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Flotation of Sub-microgram Amounts of Arsenic Coprecipitated with Iron(III) Hydroxide from Natural Waters and Determination of Arsenic by Atomic-absorption Spectrophotometry Following Hydride Generation

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A method is described for the flotation and determination of sub-microgram levels of arsenic in water. A sub-microgram amount of arsenic(III, V) in a 500-ml sample of water is coprecipitated with iron(III) hydroxide at pH 8–9. The precipitate is floated with the aid of sodium oleate and small air bubbles, then separated and dissolved in 5 M hydrochloric acid, and finally the arsenic content is determined by generation of arsine using sodium tetrahydroborate(III) as a reductant and atomic-absorption spectrophotometry with a long absorption cell (60 × 1.2 cm i.d.). This separation technique has been successfully applied to the determination of sub-microgram amounts of arsenic(III, V) in natural waters.

Keywords: *Arsenic determination*; *flotation*; *natural waters*; *atomic-absorption spectrophotometry*; *hydride generation*

Arsenic probably exists at the 1 $\mu g\ l^{-1}$ level in natural water samples. At such concentrations a precise direct determination is impracticable even by atomic-absorption spectrophotometry of arsine, which has a high sensitivity.[1–4] Accordingly, the arsenic must be concentrated from the water prior to determination.

Coprecipitation with iron(III) hydroxide is commonly used as a pre-concentration technique for the determination of arsenic in water.[5] This bulky amorphous precipitate, however, is difficult to filter, and centrifugation is cumbersome for larger volumes.

Therefore, a flotation technique[6,7] in which the precipitate of iron(III) hydroxide is floated with the aid of sodium oleate and small air bubbles (0.1–0.5 mm diameter) has been used for the pre-concentration of arsenic. The precipitate is readily separated from the mother liquor and then dissolved in hydrochloric acid for the atomic-absorption spectrophotometry of arsine using sodium tetrahydroborate(III) as a reductant. Various parameters, such as the pH of the solution, the amounts of iron(III) and surfactant added, stirring time, sample volume and foreign ions, have been investigated in order to obtain optimum conditions for the flotation and determination of the arsenic. For the atomic-absorption determination of arsenic a technique involving a long absorption cell and the argon - hydrogen flame system has been used.

The proposed method is simple and rapid, and applicable to the determination of arsenic at the low parts per billion (10^9) level in water.

Experimental

Apparatus

A Nippon Jarrell-Ash, Model AA-1, Mark II atomic-absorption spectrophotometer equipped with a Westinghouse arsenic hollow-cathode lamp and a custom-made silica absorption cell (60 × 1.2 cm i.d.) was used with a Beckman burner supplied with argon and hydrogen.

The apparatus used for hydride generation was a modified Nippon Jarrell-Ash, Model ASD-1A, arsenic measurement unit coupled to a custom-made hydride generating cell approximately 40 ml in volume. A schematic diagram of the analytical system is illustrated in Fig. 1.

