Determination of Arsenic(III) and Arsenic(V) by Hydride Generation—Atomic Absorption Spectrometry Following a Rapid Coprecipitation Technique with Hafnium(IV) Hydroxide

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Hafnium(IV) hydroxide quantitatively coprecipitates 10—120 ng of arsenic(III) and arsenic(V) from a 100—300 cm^3 sample solution at pH 6.0—10.5. After coprecipitation, arsenic(III) can be sensitively determined by heated quartz glass cell atomic absorption spectrometry utilizing arsine generation with sodium tetrahydroborate; arsenic(V) can also be determined in the same manner as above after reducing it to arsenic(III). Interference from hafnium(IV) in the determinations of arsenic (III) and arsenic (V) can be eliminated by using perchloric acid and potassium iodide, respectively. The calibration curves are linear from 0.5—6.0 ng cm^{-3} for both arsenic(III) and arsenic(V). Since this method can be used to determine arsenic(III) as well as the sum of the amounts of arsenic(III) and arsenic(V), it is possible to determine arsenic(III) and arsenic(V) consecutively.

A hydride-generation technique with subsequent atomic absorption spectrometry is widely used to analyze arsenic; it is known as being a highly sensitive determination method.[1-3] For trace amounts of arsenic, however, it is frequently necessary to concentrate it prior to the determination, even when using this analytical method.

The coprecipitation method is a useful way to concentrate trace amounts of arsenic; the hydroxides of iron(III)[4] and lanthanum[5-8] have been used for preconcentration prior to the atomic absorption spectrometry of arsine. This concentration method, however, is sometimes troublesome and time-consuming regarding filtration, especially for large-volume samples. To alleviate these disadvantages, a flotation technique[9-12] has been used to separate the precipitate from the mother liquor.

We have been examining hafnium(IV) hydroxide as a coprecipitant, and have suggested that it is useful for concentrating trace amounts of lead,[13] cadmium,[14] copper,[15] beryllium,[16] tin,[17] gallium,[18] indium,[18] and germanium[19] in water samples. This is because hafnium(IV) hydroxide is an excellent collector of these ions and coprecipitates few, or no, matrix ions, such as alkali and alkaline earth elements. This time, we found that hafnium(IV) hydroxide is also an excellent collector for arsenic(III) and arsenic(V), and that coprecipitated arsenic can be sensitivily determined by atomic absorption spectrometry utilizing arsine generation. The presence of hafnium(IV) interferes with the determination of arsenic(III) and arsenic(V). However, the effect regarding the former can be eliminated by using perchloric acid; that regarding the latter can be eliminated by potassium iodide, which has frequently been used to remove interference.[3] In this study we also tried to establish a rapid, simple coprecipitation method which does not require any filtration and complete collection of the precipitate using a known amount of hafnium(IV) and measuring the amount of both hafnium(IV) and arsenic in the final sample solution. In this case, the amount of the coprecipitant in the original sample solution must be negligibly small, and the added collector must precipitate completely. Hafnium(IV) satisfied these conditions and gave good results.

In this method, arsenic(III) can be determined without any influence from arsenic(V), and arsenic(V) can be determined as arsenic(III) after reducing it. A consecutive determination of arsenic(III) and arsenic(V) thus becomes possible. The method proposed here is simple and has good reproducibility.

This paper describes the fundamental conditions for the coprecipitation of trace amounts of arsenic(III) and arsenic(V) with hafnium(IV) hydroxide, and for their determination using arsine generation–atomic absorption spectrometry.

Experimental

Apparatus. A Hitachi 170-10 atomic absorption spectrometer with a Hitachi hollow cathode lamp made of arsenic was used for atomic absorption measurements, a Hitachi HFS-2 hydride generator for arsine generation, and a Hitachi-Horiba model M-5 glass electrode pH meter for pH measurements.

Reagents. All reagents used were of guaranteed reagent grade.

Standard Arsenic(III) Solution: A solution containing 1000 μg cm^{-3} arsenic(III) was prepared by dissolving arsenic(III) oxide (0.1320 g: Nacalai Tesque, Inc.) in 20 cm^3 of sodium hydroxide, being neutralized by 3 mol dm^{-3} of sulfuric acid, and diluting 100 cm^3 with distilled water. This solution was further diluted to the desired concentration with distilled water.

