

Accelerated Solvent Extraction of Cr(VI) from Soil

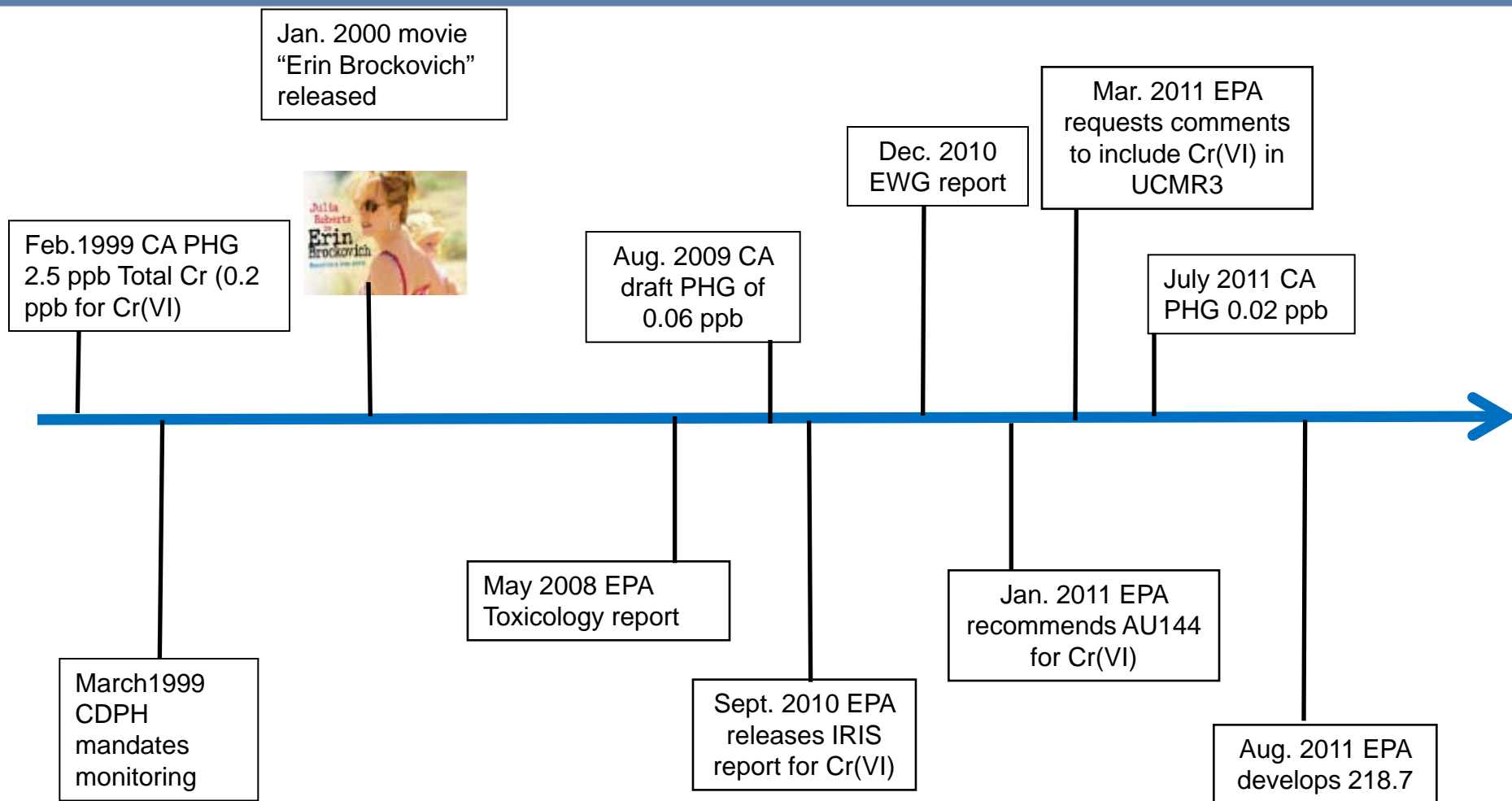
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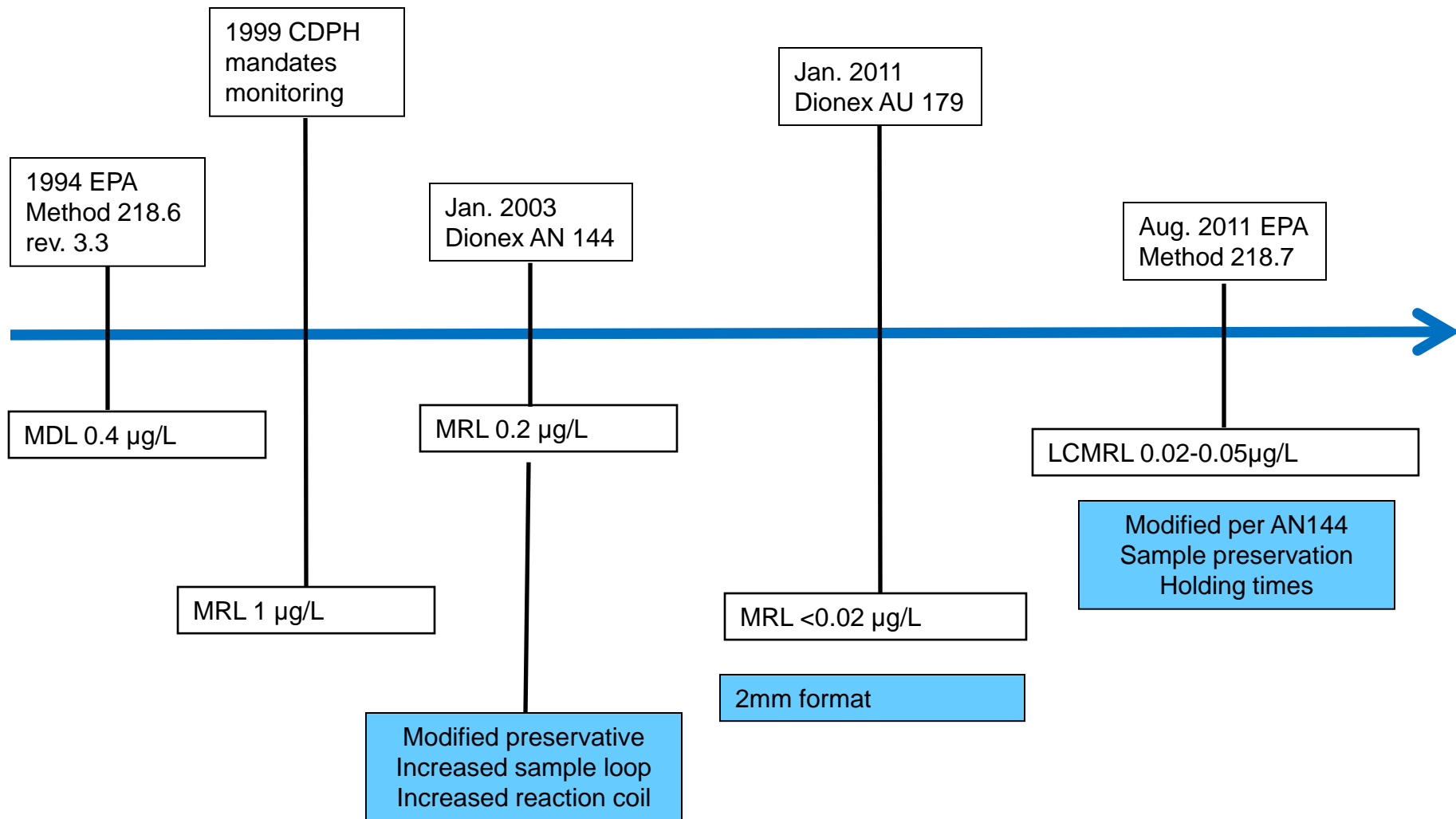
Overview

