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Speciation of Arsenic(M) and Arsenic(V) in Sediment Extracts by High-Performance liquid Chromatography-Hydride Generation Atomic Absorption Spectrophotometry

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Determining the redoxstates of arsenic (As) in environmental samples is important due to the pronounced differences in toxicity and mobility of the various forms. We have combined the separation capabilities of high-performance liquid chromatography (HPLC) with the sensitivity and element specificity of hydride generation atomic absorption spectrometry (HGAAS) to determine arsenite [As(III)] and arsenate [As(V)], which have been shown to be the most toxic and prevalent forms of As in soil and water. The HPLC-HGAAS technique gave retention times of 2.2 and 4.2 min for As(III) and As(V), respectively. Detection limits of 200 pg of As (0.8 $\mu g L^{-1}$ As in solution) were obtained for both As(III) and As(V). The technique was used to determine As(III) and As(V) in deionized water and 1 mM PO_4 sequential extracts of estuarine sediment, coal fly ash, and saline evaporation pond sediment. Coal fly ash contained no detectable deionized water-extractable As(III) or As(V), but contained appreciable PO_4-extractable As(V). The As(III) species was detected in all extracts of estuarine sediment, though 1 mM PO_4 released primarily As(V). Evaporation pond sediment also contained primarily PO_4-extractable As(V).

Introduction

Arsenic is a potentially toxic trace element that is 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. The toxicity and mobility of As depends on its chemical form or 'species' (1). Although there are several definitions of the terms species and speciation in the literature, most refer to speciation as the determination of the individual concentrations of the various chemical forms of an element that together make up the total concentration of the element (2). In this paper, we use the terms speciate and speciation to mean the separation and detection of the inorganic As(III) and As(V) species. Numerous techniques have been developed to speciate As, but most are too laborious for routine analysis, require expensive analytical equipment that is generally not available in most laboratories, or are not sensitive enough to reliably determine separate As species at trace levels. Routine and accurate techniques to separate and detect low levels of As(III) and As(V) are needed.

The soluble species of As that have received considerable attention are arsenious acid [H_3AsO_3 or As(III)], arsenic acid [H_3AsO_4 or As(V)], monomethylarsonic acid [$CH_3AsO(OH)_2$ or MMAA], and dlmethylarsinic acid [$(CH_3)_2AsO(OH)$ or DMAA]. Other organic As compounds that have been detected in seafood (3) and human urine (4) include arsenobetaine [$(CH_3)_3As^+CH_2COO^-$], arsenocholine [$(CH_3)_3As^+CH_2CH_2OH$], tetramethylarsonium ion [$(CH_3)_4As^+$], trimethylarsine oxide [$(CH_3)_3AsO$ or TMAO], and certain arsenosugar compounds. Although these compounds are of great biological importance, they are generally **not** detectable in natural waters or soil. Therefore, As(III), As(V), MMAA, and DMAA have been the focus of most analytical techniques for speciatlng As in environmental samples.

A **variety** of techniques have been proposed for separating and detecting As(III), As(V), MMAA, and DMAA. The cryogenic trap HGAAS technique has been extensively used (5-9) and is highly sensitive, being able to detect as little as 13 pg of As (7,9) The disadvantages of cryogenic trap HGAAS are (1) separate runs are required to determine As(III) and As(III + V) and (2) the technique is too time-consuming for routine analysis. Other techniques for separating As(III) and As(V) in environmental samples include solvent extraction coupled with an element-specific detector (10-14), colorimetry (15), ion chromatography-colorimeny (16, 17), suppressed ion chromatography (18), voltammetry (19), and selective HGAAS using an oxalate buffer (20). These techniques also suffer from one or more disadvantages such as the need for organic solvents, time-consuming sample preparation, determining the As(V) species by difference between separate analyses, or a lack of sensitivity.

Chromatography interfaced with element-specific detectors has been proposed as the most reliable and sensitive technique for element speciation (21, 22). The primary advantage of this approach is that unequivocal species separation by chromatography is coupled with sensitive and specific in-line detection with simple interfaces between **readily available** instrumentation. A variety of detectors have been coupled with HPLC including flame atomic absorption spectrometry (HPLC-FAAS) (23), graphite furnace atomic absorption spectrometry (HPLC-GFAAS) (24,25), inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) (26, 3,4), and atomic fluorescence spectrometry (27). Unfortunately, most of these techniques have significant disadvantages for As(III)/As(V) speciation. For example, FAAS detection lacks the sensitivity required for most environmental applications. The GFAAS technique is not a flow-through detector, and therefore fraction collection is required after HPLC. The ICP-MS detector, while being in-line and highly sensitive, suffers from interferences between As and $ArCl^+$ (both *m/z* 75) and, additionally, is not yet standard equipment in most labs.