Standard Arsenic(V) Solution: A solution containing 1000 μg cm^{-3} of arsenic(V) was prepared by dissolving sodium arsenate (0.4165 g: Kanto Chemicals) in distilled water and diluting 100 cm^3 with distilled water. This solution was further diluted to the desired concentration with distilled water.

Hafnium(IV) Solution: A solution containing about 5 mg cm^{-3} of hafnium(IV) was prepared by dissolving hafnium-

(IV) chloride (Nacalai Tesque, Inc.) in distilled water. The hafnium(IV) concentration was determined by complexometric titration using Xylenol Orange as an indicator.

Recommended Procedures. Determination of Arsenic(III): To a sample solution (100—300 cm^3) containing from between 10 to 120 ng of arsenic(III), 20 mg of hafnium(IV) is added exactly. The solution is then adjusted to a pH of about 9 with aqueous ammonia (1+5) , and allowed to stand for more than 1 h. After the supernatant solution is discarded by decantation, the remaining precipitate is washed with a small amount of distilled water, and dissolved with 3 cm^3 of perchloric acid. The solution is then made up to about 20 cm^3 with distilled water. Taking a portion of this solution (V_1 cm^3), the amount of arsenic(III) in it (M_1 ng) is measured by arsine generation-heated quartz glass cell atomic absorption spectrometry under the operating conditions shown in Table 1. Taking another portion of the solution separately (V_2 cm^3), the amount of hafnium(IV) in it (H mg) is also measured by complexometric titration (at about 90 °C and in about 1 mol dm^{-3} nitric acid) with Xylenol Orange used as an indicator. Since the amount of the arsenic(III) coprecipitated by H mg of hafnium(IV) can be calculated from these measurements, the arsenic(III) content in the original sample solution (M_0 ng) can be calculated from the amount of hafnium(IV) added to the initial sample solution by using the following equation:

$$M_0 = M_1 \times (V_2/V_1) \times (20/H).$$

Determination of Arsenic(V): To a sample solution (100—300 cm^3) containing from 10 to 120 ng of arsenic(V), 20 mg of hafnium(IV) is added exactly. The solution is then adjusted to a pH of about 9 with aqueous ammonia (1+5) and allowed to stand for more than 1 h. After the supernatant solution is discarded by decantation, the remaining precipitate is washed with a small amount of distilled water and dissolved with 4 cm^3 of hydrochloric acid. Then, 5 cm^3 of potassium iodide solution (20% w/w) is added in order to reduce arsenic(V) to arsenic(III).[3] The solution is made up to about 20 cm^3 with distilled water, warmed at 30 °C in a water bath for about 20 min, and cooled with running water. The amount of arsenic(V) in the original sample solution can then be determined using the same procedure as that for arsenic(III). If the sample solution contains both arsenic(III) and arsenic(V), their total amounts are obtained. The amount of arsenic(V), in this case, is calculated by subtracting the amount due to arsenic(III), obtained by the recommended procedure for arsenic(III) from the total amount.

Table 1. Operating Conditions for a Hydride Generator and Atomic Absoption Spectrometer

Atomic absorption spectrometer	
Analytical wavelength	193.7 nm
Lamp current	10 mA
Acetylene pressure	0.20 kg cm^{-2}
Air pressure	1.60 kg cm^{-2}
Hydride generator	
Argon flow rate	70 cm^3 min^{-1}
Concentration of NaBH$_4$	1% w/v
Concentration of HCl	5% v/v
Sampling time	0.3 min
Reaction time	0.3 min

Results and Discussion

Optimum Conditions for Coprecipitation. According to the recommended procedure for the determination of arsenic(III), the necessary amount of hafnium(IV) for coprecipitation was studied using a sample solution (100—300 cm^3) containing 40 ng of arsenic(III). The required amount of hafnium(IV) for a quantitative collection of arsenic(III) increased with increasing sample volume; more than 10 mg of hafnium(IV) was required for 300 cm^3 of the sample solution. Hence, 20 mg of hafnium(IV) was used in further experiments. The optimum pH range for coprecipitation (Fig. 1) was 6.0—10.5. Therefore, the solution pH was adjusted to about 9.0 with aqueous ammonia in further experiments. The recovery of arsenic(III) reached its maximum value at about 1 h after the formation of hafnium-

