

Simultaneous speciation of arsenic, selenium, and chromium: species stability, sample preservation, and analysis of ash and soil leachates

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Abstract An analytical method using high-performance liquid chromatography separation with inductively coupled plasma mass spectrometry (ICP-MS) detection previously developed for the determination of Cr(III) and Cr(VI) has been adapted to allow the determination of As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI) under the same chromatographic conditions. Using this method, all six inorganic species can be determined in less than 3 min. A dynamic reaction cell (DRC)–ICP-MS system was used to detect the species eluted from the chromatographic column in order to reduce interferences. A variety of reaction cell gases and conditions may be utilized with the DRC–ICP-MS, and final selection of conditions is determined by data quality objectives. Results indicated all starting standards, reagents, and sample vials should be thoroughly tested for contamination. Tests on species stability indicated that refrigeration at 10 °C was preferential to freezing for most species, particularly when all species were present, and that sample solutions and extracts should be analyzed as soon as possible to eliminate species instability and interconversion effects. A variety of environmental and geological samples, including waters and deionized water [leachates] and simulated biological leachates from soils and wildfire ashes have

been analyzed using this method. Analytical spikes performed on each sample were used to evaluate data quality. Speciation analyses were conducted on deionized water leachates and simulated lung fluid leachates of ash and soils impacted by wildfires. These results show that, for leachates containing high levels of total Cr, the majority of the chromium was present in the hexavalent Cr(VI) form. In general, total and hexavalent chromium levels for samples taken from burned residential areas were higher than those obtained from non-residential forested areas. Arsenic, when found, was generally in the more oxidized As(V) form. Selenium (IV) and (VI) were present, but typically at low levels.

Keywords Speciation · HPLC-ICP-MS · Arsenic · Selenium · Chromium · Hexavalent chromium

Introduction

In 2007–2009, California experienced many large wildfires that damaged large areas of forest and destroyed many homes and buildings. The US Geological Survey collected samples from the Harris, Witch, Grass Valley, Ammo, Santiago, Canyon, Jesusita, and Station fires for testing to identify any possible characteristics of the ashes and soils from burned areas that may be of concern for their impact on water quality, human health, and endangered species. The samples were subjected to analysis for bulk chemical composition for 44 elements by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion and deionized water leach tests for pH, alkalinity, conductivity, and anions [1, 2]. Water leach tests generated leachates ranging from pH 10–12, suggesting that ashes can generate caustic alkalinity in contact with rainwater or body fluids

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(for example, sweat and fluids in the respiratory tract). Samples from burned residential areas in the 2007 fires had elevated levels for several metals, including: As, Pb, Sb, Cu, Zn, and Cr. In some cases, the levels found were above the US Environmental Protection Agency (USEPA) preliminary remediation goals for residential soils [1].

The USGS Field Leach Test (FLT) is a deionized water leach test that can be used to estimate the potential bioaccessibility of toxic constituents from earth materials such as dusts, soils, and ash from wildfires [3]. Other tests that can be used to estimate bioaccessibility of elements in various parts of the human body include *in vitro* leach tests using simulated biological fluids as described by Plumlee, Gray, and Gammelgaard [4–6]. Because different species or chemical forms of an element exhibit different toxicities to aquatic species and impacts on human health, it is often desirable to perform speciation analysis as well as total elemental analysis on these various types of leachates to determine which particular forms or chemical species of an element may become bioaccessible [7].

The ash and soil samples collected from the wildfire impacted areas in California were subjected to the FLT procedure described by Hageman and a simulated lung fluid (SLF) leach test similar to that described by Gray [3, 5]. In addition to total elemental analysis, the resulting leachates were also subjected to speciation analysis to determine what forms of As, Cr, and Se were present. The determination of the concentration of Cr(VI) that might be released by wildfire impacted soils and ash resulting from burned wild lands and residential areas was of particular interest due to the known carcinogenicity of hexavalent chromium, Cr(VI) [8]. In addition, the caustic pH levels resulting from the interaction of water and bodily fluids with these materials would tend to stabilize any Cr(VI) present. Ash particles containing high chromium levels may also create the potential for exposure to Cr(VI), a known lung carcinogen, if inhaled. Because the various forms of arsenic and selenium have different toxicities, determination of these species is also of interest.

Typically, speciation determinations are made for the species of each element of interest separately due to different sample collection, preservation, and analysis procedures employed for each element. Using such an analytical scheme, the FLT and SLF leachates would need to be subjected to three (or more) separate determinations: arsenic species, selenium species, and chromium species. This could be a complex and time-consuming process. Since the earth materials of interest have not undergone metabolic processes, the species of interest in the leachates will be the inorganic species of each element, As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI). It would be advantageous, from a time and stability standpoint, to be able to determine all these species at the same time,

particularly since, if present, they will coexist and potentially interact with each other. A method that has been developed for the determination of Cr(III) and Cr(VI) in a wide variety of matrices was modified to also determine As(III), As(V), Se(IV), and Se(VI) species under the same chromatographic and analytical conditions for the work reported here [9].

However, little is known about the stability of these six species in the same solution or how the FLT and SLF leachate samples should be preserved and stored. There are many techniques reported in the literature for the extraction, preservation, and analysis of species of one or perhaps two elements in the same solution (As and Cr species or As and Se species), but, to our knowledge, none address these issues for all six inorganic species of interest, As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI) [10–15].

Literature reviews on species stability often comment on the contradictory results found among multiple studies [16–18]. Sample preservation schemes are dependent upon the analytical technique to be used, microbial activity, and sample matrix. Arsenic species stability has been widely studied, and there are numerous papers describing various sample preservation techniques and results [17–26]. However, in a recent review, Kumar summarized that there is no universal preservative that will work for all matrices [18]. Sample filtration, refrigeration, elimination of light, and selection of an adequate preservative (HCl, H₂SO₄, EDTA, and H₃PO₄ have all been used) are important considerations in inorganic arsenic species preservation schemes. Preservation of inorganic selenium species has also been studied, but to a lesser extent [27–31]. Again, it appears no universal preservation method for selenium exists, and noticeable differences in stabilities have been reported for freezing samples or the type of storage container used [16, 28]. There have been few recent studies on chromium species stability and preservation, although interconversion between Cr(III) and Cr(VI) is well documented [6, 9, 32–35]. Cr(VI) is known to convert rapidly to Cr(III) under acidic conditions [6, 9, 36]. As a result, aqueous samples collected for Cr(VI) analysis under regulatory programs in the USA are preserved at a pH of 9.0–9.5 according to methods specified by the USEPA and analyzed within 24 h [37, 38]. Other studies report the loss of Cr(III) in samples due to the precipitation of Cr(OH)₃ as the pH rises or from adsorption onto iron oxide particles which can precipitate at pH > 2 [9, 39]. Field methods for the separation and collection of Cr(VI) have also been developed in order to avoid the complications involved with preserving water samples for Cr(VI) determination [36].

