Speciation of Arsenic(III)/Arsenic(V) and Selenium(IV)/Selenium(VI) Using Coupled Ion Chromatography–Hydride Generation Atomic Absorption Spectrometry

Sabine Goldberg* and Bruce A. Manning

Abstract

Simple analytical methods have been developed to speciate inorganic As and Se in the microgram per liter range using coupled ion chromatography–hydride generation atomic absorption spectrometry. Because of the differences in toxicity and adsorption behavior, determinations of the redox states arsenite, As(III), and arsenate, As(V), and selenite, Se(IV), and selenate, Se(VI), are important. Anion exchange chromatography is used to separate As(III) and As(V) or Se(IV) and Se(VI) based on differences in retention times. Samples are then mixed with concentrated HCl for As or Se determination as the hydrides. Detection limits are $0.8\ \mu g\ L^{-1}$ As for both redox states, $0.68\ \mu g\ L^{-1}$ for Se(IV), and $0.55\ \mu g\ L^{-1}$ for Se(VI). Spiking of actual mixed sample solutions of both redox states showed the procedure to be accurate for solutions with As(III)/As(V) or Se(IV)/Se(VI) ratios ranging from 1:4 to 4:1. Average recoveries were 95.7% for As (III), 106% for As(V), 93.1% for Se(IV), and 108% for Se(VI). The technique can be used to determine As(III) and As(V) and Se(IV) and Se(VI) in deionized water and actual and synthetic irrigation waters.

Abbreviations: EC, electrical conductivity; HGAAS, hydride generation atomic absorption spectrometry; HPLC, high performance liquid chromatography; NIST, National Institute of Standards and Technology; SRM, standard reference material.

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A rsenic and Se are potentially toxic trace elements that are ubiquitous in rocks, soil, seawater, freshwater, and air. Adversely high concentrations of As can be found in mine drainage, coal fly ash, smelter wastes, and soil treated with arsenical pesticides. Arsenic is also a naturally occurring toxicant found in groundwater associated with As-bearing geologic deposits (Chakraborti et al., 2002; Nordstrom, 2002). Selenium concentrations can be elevated in natural waters due to runoff from mining operations (Ryser et al., 2005; Olegario et al., 2010), coal fly ash (Huggins et al., 2007), and irrigation drainage from arid-zone soils (Manning and Burau, 1995). Selenium can be present in radioactive wastes (Scheinost and Charlet, 2008). The toxicity and bioavailability of As and Se in the environment depend on the oxidation–reduction (redox) conditions of the site (Masscheleyn et al., 1990; Tokunaga et al., 1997). In typical sediment–water environments where redox conditions are mildly reducing to oxidizing (Eh = 100–700 mV), the oxyacids and associated anion species of As and Se predominate.
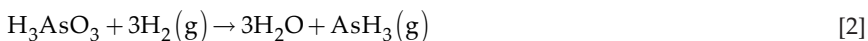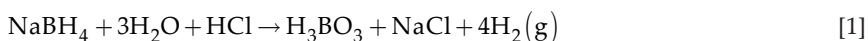
For the pH and redox conditions of most soils and surface sediments, the predominant As species are: $H_2AsO_4^-$ and $HAsO_4^{2-}$ for arsenate or H_3AsO_3 for arsenite. The As(III)/As(V) redox couple is pH dependent, but generally As(V) persists under oxidizing conditions (Eh > 100 mV) whereas As(III) is predominant under reducing to mildly reducing conditions (Eh = −50 to 100 mV). Where microbial reduction and transformations are acting under more strongly reducing conditions, monomethylarsenic acid, dimethylarsenic acid, as well as methylated arsenide [As(−III)] species can form (Gao et al., 1998). Redox transformations of As(III)/As(V) in the aquatic environment can lead to seasonal increases in total dissolved As (Jay et al., 2005).

Selenium occurs as SeO_4^{2-} for selenate and H_2SeO_3 and $HSeO_3^-$ for selenite oxyanions in mildly reducing to oxidizing wetland and aquatic conditions (Eh = −100 to 700 mV) (Séby et al., 1998). Reduction of Se(VI) to Se(IV) occurs when the sediment–water Eh is <400 mV (pH = 7). Under mildly to strongly reducing conditions where microbially mediated Fe(III) reduction is active, Se(IV) is reduced to the elemental [Se(0)] and selenide [Se(−II)] species (Dauchy et al., 1994). Both microbial and abiotic chemical processes result in the oxidation of both reduced As and Se species to the corresponding oxyanions (Osborne and Ehrlich, 1976; Oscarson et al., 1980; Tokunaga et al., 1996).