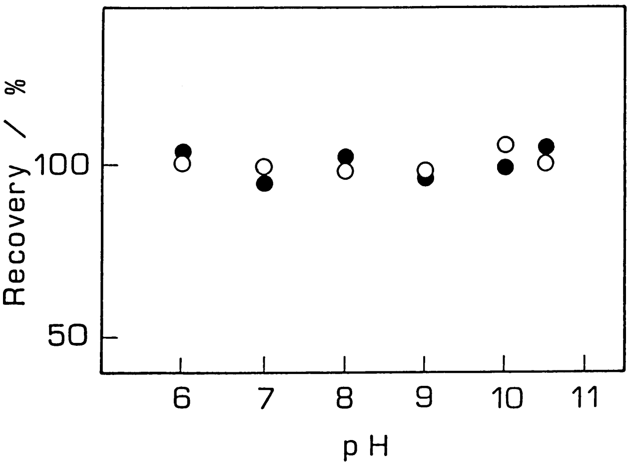

Fig. 1. Effect of pH on the recovery of arsenic(III) or arsenic(V). ○) As(III), 40 ng; Hf(IV), 20 mg; HClO$_4$, 3 cm^3. ●) As(V), 40 ng; Hf(IV), 20 mg; concd HCl, 4 cm^3; 20% w/w KI, 5 cm^3.

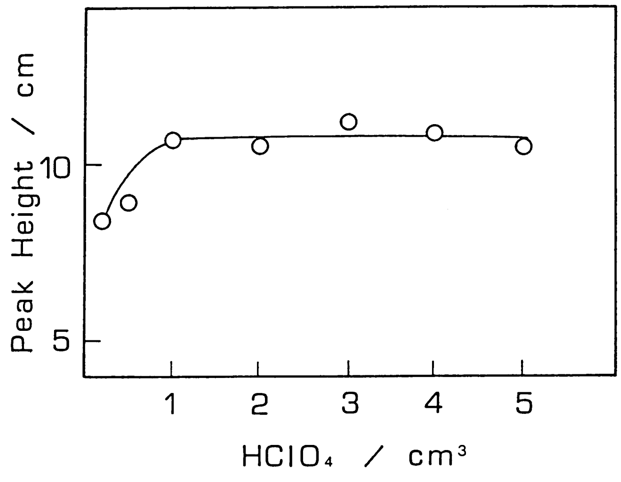

Fig. 2. Effect of the perchloric acid concentration on the peak height of arsenic(III). As(III), 40 ng; Hf(IV), 20 mg; HClO$_4$, 3 cm^3.

(IV) hydroxide, and remained unchanged for at least 3 h of standing. In the determination of arsenic(V), almost the same results as in the case of arsenic(III) were obtained.

Choice of Acids for Dissolution of Hafnium(IV) Hydroxide. Hafnium(IV) hydroxide dissolves easily in common mineral acids, except for sulfuric acid. Upon the determination of arsenic(III), perchloric acid was most suitable for dissolution of the precipitate, since interference from hafnium(IV) was eliminated due to the presence of more than 1 cm^3 of this acid, even if hafnium(IV) coexisted up to 40 mg. In Fig. 2, the effect of the concentration of perchloric acid on the peak height of arsenic(III) is given. From this, 3 cm^3 of perchloric acid was used for the determination of arsenic(III).