In review, many researchers have found acidification with various acids to be suitable for preserving inorganic arsenic species while hexavalent chromium is most stable under alkaline conditions. Reports of suitable preservation

and storage conditions for inorganic selenium species indicate that freezing may or may not be beneficial, while some studies for arsenic indicate freezing should be avoided. These contrasting conclusions indicate that a stability study for the six species to be determined by this method, As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI), should be undertaken to evaluate whether suitable sample storage and preservation conditions can be found for the matrices of interest. Once suitable sample storage and preservation conditions were evaluated, deionized water and simulated lung fluid leachates of the selected samples from wildfire impacted areas were analyzed.

Experimental

Instrumentation

A high-performance liquid chromatography (HPLC) system (PerkinElmer Series 200, Shelton, CT, USA) was coupled to a dynamic reaction cell (DRC)–ICP-MS system (PerkinElmer ELAN[®] DRC[®] II, Shelton, CT USA) for the separation and detection of the individual inorganic species of arsenic, selenium, and chromium. As previously reported, a mobile phase of 2.0 mM tetrabutylammonium hydroxide (TBAOH)+0.5 mM ethylenediaminetetraacetic acid, di-potassium salt (K₂EDTA) adjusted to a nominal pH of 7.6, with 5% methanol (added on-line by the HPLC pump) was used to effectively separate Cr(III) and Cr(VI) under the same chromatographic conditions using a Brownlee (3 cm×3 μm) C8 column at 35 °C under isocratic conditions [9]. In the method previously reported, ammonia (NH₃) was used as the reaction gas in the dynamic reaction cell in the ICP-MS to effectively reduce the ⁴⁰Ar¹²C⁺ interference on ⁵²Cr⁺. For the determination of arsenic, chromium, and selenium, a variety of different reaction gases were investigated including ammonia, oxygen, nitrogen, and hydrogen/helium. In order to evaluate the effectiveness of each reaction gas, a blank mobile phase solution containing 5% methanol was analyzed along with a standard solution prepared in the same blank solution containing 1 ppb each of As(III), Cr(III), and Se(IV). The reaction cell gas flow setting and mass rejection (RPq) parameters were optimized for each gas per the instrument manufacturer's instructions to provide the best overall detection limits for the three analytes of interest (arsenic, selenium, and chromium). Once the reaction cell parameters were optimized, the blank mobile phase solution and 1 ppb standard solution were analyzed and the resulting signal to background ratios calculated for each set of reaction cell conditions. The overall background signal reduction at ⁵²Cr⁺ was also measured in normal mode (no reaction gas) and in DRC mode (with reaction gas) to evaluate the overall ability

of the various reaction gases to eliminate the high backgrounds normally observed in ICP-MS due to ⁴⁰Ar¹²C⁺ formation in the plasma in matrices containing organics, such as the mobile phase solution containing 5% methanol.

Standards and reagents

Stock solutions of 1,000 mg/L Cr(III), Cr(VI), As(III), As(V), Se(IV), and Se(VI) were obtained from three different commercial standards suppliers (Inorganic Ventures, Christiansburg, VA, USA; Spex Certiprep, Metuchen, NJ, USA; and VHG Labs, Manchester, NH, USA). Deionized water (18 MΩ) was obtained from a commercial water polishing system equipped with an ultraviolet lamp for disinfection and a 0.2 μm final filter (Millipore, Element A-10, Billerica, MA, USA) to ensure low bacteria levels that may affect species stability or cause blockages in the HPLC system. All intermediate stock and working solutions were prepared fresh daily by appropriate dilution of the 1,000 mg/L commercial stock solutions in the prepared 2 mM TBAOH+0.5 mM K₂EDTA mobile phase at room temperature [9]. It should be noted that, due to the use of hydrochloric and nitric acids as a preservative in some of the commercially available stock solutions, care was taken to dilute each 1,000-mg/L stock solution down to separate intermediate stock solutions at 10 mg/L in the HPLC mobile phase prior to the preparation of mixed species working standards. All standards and dilutions were prepared in 15 mL polypropylene centrifuge tubes (Beckton Dickinson Labware, Franklin, NJ, P/N 352097) that had been pre-cleaned by rinsing several times with deionized water followed by soaking overnight filled with the mobile phase solution in order to leach out any possible contamination and condition the tubes prior to use. A 100-μg/L mixed species stock solution containing As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI) was prepared, taking care to add each 10-mg/L working stock solution to the test tube separately with capping and mixing in between to prevent rapid and localized changes in the pH that might cause species interconversion when the next species was added. All standard solutions containing Cr(III) were allowed to sit at room temperature (20 °C) for a minimum of 30–40 min prior to analysis to allow the Cr(III)–EDTA complex to form [9].

Calibration and analysis

Calibration standards were prepared fresh daily at 1, 2, 5, and 10 μg/L levels using the 100-μg/L mixed species working stock solution described above. Separate individual standards for each species were prepared at 10 μg/L in order to check for standard stability and purity. It was found that all sources of Se(VI) stock solutions contained

significant levels (up to 10%) of Se(IV) which had to be accounted for when determining the final concentrations of mixed species calibration standards. Calibration curves were verified using mixed species standards prepared at 1–10 µg/L from stock solutions obtained from a second commercial supplier.

Sample vials and contamination

In the work previously reported, it was found that the clear glass HPLC vials (Perkin Elmer, Shelton, CT, N9306053) were suitable for speciation determinations of Cr(III) and Cr(VI) [9]. However, preliminary investigations indicated that these vials might not be suitable for arsenic speciation due to significant levels, up to 20 µg/L, of As(V) observed during analysis of blank mobile phase solutions. A background contamination test was performed on several different types of HPLC vials and caps used directly out of the shipping container and also subjected to rinsing and washing procedures. The following treatment procedures were tested: unrinsed, vials taken directly out of shipping container and filled with blank mobile phase solution; rinsed, vials were rinsed three times with ~1 mL deionized water using polypropylene transfer pipettes prior to filling with blank mobile phase solution; washed, vials were filled with 5% HCl, covered, and allowed to soak overnight, then rinsed five times with deionized water and filled with mobile phase. Three to five vials of each type were subjected to each treatment procedure and were sampled at 2 and 24 h of contact time with blank mobile phase solution. All caps tested were equipped with polytetrafluoroethylene (PTFE) septa. Caps were not rinsed or washed prior to use.

Standard and sample stability

Finding suitable methods for the preservation of species from more than one element at the same time presents some significant challenges. For example, various acids, including hydrochloric, nitric, phosphoric, and acetic acids, as well as complexing agents, such as ethylenediaminetetraacetic acid (EDTA), have all been reported for the preservation of aqueous samples for arsenic speciation [17, 23]. However, the use of acid preservation could be detrimental to the stability of chromium species [6, 9]. Experiences in our laboratory indicate that decreases in pH of standard solutions from 7.6 to below pH 6 rapidly cause conversion of Cr(VI) to Cr(III) at the 100 µg/L level and below.

