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

Terri Christison,[1] Richard Jack,[1] Jinshui Che,[2] Lipika Basumallick,[1] and Linda Lopez[1]
[1]Thermo Fisher Scientific, Sunnyvale, CA, USA; [2]Thermo Fisher Scientific, Shanghai, People's Republic of China

Thermo
SCIENTIFIC

Overview

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

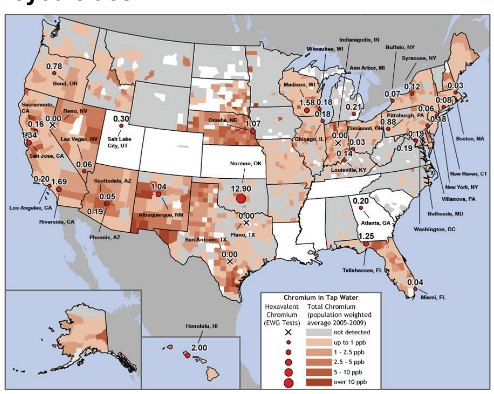
Methods: Hexavalent chromium was extracted using accelerated solvent extraction and determined by ion chromatography, absorbance detection at 530 nm aided by a post column addition.

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).[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.[2] 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.[1]



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

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

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$^+$

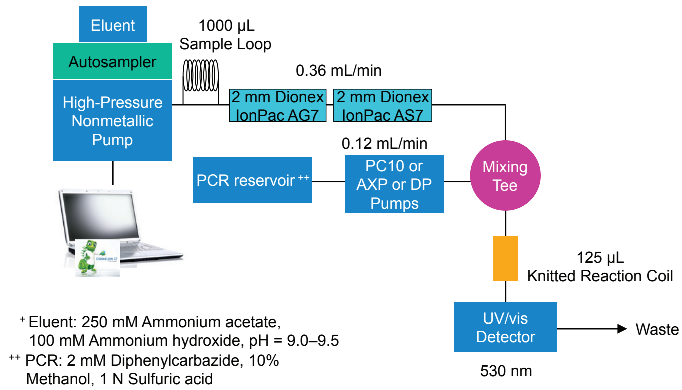
Post Column Reagent (PCR) Delivery Options:

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

Ion Chromatography Conditions

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

FIGURE 2. Flow Diagram.



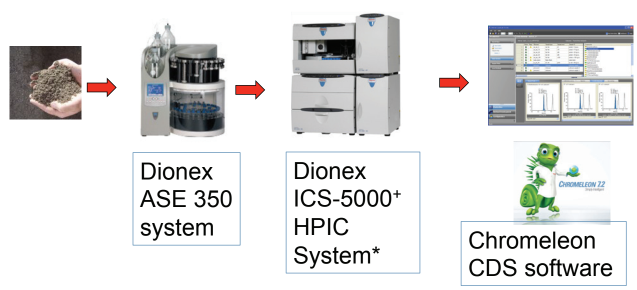
Data Analysis

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

Workflow Diagram

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

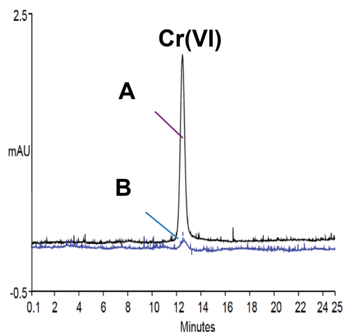
FIGURE 3. Total Workflow from Sample Preparation to Analysis and Data Management.



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.

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



Column: Dionex IonPac AS7 set, 2 mm
Eluent: 250 mM $(NH_4)_2SO_4$, 100 mM NH_4OH
Flow: 0.36 mL/min
Inj. Vol.: 1000 µL
Postcolumn Reagent: 2 mM Diphenylcarbazide, 10% methanol, 1 N sulfuric acid
PCR Flow: 0.12 mL/min
Reaction Coil: 125 µL
Flow Cell: Standard (PEEK), 11 µL
Sample Prep.: Dionex ASE 350

A. 19.1 µg/L
B. 0.9

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

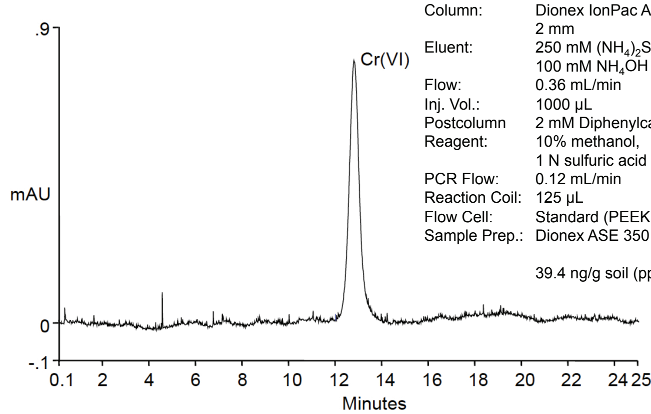
Table 1. Recoveries of Hexavalent Chromium from Dionium cells.[3]

Amount Added (µg/L)	Recovery (%)	%RSD
10	105.2	2.2%
100	105.1	0.4%

Soil Analysis[3]

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.



Column: Dionex IonPac AS7 set, 2 mm
Eluent: 250 mM $(NH_4)_2SO_4$, 100 mM NH_4OH
Flow: 0.36 mL/min
Inj. Vol.: 1000 µL
Postcolumn Reagent: 2 mM Diphenylcarbazide, 10% methanol, 1 N sulfuric acid
PCR Flow: 0.12 mL/min
Reaction Coil: 125 µL
Flow Cell: Standard (PEEK), 11 µL
Sample Prep.: Dionex ASE 350

39.4 ng/g soil (ppb)

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

1. Sutton, R. Chromium-6 in U.S. Tap Water. Environmental Working Group Report, December 2010. http://www.ewg.org/chromium6-in-tap-water. (Accessed May 2013).
2. Public Health Goal for Chromium in Drinking Water, California Office of Environmental Health Hazard Assessment. Feb 2011. http://www.oehha.ca.gov/water/phg/072911Cr6PHG.html. (Accessed May 2013).
3. Basumallick, L. Rohrer, J. Application Update 179, 282, Sensitive Determination of Hexavalent Chromium in Drinking Water, AU70415_E 12/12S. Thermo Fisher Scientific, Sunnyvale, CA, USA, 2012.

Australia +61 3 9757 4486
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
China +852 2428 3282
Denmark +45 70 23 62 60
France +33 1 60 92 48 00
Germany +49 6126 991 0
India +91 22 6742 9494
Italy +39 02 51 62 1267
Japan +81 6 6885 1213
Korea +82 2 3420 8600
Netherlands +31 76 579 55 55
Singapore +65 6289 1190
Sweden +46 8 473 3380
Switzerland +41 62 205 9966
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA and Canada +847 295 7500

Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

PN70729_E 08/16S