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Simultaneous Determination of Inorganic Arsenic and Antimony Species in Natural Waters Using Selective Hydride Generation with Gas Chromatography/Photoionization Detection

Lynda S. Cutter, Gregory A. Cutter,* and Maria L. C. San Diego-McGlone

Department of Oceanography, Old Dominion University, Norfolk, Virginia 23529-0276

Dissolved arsenic and antimony in natural waters can exist in the trivalent and pentavalent oxidation states, and the biochemical and geochemical reactivities of these elements are dependent upon their chemical forms. A method for the simultaneous determination of As(III) + Sb(III) and As(III + V) + Sb(III + V) has been developed that uses selective hydride generation, liquid nitrogen cooled trapping, and gas chromatography/photoionization detection. The detection limit for arsenic is 10 pmol/L, while that for antimony is 3.3 pmol/L; precision (as relative standard deviation) for both elements is better than 3%. The apparatus is rugged and allows determinations to be made in the field. In addition to determining dissolved arsenic and antimony species, an oxidative digest has been developed to allow the simultaneous determination of the two elements in sediments and biogenic particles. Numerous water and particulate samples have been analyzed by using the described procedures.

INTRODUCTION

In natural waters the metalloid elements (e.g., As, Sb, Se) can exist in a variety of oxidation states and chemical forms within a given oxidation state (*1-3*). Thus, the determination of the chemical forms of metalloid elements is an essential part of studying their biogeochemical cycles. Furthermore, the chemical forms of selenium and arsenic have been used to estimate the redox intensity in rainwater (e.g., refs 4, 5). The conventional method for speciating metalloids involves selective hydride generation and atomic absorption detection. While this method has sufficiently low detection limits for concentrations found in natural waters (i.e., nano- to picomolar), each element must be determined individually. The simultaneous determination of metalloid species therefore presents a significant advantage.

Recently, Vien and Fry (*6*) reported a method for the simultaneous determination of total arsenic, antimony, selenium, and tin using hydride generation, gas chromatographic separation of the volatile hydrides, and detection by photoionization. Unfortunately, the chemical conditions required to selectively generate hydrides from the different forms of these elements are mutually exclusive (i.e., iodide must be present to quantitatively generate stibine (SbH_3) from Sb(V), but iodide interferes in the determination of selenium). However, the chemical conditions for selectively generating hydrides from arsenic and antimony species are sufficiently similar to allow their simultaneous determinations. This paper describes a method that is specifically designed to determine these elements in natural waters, with the required detection limits and analytical precision. Further, the apparatus is rugged and can be used for shipboard determinations. Since the chemical forms of arsenic and antimony are not stable during conventional sample storage (e.g., acidification), de-

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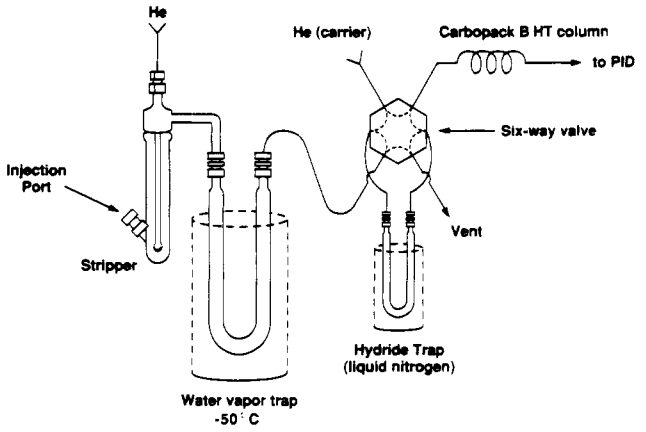

Figure 1. Appartus for the determination of arsenic and antimony species using selective hydride generation. Single lines indicate Teflon tubing, while double lines represent glass tubing.

terminations in the field are necessary. The method has been applied to the analysis of a variety of marine, fresh water, and rain water samples. In addition, a wet oxidative digest for sediments and biogenic materials has been developed to allow the simultaneous determination of total antimony and arsenic in particulate matter. When sample size is limited (e.g., filtered particles), this application of the method is extremely valuable.

