Simultaneous Speciation of Arsenic, Selenium, and Chromium by HPLC-ICP-MS

By Ruth E. Wolf, Suzette A. Morman, Jean M. Morrison, and Paul J. Lamothe

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Abstract

Title: Simultaneous Speciation of Arsenic, Selenium, and Chromium by HPLC-ICP-MS.

By: Ruth E. Wolf, Suzette A. Morman, Jean M. Morrison, and Paul J. Lamothe, U.S. Geological Survey, Minerals Resources Program, Box 25046, MS 964D, Denver Federal Center, Denver CO 80225; *rwolf@usgs.gov*

An adaptation of an analytical method developed for chromium speciation (Wolf and others, 2008) has been utilized for the simultaneous determination of As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI) species using high performance liquid chromatography (HPLC) separation with ICP-MS detection. Reduction of interferences for the determination of As, Se, and Cr by ICP-MS is a major consideration for this method. Toward this end, a Dynamic Reaction Cell (DRC) ICP-MS system was used to detect the species eluted from the chromatographic column. A variety of reaction cell gases and conditions may be utilized, and the advantages and limitations of the gases tested to date will be presented and discussed. The separation and detection of the As, Se, and Cr species of interest can be achieved using the same chromatographic conditions in less than 2 minutes by complexing the Cr(III) with EDTA prior to injection on the HPLC column. Practical aspects of simultaneous speciation analysis will be presented and discussed, including issues with HPLC sample vial contamination, standard and sample contamination, species stability, and considerations regarding sample collection and preservation methods. The results of testing to determine the method's robustness to common concomitant element and anion effects will also be discussed. Finally, results will be presented using the method for the analysis of a variety of environmental and geological samples including waters, soil leachates and simulated bio-fluid leachates.

Introduction

This Open-File Report contains illustrative materials, in the form of PDFs of PowerPoint slides, used for an oral presentation given at the 2008 Winter Plasma Conference on Plasma Spectrochemistry in Temecula, California, January 6–12, 2008. The conference is primarily an analytical chemistry conference that focuses on new methods for trace metals analysis using Inductively Coupled-Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrumentation.

The individual slides summarize work done to date by on an analytical method to determine the inorganic forms of arsenic (As^{+3} and As^{+5}), selenium (Se^{+4} and Se^{+6}), and chromium (Cr^{+3} and Cr^{+6}) in waters, soil extracts, and simulated biological fluids under the same chromatographic conditions. The method discussed in the presentation is an adaption of a previously published method (Wolf and others, 2007) for the determination Cr^{+3} and Cr^{+6} in waters and soil extracts. The method consists of separation of the individual species using High Performance Liquid Chromatography (HPLC) followed by detection using ICP-MS instrumentation.

The presentation contains preliminary values that were obtained on leachates (prepared with deionized water) of soils and ashes from several sites sampled after the California fires in 2007. These preliminary values indicate that in soil and ash samples containing measurable levels of chromium the predominate form of the chromium in a 5-minute deionized water leach is hexavalent chromium (Cr^{+6}), which is of interest from a human and ecosystem health perspective due to the toxicity of this form of chromium. Preliminary data for total metal analysis of ash and soil samples from the 2007 California wildfires can be found in a separate report by Plumlee and others (2008).

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United States Geological Survey, Denver Federal Center, MS 964D,
Denver, CO 80225, USA

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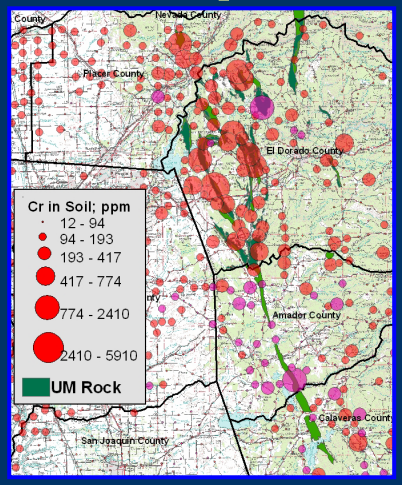
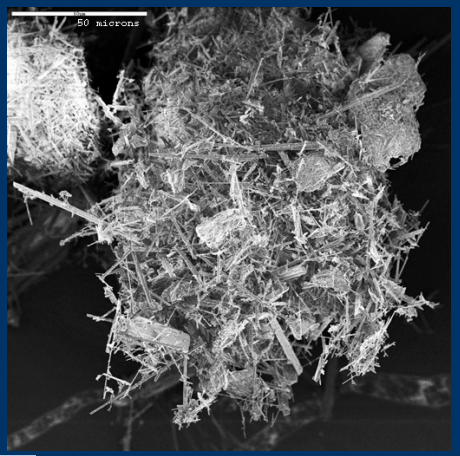
Why USGS and Speciation?

- Need for a rapid response method for speciation of key toxic elements
  - Watershed and environmental monitoring
  - Study of natural weathering processes
  - Disaster response
  - Biological response and ecosystem health studies
  - Remediation strategies for contaminated sites

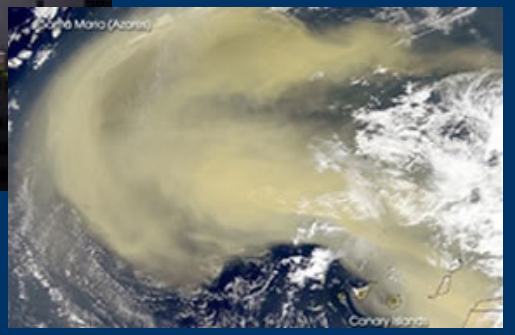


Cr in Soils in Western Metamorphic Belt, CA



Asbestiform amphiboles (Libby, MT)

Hurricane Katrina floodwaters



Satellite view of Saharan sandstorm

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Instrumentation Used†

- HPLC: PerkinElmer Series 200
  - Column Oven - 35º C
  - Autosampler - 10º C
  - Column: Brownlee C8
    - 3.3 cm X 3um, Si-based*
  - Mobile Phase:
    - 2mM TBAOH + 0.5mM K_2EDTA in 5% MeOH, pH = 7.4 – 7.6
- ICP-MS: PerkinElmerSciex DRC II
  - RF Power: 1300W
  - Nebulizer: Meinhard TQ-30-A3
  - Spray Chamber: Baffled cyclonic
  - Chromera Software ver. 1.2

The use of company, trade, and/or product names is for identification purposes only and does not imply endorsement by the United States Government.