Coupling HPLC with hydride generation has been shown to be the most routine and sensitive means of speciating As using standard analytical instrumentation. The technique has been used to speciate As(III), As(V), MMAA, and DMAA in food extracts (28), human urine (29, 30), and soil pore waters (31, 32). The use of HPLC with hydride generation and ICP as an element-specific detector (HPLC-HGICP) has been reported (33), although HGAAS is more sensitive and allows more **flexibility** in the use of different types of atomizers in the light path.

Studies that have used sensitive techniques such as cryogenic trap HGAAS (34,8), HPLC-HGAAS (31)) and HPLC-

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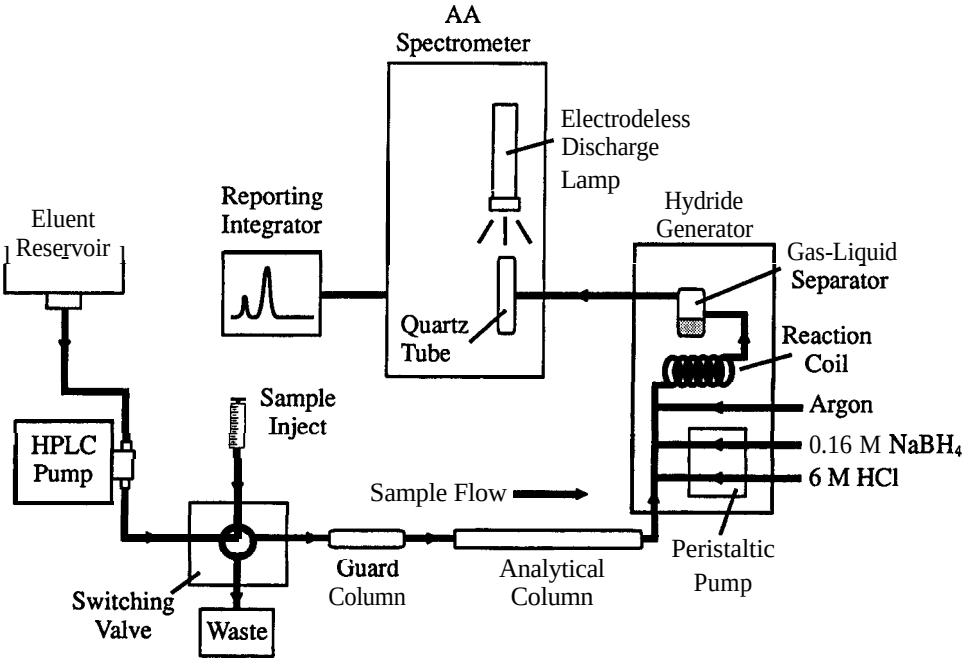

FIGURE 1. Schematic diagram of the high-performance liquid chromatography-hydride generation atomic absorption spectrophotometry (HPLC-HGAAS) system.

ICP-MS (26) to speciate As(III), As(V), MMAA, and DMAA in soil and water have shown that the predominant species are inorganic As(III) **and As(V).** Andreae (5) used cryogenic trap HGAAS and found that organoarsenicals (MMAA and DMAA) constituted a maximum of 5% and typically less than 1% of total soluble As in natural waters. Also using cryogenic trap HGAAS to measure the seasonal variation in As(III), As(V), MMAA, and DMAA speciation in surface seawater, Comber and Howard (7) measured **predominantly** As(V) In addition, Haswell et al. (32) speciatedAs(III), As(V), MMAA, and DMAA in soil pore waters by HPLC-HGAAS and found that the predominant species were As(III) and As(V).

We report here on **a** robust, sensitive, and routine analytical technique for the direct, simultaneous determination of inorganic As(III) and As(V) using HPLC-HGAAS. The technique has been applied to sediment and coal fly ash extracts containing As(III) and/or As(V). Because previous work has demonstrated the importance of the inorganic As(II1) and As(V) species (26,12,8), we have concentrated on optimizing the HPLC-HGAAS system for rapid separation and detection of As(III) and As(V).

Experimental Section

Reagents. All chemicals used were of reagent grade. Deionized (DI) water was produced with Millipore deionizing cartridges. Mobile phase was prepared by degassing DI water while stirring and boiling under vacuum for 15 min followed by cooling. An appropriate volume of 50% w/w NaOH solution (Fisher) was pipetted into the degassed water followed by vacuum filtration through a 0.1-μm membrane. The solution was decanted into a polyethylene bladder with the addition of 10 mL of methanol (Fisher) L^{-1} resulting in final mobile phases of 25,30, or 40 mM NaOH in 1% methanol. The 0.16 M NaBI-IJ0.12 M NaOH solution was also vacuum filtered prior to analyses. Instrapure HCl (Baker) was used to make 6 M HCl. Separate stock solutions of 1000 mg L^{-1} A.s(III) or As(V) were made by dissolving 0.86 g of $NaAsO_2$ or 2.08 g of $Na_2HAsO_4 \cdot 7H_2O$ in 500 mL of 0.1 M NaCl. Single ion and mixed ion [As(III) + As(V)] working standards (5-30 $\mu g\ L^{-1}$) were prepared fresh daily in the appropriate matrix for the analysis.