Accurate and routine analytical separation and detection of the dissolved As(III)/As(V) and Se(IV)/Se(VI) redox couples is an important goal of many environmental scientists, engineers, and local, state, and federal agencies concerned with drinking water monitoring and quality. Regardless of the final method used, the analytical demands include: (i) low microgram per liter or nanogram per liter limits of detection (LOD); (ii) unequivocal separation of the target species (speciation accuracy); (iii) excellent reproducibility (precision); (iv) good dynamic range; and (v) the ability to accommodate complex environmental sample matrices. There are few routine techniques that are capable of fulfilling all of these criteria. However, the increased awareness of the importance of As(III)/As(V) and Se(IV)/Se(VI) speciation has resulted in an increase in the demand for such techniques (Greenway, 2001; Guerin et al., 1999; Harrington et al., 2010).

There are several techniques currently available for the speciation of As(III)/As(V) and Se(IV)/Se(VI). Due to the chemical similarities of As and Se (both form oxyanions as well as volatile reduced hydrides), most techniques are capable of speciating both As and Se. For a comprehensive overview of the subject of As and Se speciation, the reader is directed to the thorough reviews by Dauchy et al. (1994), Guerin et al. (1999), Greenway (2001), and Terlecka (2005). The As(III)/As(V) and Se(IV)/Se(VI) speciation techniques currently used in most laboratories involve high performance liquid chromatography (HPLC) of the dissolved As and Se species linked to a highly sensitive detector, typically either inductively coupled plasma–mass spectrometry (ICP–MS) or hydride generation atomic absorption spectrometry (HGAAS). Both techniques determine both redox states simultaneously and are relatively rapid and sensitive. The ICP–MS detector, while highly sensitive (LOD = 0.01 μg L^{-1}), can suffer from polyatomic, isobaric interferences between ^{75}As$^+$ and ArCl$^+$ (both m/z = 75) and ^{80}Se$^+$ and ^{40}Ar$_2^+$ (both m/z = 80), necessitating reaction cell technology, which is not yet standard equipment in most laboratories. Although HGAAS is somewhat less sensitive than ICP–MS (LOD = 0.5 μg L^{-1}), it has excellent selectivity in complex sample matrices by simple As and Se gas stripping. This chapter discusses a routine HPLC–HGAAS technique that can be configured for speciation of either As(III)/As(V) or Se(IV)/Se(VI). This chapter combines a technique previously described for simultaneous determination of As(III)/As(V) (Manning and Martens, 1997) with a similar technique specific for Se(IV)/Se(VI) (Goldberg et al., 2006). These methods have been previously validated using standard reference materials and extracts from environmental samples and offer a sensitive alternative to laboratories that do not have ICP–MS with reaction cell technology.

Separation of As(III) from As(V) and Se(IV) from Se(VI) is accomplished by anion exchange liquid chromatography. For As, the chromatographic separation of As(III)/As(V) is directly followed by in-line HGAAS converting both As(III) and As(V) to arsine (AsH$_3$) with NaBH$_4$ (Pohl and Prusisz, 2004):

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 4H_2(g) \tag{1}$$

$$H_3AsO_3 + 3H_2(g) \rightarrow 3H_2O + AsH_3(g) \tag{2}$$

$$HAsO_4^{2-} + 2H^+ + 4H_2(g) \rightarrow 4H_2O + AsH_3(g) \tag{3}$$

In this technique, both As(III) and As(V) are converted to AsH$_3$ at separate times after column separation. The separation of Se(IV) and Se(VI) must be followed by in-line reduction of Se(VI) to Se(IV) using a heated HCl pretreatment before HGAAS. The Se(IV) species is then converted to hydrogen selenide (H$_2$Se) by NaBH$_4$:

$$SeO_3^{2-} + 2H^+ + 3H_2(g) \rightarrow 3H_2O + H_2Se(g) \tag{4}$$
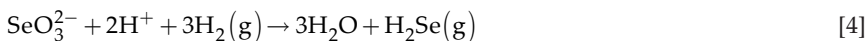
The gaseous AsH$_3$ and H$_2$Se products are transported by a neutral inert carrier (Ar or He) to a heated quartz tube atomizer in the atomic absorption spectrometer

light path. Data collection using a standard chromatography integrator (or suitable software) completes the analysis. The use of HPLC combined with hydride generation has been extensively developed and applied for both As(III)/As(V) (Tye et al., 1985; Maitani et al., 1987; Stummeyer et al., 1996; Gomez et al., 1997; Manning and Martens, 1997) and Se(IV)/Se(VI) (Cobo-Fernández et al., 1995; Ellend et al., 1996; Pitts et al., 1995; Goldberg et al., 2006) speciation. The objective of this chapter is to demonstrate the effective application of HPLC-HGAAS for the speciation of As(III)/As(V) and Se(IV)/Se(VI) using standard reference materials and environmental soil and water samples.

EQUIPMENT AND INSTRUMENTATION

The analytical equipment required for direct simultaneous hydride generation and determination of inorganic As and Se species is:

- High-performance liquid chromatography pump (e.g., Dionex DQP-1)
- Anion exchange column (e.g., Dionex IonPac AS11)
- Guard column (e.g., Dionex IonPac AG11)
- Atomic absorption spectrophotometer (e.g., PerkinElmer Model 3030B)
- Arsenic or Se electrodeless discharge lamp (EDL)
- Hydride generator (e.g., Varian Model VGA-76)
- Quartz absorption cell and mount
- Data acquisition system (e.g., Hewlett-Packard integrator Model 3393A)

Additional requirements for the Se method are a heated sand bath and an ice bath. Components of the apparatus and their corresponding operating parameters are provided in Table 41-1 for both As and Se. Schematic drawings of the experimental setups are shown in Fig. 41-1 for As and Fig. 41-2 for Se. Separation of the As and Se redox states is accomplished by passing solutions first through a guard column and then through an analytical anion exchange column. The analytical column has a multiphase structure. The column packing is composed of an anion exchange layer functionalized with quaternary ammonium groups attached to the surface of a core consisting of ethylvinylbenzene cross-linked with divinylbenzene.

REAGENTS AND MATERIALS

All chemicals to be used must be of reagent-grade purity. Deionized (DI) water can be produced using Millipore deionizing cartridges or absorber and ion-exchange cartridges. These types of cartridges remove free chlorine, organics, and essentially all ions. All DI water must be degassed under vacuum for at least 15 min before use in the preparation of the mobile-phase eluent.

Reagents—Arsenic

- Mobile phase: Pipet an appropriate amount of 50% (w/w) NaOH solution into degassed DI water. Vacuum filter the solution and decant into a polyethylene bladder and add an appropriate amount of methanol to make a final mobile

Table 41-1. The high-performance liquid chromatography–hydride generation atomic absorption spectrophotometry (HPLC-HGAAS) system and operating parameters.

Parameter	Arsenic	Selenium
HPLC		
Pump	Dionex DQP-1	Dionex DQP-1
Switching valve gas	62 MPa N_2	62 MPa N_2
Guard column	Dionex IonPac Guard AG11	Dionex IonPac Guard AG11
Size	4 by 50 mm	4 by 50 mm
Analytical column	Dionex IonPac Analytical AS11	Dionex IonPac Analytical AS11
Size	4 by 250 mm	4 by 250 mm
Mobile phase	30 mmol L^{-1} NaOH/1% methanol	10 mmol L^{-1} NaOH
Flow rate	1 mL min^{-1}	1 mL min^{-1}
Sample inject volume	250 μL	200 μL
Hydride generator		
Model	Varian VGA-76	Varian VGA-76
Ar flow rate	40 mL min^{-1}	40 mL min^{-1}
0.16 mol L^{-1} $NaBH_4$ flow rate	1 mL min^{-1}	1 mL min^{-1}
HCl concentration	6 mol L^{-1}	12 mol L^{-1}
Flow rate	1 mL min^{-1}	1 mL min^{-1}
Atomic absorption spectrometer		
Model	Perkin Elmer 3030B	Perkin Elmer 3030B
Electrodeless discharge lamp (EDL)	Perkin Elmer EDL	Perkin Elmer EDL System 2
EDL power	8 W	230 mA
Wavelength	193.7 nm	196.0 nm
Bandwidth	0.7 nm	2.0 nm
Flame	air + acetylene	air + acetylene
Integrator		
Model	Hewlett Packard 3393A	Hewlett Packard 3393A
Zero setting	10	0
Attenuation (ATT2^)	7	8
Chart speed	0.5 cm min^{-1}	0.4 cm min^{-1}
Area reject	500,000	3,000,000
Threshold	6	8
Peak width	0.16	0.30