EXPERIMENTAL SECTION

Apparatus. The apparatus used to generate and collect the hydrides from aqueous solutions is shown in Figure 1. The glass stripping vessel and water trap (glass U-tube immersed in 2-propanol at −50 °C by using an immersion cooler) are exactly the same as those described by Cutter (*7, 8*). For samples of anoxic water, a 5 cm long, 6-mm (o.d.) glass tube that is loosely packed with glass wool soaked in 1 M zinc acetate is placed between the stripper and water trap to remove hydrogen sulfide. The generated arsine (AsH_3) and stibine are collected in a glass U-tube (16 cm long, 6 mm o.d.) packed with glass wool treated with dimethyldichlorosilane. This trap is interfaced to the gas chromatograph/photoionization detector (HNU Model 321 with a 10.2-eV lamp; attenuation ×10) by using a six-way, stainless steel chromatographic valve (Whitey). The valve is plumbed so that there are two positions; strip/trap and column/inject. In the strip/trap position, the effluent from the stripping apparatus passes through the hydride trap and is then vented to the atmosphere; carrier gas passes directly into the GC column. In the column/inject position, the carrier gas passes through the hydride trap and into the GC column, while the stripping gas is vented directly to the atmosphere. All glass surfaces are treated with dimethyldichlorosilane, and all connections are made with Teflon Swagelok connectors and Teflon tubing.

The gas chromatographic column consists of a 4-m, $^1/_8$-in. Teflon (TFE) tube packed with Carbopack B HT 100 (40/60 mesh, Supelco). The following gas flow rates and column conditions are used: stripping gas, 100 mL/min helium; carrier gas, 30 mL/min helium; column temperature, 30 °C (70 °C when not in use); detector temperature, 125 °C. An integrator/plotter (HP 3392A) is used to record chromatograms and determine peak areas.

Reagents and Standards. Reagents for the hydride determination are exactly as described by Andreae et al. (*9*). All reagents and acids are reagent grade (Baker) with the exception of Baker "Instra-analyzed" nitric acid. Zero grade helium is used for both stripping and carrier gas with additional in-line oxygen and activated charcoal traps. The hydrochloric acid is bubbled with a stream of helium (30 mL/min) for 3 h (for a 2.4-L bottle) to remove free chlorine gas. It is subsequently passed through 10 mL of AG1×8 resin (100/200 mesh, Bio-Rad; washed with 4 M HCl) held in a chromatographic column (Econo-column, Bio-Rad) to remove any arsenic and antimony contamination and stored in a glass bottle until dispensed. Potassium iodide (1 M) and 4% (w/v) sodium tetrahydridoborate (Alfa) are made fresh every 4 h, since they are not stable with storage. Tris–HCl is 2.5 M and is stored in a glass reagent bottle until use. A 1-ml aliquot of this solution should adjust the pH of a 50-mL sample to 6.2. Potassium persulfate is 4% (w/v) and is made fresh daily. Distilled, deionized water (DDI) is used throughout the procedure for reagents and sample dilutions.

The following standard reference materials were employed: National Institute of Standards and Technology (NIST) Bovine Liver (SRM 1577), River Sediment (SRM 1645), Estuarine Sediment (SRM 1646), and International Atomic Energy Agency (IAEA) Copepod Homogenate (MA-A-1). Standards [1000 ppm of As(V) and Sb(V)] were obtained from Baker. Ultrapure antimony trioxide (Sb_2O_3, Alfa) and arsenic trioxide (As_2O_3, MCB) were used to make Sb(III) and As(III) standards (1000 ppm), respectively.

Procedures. *Sample Processing.* Water samples that cannot be analyzed within approximately 12 h of collection should be placed in high-density polyethylene bottles (three-fourths full) and rapidly frozen by immersion in liquid nitrogen. Sediments and biogenic matter should be kept frozen prior to processing. Particulate matter is dried at 40 °C, ground with an agate mortar and pestle, sieved through a 150-μm mesh polyethylene screen, and stored in a clean polyethylene bottle. Filtered particulate material is stored frozen in polyethylene vials until digested. Water samples are thawed by using a microwave oven (do not allow temperature to rise above 30 °C) just prior to analysis.