Apparatus. The equipment required for the separation, hydride generation, and detection of As(III) **and** As(V) is listed in Table 1 and shown schematically in Figure 1. The separation of As(III) and As(V) was achieved using a Dionex OmniPac PAX-500 (4.6 x 250 mm) analytical anion-exchange column (Dionex Corp., Sunnyvale, CA) preceded by an OmniPac PAX-500 guard column (4.6 x 45 mm). The stationary phase is composed of a multiphase substrate with a highly cross-linked ethylvinylbenzene/divinylbenzene polymeric core coated with a quatemary ammonium functionalized colloid allowing both anion and reversed phase chromatography. We also used Dionex **IonPac AS1** 1 analytical

TABLE 1. HPLC-HGAAS System and Operating Parameters

	HPLC
pump	Dionex DQP-1
switching valve gas	90 psi N_2
guard column (size)	Dionex OmniPac Guard PAX-500 (4.6 x 45 mm) or Dionex IonPac AS11 (4.6 x 45 mm)
column (size)	Dionex OmniPac PAX-500 (4.6 x 250 mm) or Dionex IonPac AS1 1 (4.6 x 250 mm)
mobile phase (flow rate)	30 mM NaOH/1% methanol (1 mL min^{-1})
sample inject volume	250 μL
	Hydride Generation
model	Varian VGA-76
argon flow rate	40 mL min^{-1}
0.16 M $NaBH_4$ flow rate	1 mL min^{-1}
6 M HCl flow rate	1 mL min^{-1}
	Atomic Absorption Spectrophotometer
model	Perkin Elmer 30308
lamp	Perkin Elmer EDL
EDL power	8 W
wavelength	193.7 nm
bandwidth	0.7 nm
flame	air-acetylene
	Integrator
model	Hewlett Packard 3393A
zero setting	10
attenuation (ATT 2^)	7
chart speed	0.5 cm min^{-1}
area reject	500 000
threshhold (THRSH)	6
peak width (PK WD)	0.16

TABLE 2. Deionized Water. and 1 mM PO_4-Extractable As(III) and As(V) in Estuarine Sediment, Coal Fly Ash, and Evaporation Pond Sediment as Determined by HPLC–HGAAS[a]

	DI water		1 mM PO4	
sample	As(III)	As(V)	As(III)	As(V)
MESS-1	21.5	65.0	20.5	215
PACS-1	24.6	ND[b]	51.2	950
NBS 1646	22.6	ND	12.0	194
NBS 1633b	ND	ND	ND	1490
KRS pond 2[c]	23.0	ND	ND	137
KRS pond 7	ND	40.0	ND	65.0
KRS pond 9	ND	15.0	ND	59.0

[a] As(III) and As(V) contents are expressed in μg kg-'. [b] ND, not detected. [c] KRS, Kesterson Reservoir Sediment.

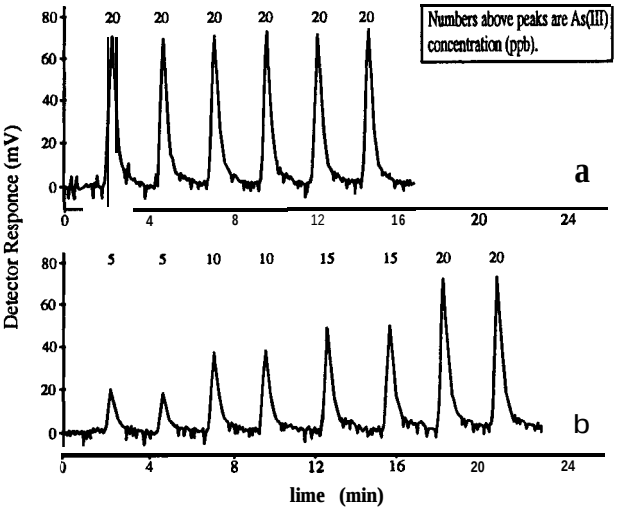

FIGURE 2. HPLC-HGAAS chromatograms using the OmniPac PAX-500 column showing multiple injections of 20 ppb As(III) standard solution (a) and duplicate injections of 5, IO, 15, and 20 ppb As(III) standard solutions (b). See Table 1 for run parameters.

and guard columns, which provided better separation and overall performance than the OmniPac PAX-500 columns. Occasionally, a manufacturer-recommended column regeneration sequence was used to remove hydrophilic and hydrophobic contaminants from the columns (originating from soil and sediment extracts), which can be retained by the stationary phase causing fewer of the anion exchange sites to be available for sample ions. The sequence involved allowing 1 M HCl, 10% methanol, and 1 M NaOH solutions to flow through the columns (1 mL min^{-1}) for **15 min each step with 5-min** DI water rinse steps between each step.