    phase of 30 mmol L^{-1} NaOH/1% methanol solution.

- Hydride solution: Combine $NaBH_4$ and NaOH to make a final solution consisting of 0.16 mol L^{-1} $NaBH_4$ and 0.12 mol L^{-1} NaOH. Vacuum filter before use.
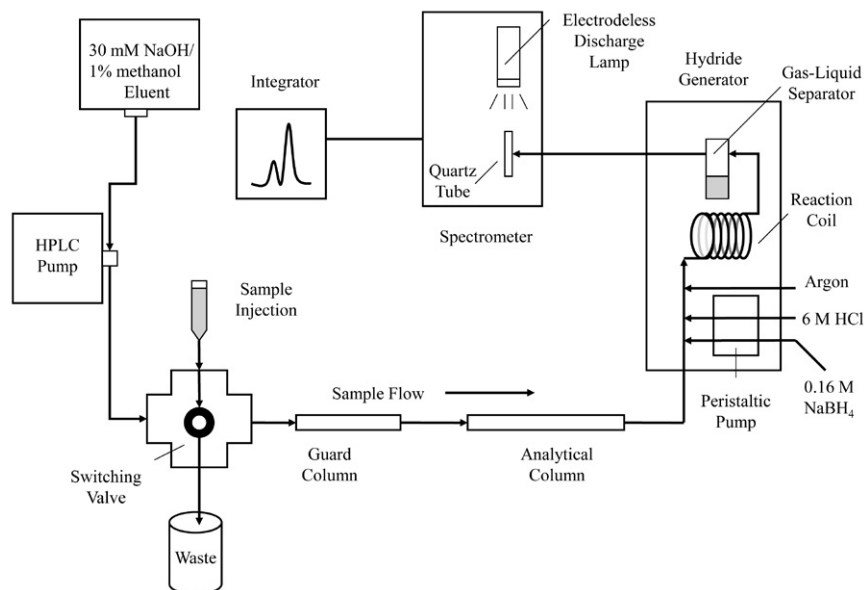- Acid solution: Dilute concentrated instra-analyzed HCl to make a 6 mol L^{-1} solution.

Fig. 41-1. Diagram of the high-performance liquid chromatography–hydride generation atomic absorption spectrophotometry (HPLC-HGAAS) system for As analysis (from Manning and Martens, 1997).
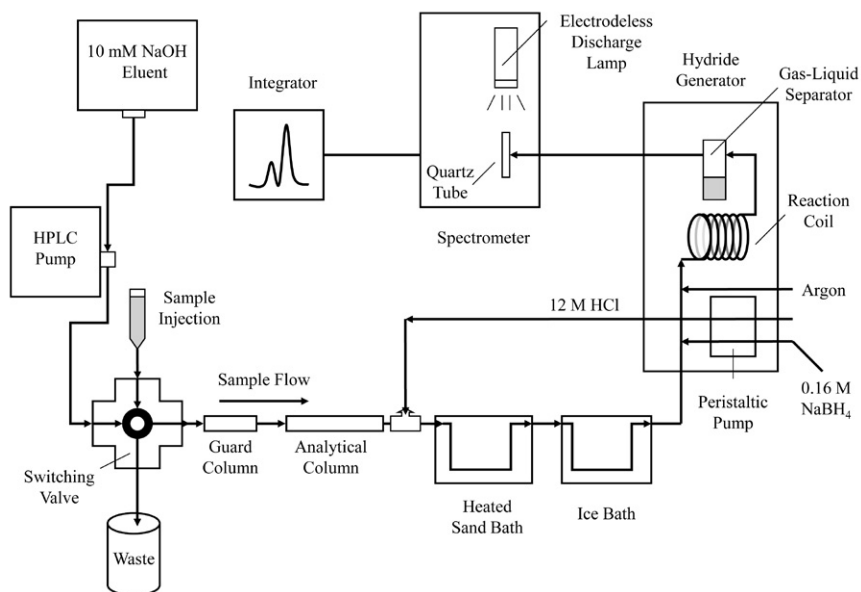

Fig. 41-2. Diagram of the high-performance liquid chromatography–hydride generation atomic absorption spectrophotometry (HPLC-HGAAS) system for Se analysis (from Goldberg et al., 2006).

