Trace Determinations of Hexavalent Chromium in Soil Using Automated Extractions and Ion Chromatography

Terri Christison, Richard Jack, Jinshui Che, Lipika Basumallick, and Linda Lopez

Thermo Fisher Scientific, Sunnyvale, CA, USA; Thermo Fisher Scientific, Shanghai, People’s Republic of China
Overview

Purpose: Demonstrate automated extractions used to determine trace hexavalent chromium, Cr(VI) in soil samples.

Methods: Hexavalent chromium was extracted using accelerated solvent extraction and determined by ion chromatography, absorbance detection at 530 nm aided by a post column addition.

Results: Hexavalent chromium was extracted from soil samples using an automated alkaline extractions with the alkaline compatible Thermo Scientific™ Dionex™ Dionium™ extraction cells. Ten-fold lower blanks were achieved with the Dionium cells than the stainless steels cells. Chromate MDLs were improved to 0.5 ng/g of soil with automated extraction using ion chromatography, post column derivitization, and selective detection at 530 nm.

Introduction

Chromium(VI), Cr(VI), is an industrial contaminant from plating, steel production, chemical, and leather tanning industries. The 2010 environmental health hazard evaluation found that the majority (31) of the 35 cities surveyed had chromium(VI) in their drinking water (Figure 1). Although chromium(III) is an essential nutrient, chromium(VI) (hexavalent chromium) compounds are classified as mutagenic carcinogens, associated with various cancers of internal organs. Consequently, the U.S. EPA has defined hexavalent chromium as a regulated toxic contaminant and in 2009 the state of California proposed reducing the Public Health Goal (PHG) from 0.2 to 0.02 µg/L hexavalent chromium and 2.5 µg/L total chromium in drinking water. This new PHG requires a method with 10-fold increased sensitivity and additional attention on chromate-contaminated soils.

Figure 1. Map of chromate levels in US cities; Chromate was found in the drinking water of 31/35 surveyed cities.

Methods

Sample Preparation Equipment and Reagents
- Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor system
- Dionium Extraction Cells, 66 mL
- Ottawa Sand (Fisher Scientific)
- Standard Laboratory Grinder or Mill
- Sample pH Adjustment Solution: 5 M Nitric acid
After extraction, the soil extractant was adjusted to derivitization, and selective detection at 530 nm. MDLs were improved to 0.5 ng/g of soil with automated extraction cells. Ten-fold lower blanks were achieved with evaluation found that the majority (31) of the 35 cities plating, steel production, chemical, and leather tanning results:

Hexavalent chromium was extracted from soil by a post column addition.

Chromate was found in the drinking water of 31/35 cities.1 Toxic contaminant and in 2009 the state of California various cancers of internal organs. Consequently, the U.S. survey cities.1

**Trace Determinations of Hexavalent Chromium in Soil Using Automated**

1 Thermo Fisher Scientific, Sunnyvale, CA, USA

2 Thermo Fisher Scientific, Shanghai, People’s Republic of China

* Or Dionex ICS-2100, ICS-1600, ICS-1100, or ICS-5000+

**Conditions**

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Mix 10 g of pulverized soil dried at 50 °C with Ottawa sand. Extract to 100 mL constant volume, filter (0.45 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>100 °C</td>
</tr>
<tr>
<td>Solvent:</td>
<td>10 mM NaOH, 4 g/L NaCl, pH &gt;11.5</td>
</tr>
<tr>
<td>Preheat Time:</td>
<td>5 min</td>
</tr>
<tr>
<td>Static Time:</td>
<td>5 min</td>
</tr>
<tr>
<td>Static Cycles:</td>
<td>2</td>
</tr>
<tr>
<td>Flush:</td>
<td>60 %</td>
</tr>
<tr>
<td>Purge:</td>
<td>90 s</td>
</tr>
<tr>
<td>Total Time:</td>
<td>~ 20 min</td>
</tr>
</tbody>
</table>

After extraction, the soil extractant was adjusted to pH = 7.5 ± 0.5 with 5 M nitric acid.

**Ion Chromatography Instrumentation**

Thermo Scientific Dionex ICS-5000 system* including:

- SP Single Pump or DP Dual Pump module
- DC Detector/Chromatography module
- Injection Loop, 1000 µL
- Reaction Coil, 125 µL
- Sample Syringe, 5 mL
- ICS Series VWD Variable Wavelength Absorbance Detector
- PEEK Cell (Standard, 11 µL)
- Thermo Scientific Dionex AS-AP Autosampler

* Or Dionex ICS-2100, ICS-1600, ICS-1100, or ICS-5000+

Post Column Reagent (PCR) Delivery Options:

- PC-10 Pneumatic Delivery
- Second Pump of Dionex ICS-5000+ DP
- Thermo Scientific Dionex AXP Auxiliary Pump

**Ion Chromatography Conditions**

<table>
<thead>
<tr>
<th>IC Conditions</th>
<th>Thermo Scientific™ Dionex™ IonPac™ AS7, 2 mm guard and separation columns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluent:</td>
<td>250 mM Ammonium sulfate, 100 mM ammonium hydroxide</td>
</tr>
<tr>
<td>Flow Rate:</td>
<td>0.36 mL/min</td>
</tr>
<tr>
<td>Inj. Volume:</td>
<td>1000 µL</td>
</tr>
<tr>
<td>Temperature:</td>
<td>30 °C</td>
</tr>
<tr>
<td>PCR:</td>
<td>2 mM Diphenylcarbazide, 10% methanol, 1 N sulfuric acid</td>
</tr>
<tr>
<td>PCR Flow Rate:</td>
<td>0.12 mL/min</td>
</tr>
<tr>
<td>Detection:</td>
<td>Visible absorbance, 530 nm</td>
</tr>
</tbody>
</table>