Stability tests were performed on single species and mixed species calibration standards at 50 µg/L prepared in the mobile phase under three different storage conditions: room temperature at 20 °C, refrigerated at 10 °C, and frozen at –21 °C. A concentration of 50 µg/L was selected

for testing because 50 µg/L has been proposed as a regulatory limit for Cr(VI) in drinking water in the USA. All tests were carried out in polypropylene HPLC autosampler vials or pre-cleaned and preconditioned 15 mL polypropylene centrifuge tubes. All solutions were analyzed at 0, 24, 48, and 120 h, and signals were normalized against a freshly prepared check standard run before and after each sample set in order to eliminate the effects of instrument signal drift over time. Samples initially stored at –21 °C were allowed to thaw for sampling at 24 h and were returned to the freezer as quickly as possible for storage until the next sampling period. Although previous studies have found that the thawing and refreezing of samples for arsenic and selenium speciation is not recommended, no data is available to our knowledge for chromium speciation [16, 18, 26, 28].

In order to test the effect of common concomitant elements on species stability, aliquots of two USGS reference water solutions, M-172 and M-176 (<http://bqs.usgs.gov/srs>), were spiked with individual species and mixed species standards as described above and evaluated at the same storage temperatures and time intervals as the standard solutions in the HPLC mobile phase. These reference waters are surface waters with major ion inorganic constituents and have been chlorinated to 5 mg/L chlorine with sodium hypochlorite as a preservative to prevent microbial growth. The anion and element concentrations in these reference waters have been discussed previously but are typical of those found in natural waters from which they are derived [9]. Electronic Supplementary Material Table S1 shows the major cation and anion concentrations present in M-172 and M-176. Since these waters have been preserved with sodium hypochlorite, this makes them a useful surrogate for drinking waters coming from municipal sources using chlorination disinfection processes, since there has been some discussion on the stability of Cr(VI) in chlorinated drinking water supplies [40, 41]. These waters also have the same major constituents, Ca, Mg, K, Na, Al, and Fe, albeit at lower levels, as the FLT leachates of wildfire impacted soils and ashes [1].

Others have reported successful use of EDTA as a preservative for speciation analysis [19, 20, 23, 24]. Since the M-172 and M-176 natural waters have significant levels of major cationic species, such as Ca, K, Mg, and Na as well as trace levels of Al and Fe, the use of EDTA was also investigated as a preservative to see if complexation of these concomitant cationic species improved stability over the conditions tested. Prior to spiking with individual and mixed species, separate aliquots of the M-172 and M-176 water standards were prepared and spiked with 10.0 mM K₂EDTA, and are designated as E-172 and E-176, respectively. All signals (in area counts per second) were normalized to those of freshly prepared standards (in mobile phase) analyzed just prior to each set of samples analyzed.

Based upon the results obtained from the stability testing in the reference water samples, a single temperature stability test using mixed species spikes was performed on the blank SLF solution and sample duplicates at 10 °C in order to evaluate stability during the course of analysis in the Peltier-cooled autosampler tray.

Quality control

One of the difficulties in performing speciation analyses is providing some measure of the quality of the data provided. Usually, methods are validated by analyzing certified reference materials of a similar type or matrix to the samples to be analyzed to ensure the data are not biased. Routine quality control samples, such as spikes, duplicates, and check samples, are also analyzed to provide a measure of the overall quality of the data. In the case of speciation analyses, the availability of certified reference materials is extremely limited and many are only available for a single elemental species or in a non-complex matrix and may themselves be subject to stability issues [42]. The approach used in this paper to provide some estimate of data quality is to use a second source of commercially available standard stock solutions to verify calibrations and to perform an analytical spike on every sample for all species using the same stock solutions employed in calibration. The analytical spikes were prepared at the same time the samples were diluted with mobile phase for analysis. The analytical spike provides some measure of what effect the sample matrix has on signal intensities, species stability, retention time, and chromatographic separation. Duplicate sample and spiked sample analyses over the course of an analytical run were also used to evaluate species stability in a specific sample matrix. In addition, since a mass spectral internal standard is not being used to compensate for instrumental drift, calibration check standards are run periodically to determine and correct for any instrumental signal drift, if necessary. Check standard results are generally acceptable if measured concentrations are within $\pm 10\%$ of the prepared or calculated value. Analytical spikes are considered acceptable if the spike recovery is within $\pm 25\%$ of the spiked value. Duplicate sample and duplicate spiked sample analyses are acceptable if the relative percent different is $\leq 20\%$. These acceptance limits are consistent with those utilized by many USEPA methodologies, including elemental analysis by ICP-MS [43]. If spike recoveries are not acceptable, the data may be reported as informational values and flagged as unacceptable spike recovery. Samples that show significant retention time shifts due to the sample matrix are also flagged, and the analytical spikes may be used to validate the identity of the peaks. For samples exhibiting significant matrix effects such as retention time shifts,

species interconversions, elevated or noisy backgrounds, or the appearance of unknown peaks, the sample is subjected to two or more levels of additional dilution to see if the matrix effects can be eliminated while still obtaining usable analytical signals.

Figure 1 shows the retention time shifts, species interconversions, and peak splitting effects that can be observed in an analytical spike of the M-172 water sample, illustrating the need to evaluate the effect of all sample matrices on the separation chemistry and species stability. Figure 1a shows the chromatograms for a 50 $\mu\text{g/L}$ standard containing As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI) prepared in the mobile phase. Figure 1b shows the chromatograms for a 50 $\mu\text{g/L}$ spike of these same species in the M-172 water matrix. Comparing the chromatograms for ^{52}Cr (solid black line) in Fig. 1a, b, it

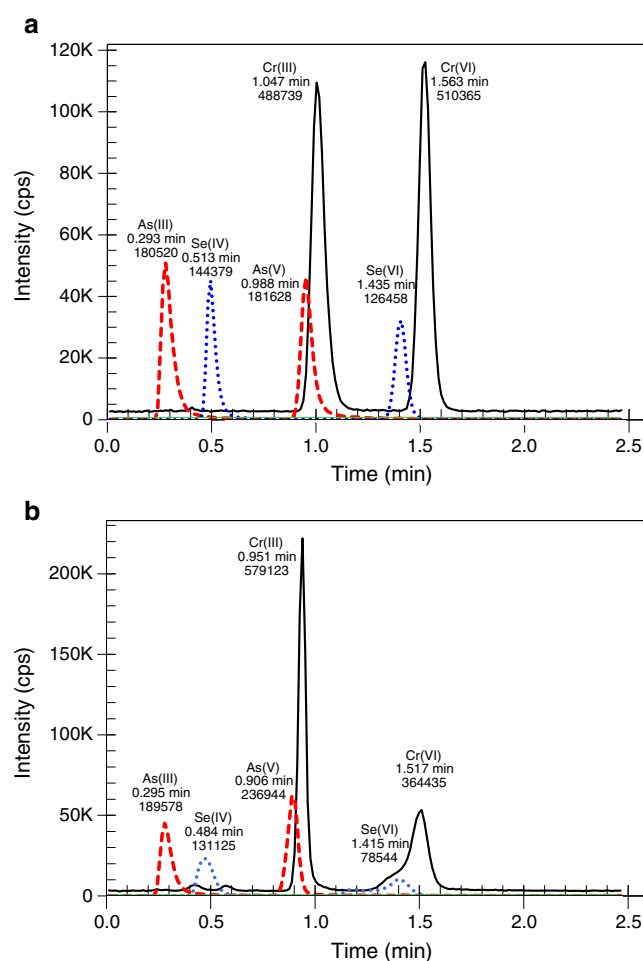


Fig. 1 **a** Shows a chromatogram for a 50- $\mu\text{g/L}$ standard containing As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI) prepared in the mobile phase. Peak labels immediately adjacent to the peak indicate species identity, retention time, and integrated area counts. **b** Shows the chromatograms for a 50- $\mu\text{g/L}$ analytical spike in reference water sample M-172. The solid black line is the chromatogram for ^{52}Cr . The dotted blue line is the chromatogram for ^{78}Se . The dashed red line is the chromatogram for ^{75}As