- 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



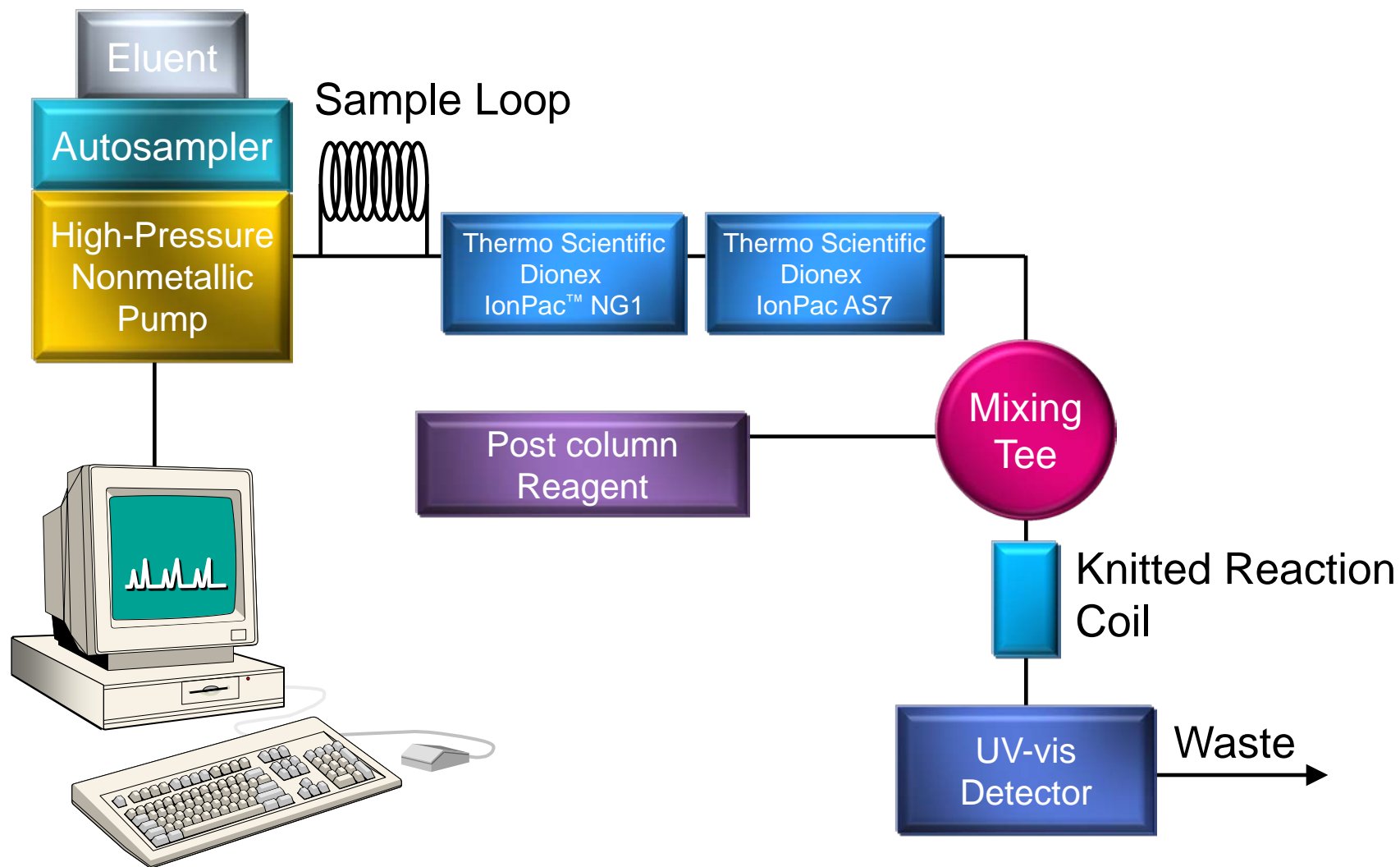
15 + year Analytical Timeline for Cr(VI) in Water