† Complete description in JAAS, 22, 1051-1060

* Stated column working range to pH=7; however, have run up to pH=8 without significant column life issues

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Challenges for As Se Cr Speciation by ICP-MS

- ArC^{+} interferences on $^{52}Cr^{+}$
  - Limits use of most abundant mass
  - Requires use of HR-ICP-MS
    - HR-ICP-MS has scan speed limitations
- $ArCl^{-}$ interferences on ^{77}Se and ^{75}As
  - Limits detection capabilities in chloride matrices

- Reaction cell technology can improve detection capabilities for As, Se and Cr
  - But can conditions be found to improve all three for transient signal analysis?

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DRC Reaction Schemes

- N_2 Reaction Gas offers best compromise conditions for all three elements
- If Cr DLs important and [Cl-] is low, N_2 or NH_3 can be used
- If As DLs important and [Cl-] is high, O_2 can be used

Signal (1 ppb)* / Background	N_2 =1.0 RPq = 0.50	O_2 = 0.75 RPq = 0.55	NH_3 = 0.65 RPq = 0.60	7%H_2/He = 1.0 RPq = 0.70
^{52}Cr	6.4	4	7	1
^{75}As	51	25	290	200
$^{75}As^{16}O$	---	340**	---	---
^{78}Se	35	18	9	1.5
Normal Mode Bkg ^{52}Cr	2,377,440	5,507,800	5,155,460	5,725,700
DRC Mode Bkg ^{52}Cr	1480 cps	6320 cps	4070 cps	4,653,150

* in mobile phase + 5% MeOH

** ~ 90% conversion of As to AsO (AFT=200V must be optimized)

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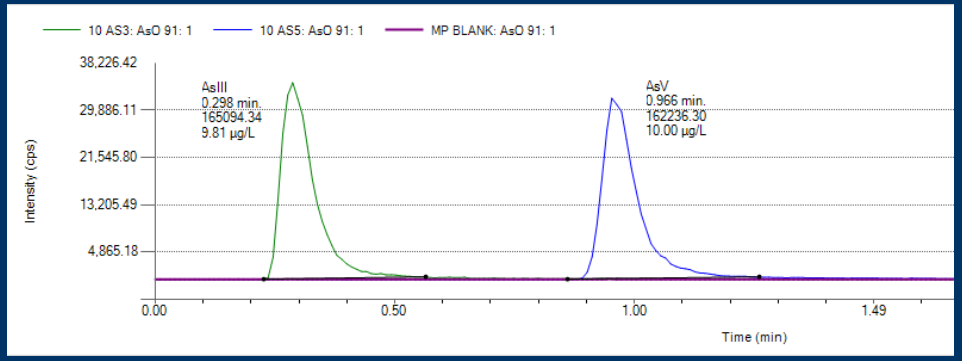
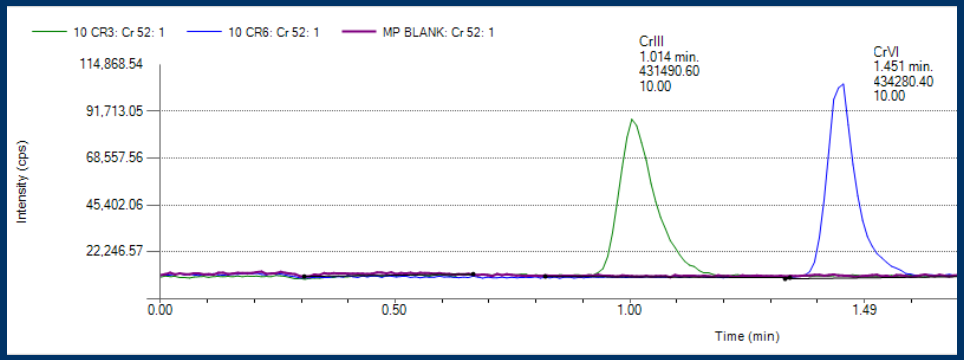
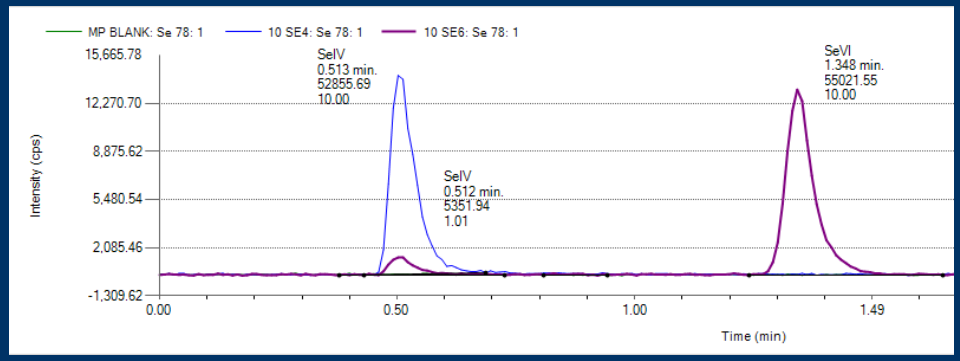
Calibration & Issues

