Accelerated Solvent Extraction of Cr(VI) from Soil

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Overview

- Hexavalent Chromium
  - Background
  - Current Methods
- Analysis Improvements
  - EPA 218.6, 218.7, 7136,
- Soils extraction using EPA 3060A
  - Interferences, challenges
- Conclusions
Cr(VI) Regulatory Timeline

- May 2008 EPA Toxicology report
- Sept. 2010 EPA releases IRIS report for Cr(VI)
- Feb. 1999 CA PHG 2.5 ppb Total Cr (0.2 ppb for Cr(VI))
- March 1999 CDPH mandates monitoring
- Aug. 2009 CA draft PHG of 0.06 ppb
- May 2008 EPA Toxicology report
- Aug. 2011 EPA develops 218.7
- Jan. 2000 movie “Erin Brockovich” released
- Dec. 2010 EWG report
- Jan. 2011 EPA recommends AU144 for Cr(VI)
- Mar. 2011 EPA requests comments to include Cr(VI) in UCMR3
- July 2011 CA PHG 0.02 ppb
15 + year Analytical Timeline for Cr(VI) in Water

- **1994 EPA Method 218.6 rev. 3.3**
  - MDL 0.4 µg/L
  - MRL 1 µg/L

- **1999 CDPH mandates monitoring**
  - Jan. 2003 Dionex AN 144
  - MRL 0.2 µg/L

- **Jan. 2011 Dionex AU 179**
  - MRL <0.02 µg/L

- **Aug. 2011 EPA Method 218.7**
  - LCMRL 0.02-0.05µg/L

- **Modified per AN144**
  - Sample preservation
  - Holding times

- **2mm format**

- **Modified preservative**
  - Increased sample loop
  - Increased reaction coil
# Summary of Methodologies for Chromium VI Analysis

<table>
<thead>
<tr>
<th>EPA Method</th>
<th>Sample Types</th>
<th>Sample Conc. Limits (µg/L)</th>
<th>Technique</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>218.6</td>
<td>Drinking Water, Groundwater, Industrial Effluents</td>
<td>-</td>
<td>IC with post column derivatization</td>
<td>0.3 µg/L (0.001 µg/L with modifications outlined in Dionex AN 179)</td>
</tr>
<tr>
<td>218.7</td>
<td>Drinking Water</td>
<td>-</td>
<td>IC with post column derivatization</td>
<td>0.3 µg/L (0.001 µg/L with modifications outlined in Dionex AN 179)</td>
</tr>
<tr>
<td>1636</td>
<td>Ambient Waters (river/lake water)</td>
<td>-</td>
<td>IC with post column derivatization</td>
<td>0.3 µg/L (0.001 µg/L with modifications outlined in Dionex AN 179)</td>
</tr>
<tr>
<td>7199</td>
<td>Drinking Water, Groundwater, Industrial Effluents</td>
<td>-</td>
<td>IC with post column derivatization</td>
<td>0.3 µg/L (0.001 µg/L with modifications outlined in Dionex AN 179)</td>
</tr>
<tr>
<td>218.4</td>
<td>Drinking Water, Surface/Saline Water</td>
<td>10 - 250</td>
<td>Chelation Extraction with Flame AA</td>
<td>10 – 25 µg/L</td>
</tr>
<tr>
<td>7197</td>
<td>Ground Water, Leachates, Soils</td>
<td>1 - 25</td>
<td>Chelation Extraction with Flame AA</td>
<td>10 – 25 µg/L</td>
</tr>
<tr>
<td>7196</td>
<td>Ground Water, Leachates, Soils</td>
<td>500 – 50,000</td>
<td>Colorimetric Analysis</td>
<td>&lt;50 µg/L</td>
</tr>
<tr>
<td>7195</td>
<td>Ground Water, Leachates, Soils</td>
<td>&gt;5</td>
<td>Co-precipitation with AA</td>
<td>10 – 25 µg/L</td>
</tr>
</tbody>
</table>
System Configuration for Hexavalent Chromium by U.S. EPA Method 218.6
## Achieving a Lower Method Detection Limit (MDL)