Summary of Methodologies for Chromium VI Analysis

EPA Method	Sample Types	Sample Conc. Limits (µg/L)	Technique	MDL
218.6	Drinking Water, Groundwater, Industrial Effluents	-	IC with post column derivatization	0.3 µg/L (0.001 µg/L with modifications outlined in Dionex AN 179)
218.7	Drinking Water	-		
1636	Ambient Waters (river/lake water)	-		
7199	Drinking Water, Groundwater, Industrial Effluents	-		
218.4	Drinking Water, Surface/Saline Water	10 - 250	Chelation Extraction with Flame AA	10 – 25 µg/L
7197	Ground Water, Leachates, Soils	1 - 25		
7196	Ground Water, Leachates, Soils	500 – 50,000	Colorimetric Analysis	<50 µg/L
7195	Ground Water, Leachates, Soils	>5	Co-precipitation with AA	10 – 25 µg/L

System Configuration for Hexavalent Chromium by U.S. EPA Method 218.6



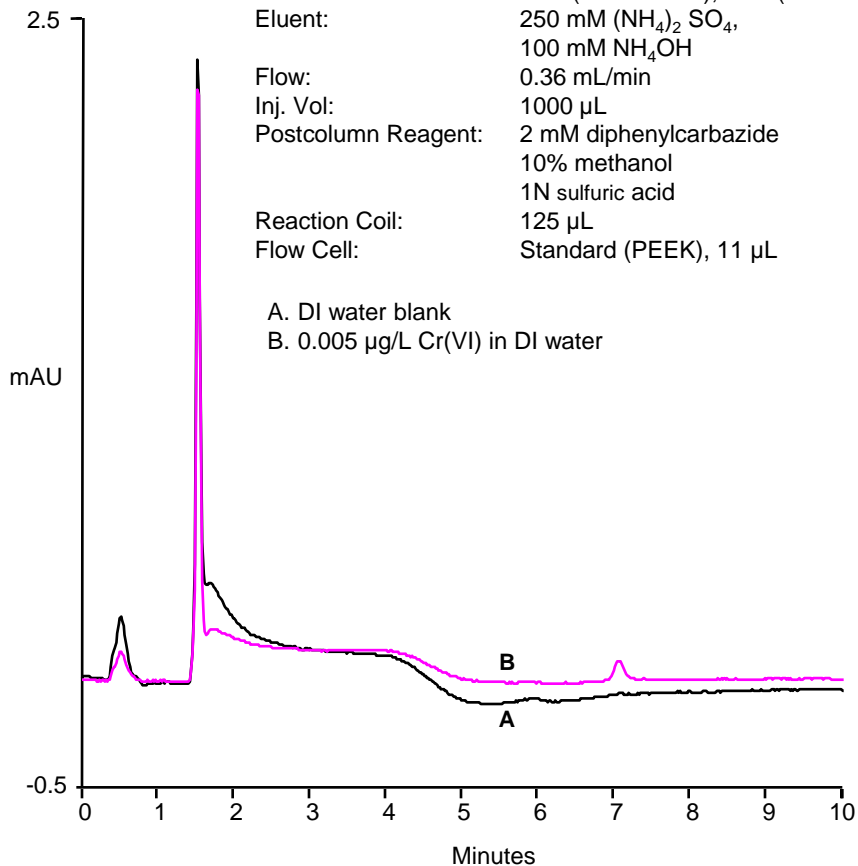
Achieving a Lower Method Detection Limit (MDL)

Method	Column Set	Reaction Coil Volume (μL)	Eluent Flow Rate (mL/min)	Postcolumn Flow Rate (mL/min)
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