- 1000 mg/L stocks diluted separately to 10 ppb in mobile phase (pH=7.6)
  - As^{+3}, As^{+5}, Cr^{+3}, Cr^{+6}, Se^{+4}, Se^{+6} (Source:Spex Certiprep)
  - Cr^{+3} is converted to an anion by complexation with EDTA
    - Prepared solutions with EDTA in mobile phase allowed to sit ~30 min for Cr^{+3}-$EDTA^{-}$ complex to form
- Determine retention times
- Evaluate standard stability and contamination issues
  - Acps for As^{+3} / As^{+5} ± 2%
  - Acps for Cr^{+3} / Cr^{+6} ± 1%
  - Acps for Se^{+4} / Se^{+6} ± 4%
    - Se^{+6} contains ~10% Se^{+4} as a contaminant
    - Issue for multi-component calibrations







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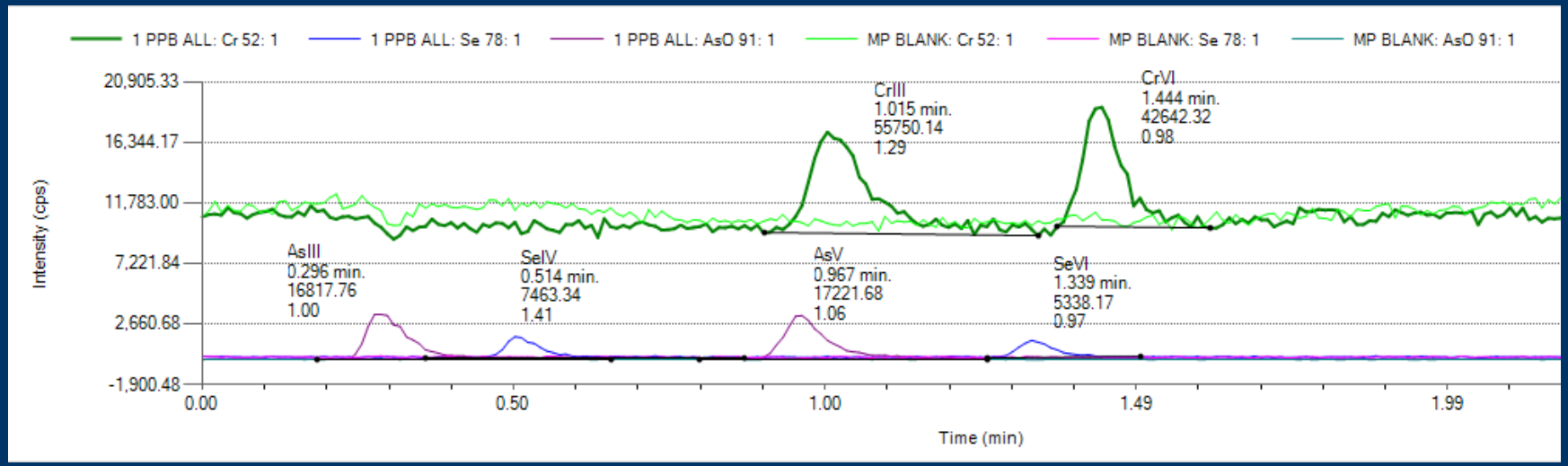
O_2 reaction gas

National Scientific PP vials and PKI black/Teflon caps

Multi-component Calibrations

- Combined 1 ppb standards
  - Run against separate standard curves
- Se^{+4} and Cr^{+3} are high
  - Contamination issue for Se^{+4}
  - Peak detection issue for Cr^{+3}
  - Noticed small As peaks in blank MP runs



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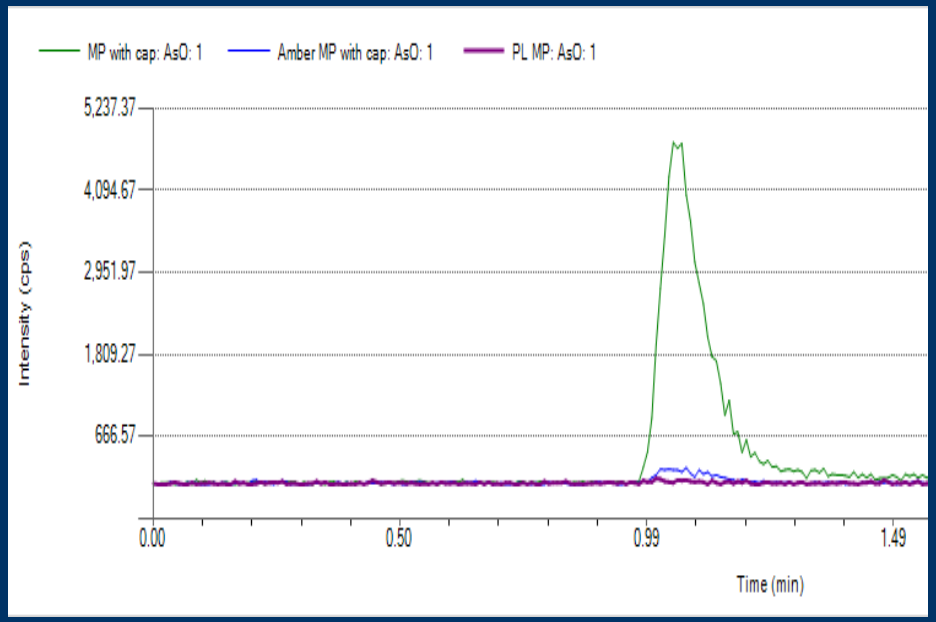
O_2 reaction gas