<table>
<thead>
<tr>
<th>Method</th>
<th>Column Set</th>
<th>Reaction Coil Volume (µL)</th>
<th>Eluent Flow Rate (mL/min)</th>
<th>Postcolumn Flow Rate (mL/min)</th>
</tr>
</thead>
</table>
| **Modified Version of 218.6** | Thermo Scientific Dionex IonPac™ NG1 Guard 4 × 50 mm  
Dionex IonPac AS7 Analytical 4 × 250 mm | 750                        | 1.0                       | 0.3                          |
| **AU179**             | Dionex IonPac AG7 Guard 2 × 50 mm  
Dionex IonPac AS7 Analytical 2 × 250 mm | 125                        | 0.36                      | 0.12                         |
Chromate Detection

Column: Thermo Scientific Dionex IonPac™ AS7 (2 × 50 mm), AS7 (2 × 250 mm)

Eluent: 250 mM (NH₄)₂ SO₄, 100 mM NH₄OH

Flow: 0.36 mL/min

Inj. Vol: 1000 µL

Postcolumn Reagent: 2 mM diphenylcarbazide, 10% methanol, 1N sulfuric acid

Reaction Coil: 125 µL

Flow Cell: Standard (PEEK), 11 µL

A. DI water blank
B. 0.005 µg/L Cr(VI) in DI water

Comparison of chromate in high ionic-strength water (HIW) and Sunnyvale tap water

Column: Dionex IonPac™AS7 (2 × 50 mm), AS7 (2 × 250 mm)

Eluent: 250 mM (NH₄)₂ SO₄, 100 mM NH₄OH

Flow: 0.36 mL/min

Inj. Vol: 1000 µL

Postcolumn Reagent: 2 mM diphenylcarbazide, 10% methanol, 1N sulfuric acid

Reaction Coil: 125 µL

Flow Cell: Standard (PEEK), 11 µL

A. 0.1 µg/L Cr(VI) in DI water
B. 0.1 µg/L Cr(VI) in HIW
C. 0.1 µg/L Cr(VI) spiked in Sunnyvale, CA tap water

1 ppt Detection can be achieved!
Analytical Issues involving Cr(VI) determination in water

- IC is extremely sensitive and can measure down to 1ppt MDL
- Cr(VI) is very stable in most waters
  - Holding time in EPA 218.7 is 14 days
- Cr(VI) contamination has been found in chemicals used for eluents and preservation buffers
- EPA 218.7 allows easier pH adjustment to pH 8.0
  - Also uses weaker buffers to prevent column overloading
- Free chlorine will oxidize Cr(III) to Cr(VI)
  - Need to minimize impact with NH₄SO₄ addition to form chloramines
  - Chlorine must be <0.1 ppm prior to collection
- Filtering samples is not required
- Preservative is prepared once every 30 days
  - Can add preservative to bottles prior to sample addition
- Chilling of samples is not required.
Cr(VI) from soil

• **Step 1:** Extraction Method 3060A – alkaline digest
  • Extraction also removes anions and metals in the soil sample
  • redox, pH, sulfides, Mg$^{2+}$, Fe$^{2+}$ affect extraction, oxidation and reduction between Cr(III) and Cr(VI).

• **Step 2:** Analysis Method 7199 – IC with post column same as EPA 218.6

• Under reporting in soil extracts
Focus has been on Analysis Techniques
Sample Preparation…
Sample Preparation: What and Why

- Prepare sample for analysis
- Concentrate analytes
- Eliminate matrix effects

- Sample Prep is…
- Most time consuming part of analytical procedure (61%*)
- Single largest source of errors(<30% by some reports**)

Importance of Sample Preparation

“Eighty Percent of the Variance in an Assay Usually Arises from the Sample Prep.”