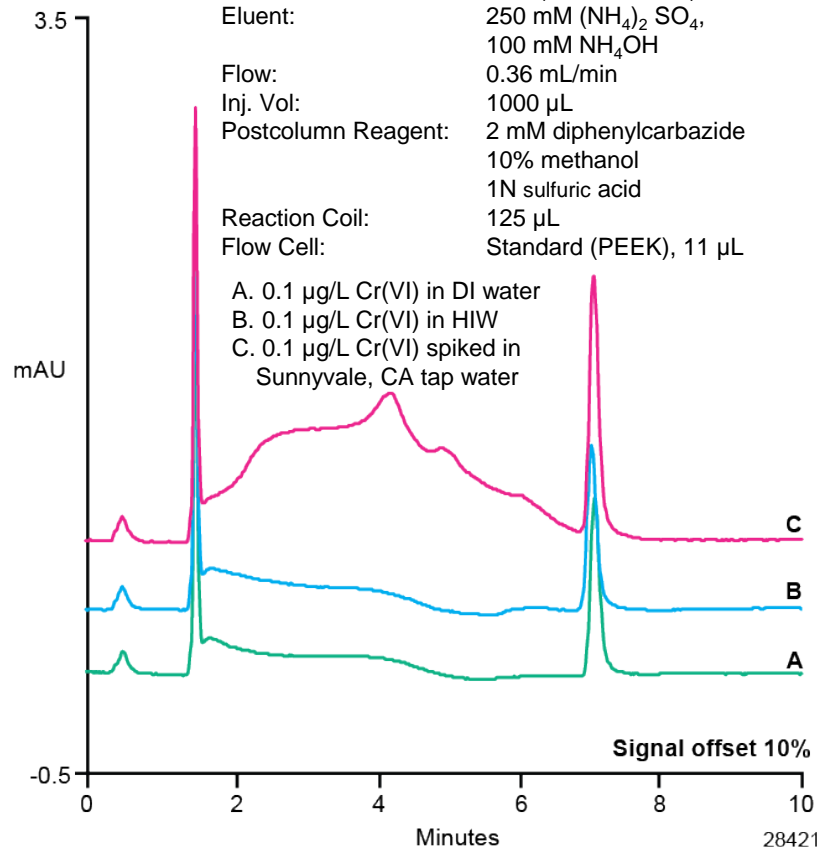
A. DI water blank
 B. 0.005 µg/L Cr(VI) in DI water



Blank and low-level chromate

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



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

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 NH_4SO_4 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**)

*Majors, R.E. *LC-GC*, **1995**, 13, 742-749, and **Majors, R.E. *LC-GC*, **1999**, 17, S8 - S13

Importance of Sample Preparation

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

R. Stevenson, “Pittcon® ‘98: Part 3 Sample Prep: The Place to Make a Difference” American Laboratory, Vol. 30, No. 14 p.21, 1998

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).

3060A

- Procedure
 - 2.5 g sample
 - 50 mL \pm 1 mL of digestion solution
 - 400 mg MgCl₂
 - 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 μ m 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

Eluent	NIST Standard Soil 2701 (550 mg/Kg per ICP-MS)	Cr(VI) (mg/kg)	Cr(VI) (mg/kg) (total from 2 extractions)
NH_4OH and $(\text{NH}_4)_2\text{SO}_4$	550	384	458

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

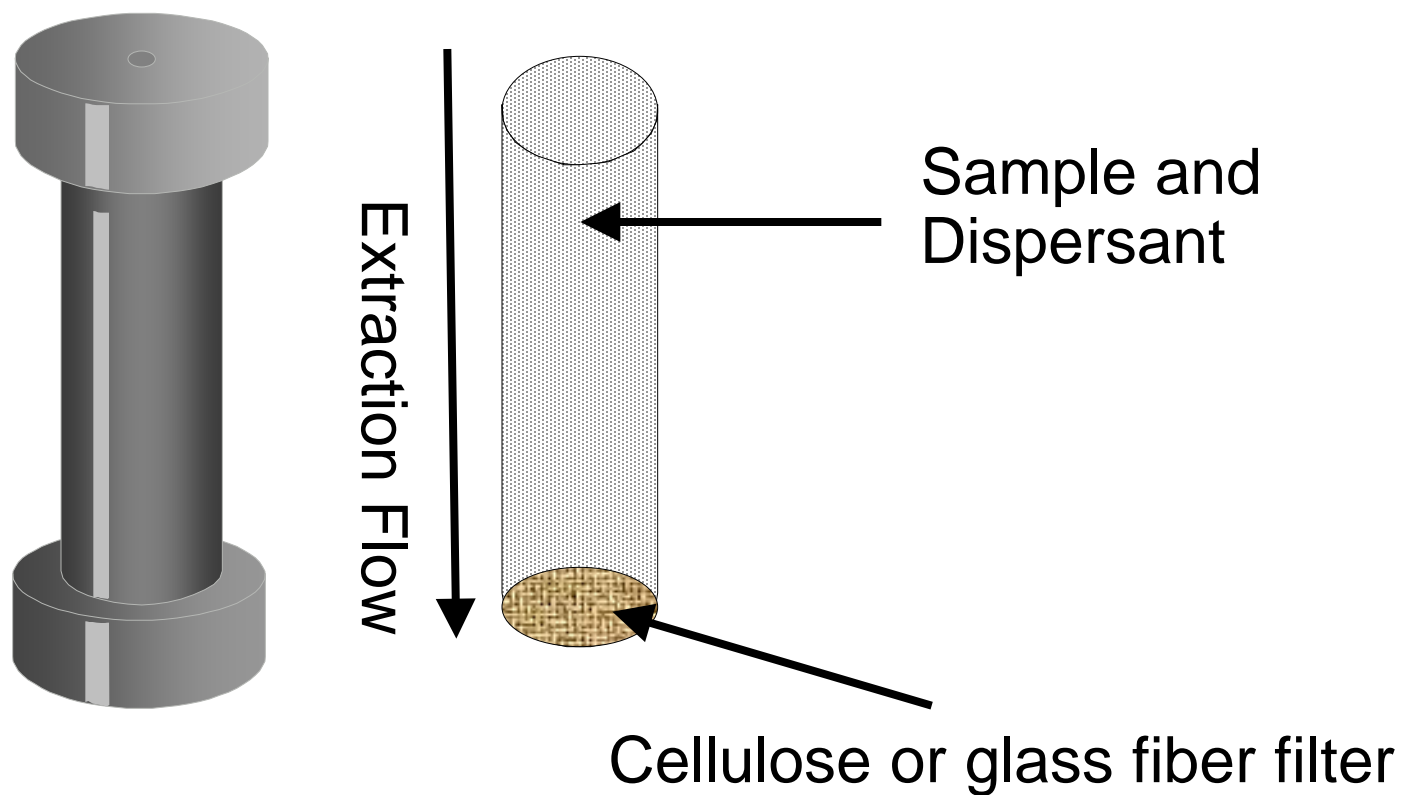
ASE is approved as US EPA Method 3545A
Pressurized Fluid Extraction