Upon the determination of arsenic(V), the use of hydrochloric acid was preferable for dissolving the precipitate, since potassium iodide was used to reduce arsenic(V) to arsenic(III). From the results shown in Fig. 3, 4 cm^3 of concentrated hydrochloric acid was used in further experiments. The reduction from arsenic(V) to arsenic(III) by potassium iodide is slow at room temperature; it was hastened by heating. In this experiment, the solution was warmed at 30 °C in a water bath for 20 min. Interference from hafnium(IV) in this determination could be effectively eliminated by potassium iodide added as the reductant of arsenic(V). The

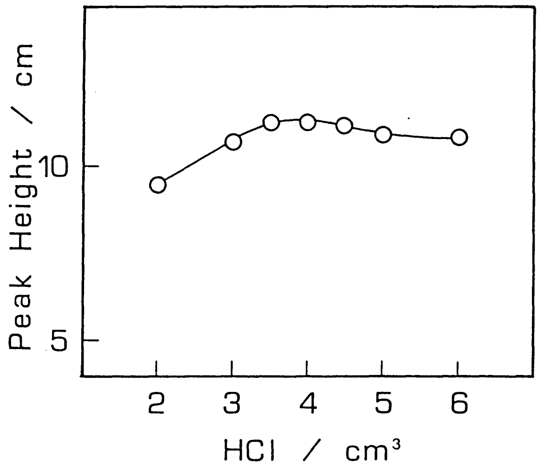

Fig. 3. Effect of the hydrochloric acid concentration on the peak height of arsenic(III). As(III), 40 ng; Hf(IV), 20 mg; concd HCl, 4 cm^3; 20% w/w KI, 5 cm^3.

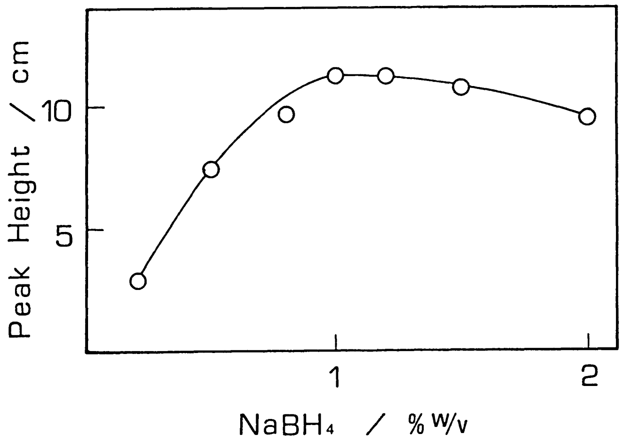

Fig. 4. Effect of the sodium tetrahydroborate concentration on the peak height of arsenic(III). As(III), 40 ng; Hf(IV), 20 mg; concd HCl, 4 cm^3; 20% w/w KI, 5 cm^3.

Table 2. Effect of Diverse Ions on the Determination of Arsenic

Tolerance limit	Ion	
[Ion]/[As(III)]	A	B
<25000	$Li^{+}, Be^{2+}, Ca^{2+}, Ba^{2+}$	$Li^{+}, K^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$
<2500	$Mg^{2+}, Sr^{2+}, Al^{3+}, In^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, La^{3+}, Zr^{4+}, Th^{4+}, Cr^{3+}$, W(VI), Mn^{2+}, Fe^{3+}	$Al^{3+}, In^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, La^{3+}, Zr^{4+}, Th^{4+}, Cr^{3+}$, Mo(VI), W(VI), $Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}$
<1250	Co^{2+}, Sb^{3+}	Sn^{4+}
<250	Sn^{4+}, Bi^{3+}, Mo(VI), Ni^{2+}	Bi^{3+}, Fe^{3+}
<25	Te(IV), Se(IV)	Sb^{3+}, Te(IV), Se(IV)
[Ion]/[As(V)]	A	
<25000	$Li^{+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$	
<2500	$Al^{3+}, In^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, La^{3+}, Zr^{4+}, Th^{4+}, Cr^{3+}$, Mo(VI), W(VI), $Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}$	
<250	Sn^{4+}, Bi^{3+}	
<25	Sb^{3+}, Te(IV), Se(IV)	

40 ng of arsenic(III) or arsenic(V) was taken. A: Recommended procedure for arsenic(V) was used. B: Recommended procedure for arsenic(III) was used. The results are the average of duplicate determinations. The tolerance limit of an ion was fixed as the amount causing an error not more than 5% for arsenic recovery.