- Stock solutions: Dissolve 0.867 g of $NaAsO_2$ or 2.08 g of $Na_2HAsO_4 \cdot 7H_2O$ into 500 mL of 0.1 mol L^{-1} NaCl to make separate stock solutions of 1000 mg L^{-1} As(III) or As(V), respectively.
- Standards: Prepare fresh working standards daily in the appropriate background matrix and range (5–30 μg As L^{-1}) for analysis. Make both single ion and mixed As(III) + As(V) ion standards as needed.

Reagents—Selenium

- Mobile phase: Pipet an appropriate amount of 50% (w/w) NaOH solution into degassed DI water. Vacuum filter the solution and decant into a polyethylene bladder to make a final mobile phase of 10 mmol L^{-1} NaOH solution.
- Hydride solution: Combine $NaBH_4$ and NaOH to make a final solution consisting of 0.16 mol L^{-1} $NaBH_4$ and 0.12 mol L^{-1} NaOH. Vacuum filter before use.
- Acid solution: Concentrated instra-analyzed HCl, 12 mol L^{-1} solution.
- Stock solutions: Dissolve 1.1 g of Na_2SeO_3 or 1.2 g of Na_2SeO_4 into 500 mL of DI water to make separate stock solutions of 1000 mg L^{-1} Se(IV) or Se(VI), respectively.
- Standards: Prepare fresh working standards daily in the appropriate background matrix and range (5–30 μg Se L^{-1}) for analysis. Make both single ion and mixed Se(IV) + Se(VI) ion standards as needed.

Materials

Standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) were used to evaluate the accuracy of the methods for determining trace element concentrations in fresh water; SRM 1640 is a natural fresh water collected from Clear Creek, CO, and certified as 26.7 ± 0.4 μg As L^{-1} and 22.0 ± 0.5 μg Se L^{-1}; SRM 1643e is a simulated fresh water certified as 60.5 ± 0.7 μg L^{-1} As and 12.0 ± 0.1 μg Se L^{-1}.

The capability of the procedures to determine As and Se in simulated irrigation waters of varying As(III)/As(V) and Se(IV)/Se(VI) ratios was tested by spiking sample solutions. Two Se solutions were prepared for this study: (i) a Se-free synthetic irrigation water containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}, and electrical conductivity (EC) = 4.77 dS m^{-1} and (ii) the synthetic irrigation water diluted to an EC = 0.95 dS m^{-1}. An As-free synthetic irrigation water containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} was spiked with As(III) and As(V) and analyzed before and after removal of Ca because high concentrations of Ca interfere with the determination of arsenate. Calcium was removed using a no. 2 Dowex 50W-X8 cation exchange resin that was slurry-packed into solid-phase extraction columns. The three spikes added to each solution varied in As(III)/As(V) or Se(IV)/Se(VI) ratio from 1:4 to 4:1 and are shown in Tables 41-2 and 41-3. Recoveries of As(III) and As(V) or Se(IV) and Se(VI) were calculated as the differences between concentrations found in spiked and unspiked samples.

Table 41-2. Selenium concentrations and recoveries of spiked sample solutions (after Goldberg et al., 2006).

Sample	Treatment spike		Sample + treatment spike		Recovery	
	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)
	—————————— μg L^{-1} ——————————				———— % ————	
Synthetic irrigation water	0.0	0.0	–	–	–	–
	7.5	22.5	4.0	9.1	53.3	40.4
	15.0	15.0	6.8	6.7	45.3	44.7
	22.5	7.5	9.6	2.7	42.7	36.0
Average recovery					47.1	40.4
Diluted synthetic irrigation water	0.0	0.0	–	–	–	–
	7.5	22.5	7.0	23.6	93.3	105
	15.0	15.0	14.0	15.3	93.3	102
	22.5	7.5	21.7	7.8	96.4	104
Average recovery					94.3	104

Table 41-3. Arsenic concentrations and recoveries of spiked sample solutions.