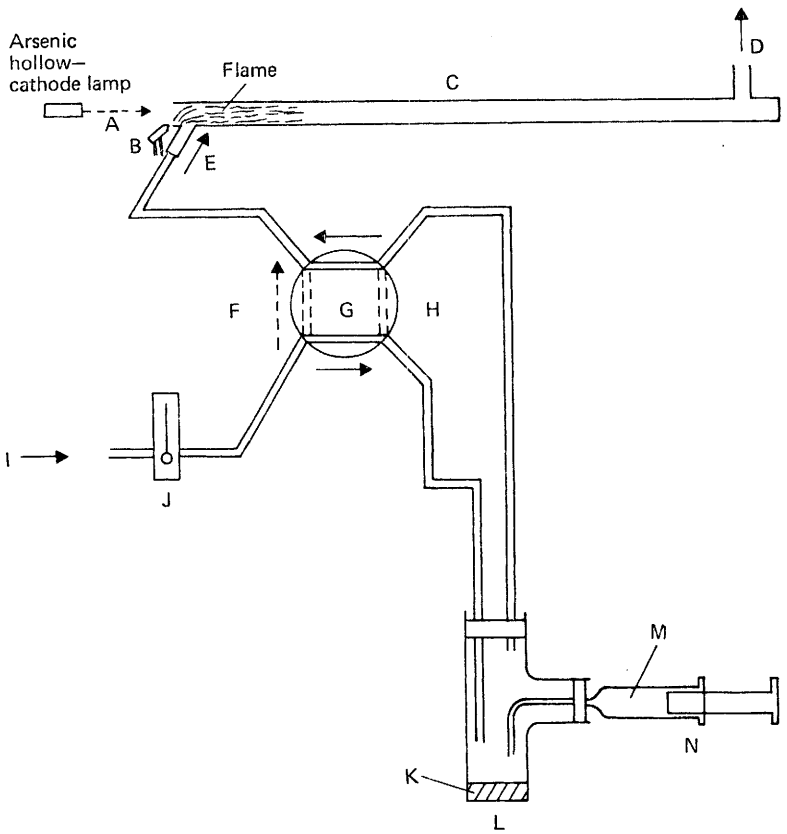

Fig. 1. Schematic diagram of analytical system. A, Light from hollow-cathode lamp; B, Beckman burner; C, silica absorption tube (60 × 1.2 cm i.d.); D, outlet from tube; E, argon gas flow containing arsine; F, by-pass; G, four-way stopcock, alternative gas passages shown by broken lines; H, gas flow with valve in sweep position; I, argon supply; J, flow meter; K, sodium tetrahydroborate(III) solution; L, hydride generating cell; M, sample solution; and N, syringe.

All pH readings were made with a Hitachi-Horiba, Model M-5, pH meter together with a combined glass electrode.

The flotation and separation apparatus was similar to that described by Mizuike and co-workers.[6,7] The flotation cell, shown in Fig. 2, was a glass cylinder, 40 × 6.5 cm i.d., which was fitted with a sintered-glass filter (No. 4) to generate small bubbles.

The air that served as the inert gas was supplied by a Nippon Jarrell-Ash, Model AMD-B1, air pump unit.

Reagents

All reagents were of analytical-reagent grade except for sodium oleate. Aqueous reagents were prepared in de-ionised, distilled water. Arsenic standard solutions were freshly prepared by diluting stock solutions before use.

Arsenic(III) stock solution, 1 mg ml^{-1}. Dissolve 1.321 g of diarsenic trioxide in a minimum amount of 20% *m*/*V* sodium hydroxide solution, acidify with 5 M hydrochloric acid and dilute to 1000 ml with water.

Arsenic(V) stock solution, 1 mg ml^{-1}. Dissolve 4.165 g of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) in 1000 ml of water.

Iron(III) solution, 5 mg ml^{-1}. Dissolve 43.17 g of ammonium iron(III) sulphate [$Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$] in water and dilute to 1 000 ml in 1 M hydrochloric acid with hydrochloric acid and water.

Sodium oleate solution, 1 mg ml^{-1}. Dissolve sodium oleate (powder, extra-pure reagent, Wako Pure Chemicals Co.) in 99.5% *V/V* ethanol with magnetic stirring.

Sodium tetrahydroborate(III) solution, 5% *m/V*. Dissolve sodium tetrahydroborate(III) in water.

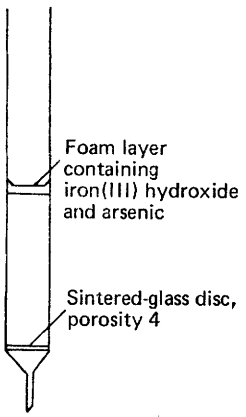

Fig. 2. Flotation cell for pre-concentration of arsenic.

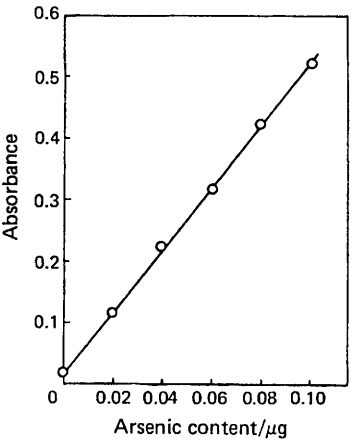

Fig. 3. Typical calibration graph for determination of arsenic in 1 ml of solution.

Recommended Procedure for the Determination of Arsenic

Transfer 1 ml of freshly prepared 5% *m/V* sodium tetrahydroborate(III) solution into an arsine-generating cell and attach the cell to the apparatus. Insert the needle of a plastic syringe containing 1 ml of sample solution that contains less than 0.10 μg of arsenic through the side-arm seal of the cell. Turn the four-way stopcock of the apparatus to the sweep position in order to introduce argon into the system and inject the sample into the cell. Sweep the arsine thus generated into the long absorption cell with the argon so that it is atomised in the argon - hydrogen flame and record the absorption signal on a recorder. Return the stopcock to the by-pass position. Rinse the cell carefully with distilled water and re-charge with sodium tetrahydroborate(III) solution ready for the next sample. If the concentration of arsenic exceeds 0.10 μg ml^{-1}, dilute the solution further, adjusting the hydrochloric acid and iron(III) concentrations accordingly.