Table 3. Measurement of Arsenic(III) and Arsenic(V) in Spiked Water Samples

Sample	Sample volume/ cm^3	As(III) added/ ng	As(V) added/ ng	As(III) found/ ng	RSD[a] %	As(V) found/ ng	RSD[a] %
Distilled water	300	10	10	7.8	1.1	14.0	0.2
	300	10	40	10.7	2.0	41.0	1.5
	300	40	10	37.7	0.3	9.2	0.4
	300	40	40	43.8	1.3	34.1	1.0
River water	300	60	60	63.8	2.3	63.2	2.4
Tap water	300	60	60	n.d.	—	86.1	3.8

The results obtained are the average of five replicate determinations. a) Relative standard deviation. n.d., not detected.

Table 4. Results for Arsenic(III) and Arsenic(V) in a River-Water Sample

Sample	Sample volume	Calibration method		Standard addition method	
	cm^3	As(III) found/ng cm^{-3}	As(V) found/ng cm^{-3}	As(III) found/ng cm^{-3}	As(V) found/ng cm^{-3}
Kanakusari river the upper stream (RSD[a])	300	0.123 (11.3%)	0.540 (6.4%)	0.127 (3.5%)	0.490 (8.2%)

The results obtained are the average of four replicate determinations. a) Relative standard deviation.

addition of more than 5 cm^3 of a 20% w/w solution of potassium iodide was adequate for this purpose.

Optimization of Operating Conditions. The optimum conditions for measuring the atomic absorbance of arsenic(III) were studied. In hydride generation, the optimum concentration of sodium tetrahydroborate solution was 1% w/v (Fig .4), and that of hydrochloric acid was 3—10% v/v. Regarding the argon gas-flow rate, its increase within the 50—250 $cm^3 min^{-1}$ range gradually decreased the atomic absorbance of arsenic(III). From these results and other instrumental conditions, such as the analytical wavelength, lamp current, as well as acetylene and air pressure, the optimum measurement conditions for the atomic absorption of arsenic(III) were determined (Table 1). For the determination of arsenic(V), the same operating conditions were suitable.

Calibration Curve. The relationship between the peak height and the arsenic concentration was examined according to the recommended procedures. A straight line through the point of origin was obtained over a range of 0.5 to 6.0 ng cm^{-3} of arsenic for determinations of both arsenic(III) and arsenic(V). The reproducibilities of these methods (relative standard deviation) for the peak height obtained from five repeated determinations were 0.46% for 60 ng of arsenic(III) and 0.84% for 60 ng of arsenic(V) in 300 cm^3 of water. The detection limits (signal/noise=2) were 6.0×10^{-4} ng cm^{-3} and 6.5×10^{-4} ng cm^{-3} in 300 cm^3 of the initial sample solution, respectively.

Interferences. The influences of each of 29 diverse ions on the determination of arsenic(III) or arsenic(V) were examined according to the recommended procedures. As shown in Table 2, arsenic(III) could be recovered within a 5% error in the presence of large amounts of alkali and alkaline earth metals. Although antimony(III), bismuth(III), iron(III), selenium(IV), or tellurium(IV) interfered with the determination, 10 μg of bismuth(III) or iron(III), or 1 μg of antimony(III), selenium(IV), or tellurium(IV) could coexist. Almost the same results were obtained for the determination of arsenic(V). In Table 2, the results of arsenic(III) examined under the same procedure as that for arsenic(V) are appended.

Measurement of Arsenic in Spiked Water Samples. Using the recommended procedures, the amount of arsenic(III) or arsenic(V) in some water samples spiked with arsenic(III) and arsenic(V) were measured. The samples were filtered through a Fuji Photo Film FR-40 membrane filter (pore size of 0.4 μm) as soon as possible after sampling. The obtained results are shown in Table 3. Although arsenic(III) and arsenic(V) in distilled and river water samples could be measured, arsenic(III) could not be recovered from tap water.

Based on the results obtained from these experiments, the determination of arsenic(III) and arsenic(V) in river water (located in Ishikawa prefecture) was tried. As is shown in Table 4, the results obtained using the calibration and standard addition methods were in good agreement with each other.

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