Sample	Treatment spike		Sample + treatment spike		Recovery	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
	—————————— μg L^{-1} ——————————				———— % ————	
Synthetic irrigation water	0.0	0.0	–	–	–	–
	7.5	22.5	7.4	0	99.2	0
	15.0	15.0	14.8	0	98.4	0
	22.5	7.5	24.4	0	108	0
Average recovery					102	0
Filtered synthetic irrigation water	0.0	0.0	–	–	–	–
	7.5	22.5	6.2	21.9	82.7	97.3
	15.0	15.0	14.6	19.0	97.3	108
	22.5	7.5	24.1	8.7	107	112
Average recovery					95.7	106

SAMPLE PREPARATION

The preservation and stabilization of As and Se redox states in natural waters is of major concern. After collection in the field, samples should be filtered immediately through a 0.45-μm filter. Filtration through a 0.1-μm filter compared with a 0.45-μm filter did not affect the speciation of As (McCleskey et al., 2004). Maintaining samples in the dark also aids in preserving redox states. It is also recommended that samples be stored at 4°C to maintain As (Hall et al., 1999) and Se (Héninger et al., 1997) speciation. The USEPA recommends that water samples for trace metal analysis be acidified to pH <2 with HNO_3 (USEPA, 1982); however, HNO_3 is not recommended for use with HGAAS because of NO_3^- interference in the analysis (Gómez Ariza et al., 2000). McCleskey et al. (2004) recommended HCl

for preservation of As redox states. For Se analysis, however, HCl is not recommended because it reduces selenate to selenite. Therefore, Héninger et al. (1997) recommended H_2SO_4 for preservation of Se redox states. Preservation of redox states using ethylenediaminetetraacetic acid (EDTA), as recommended by Bednar et al. (2002), is not recommended for HGAAS because the metals sequestered by EDTA can cause interference in the analysis (McCleskey et al., 2004).

PROCEDURE

To achieve separation of the inorganic As and Se species, the sample and eluent are first passed through a Dionex IonPac AG11 (4 by 50 mm) guard column and then passed through a Dionex IonPac AS11 (4 by 250 mm) analytical column.

Procedure—Arsenic

The analytical column is linked to the hydride generator with a 0.1-m piece of polyethylene tubing to allow continuous flow of the column effluent to the hydride generator. The arsine generated from dissolved As(III) and As(V) is mixed with 6 mol L^{-1} HCl and 0.16 mol L^{-1} $NaBH_4$/0.12 mol L^{-1} NaOH and then stripped from solution with Ar and swept into an air–acetylene flame heated quartz tube in the spectrophotometer light path.

Procedure—Selenium

The sample, eluent, and 12 mol L^{-1} HCl are pumped into a PEEK tee (0.127-cm through hole, 3.06-μL swept volume) and mixed with the sample to begin the reduction of Se(VI) to Se(IV). The acidified sample and eluent are passed from the tee into a 1.5-m length of PEEK tubing (0.16-cm o.d., 0.10-cm i.d.) that has been coiled to a diameter of 15 cm so as to fit inside an aluminum sand bath box (17.8 by 17.8 by 10.2 cm) containing sand 5 cm deep. The sand bath box rests on a hotplate that maintains the sand at 130°C. Heating of the acidified sample greatly enhances the reduction of Se(VI) to Se(IV). The heated, acidified sample is passed from the sand bath into a 1-m length of PEEK tubing (0.16-cm o.d., 0.05-cm i.d.) coiled inside a 15-cm-diameter reservoir that is 7.6 cm in height. This reservoir is filled with ice and serves as an ice bath to cool the heated, acidified sample. The cooled, acidified sample then passes from the ice bath into a polypropylene tee (0.16 by 0.16 by 0.16 cm) linked to the hydride generator. Hydride solution containing 0.16 mol L^{-1} $NaBH_4$ and 0.12 mol L^{-1} NaOH is also pumped into the tee and mixed with the sample to form the arsine. The arsine is then stripped from solution with Ar and swept into an air–acetylene flame heated quartz tube in the light path of the atomic absorption spectrometer.