The HPLC column was linked to the continuous hydride generator with a IO-cm piece of polyethylene tubing allowing column effluent to flow continuously to the hydride generator. The arsine generated from dissolved As(III) and As(V) upon **mixing with 6 M HCl and 0.16 M $NaBH_4$/0.12 M NaOH reagents** was stripped from solution with Ar and swept into an air-acetylene flame heated quartz tube in the spectrophotometer light path. Absorbance signal peak areas were recorded by linking a Hewlett Packard 3393A integrator with the Perldn Elmer 3030B AA spectrophotometer by the 1-V recorder output. Samples were also analyzed by conventional flow-through HGAAS without HPLC for comparison.

The parameters listed in Table 1 were optimum for determination of As(III) and As(V) in the concentration range from 1 to 30 $\mu g\ L^{-1}$ in sediment extracts, although these parameters can be adjusted to suit the needs of the analyst. For example, the overall sensitivity of the technique can be controlled with the integrator attenuation function. Increasing the sample injection volume and $NaBH_4$ concentration

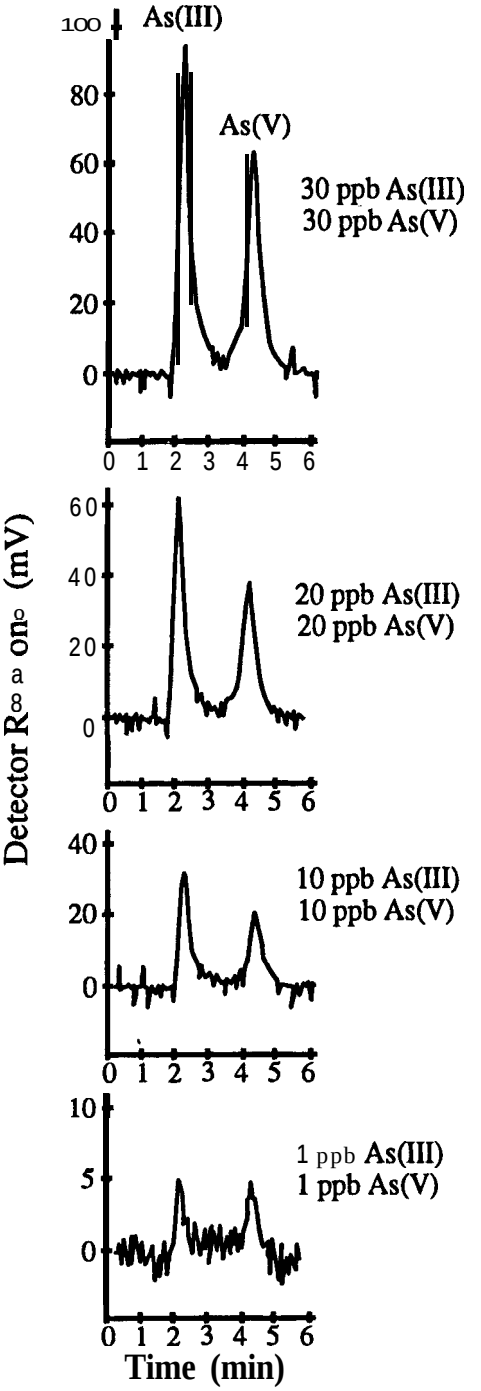

FIGURE 3. Representative HPLC-HGAAS chromatograms using the OmniPac PAX-500 column showing injections of As(III) + As(V) mixed standard solutions. Retention times for As(III) and As(V) were 2.2 and 4.2 min, respectively. All run parameters are those given in Table 1, except for 1 ppb As(III) + 1 ppb As(V) where the 3393A integrator attenuation (ATT 2^) was set at 5.

will decrease the effective detection limit and the As(III) and As(V) peak separation can be increased by using a less concentrated mobile phase.

Sequential Extracts The materials used in this study were estuarine sediment **standard reference** material (MESS-l and PACS-1, National Research Council, Ottawa, Canada), coal fly ash standard reference material (1633b, National Institute of Standards &Technology), and evaporation pond sediments from Kesterson Reservoir (Merced Co., CA). Sequential extracts of materials were created by weighing 2 g of solid directly into polycarbonate centrifuge tubes. Distilled deionized water (20 mL) was added to the solids, and the tubes