is apparent that the M-172 matrix is causing retention time shifts for both Cr(III) and Cr(VI) and that Cr(VI) is reducing to Cr(III). In the chromatograms for ^{78}Se (blue dotted line), the matrix of the M-172 water causes a slight shift in retention time for both the Se(IV) and Se(VI) peaks. The Se(VI) peak also appears to be splitting into two peaks, or perhaps forming a different Se species. In the ^{75}As chromatogram (dashed red line), the As(V) peak undergoes a significant retention time shift from 0.988 min in the mobile phase standard to 0.906 min in the M-172 water matrix. This example illustrates that the use of analytical spikes can be very useful in evaluating the effects of the sample matrix on the chromatographic separation, species stability, species recoveries, and peak identification on data quality.

Analysis of ash and soil leachates

In 2007–2009, the state of California experienced many large wildfires. Samples were collected from a variety of locations affected by the 2007 wildfires and were subjected to a variety of analyses to determine overall potential impact on water quality, human health, endangered species, and debris-flow or flooding hazards [1, 2]. A subset of these samples where total values reported for As, Cr, or Se were at elevated levels were subsequently re-leached using the FLT procedure described by Hageman or using a SLF leaching procedure similar to that described by Gray [3, 5]. In the FLT procedure, deionized water and a solid-to-liquid ratio of 1:20 is used to leach the <2-mm fraction of unground sample splits. After shaking for 5 min, the leachates are filtered using a 0.45- μm nitrocellulose syringe filter into pre-cleaned high-density polyethylene (HDPE) bottles.

The simulated lung fluid used a modified Gamble's solution adapted from previous studies and is designed to model interactions of particles with extracellular lung fluids [44–48]. The simulated lung fluid contained NaCl (6780 mg/L), NH_4Cl (535 mg/L), NaHCO_3 (1770 mg/L), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (166 mg/L), Na_2CO_3 (630 mg/L), glycine (450 mg/L), H_2SO_4 (51 mg/L), $\text{Na}_3\text{-citrate} \cdot 2 \text{H}_2\text{O}$ (59 mg/L), and $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$ (29 mg/L) which was adjusted to pH 7.4 at 37 °C using HCl. The batch extractions are done using a solid-to-liquid ratio of 1:100 based on results from previous studies. The solid materials, previously sieved to <20 μm , are placed in new, acid-washed HDPE bottles to which the simulated lung fluid is added. The bottles are placed in a preheated (37 °C) incubator to provide both constant rotation and temperature for 24 h. When removed, the SLF leachates are centrifuged at 2,000 rpm for 2 min and then filtered into a new acid-washed HDPE bottle using a 0.45- μm nitrocellulose syringe filter.

Aliquots of FLT and SLF leachates submitted for total metals analysis were acidified with concentrated nitric acid

to pH <2 and analyzed by ICP-MS as described by Taggart [49]. For speciation analysis, separate aliquots were taken from FLT leachates for each sample and placed inside the same type of new, unwashed polypropylene HPLC vials with PTFE-lined caps used for analysis. No preservative was added to the aliquots for speciation analysis, and they were refrigerated at 10 °C until analysis. Separate aliquots were collected from the SLF leachates for total elemental analysis and for speciation analysis. The aliquots of SLF leachates for speciation analysis were stored unpreserved in new, unwashed HPLC vials and caps as described above at 10 °C. Both the FLT and SLF leachates were analyzed as quickly as possible after receipt and storage time was generally less than 1 h before the samples were prepared for analysis by performing appropriate dilutions and preparing spikes. All samples for speciation analysis were diluted a minimum of 1:1 in the blank mobile phase solution to minimize matrix effects and to provide some buffering of the sample pH. The SLF leachates were diluted a minimum of 1:5 in mobile phase to minimize detrimental effects on the chromatographic background signals due to the complex matrix of the SLF solution. Analytical spikes of each sample were prepared by spiking separate aliquots with a stock mixed species standard at 2–10 $\mu\text{g/L}$. All samples and standards were held in the HPLC autosampler at 10 °C until analysis was complete. All sample results and associated reporting limits were multiplied by appropriate dilution factors.

Results and discussion

Determination of DRC reaction gas

Comparing the DRC mode background count rates to normal mode background count rates in Table 1, it is apparent that oxygen, ammonia, and nitrogen are all quite effective at reducing the overall background observed at $^{52}\text{Cr}^+$ due to the formation of $^{40}\text{Ar}^{12}\text{C}^+$ in the plasma. The mixture of hydrogen and helium gas was not found to be effective for this application. Nitrogen, N_2 , was found to provide the best overall signal-to-noise ratios for all three analytes of interest and was subsequently used as the reaction gas for the speciation of arsenic, selenium, and chromium. However, the selection of the reaction gas may be changed if better detection limits are required for one particular analyte. For example, if better detection limits are required for arsenic, then the use of oxygen as the reaction gas and subsequent determination of arsenic as $^{75}\text{As}^{16}\text{O}^+$ at mass 91 would be the condition of choice. For this report, N_2 was used as the reaction gas, and the isotopes monitored were ^{52}Cr , ^{75}As , and ^{78}Se .