Determination of Aqueous As(III) and Sb(III). Between 5 and 50 milliliters (depending on concentration) of fresh or thawed sample is transferred to the stripper bottom and the volume brought to 50 mL with DDI. A 1-mL aliquot of 2.5 M Tris–HCl is added (the pH at this point should be 6.2), the bottom is reattached to the stripper, and the system is allowed to purge for 2 min. After purging, the hydride trap is placed in liquid nitrogen and 1.2 mL of 4% $NaBH_4$ is injected into the stripper through the septum. After stripping for 7 min, the six-way valve is turned to the column/inject position, and 1 min later the trap is pulled from the liquid nitrogen; the integrator is started at this time. After 45 s, the valve is returned to the strip/trap position so that high boiling point substances (e.g., water) do not enter the column. Arsenic has a retention time of approximately 3 min, while that of antimony is approximately 7 min, depending on exact column length, carrier flow rate, and oven temperature.

Determination of Aqueous As(III + V) and Sb(III + V). From 1 to 50 mL of sample (fresh, thawed, or stored) is added to the stripper bottom and the volume adjusted to 50 mL with DDI. A 2-ml aliquot of concentrated HCL and 3 mL of KI solution are added, and the stripper is assembled and purged for 3 min. $NaBH_4$ solution (4 mL) is injected slowly over 1 min, and the hydrides are collected over a 7-min strip/trap time. Determination of the hydrides then follows the procedure above. As(V) is calculated to be the difference between As(III + V) and As(III) determinations, while Sb(V) is the difference between the Sb(III + V) and Sb(III) determinations.

Particulate Digestion. Approximately 0.1 g of dried and ground sediment is weighed into an acid-cleaned, 50-mL beaker. Concentrated nitric acid (5 mL) is added, the beaker covered with a watch glass, and the sample allowed to reflux gently on a warm hot plate for 6 h. The watch glass is then removed and the nitric acid evaporated until the sample is completely dry (*but not charred*). An 8-mL aliquot of 4% (w/v) potassium persulfate is added, and the sample is again refluxed for 6 h. After the watch glass is removed, the persulfate solution is evaporated to dryness; a white residue remains at this point. A 10-mL aliquot of 6 M HCl is added and the sample gently heated for 1 h. If needed, sediment samples can be filtered through 0.4-μm membrane filters to remove any undigested mineral phases. Samples are stored in 30-mL high-density polyethylene bottles until analysis.

Any amount of the digest can be analyzed, but typically, 0.1–2.0-mL aliquots are diluted to 50 mL with DDI and analyzed by using the As(III + V) and Sb(III + V) procedure.

RESULTS AND DISCUSSION

Sample Processing and Storage. *Aqueous Samples.* The conventional means of storing water samples for trace element analyses uses polyethylene containers and acidification to a pH less than 2 in order to prevent adsorption or precipitation (*10*). However, previous studies (*9, 11*) have shown that

Table I. Storage Results for Oxic and Anoxic Seawater Samples Taken in the Black Sea (43°04′N, 34°00′E) in June 1988 (All Concentrations in nmol/L)[a]

	shipboard		stored	
depth, m	As(III + V)	Sb(III + V)	As(III + V)	Sb(III + V)
	Oxic Water Column			
5	3.72 ± 0.02	1.36 ± 0.05	3.62 ± 0.14	0.93 ± 0.06
30	5.17 ± 0.36	0.83 ± 0.12	5.22 ± 0.20	0.75 ± 0.04
90	36.1 ± 0.05	0.33 ± 0.02	36.2 ± 0.3	0.37 ± 0.04
	Anoxic Water Column			
500	11.4 ± 0.1	0.61 ± 0.02	32.8 ± 0.2	0.40 ± 0.01
800	10.4 ± 0.2	0.92 ± 0.02	31.3 ± 0.4	0.34 ± 0.04
1500	7.01 ± 0.41	0.55 ± 0.05	27.0 ± 0.2	0.28 ± 0.01

[a] All determinations made in triplicate.

trivalent forms of arsenic and antimony will oxidize during such storage. Thus, the samples must either be analyzed immediately after collection (e.g., on board ship) or stored in a manner that does not compromise the chemical forms of arsenic and antimony. Rapid freezing at liquid nitrogen temperatures and subsequent storage below −40 °C have been shown to preserve the original chemical forms (*1*). Rapid freezing is particularly important for saline waters since the ionic strength of brines formed during slow freezing can promote changes.