- 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*

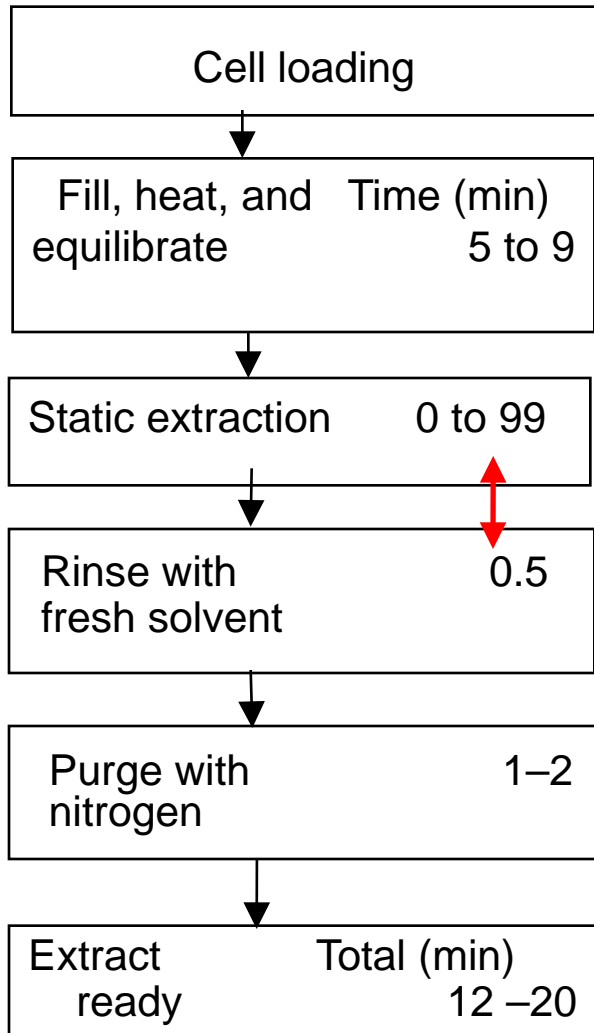
Schematic of ASE Cell



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

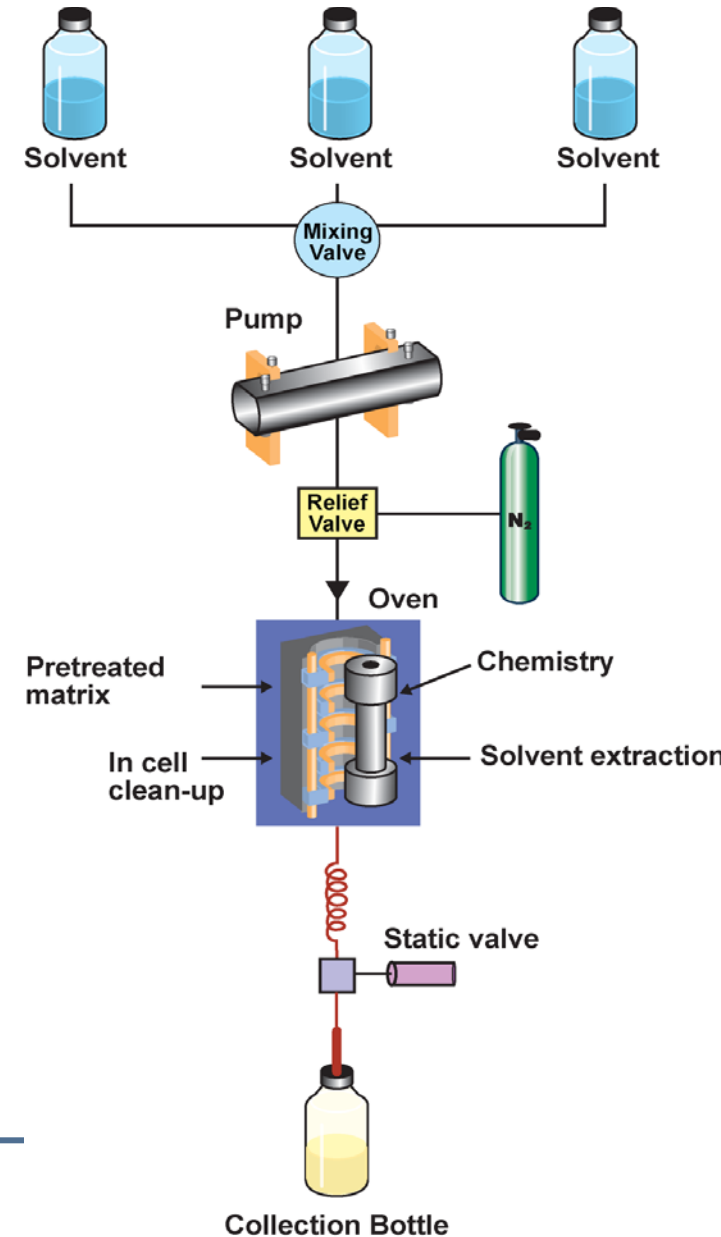
ASE[®] Schematic



dynamic extraction

static cycle

static extraction



ASE Extraction Conditions

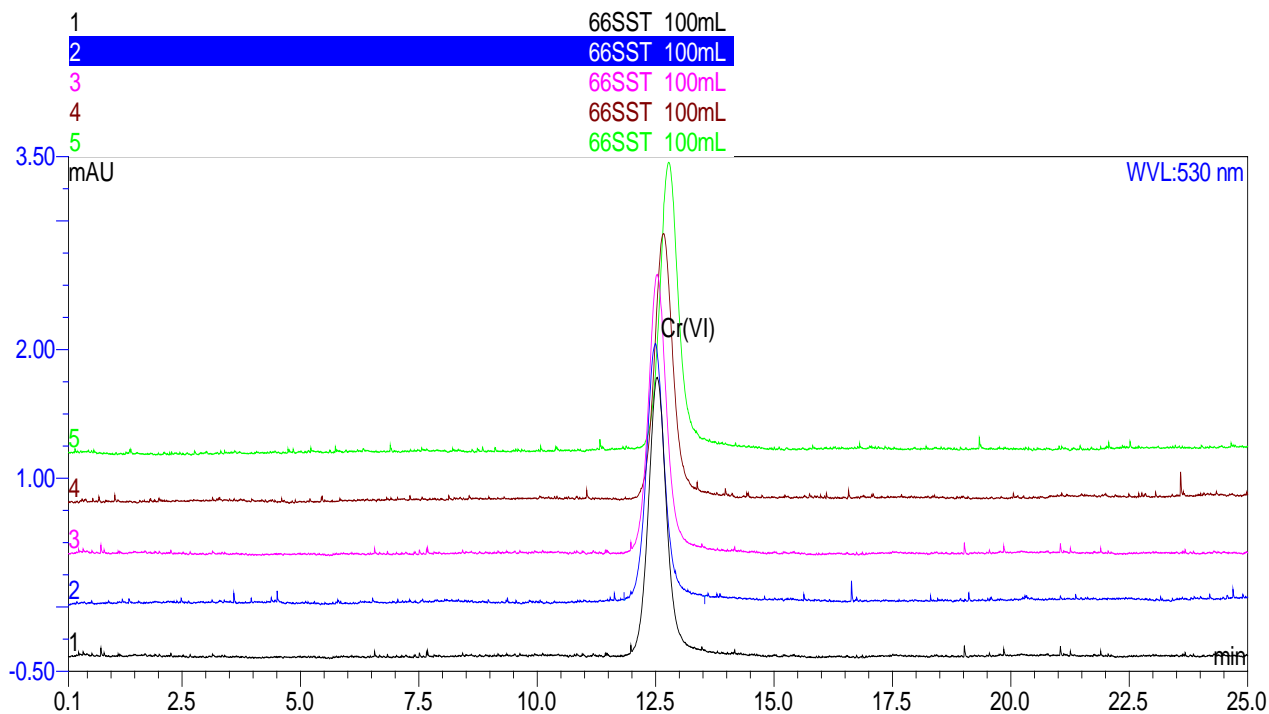
- Extraction Solvent: 10mmol/L NaOH, 4g/L NaCl (pH>11.5)
- Extraction Temperature: 100°C
- Pre-heat time: 5min
- Static Extraction Time: 5min
- Cycle Time: 2
- Flush Volume: 60%
- Purge Time: 90s
- Extraction Cell: 66mL cell
- Total extraction time: about 20 min
- Automation allows multiple extractions 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)