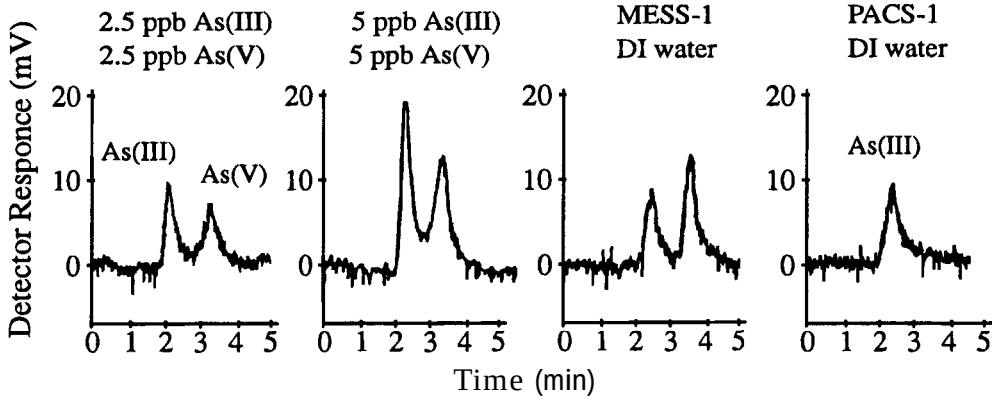

FIGURE 4. HPLC-HGAAS chromatograms using the OmniPac PAX-500 column of two As(III) + As(V) mixed ion standard solutions and the DI water extracts of MESS-1 and PACS-1 estuarine sediment The DI water extracts were spiked with 100 mM PO, solution to make 1 mM PO_4 final concentration in the extracts. For these injections, the 3393A integrator attenuation (All 2^) was set at 6.

were shaken on a reciprocating shaker for 2 h. The tubes were centrifuged (12500g), and the supematants were decanted and filtered through 0.1-μm Whatman membranes. In some cases, 100 mM PO_4 solution (50:50 KH_2PO_4:K_2HPO_4) was added to DI water sample extracts to make a 1 mM PO_4 concentration. The presence of 1 mM PO_4 in sample injections decreased the As(V) retention time and improved As(V) peak shape for integration when using the OmniPac PAX-500 column. The separation and detection of As(III) and As(V) using the IonPac AS11 column was less sensitive to the presence of 1 mM PO_4.

The second extract was created by resuspending the solids in 20 mL of 1 mM PO_4 (50:50 KH_2PO_4:K_2HPO_4) followed by the same procedure as the DI water extract. The PO_4 concentration in standards was matched with that of samples for all HPLC-HGAAS analyses. The effects of the PO_4 concentration in the sequential extraction solution were investigated by extracting standard reference materials first with DI water and then different sample suspensions were treated with 1, 10, 20, and 50 mM PO_4 concentration. The MESS-l, PACS-1, and NBS 1633b reference materials contain certified total As values of 10.6,211, and 136.2 mg kg^{-1}. We recognize that these As levels are not recoverable in aqueous extracts but require total dissolution of As in the solid phase. This experiment was designed to investigate the quantity and speciation of PO_4-extractable As and was not designed to recover total As in the solid phase.

In a preliminary investigation, conventional spike and recovery of added As(III) and As(V) to extracts revealed poor recoveries of As(V) added to Kesterson Reservoir sediment (KRS) sample DI water extracts when measured by HPLC-HGAAS. Further investigation revealed that high concentrations of Ca^{2+} in KRS DI water extracts may complex $HAsO_4^{2-}$ anions and become bound on the anion exchange column. This problem was avoided by removing Ca^{2+} with no. 2 Dowex 50W-X8 cation exchange resin (100-200 mesh, H^+ form) that was slurry-packed in 0.9 cm (i.d.) x 6.5 cm SPE columns. Good recoveries of As(V) added before and after Dowex resin cleanup were then obtained. This problem was not encountered with the other materials studied. All As(III) and As(V) values reported in KRS DI water extracts (Table 2) were derived from extracts subjected to Ca^{2+} removal.

All extracts were analyzed immediately by HPLC-HGAAS in our experiments. However, in cases where environmental sampling requires a substantial storage time prior to analysis, a sample preservation scheme must be considered to minimize conversion between the As(III) and As(V) oxidation states. Studies of the stability of As(III) and As(T) in sediment interstitial water (35) have shown that samples are best preserved by acidification to pH 2, deaeration with On-free N_2, and refrigeration at 2 °C. Decreases in As(III) and As(T) were found when samples were not treated due to oxidation of As(III) and precipitation of Fe(III) and Mn(IV) during storage.