Table 1 Optimized parameters (gas flow and RPq setting) for different DRC reaction gases

Reaction gas	N ₂	O ₂	NH ₃	7%H ₂ /He
Gas flow	Flow=1.0	Flow=0.75	Flow=0.65	Flow=1.0
DRC cell setting	RPq=0.50	RPq=0.55	RPq=0.60	RPq=0.70
⁵² Cr ⁺ signal/background	6.4	4	7	1
⁷⁵ As ⁺ signal/background	51	25	290	200
⁷⁵ As ¹⁶ O ⁺ signal/background	—	340	—	—
⁷⁸ Se ⁺ signal/background	35	18	9	1.5
Normal mode Bkg ⁵² Cr ⁺ (cps)	2,377,440	5,507,800	5,155,460	5,725,700
DRC mode Bkg ⁵² Cr ⁺ (cps)	1,480	6,320	4,070	4,653,150

Measured signal-to-background ratios for 1 ppb standard in HPLC mobile phase and blank mobile phase solution. Background count rates (Bkg) for ⁵²Cr⁺ at for each reaction gas in normal (no gas) mode and DRC (with gas) mode, showing overall reduction of background due to ⁴⁰Ar¹²C⁺ plasma species

Calibration and analysis

The calibration curves were found to be linear up to 100 µg/L. Using a 50-µL injection volume, standards were analyzed at 0.025, 0.05, 0.1, 0.2, and 0.5 µg/L. A practical quantitation limit (PQL) for each species was determined as the lowest standard analyzed that read back to within ±20% of the prepared value. For As(III), As(V), Se(IV), and Se(VI), the PQL was determined to be 0.05 µg/L. The PQL determined for Cr(III) and Cr(VI) in this method using N₂ as the reaction gas to remove the ⁴⁰Ar¹²C⁺ was 0.1 µg/L. A summary of the method and figures of merit are given in Table 2.

Sample vials and contamination

The detailed results of the sample vial background contamination test are shown in Electronic Supplementary Material Table S2. Significant levels of As(V), 0.3–20 µg/L, were

found in both clear and amber glass vials, which is to be expected due to the use of arsenic in glass manufacturing [25, 50]. Although the arsenic levels were found to be reduced by the cleaning procedures tested, pre-cleaning of a large quantity of small-volume (1–2 mL) HPLC vials is highly impractical. Overall contamination levels for all species in polypropylene vials obtained from National Scientific (Rockwood, TN, USA) were non-detectable or very low (less than 0.1 µg/L). For all subsequent studies, polypropylene vials with Teflon-lined caps (National Scientific, C4000-57-R) were used without any washing or rinsing before use. It is highly recommended that each new supplier and lot of vials be tested for contamination levels prior to use.

Standard and sample stability

Cr(III) and Cr(VI) species standards prepared in the mobile phase solution were found to be stable to within ±5% of

Table 2 Analytical figures of merit, using N₂ reaction gas in DRC cell

Species detected	PQL (±20%)	Retention time	%RSD (2 ppb, n=4)
As(III)	0.05 µg/L	0.293 min	5.4
As(V)	0.05 µg/L	0.988 min	8.7
Cr(III)	0.1 µg/L	1.047 min	2.8
Cr(VI)	0.1 µg/L	1.563 min	7.0
Se(IV)	0.05 µg/L	0.513 min	7.5
Se(VI)	0.05 µg/L	1.435 min	4.5
HPLC column	C8, 3 cm×3 µm, 35 °C		
Mobile phase	2.0 mM tetrabutylammonium hydroxide+0.5 mM K ₂ EDTA, pH=7.6, 5% methanol added on-line via HPLC pump		
Flow rate	1.5 mL/min, isocratic		
Injection volume	50 µL, 200 µL sample loop		
Autosampler	10 °C, polypropylene vials, Teflon-lined caps		

Practical quantitation limit (PQL) defined as lowest standard analyzed reading ±20% of prepared value. Relative standard deviation (% RSD) calculated for four single injections of a 2-ppb standard analyzed periodically over the course of a single analytical run of over 4 h duration

the original value in individual solutions and mixed with all chromium, selenium, and arsenic species (mixed species solution) present for up to 48 h at both 20 °C and 10 °C. After 48 h at 20 °C, there was significant (more than 5%) conversion of Cr(VI) to Cr(III) in the mixed-species solution. Individual and mixed-species solutions maintained at 10 °C showed no significant conversion of chromium species for up to 120 h. However, freezing mixed-species solutions showed significant (approximately 50%) conversion of Cr(VI) to Cr(III) after just 24 h, although the single-species solutions were stable over the entire 120-h time period tested at −21 °C, as is illustrated by Fig. 2a.

As(III) and As(V) in single component and mixed-species standards were stable within $\pm 5\%$ of the original value for the entire 120 h at both 20 °C and 10 °C. However, freezing at −21 °C was detrimental to arsenic species, resulting in greater than 20% conversion of As(V) to As(III) in 24 h in the single species solutions. Conversely, in the mixed species solutions stored at −21 °C

over 50% of the As(III) was converted to As(V) as illustrated in Fig. 2b.

Selenium (IV) and (VI) standards were stable in all solutions to within $\pm 5\%$ of the original values at storage temperatures of 20 °C and 10 °C over the entire 120 h period. However, the separate Se(IV) and Se(VI) solutions showed up to 8% conversion of Se(IV) to Se(VI) with freezing at −21 °C after 24 h.

The stability test results for the reference water samples are shown in the Electronic Supplementary Material Figs. S1, S2, S3, and S4. In the single-species solutions (see Electronic Supplementary Material Fig. S1a–c), a significant amount (30–50%) of the Cr(III) added to the M-172 water appears to be oxidized to Cr(VI) in 24 h at all storage temperatures tested. This is consistent with reports by others that free chlorine present in water can oxidize Cr(III) to Cr(VI) [40, 41]. However, in the mixed species solutions, results are more variable. Cr(VI) is reduced to Cr(III) in this same water matrix at the 20 °C and −21 °C storage temperatures, but over 10% of the Cr(III) is oxidized to Cr(VI) at the 10 °C storage temperature.

The addition of 10 mM EDTA as a preservative to M-172, denoted as E-172, (see Electronic Supplementary Material Fig. S1d–f) has the effect of dramatically stabilizing the Cr(III) and Cr(VI) present in the single-species solutions, so the values measured are within 5% of the starting values at the 20 °C and 10 °C storage temperatures for up to 48 h. In the mixed-species solutions, the amount of reduction of Cr(VI) to Cr(III) is reduced and is less than 25% at times up to 48 h at the 20 °C and 10 °C storage temperatures. Freezing the samples at −21 °C appears to be more detrimental to Cr species stability for separate standards as well as for mixed-species solutions.

The stability of Cr(III) and Cr(VI) in the other USGS reference water sample, M-176 and the EDTA-preserved aliquot of this sample, E-176, is shown in Electronic Supplementary Material Fig. S2a–f. Storage at 20 °C showed less conversion of Cr(III) to Cr(VI) in this matrix after 24 h in the single species solutions, however, the mixed-species solutions showed significant conversion of Cr(VI) to Cr(III). Solutions kept at 10 °C for up to 48 h showed only 10% or less conversion of Cr(VI) to Cr(III). In contrast, at 120 h, the single-species solutions showed significant conversion of Cr(III) to Cr(VI), while the mixed-species solutions remained stable as compared with those tested after 48 h. Freezing the single-species and mixed-species solutions was detrimental to species stability at all times tested and had a greater impact on Cr(III) and Cr(VI) stability in the mixed-species solutions. Electronic Supplementary Material Fig. S2d–f shows the impact of using EDTA as a preservative on the M-176 water matrix. At 20 °C, the addition of EDTA appears to inhibit the oxidation