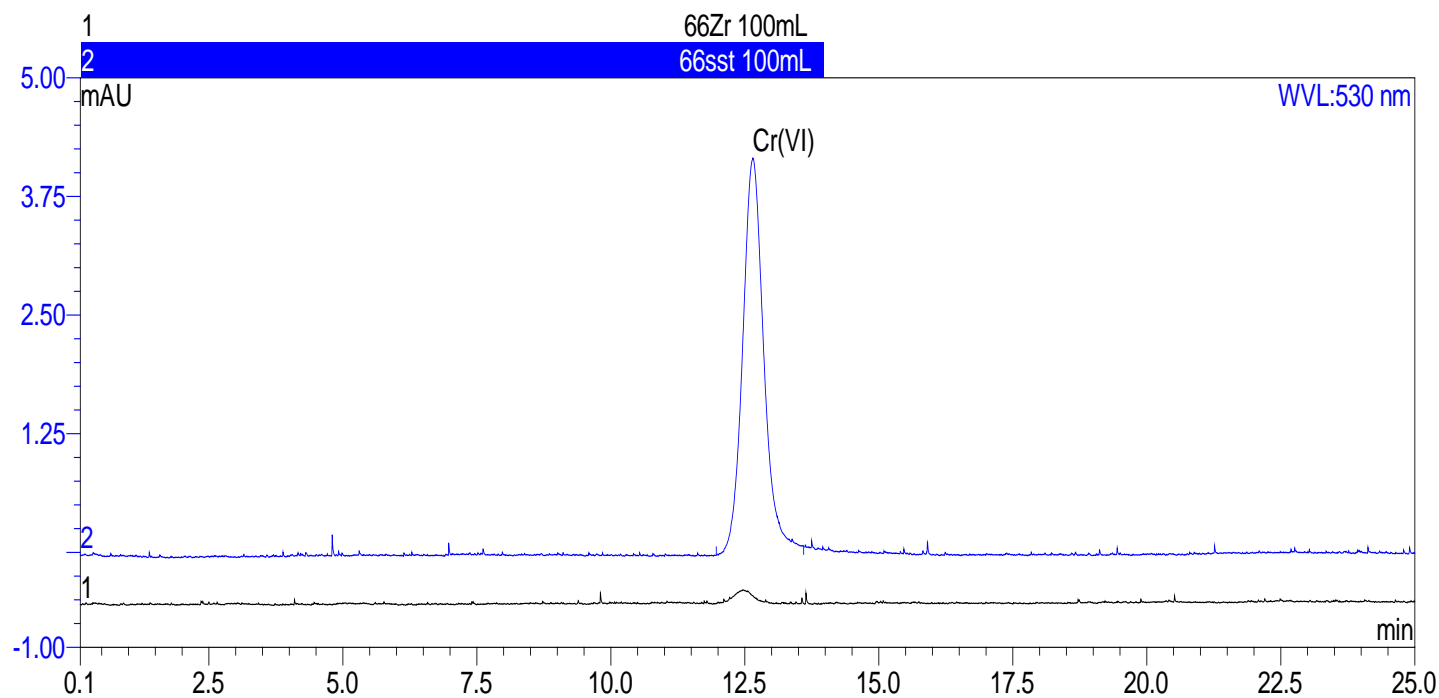
Results from Blanks

- Stainless Steel extraction cell
- 19 $\mu\text{g/L}$



Results from ASE Cell Blanks

- Comparison between stainless steel vs. Dionium extraction cells
- Dionium cell 0.9 $\mu\text{g/L}$