While previous investigators have reported that acidified storge for total inorganic (i.e., (III + V)) arsenic and antimony is acceptable (*9*, *11*), the results in Table I indicate that there may be storage artifacts when anoxic water samples are kept in this manner. In particular, As(III + V) concentrations determined on samples stored via acidification are an average of 225% higher than those determined immediately at sea; shipboard and stored concentrations in the oxic water column are identical. In contrast, Sb(III + V) in the anoxic water samples that were stored are an average of 49% lower than those determined at sea. Again, the oxic samples did not show this trend. All of the samples were filtered through 0.4-μm filters, and possible explanations for the behavior of arsenic include the oxidation of organic arsenic species not detected by the inorganic methods or the oxidation of an inorganic, colloidal form that passed through the filter (e.g., As_2S_3). The loss of antimony during storage may be due to adsorption. In any case, these data argue for the determination of arsenic and antimony species in the field.

Particulate Samples. The handling and storage of samples must not alter the concentration of particulate arsenic and antimony. For biogenic materials and sediments, changes in concentration may occur via bacterial degradation during storage. In order to prevent this, samples are placed in acid-cleaned polyethylene vials or bags and frozen immediately. Samples are dried slowly at 40 °C to prevent potential losses from volatilization. To ensure homogeneity, samples are sieved through a polyethylene mesh after grinding with an agate mortar and pestle. Dried and ground samples are stored in clean polyethylene bottles.

Hydride Generation and Chromatographic Separation. *Chromatographc Separation.* The operation of the photoionization detector (PID) is based on the absorption of ultraviolet radiation causing molecules in the detector chamber to ionize (if their ionization potentials are less than that of the UV source, 10.2 eV). Thus, the PID is capable of detecting arsine (IP of 10.03 eV) and stibine (IP of 9.58 eV), but as a nonspecific detector, these hydrides must be chromatographically separated from other coeluting compounds. Among the known compounds produced by the hydride generation conditions used here are carbon dioxide, diborane, and hydrogen sulfide, as well as methylated arsine (*11*) and stibine (*9*). Carbopack B HT 100 (Supelco) was chosen as the chromatographic packing because of its ability to separate most volatile sulfur compounds and because of the similarities (e.g., boiling points) between these compounds and the inorganic hydrides. An example chromatogram is shown in Figure 2, where arsine has a retention time of ca. 3 min and that of stibine is ca. 7 min. Methylated arsine and stibine (e.g., CH_3AsH_2, $(CH_3)_2SbH$) do not elute from the Carbopack column at 30 °C. This eliminates any interference from the methylated species, but it also precludes their simultaneous determination with the inorganic species.

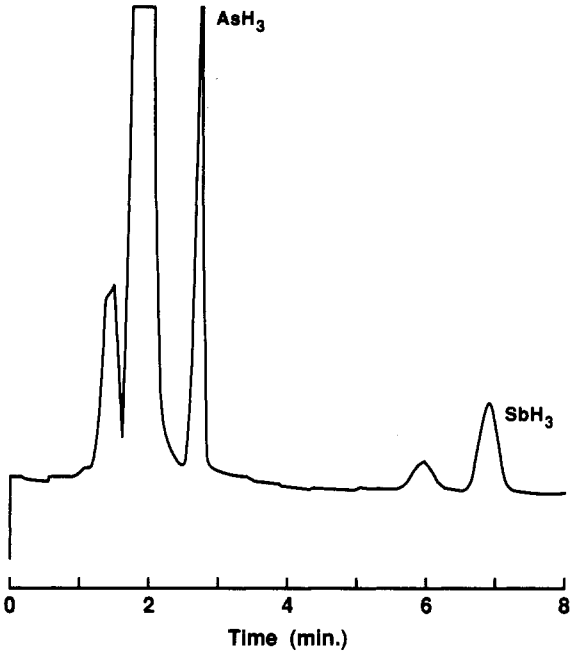

Figure 2. Typical chromatogram showing the separation of arsine (ca. 5 ng) and stibine (ca. 2 ng) in a seawater sample.

