, As, B, Ba, Be, Ca, Cd, Ce, Cr, Co, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si (Silica), Sn, Sr, Ti, Tl, V, Zn
- Ce is used for monitoring spectral interferences
- *Not suitable for silica determination in solids*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

133



USEPA 2005

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

134

**CAN DRINKING WATER BE ANALYZED
USING ICP-AES ACCORDING TO
COMPLIANT US EPA 200.5?**

***CRITICAL EXAMINATION OF RADIALY
(RV) AND AXIALLY VIEWED (AX) ICPS.***

I.B. Brenner

Environmental Analytical Laboratory

9 Dishon Street, Malkha, Jerusalem, 96956, ISRAEL

Telephone 972-2-6797-255 FAX 972-2-6797-145,

Mobile 972-54-424403

e-mail: BRENNER@cc.huji.ac.il

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

135

Analysis of drinking water by ICP-AES



08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

136

Challenges of ICP-AES

- Lowering of regulation limits of toxic elements in drinking water
- RV-ICP-AES fails to meet new concentrations
✓ 200.7 will be withdrawn
- Improvement of IDLs by 5-10 using USN ineffective due EIE interference effects
- USEPA published new SOP (EPA 200.5) for analysis of drinking water using AX-ICP-AES.
- Are enhanced AX-ICP-AES IDLs (x 5-20) sufficient ?

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

137

Plasma-based compliant procedures for multielement analysis of surface, ground, and drinking water, liquid, solid and semi-solid wastes, sludge, and sediments.

Sample preparation protocols allow for determination of dissolved, particulate and total concentrations

ICP-MS

EPA 200.8
SW846-6020 B,
EPA CLP ILM05.2D
DOD
Standard Methods
ASTM
ISO 17294
AOAC

ICP-AES

ISO 11885
EPA 200.7
EPA 6010 B and C
Standard Methods
ASTM
AOAC
EPA-CLP

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

138

**METHOD 200.7 TRACE ELEMENTS IN WATER,
SOLIDS, AND BIOSOLIDS BY INDUCTIVELY
COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRY**

**Revision 5.0, August 1998, Draft 1
U.S. Environmental Protection Agency,
Office of Water,
Office of Science and Technology,
Engineering and Analysis Division (4303),
401 M Street SW, Washington, D.C. 20460**

Will be withdrawn !

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

139

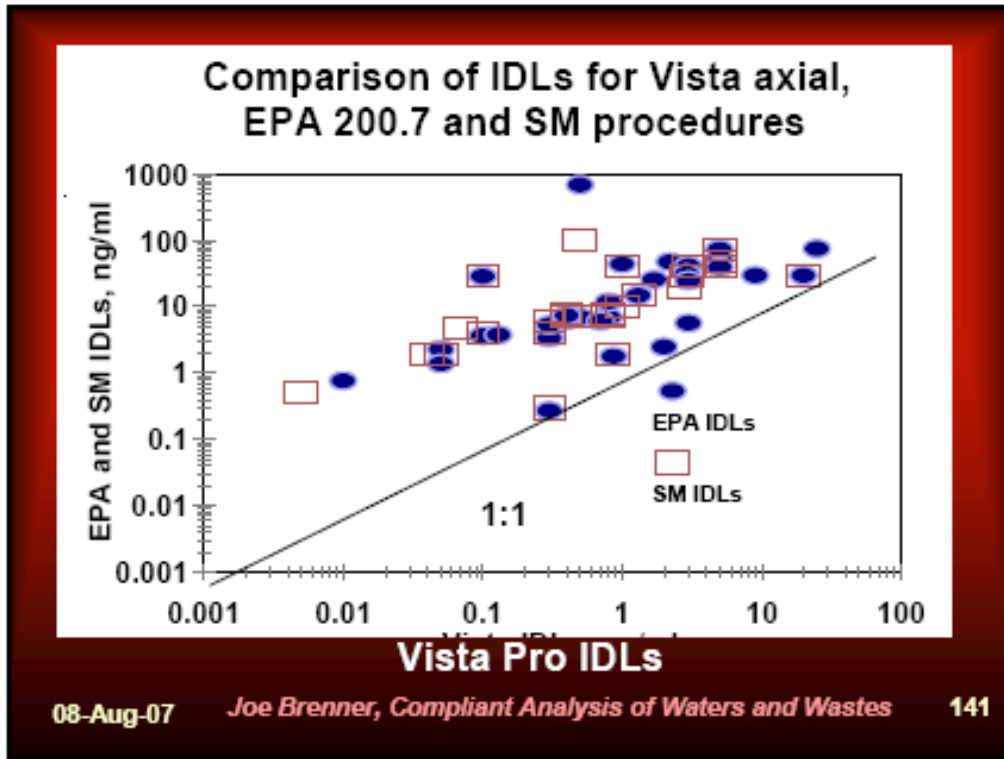
Federal Register

- <http://www.epa.gov/EPA-WATER/2005/March/Day-25/w7848.htm>
- the page for 200.7 as an approved method. - 141.23 - National
- Primary Drinking Water Regulations (toward the bottom of the document.) It - effective January 23, 2006, EPA 200.7 will no longer be an
- approved method for DRINKING WATER analysis. This is due to the changes in
- the maximum contaminant level (MCL) for Arsenic. The MCL for arsenic is
- going from 0.050 mg/L to 0.010 mg/L. Per the EPA, method 200.7 has a method
- detection limit (MDL) of 0.008 mg/L or higher. The interpretation is that
- 200.7 does not have sufficient sensitivity to reliably monitor at the new
- compliance limit. Methods other than 200.7 are approved for Arsenic
- monitoring in Drinking Water. They are Furnace-AAS, Hydride-AAS & ICP-MS
- methods
-
- As of April 2004, Method 200.7 Rev
- 4.4 (1994) was still approved for waste water monitoring.
- <http://www.epa.gov/EPA-WATER/2004/April/Day-06/w6427.htm>
- Here is a clip of the relevant text of the drinking water regs:
- < 16\ The value for arsenic is effective January 23, 2006. Until then, the
- MCL is 0.05 mg/L.
- < 17\ The MDL reported for EPA Method 200.9 (Atomic Absorption;
- Platform—Stabilized Temperature) was determined
- < using a 2x concentration step during sample digestion. The MDL
- determined for samples analyzed using direct
- analyses (i.e., no sample digestion) will be higher. Using multiple
- determinations, EPA 200.9 is capable of

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

140



**METHOD 200.5 - DETERMINATION OF
TRACE ELEMENTS IN DRINKING
WATER BY AXIALLY VIEWED
INDUCTIVELY COUPLED PLASMA -
ATOMIC EMISSION SPECTROMETRY**

Revision 4.2, October 2003

NATIONAL EXPOSURE RESEARCH LABORATORY OFFICE OF
RESEARCH AND DEVELOPMENT U. S. ENVIRONMENTAL
PROTECTION AGENCY CINCINNATI, OHIO 45268

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 142

Scope and application of EPA 200.5

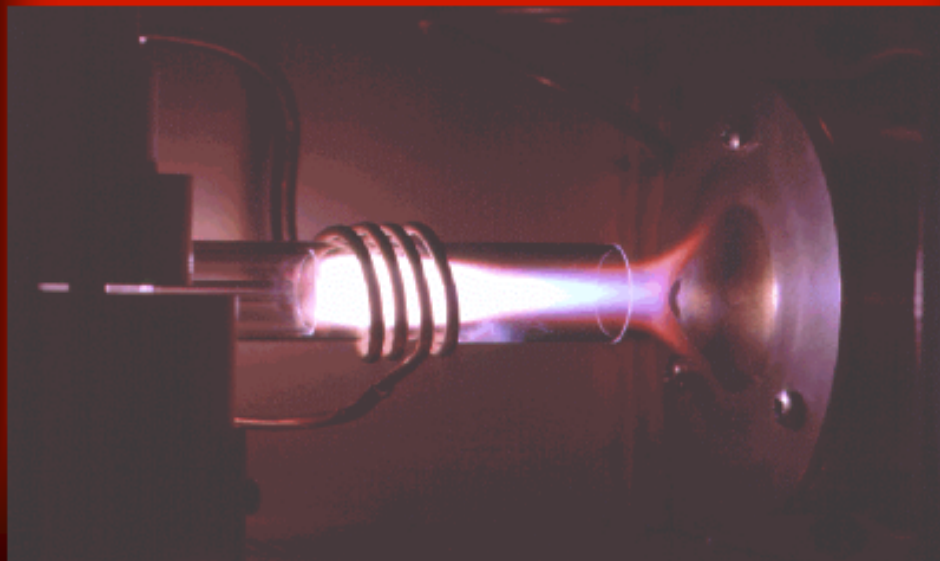
- Determination of dissolved and acid extractable trace and matrix elements, in drinking water in compliance with monitoring programs (e.g., Safe Drinking Water Act [SDWA])
- Procedure utilizes AXV ICP-AES and pneumatic nebulization using CTDs and conventional PMT based systems (?)
- In EPA 200.5, IDLs were obtained using a conventional PMT-based multichannel spectrometer and not a CTD!

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

143

Cooled Cone Interface



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

144

Topics and issues

- Examination of IDLs of axially viewed CT ICPs to determine if 200.5 limits can be obtained using pneumatic sample introduction
 - ✓ Dual view AX-RAD segmented CCD
 - ✓ Dual view AX-RAD CID instrument
 - ✓ Mono view AX-ICP-AES where CCDs are installed on the Rowland Circle of a Paschen Runge configuration
 - ✓ High resolution PMT-based RAD-ICP-AES.
 - ✓ Anonymity - instruments manufacturers not addressed directly for obvious reasons, and will not be denoted directly
- Data employed - available but may be improved with technological development
- Comparison with EPA Contamination List (CCL)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

145

QC tests for complaint laboratory SOPs - *Figures of merit*

- IDLs
- MDLs
- Calibration and calibration verification
- Initial precision and recovery
- Ongoing precision and recovery (OPR)
- Analysis of blanks
- Matrix spike and matrix spike duplicate analyses
- CRMs and PTs

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

146

EPA 200.5 IDLs

- INSTRUMENT DETECTION LIMIT (IDL) -
Concentration equivalent to analyte signal equal to 3 X standard deviation of 10 replicate measurements of calibration blank signal
- For SDWA compliance monitoring MDLs for As, Be, Cd, Sb, Se, and Pb must be 1/5 their MCLs (CCL)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

147



United States
Environmental Protection
Agency

Office of Water
Office of Science and Technology
(43041)

EPA-822-R-02-047
November 2002

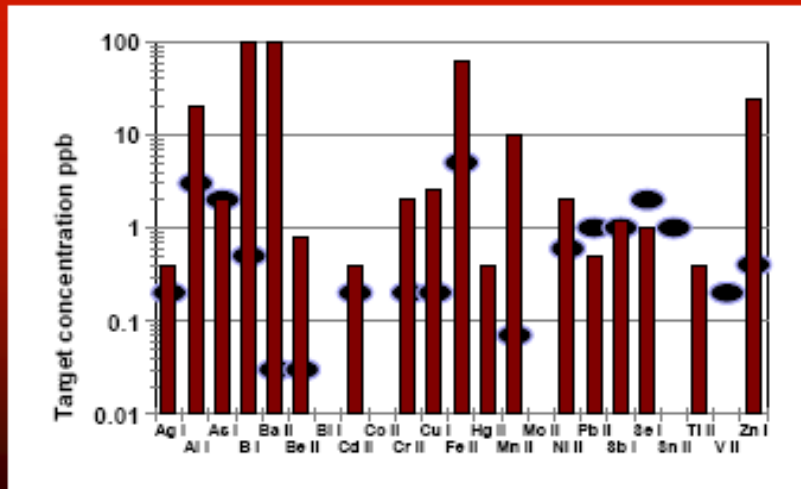
National Recommended Water Quality Criteria: 2002

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

148

EPA 200.5 IDLs conform to target concentrations for primary and secondary contaminants (1/5 CCL, 2004) – except Pb, Se