Results and Discussion

Standard Injections. The precision and sensitivity of the HPLC-HGAAS technique was determined by the injection of standard solutions. Multiple injections of As(III) alone (Figure 2a) and duplicate injections of As(II1) from 5 to 20 $\mu g\ L^{-1}$ As (Figure 2b) showed that both peak area and peak height were highly reproducible measurements with a precision typically better than ±4%. Mixed standards containing ($\mu g\ L^{-1}$) concentrations of both As(III) and As(V) were used to optimize the HPLC separation, i.e., provide adequate resolution of the two species, maintain good peak shapes for integration, and minimize the overall run time. The final conditions used are given in Table 1, and chromatograms of mixed standards are shown in Figure 3. The following expression was used to calculate the detectionlimit for the HPLC-HGAAS technique:

$$x - x_B = 3s_B \quad (1)$$

where x is the signal with minimum detectable As concentration, x_B is the average signal of several blank injections (n > 10), and s_B is the standard deviation of the blank injection readings (36,37). The calculated detection limit was 0.8 $\mu g\ L^{-1}$ As or 200 ug As using a 250-μL inject volume. The baseline noise in Figure 3 is typical of that used to calculate the detection limit.

Sequential Extraction. To assess the applicability of the technique to samples of environmental importance, we chose to determine the As(III)/As(V) speciation in the soluble fractions of standard reference materials and saline evaporation pond sediment. Representative chromatograms of two standard solutions containing ($\mu g\ L^{-1}$) concentrations of As(III) +As(V) and the DIwater extracts of MESS-l andPACS-1 estuarine sediment are shown in Figure 4. Table 2 contains solid-phase concentrations of DI water-extractable and 1 mM PO_4-extractable As(III) and As(V) for all materials studied. The MESS-l material contained both DI water extractable As(III) and As(V), whereas only As(III) was released from PACS-1 sediment. The As(III) species is weakly bound to sediment particles (38,39) and is expected to be more soluble than As(V) because As(III) is predominantly $H_3AsO_3^0$ at environmental pH values and has a first pK_a of 9.2. Arsenic(V) anions ($H_2AsO_4^-$ and $HAsO_4^{2-}$) form strong surface complexes at the mineral-water interface and undergo ligand exchange reactions with $H_2PO_4^-$ and HPO_4^{2-} anions.

The accuracy of the measurement of the As(V) peak area by the integrator was improved when sample matrixes contained 1 mM PO_4 (as 50:50 KH_2PO_4:K_2HPO_4). We suspect

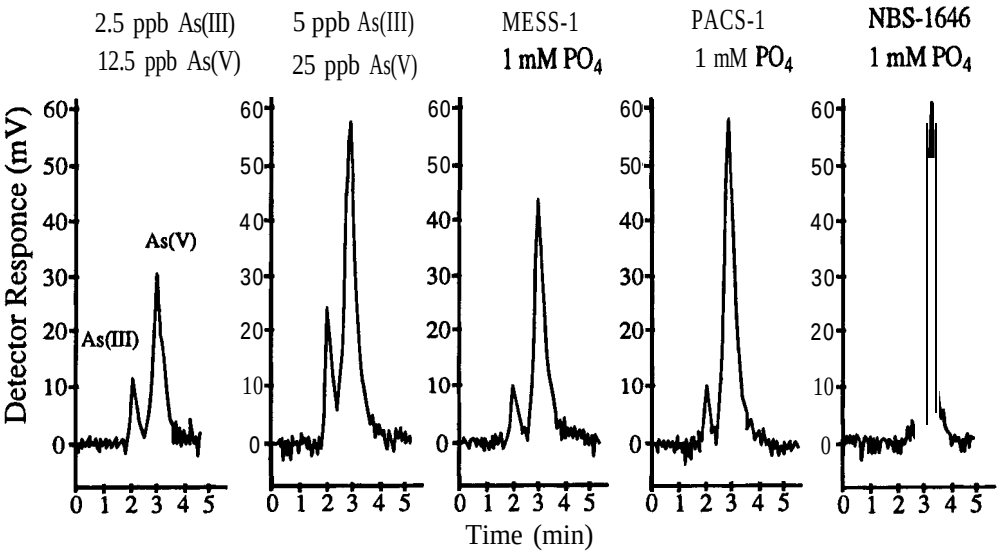

FIGURE 5. HPLC-HGAAS chromatograms using the OmniPac PAX-500 column showing two As(III) + As(V) mixed standard solutions and the 1 mM PO_4 extracts of MESS-I, PACS-1, and NBS-1646 estuarine sediments. Standards and extracts were diluted with 1 mM PO_4.

