Meeting Summary
Joint IDQTF/DoD EDQW Roundtable
State of the Art in Analysis of Perchlorate in Environmental Samples
Thursday, October 23, 2003
Dallas, Texas

Introduction

The DoD Environmental Data Quality Workgroup (EDQW) and the Intergovernmental Data Quality Task Force (IDQTF) convened this national, multi-disciplinary task force to examine problems/limitations with current perchlorate sampling and testing methods, discuss emerging technology, and recommend a path forward for developing, validating, and publishing improved, performance-based methods.

Jim Woolford [Director of the EPA Federal Facilities Restoration and Reuse Office (FFRRO) and Chair of the IDQTF] and Jackie Sample [Director of Navy's Laboratory Quality and Accreditation Office and Chair of the EDQW] welcomed participants and thanked them for their contributions to this effort, noting that this meeting was just the beginning of a process. Three specific objectives of the discussions are to:

1 Identify the most promising laboratory technologies for the analysis of perchlorate in environmental samples.
2. Determine what must be done to validate and publish these methods.
3. Identify what steps data users and other stakeholders can/should take in the meantime to ensure the collection of usable data for the purpose of assessing perchlorate contamination in the environment.

Mr. Woolford explained that while the meeting's sponsors intend to identify a path forward and take the appropriate next steps, what those specific actions will look like is uncertain at this point. The first step will be to prepare a meeting summary and post the technical presentations on the Navylabs website: www.navylabs.navy.mil. Once a follow-up strategy is developed, it also will be posted on the Navylabs website. Mr. Woolford noted that toxicology, risk assessment, regulatory, legal, and policy issues were outside the scope of this effort and would not be discussed.

Attachment A provides the Roundtable agenda. Attachment B provides contact information for participants. Handouts and copies of presentations are posted on the Navylabs website.

Overview of EPA's Method-development and approval process

Elizabeth Hedrick, with EPA's Office of Research and Development (ORD), discussed the ORD process for method development and the alternative test procedure (ATP) approval process. ORD starts with a research plan, which the Office of Water (OW) approves. Proposed methods are published in the federal register and undergo the review and comment process. Ms. Hedrick stated that there is some flexibility in OW methods. Due to limited funding for approving ATPs, there currently is a significant backlog; therefore, this process would likely be too slow to work for the development of alternative perchlorate testing methods. EPA's Laboratory Technical Issues Group is pursuing alternative method development/approval processes, such as publication

through the American Society of Testing and Materials (ASTM), which would be followed by EPA review and acceptance.

Shen-yi Yang, with EPA's Office of Solid Waste (OSW), discussed the procedure to develop SW-846 methods, pointing out that SW-846 methods generally are not prescriptive and OSW promotes the performance-based measurement approach. The performance data provided in SW-846 methods are intended to be used as guidance to help select appropriate methods; they are not intended to be used as absolute quality control (QC) acceptance criteria. Except where explicitly stated in regulations, the use of SW-846 methods is not mandatory. Ms. Yang stated that OSW had intended to finalize proposed Method 9058 (perchlorate by ion chromatography) by the end of the year. Several participants expressed concern over its publication, however, because Method 9058 does not make use of current IC technology, and its quality control procedures are not as rigorous as those specified in Method 314.0. One State participant noted that while SW-846 methods are intended to be used as guidance, States can write them into regulations, making their application prescriptive and their use mandatory.

Ms. Yang also discussed the implementation of the Methods Innovation Rule (MIR), emphasizing that method flexibility is needed to address *specific analytes of concern, in matrices of concern, at specific levels of concern.* The MIR, which is expected to be finalized in December 2003, will eliminate the need to publish SW-846 Updates as regulations; instead, Updates will be published in the *Federal Register* as Notices of Data Availability (NODA), with opportunity for public comment. The Resource Conservation and Recovery Act (RCRA) method development guidelines for both modifying a procedure and developing a new procedure are available on the OSW website: http://www.epa.gov/epaoswer/hazwaste/test/methdev.htm.

Presentations

1 *EPA Perchlorate Method Development Activities*, Elizabeth Hedrick, EPA/ORD.