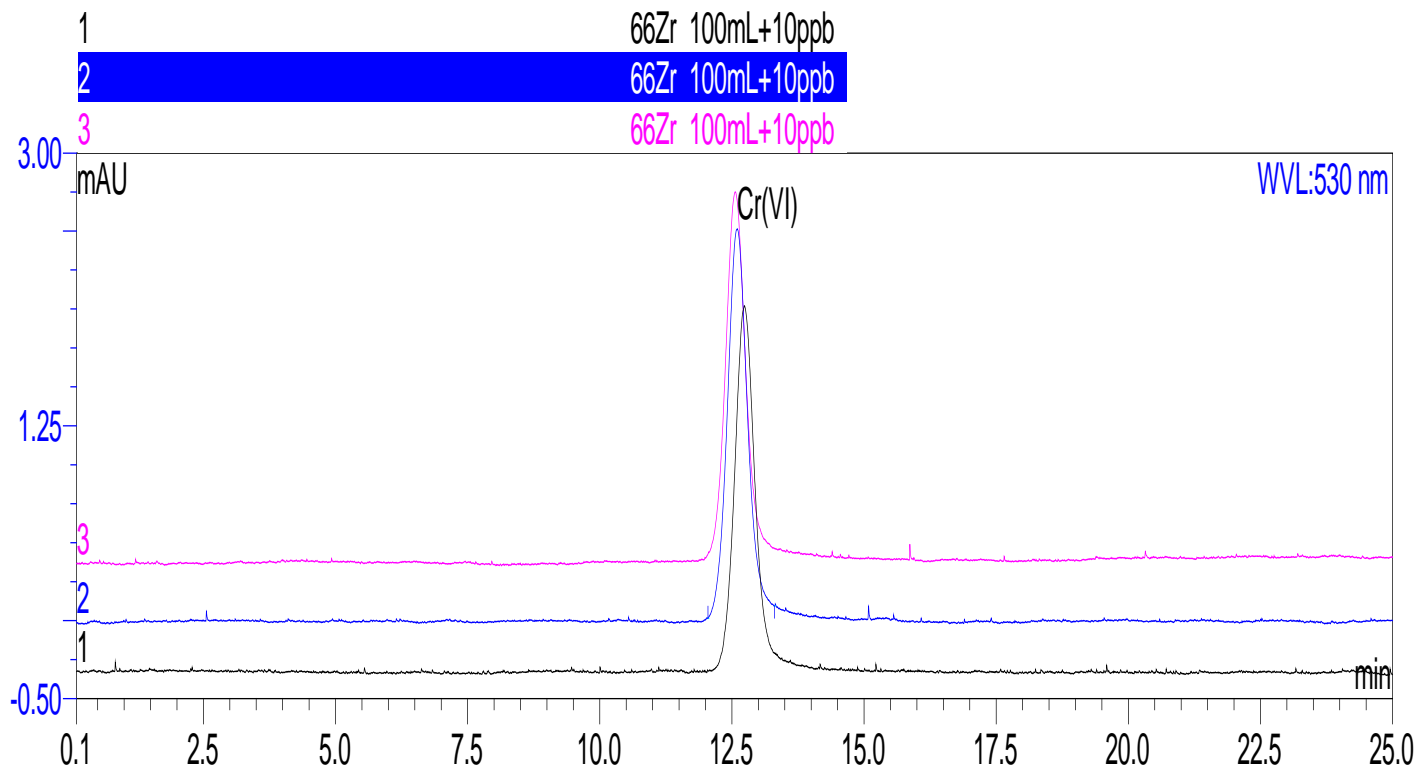
Recoveries

Table1. Recoveries and their relative standard deviations (n=3)

Added	Recovery/ %	Avg. Recovery/%	RSD
	105.6		
10 µg/L	107.2	105.2	2.2%
	102.6		
	104.6		
100 µg/L	105.4	105.1	0.4%
	105.4		

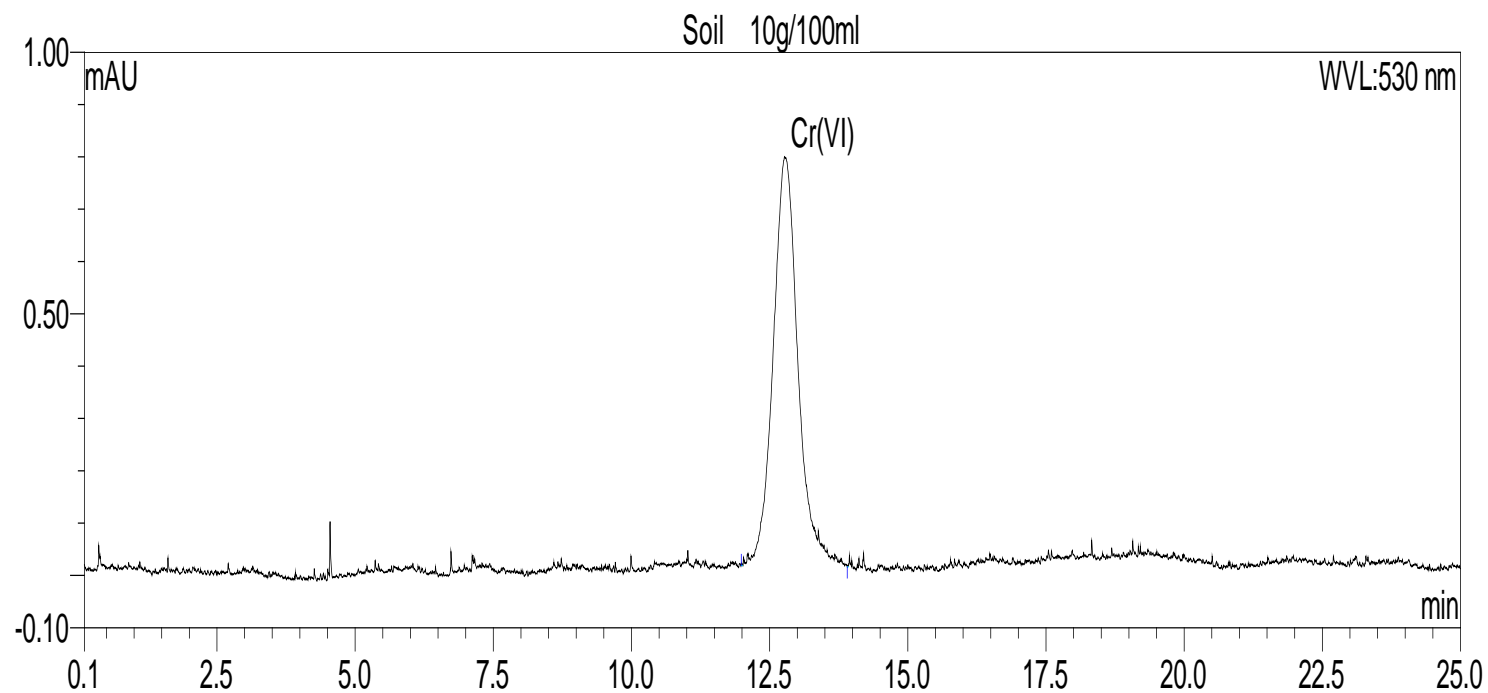
Results of Spiked Samples

- Chromatograms of spiked quartz sand (added 10 $\mu\text{g/L}$)



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!