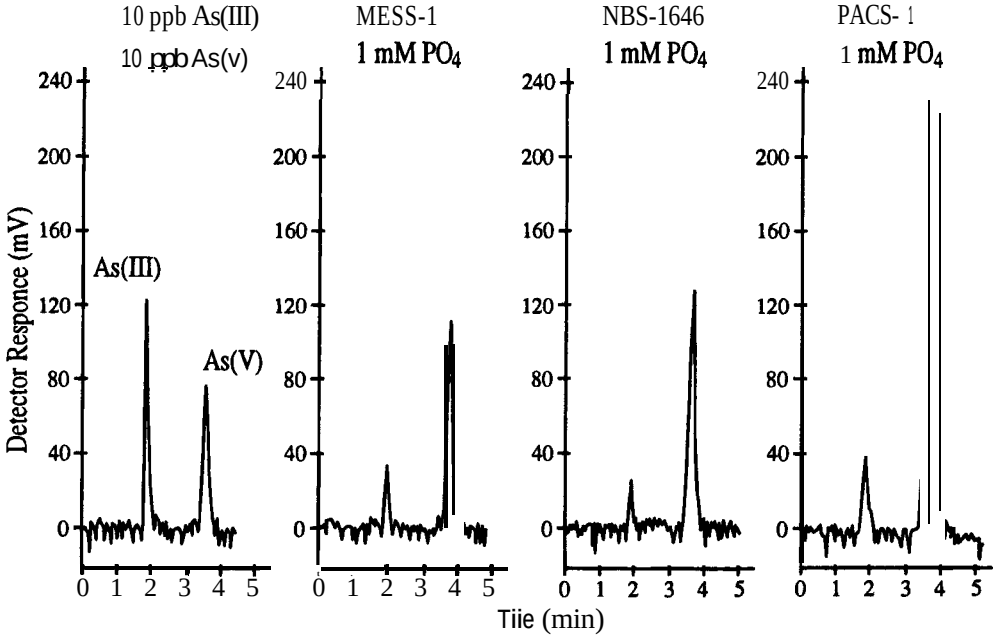

FIGURE 6. HPLC-HGAAS chromatograms using the IonPac AS11 column showing one As(III) + As(V) mixed standard solution and the 1 mM PO_4 extracts of MESS-I, PACS-1, and NBS-1646 estuarine sediments. Retention times for As(III) and As(V) were 1.9 and 3.8 min, respectively. Standards and extracts were dilated with 1 mM PO_4.

that HPO_4^{2-} anions compete with $HAsO_4^{2-}$ anions for anion exchange sites on the column which decreases the As(V) retention time and decreases As(V) peak broadening. Standards used for quantitation should be matrixmatched as closely as possible to samples and should contain a similar As (III) / As(V) relative concentration as in samples for maximum accuracy.

Representative chromatograms of the 1 mM PO_4 extracts of three estuarine standard reference materials using the PAX-500 analytical column are shown in Figure 5. These extracts were also analyzed with the IonPac AS11 column, which provided better resolution of As(III) and As(V) and smaller peak widths (Figure 6). All estuarine sediments contained a similar As(III)/As(V) ratio in the 1 mM PO_4 extract with a low concentration of As(III) relative to As(V). The 1 mM PO_4 extract gave evidence for the persistence of As(III) in air-dried estuarine sediment materials. Shnilar results were obtained by Tye et al. (31), who measured a predominance of As(V) with measurable As(III) in aerated soil. Spiking the 1 mM PO_4 extract of MESS-l with As(III) verified the identity of the small peak at 2.2 min as As(III). The importance of these findings are 2-fold: (1) some As(III) is stable in an air-dry sediment sample and (2) measuring total As in soil, sediment, or water probably does not give sufficient information about the disposition of As in natural samples.

Extracts of coal fly ash indicated that the PO_4-extractable As in this material was exclusively As(V) but that As(V) was not soluble in the DI water extract (Figure 7). For this application, it was appropriate to use As(V) single-ion standards for accurate quantitation. The two-step sequential extraction was not intended to affect the dissolution of total As in coal fly ash because to do so would alter the speciation of soluble As. Moreover, total As is easily determined by conventional HGAAS without HPLC separation. Therefore, the HPLC-HGAAS is appropriate for separating and detecting the As(III) and As(V) species in aqueous samples (either extracts, natural waters, or wastewaters) where the determination of the As(III) and As(V) is important.