National Scientific PP vials and PKI black/Teflon caps

Initial Studies - Contamination

- Used standard glass HPLC vials (PKI) with Teflon-lined caps (reported from previous Cr speciation studies)
- Large peak from As^{+5} at RT=1 minute
  - Suspect As leaching from glass, vials not pre-cleaned
- Much less As leaches from Amber glass vials
- No As apparent in plastic vials
  - At this scale
  - Plastic vials resulted in Cr^{+6} ➔ Cr^{+3} conversion in previous work



Clear glass, amber glass, polypropylene vials – all PerkinElmer (PKI)

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O_2 reaction gas

Vials/Caps Tested

- PKI caps - black with Teflon septa
  - N9306062, Lots 55402, 63800
- PKI clear glass, 1.5 mL
  - N9306053, Lot 12057261
- PKI amber glass, 1.5 mL
  - N9306057, Lot 01065091
- PKI polypropylene (PP), 600 uL
  - N9302130, no caps, no lot number
- National Scientific Polypropylene (PP), full volume, 700 uL
  - Actual volume capacity = 800 uL
  - C4010-14, lot 00069806
- National Scientific Target DP Red Caps with TEF/RR Septa
  - C4000-57-R, lot 00097080411
- National Scientific Amber Glass Vials with Natural PP caps
  - C4000-2W, lot 05183153, Wheaton W225333-03 SP cap (no lot #)

- For 24 hour data, samples kept in autosampler tray at 10ºC overnight, MP also kept in refrigerator at 4ºC

Washing/Rinsing Procedures

- Rinsed vials
  - Vials rinsed 5 times with DI water, then 2 times with mobile phase (MP) prior to filling with MP blank
- Washed vials
  - Vials filled with 5% HCl – no caps
    - Batch soaking not used – ink on vials dissolves
  - Covered with plastic wrap overnight
  - Emptied and rinsed 5 times with DI water
  - Filled with either DI water or Mobile Phase
    - Capped with suitable cap to be tested
- Run #1: Ran as soon as possible within 2-3 hours
- Run #2: Left in AS tray overnight, ran ~24 hours later

Feasibility: Vial Contamination

Vial and cap type	As III (ppb)	As V (ppb)	Se IV (ppb)	Se VI (ppb)	Cr III (ppb)	Cr VI (ppb)
Unrinsed Clear Glass w/PKI cap	nd	9-20	nd	nd	nd	nd
Rinsed Clear Glass w/PKI cap	nd	6-10	nd	nd	nd	nd
Washed Clear Glass w/PKI cap	nd	0.1-0.4	nd	nd	nd	nd
Amber Glass w/PKI cap	nd	0.3-0.7	nd	nd	0.2-0.6	nd
Rinsed Amber Glass w/PKI cap	nd	0.1-0.2	nd	nd	nd	nd
Washed Amber Glass w/PKI cap	nd	0.04-0.07	nd	nd	nd	nd
PKI PP no cap	nd	0.1-0.3	nd	nd	nd	nd
N-Sci PP no cap	nd	0.01-0.03	nd	nd	0.1?	nd
N-Sci PP w/PKI cap	nd	0.02-0.04	nd	nd	nd	nd
Rinsed N-Sci PP w/PKI cap	nd	0.03-0.06	nd	nd	nd	nd
Washed N-Sci PP w/PKI cap	nd	0.01-0.03	nd	nd	nd	nd
Rinsed N-Sci PP w/TargetDP cap	nd	0.02-0.06	nd	nd	nd	nd
N-Sci Amber Glass / Nat PP cap	nd	0.06-0.2	nd	nd	nd	0.4-0.6

nd = not detected

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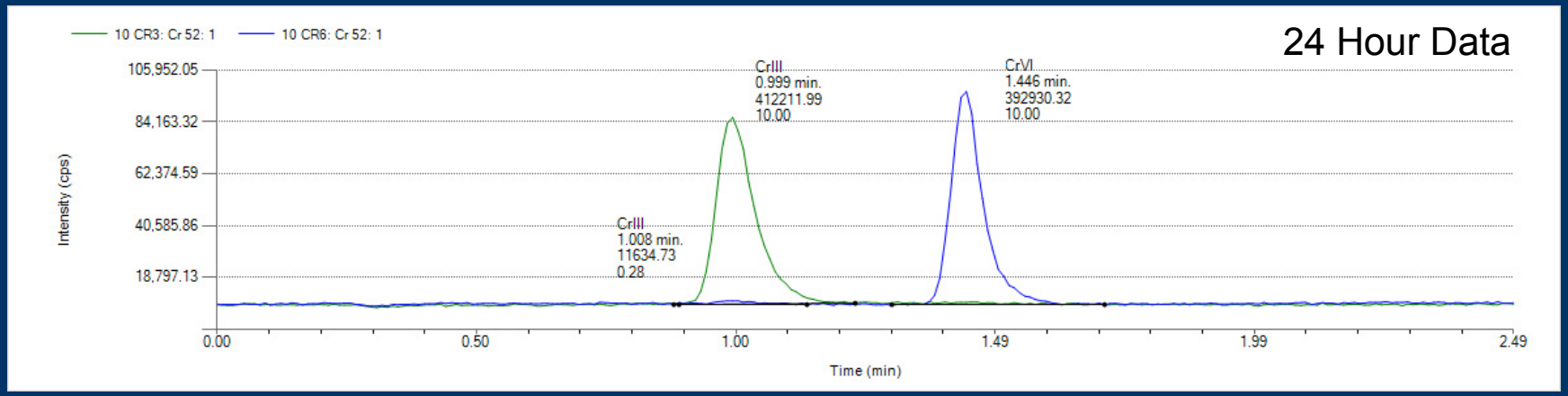
Cr Stability - 24+ Hours