Hydrogen sulfide elutes before arsine (i.e., with the unresolved peaks preceding arsine; Figure 2), and since the PID is an extremely sensitive detector for H_2S (e.g., ref 12), this sulfur gas can interfere with the determination of arsenic in anoxic waters (i.e., the arsine peak is only a shoulder on the larger H_2S peak). In order to remove this interference an H_2S trap, consisting of a small tube filled with glass wool that is soaked in zinc acetate, is placed in-line between the stripper and the water trap. This trap efficiently removes hydrogen sulfide concentrations up to 2.0 mmol of S/L. Analyses of arsenic and antimony standards with and without the sulfide trap show identical peak areas. Thus, the zinc acetate trap eliminates hydrogen sulfide interference without affecting the determinations of arsenic and antimony.

The only other chromatographic interferents are high boiling point compounds (e.g., water) that have retention times longer than 10 min and elute during subsequent chromatograms. These compounds can be eliminated by returning the six-way valve to the strip/trap position 45 s after pulling the hydride trap from the liquid nitrogen. Within this time span, arsine and stibine are revolatilized, but higher boiling point substanes remain in the trap. If the valve is not switched back to the strip/trap position, at least 1 h is required to elute all of these substances.

Selective Hydride Generation. In order to determine the concentration of inorganic arsenic and antimony species, arsine and stibine must be generated from their trivalent states without affecting the pentavalent forms. Subsequently, As(III + V) and Sb(III + V) must be reduced quantitatively to their respective hydrides and the concentrations of As(V) and Sb(V) calculated by difference. Examination of the published

Table II. Recoveries of Total Arsenic and Antimony for Various Wet Oxidative Digests[a,b]

material	certified value	digest recovery				
		HNO_3	HNO_3 + $HClO_4$ (*8*)	HNO_3 + V_2O_5 + H_2SO_4 (*15*)	HNO_3 + S_2O_8, HCl (*16*)	HNO_3, S_2O_8, HCl (this work)
NIST River Sediment SRM 1645	As: 66[c]	57.6 ± 3.0	59.5 ± 2.9	48.3 ± 2.1	41.7 ± 2.1	65.5 ± 6.8
	Sb: 51[c]	44.4 ± 2.3	6.76 ± 0.34	ND[d]	35.5 ± 1.7	48.9 ± 2.9
NIST Estuarine Sediment SRM 1646	As: 11.6 ± 1.3	8.59 ± 0.43	7.99 ± 0.36	9.24 ± 0.28	5.16 ± 0.17	11.2 ± 0.6
	Sb: 0.4[c]	ND	0.20 ± 0.02	ND	0.06 ± 0.01	0.49 ± 0.05
NIST Bovine Liver SRM 1577	As: 0.047 ± 0.006	0.014 ± 0.001	*e*	*e*	0.050 ± 0.003	0.042 ± 0.002
	Sb: 0.003[c]	ND	*e*	*e*	ND	0.003 ± 0.001
IAEA Copepod Homogenate MA-A-1	As: 7.6 ± 0.7	*e*	6.90 ± 0.28	6.59 ± 0.26	0.18 ± 0.01	7.51 ± 0.54
	Sb: 0.08 ± 0.04	*e*	ND	ND	0.049 ± 0.001	0.069 ± 0.004

[a] Concentrations in micrograms As or Sb per gram. [b] All digests performed at least in triplicate. [c] Only noncertified value is available. [d] Non-detectable. [e] Digest was not tested.

methods of Andreae (*11*) for arsenic and Andreae et al. for antimony (*9*) revealed that conditions for hydride generation from the trivalent ions [As(III) and Sb(III)] are nearly identical, while those for Sb(III + V) are more rigorous (i.e., requiring higher acid concentration and the addition of KI) than those for As(III + V). Thus, we initially selected the antimony procedure for the simultaneous determination of both elements.

Standards of As(V) and Sb(V) subjected to the Sb(III) method showed no detectable recoveries, indicating that the Sb(III) method is specific for the trivalent forms. Moreover, the recoveries of As(III) and As(III + V) using the Sb(III) and Sb(III + V) methods are identical with those obtained by using the arsenic-only methods. Thus, the recommended conditions are capable of selectively volatilizing the trivalent and pentavalent forms of both arsenic and antimony. The only other parameter that required evaluation was the reaction/stripping time to ensure quantitative recoveries of the hydrides with our apparatus. In Figure 3 it can be seen that the recoveries of arsine and stibine are essentially complete by 7 min; this time is similar to the 6-min strip/trap time used by Andreae et al. (*9*).