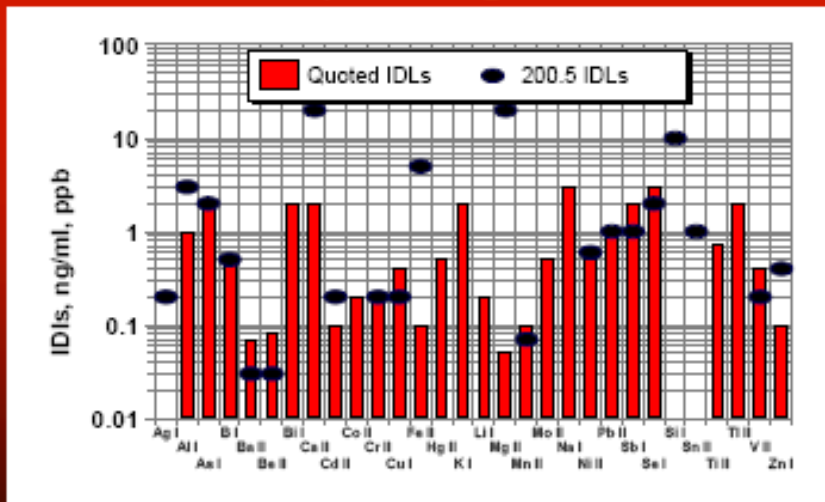


08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

149

Comparison of quoted IDLs vs EPA 200.5 Instrument A, AXV segmented CCD



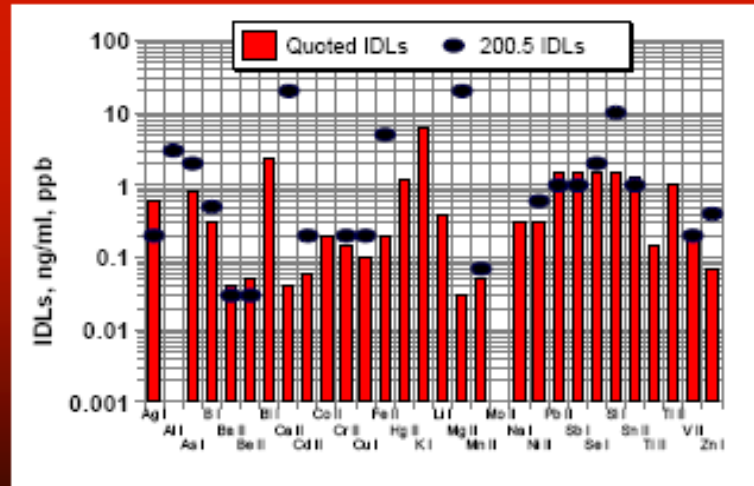
As, B, Ba, Be, Cr, Cu, Mn, Ni, Pb, Sb, Se, V

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

150

Comparison of *quoted* IDLs vs EPA 200.5 Instrument B, high resolution RV Seq ICP-AES – PMT



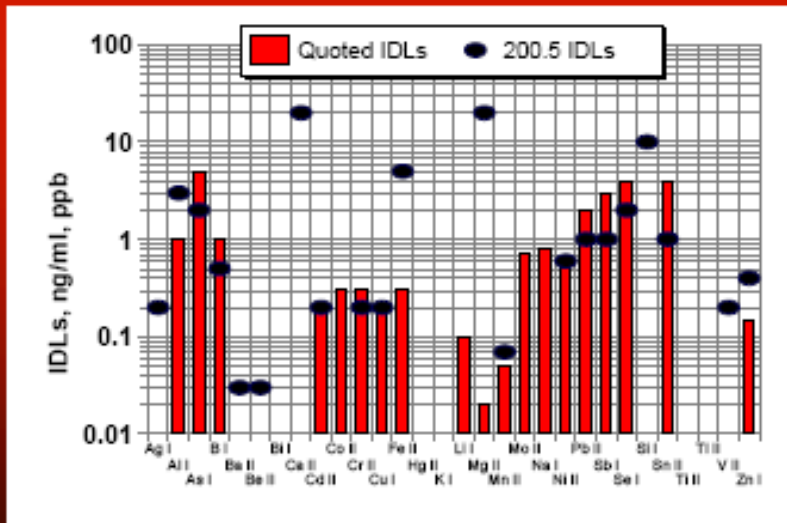
Ag, Ba, Be, Pb, Sb, Sn, V

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

151

Comparison of *quoted* IDLs vs EPA 200.5 Instrument C, medium resolution AXV Seq ICP-AES – CCD



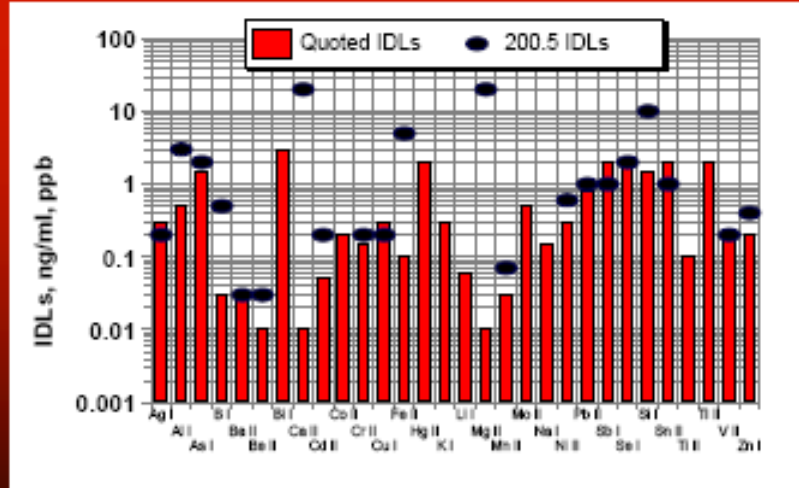
As, Cd, Cr, Cu, Pb, Sb, Sn

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

152

Comparison of *quoted* IDLs vs EPA 200.5 Instrument D, AXV ICP-AES – CCD



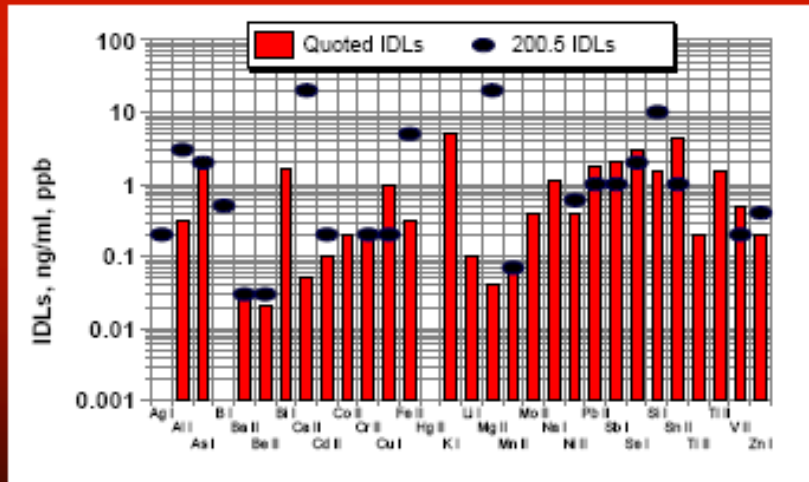
Ag, Ba, Cu, Sb, Se, Sn, V

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

153

Comparison of *quoted* IDLs vs EPA 200.5 Instrument E, AXV ICP-AES – CID



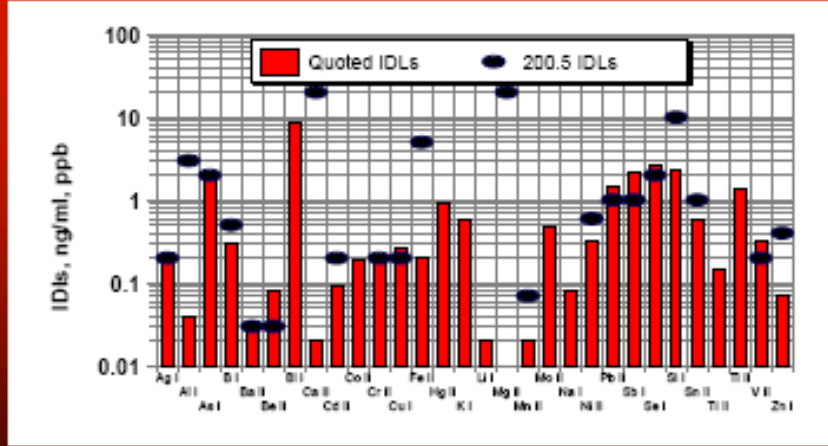
As, Ba, Cr, Cu, Mn, Pb, Se, Sn, V

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

154

Comparison of *quoted* IDLs vs EPA 200.5 Instrument F, AXV ICP-AES – CCD – Paschen Runge



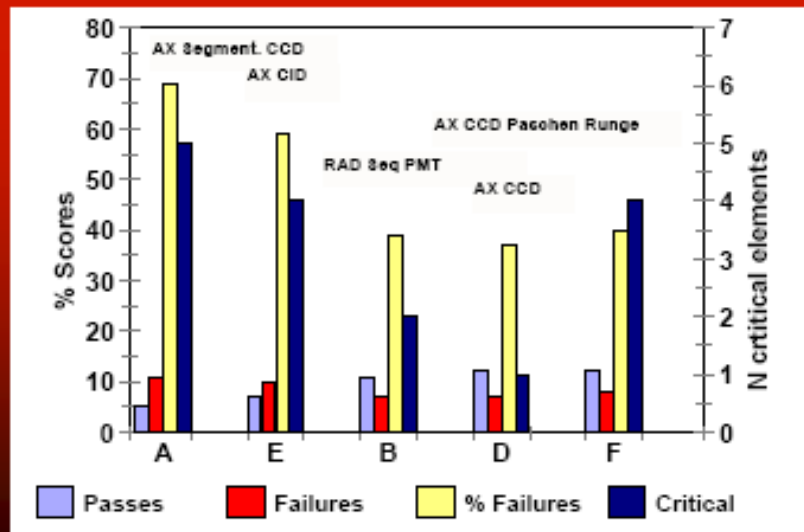
Ag, As, Ba, Cu, Pb, Sb, Se, V

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

155

Vendor vs. EPA IDLs – Scores and failures

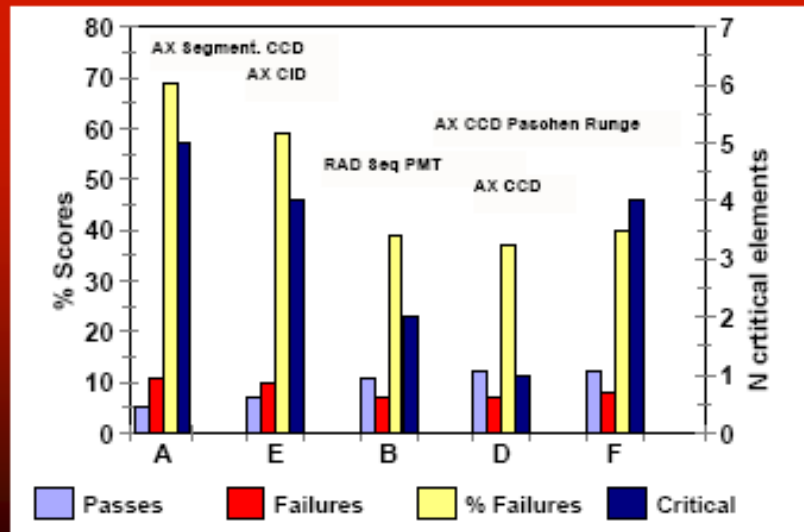


08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

156

Vendor vs. EPA IDLs – Scores and failures



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

157

Scores and failures

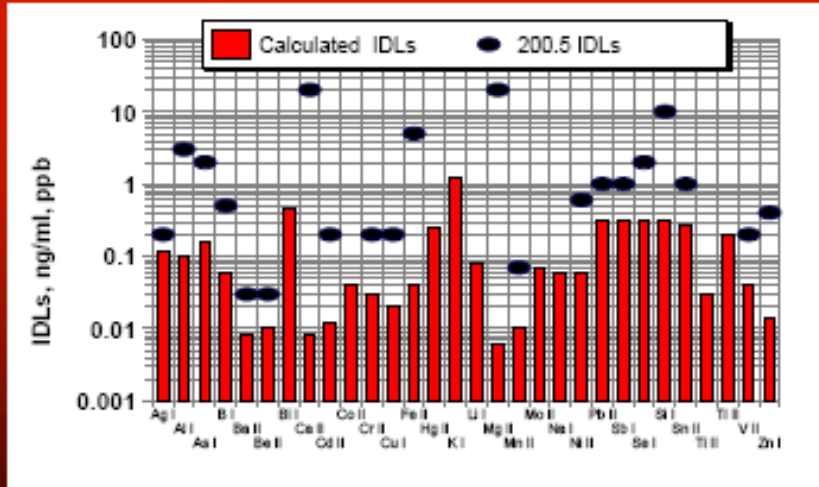
- None of the instruments fully meet EPA 200.5 regulation IDLs
- Failures vary from 40-70 %
- Critical failures vary from 1-5 elements
- The high res RV instrument score is among the lowest with only 2 element failures.
- If this evaluation represents current performance of AX-ICP-AES, it may be concluded that AX-CCD-CID-ICP-AES instruments do not meet EPA 200.5 compliant limits and therefore cannot be used for the determination of the trace elements in drinking water with this SOP.
- An AX-high resolution instrument should easily meet defined 200.5 limits. However, such an instrument is not commercially available.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

158

**Axially viewed high resolution spectrometer.
A 10-fold enhancement has been applied**



No failures

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

159

SW 846-6010

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

160



Performance Data

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 161



Detection limits

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 162

Sensitivity and LODs- EPA

○ Sensitivity:

- ✓ Slope of analytical curve, i.e., relationship between intensity and concentration.