- National Scientific PP Vials w/PKI black/teflon cap
- Cr(III) and Cr(VI) standards run separately
- Autosampler tray kept at 10ºC overnight

- ~3% of Cr(VI) is converted to Cr(III) over ~28 hours

Area cps	2 Hr	24 Hr	24/2 Hr
Cr(III)	431491	412212	95.5%
Cr(VI)	434280	392930	90.5%
Cr(VI)/Cr(III)	1.006	0.953	94.7%
Cr(III) in Cr(VI)	0.00	0.030	



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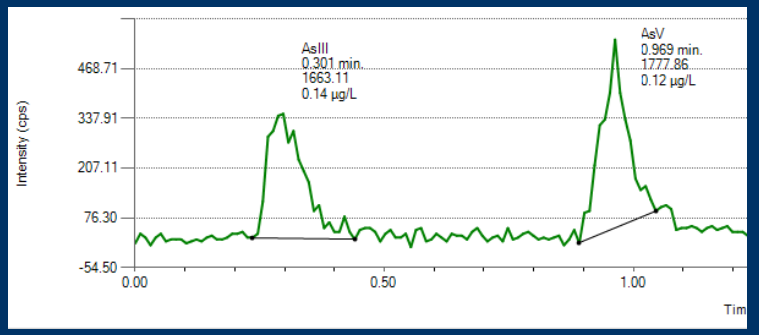
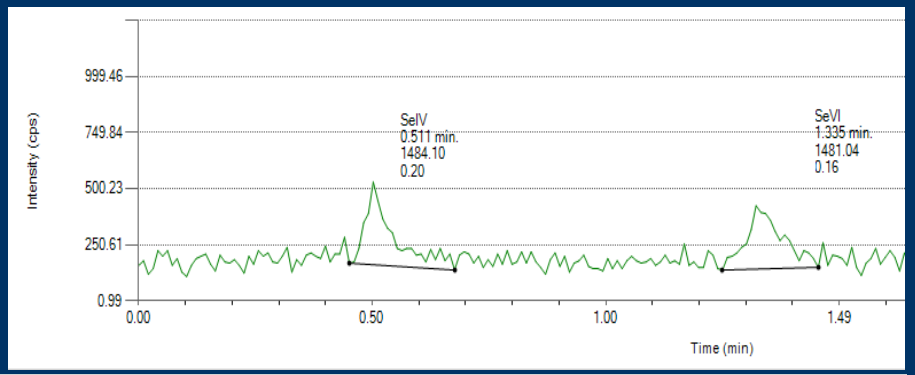
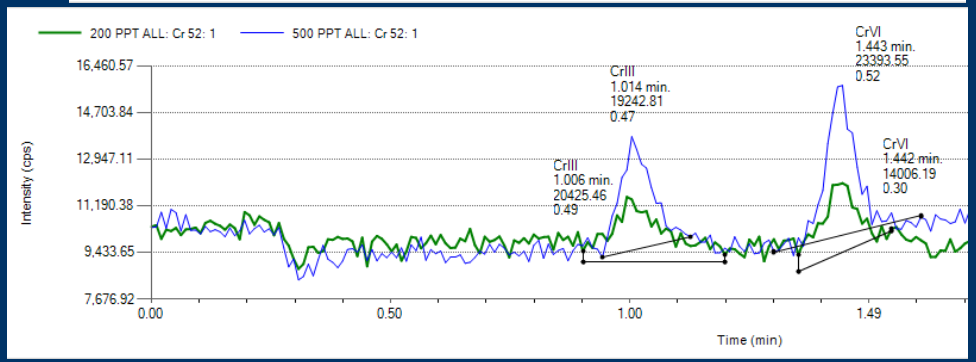
Detection Capabilities – O_2 Reaction Gas

- Calibrated at 1, 5, 10 ppb
  - Ran 100, 200, 500 ppt standards
  - Look at accuracy of result at low levels

- As PQL* ~ 100 ppt
- Se PQL ~ 200 ppt
- Cr PQL ~ 500 ppt
  - Better using NH_3 gas
  - Issues with Cr baseline and peak detection parameters in software