Elizabeth Hedrick presented a summary of ORD and OW activities in the development of an Ion Chromatograpy/Mass Spectrometry (IC/MS) method using isotope dilution (oxygen-18). She reported that the method detection limit (MDL) was between 0.02 and 0.06 parts per billion (ppb). Dr. Hedrick discussed method performance issues such as interference by sulfate, loss of sensitivity in high ionic strength matrices, and cone fouling in the MS. She also pointed out that it is essential to monitor ion ratios when using MS methods. EPA hopes to have the peer review completed in December 2003 and the method finalized by February 2004. Some method implementation issues include the cost and availability of mass spectrometry and availability of the oxygen-18 standard.

2 *Perchlorate by Ion Chromatographic Methods*, Douglas Later, Dionex

Doug Later discussed modifications and improvements to Method 314.0, including improved instrumentation, ion suppression, pretreatment, preconcentration, and second-column confirmation. He reported that the Method 314.0 improvements have worked to reduce interferences from samples with high levels of total dissolved solids (TDS) (in particular chloride, sulfate, and carbonate). He also discussed IC/MS methodology, which is capable of greatly reducing detection limits, but requires higher operator skill than traditional IC

methods. Dr. Later reported that Dionex is currently working to address some problems with the implementation of IC/MS technology in a production laboratory.

3. *Determination of Perchlorate in Water and Soil by IC Following EPA Method 314.0*, Bob DiRienzo, DataChem.

   Bob DiRienzo reported on a modification to Method 314.0. The modification, which employs a pre-concentration setup, allows DataChem to analyze samples with much higher total dissolved solid (TDS) levels than Method 314.0. Dr. DiRienzo stated there is a need for guidance on validating perchlorate data.

4. *Determination of Trace Perchlorate in High Salinity Matrices by IC with On-line Pre-concentration and Pre-elution*, Rashila Patel, Texas Tech

   Rashila Patel presented the pre-concentration method developed by Texas Tech University used to manage matrix interferences. Similar to work conducted by DataChem, Texas Tech has been able to analyze samples in various complex matrices with high TDS levels. Ms. Patel noted the need to optimize the wash volume for specific matrices. Texas Tech has used MS to confirm many IC results.

5. *Trace-Level Analysis of Perchlorate by IC/MS*, Jay Ghandi, Metrohn-peak, Inc.

   Jay Ghandi discussed the use of IC/MS for perchlorate. He noted that the configuration of their instrument [Agilent] allows method ruggedness, but added that sulfonate detergents can interfere with the detection of perchlorate by IC/MS.

6. *Mass Spectrometric Methods for Definitive Analysis of Perchlorate Compared to IC/Conductivity Methods*, Larry Penfold, STL

   Larry Penfold presented the use of IC/MS/MS for perchlorate analysis, noting that essential QC procedures for MS methods include ion-ratio monitoring, MDL verification, and the measurement of method accuracy in every sample. Dr. Penfold compared the performance of IC, LC/MS, LC/MS/MS, and IC/MS/MS in difficult matrices, noting that matrix effects can result in false positive results, false negative results, and retention time shifts. He provided examples illustrating the occurrence of false positives when using Method 314.0 that were uncovered using IC/MS/MS.

7. *Definitive Perchlorate Analysis by LC/MS/MS*, Janice Willey, GEL

   Janice Willey presented GEL's LC/MS/MS method, which includes sample pretreatment to reduce interferences caused by carbonate and sulfate. Ms. Willey stressed the importance of proper method QC including matrix-specific MDL verification, and ion-ratio monitoring. She also discussed the importance of routine instrument maintenance, which should include weekly cone cleaning.

8. *Analysis of Perchlorate in the Sub-ppb Range Using Ion Chromatography*, Ali Haghani, MWH

Ali Haghani discussed enhancements to Method 314.0 including the use of dual columns and concentrators in series with conductivity detection. The primary concentrator was a Cryptand column and the secondary was a TAC-LP1. Other enhancements included chromatogram 'heart-cutting' to eliminate matrix effects, suppressor noise control, and use of chromatogram 'smoothing' algorithms.

9. *Data Quality Issues and Data Review for Low-Level Perchlorate Analysis*, Nora Conlon, EPA Region 1

Nora Conlon presented a summary of data quality issues for perchlorate analysis at the Massachusetts Military Reservation (MMR), where a modified Method 314.0 has been used to determine perchlorate concentrations as low as1 ppb in groundwater samples with very low TDS. Method QC includes daily MDL checks at 0.5 ppb (acceptance criterion is 50-150%), method blanks (results must be < MDL) Laboratory Control Samples (LCS) and matrix spikes/matrix spike duplicates (MS/MSD).