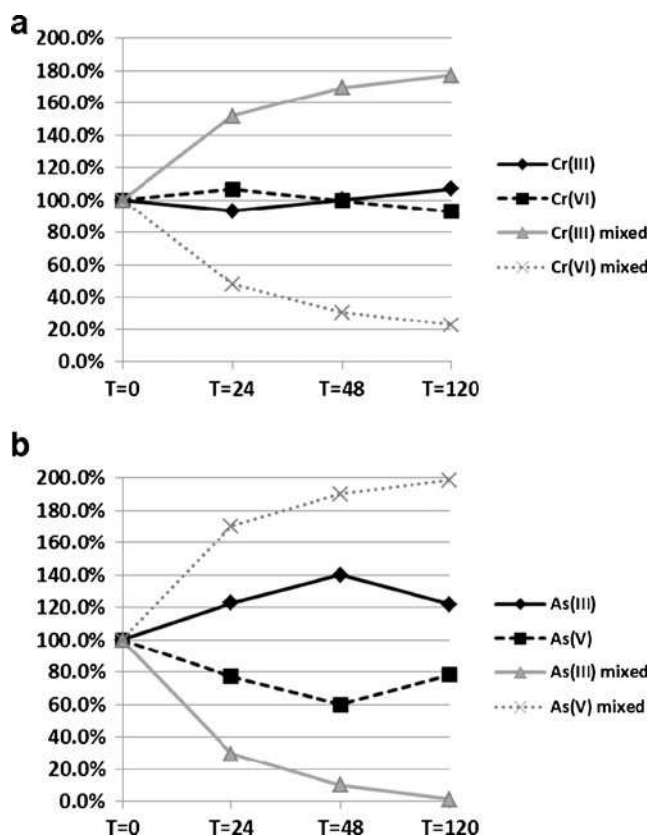


Fig. 2 Chromium and arsenic stability measured in individual 50 $\mu\text{g/L}$ Cr(III), Cr(VI), As(III), and As(V) solutions over 120 h at −21 °C and of mixed-species solutions (designated as “mixed”) containing Cr(III), Cr(VI), As(III), As(V), Se(IV), and Se(VI) at 50 $\mu\text{g/L}$ each. Y-axis is normalized percent recovery based on freshly prepared standards at time (t)=0. **a** Shows the plot of the Cr species stability over 120 h when stored frozen at −21 °C. **b** Shows As species stability at −21 °C

of Cr(III) to Cr(VI), which may suggest that the EDTA is forming a complex with some concomitant metal, perhaps Fe, present at 50 $\mu\text{g/L}$, which is involved in the redox chemistry of chromium in this matrix. At 10 $^{\circ}\text{C}$, the addition of EDTA does not improve the stability of the chromium species in either the single-species or mixed-species solutions for solutions tested at 24 and 48 h. However, stability of the single species solutions is improved for solutions tested after 120 h. Stability for all solutions held at -21°C is somewhat improved with the addition of EDTA at all times tested.

Stability of As(III) and As(V) in the M-172 water is shown in Electronic Supplementary Material Fig. S3a–c. At 20 $^{\circ}\text{C}$, the mixed-species solutions show more conversion of As(III) to As(V), which increases slightly with time. Storage at 10 $^{\circ}\text{C}$ shows good stability of both As(III) and As(V) over the total time tested of 120 h where the measured values are within $\pm 5\%$ of the initial values. Freezing the solutions at -21°C is particularly detrimental to the mixed-species solutions, whereas the single-species solutions appear to be more stable, but still exhibit 10–20% conversion. The addition of EDTA to water M-172 as a preservative, designated as E-172 in Electronic Supplementary Material Fig. S3d–f, seems to have little effect on the single-species solutions at any temperature but is detrimental to mixed-species solutions stored at 10 $^{\circ}\text{C}$.

Spikes of arsenic species in the M-176 water sample held at 20 $^{\circ}\text{C}$ were stable to within $\pm 10\%$ of the original values for up to 48 h, after which significant conversion of As(III) to As(V) occurred in the mixed-species solutions (see Electronic Supplementary Material Fig. S4a). Individual and mixed-species spikes of arsenic species in M-176 held at 10 $^{\circ}\text{C}$ were stable to within $\pm 5\%$ of the original value for the entire 120 h monitored. Freezing the solutions at -21°C resulted in nearly complete conversion of As(III) to As(V) within 24 h in the mixed-species spikes while the individual species spikes were stable for approximately 48 h (see Electronic Supplementary Material Fig. S4b, c). When EDTA was added to water M-176 as a preservative (see Electronic Supplementary Material Fig. S4d–f), the stability of mixed-species solutions stored at 10 $^{\circ}\text{C}$ (see Electronic Supplementary Material Fig. S4e) was decreased as compared with that without the EDTA preservative (see Electronic Supplementary Material Fig. S4b). The addition of EDTA as a preservative had little effect for the solutions at the other storage temperatures.

Selenium proved to be the most stable species in both M-172 and M-176, with less than 10% conversion of Se(VI) to Se(IV) at all storage temperatures for the entire 120-h time period. The addition of EDTA as a preservative to either M-172 or M-176 waters had no observed effect on the stability of either Se(IV) or Se

(VI) in either water matrix over the entire 120 h time period and at all storage temperatures.

As a result of these experiments, it is apparent that the stability of the chromium and arsenic species tested, Cr(III), Cr(VI), As(III), and As(V), is highly variable and varies with the concomitant species and elements present and the storage temperature of the solutions. It is not apparent from the experiments conducted that the addition of EDTA to aqueous samples as a preservative is advantageous for all the species tested, and further experiments should be conducted with a wide array of sample types to evaluate its effectiveness. It also appears that freezing the samples at -21°C can be detrimental to chromium and arsenic species and will thus be avoided for future studies.

Additional testing performed on mixed-species spikes containing As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se (VI) on blank SLF solutions, sample duplicates, and spiked sample duplicates were found to be stable to within $\pm 10\%$ of the original value for up to 4 h when held at 10 $^{\circ}\text{C}$ in the Peltier-cooled autosampler during analysis. Additional long-term stability testing is needed in this matrix and in actual sample leachates. Based on the data from these experiments, it has thus been concluded that samples for speciation analysis using the method described herein should be stored refrigerated at 10 $^{\circ}\text{C}$ without the addition of any preservative and analyzed as soon as possible (preferably within 24 h).

Analysis of ash and soil leachates

Figure 3 shows example chromatograms from one of the actual SLF leachate samples and its analytical spike. Each element is plotted separately in Fig. 3a–c for clarity due to the different signal intensities. In each chromatogram, a 5 ppb standard in the mobile phase is also overlaid with the sample and spike chromatograms, so comparisons can be made on the effects of the sample matrix on retention time, peak shape, and overall integrated signal intensity. It is important to evaluate the peaks in the chromatograms from the analytical spikes in order to determine if adjustments are necessary in the peak detection parameters prior to quantitation. As Fig. 3 shows, the sample matrix causes some retention time shifts for all species except As(III). In Fig. 3c, it is evident that Se(IV) also undergoes significant peak broadening, illustrating the need for calculations to be performed on integrated peak areas and not on peak height, due to the possibility of peak broadening or tailing that may change with different sample matrices.