RESULTS

Standard solutions of As and Se were used to test the sensitivity of the speciation technique. Multiple injections of As(III) and As(V) or Se(IV) and Se(VI) gave highly reproducible measurements with precision typically better than ±5%. The

detection limits, calculated as three times the standard deviation of more than 10 blank readings were $0.68\ \mu g\ L^{-1}$ for Se(IV) and $0.55\ \mu g\ L^{-1}$ for Se(VI) using a 200-μg injection loop or $0.8\ \mu g\ L^{-1}$ for both As species using a 250-μg injection loop. Mixed standards containing equimolar amounts of both redox states were analyzed in the range of 1 to $30\ \mu g\ L^{-1}$. The results are presented in Fig. 41-3 for As(III)/As(V) and Fig. 41-4 for Se(IV)/Se(VI). Our method provides complete resolution of the two redox states while minimizing the overall run time to <6 min per sample for As(III) and As(V) and 8 min per sample for Se(IV) and Se(VI). Advantages of the coupled methodology include less use of and exposure to acids because a digestion step in the fume hood is eliminated and shorter analysis time because both redox species can be analyzed in one chromatographic run.

To evaluate the ability of our methods to accurately determine known concentrations of As and Se, we analyzed two SRMs from the NIST intended for use in evaluating methods for determining trace elements in freshwater. Certification of SRM 1640 is $22.0 \pm 0.5\ \mu g\ Se\ L^{-1}$. Sextuplicate analyses with our speciation method determined the concentration of SRM 1640 to be $21.0 \pm 1.0\ \mu g\ Se\ L^{-1}$ (96% recovery), with all Se being present as Se(VI). Certification of SRM 1643e is $12.0 \pm 0.1\ \mu g\ Se\ L^{-1}$. Sextuplicate analyses with our speciation method determined the concentration of SRM 1643e to be $12.0 \pm 1.1\ \mu g\ Se\ L^{-1}$ (100% recovery), with all Se being present as Se(IV). Our results for both SRMs are not statistically significantly different than the NIST results at the 95% level of confidence. The SRMs contain a background of 0.5 or $0.8\ mol\ L^{-1}\ HNO_3$. This apparently interferes with the As analyses (Gómez Ariza et al., 2000) because our recoveries were low. Acidification with HNO_3 has been observed to change the redox species distribution by reducing arsenate to arsenite (Hall et al., 1999). In our analyses, we observed reduction of arsenate in mixed As(III)/As(V) standards contained in $0.5\ mol\ L^{-1}\ HNO_3$.

The capability to determine As and Se in simulated irrigation waters of varying As(III)/As(V) and Se(IV)/Se(VI) ratios in spiked sample solutions was tested. As shown in Table 41-2, Se spike recoveries deviated by $\leq 1.8\ \mu g\ L^{-1}$ for Se(IV) and $\leq 1.5\ \mu g\ L^{-1}$ for Se(VI) from the expected values at all addition ratios in the diluted synthetic irrigation water. Recoveries of Se(IV) were consistently less than the spike concentrations by an average of 6%, while recoveries of Se(VI) were consistently greater than the spike concentrations by an average of 6%. For the undiluted synthetic irrigation water, spike recoveries for both Se redox states were very poor, ranging from only 36 to 53%. We believe this was the result of the saturation of exchange sites on the column because chromatographic resolution was compromised. Peak width was broadened and peak height was reduced. These results indicate that the Se speciation method should not be used on sample solutions having EC values $>1\ dS\ m^{-1}$.