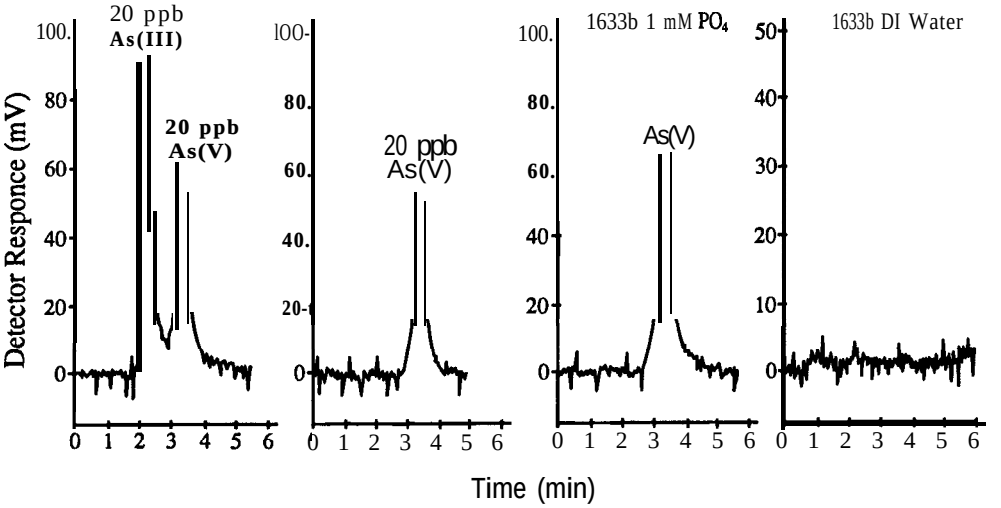

FIGURE 7. HPLC-HGAAS chmmatograms of a mixed As(III) + As(V) standard, a single-ion As(V) standard, and the DI water and 1 mM PO_4 extracts of coal fly ash (NBS-1633b).

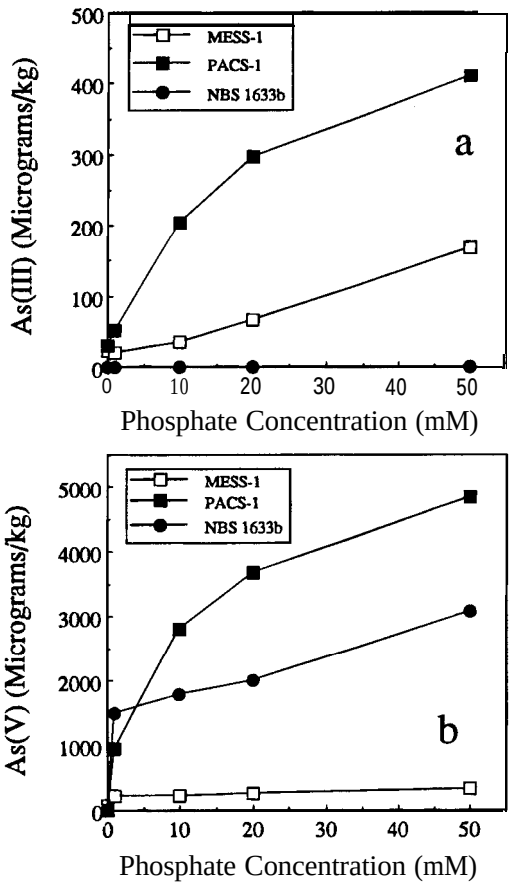

FIGURE 8 Effects of PO_4 extract solution concentration on extractable As(III) (a) and As(V) (b)from estuarine sediments(MESS-1 and PACS-1) and coal fly ash (NBS-1633b).

The extraction of As(III) and As(V) from three reference materials as a function of PO_4 concentration is represented in Figure 8. Data points corresponding to zero PO_4 concentration are the DI water extracts. The PO4 solution concentration had a similar curvilinear effect on both As(III) and As(V) extraction in PACS- 1 estuarine sediment, whereas a linear relationship was found for the other materials. Extraction of PACS-1 with 50 mM PO_4 resulted in the removal of 412 and 4800 mg kg^{-1} As(III) and As(v), respectively, accounting for only 2.2% of the certified solid phase As content. These data suggest that the majority of total As (>95%) is tightly held in the solid phase of these materials.

Kesterson Reservoir sediment (KRS) samples, which are saline (40) and contain a range of soluble As, were also extracted (Table 2). These materials contain predominantly PO_4-extractable As(V) Total As in all extracts was analyzed separately by conventional flow-through HGAAS, and excellent agreement was found with the HPLC-HGAAS technique. We found that samples can be conveniently run by conventional flow-through HGAAS following HPLC-HGAAS analysis by simply disconnecting the HPLC column from the hydride generator. This is recommended for sample matrixes typical of sediment extracts, brines, or wastewaters where high salt backgrounds are expected.

The application of HPLC to separate As(III) and As(V) coupled with HGAAS element-specific detection is a simple, reliable, and sensitive means of determining these species. The technique has proven useful for investigating the speciation of soluble As in estuarine sediment, coal fly ash, and evaporation pond sediment. The two-step sequential extraction scheme designed to extract soluble (DI water-extractable) and adsorbed (1 mM PO_4-extractable) As was shown to primarily remove the more soluble As(III) species with DI water and the more strongly adsorbed As(V) species in the PO_4 extract. Our results suggest that the soluble and readily exchangeable As is a minor fraction (< 5%) of the total solid-phase As in estuarine sediment and coal fly ash standard reference materials. In addition to the application investigated in this study, other potential uses of HPLC-HGAAS include studying rates of transformation between As(III) and As(V) in soil and sediment or assessing the levels of As(III) and As(V) in groundwater, industrial wastewaters, or drinking water.

Acknowledgments

The use of product or trade names in this publication is for descriptive purposes only and does not imply a guarantee or endorsement by the U.S. Department of Agriculture or the U.S. Government.

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