○ Instrumental LODs (IDL's). Concentration equivalent to analyte signals equal to 3 sd of 10 calibration blank measurements – constrained by contamination

○ Method LODs (MDLs) - minimum concentration that can be determined with 99 % confidence that the concentration is > zero

- ✓ MDLs are determined from analysis of a given matrix containing analytes, processed through entire preparative procedure. **MDL determined according to 40 CFR Part 136, Appendix B**
- ✓ MDLs 3-5 times higher than IDLs.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

163

Instrumental detection limits (IDLs)

○ Determine IDLs and precision using 1000 µg/l standard, by nebulizing calibration blank 10 times

- ✓ Performed on regular basis and when new conditions are employed.
- ✓ Register results in QA/QC media.

○ $LOD = [3 Sd_{blank} \times 100^*] / (\text{Intensity of } 100 \mu\text{g/l standard} - \text{intensity}_{blank})$

- 100 µg/l ME standard
- LODs should be determined once a month or when excitation and sample introduction systems are replaced or when new matrix is analyzed

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

164

VISTA AX LODs

Element	LOD rad Liberty	LOD axial Liberty
Ag 328.068	2	0.7
As 188.980	12	5
B 249.773	1	0.4
Ba 455.403	0.06	0.01
Be 234.861	0.15	0.05
Bi 223.061	9	0.8
Cd 228.802	1.2	0.3
Co 238.892	4	0.25
Cr 267.716	3	0.2
Cu 324.754	2	0.6
Fe 259.940	1	0.2
Mn 257.610	0.2	0.06
Mo 202.032	4	0.6
Ni 231.604	5	0.6
Pb 220.353	10	1.5
Sb 217.582	14	2.5
Se 196.026	30	3
Sr 407.771	0.03	0.01
Tl 190.790	12	3
V 292.401	2	0.8
Zn 213.857	1	0.4

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

165

WAVELENGTHS, IDL

Analyte	Estim.,OD.(µg/L)	Wavelength.(nm)
Aluminum	45	308.215
Antimony	32	206.833
Arsenic	53	193.759
Barium	2.3	493.409
Beryllium	0.27	313.042
Boron	5.7	249.678
Cadmium	3.4	226.502
Calcium	30	315.887
Cerium	48	413.765
Chromium	6.1	205.552
Cobalt	7.0	228.616
Copper	5.4	324.754
Iron	6.2	259.940
Lead	42	220.353
Lithium	3.7	670.784
Magnesium	30	279.079
Manganese	1.4	257.610
Mercury	2.5	194.227
Molybdenum	12	203.844
Nickel	15	231.604
Phosphorus	76	214.914
Potassium	700	766.491
Selenium	75	196.090

08-Aug-07

166

Limits of detection, ng/ml. Axial plasma and comparisons

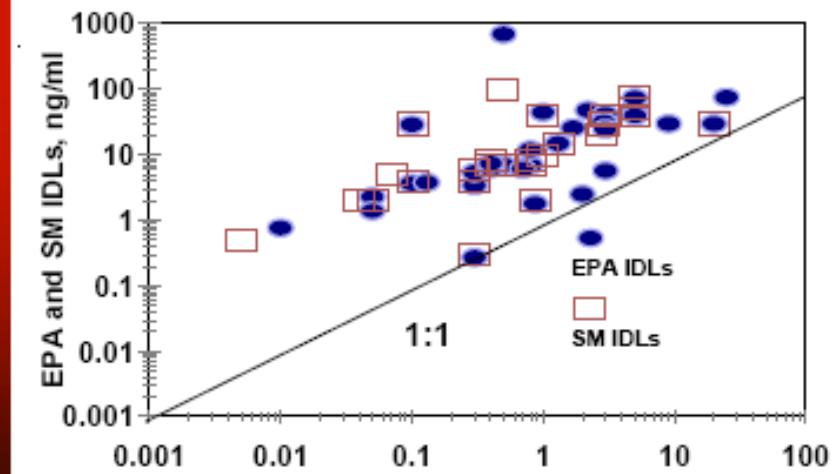
Element	Wave, nm	RP	RP+USN	AP	AP+USN
Al	I 396.152	5	0.5	1	0.15
As	I 193.759	10	10	4	1
Be	II 234.861	0.15	0.01	0.05	0.005
Cd	II 226.502	2	0.3	0.3	0.05
Co	II 238.892	4	0.2	0.15	0.05
Cr	II 267.716	4	0.2	0.2	0.03
Mo	II 202.030	4	0.2	0.6	0.04
Ni	II 231.604	5	0.5	0.75	0.06
Pb	II 220.353	12	1.5	1.5	0.2
Se	II 196.090	30	4	3	0.8
V	II 292.402	2	0.3	0.8	0.05

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

167

Comparison of IDLs for Vista axial, EPA 200.7 and SM procedures



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

168

Effect of Integration Time on LOD (3σ $\mu\text{g/L}$)

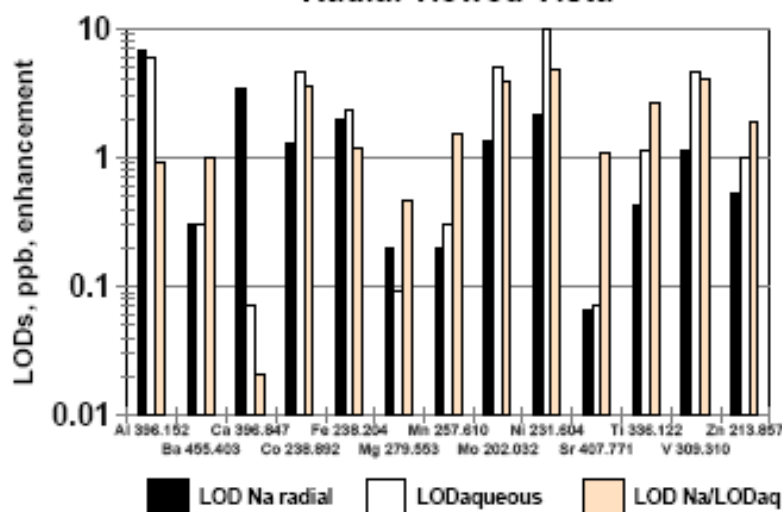
	10 s	50 s
As 188.979	3	1.3
As 193.696	4	1.5
Cd 214.438	0.2	0.07
Cd 228.802	0.3	0.14
Pb 220.353	2.8	1.5

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

169

LOD in 10 % NaCl vs Aqueous Radial viewed Vista



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

170

**Comparison of toxic element LODs (ppt)
ICP-QMS, axially viewed ICP-USN-AES, GFAAS**

Element	ICP-MS*	AX-ICP-AES-USN	GFAAS
75As	3**	Volatile	
9Be	0.1	9	10
209Bi	0.01	200	100
111Cd	0.02	40	3
59Co	1	50	10
52Cr	3**	30	10
202Hg	1	200 (Volatile)	1000
95Mo	0.02	40	40
60Ni	5	20	100
208Pb	0.05	200	250
80Se	2**	800	200
118Sn	2	500	200

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

171

Enhancement factors, Axial ICP

Element	Wavelength	AP-RP	RPUSN-RP	APUSN-RP USN
Al	I 396.152	5	10	7
As	I 193.759	2.5	2	4
Be	II 234.861	3	15	10
Cd	II 226.502	13	7	3
Co	II 238.892	16	20	5
Cr	II 267.716	20	20	7
Mo	II 202.030	7	20	15
Ni	II 231.604	7	10	13
Pb	III 220.353	8	8	7.5
Se	II 196.090	7.5	7.5	4
V	II 292.402	2.5	7	16

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

172

Method Detection Limits

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

173

Method detection limit (MDL)

- Ability to detect analyte(s) by determining MDLs for analytes according to 40 CFR 136, Appendix B using apparatus, reagents, and standards used in practice
- **MDLs MUST be < or equal to MDLs specified in Section 1.11 or one-third regulatory compliance limit, whichever is greater**
- **MDLs MUST be determined when a new operator begins work or whenever a change in instrument hardware or operating conditions is made that MAY affect the MDL**
- **MDLs MUST be determined for solids with clean sand or soil matrix (NRC CRMs) for solids and sludge samples and/or with reagent water for aqueous samples**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

174

Method detection limits (MDLs)

- Spike reagent blank with all elements at concs. 3 x IDLs.
- Process seven different aliquots of solution through entire analytical process
- Calculate MDLs as follows:

$$MDL = t \times SD \quad \text{where}$$
 - $t =$ students t for 99 % confidence limit and standard deviation with $n-1$ degrees of freedom ($t = 3.14$ for 7 replicates)
 - Rounding to number nearest (2, 5, or 10 X 10ⁿ) where $n = +$ or $-$
 - SD - standard deviation of replicates

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 175

Determination of MDLs and LOQs

- 7 integrations, determine sd and multiply by T value of 3.14 - *estimated MDL*
- Aspirate 7 spiked aliquots containing 3-5 x estimated MDL.
- These then treated as samples (e.g., digested) and analyzed
- Determine sd and multiply by 3.14 - MDL for the method and given matrix
- LOQs – 3-5 x MDL. (LOQ is defined as concentration at which there is a 99% confidence level that the concentration is greater than zero)

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 176

Method Detection Limit (MDL)

Element	MDL	Element	MDL
Ag 328.068	.239	Fe 271.441	2.10
Al 308.215	2.48	K 766.491	.583
As 188.980	1.32	Mg 279.078	.276
B 249.678	1.29	Mn 257.610	.054
Ba 493.408	.070	Na 589.592	.255
Be 313.042	.050	Ni 231.604	.641
Ca 315.887	2.09	Pb 220.353	.602
Cd 2263502	.054	Sb 206.834	.958
Co 228.615	.619	Se 196.026	2.78
Cr 267.716	.145	Tl 190.794	1.38
Cu 324.754	.397	Zn 206.200	.205

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

177

CRQLs vs. Vista-PRO MDLs (1)

Analyte	CRQL (ppb)	CRQL/2 (ppb)	Vista-PRO MDL (ppb)	Ratio Required / Observed
Antimony	60	30	.96	31
Arsenic	10	5	1.32	3.8
Barium	200	100	.07	1430
Beryllium	5	2.5	.05	50
Cadmium	5	2.5	.05	50
Chromium	10	5	.15	33
Cobalt	50	25	.62	40
Copper	25	12.5	.40	31

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

178

CRQLs vs. Vista-PRO MDLs (2)

Analyte	CRQL (ppb)	CRQL/2 (ppb)	Vista-PRO MDL (ppb)	Factor
Iron	100	50	2.10	24
Lead	10	5	.60	8.3
Manganese	15	7.5	.05	150
Nickel	40	20	.64	31
Selenium	35	17.5	2.78	6.3
Silver	10	5	.24	21
Thallium	25	12.5	1.38	9
Zinc	60	30	.21	143

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

179

CRI

- ILM - 'verify linearity near CRQL'. Lab required to analyze a standard at a concentration of 2 X CRDL or IDL whichever is greater' at beginning and end of each sample analysis run of up to 20 samples'.
- CRI is measured after the ICV but before the ICS. (Note: acceptance limits are not specified in the SOW).

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

180

LLCCV

- According to 6010c section 10.4.5, if a single calibration standard and blank are used to establish initial calibration curve, then calibration curve must be verified prior to sample analysis of use of a low-level CCV standard.
- LLCCV should be made from the same material as the ICV standards at the *quantitation limit* as reported by the laboratory.
- Acceptance criteria for LLCCV standard must be +/- 20% of its true value

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

181

CRI / LLCCV Performance Data (1)

	Ag 328.068	As 188.980	B 249.678	Be 312.042	Cd 226.502
read 1	5.02	4.35	5.70	4.95	4.84
read 2	5.11	4.29	5.60	4.95	4.86
read 3	5.06	4.79	5.32	4.97	4.86
read 4	5.08	3.72	5.53	4.95	4.88
read 5	5.07	4.08	5.24	4.96	4.85
read 6	5.16	3.80	5.26	4.93	4.84
read 7	5.05	4.65	5.18	5.00	4.88
Avg % rec	101.5	84.8	108.1	99.2	97.2

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

182

CRI / LLCCV Performance Data (2)

	Co 228.615	Cr 267.716	Ni 231.604	Pb 220.353	Sb 206.834
read 1	4.73	4.97	5.37	5.29	5.81
read 2	4.88	4.93	4.94	5.18	5.33
read 3	4.97	5.07	5.14	5.03	4.80
read 4	5.28	4.97	5.44	5.36	5.17
read 5	5.24	5.03	5.38	4.88	4.99
read 6	5.09	5.04	4.99	5.31	5.44
read 7	4.86	5.01	5.31	5.10	5.30
Avg % rec	100.1	100.1	104.5	103.3	105.3

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

183

CRI / LLCCV Performance Data (3)

	Se 196.026	Tl 190.794	V 292.401	Zn 206.200
read 1	5.23	4.54	5.05	4.89
read 2	6.30	5.07	5.09	4.90
read 3	4.99	4.57	5.12	4.99
read 4	4.87	5.40	5.02	5.03
read 5	4.28	5.12	4.92	5.10
read 6	4.67	5.20	5.00	5.02
read 7	5.12	5.13	5.06	5.24
Avg % rec	101.3	100.1	100.7	100.5