**FIGURE 2. Flow Diagram.**

**FIGURE 4. Chromate Blanks in 66 mL A) Stainless Steel and B) Dionium Accelerated Solvent Extraction cells.3**

**FIGURE 5. Hexavalent Chromium Results.**

Thermo Scientific™ Dionex™ CDS software

Legend:

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After extraction, the soil extractant was adjusted to derivitization, and selective detection at 530 nm. Chromate extraction cells. Ten-fold lower blanks were achieved with plating, steel production, chemical, and leather tanning samples using an automated alkaline extractions with the Dionium cells than the stainless steels cells. Chromate was found in the drinking water of 31/35 * Or Dionex ICS-2100, ICS-1600, ICS-1100, or ICS-5000+ samples.

**Purpose:**
Demonstrate automated extractions used to trace determinations of hexavalent chromium in soil using automated extractions and ion chromatography.

**Results:**
Some reagents contain trace amounts of chromate, therefore system blanks were determined with the previous stainless steel cells and the new Dionium cells. Figure 4 shows a 20-fold decrease in baseline chromium levels when using the Dionium extraction (66 mL) cells, demonstrating the better suitability of these cells.

**Data Analysis**
Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software

**Workflow Diagram**
Figure 3 shows the total workflow for chromate analysis in soil samples.

**FIGURE 2. Flow Diagram.**

![Flow Diagram Image]

* Eluent: 250 mM Ammonium acetate, 100 mM Ammonium hydroxide, pH = 9.0–9.5
** PCR: 2 mM Diphenylcarbazide, 10% Methanol, 1 N Sulfuric acid

**FIGURE 3. Total Workflow from Sample Preparation to Analysis and Data Management.**

![Workflow Diagram Image]

**Results**
Some reagents contain trace amounts of chromate, therefore system blanks were determined with the previous stainless steel cells and the new Dionium cells. Figure 4 shows a 20-fold decrease in baseline chromium levels when using the Dionium extraction (66 mL) cells, demonstrating the better suitability of these cells.
After extraction, the soil extractant was adjusted to derivitization, and selective detection at 530 nm. MDLs were improved to 0.5 ng/g of soil with automated extraction cells. Ten-fold lower blanks were achieved with Chromium(VI), Cr(VI), an industrial contaminant from samples using an automated alkaline extractions with the accelerated solvent extraction and determined by ion Hexavalent chromium was extracted using samples.

Purpose:

- Thermo Fisher Scientific, Shanghai, People’s Republic of China
- Extractions and Ion Chromatography
- EPA has defined hexavalent chromium as a regulated
- various cancers of internal organs. Consequently, the U.S.
- chromate-contaminated soils.
- Chromate was found in the drinking water of 31/35
- Thermo Scientific™ Dionex™ ASE™ 350
- Dionium Extraction Cells, 66 mL
- Sample pH Adjustment Solution: 5 M Nitric acid
- Standard Laboratory Grinder or Mill
- Ottawa Sand (Fisher Scientific)
- Dionium cells.3
- Figure 4 shows a 20-fold decrease in baseline chromium levels when using the system blanks were determined with the previous stainless steel cells and the new Dionium cells. Figure 4 shows a 20-
- Thermo Scientific Dionex ICS-5000 system* including:
- Purge: 90 s
- Static Time: 5 min
- Preheat Time: 5 min
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography
- Detection/Chromatography module
- Columns: Thermo Scientific™ Dionex™ IonPac™ AS7
- Nonmetallic Pump
- Flow Rate: 0.12 mL/min
- PCR Flow: 0.36 mL/min
- 2 mM Diphenylcarbazide, 10% methanol, 1 N sulfuric acid
-反應合適
- 0.12 mL/min
- Reaction Coil: 125 µL
- Flow Cell: Standard (PEEK), 11 µL
- Sample Prep.: Dionex ASE 350
- Flow Cell: Standard (PEEK), 11 µL
- Sample Prep.: Dionex ASE 350
- * Or Dionex ICS-2100, ICS-1600, ICS-1100, or ICS-5000+
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- * Or Dionex ICS-2100, ICS-1600, ICS-1100, or ICS-5000+

Table 1 summarizes the recoveries of chromate added to the Dionium cells, with similar recoveries at both concentrations, 105%, and RSD < 2.5%.

Table 1. Recoveries of Hexavalent Chromium from Dionium cells.

<table>
<thead>
<tr>
<th>Amount Added (µg/L)</th>
<th>Recovery (%)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>105.2</td>
<td>2.2%</td>
</tr>
<tr>
<td>100</td>
<td>105.1</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

Soil Analysis

Figure 5 shows high hexavalent chromium results from a soil extraction sample, which had ~ 40 ng per g of soil (ppb).

FIGURE 5. Hexavalent Chromium Results.
Conclusion

- Automated accelerated solvent extraction of soil samples are a viable alternative to manual digestions and extractions, and provide sample solutions within 20 min.
- The Dionium alkaline compatible cells allow alkaline extractions needed for hexavalent chromium determinations and have 20-fold less baseline contamination than stainless steel cells.
- Baseline chromium extractions of 0.9 µg/L were obtained when using accelerated solvent extraction, with 66 mL Dionium extraction cells.

References