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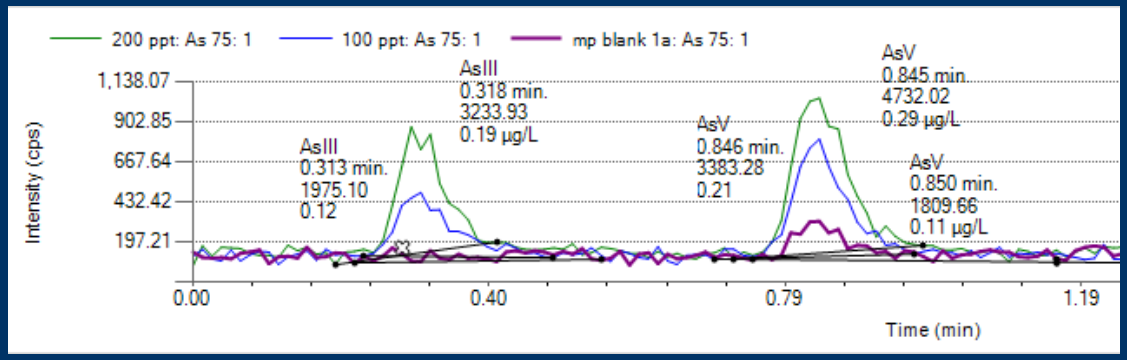
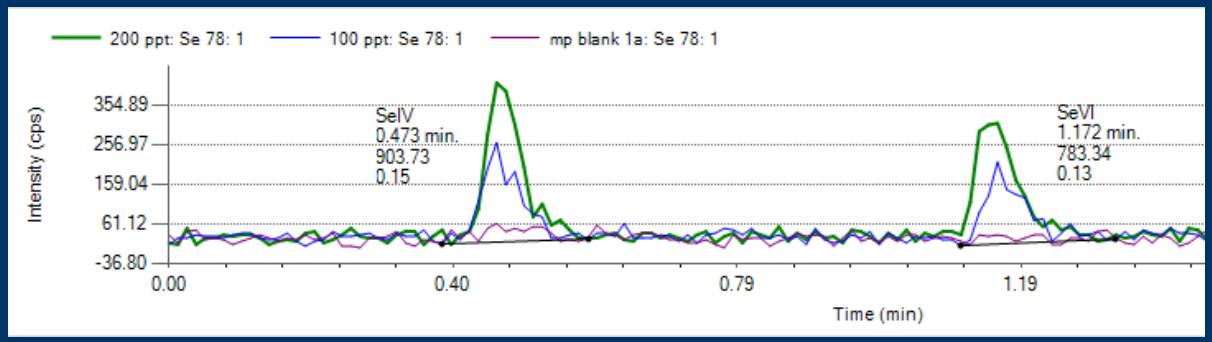
***PQL = Practical Quantitation Limit**
PQL = Concentration determined within ± 20% of true value

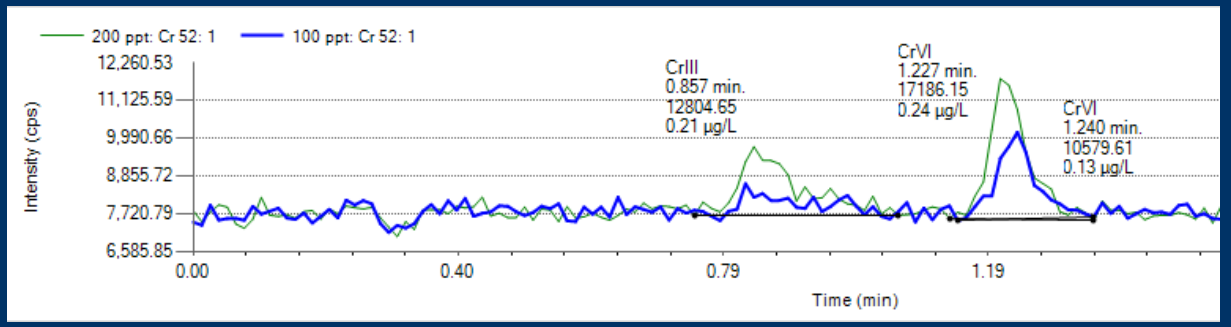
Detection Capabilities – N_2 Reaction Gas

- Calibrated at 1, 5, 10 ppb
  - Ran 100, 200, 500 ppt standards
  - Look at accuracy of result at low levels



- As PQL ~ 50 ppt
- Se PQL ~ 50 ppt
- Cr PQL ~ 100 ppt CrVI
  - Best using NH_3 gas





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Validation: Water Analysis

- USGS WRD reference water samples
- Cover a range of anion and element concentrations
  - Prepared from natural waters

Sample	*Fe* µg/L	*Al* µg/L	*Ba* µg/L	*Mo* µg/L	*Ca* mg/L	*K* mg/L	*Mg* mg/L	*Na* mg/L	*Sr* µg/L	*V* µg/L	Cl^- mg/L[a]	F^- µg/L[a]	SO_4^{2-} mg/L[a]	pH[a]
M-170	---	---	---	---	5.74	2.1	3.7	9.5	42.6	2.91	8.9	254	8.33	7.85
M-172	30	6.2	24	0.35	8.7	3.6	5.2	10.7	54	11.3	16	381	12.3	8.77
M-174	46	6	20	0.62	12.7	1.9	10.3	18.6	75	4.7	32	265	7.68	9.65
M-176	50	18.4	23	19.7	14.3	2.3	2.8	8.9	73	2.6	16.8	200	18.2	7.51
M-178	185	1.7	34	0.47	55.7	5.9	17.7	29.1	354	3.1	59.4	264	178	7.50
M-180	68	12.6	31	0.57	20.1	9.7	11.3	15	220	2.1	30.5	256	38.3	9.71

Total element concentrations were measured via ICP-MS. [a]Stated values for anions and pH are from published concentrations (source: http://qadata.cr.usgs.gov/srs_study/reports/index.php).