Table 3 contains results for samples analyzed from the 2007 Grass Valley and Harris fires from Southern California. Data for the FLT leachate pH and total As, Cr, and Se values were taken from Plumlee [1]. Approximately 1 year

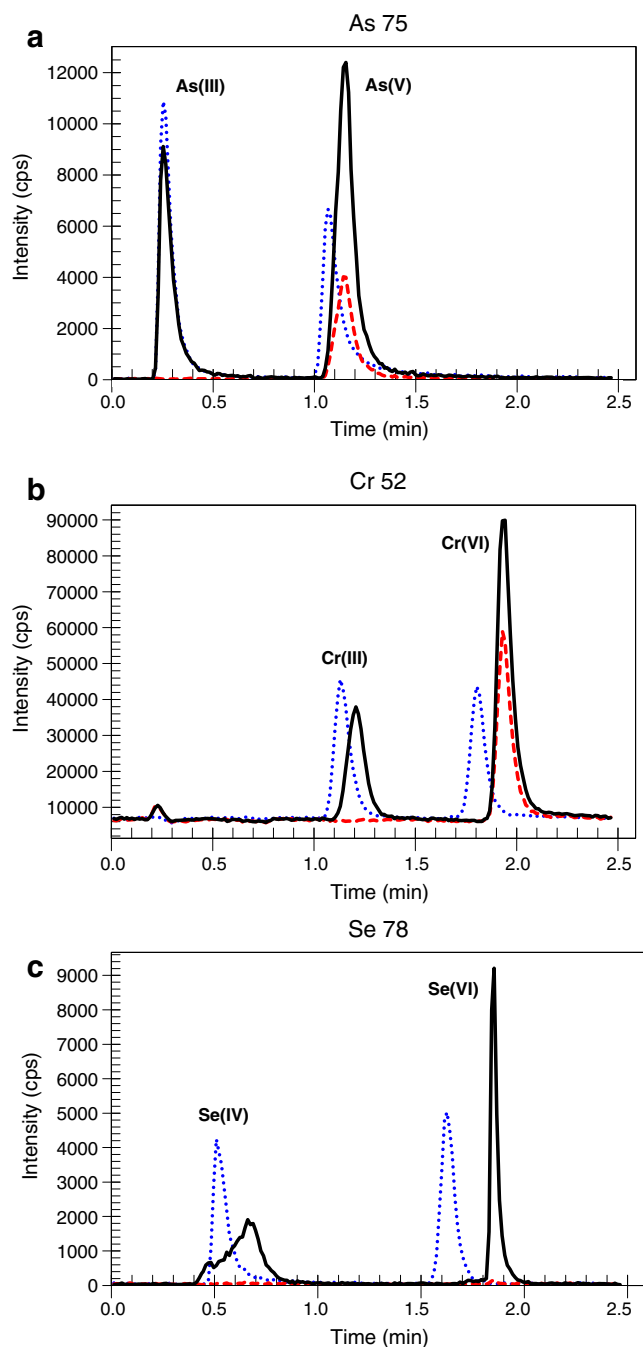


Fig. 3 Chromatographic plots of GrassValley01 ash sample in simulated lung fluid (SLF) leachate. Each element is plotted separately for clarity. **a** Shows the chromatograms for the As species monitored at mass 75. **b** Shows the chromatograms for the Cr species monitored at mass 52. **c** Shows the chromatograms for the Se species monitored at mass 78. The red dashed line in each figure is the unspiked leachate sample (1:10 dilution). The blue dotted line is a 5- $\mu\text{g/L}$ standard mixed-species standard prepared in the HPLC mobile phase. The solid black line is a 5- $\mu\text{g/L}$ analytical spike of the GrassValley01 ash sample

after these samples were originally collected, new portions of the solid samples were leached using both the FLT method and the SLF method described above. In general,

the SLF leachate contained higher concentrations of As and Cr than did the FLT leachate from the same sample. This is not surprising since the SLF procedure is a 24-h leach as compared with the 5-min FLT procedure, and there could be some additional complexation of the As and Cr present by the organic constituents in the simulated lung fluid. In most cases, the predominant form of arsenic and chromium species present were the more oxidized As(V) and Cr(VI) forms. This again is expected due to the highly oxidizing environment of a wildfire. As Table 3 illustrates, the amount of Cr(III) measured in all the leachates is very low. This can be explained by the filtration of the leachates prior to analysis, which would probably remove any Cr(III) that had either adsorbed onto iron oxide particles or precipitated as insoluble $\text{Cr}(\text{OH})_3$ at the higher pH values of the leachates [9]. Se(IV) and Se(VI) values were very low, at less than 3 $\mu\text{g/L}$ for most samples. For some samples, the sum of the individual element species may not approximate the total measured elemental concentration in the leachates. For the results reported in Table 3, this difference can possibly be explained by the use of previously analyzed FLT leachates for the total element content and a separate FLT leachate for the speciation analyses. It is also probable that the FLT and SLF solutions may interact differently with elements occurring in colloidal particles that pass through the 0.45- μm filter due to their pH and, in the case of the SLF, the presence of organic constituents. Another possibility is that some, perhaps unidentified, species are possibly retained on the column, not retained on the column at all, or filtered out by the column filter. Again, the use of an analytical spike can help elucidate the possible causes of elemental species totals that are different than total elemental results. Analytical spike recoveries in FLT leachates ranged from 98% to 125% for Cr(III), 54–101% for Cr(VI), 99–124% for As(III), 72–126% for As(V), 88–109% for Se(IV), and 89–109% for Se(VI). High spike recoveries for Cr(III) in conjunction with low spike recoveries for Cr(VI) in the same sample indicate that species interconversion may be occurring during leaching and analysis. Low spike recoveries for Cr(VI) in conjunction with unknown peaks appearing in the chromatogram may indicate other types of species conversions. In the SLF leachates, spike recoveries ranged from 96% to 104% for Cr(III), 96–114% for Cr(VI), 87–106% for As(III), 130–143% for As(V), 96–113% for Se(IV), and 89–110% for Se(VI). In the SLF leachates, low spike recoveries for As(III) in conjunction with high spike recoveries for As(V) in the same sample could be an indication that oxidation of As(III) present in the sample to As(V) may be occurring. However, in Table 3, the high spike recoveries for only As(V) without an offsetting low spike recovery for the As(III) species in multiple samples may be an indication that the sample matrix is causing signal

Table 3 Results for total and speciated analysis of FLT and SLF leachates of samples from 2007 California wildfires