Several modifications to the Andreae et al. (*9*) technique were developed, primarily to reduce reagent blanks and intereferences. First, it was found that Sb(III + V) could not be quantitatively recovered by using certain batches of hydrochloric acid. However, after bubbling helium through the acid for 3 h, full recovery was regained. Since the interferent appears to be volatile, we speculate that it is free chlorine gas in the hydrochloric acid. In addition to purging with helium, the HCl is passed through the anion-exchange resin AG1×8 to eliminate the large arsenic and antimony blanks associated with the acid (*13*). This blank varies considerably from lot to lot, and ranges from <1 to 5 μg of As/mL. After treatment the HCl blank was reduced to less than 0.1 ng of As/mL.

For samples where strong oxidants such as peroxide may be present (e.g., rain water), the solution turns yellow after the addition of potassium iodide (triiodide formation) and the recovery of Sb(III + V) drops significantly. To prevent this occurrence, the KI solution is injected into the stripper with a syringe just prior to injecting the $NaBH_4$.

Total Particulate Arsenic and Antimony Determination. In order to determine total arsenic and antimony in sediments and biogenic particles, the elements must be quantitatively solubilized, but the resulting solution must be amenable to analysis using hydride generation (i.e., oxidized to inorganic As(III + V) and Sb(III + V) with minimal interference). This presents a problem, since arsenic can occur as refractory organic compounds such as arsenocholine in biogenic materials (*14*). To meet these criteria, a variety of wet oxidative digests were investigated. The general procedure for all of the digests involved placing the particulate matter

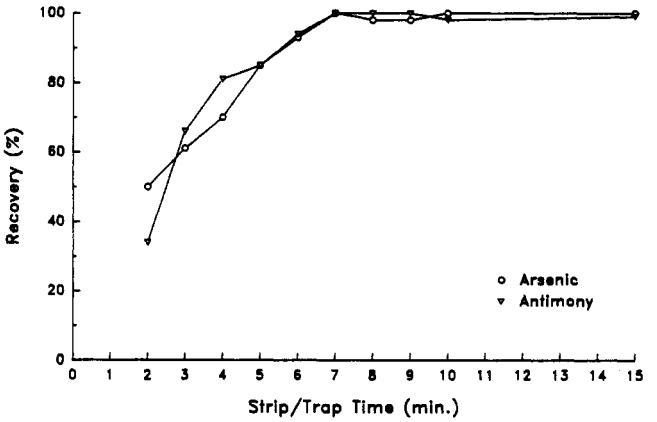

Figure 3. Recovery of arsenic (i.e., arsine) and antimony (i.e., stibine) as a function of reaction/stripping time (see text for operating conditions). Full recovery is 4.0×10^6 integrator counts for antimony and 6.2×10^6 for arsenic.

in a 50-mL beaker, adding the digestion solution, covering with a watch glass, and refluxing at low heat. In order to assess accuracy, standard reference materials (NIST Bovine Liver, River Sediment, and Estuarine Sediment, and IAEA Copepod Homogenate) were used; results are presented in Table II.

Wet oxidative digestions using nitric acid or nitric/perchloric acids similar to those used for other metalloids such as selenium (*8*) did not interfere with hydride generation but gave incomplete recoveries of arsenic and antimony (Table II). The technique of Uthe et al. (*15*) using a mixture of HNO_3, V_2O_5, and H_2SO_4 worked well for arsenic but gave no recovery for antimony. Antimony determinations using the standard additions method of calibrtion indicated that the lack of antimony recovery was most likely due to V_2O_5 interference with the formation of stibine. The technique of Nygaard and Lowery (*16*) that uses sequential treatments of weak nitric acid and potassium persulfate and then hydrochloric acid also gave satisfactory recoveries for arsenic in sediments but could not solubilize arsenic or antimony in the biogenic matrices (e.g., NIST Bovine Liver, IAEA Copepods; Table II). Finally, a combination of techniques using wet oxidation with HNO_3, evaporation, followed by another strong oxidant ($K_2S_2O_8$), evaporation, and storage in 6 M HCl yielded quantitative recoveries from all reference materials (Table II).