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

184

Blanks

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

185

Blanks -purpose

- **Field blank**
 - ✓ Reliability of sampling procedure – contamination
- **Calibration blank**
 - Establishing analytical curve
- **Method Blank.**
 - ✓ Assess contamination from sample preparation procedure
- **Reagent blanks**
 - *SHOULD be subtracted from all samples. Important for digested samples requiring large quantities of acids to complete digestion*
- **Rinse blank**
 - ✓ Flush sample introduction system between standards, check solutions, and samples to reduce memory interferences

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

186

FIELD BLANK

- *Aliquot of reagent water or other blank matrix* placed in sample container in laboratory and treated as sample in all respects, including shipment to sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures
- *Field blank* is analyzed to determine if method analytes or other interferences are present in field environment.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

187

Field blank

- Analyze field blank(s) shipped with each batch (samples collected from same site at same time), maximum 1/20 samples
- Analyze blank immediately before analyzing samples
- If analyte(s) of interest or any potentially interfering substance is found in field blank at concentration = or \geq than ML or $>$ than one-fifth level in associated sample, whichever is greater, results for associated samples MAY be result of contamination and MAY not be reported for regulatory compliance purposes.
- Alternatively, if a sufficient number of field blanks (3 minimum) are analyzed to characterize field blank, average concentration plus 2 sd's MUST be less than regulatory compliance level or less than one-half level in associated sample, whichever is greater.
- If contamination of field blanks and associated samples is known or suspected, laboratory SHOULD communicate this to sampling team so that source of contamination can be identified and corrective measures taken prior to next sampling event

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

188

Blanks

- **CALIBRATION BLANK** – *ultrapure water containing same acid concentration as calibration standards. Calibration blank is zero standard for calibration*
- **Method (REAGENT) BLANK** - *Water or other blank matrix treated exactly as sample (containing same acids used in decomposition, calibration standards and samples), exposed to all glassware, equipment, solvents, reagents, internal standards used with samples*
 - ✓ *Used to determine if method analytes or other interferences are present in laboratory environment, reagents, or apparatus*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

189

Equipment blanks

- Before **sampling equipment** is used at a given site, it is recommended that laboratory or cleaning facility generate **equipment blanks** to demonstrate that equipment is free from contamination
- Two types of equipment blanks are recommended: **bottle blanks and sampler check blanks.**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

190

Sampler check blanks

- Sampler check blanks **SHOULD** be run on *all* equipment that **WILL** be used in the field. Precautions used in field **SHOULD** also be used to generate these blanks.
- Sampler check blanks are generated in lab by processing reagent water through sampling devices using same procedures used in field.
- Fill large carboy or other container with reagent water and process equipment using procedures used in field
 - ✓ E.g., grab sampler blanks are collected by directly submerging sample bottle into water, filling bottle, and capping
- Subsurface sampler blanks collected by immersing sampler into water and pumping water into sample container
- Sampler check blank **SHOULD** be analyzed using the procedures in this method.
- If target analyte(s) or any potentially interfering substance is detected in blank, source of contamination or interference **MUST** be identified and problem corrected
- Equipment **SHOULD** be demonstrated to be free from contamination before the equipment is used in field.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

191

Bottle blanks

- After cleaning bottles **SHOULD** be subjected to conditions of use to **VERIFY** effectiveness of cleaning procedures
- A representative set of sample bottles **SHOULD** be filled with reagent water acidified to pH < 2 and allowed to stand for a minimum of 24 h
- The time that bottles are allowed to stand **SHOULD** be as close as **POSSIBLE** to time that sample **WILL** be in contact with bottle
- After standing, water **SHOULD** be analyzed
- If any bottle shows contamination, the problem **MUST** be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

192

Calibration blank

- Analyze calibration blank at frequency of 10%
- Result *SHOULD* be within 2 sd of mean
 - ✓ If not, repeat analysis 2 more times and average 3 results
 - ✓ If average is not within control limit, terminate analysis, correct problem and recalibrate

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

193

Method blanks

- Method blank using all acids in sample preparation, *SHOULD* be carried through entire sample preparation and analytical process.
- This test is to determine if contamination occurred in preparation.
- Analyze method blank at frequency of 10%
- Method blank *SHOULD* be < MDLs (usually 5 x IDLs)
 - ✓ If not, repeat 2 more times and average the 3 results
 - ✓ If average not within control limit, terminate analysis.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

194

Method blank

- Prepare method blank with batch (samples of same matrix) taken through sample preparation process on the same 12-hour shift, to a maximum of 20 samples).
- Analyze method blank immediately after OPR (ongoing precision and recov) is analyzed to demonstrate freedom from contamination.
- If analyte(s) of interest or any potentially interfering substance is found in method blank at concentration equal to or > than ML or 1/3 regulatory compliance level, whichever is greater, sample analysis MUST be halted, source of contamination determined, samples MUST be prepared again with a fresh method blank and OPR and analyzed again.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

195

Method blanks-2

- Alternatively, if at least 3 method blanks are analyzed, average concentration plus 2 sd standard deviations MUST be < than regulatory compliance level
- If result for single blank remains above ML or if result for average concentration (n=3) plus 2 sd exceeds regulatory compliance level, results for samples associated with those blanks MAY not be reported for regulatory compliance purposes.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

196

Blank correction

- Blank correction CAN BE MADE using instrument routines
- ENSURE that blanks are not contaminated by carry over
- Separate calibration blanks from flush solutions.
- Method blank correction - compensate for method contaminations

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

197

Calibration

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

198

Calibration standards

According to EPA Method 200.9 (STPF, revision 2.2, May 1994), calibration standards ***should*** be prepared every 2 weeks or as needed. EPA methods 200.8 (ICP-MS) and 200.7 (ICP-OES) are more vague, saying the calibration standards should be prepared again when their concentrations cannot be confirmed by the Quality Control Sample

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

199

Calibration strategies

- *Calibration with synthetic standards*
Stock standard solutions diluted into calibration range. Matrix matched in acid and fusion reagents Matrix match with major element concomittants
- *Calibration with internal standards for compensating signal v ariations in the sample introduction system, plasma and plasma-MS interface*
Response of the internal standard elements must be identical to those of the anytes, similar mrgy potentials, close in wavelength and mass, chemical compatibility
In certain cases a major element can be used if its concetration is constant or known
- Calibrations verified using ICV and CCV
- *Method of standard addition (MSA)*
Increasing concentrations of analyte spikes to sample aliquot
MSA does not compensate for spectroscopic interferences
(Spectral overlap in ICP-AES and isobaric and polyatomic ions in ICP-MS.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

200

Calibration

- **Standard stock solution –**
concentrated solution containing one or more method analytes prepared in laboratory using assayed reference materials or purchased from reputable commercial source

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

201

Calibration solutions

- **Multielement Stock Solutions**
 - ✓ Commercial Multielement standard
 - ✓ *Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.*
- **Stock solutions of majors and minors -**
Na, Ca, Na, S, Si

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

202

Calibration protocol - EPA 200.7

- Calibration blank
 - ✓ 1 % HNO₃ (Ultrapure). Zero standard
- Rinse blank
 - ✓ Flush between standards. 1 % HNO₃
- Mixed calibration standards (ICL)
 - ✓ 100-500 ng/ml). Prepared from Spex QC 21 stock solution
- Initial calibration/verification (Primary and secondary (ICV and CCV)
- Instrument performance check (IPC)
 - ✓ Control standard - synthetic standard
- Method, instrument validation
 - ✓ SRM and quality control sample (QCS)

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

203

Calibration

- **Minimum 2 point calibration - blank and high**
- **Check for spectral interferences in high concentration standard.**
- **For low-level determinations (< 100 µg/L), reduce upper calibration standard to 1 mg/l.**
- **Take into account memory effects when going from high to low trace metal concentrations. Evaluate instrumental blanks < MDLs.**
- **Store mixed standards in PTFE or unused LDPE bottles**
- **Use LDPE or PTFE for B and Si determinations, from collection to completion of analysis**
- **High concentrations of Ba MAY not stay in solution if even small amounts of sulfate are present.**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

204

EPA 200.7 - LINEARITY

- **LDR - Analyze standards at higher concentrations until recovery falls below 90%.**
- **Dilute samples < 90% of LDR.**
- **Operating conditions, spectral lines and matrices affect linearity**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

205

Linear Dynamic Range (LDR)

Element	LDR in ppm	Element	LDR in ppm
Ag	100	Mg	5000
Al	2000	Mn	1000
As	500	Mo	200
B	1000	Na	5000
Ba	1000	Ni	200
Be	1000	Pb	2000
Ca	5000		
Cd	100		
Co	300		
Cr	500		
Cu	1000		
Fe	2000		
K	5000		
		Sb	1000
		Se	500
		Sr	1000
		Ti	300
		Tl	1000
		V	500
		Zn	1000

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

206

Linear dynamic range (LDR)

- **Determine upper limit of linear calibration for each wavelength using linear calibration with established operating conditions**
- **VERIFY by analyzing high concentration standard.**
 - ✓ In axial viewed ICP range MAY be reduced.
 - ✓ Calculate recoveries for intermediate standards
- **LDRs SHOULD not deviate by more than 10 % of analyte concentration.**
- **LDRs MUST be documented**
- **If sample deviates > 10 %, dilute or use alternate spectral lines**
- **LDRs SHOULD be verified when sample introduction and excitation systems are replaced**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

207

Calibration and lowest limit determination (QLOD)

- **Minimum level (ML) – lowest level at which entire analytical system gives recognizable signal and acceptable calibration point for analyte.**
 - ✓ Equivalent to concentration of lowest calibration standard, assuming that all method-specific sample weights, volumes and cleanup procedures have been employed.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

208

Signal Stability - 4 hours (1), 0.5 mg/L Standard

Element		Integration (sec)	%
Al	396.152	0.1	0.8
As	188.979	5	1
Ba	455.403	0.01	1.2
Cd	214.438	1	0.8
Cu	324.754	0.2	0.8
Cu	327.396	0.1	0.9

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

209

QA/QC, Verification and Validation

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

210

QA/QC

- **MUST** operate formal QA
 - ✓ *Initial demonstration of laboratory capability*
 - ✓ *Analysis of samples spiked with analyte(s) of interest to evaluate and document data quality*
 - ✓ *Analysis of standards and blanks as tests of continued performance.*
- Lab performance compared to established performance criteria to determine that results meet performance characteristics of method.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

211

Daily performance tests

- Torch – condition, alignment, injector, connections,
 - ✓ Check alignment when torch or injector are changed
- Nebulizer and peristaltic tubes.
- Check profile positions
 - ✓ If unaligned perform wavelength calibration.
- After 30 min warm up, check intensities and ratio of CuI 324.75 and MnII 257.61 using high calibration standard
 - ✓ *Keep daily reports of intensities, % RSDs and intensity ratio.*
 - ✓ *Record aerosol flow rate - nebulizer pressure, RF power peristaltic tube type and delivery rates, pre-integration and integration time, number of measurements in appropriate documents and files.*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

212

Figures of merit in accreditation

- LODs (IDLs, MDLs)
- LQDs – lowest point on calibration curve
- Sensitivity
- Matrix effect - bias
- Accuracy – Recovery (also at LQDs, CRMs)
- RSDs – long and short term
- Linear range of calibration

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

213

QC tests for modified method

Figures of merit for comparison

- MDLs
- Calibration and calibration verification
- Initial precision and recovery
- Ongoing precision and recovery (OPR)
- Analysis of blanks
- Matrix spike and matrix spike duplicate analyses

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

214

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

215

Types of calibration and QC standards

- **CALIBRATION STANDARDS**
- **CALIBRATION VERIFICATION (CV) (200.7). QC REFERENCE SOLUTION, INSTRUMENT CHECK STANDARD – ICS (STANDARD METHODS)**
- **REFERENCE SAMPLE (200.7) INSTRUMENT QUALITY CONTROL SAMPLE (IQCS)(SM)**
- **MINIMUM LEVEL STANDARD (ML)**
- **METHOD QUALITY CONTROL SAMPLE (MQCS). SPIKED QC REFERENCE STANDARDS ICS, ICQS)**
- **ONGOING PRECISION and RECOVERY STANDARD (OPR)**
- **MATRIX INTERFERENCE SAMPLE (MIS), MATRIX SPIKE**
- **SPECTRAL INTERFERENCE CHECK (SIC)**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

216

CALIBRATION VERIFICATION

- **CALIBRATION VERIFICATION (CV) (200.7). QC REFERENCE SOLUTION, INSTRUMENT CHECK STANDARD – ICS (Standard Methods). Reference sample (200.7) Instrument Quality Control Sample (IQCS)(SM). Used to check laboratory and instrument performance**
 - ✓ Aliquot of external *certified aqueous reference standard* - different from source of calibration standards. Contains same acid matrix as in calibration standards.
 - ✓ *Independent certified standard containing method analytes in the calibration blank. Used to evaluate performance of instrument system with respect to method criteria; e.g., calibration verification, calibration linearity, repeatability. Contains intermediate analyte concentrations.*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

217

Calibration verification (CV) solution

- Analyte concentration **SHOULD** be 2 mg/L, except Ag which **MUST** be 0.5 mg/L for stability
- K and P because of higher MDLs, and silica, because of potential contamination, **SHOULD** be 10 mg/L.
- CV solution can be prepared from commercial multielement standard stock solution and stored in FEP bottle
- **Analyzed as needed by QC**
- **Fresh solution SHOULD be prepared quarterly or more frequently as needed**
- **Alternatively, reference sample MAY be a standard or certified reference material traceable to NIST**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