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Spike Recoveries

- Waters diluted 1:1 with mobile phase
- Waters spiked at 2.5 ppb
  - Diluted 1:1 with 5 ppb standard in MP
- Recoveries within ± 20% with a few exceptions
  - Cr(VI) in M-178 & M-180
    - Samples have high Fe and SO_4^{2-} levels

	Cr(III) Recovery		Cr(VI) Recovery		As(III) Recovery		As(V) Recovery		Se(IV) Recovery		Se(VI) Recovery	
Sample	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr
MP spike	109	106	104	100	107	104	105	95	109	97	101	100
M-170	98	107	94	88	92	103	106	102	102	96	101	99
M-172	99	99	95	87	100	105	107	104	106	97	101	96
M-174	103	98	78	81	104	82	103	122	101	97	104	105
M-176	100	99	80	85	106	97	101	102	106	93	101	97
M-178	97	112	33	31	102	107	91	89	87	86	96	83
M-180	104	104	64	57	104	98	95	88	99	92	101	94

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Analysis of Fire Ash/Soils

- Large forest fires in Northern CA Fall 2007
  - Burned many homes
- Assessing potential risks to human health from residential and non-residential fire ash
  - Expected to vary with particle size and speciation
- Preliminary Report
  - http://pubs.usgs.gov/of/2007/1407/

Composite photo of house burning and fireman, Credit: http://www.usgs.gov/hazards/wildfires/ca/

Satellite image of smoke from California fires, Credit: NASA

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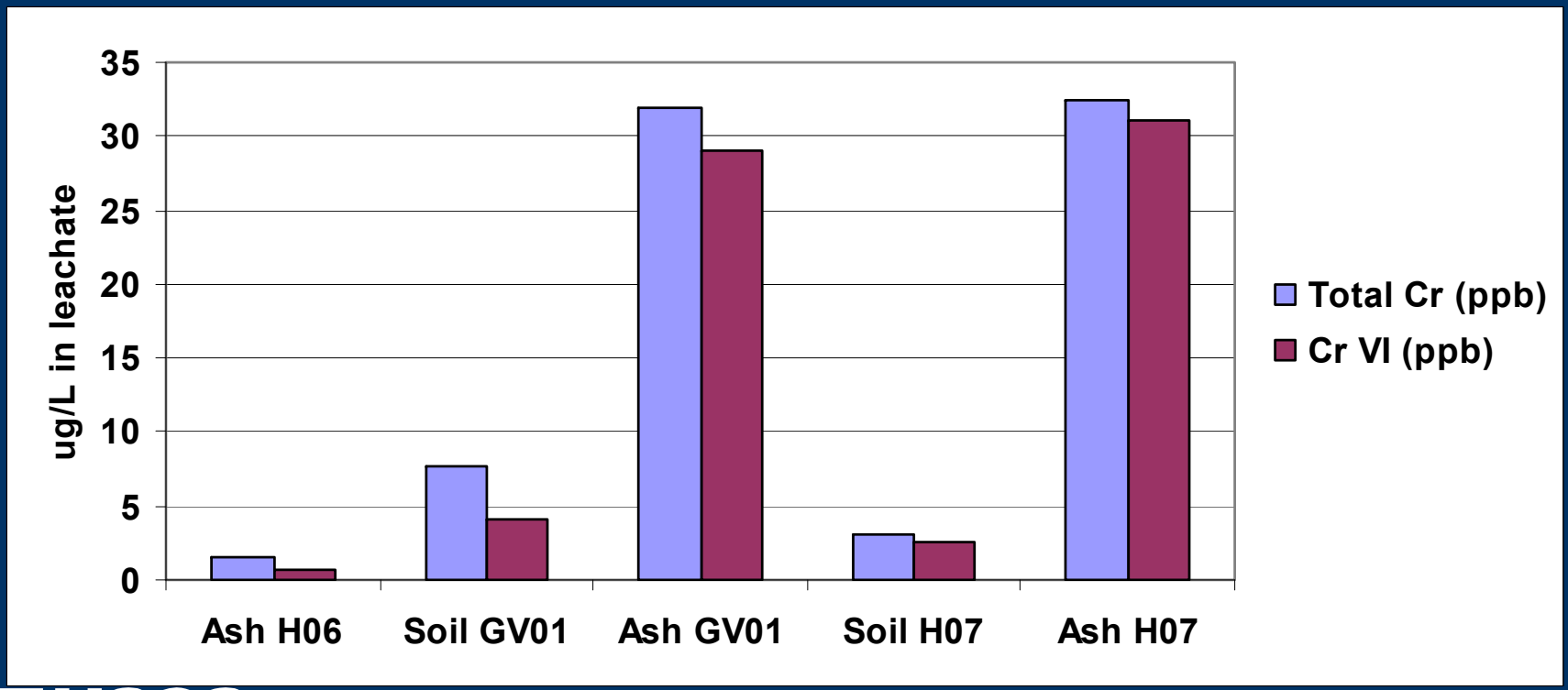
Total Cr vs. Cr(VI)

- In filtered DI-water leachate
  - 1 part ash to 20 parts water, shaken for 5 minutes, filtered
- pH > 10, Cr(III) precipitates – filtered out
- At pH > 8, Cr(VI) stable as CrO_4^{2-}



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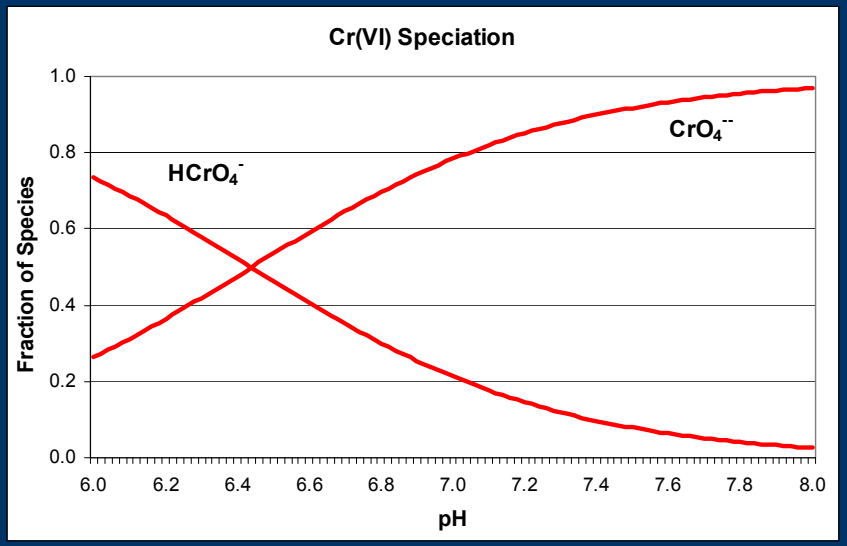
Cr Species Stability vs. pH