Construct a calibration graph using 5 M hydrochloric acid solutions containing 1 mg ml^{-1} of iron(III) and 0–0.10 μg ml^{-1} of arsenic(III). A typical calibration graph for arsenic is illustrated in Fig. 3, which is linear up to 0.10 μg of arsenic. The same result was obtained by using an arsenic(V) solution containing 1 mg ml^{-1} of iron(III) as a standard. The coefficient of variation based on 10 replicate runs of a solution containing 0.05 μg ml^{-1} of arsenic was within 1.5%.

The atomic-absorption equipment was operated under the following conditions: wavelength, 193.7 nm; lamp current, 16 mA; gas flow-rates, argon 1.5, hydrogen 1.5 and auxiliary argon 6 l min^{-1}; slit (spectral band width), 1 nm.

The 60-cm tube system described in this paper cannot be used with most commercial atomic-absorption spectrophotometer units. However, the arsenic in a sample solution can also be determined by atomic-absorption spectrophotometry, using an arsine generation - electrically or flame-heated silica tube. Moreover, nitrogen can be substituted for the more expensive argon.

Procedure Recommended for the Flotation Step

Place 500 ml of the water sample in a 500-ml beaker and add 2 ml of iron(III) solution and 1 ml of sodium oleate solution. Adjust the pH to 8–9 with aqueous ammonia solution (5 and 0.1 M) in order to precipitate iron(III) hydroxide, while stirring magnetically, and stir the solution for 15 min. Transfer the contents of the beaker (excluding the stirring bar) to a flotation cell and wash the residue in the beaker into the cell by using two small portions of water. Pass air at a flow-rate of 50 ml min^{-1} from the lower end of the cell for about 30 s, in order to obtain complete mixing and flotation of the precipitate. Suck off the mother liquor through the sintered-glass disc and wash the precipitate with 30 ml of water. Add 5 ml of 5 M hydrochloric acid to the cell to dissolve the precipitate, collect the filtrate by suction in a 10-ml calibrated flask, wash the sintered-glass disc with hydrochloric acid, add the washings to the flask and dilute to the mark with 5 M hydrochloric acid.

Results and Discussion

Determination of the Optimum pH for Collection of Arsenic

The effect of the pH of the 500 ml of solution containing 0.5 μg of arsenic(III, V), 10 mg of iron(III) and 1.0 mg of sodium oleate on the coprecipitation of arsenic was studied. Hydrochloric acid and aqueous ammonia solution were used to adjust the pH to values within the range 4–10. As a result satisfactory recoveries of both trivalent and pentavalent states of arsenic were obtained over this range. The most stable layer of surface foam supporting the precipitate of iron(III) hydroxide was formed within the pH range 7–9.5; the pH range of 8–9 was used throughout the work.

At a pH below about 6.5, a stable surface-foam layer was obtained by using sodium lauryl sulphate as a surfactant.

Determination of Optimum Amounts of Iron(III) and Surfactant

Table I shows the percentage of arsenic recovered as a function of the amount of iron(III) added to the solution. Quantitative recoveries of arsenic were obtained above 2.5 mg of iron(III). In this work 10 mg of iron(III) were added to 500 ml of the solution.

The amount of sodium oleate required for complete flotation of the precipitate was investigated. Quantitative recoveries of arsenic were obtained between 0.2 and 4.0 mg of sodium oleate and 1.0 mg in 500 ml of solution was adopted in further work.

TABLE I

RELATIONSHIP BETWEEN AMOUNT OF IRON(III) ADDED AND RECOVERY OF ARSENIC

Solution contained 0.5 μg of As(III) and 1 mg of sodium oleate; pH, 8–9; volume, 500 ml.

Fe(III) added/mg	2.5	5.0	7.5	10.0	15.0	20.0
As recovered, %	98	100	101	100	98	99

Stirring Time

The relation between stirring time and recovery of arsenic was investigated. The results are shown in Table II. Coprecipitation was quantitative over the range 5–40 min and stirring for 15 min was found to be best.

TABLE II

RELATIONSHIP BETWEEN STIRRING TIME AND RECOVERY OF ARSENIC

Solution contained 0.5 μg of As(III) and 10 mg of Fe(III); pH, 8–9; volume, 500 ml.

Stirring time/min	5	10	15	20	25	30	40
As recovered, %	99	101	101	100	98	99	97

Solution Volume

The effect of variation of the volume of solution containing 0.5 μg of arsenic(III), 10 mg of iron(III) and 1.0 mg of surfactant was studied. Arsenic was recovered quantitatively from volumes of up to at least 1 000 ml. Taking the arsenic content (1 $\mu g\ l^{-1}$ level) in natural waters and the sensitivity of analytical equipment into account, 500 ml of water sample was considered to be a suitable volume.