Method Discussion

Group discussion was structured to collect information about applicability, limitations, costs, and QC issues for methods described in the presentations. The following discussion divides methods into three categories: 1) Ion Chromatograpy/Conductivity (compliant with Method 314.0); 2) Enhanced Ion Chromatography/Conductivity (Modified Method 314.0), and 3) IC-LC/MS and IC-LC/MS/MS. **Note: while there was general agreement among participants concerning the following technical issues, this summary is preliminary and does not represent formal consensus by either the IDQTF or EDQW.**

1) Ion Chromatograpy/Conductivity (Compliant with Method 314.0)

Applicability

- Use is mandatory for drinking water samples under the Unregulated Contaminant Monitoring Rule (UCMR)
- Suitable for use when:
  - Samples contain low dissolved solids (conductivity < 1mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 ppm each
  - There is a confirmed source of perchlorate at concentrations exceeding the Method Reporting Limit
  - Used as a screening method, subject to confirmation by definitive technology
- Reporting limit: 0.5 – 5ppb

Limitations

- Analysis is subject to false positives due the unspecific nature of the conductivity detector
- Inappropriate for use in samples with high TDS
- The lower reporting limit of 0.5 ppb is achievable only in samples with very low TDS
- Confirmation of perchlorate by specific method is required

- Method has been validated in drinking water only; no guidance provided for use with soils, solids

Cost/Availability
- Widely available
- Instrument cost: $40 – 65K
- Per-sample analytical cost: $60 – 125K (extra for confirmatory analysis)
- Operator qualifications and experience: BS chemist
- Capacity: 500 samples/mo/instrument
- Run time: approximately 15 – 20 min/sample
- Maintenance: 6 – 8 hrs per 1000 samples

Recommended Quality Assurance and Quality Control
- Determine maximum conductivity threshold (MCT) at reporting limit
- Conduct MDL study at MCT
- Signal to noise ratio: 5:1 at RL and 3:1 at MDL
- Lowest calibration standard at or below RL
- MS/MSD and LCS spike concentrations should be close to level of concern
- Continuing calibration verification sample (CCV) after every 10 field samples
- Surrogate or internal standard in each sample to check for retention time shifts

2) Enhanced Ion Chromatography/Conductivity (Modified Method 314.0)

Applicability
- Can accommodate more difficult matrices
  - Samples with up to 10 mS/cm TDS
- Reporting limit: 0.5 –1 ppb
- Reduces false positives
- Second column aids in confirmation
  - 2nd channel method offers built-in confirmation

Limitations
- Lower reporting limit: 0.5 ppb
- False positives will be reduced but not eliminated
- No EPA-approved methods

Cost/Availability
- Initial set-up instrument cost: $75- 100K
- Modification to existing 314.0 set-up: $10K
- Per-sample analytical cost: $75 –150
- Pre-concentration columns not widely available
- Currently 6 -12 laboratories are able to use pre-concentration
- Start up time to implement this method: 6-8 months
- Operator qualifications and experience: BS chemist plus1 yr experience in LC or IC
- Run time: 30 min
- Maintenance: Somewhat higher than maintenance costs for standard IC, depending on the nature of the instrument modifications

Recommended Quality Assurance/Quality Control

- Same as Method 314.0

3) **IC-LC/MS, IC-LC/MS/MS**

Applicability

- Much greater sensitivity (Reporting Limit: approx 200ppt; MDL: approx 50 ppt)
- Eliminates matrix interferences (false positives)
- High confidence in compound identification with IC/MS
- Extremely high confidence with IC/MS/MS

Limitations

- Few available (2 – 4 laboratories have the instrumentation)
- Need to monitor accuracy in every sample due to ionization suppression which can result in low bias
- Need to monitor for cone fouling

Cost/Availability

- Instrument cost: IC-LC/MS $150-175K; IC-LC/MS/MS $250-300K
- Per-sample analytical cost: $120- 250
- Approximately 4 – 6 commercial laboratories currently have this instrumentation
- Limited availability of internal standards
- Analysis requires a highly knowledgeable analyst with experience in liquid chromatography and mass spectroscopy
- Maintentance contract: 10% of capital cost per year
- Operator qualifications and experience: MS Chemist

Recommended Quality Assurance/Quality Control

- Signal-to-noise ratio should be 5:1 at reporting level
- Lowest calibration standard should be run at or below reporting level
- Isotope ratio monitoring
- Daily MS tuning check standard must be run
- MS/MSD and LCS should be run at level of concern
- Continuing Calibration Verification sample should be run every 10 samples.
- A QC sample must be run to monitor for cone fouling
- A QC sample must be run to check shifts in retention time
- A QC sample must be run to monitor for low-level standard suppressions
- Specify best run sequence

Summary/Conclusions:

While participants were not polled for formal consensus, there was general agreement on the following:

1) Proposed Method 9058 not be finalized as written, because it employs older column technology than Method 314.0, and it does not meet the current need for the development of a perchlorate-specific method suitable for use with

solid matrices and high-conductance water. EPA OSW (S-Y Yang) requested technical comments on improving Method 9058.