- Cr(VI) exists in solution in several forms
  - H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$
  - Stable form is highly pH dependent
    - Method robustness
    - Ability to work on all leach types
  - Reduction by Fe(II) and TOC in soils
- Cr(III) present as cation, Cr^{3+} at pH < 3.5
  - As pH increases hydrolysis yields $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^+$
  - Precipitates at slightly acidic to alkaline pH as $Cr(OH)_3$
  - Oxidation by MnO_2 and dissolved O_2



Cr(VI) stability vs. pH

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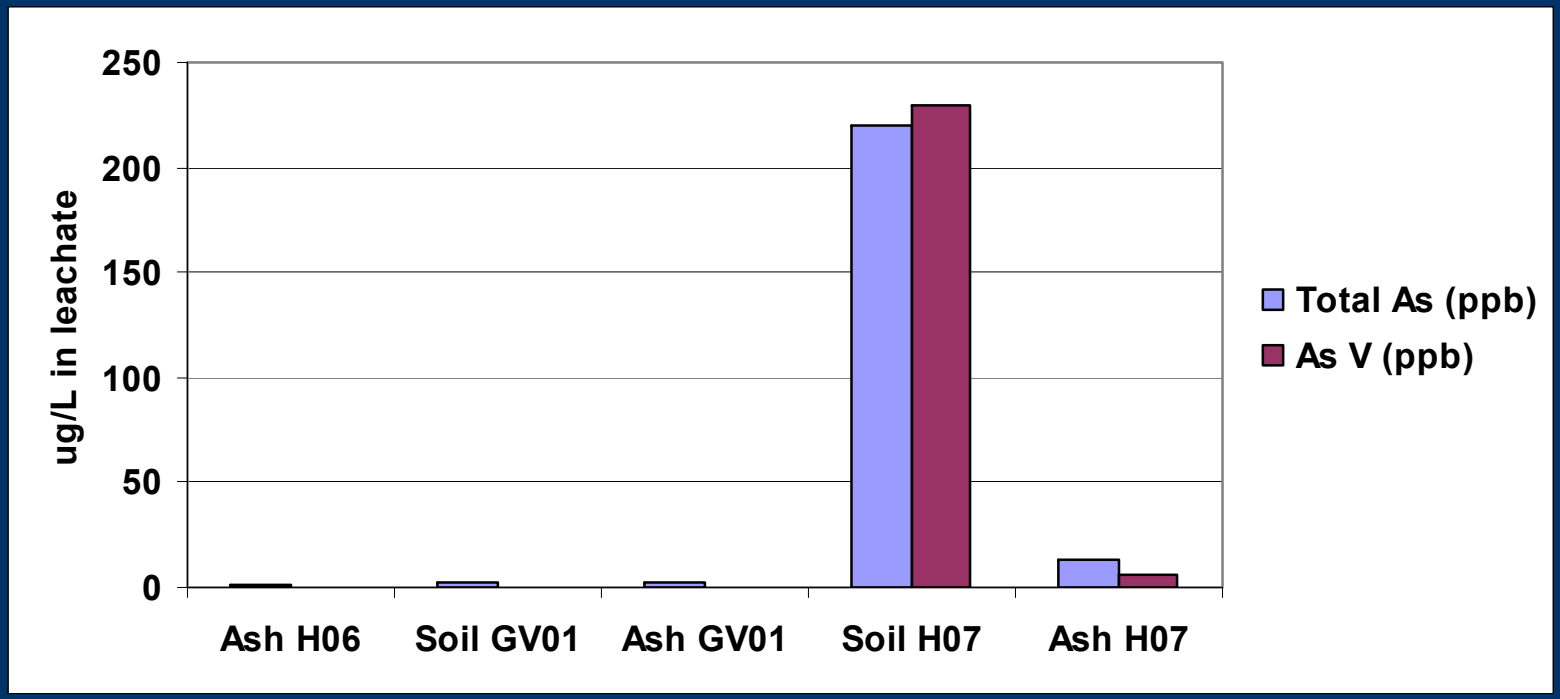
References: EPA/540/5-94/505; JAAS 2007, 22, 1051.

Total As vs. As(V)

- In filtered DI-water leachate
- Se < 2 ppb (all forms)



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Conclusions

- Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6} determined in a single run
  - C8 column used allows rapid separation in under 2 minutes
  - A variety of reaction gases may be used, depending on matrix & analytical needs
- Some difficulties finding suitable HPLC vials without contamination
  - Most vials are cleaned for organic contamination
- Need to verify single species stocks not contaminated prior to use in preparing multi-component calibration mixes
  - Need to find alternative Se(VI) source
- Method demonstrated with reference waters and fire soil/ash leachates
  - Samples diluted 1:1 or 1:10 with mobile phase
    - Allow 30-minute reaction time for Cr(III)-EDTA complex to form

- Next Steps: Investigations of sample collection/preservation methods
  - Stability of samples collected in the field
    - Typical field sampling trips are from 1 to 3 weeks in length - finding suitable collection, preservation, and shipping conditions are critical
  - Expect issues with presence of bacteria in soil and arsenic species

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- John Garbarino, USGS/WRD, Denver, CO

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