Effect of Foreign Ions

By following the recommended procedure, the effect of various ions on the separation and determination of arsenic was investigated. Table III shows permissible amounts of foreign ions for the determination of 0.5 μg of arsenic(III) in 500 ml of solution with 10 mg of iron(III) added. As can be seen, the determination of arsenic is scarcely affected by the amounts of foreign ions normally present in natural waters. Of these ions, hydride-forming elements such as selenium(IV), antimony(III) and tin(IV) are coprecipitated with iron(III) hydroxide in the same way as arsenic and would have a relatively strong effect on the arsine generation. However, these ions occur at extremely low levels in natural waters in comparison with arsenic. Therefore, this method can be employed for the determination of arsenic in natural waters without any interference from co-existing ions.

TABLE III

PERMISSIBLE AMOUNTS OF FOREIGN IONS FOR DETERMINATION OF ARSENIC

Solution contained 0.5 μg of As(III) and 10 mg of Fe(III); volume, 500 ml.

Ion	Limit [Ion]/[As]	Ion	Limit [Ion]/[As]	Ion	Limit [Ion]/[As]
Na^+	20 000	Cd^{2+}	2 000	Co^{2+}	2 000
K^+	20 000	Zn^{2+}	2 000	PO_4^{3-}	2 000
Ca^{2+}	20 000	Mn^{2+}	2 000	V^{5+}	1 000
Mg^{2+}	20 000	Al^{3+}	2 000	Bi^{3+}	400
Cl^-	20 000	Cr^{3+}	2 000	Te^{4+}	400
NO_3^-	20 000	Cr^{6+}	2 000	Ni^{2+}	400
SO_4^{2-}	20 000	Mo^{6+}	2 000	Cu^{2+}	200
SiO_3^{2-}	20 000	Pb^{2+}	2 000	Sb^{3+}	60
Sr^{2+}	2 000	Hg^{2+}	2 000	Sn^{4+}	60
Ba^{2+}	2 000	Se^{6+}	2 000	Se^{4+}	10

Recovery of Arsenic

Solutions (500 ml) at pH 8–9 containing 10 mg of iron(III), 1.0 mg of sodium oleate and 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 μg of arsenic(III, V) were analysed by the recommended procedure. Recoveries of the arsenic that had been added were greater than 95% in all instances. Recommended conditions, therefore, appear to be optimum for 500-ml volumes of solutions containing up to at least 10 μg of arsenic.

The relative standard deviation of 10 analyses of solutions containing 0.5 μg of arsenic(III) per 500 ml was less than 3%.

Determination of Trace Amounts of Arsenic in Natural Water

The analyses were carried out on 500-ml aliquots of clear, uncontaminated water (river, well and tap waters), filtered through 0.45-μm Millipore filters after addition of 10 ml of hydrochloric acid per 1 000 ml of sample immediately after collection.

Table IV presents analytical results for natural water samples by the procedure recommended. A known amount of arsenic(III) was added to water samples and the recovery was measured. In these instances the recoveries were from 94 to 103%. The arsenic concentrations in the waters analysed were 1.59, 0.63 and 0.71 $\mu g\ l^{-1}$ for Takahashi River water (Okayama Prefecture, Japan), well water and laboratory tap water, respectively.

TABLE IV

DETERMINATION OF ARSENIC IN NATURAL WATER SAMPLES

Volume of sample, 500 ml.

Sample	Amount of arsenic/μg Added	Found	Recovered	Recovery, %	Arsenic in sample/μg l^{-1}
River water	None	0.795			1.59
	0.200	1.001	0.206	103	
	0.400	1.200	0.405	101	
Well water	None	0.315			0.63
	0.200	0.502	0.187	94	
	0.400	0.700	0.385	96	
Tap water	None	0.357			0.71
	0.200	0.560	0.203	102	
	0.400	0.734	0.377	94	

Conclusions

The flotation of sub-microgram amounts of arsenic coprecipitated with iron(III) hydroxide is useful as a pre-concentration technique for extraction of arsenic from a large volume of water, and subsequent atomic-absorption spectrophotometry in a long absorption cell of the arsine generated from the arsenic is an accurate method for the determination of arsenic.

The method offers a rapid and precise procedure for the routine determination of arsenic in natural fresh waters. This method is also applicable to the flotation of arsenic in artificial sea water. With suitable modifications, the procedure can be applied to determining sub-microgram levels of metals, such as tin(IV), antimony(III, V) and selenium(IV), which readily form volatile hydrides in water.

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