2) Positive results for perchlorate obtained using Method 314.0 should be confirmed because the conductivity detector is non-selective. False positive results have been shown to occur due to interferences from numerous sources (see presentation number 6)
3) While modifications to Method 314.0 can be effective at reducing background interference, improving method ruggedness for use with higher dissolved solid matrices, the modifications do not improve method selectivity. The only way to improve selectivity is to use an alternative detection technology (e.g. mass spectrometry).
4) As documented in the accompanying presentations, the lower reporting limit for ion chromatographic methods, including Method 314.0 and its modifications, ranges from 0.5 to 5 ppb. The lower reporting limit for methods employing MS ranges from 50 to 200 parts per trillion (ppt).
5) This workshop provided an effective forum for gathering both government and private-sector technical experts from to discuss a current environmental problem and begin to develop joint, workable solutions. Participants suggested that DoD and EPA consider institutionalizing this type of workshop in conjunction with future EPA headquarters or regional quality assurance meetings.

Next Steps:

Representatives from DoD and EPA will meet to discuss next steps. Next steps suggested by DoD representatives include the following:

1) EDQW provide technical comment to OSW (S-Y Yang) on improving SW-846 Method 9058 (draft).
2) Discuss the process and timeframe for EPA approval of perchlorate methods employing mass spectrometry and facilitate process.
3) Develop procedures to characterize site-specific background contamination by perchlorate.
4) Investigate sources of laboratory contamination by perchlorate, including glassware detergents.
5) Investigate availability of internal standards (e.g. oxygen-18).
6) Pursue the development of a DoD guidance document to address sampling and testing of perchlorate.
7) Institutionalize the government-private, multidisciplinary task force approach for technical problem-solving.

Attachment A: *State of the Art in Analysis of Perchlorate in Environmental Samples*

Agenda

Thursday, October 23, 2003

Dallas, Texas

Welcome, Introductions, Ground Rules 8:00 – 8:30

EPA Method-development and approval process 8:30 – 9:00

Elizabeth Hedrick, EPA/ORD

Shen-yi Yang, EPA/OSW

Invited Presentations

1) EPA Perchlorate Method Development Activities 9:00 – 9:25

Elizabeth Hedrick EPA/ORD

2) Perchlorate by Ion Chromatographic Methods 9:25 – 9:50

Douglas Later Dionex

3) Determination of Perchlorate in Water and Soil by IC Following EPA Method 314.0 9:50 – 10:15

Bob DiRienzo DataChem

Break *10:15 – 10:30*

4) Determination of Trace Perchlorate in High Salinity Matrices by IC with On-line Pre-concentration and Pre-elution

Rashila Patel Texas Tech 10:30 – 10:55

5) Trace-Level Analysis of Perchlorate by IC/MS 10:55 – 11:20

Johnson Matthew EPA Region 6

Joe Hedrick Agilent Technologies

Jay Ghandi Metrohn-peak, Inc.

6) Mass Spectrometric Methods for Definitive Analysis of Perchlorate Compared to IC/Conductivity Methods

Larry Penfold STL 11:20 – 11:55

Lunch *11:55 – 1:00*

7) Definitive Perchlorate Analysis by LC/MS/MS 1:00 – 1:25

Janice Willey GEL

8) Title TBD 1:25 – 1:50

Ali Haghani MWH

9) Data Quality Issues and Data Review for Low-Level Perchlorate Analysis

Nora Conlon EPA Region 1 1:50 – 2:15

Steve DiMattei EPA Region 1

Break *2:15 – 2:30*

Next Steps 2:30 – 5:00

[Developing, validating and publishing improved, performance-based methods]

Attachment B – Roundtable Participants

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[Note: States with current advisory levels include AZ, CA, MD, MA, NV, NM, NY, and TX]

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