218

Calibration verification (CV) (SM)

- Laboratory **MUST** analyze CV solution and calibration blank **immediately following daily calibration**, after every 10th sample (or more frequently, if REQUIRED) and at **end of sample run**
- Analysis data of calibration blank and CV solution **MUST** be kept on file with sample analyses data
- Result of calibration blank **SHOULD** be less than analyte ML or one-third regulatory compliance level, whichever is greater.
- Analysis of CV solution immediately following calibration **MUST VERIFY** that instrument is within performance criteria
- If calibration cannot be verified within specified limits, both CV solution and calibration blank **SHOULD** be analyzed again
- If second analysis of CV or calibration blank confirm calibration to be outside limits, sample analysis **MUST** be discontinued, cause determined, corrected, and/or instrument recalibrated
- **All samples following last acceptable CV solution MUST be analyzed again.**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

219

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

220

Reference sample – initial calibration verification (ICV)

- Analysis of reference sample for initial and periodic verification of calibration standards to **VERIFY** instrument performance
- Reference sample **MUST** be obtained from **outside source different from standard stock solutions** and prepared in same acid mixture as calibration standards

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

221

Calibration - **total recoverable elements**

- Multielement standard prepared by taking aliquot of 100 mg/l stock solution in 500 mL volumetric flasks containing **20 mL (1+1) HNO₃ and 20 mL (1+1) HCl** and diluting to volume
- Commercial standards **MUST** be traceable to NIST single element stock solutions. Standards **MUST** be certified for stability for specified time
- Avoid contamination by transferring standard solutions to acid-cleaned, **never-used** FEP fluorocarbon bottles for storage.
- Calibration standards not prepared from primary standards **MUST** be initially verified using certified reference solutions
- NOTE: *If presence of Ag in mixed-acid calibration standard results in precipitation, add 15 mL reagent water and warm until solution clears.*
- For this acid combination, Ag concentration **SHOULD** be limited to 0.5 mg/L.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

222

Initial precision and recovery (IPR)

- To establish ability to generate acceptable precision and recovery, the following operations SHALL be performed:
- Spike four aliquots of reagent water (for aqueous samples) or clean sand or soil (for solid and sludge) with analyte(s) at 1-5 times ML (minimum level).
- Analyze four aliquots according to the EPA 200.7 procedures
- This test MUST use containers, labware, and reagents that WILL be used with samples and all digestion, extraction, and concentrations steps

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

223

Initial precision and recovery (IPR)

- Using results of the four analyses, compute average % recovery (X) for the analyte(s) in each aliquot and the sd of the recovery (s) for each analyte.
- For each analyte, compare sd and X with corresponding limits for IPR (initial precision and recovery)
- If sd and X for all analyte(s) meet acceptance criteria, system performance is acceptable and analysis of blanks and samples MAY begin
- If, however, any individual sd exceeds precision limit or any individual X falls outside range for accuracy, system performance is unacceptable for that analyte.
- Correct the problem and repeat the test.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

224

Ongoing precision and recovery standard (OPR)

- *OPR used to ENSURE that laboratory meets performance criteria during analysis*
- *Separates laboratory performance from method performance on sample matrix.*
- *For aqueous samples, OPR solution is an aliquot of method blank to which method analytes are added in laboratory.*
- *For solid samples, use of clean sand or soil (NRC CRM) to which known quantities of method analytes are added in laboratory*
- *OPR is analyzed in same manner as samples*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

225

Ongoing precision and recovery (OPR) - Aqueous samples

- Prepare OPR sample (LABORATORY FORTIFIED METHOD BLANK - LFMB) identical to IPR (initial precision and recovery) aliquots with each preparation batch (samples of same matrix taken through sample preparation process on same 12-hour shift, to a maximum of 20 samples) by spiking aliquot of reagent water with the analyte(s) of interest.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

226

Ongoing precision and recovery (OPR) - Solid samples

- Use fortified “clean sand or soil”(NRC CRM)
- Analyze this OPR sample immediately **before** method blank and samples from the same batch.
- Compute % recovery of each analyte in OPR sample.
- Compare each analyte concentration to limits for ongoing recovery
- If all analyte(s) meet acceptance criteria, system performance is acceptable and analysis of blanks and samples MAY proceed.
- If, however, any individual recovery falls outside of range given, analytical processes are not being performed properly for that analyte
- Correct problem, prepare sample batch again with fresh OPR and method blank, and reanalyze the QA/QC and samples.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

227

INTERFERENCES

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

228

Spectral interferences

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

229

Spectroscopic interference effects

○ Spectroscopic

✓ Background - Continuum, stray light

○ Spectral line interferences

✓ Overlap from matrix spectra lines – Fe.

✓ Select different lines, make corrections

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

230

Spectral interferences

- **Background emission** from continuous or recombination phenomena
- **Stray light** from line emission of high concentration elements
- **Overlap** of spectral line from another element
- **Unresolved overlap** of molecular band spectra

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

231

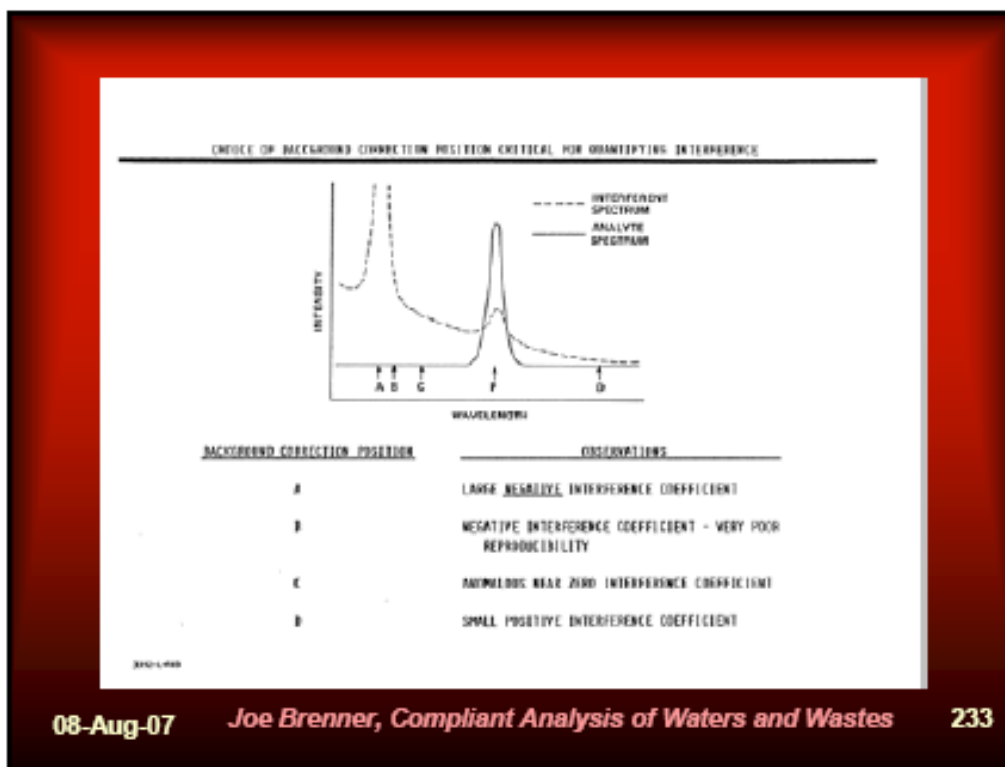
Background emission and stray light

- *Compensated by subtracting background emission adjacent to analyte wavelength peaks*
- *Spectral scans of samples or single element solutions in analyte regions*
 - ✓ *indicate when alternate wavelengths are desirable because of severe spectral interference*
 - ✓ *Show structure and whether estimate of background emission is provided by interpolation from measurements on either or both sides of analyte peak*
 - ✓ *Location (s) for measurement of background determined by spectral complexity adjacent to wavelength peak.*
- Positions for measurement **MUST** be free of spectral interference (interelement or molecular) or **adequately corrected to reflect same change in background intensity as occurs at wavelength peak.**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

232

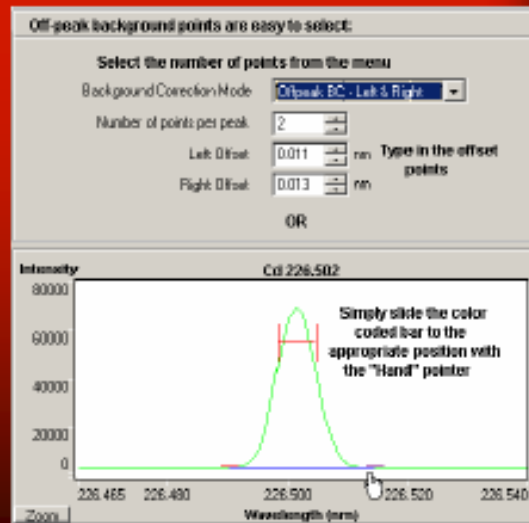


Background correction

- Determine appropriate positions by scanning one or both sides adjacent to wavelength
 - ✓ record emission intensity from all other method analytes.
- Spectral information **MUST** be documented and kept on file.
- Location selected for background correction **MUST** either be free of spectral interference or a computer routine **MUST** be used for automatic correction on all determinations.

Background Correction Off Peak

View actual signals to set background positions - left, right, or left & right selection truly simultaneous correction



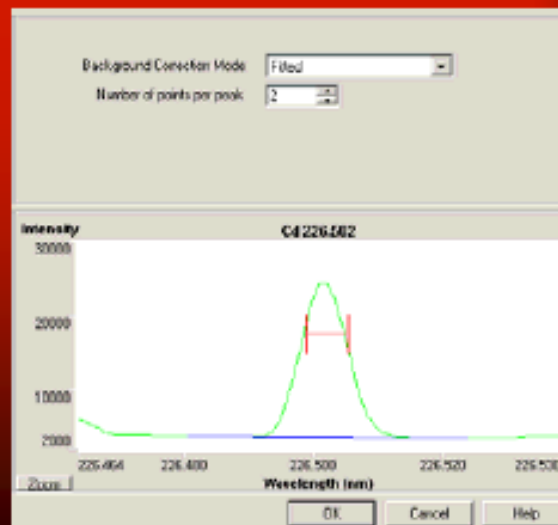
08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

235

Background Correction Fitted

Fitted Background Correction automatically selects positions



08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

236

Spectral overlap

- MAY be avoided by using alternate wavelength
- Can be compensated by equations that correct for interelement contributions
 - ✓ involves measuring interfering elements.
- When operative and uncorrected, interferences produce **false-positive** determinations and WILL be reported as analyte concentrations.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

237

Spectral Interference - procedure

- VERIFY spectral interferences and background correction positions using typical sample containing *minimum* trace element concentrations.
- In case of overlap, select alternate lines with adequate LODs
- Analyze *spectral interference solutions (SIS)*.
 - ✓ Spike low trace element concentration sample containing matrix after digestion with 10 mg/l, Fe, Al and Mn.
 - ✓ Spike aliquot with 1 mg/l ME std. Determine original concentration and spike recoveries.
- Analyze spectral interference check sample at beginning and end of run.
- Recovery SHOULD be +/- 5 % of spike value or +/- 2 SD around mean.
- Register results in QC/QA media

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

238

Spectral interferences

- Interferences listed are *only* those that occur between method analytes
- Only direct overlap with instrument having a resolution of 0.035 (in VISTA about 0.010) nm are listed.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

239

SPECTRAL INTERFERENCES AT 100 mg/L

Analyte	Wavel	Interferant *	
Ag	328.068	Ce, Ti, Mn	<i>Interferences using 0.035 nm resolution. VARIAN VISTA 0.015</i>
Al	308.215	V, Mo, Ce, Mn	
As	193.759	V, Al, Co, Fe, Ni	<i>Interferants ranked by magnitude with most severe listed first</i>
B	249.678	None	
Ba	493.409	None	<i>Very few in normal contaminated samples</i>
Be	313.042	V, Ce	
Ca	315.887	Co, Mo, Ce	
Cd	226.502	Ni, Ti, Fe, Ce	
Ce	413.765	None	
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce	
Cr	205.552	Be, Mo, Ni	
Cu	324.754	Mo, Ti	
Fe	259.940	None	
Hg	194.227	V, Mo	
K	766.491	None	
Li	670.784	None	
Mg	279.079	Ce	

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

240

SPECTRAL INTERFERENCES AT 100 mg/L

Analyte	Wave	Interferent
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Ti
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO	2251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 241

IECs

- IECs are determined by aspirating single solutions of major concomitants (in case of waters and wastes - Ca, Mg, Al, Fe) of maximum anticipated concentrations (500, 100, 10, and 10 mg/l respectively)
- Before determining IECs, check Cu/Mn and MgII/MgI ratios and ENSURE that values are similar to those used for sample analysis

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 242

IEC for 1000 mg/l Fe, mg/l

Element	Soln Conc
Ag 328.068	0.002202
Al 398.152	0.228158
As 188.980	-0.02077
As 193.696	-0.01853
B 208.958	0.180285
B 249.678	-0.00757
Ba 455.403	0.00162
Be 313.042	0.000499
Ca 317.933	0.606777
Cd 228.502	0.073588
Co 228.615	0.016503
Co 230.788	0.054558
Cr 267.716	0.005076
Cu 327.395	0.001478
K 766.491	0.001525
Li 670.783	0.000365
Mg 279.078	0.12768
Mn 257.610	0.002215
Mo 202.032	0.002451
Ni 231.604	-0.00453
P 213.618	0.00138
Pb 220.353	0.009797

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

243

Interference Avoidance

- **Method 200.7 section 4.1.2** Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for inter-element contributions, which involves measuring the interfering
- **Method 6010, section 4.1.3** Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

244

IECs

- IECs are determined by aspirating single solutions of major concomitants (in case of waters and wastes - Ca, Mg, Al, Fe) of maximum anticipated concentrations (500, 100, 10, and 10 mg/l respectively)
- Before determining IECs, check Cu/Mn and MgII/MgI ratios and ENSURE that values are similar to those used for sample analysis

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

245

IECs (1)

- IEC a ratio of observed concentration of interferent at the analyte wavelength to the concentration of the interferent at it's analytical wavelength.
- For accurate IEC factors intereferent concentrations must be determined within their linear range.
- A Multi-cal can correct across all concentration levels.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

246

IECs (2)

Calculate IEC factors with each run
OR store factors for re-use.