In the recommended procedure, the evaporation steps are included to remove all of the oxidants (e.g., nitric acid) since they may interfere with later hydride analysis. The breakdown of lipids to ensure solubilization of organic–arsenic compounds must be complete, and additional nitric acid plus drying steps may be required if an oily residue remains. The subsequent potassium persulfate digest is added to help ensure the complete oxidation of dissolved organic compounds, and storage

Table III. Amounts of Arsenic and Antimony in Natural Waters and Particulate Materials[a]

A. Water Samples (nmol/L)

Type, Location	As(III)	As(V)	Sb(III)	Sb(V)
mid-Chesapeake Bay, 4 m, 6/14/88	1.84 ± 0.08	0.78 ± 0.08	<0.003	0.48 ± 0.01
sediment porewater, mid-Chesapeake Bay, 6/15/88	195 ● 2	734 ± 16	3.41 ± 0.14	15.8 ± 0.3
Sacramento River, CA, 9/24/86	0.07 ± 0.01	11.5 ± 0.3	<0.003	0.55 ± 0.04
rain water, Bermuda, 1/25/89	<0.011	0.093 ± 0.001	<0.003	0.041 ± 0.001

B. Biogenic Materials and Sediments (μg/g)

Type, Location	total As	total Sb
Black Sea sediment, 6/14/88		
0–1 cm	16.0 ± 0.5	1.37 ± 0.05
10–11 cm	6.34 ± 0.22	0.67 ± 0.04
diatoms, North Pacific Ocean	2.18 ± 0.10	1.20 ± 0.06
80-m sediment trap material, North Pacific Ocean	3.54 ± 0.21	0.49 ± 0.01

[a] All determinations made in triplicate.

in hydrochloric acid ensures sample integrity (i.e., no loss through adsorption to container walls).

Analytical Figures of Merit. *Detection Limits.* The detection limit for As(III) and As(III + V) was evaluated by using five determinations of the reagent blank. The absolute detection limit for arsenic is 40 pg (3 σ); for a 50-mL sample this corresponds to a relative detection limit of 11 pmol of As/L. The detection limit for Sb(III) and Sb(III + V) was determined in a similar fashion. The absolute detection limit for antimony is 20 pg (3 σ), corresponding to a relative detection limit of 3.3 pmol of Sb/L for a 50-mL sample. On the basis of these absolute detection limits, the relative detection limits for particulate arsenic and antimony are 5.3 pmol of As/g and 1.6 pmol of Sb/g, using a 0.1 g sample.

Precision. Precision for both arsenic and antimony at low concentrations (i.e., 0.03 nmol of As/L, 0.02 nmol of Sb/L) is 3% relative standard deviation (n = 8) and at high concentration (1.9 nmol of As/L, 3.0 nmol of Sb/L) is 0.5% (relative standard deviation, n = 6).

Linearity. The linear range extended from the detection limit to about 75 ng (r = 0.9999, n = 6) for arsenic and to 50 ng (r = 0.9980, n = 6) for antimony, at which point it exceeds the dynamic range of the HP 3392A integrator (i.e., the response exceeded 1000 mv). Higher concentrations can be determined by using smaller sample volumes or by dilution.

Sample Analysis Time. The analysis time for an individual sample includes the strip/trap time (7 min) and the elution time for the chromatogram (ca. 9 min). However, to reduce the sample-to-sample time, one sample can be in the strip/trap phase while the previous sample is being chromatographed. In this manner, the sample-to-sample analysis time is reduced to 12 min.

Interferences. A number of substances may interfere with the generation of arsine and stibine or with their chromatographic separation. As mentioned earlier, oxidants used in the particulate digests must be removed to minimize their interference. Hydrogen sulfide is a chromatographic interferent and must be chemically removed during analysis. Other ions (e.g., Cu^{+2}, NO_2^-) have been shown to be possible interferents in hydride generation (*9*, *11*, *17*, *18*), but the concentrations at which they interfere are several orders of magnitude higher than those found in the environment. However, it is recommended that the standard additions method of calibration be used to assure accuracy.

Application to Field Samples. The methods described here have been used to determine arsenic and antimony species in a variety of natural water samples; Table III contains some of the results. In addition to water samples, the particulate digestion method has been applied to samples of particulate matter from the water column and sediments. These results show that the methods described here can be used for many different sample types and widely varying concentrations. It is interesting to note that the 3-fold lower detection limit for antimony is perfectly suited to the analysis of environmental samples. In particular, the concentrations of dissolved and particulate antimony are 1–2 orders of magnitude lower than those of arsenic.

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