EPA 3060A

- *Alkaline digestion for Hexavalent Chromium*
- Designed for soil, sludges, and sediments.
- Must meet 3 criteria
  1. The extracting solution must solubilize all forms of Cr(VI),
  2. The conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III),
  3. The method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI).
• Procedure
  • 2.5 g sample
  • 50 mL ± 1 mL of digestion solution
  • 400 mg MgCl$_2$
  • 0.5 mL phosphate buffer
  • Heat digestion solution to 90 – 95°C for 60 minutes
  • Let cool, rinse vessel 3x
  • Filter through a 0.45 µm filter
  • pH adjust to 7.0 for 7196, pH 9.0 for 7199
Cr(VI) from soil - EPA 3060A and 7199

- Results from soil extracts
- Second extraction resulted in more Cr(VI) suggests that extraction is inefficient

<table>
<thead>
<tr>
<th>Eluent</th>
<th>NIST Standard Soil 2701 (550 mg/Kg per ICP-MS)</th>
<th>Cr(VI) (mg/kg)</th>
<th>Cr(VI) (mg/kg) (total from 2 extractions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$OH and (NH$_4$)$_2$SO$_4$</td>
<td>550</td>
<td>384</td>
<td>458</td>
</tr>
</tbody>
</table>
ASE 350 and 150

• Goal: Automate 3060A using Accelerated Solvent Extraction
What Is ASE?

• A device that automates sample preparation for **solid** samples using solvent extraction
• Operates above the boiling point of most extraction solvents
• Pressure is used to keep solvents liquid during extraction

ASE is approved as US EPA Method 3545A
Pressurized Fluid Extraction

• A procedure for extracting water insoluble or slightly water soluble **semivolatile organic compounds** from soils, clays, sediments, sludges, and waste solids.
Examples of Metal Extraction using ASE

• **Pressurized Extractions for the Remediation of Heavy Metal contaminants in Soil and Sediments.**
  - Pb, Mn, Cu

• **Selenium Speciation analysis of selenium enriched supplements by HPLC with ultrasonic nebulization ICP-MS and MS-MS**

• **Simultaneous Extraction of Organometallic species of As, Se, and Hg by Accelerated Solvent Extraction and analysis by ICP-MS coupled to Liquid and Gas chromatography**
Schematic of ASE Cell

- Sample and Dispersant
- Cellulose or glass fiber filter
- Extraction Flow
ASE extraction cells

- First generation extraction cells are stainless steel
- Second generation are Dionium Cells, a zirconium alloy
  - A new alloy specifically developed for high and low pH extractions
- Allows acidic or alkaline pretreated samples
- Improved overall longevity of system
Cell loading

- Fill, heat, and equilibrate: 5 to 9 min

Static extraction: 0 to 99

Rinse with fresh solvent: 0.5 min

Purge with nitrogen: 1–2 min

Extract ready: Total (min) 12–20

Dynamic extraction

Static cycle

Static extraction

ASE® Schematic
ASE Extraction Conditions

- Extraction Solvent: 10mmol/L NaOH, 4g/L NaCl (pH>11.5)
- Extraction Temperature: 100°C
- Pre-heat time: 5min
- Static Extraction Time: 5min
- Cycle Time: 2
- Flush Volume: 60%
- Purge Time: 90s
- Extraction Cell: 66mL cell
- Total extraction time: about 20 min
- Automation allows multiple extractions without labor
Sample Preparation

- Soil samples were dried at of 50°C,
- Pulverized
- 10g soil sample, mixed with quartz sand and filled to 66mL Zr extraction cell,
- ASE extracted
- Analysis by EPA 7199 (Ion Chromatography)
Results from Blanks

- Stainless Steel extraction cell
- 19 µg/L
Results from ASE Cell Blanks

- Comparison between stainless steel vs. Dionium extraction cells
- Dionium cell 0.9 µg/L
Recoveries

Table 1. Recoveries and their relative standard deviations (n=3)

<table>
<thead>
<tr>
<th>Added</th>
<th>Recovery/ %</th>
<th>Avg. Recovery/ %</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μg/L</td>
<td>105.6</td>
<td>105.2</td>
<td>2.2%</td>
</tr>
<tr>
<td></td>
<td>107.2</td>
<td>105.1</td>
<td>0.4%</td>
</tr>
<tr>
<td>100 μg/L</td>
<td>105.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>105.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results of Spiked Samples

- Chromatograms of spiked quartz sand (added 10 µg/L)
Results

- Soil sample
Conclusions

• Preliminary results show that ASE can be used to extract hexavalent chromium from soil and spiked quartz

• Background issue

• Further studies will attempt using NIST standards and different soil matrices.

• Eventual goal to develop ASE method for EPA’s ATP approval.
Thank You!