Tube	Sample Label	Al 308.215	Ca 315.807	Co 228.615	Cr 207.716	Fe 271.441	Mg 279.076	Mn 257.616	Mo 202.302	V 232.401
1-1	IEC Blank	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1-2	SI									
1-3	Ag SI									
1-4	B SI									
1-5	AM/Fe SI									
1-6	AL/Fe SI									
1-7	Si/Fe SI									
1-8	Si, Fe, Si, Si									
1-9	Al INT	500.00								
1-10	Ca INT		1000.0							
1-11	Co INT			20.000						
1-12	Cr INT				20.000					
1-13	Fe INT					500.00				
1-14	Mg INT						500.00			
1-15	Mn INT							25.000		
1-16	Mo INT								30.000	
1-17	V INT									20.000

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes
coded bar to the proper location with the hand pointer.

247

IECs (3)

Select IEC icon from tool bar to view correction factors during analysis.

INTERFERENTS		Al 308.215	Ca 315.807	Co 228.615	Cr 207.716	Mg 279.076	Mn 257.616	Mo 202.302	V 232.401	Fe 271.441
ANALYTE	Cr 207.716	0.00001	0.00000	-0.00010	0.00000	0.00005	0.00027	-0.00015	-0.00002	0.00005
	Co 324.756	-0.00006	-0.00000	-0.50000	-0.00210	0.00000	-0.00000	0.00000	-0.12229	-0.11042
	Fe 271.441	0.00000	0.00000	0.00010	0.00000	0.00005	0.00005	0.00016	0.00000	0.00000
	Mg 279.076	0.00000	0.00000	-0.00000	0.00017	0.00000	0.00000	0.00000	0.00000	0.00000
	Mn 257.616	0.00000	0.00000	-0.00000	0.00000	0.00010	0.00000	0.00000	0.00000	0.00000
	Mo 202.302	0.00000	0.00000	-0.00000	0.00000	0.00000	-0.00004	0.00000	0.00000	-0.00004
	Pb 208.383	-0.00004	-0.00000	0.00000	0.011295	0.00000	0.00000	-0.00000	-0.00000	0.00000
	Si 226.634	-0.00421	0.00000	0.002184	10.00000	0.00000	-0.00000	0.00000	0.17282	-0.00000
	Si 196.035	0.00001	0.00000	-0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	V 232.401	0.00000	0.00000	0.00000	-0.001200	0.00000	-0.00000	-0.00000	-0.00000	-0.00000
	Zn 200.200	0.00000	0.00000	-0.00000	-1.252445	0.00000	0.00000	0.00000	0.00000	0.00000
	Ni 225.694	0.00047	0.000185	0.248650	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	Ca 226.692	-0.00000	0.00000	-0.00000	0.00000	-0.00000	0.00000	0.00000	-0.00000	-0.00000
	Na 283.532	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	Se 213.942	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	Fe 271.441	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	Ti 307.724	-0.00041	0.001145	0.00000	0.100000	0.00000	0.00000	0.00000	0.00000	0.00000
	Si 201.758	0.00005	0.00000	-0.00000	-0.00000	-0.00000	0.00000	0.00000	0.00000	0.00000
	Si 193.927	-0.00001	0.00000	-0.00000	-0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

08

8

Spectral interference check (SIC) solutions – 200.7

- SIC solutions contain interferences expected in samples.
 - ✓ Used to VERIFY on-peak and off peak interferences
- Various solutions can be used, provided an analyte is not subject to interference *from more than one* interferant in the solution
- **MUST** be prepared in same acid mixture as calibration standards and stored in FEP bottles
- Used to determine correction factors for EPA 200.7 recommended wavelengths
- Coefficients are determined from single element solutions.
 - ✓ E.g., 300 mg/L Fe, 200 mg/L Al, 5 mg/L Ba, Co, Cr; Cu, Ni, Ti, V, 10 mg/L Mn
- NOTE: *If wavelengths other than those recommended in 200.7 are used, solutions other than those above MAY be REQUIRED.*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

249

Spectral interference corrections using interference equivalent concentrations (IECs)

- Perform spectral line interference corrections using IECs
- Corrected concentration is:

$$\text{Corr conc} = \text{Observed conc} - \text{ICF} \times \text{meas. conc of interferent}$$

Where

- ICF = *Apparent concentration of analyte due to interferent concentration*
- *Apparent conc. is observed conc. of analyte when interferent is nebulized as if it was a sample with background correction.*
- When several interferences occur, corrected concentrations are calculated by subtracting effects of all interferents

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

250

Interelement corrections

- VERIFY accuracy by analyzing *spectral interference check solutions*
- Interelement corrections depend on background positions. Avoid positions with interfering lines
- Interelement corrections that constitute major portion of emission signal *MAY* not yield accurate data
- Some samples *MAY* contain uncommon elements that *could* contribute spectral interferences

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

251

Testing of correction factors

- If daily correction factors are within 10% criteria for 5 consecutive days, REQUIRED verification frequency of those factors in compliance *MAY* be extended to a weekly basis
- Also, if nature of samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of interfering elements at 10 mg/L level, daily verification is not REQUIRED
- However, all interelement spectral correction factors **MUST** be verified annually and updated if necessary.
- All interelement spectral correction factors **MUST** be verified whenever there is a change in instrument operating conditions
 - ✓ rigorous verification of spectral correction factors are: changes in power, nebulizer gas flow, installation of a new torch injector with a different orifice.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

252

Spectral interference check (SIC) solution

- Laboratory **MUST periodically VERIFY** interelement spectral interference correction routine by analyzing SIC solutions
- *For interferences from Fe and Al only those correction factors (positive or negative) which, when multiplied by 10, exceed analyte ML, or one-third regulatory compliance, whichever is greater, or fall below the lower limit for calibration blank, need be tested on a daily basis.*

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

253

Nonspectroscopic effects

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

254

Nonspectroscopic interference effects

- Physical - efficiency of aerosol production and transport – high salt
- Memory effect – optimize rinse time
- Plasma – energy withdrawal
- Matrix matching, addition method, internal standards, dilution
- Optimize ICP

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

255

Nonspectroscopic effects

- *Physical interferences* - variation of efficiency of aerosol production and transport, when salt and acid concentrations exceed 0.5 % and > 20 % respectively.
- *Changes in energy regime of the plasma* when high concentrations (about 500 mg/l) of Na and Ca are introduced into the ICP.
- Matrix matching, addition methods and internal standardization can overcome these effects.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

256

Nonspectroscopic interference effects

- Physical - efficiency of aerosol production and transport – high salt
- Memory effect – optimize rinse time
- Plasma – energy withdrawal
- Matrix matching, addition method, internal standards, dilution
- Optimize ICP

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

257

Overcoming interference effects in axially viewed ICPS

- Improve plasma robustness
- Add “buffer” e.g., Cs – problem contamination, salt concentration
- Use internal standards
- Dilute sample – problem with LODs
- Use low consumption nebulizers

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

258

Memory effect

- Memory effect - when analytes in previous sample contribute to signals measured in new sample
- Deposition in sample intro system and torch
- Element and matrix dependant
- Minimized by flushing system with rinse blank between samples

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

259

Memory effects - 2

- Optimize rinse time
- Aspirate standard containing elements corresponding to **LDR or 10 x concentration** usually encountered
- Aspiration time **SHOULD** be same as normal sample analysis period, followed by analysis of rinse blank at designated intervals.
- Note time **REQUIRED** to reduce analyte signals to within **factor of 2 of MDL**
- **Until REQUIRED rinse time is established, use rinse period of at least 60 s between samples and standards.**
- **If memory interference is suspected, sample MUST be analyzed again after longer rinse period**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

260

Matrix effects - procedures

- Matrix interference solutions – real sample matrices spiked with method analytes – recoveries +/-10 %
- Spiked laboratory samples – duplicate. 5 % frequency
- Spiked sea water
- Spikes added before and after sample prep.
- Dilution tests
- Addition method
- Internal standards
- CRMs and PT
- Other methods

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 261

Determination of non spectral interferences using matrix interference solutions (MIS)

- Pipette 10 ml well-mixed sample into tube.
- Add acids in accordance with decomposition procedure
- Sample **SHOULD** contain *high Ca and Na and low trace element concentrations*
- Spike 0.5 ml CPI standard so that concentration is 1 mg/l
- Analyze original and spiked sample and determine % recoveries for all elements.
- Recovery **SHOULD** be +/- 5 % of spike value or +/- 2 SD around mean

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 262

Matrix interference sample (MIS) Matrix spike (200.7)

- **Matrix spike (MS) and matrix spike duplicate (MSD) –**
Two sample aliquots to which known quantities of method analytes are added in laboratory
- MS and MSD are treated and analyzed exactly like samples
- Used to determine whether sample matrix contributes bias to analytical results *and to indicate precision of laboratory procedures.*
- Concentrations of analytes in original sample **MUST** be determined in separate aliquot and measured values corrected for **background concentrations.**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

263

Matrix spike (MS) and matrix spike duplicates (MSD) – determination of spike concentration

- If in compliance monitoring, analyte concentrations are checked against a regulatory concentration limit, *the spiking level SHALL be at that limit or at 1- 5 times the background concentration of the sample, whichever is greater*
- If concentration is not checked against a regulatory limit, the spike **SHALL** be **1-5 times the background concentration.**
- For solid and sludge samples, the concentration added **SHOULD** be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the *conversion factor* $100 \text{ (mg/L} \times 0.1\text{L}/0.001\text{kg)} = 100$,

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

264

Comparison of % recovery with QC acceptance criteria

- If P falls outside designated range for recovery in specs then it fails to meet established analytical performance criteria
- If P is unacceptable, analyze OPR standard.
- If OPR is within performance criteria, the analytical system is within specification then problem can be attributed to a matrix interference
- Data user *SHOULD* be informed that result for that analyte in unfortified sample is suspect due to either heterogeneous nature of sample or matrix effects, and that standard addition or an internal standard(s) *SHOULD* be considered.
- If results of both spike and OPR fall outside acceptance criteria, analytical system is outside specified limits
- Analyst **MUST** identify and correct problem and analyze sample batch again.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

265

Recovery

- After analysis of five samples of a given matrix (river water, lake water, etc.), compute average percent recovery (R) and sd (SdR)
- Express accuracy as a percent recovery interval from $R - 2SdR$ to $R + 2SdR$ for each matrix.
 - ✓ E.g., if $R=90\%$ and $SdR = 10\%$ for 5 analyses of river water, accuracy interval is expressed as 70-110%.
- Update accuracy assessment for each metal in each matrix regularly (e.g., after each 5-10 new measurements).