As shown in Table 41-3, As spike recoveries deviated by $\leq 1.9\ \mu g\ L^{-1}$ for As(III) and $\leq 1.5\ \mu g\ L^{-1}$ for As(V) from the expected values at all addition ratios in the synthetic irrigation water. Recoveries of As(V) were consistently zero in the unfiltered synthetic irrigation water because the presence of Ca interfered with the determination of As(V). These results indicate that the As speciation method should be used only on sample solutions that have been filtered to remove Ca before analysis.
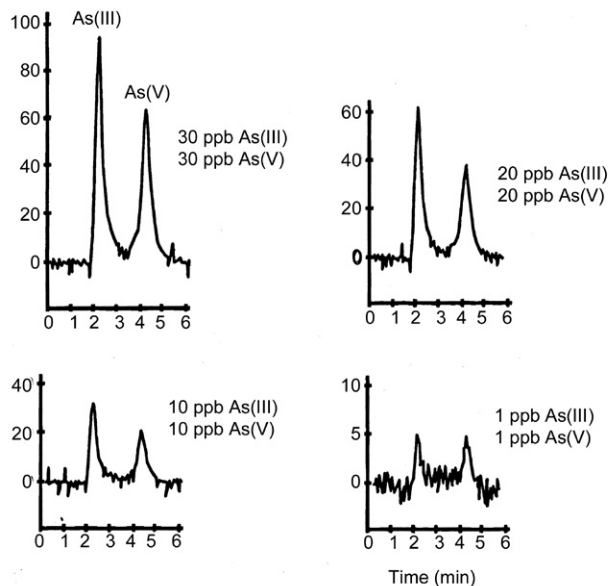
Fig. 41-3. Ability of the speciation method to analyze mixed standards in the range of 1 to 30 µg As L⁻¹ (from Manning and Martens, 1997).
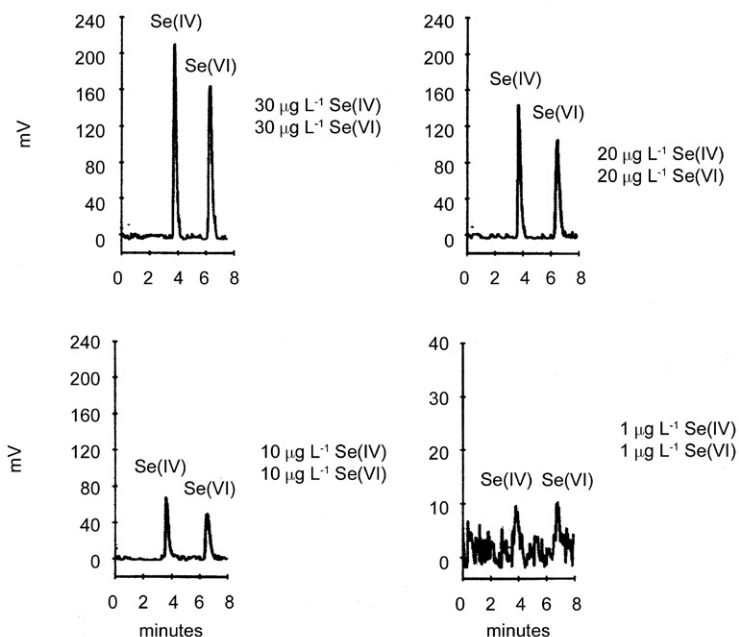

Fig. 41-4. Ability of the speciation method to analyze mixed standards in the range of 1 to 30 µg Se L⁻¹ (from Goldberg et al., 2006).

CONCLUSIONS

The results of this study show that the HPLC–HGAAS technique for speciation of As(III)/As(V) and Se(IV)/Se(VI) has both advantages and disadvantages. The primary advantage is that the HGAAS technique gives excellent, element-specific detection. Proper As(III)/As(V) and Se(IV)/Se(VI) species preservation and reasonably good chromatographic separation yield good results that are reliable and useful in monitoring As(III)/As(V) and Se(IV)/Se(VI) redox speciation.

The primary disadvantages of the HPLC–HGAAS technique involve challenging sample matrices that limit the overall accuracy of the technique. The presence of a high salt concentration (EC = 4.77 dS m^{-1}) in a synthetic irrigation water resulted in poor recoveries (36–53%) of both Se(IV) and Se(VI) added in various ratios. Recoveries were greatly improved (93–105%) when the EC was lowered to 1 dS m^{-1} by including a dilution step. The speciation of As(III)/As(V) was also sensitive to high EC; however, this problem was probably due to a specific interference of Ca with the recovery of As(V). Sample dilution or Ca removal by filtration is necessary for accurate determination of As(V). Sample matrices that contain HNO$_3$, for example when added as an acidification/preservation step, can also interfere with accurate As(III)/As(V) quantification by reduction of As(V) to As(III). This problem can be overcome by the choice of an alternative acid such as HCl for As or H$_2$SO$_4$ for Se as needed.

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