Sample ID (leach method)	Area type	Leachate pH	Measured in leachate, µg/L			Measured in leachate, µg/L			Measured in leachate, µg/L		
			Total As	As(III)	As(V)	Total Cr	Cr(III)	Cr(VI)	Total Se	Se(IV)	Se(VI)
Grass Valley 01 ash (FLT)	R	12.7	2	<1	<1 (L)	32	3	29	3.5	2	<1
Grass Valley 01 ash (SLF)	R	9.1	22	<2	31 (H)	73	<2	76	3.4	<2	<2
Grass Valley 01 soil (FLT)	R	10.9	2	0.6	0.7	7.7	1	4.1 (L)	1.6	<0.4	<0.4
Grass Valley 01 soil (SLF)	R	7.3	19	<2	28 (H)	16	<2	5.0	<1	<2	<2
Harris 06 ash (FLT)	WL	10.9	1	<0.4	0.9	1.5	<0.4	0.7 (L)	7.2	1.7	1.1
Harris 06 ash (SLF)	WL	9.2	7	<2	8 (H)	5.4	<2	<2	8.2	<2	6
Harris 07 ash (FLT)	R	12.5	13	<1	6	32	<1	31	6.3	<1	<1
Harris 07 ash (SLF)	R	11.1	13	<2	17 (H)	102	<2	104 (H)	8.3	<2	<2
Harris 07 soil (FLT)	R	10.6	219	1.4	230	3	<1	2.7	2.7	2.4	<1

Values for As, Cr, and Se in FLT leachates were determined from different leachate solutions than the total element concentrations (see text). Reporting limits were determined by multiplying PQL by dilution factor used. Total element and pH values for FLT leachates are taken from Plumlee [1]. Samples taken from residential areas where houses or outbuildings burned are designated in the “Area type” column as *R* for residential or *WL* for unimproved or wild land. Spike recovery <75% indicated by (L). Spike recovery >125% indicated by (H)

enhancement or that the analytical spiking solution may have been contaminated. In all cases, spike recoveries should be considered and evaluated during interpretation of the results.

Table 4 shows the results obtained for only FLT leachates of selected samples taken from the Jesusita and Station fires which burned significant portions of California in 2009. For these samples, the same FLT leachate was used for both total elemental analysis (after acidification) and for speciation analysis which was performed as soon as possible after extraction with refrigeration of the prepared samples at 10 °C. Again, the predominant form of Cr found in the leachates is the more toxic and more oxidized Cr(VI) form.

As(V) is also the most predominant form of As measured in these samples. Selenium is generally low in both total Se concentration and individual species. For the sample results reported in Table 4, spike recoveries ranged from 74% to 127% for Cr(III), 70–125% for Cr(VI), 80–124% for As(III), 80–132% for As(V), 80–120% for Se(IV), and 70–120% for Se(VI).

For all the leachate samples analyzed, samples taken from residential areas where houses or outbuildings burned contained higher levels of leachable arsenic and chromium than samples from unimproved or wild land areas. These higher levels are likely the result of these elements being present in the building structures or furnishings or from the

Table 4 Total and speciated analysis of selected samples collected from 2009 California wildfires in FLT leachates

Sample ID (leach method)	Area type	Leachate pH	Measured in leachate, µg/L			Measured in leachate, µg/L			Measured in leachate, µg/L		
			Total As	As(III)	As(V)	Total Cr	Cr(III)	Cr(VI)	Total Se	Se(IV)	Se(VI)
JSA09-05 ash (FLT)	WL	12	2	<1	<1	5.6	<1	5.3	6.3	<1	<1
JSA09-05 ash duplicate (FLT)	WL	12	2	<1	<1	5.3	<1	4.6	6.3	<1	<1
JSA09-06 ash (FLT)	R	11.9	4.2	<0.2	1.8	17.2	0.3	13.5	4.3	0.9	<0.2
JSA09-07 ash (FLT)	R	12.3	10.2	<1	<1	541	<1	492	14.8	<1	<1
JSA09-01 soil (FLT)	WL	9.5	1	<0.2	0.8	<1	<0.2	<0.2	<1	<0.2	<0.2
JSA09-02 soil (FLT)	WL	8.2	3	0.3	1.3	2	<0.2	<0.2	<1	<0.2	<0.2
JSA09-7 soil (FLT)	R	10.2	7.2	0.2	6.5	32	2.2	22	1.2	0.7	<0.2
STN09-10A ash (FLT)	R	12.1	3	<1	<1	944	5.4	893	12	<1	1.5
STN09-13A ash (FLT)	R	12.3	8.8	<1	2	193	14	128	13	4	1
STN09-22A ash (FLT)	WL	11.1	1	<0.2	3.8	8.6	<0.2	9	9.6	2.3	2.8
STN09-26R ash (FLT)	WL	10.5	2	<0.2	<0.2	12	<0.2	10	1.8	1	<1

Total element concentrations were determined on separate aliquots of the leachates that were acidified to pH<2 prior to analysis by ICP-MS according to Taggart [49]. Samples taken from residential areas where houses or outbuildings burned are designated in the “Area type” column as *R* for residential or *WL* for unimproved or wild land

use of chemical pesticides, herbicides, or wood preservatives that contained chromium and arsenic.

Conclusions

The results from stability tests performed on standards prepared in the HPLC mobile phase indicated that mixed-species standards containing As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI) were stable to within $\pm 5\%$ of the original values if stored at 10 °C for up to 120 h. Freezing at -21 °C was detrimental to both chromium and arsenic species stability, particularly when the species of all three elements, As, Se, and Cr, were present.

In the stability testing performed on the reference water samples preserved with sodium hypochlorite, addition of EDTA as a preservative was not found to improve stability for all species, although it was found to reduce the oxidation of Cr(III) to Cr(VI) in the single-species solutions. The most suitable preservation scheme for the determination of As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI) in the reference water samples was found to be refrigeration at 10 °C with no preservative followed by analysis as soon as possible (preferably within 24 h).

In the blank SLF solution and the sample duplicates analyzed, all species were found to be stable to within $\pm 10\%$ of the original values if stored at 10 °C for up to 4 h. However, based on the results of the stability testing from the reference water samples, there may be effects from concomitant elements or species present in the SLF leachates from the samples due to the significant levels of Al, Ca, K, Mg, Na, and Fe leached from the wildfire ashes and soils [1]. Further stability testing with additional soil SLF leachates will be necessary to explore these effects and better evaluate long-term stability. From the work presented here, we have concluded that the FLT and SLF leachates from the ash and soil samples should be stored at 10 °C and be analyzed as soon as possible after leaching.

For the ash and soil samples analyzed from wildfire impacted areas in California, the predominant forms of arsenic and chromium found were the more oxidized forms, which is consistent with the oxidizing conditions experienced in a wildfire. Samples from burned residential areas had higher values of arsenic and chromium species in both types of leachates performed than did samples from unimproved or wild land areas.

Observations during stability testing indicate that the stability of mixed species solutions is highly variable and may be affected by interactions with concomitant elements and species. As a result, it is recommended that stability tests should always be performed on new matrices. In addition, the use of analytical spikes has been shown to be extremely useful in assessing the data quality in speciation

analyses. This study has shown that it is possible to determine all the inorganic forms of arsenic, chromium and selenium: As(III), As(V), Cr(III), Cr(VI), Se(IV), and Se(VI), in a single analytical run using the same chromatographic conditions via HPLC-ICP-MS.

Disclaimer

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

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