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

266

Precision and Accuracy

- **Routine analysis of replicate and spiked replicate samples (Ca, Mg, Na, Fe, Al)**
 - ✓ Spiked replicate samples - used to determine accuracy and precision.
 - ✓ Frequency of repetition WILL depend on number of samples – 5 % recommended.
 - ✓ Spike addition SHOULD be minimum of 10 X to maximum 100 times IDLs
 - ✓ +/- 5-10 % recoveries
 - ✓ Reportable values

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

267

Laboratory duplicates

- **Two aliquots of same sample taken in laboratory and analyzed separately with identical procedures.**
- **Analyses of duplicates indicate precision associated with laboratory procedures**

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

268

RPD Criteria

- RPD (rel % diff) for MS/MSD pair **MUST** not exceed acceptance criteria
- If criterion not met system is outside limits of performance
- Problem **MUST** be identified and corrected, and analytical batch **MUST** be reanalyzed

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

269

Precision of matrix spike and duplicates *Relative % difference (RPD)*

- Compute RPD between MS and MSD using following equation

$$RPD = 200 \times (D1 - D2)_{abs} / (D1 + D2)$$

where

RPD = Relative percent difference

D1 = Analyte concentration in MS sample

D2 = Analyte concentration in duplicate

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

270

Total recoverable analytes in solid and sludge samples

- Report data up to 3 significant figures as mg/kg dry-weight basis unless specified otherwise
- Calculate concentration using following equation:

$$C_s = C \cdot V \cdot D / W$$

where:

C_s = Sample concentration (mg/kg, dry-weight basis)

C = Concentration in extract (mg/L)

V = Volume of extract (L, 100 mL = 0.1L)

D = Dilution factor (undiluted = 1)

W = Weight of sample aliquot extracted (kg, 1g=0.001kg)

- Do not report data below solids MDL
- QC data obtained during analyses indicate quality of data and SHOULD be provided with results.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

271

Dilution Test

- If analyte concentration is sufficiently high (minimally, x 50 IDLs in original solution but < 90% of LDR), analysis of 1+4 dilution SHOULD agree (after correction for fivefold dilution) within $\pm 10\%$ of original determination
- If not, chemical or physical interference effect SHOULD be suspected
- MSA or IS's MAY provide more accurate data for samples failing this test.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

272

Standard addition and internal standards

- **Standard Addition** - Addition of known amount of analyte to sample in order to determine response of detector to analyte in sample matrix
 - ✓ Response used to assess matrix effect and analyte concentration
- **Internal Standard (IS)** - Pure analyte(s) added to sample, extracts and standards in known amount(s).
 - ✓ Used to measure relative responses of other analytes in same sample or solution.
 - ✓ IS MUST be an analyte that is not a sample component.
 - ✓ IS's compensate for various nonspectroscopic interferences.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

273

METHOD OF STANDARD ADDITIONS (MSA)

- This technique is valid when:
 - a. When interference effect is constant over linear range
 - b. When added analyte responds in same way as endogenous analyte
 - c. Signal is corrected for additive interferences.
 - d. Simplest version is single-addition method.
 - e. Procedure calls for two identical aliquots of sample solution
 - f. To first aliquot, a small volume of standard is added
 - g. To second aliquot, a volume of acid blank is added equal to the standard addition

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

274

Validation - Addition method SM

- Matrix effects (not spectral) can be compensated by addition method
 - ✓ Analyte added to sample prior to sample treatment.
 - ✓ Effects due to sample prep can also be defined
- Additions **MUST** not exceed linear calibration range
 - ✓ *Multielement spike SHOULD not be less than 50 % nor more than 100 % of element concentration in the sample so that precision WILL not affect result.*
- Standard addition does not compensate for spectral line interferences
 - ✓ Apply instrument routine
- Register results in QC/QA media

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

275

Method of standard additions (MSA)

- Analyte(s) spike added to portion of prepared sample, or its dilution, **SHOULD have a recovery of 85% to 115% of known value**
- Analyte(s) addition **SHOULD not be < 20 times and not more than 100 times MDL**
- If analyte addition is < 20% of sample analyte concentration, **dilution test** SHOULD be used.
- ***If analyte recovery is not within specified limits, a matrix effect SHOULD be suspected, and associated data flagged accordingly.***
- ***Method of additions or internal standard MAY provide more accurate data***

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

276

internal standard technique

○ Alternative to MSA

- ✓ ***adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.***

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

277

Method validation

- Analyze *certified reference materials (CRM)* for determination of accuracy**
- CRMs SHOULD be included with each batch and when new sample matrix is analyzed.**
- *Interlaboratory proficiency tests***
 - ✓ **Distribute and receive samples for trace determinations by this method**
- Compare with alternate methods e.g., FAAS**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

278

Certified reference materials

- *Reference material analysis can provide additional interference data.*
- *Analysis of reference samples can demonstrate ability to perform method*
- *Reference materials containing high concentrations of analytes can provide additional information on performance of spectral interference correction routine.*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

279

CRM Trace Metals in Drinking Water Vista AX (µg/L)

Element	Measured	Certified
Ag 328.068	2.22	2.0
As 188.979	80.6	80
Ba 455.403	49.3	50
Cd 214.438	9.3	10
Co 238.892	22.1	25
Cr 205.552	18.3	20
Cu 324.754	19.0	20

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

280

CRM Trace Metals in Drinking Water Vista AX ($\mu\text{g/L}$) - 2

Element	Measured	Certified
Mn	260.569	42.7
Ni	231.604	61.0
Pb	220.353	35
Sb	206.833	9.1
Tl	190.790	14
V	292.402	25
Zn	206.200	69.7

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

281

SLRS-1 and NIST 1643 B by USN, data in $\mu\text{g/l}$ except where indicated in mg/l. Blank values indicate not detected. Recommended values are from NIST and NRC

	SLRS-1		NIST 1643B		
	Det	Rec	Det	% RSD	Rec.
Al	18	23	15	2	
As			53	5	49
B	180		87	5	100
Ba	20.7	22.2	42.4	1.8	44
Be			18.5	2	19
Cd			23	1.4	20
Co			29.5	2.2	26
Cr	0.3	0.4	22.4	2.6	19
Cu	3.5	3.6	20.3	1.5	21.9
Fe	32	31.5	93	1.8	99
Mn	1.6	1.8	28	1.8	28
Mo	0.9	0.8	89	2.2	85
Ni	1.8	1.1	50	1.6	49
Pb			21	10	24
Se			12.5	8	10
Sr ⁺	135	136	225	1.2	227
V	0.87	0.66	43	1.4	45
Zn	2.1	1.34	61	1.9	66

Data mg/l

Rec.	SLRS-1		NIST 1643B		
	Det	Rec	Det	% RSD	Rec.
Ca	26.4	25.1	29.9	1.2	30
Mg	5.8	5.99	6.9	1.4	8
Na	9.9	10.4			
K	0.97	1.3			

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

282

Analysis of NIST 1643c

Element	Measured	Certified
Cu 324.745	16.2	22.3 ± 2.8
Mn 257.610	35.7	35.1 ± 2.2
Mo 202.030	100	104.3 ± 1
Ni 231.604	58.0	60.6 ± 7.3
Pb 220.353	32.7	35.3 ± 0.9
Tl 190.790	6.0	7.9
V 292.402	28.1	31.4 ± 2.8

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

283

NIST 1643 B TRACE ELEMENTS in WATER

Pneumatic neb. Data in µg/l except where indicated in mg/l.

	Det val	% RSD	NBS value
Ca mg/l	29.90	1.8	30
Mg mg/l	7.5	1.4	8
Ba	41.4	1.5	44
Cd	24	1.1	20
Cr	21	2.1	19
Co	29	2.0	26
Cr	21.4	3.0	19
Cu	19	1.5	21.9
Fe	94	2	99
Mn	28	1.5	28
Mo	89	2.2	85
Ni	49	2.6	49
Pb	21	5	24
Sr	224	1.1	227
V	43	1.4	45
Zn	56	2	66
Be	18	1.2	19
B	93	5	100
As	58	30	49

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

284

Long term % RSDs and mean recoveries with and without internal standard (Co). 60 min. 100 µg/l Multiellement spike in 0.1 % NaCl .

Elem	Without internal reference			With Internal reference		
	Mean	STD	% RSD	Mean	STD	% RSD
Zn	101.7	0.9	0.9	100.9	0.5	0.5
Pb	100.8	0.8	0.8	101.4	0.6	0.6
Cd	99.1	0.9	0.9	100.2	0.5	0.5
Ni	98.9	1.1	1.1	98.6	0.6	0.7
Ba	99.5	0.8	0.8	99.2	0.4	0.4
Co	100.3	0.7	0.7			
Mn	101.5	0.8	0.8	101.2	0.7	0.7
Fe	97.9	1.2	1.2	99.9	0.7	0.7
Cr	99.4	0.7	0.7	99.2	0.3	0.3

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

285

Background values for sea water

Very low values in comparison to surface water

Li	175 ug/l	Zn	500 ppt
Ba	21 ug/l	Sb	200 ppt
Rb	120 ug/l	Cr	200 ppt
U	3 ug/l	Cu	300 ppt
Mo	11 ug/l	Mn	10 ppt
V	1.5 ug/l	Fe	30 ppt
As	1.4 ug/l	Cd	80 ppt
Ni	500 ppt	Co	1 ppt
		Pb	1 ppt

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

286

Spiked recoveries for 0.5 % NaCl Calibration with Matrix Match Procedure

Element	10 µg/l	50 µg/l	100 µg/l
Cd	11.3	52	98
Cu	9.6	47	103
Cr	12.4	51.7	102
Fe	9.75	50.5	101
Mn	9.2	48.5	99
Mo	11.8	49	102

Pb spike	5	10	20	30	40	50
Pb Deter	7	12	19.8	28.5	39	51.5

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 287

Effect of 1 % NaCl in the Vista axially viewed ICP. Without IS

Analyte	Content	% Difference
Cr II 267	9.7	-3
Cu I 324	9.5	-5
Fe II 259	9.2	-8
Mg II 279	8.9	-11
Mn II 256	8.9	-11
Zn II 202	10.15	+1.5

Relative to DI water

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 288

% RSD 1 % NaCl, using Meinhard high salt nebulizer (type c), with and without Sc II 361.384 nm as internal standard. 60 min continuous, 100 µg/l)

Element	Wave	Without IS	With IS
Mo II	202.03	2.5	0.8
Pb II	220.353	2.1	1
Co II	228.616	1.6	0.9
Ni II	231.604	2.8	0.8
Mn II	256.71	1.6	0.7
Cr II	267.716	2.5	1.2

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

289

Background values for sea water

Very low values in comparison to surface water

Li	175 ug/l	Zn	500 ppt
Ba	21 ug/l	Sb	200 ppt
Rb	120 ug/l	Cr	200 ppt
U	3 ug/l	Cu	300 ppt
Mo	11 ug/l	Mn	10 ppt
V	1.5 ug/l	Fe	30 ppt
As	1.4 ug/l	Cd	80 ppt
Ni	500 ppt	Co	1 ppt
		Pb	1 ppt

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

290

Trace element spike recoveries. NASS-2 standard sea water using conventional pneumatic nebulization. Data $\mu\text{g/l}$ except where indicated. Sc used as internal standard

ELEM	REC.*	SPIKE	RECOV/DET
Ba	nd		9
Be	nd	40	40
Cd	0.03	40	36
Co	0.004	40	40
Cr	0.18	40	43
Cu	0.23	40	38
Mn	0.38	80	75
Mo	8.84	40	53
Ni	0.228	40	45
Pb		100	110
V	nd	40	45
Zn	0.18	80	95

* Recommended values of NASS-2 standard sea water according to NRCC certificate

nd - Not determined or not recommended.

RSDs varied from 1-15 %

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

291

Trace element spike recoveries. NASS-2 standard sea water using conventional pneumatic nebulization. Data $\mu\text{g/l}$ except where indicated. Sc used as internal standard

ELEM	REC.*	SPIKE	RECOV/DET
Ba	nd		9
Be	nd	40	40
Cd	0.03	40	36
Co	0.004	40	40
Cr	0.18	40	43
Cu	0.23	40	38
Mn	0.38	80	75
Mo	8.84	40	53
Ni	0.228	40	45
Pb		100	110
V	nd	40	45
Zn	0.18	80	95

* Recommended values of NASS-2 standard sea water according to NRCC certificate

nd - Not determined or not recommended.

