An Update on the OSW Methods Development Activities for Perchlorate in Solids

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Presentation Outline

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Background

- Perchlorate ($\text{ClO}_4^-$) is an oxidant used primarily in the manufacture of solid propellant.

- Other sources include fireworks, highway safety flares, airbag inflators and some nitrate-based fertilizers.

- Perchlorate inhibits the iodine uptake by the thyroid gland and thus affects:
  - Thyroid hormone production
  - Thyroid regulation of metabolism, and
  - Neurological development of fetus and newborn

- Presently, perchlorate has been detected in twenty (20) States, various aquifers, crops, and milk

- The EPA proposed drinking water action level is $1 \mu g/L$; State action levels range from $1$ to $31 \mu g/L$. 
The EPA has not yet set an action level for perchlorate in soil, however, EPA Region 9 has identified a Preliminary Remediation Goal (PRG) of 7.8 mg/kg.

The current method for perchlorate in solids is Method 9058.

There are analytical issues with the current published methods (314.0 for water and 9058 for solids).
Perchlorate in Soil

- Very little information and data are available about:
  - The ionic strength of soils.
  - How perchlorate behaves in solid matrices along with the stability in soil.
  - What are the inorganic and organic compounds in soil that may interfere with the analysis of perchlorate?
  - Are the compounds that interfere with perchlorate analysis in water the same for soil and soil extracts?

- The conductivity range for 270 soil sample extracts analyzed by the Texas Tech, Groundwater Analysis Laboratory in 2002 and 2003, was low (no more than 800 μS/cm).

- It is believed that perchlorate migrates through soils with little, if any, absorption occurring, however, the studies and literature to support this hypothesis are limited.
Perchlorate in Soil (cont.)

- Studies by the U.S. Army Engineer Research & Development Center in Vicksburg, MS and Omaha, NE, show that:
  - As expected, the majority of perchlorate was recovered in the exposure solution.
  - Perchlorate soil absorption did not appear to be affected by various soil types or oxygen conditions (oxic verses anoxic).
  - However, of the five soils tested, the high pH soil demonstrated the highest level of perchlorate in the leachates.
The OSW Perchlorate Task Force

- OSW
- ORD
- LTIG
- DOD
- Instrument Vendors / Method Developers
- Commercial Laboratories
Analytical Methods for the Determination of Perchlorate in Solids

- Method 9058 (Ion Chromatography with Chemical Suppression and Conductivity Detection).
- Method 6850 (High Performance Liquid Chromatography / Mass Spectrometry).
- An Anticipated New Method (ion Chromatography / Mass Spectrometry).
Method 9058 (IC)

- Method was proposed in November 2000.
- The scope and applicability of Method 9058, as currently written:
  - 4 μg/L lower limit of detection for spiked reagent water samples.
  - Performs adequately on water samples with conductivities up to 1000 μS/cm. Water samples with conductivities >1000 μS/cm have not been tested.
  - The method could produce false positive and false negative results due to sample matrix interferences attributed to co-eluants and high total dissolved solids.
Method 9058 (IC) (Cont.)

- When this method is used to analyze unfamiliar samples, perchlorate identification should be supported by a demonstration of performance. The method recommends that the detected concentrations be confirmed using either another analytical column with dissimilar ion chromatographic conditions or other approved analytical techniques such as IC/MS, LC/MS, LC/MS/MS, or ion selective electrode.
- This recommendation is especially important for situations where the data will be used for compliance or other regulatory purposes.

- Our goals for refining Method 9058
  - Broaden the scope such that the method is applicable for aqueous and leachate samples having high total dissolved solids,
  - Lower the level of detection for perchlorate to sub-ppb level,
  - Have better chromatographic separation,
  - Minimize false positive and negative results,
  - Include extraction procedures for solids.
Method 9058 (IC) (Cont.)

- We will continue our refinement of Method 9058 for the intended use.

- Current Status: Evaluating the sample preparation procedures to be included in Method 9058
  
  - Reviewed five currently available extraction procedures for soils.
  - Spiked four soil samples containing perchlorate and extracted them using two of the selected procedures.

<table>
<thead>
<tr>
<th>Alliant Techsystems (ATK)</th>
<th>Texas Tech (GAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution Ratio</td>
<td>1:10</td>
</tr>
<tr>
<td>Extractant</td>
<td>water</td>
</tr>
<tr>
<td>Drying</td>
<td>air-dried</td>
</tr>
<tr>
<td>Clean-up</td>
<td>none</td>
</tr>
</tbody>
</table>

- Percent recoveries in soils extracted with these two procedures are comparable.
Method 9058 (IC) (Cont.)