RSDs varied from 1-15 %

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

292

PT Spex NVLAP – Soil 1

Element	average	average	true value
Date of Analysis			
Ag 328.088*	60.1	63.7	60.1
As 188.980	61.2	64.9	58.6
B 208.956	43.4	46.0	46.4
Ba 455.403	107.2	113.7	94.0
Be 313.042	34.0	36.1	33.9
Cd 226.502	39.5	41.9	39.0
Co 230.786	51.8	54.9	51.8
Cr 287.716	43.6	46.2	40.3
Cu 324.754	42.4	44.9	44.3
Mn 257.610	719.3	762.8	753.0
Mo 202.032	13.8	14.7	14.1
Ni 231.604	50.6	53.7	51.5
Pb 220.353	60.7	64.4	58.7
Sb 206.834*	63.2	67.1	43.0
Se 196.026	43.9	46.5	42.5
Sr 407.771	21.6	23.0	20.1
Tl 190.807	62.6	66.3	75.6
V 292.401	77.2	81.9	75.4
Zn 213.857	109.4	116.1	111.0

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

293

Trouble shooting

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

294

Trouble shooting - 1

- **Low sensitivity**
 - ✓ **Blocked nebulizer, torch injector - Replace**
- **Incorrect Cu/Mn ratio**
 - ✓ **Low RF power, large matrix effect (high Na, Ca concentrations), incorrect torch position**
 - ✓ **Realign, increase power**
- **High short and long term RSDs**
 - ✓ **Nebulizer and injector blockage, gas leaks, punctured peristaltic tubes**
 - ✓ **Replace or clean**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

295

Trouble shooting - 2

- **Negative analytical results**
 - ✓ **Spectral line interference in background position**
 - ✓ **Check profile, change background positions, perform interference correction or change spectral line**
- **Inaccurate results for different spectral lines**
 - ✓ **Linear range exceeded.**
 - ✓ **Matrix effects on very high or very low energy lines**
 - ✓ **Dilute sample, use lines of lower sensitivity.**
 - ✓ **Use internal standard**

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

296

Trouble shooting - 3

- **Sample related instrument drift**
 - ✓ Variations in salt and acid concentrations
 - ✓ Use internal standards
- **Inaccurate results between high and low concentrations**
 - ✓ Carry over
 - ✓ Increase washout times.
 - ✓ Flush sample introduction system with 2 N HNO₃ until signals are < then MDLs

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

297

Proficiency Testing

- Sample Preparation - dilution of PT ampoule and handling the actual test material.
- EPA methods.
- PT Report contains fields for registration of data. Data are graded
- Report - True Values are based on compilation of data by other analysts using NIST SRMs and commercially available of certified materials of similar composition
- Control Limits - Based on the EPA's QA-QC criteria
- Summary Report - Provides evaluation on laboratory performance
- population performed.
- Examples, Spex Certiprep.
- Accustandards. Fax 203-786-5287, 800-442-5290 / 203-786-5290
www.accustandard.com

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

298

Uncertainty - definitions

- *Error Budget* - random and fixed errors, absolute values, and distribution (rectangular or Gaussian).
- *Accuracy* nearness of result (X_i) or arithmetic mean (\bar{M}) of a set of results to true value (μ).
- *Error* expresses accuracy, $X_i - \mu$ (or $\bar{M} - \mu$). Difference between true value (unknown) and experimental value or mean.
- *Absolute Error* is equal to $X_i - \mu$ and is expressed in the dimension of the two numbers.
- *Relative Error* - absolute error divided by true value (μ). Relative error calculated from absolute error and actual measurement
- *Systematic Errors* are of the same sign and magnitude and produce bias.
- *Random Errors* vary in sign and magnitude and are unpredictable. Random errors average out and approach zero if enough measurements are made.
- *Blunders* are mistakes that occur on occasion and produce erroneous results that are outliers and may be recognized as such by statistical procedures. They cannot be treated by statistics.
- *Precision* expressed in terms of deviation of a set of experimental results from the arithmetic mean of the set.
- *Deviation* is the difference between the mean and an individual result.
- *Average Deviation* refers to the summation of the deviation divided by the number of results.
- *Standard Deviation* of a sample is the square root of the average of the square of the individual deviations from the mean divided by $n-1$, where n is the number of measurements.
- *Uncertainty* - estimate of error in mathematical terms. Expressed using the standard deviation. Error is the difference between true value and a result or mean. Uncertainty is calculated from the deviation (difference between mean and individual result).

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 299

Figures of merit in accreditation

- LODs (IDLs, MDLs)
- LQDs – lowest point on calibration curve
- Sensitivity
- Matrix effect - bias
- Accuracy – Recovery (also at LQDs, CRMs)
- RSDs – long and short term
- Linear range of calibration

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 300

Sources of uncertainty

- Inhomogeneity of samples
- Analyte measurement instrumental variations
- Sample preparation - contamination, analyte losses

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

301

Uncertainty

- Uncertainty – all operators, procedures – all the time
- Sources of uncertainty
 - ✓ Sample prep, collection and preservation – 70 %
 - ✓ LODs
 - ✓ Calibration linearity
 - ✓ Matrix effects
 - ✓ Contamination
 - ✓ Precision
 - ✓ Operator error

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

302

Uncertainty

Ongoing precision and recovery OPR

- Add results that pass specs to IPR and previous OPR data for each analyte in each matrix.
- Update QC charts to form a graphic representation of continued laboratory performance.
- *Develop a statement of laboratory accuracy for each analyte in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR)*
- *Express the accuracy as a recovery interval from $R-2SR$ to $R+2SR$. For example, if $R = 95\%$ and $SR = 5\%$, the accuracy is 85-105%*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

303

Validation contd

- *Dilution data, differentiating between dilution of sample or extract*
- *Instrument and operating conditions (make, model, revision, modifications)*
- *Sample introduction system (ultrasonic nebulizer, flow injection system, etc.)*
- *Preconcentration system*
- *Operating conditions (background corrections temperature program, flow rates, etc.)*
- *Detector (type, operating conditions, etc.)*
- *Mass spectra, printer tapes, and other recordings of raw data*
- *Quantitation reports, data system outputs, and other data to link raw data to results reported*

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

304

Analytical factors influencing uncertainty

- Sampling
- Data handling
 - ✓ Weighing and seiving
- Sample preparation
 - ✓ Chemical extractability – digestion
- Chemical stability of standards and samples
- Spectroscopic interferences
- Matrix nonspectroscopic interferences
 - ✓ Salt effects in nebulization
 - ✓ EIE effects in plasma
- Compensation of internal standards
- Recovery – addition method and spikes
- Within batch and day-to-day drift
- MDLs and
- Ongoing precision and accuracy
- Spikes, CRMs, PT

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 305

EURACHEM Guide - Uncertainty

- Uncertainty of procedures, labs or chemists ?
- ONE chemist usually contributes to the test
- Therefore one calculation of uncertainty in a laboratory with one chemist will not provide "better" data, nor will these uncertainty data be associated with "real" uncertainty
- In order to determine uncertainty, we need to do this not only on a chemist basis but on a procedure basis as well

08-Aug-07 Joe Brenner, *Compliant Analysis of Waters and Wastes* 306

MDLs as a "real world" measure of uncertainty – why?

- MDLs - is the recovery of a low level spiked sample
- Since spike is a "true value" (with some definable uncertainty") variance can be referred to as "error."
- Low level spikes provide larger standard deviation due to recovery variance
- Low-level spikes provide an approximate measure of "variance" that can be related to laboratory uncertainty

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

307

EURACHEM Guide - Quantifying Uncertainty in Analytical Measurement.

- Estimating sources of error
- "Repeatability variation" is significant, if not largest contributor to uncertainty - directly related to operator - proficiency
- For estimation of uncertainty current data is used - if operator is changed, revalidation is necessary
- "Horwitz Curve" shows that coefficient of variation increases exponentially with decrease in concentration
- Horwitz Curve indicates interlaboratory variation - z-scores

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

308

EURACHEM CITAC

- Uncertainty is calculated once, unless procedure or equipment is changed.
- Uncertainty is then recalculated in a revalidation
- Performance Tests, validation studies and uncertainty measures are done ONLY by most senior or "best" chemists
- Thus laboratory will typically produce data that has a greater uncertainty on day to day samples.
- if lab A has a good z-score (measure of standard deviation) and lab B has a larger z-score they may both have similar uncertainties
- Uncertainty like interlaboratory variation, increases dramatically at lower concentrations

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

309

Z- values

- Good z values obtained in interlaboratory comparisons is more meaningful than low estimated uncertainties
- Good z values and low uncertainty derived from ONE chemist is only a measure of this chemist
- Since neither ISO 17025 nor the EURACHEM guide requires this measure from EVERY chemist, a laboratory will generally have lower performance on "every day" samples

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

310

Safety

Toxicity or carcinogenicity of reagents

- *OSHA regulations regarding safe handling of chemicals*
- Reference file of material handling **SHOULD** be made available to all personnel involved in chemical analysis.
- Use toxic reagents in fume hood and if eye or skin contact occurs, flush with large volumes of water
- Always wear safety glasses or shield for eye protection, protective clothing
- Acidification of samples containing reactive materials **MAY** result in release of toxic gases, such as cyanides or sulfides. Acidification and digestion **SHOULD** be done in fume hood.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

311

Safety

- Operators handling human waste **SHOULD** be immunized against known disease causative agents.
- **COMPLY** with relevant disposal and waste regulations.

08-Aug-07

Joe Brenner, *Compliant Analysis of Waters and Wastes*

312

Waste Management

- EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations
- Minimizing and control releases from hoods and bench operations, drains

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

313

REFERENCES – EPA 200.7

1. U.S. Environmental Protection Agency. *Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes-Method 200.7*, Dec. 1982. EPA-600/4-79-020, revised March 1983.
2. U.S. Environmental Protection Agency. *Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010, SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition*, 1986.
3. U.S. Environmental Protection Agency. *Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, revision 3.3*, EPA 600 4-91/010 June 1991.
4. U.S. Environmental Protection Agency. *Inductively Coupled Plasma-Atomic Emission Spectrometry Method for the Analysis of Waters and Solids*, EMMC, July 1992.
5. Fassel, V.A. et al. Simultaneous Determination of Wear Metals in Lubricating Oils by Inductively-Coupled Plasma Atomic Emission Spectrometry. *Anal. Chem.* 48:516-519, 1976.
6. Merryfield, R.N. and R.C. Loyd. Simultaneous Determination of Metals in Oil by Inductively Coupled Plasma Emission Spectrometry. *Anal. Chem.* 51:1965-1968, 1979.
7. Wings, R.K. et al. *Inductively Coupled Plasma-Atomic Emission Spectroscopy: An Atlas of Spectral Information*, Physical Science Data 20. Elsevier Science Publishing, New York, New York, 1985.
8. Boumans, P.W.J.M. *Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry*, 2nd edition. Pergamon Press, Oxford, United Kingdom, 1984.
9. *Carcinogens-Working With Carcinogens*, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977. Available from the National Technical Information Service (NTIS) as PP-277256.
10. OSHA Safety and Health Standards, General Industry, (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

314

References

11. *Safety in Academic Chemistry Laboratories*, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
12. Proposed OSHA Safety and Health Standards, Laboratories, Occupational Safety and Health Administration, Federal Register, July 24, 1988.
13. Rohrbough, W.G. et al. *Reagent Chemicals*, American Chemical Society Specifications, 7th edition. American Chemical Society, Washington, D.C., 1988.
14. American Society for Testing and Materials. *Standard Specification for Reagent Water*, D1193-77. Annual Book of ASTM Standards, Vol. 11.01. Philadelphia, PA, 1991.
15. *Code of Federal Regulations* 49, Ch. 1, Pt. 198 Appendix B.
16. Maxfield, R. and B. Mindak. EPA Method Study 27, Method 200.7 Trace Metals by ICP, Nov. 1983. Available from National Technical Information Service (NTIS) as PB 85-248-858.
17. Boffo, R.L. *Quality Assurance in Operating a Multielement ICP Emission Spectrometer*. *Spectrochim. Acta*, 39B(1):86-113, 1984.
18. Wallace, G.F. *Some Factors Affecting the Performance of an ICP Sample Introduction System*. *Atomic Spectroscopy*, Vol. 4, p. 188-192, 1983.
19. Koirtyohann, S.R. et al. *Nomenclature System for the Low-Power Argon Inductively Coupled Plasma*, *Anal. Chem.* 62:1965, 1990.
20. Deming, S.N. and S.L. Morgan. *Experimental Design for Quality and Productivity in Research, Development, and Manufacturing*, Part III, pp 119-123. Short course publication by Statistical Design, 9941 Rowlett, Suite 8, Houston, TX 77076, 1989.
21. Winefordner, J.D., *Trace Analysis: Spectroscopic Methods for Elements*, *Chemical Analysis*, Vol. 48, pp. 41-42.
22. Jones, C.L. et al. *An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 8010 and Digestion Method 3050*. EPA-806/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.
23. Martin, T.D., E.R. Martin and S.E. Long. *Method 200.2: Sample Preparation Procedure for Spectrochemical Analysis of Total Recoverable Elements*, EMSL ORD, USEPA, 1989.
24. *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*; U.S. Environmental Protection Agency. EMSL-Cincinnati, OH, March 1979.

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

315

CONCLUSIONS – rewards

- Trace metal water quality data bases - background and natural (rock-water, sea-water salinization) and anthropogenic contamination
- Trace metal concentrations used to characterize aquifer and surface waters, wastes, sediments
- Data provided for long and short-term planning of water management programs.
- Establishment of diagnostics to model the origin, migration, and evolution of water entities in the Guadiana Basin

08-Aug-07

Joe Brenner, Compliant Analysis of Waters and Wastes

316

Acknowledgements



Tel Aviv Towns Association of Effluent Disposal
Daniel Salomon, director Environmental Division
Varian OSI, Melbourne, Australia
Andy Zander, (Molecular Devices CA.) previously
Varian GRC, Palo Alto, California

08-Aug-07 *Joe Brenner, Compliant Analysis of Waters and Wastes* 317



Kent Porter / The Santa Rosa Press Democrat

08-Aug-07 *Joe Brenner, Compliant Analysis of waters and wastes* 318

AUTHOR INDEX

**NATIONAL ENVIRONMENTAL MONITORING CONFERENCE
PROCEEDINGS 2008****AUTHOR INDEX**

Bowerbank, Christopher.....	72, 73
Brenner, Isaac.....	128, 129
Eaton, Andrew.....	109, 114
Fitzpatrick, Timothy	89
Griedman, David.....	98
Grosser, Zoe.....	98
Hammersla, Mark	45, 46
Moore, Stephen.....	28, 35
Parshionikar, Sandhya.....	2
Proper, Wim	51, 60
Timm, Gary.....	15
Wilbur, Steve.....	51, 60
Wood, Curtis.....	127