- Continuing to gather information and data to help determine if pre-treatment, pre-concentration, and pre-elution steps are necessary.
  - Conductance ranges for various types/locations of soils, sediments, and sludges.
  - Identify possible inorganic and organic compounds that may interfere with the analysis of perchlorate in soil, sediment, and sludge sample matrices.

- Next Steps: Will perform further extraction studies to further develop the recommended sample extraction and preparation procedures.
  - Compare extraction efficiency on native soils due to drying (air-dried verses as-received).
  - Compare extraction efficiency on high conductivity soils (samples will be spikes with a combination of chloride, sulfate, carbonate, nitrate, and phosphate salts prior to extraction to yield an approximate extract conductivity of 2,500 μS/cm in one set of extracts and 5,000 μS/cm in another set of extracts).
  - Determine if a pre-treatment procedure is needed.
Method 9058 (IC) (Cont.)

- We will determine if pre-concentration and pre-elution steps are needed pending the outcome of the following:
  - Conductance range of soil extracts, sediments, and sludges;
  - Possible inorganic and organic interferents;
  - Sample size;
  - Level of detection

- Should pre-concentration and pre-elution steps be necessary, two possible techniques will be evaluated:
  - Dionex (Cryptand C1 Concentrator Column)
  - Texas Tech, Groundwater Analysis Laboratory, Standard Operating Procedure

- Will include an improved system (i.e., AG/AS 16 columns and improved suppressor ASRS Ultra II)

- Will consider whether or not to include a new eluant generator and / or a second confirmatory column
Method 6850 (HPLC/MS)

- The draft method was submitted for evaluation July 2004.
- The method uses a high performance liquid chromatography / mass spectrometry (HPLC/MS).
- The method will be applicable to the determination of perchlorate in soil, sediment, and sludge.
- This method may be applicable to other matrices (e.g., biota), but these types of matrices will not be evaluated.
- A 100 μL portion of the sample or extract is introduced into the HPLC/MS. Perchlorate is separated by the HPLC, and partially fragmented by the MS using masses 83, 85, and 89.
- The 83/85 isotopic ratio reflects the isotopic ratio of naturally occurring $^{35}\text{Cl}$ to $^{37}\text{Cl}$ and is used for additional identification of perchlorate.
- An oxygen-18 isotopic labeled perchlorate is used as an internal standard and is monitored at mass 89.
- The method requires less sample preparation (without sample pre-treatment). A single lab validation study results look very promising.
Method 6850 (HPLC/MS) (Cont.)

- Proposed HPLC/MS Operating Conditions Using Agilent 1100 HPLC/MS

- Pump Control
  - Flow Rate: 0.5 mL/min
  - Run Time: 10.0 min
  - HPLC Mobile Phase: Isocratic 53.00% Solvent A (95% ACN / 4.5% Water / 0.5% Acetic Acid) 47.00% Solvent B (94.5% Water / 5% CAN / 0.5% Acetic Acid)

- Mass Spectrometer
  - Ionization Mode: Electrospray
  - Polarity: Negative

- SIM Parameters
  - | SIM Ion | Fragmentor | Gain (EMV) | Actual Dwell |
  - | 83.00   | 160V       | 3.0        | 192 msec     |
  - | 85.00   |            |            | 192 msec     |
  - | 89.00   |            |            | 192 msec     |
Method 6850 (HPLC/MS) (Cont.)

- Spray Chamber
  - Gas Temp: 320°C
  - Drying Gas (Nitrogen): 12.0 L/min.
  - Nebulizer Pressure: 50 psig

- Capillary Voltage
  - Negative: 1450 V

- Autosampler and Column
  - Injection Volume: 100 µL
  - Column Temp: 30°C
Method 6850 (HPLC/MS) (Cont.)

- Current Status:
  - The OSW Perchlorate Task Force completed a preliminary review.
  - The comments received thus far will be forwarded to Data Chem Laboratories (method developer) this week.
  - A revised method will be forwarded for further Task Force review and approval before it is sent for the OSW Inorganic Methods Workgroup review.
  - A multi-laboratory validation study is planned for next year.
Anticipated New Method

- Determination of perchlorate in solids by IC/MS.
- An instrument vendor contacted OSW for submission of a proposed method for our evaluation.
- The draft version of this method should be received within the next few months.
Relevant Contact Addresses and Phone Numbers

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

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

- Shen-yi Yang
  - Phone No.: (703)-308-0437
  - E-mail: yang.shen-yi@epa.gov
The OSW Perchlorate Task Force consists of chemists from seven EPA Regions (3, 4, 5, 6, 7, 9, and 10). I am also seeking support from outside experts and encourage your participation in further developing Method 9058 and the additional development and validation of new perchlorate methods.