The Determination of Antimony in Water by Atomic-absorption Spectrophotometry Following Flotation Separation

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Synopsis. A flotation method which utilizes an iron(III) hydroxide–surfactant–air system at pH 4 is described for the separation of sub-microgram levels of antimony(III,V) in water. The antimony content is determined by the generation of stibine, followed by atomic-absorption spectrophotometry with a long absorption cell (60 cm× 1.2 cm i.d.).

From the viewpoints of environmental science and geochemistry, there is an increasing need for a rapid and accurate method for determining low parts per billion (ppb) of antimony in water. At a less than 1 μg dm^{-3} level of antimony in water, a precise direct determination is difficult even by the atomic-absorption spectrophotometry of stibine, which has a high sensitivity.[1–4] Accordingly, the antimony must be concentrated from the water prior to determination.

In previous papers,[5–8] a flotation technique,[9,10] one in which the precipitate of iron(III) hydroxide is floated with the aid of a surfactant and small air bubbles, was used for the pre-concentration of arsenic(III,V)[5,6] selenium(IV),[7] and tin(II,IV)[8] in water. The present paper will describe the application of the separation technique mentioned above to the pre-concentration of antimony(III,V), in water and the determination of antimony by atomic-absorption spectrophotometry, following stibine generation.

Experimental

Apparatus. The apparatus employed in this work has all been previously described[5–8] except for the light source, a Hamamatsu TV antimony hollow-cathode lamp.

Reagents. The reagents were the same as those described previously[7,8] except for those mentioned below. The antimony standard solutions were freshly prepared by diluting stock solutions before use. An antimony(III) stock solution (1 mg Sb cm^{-3}) was prepared by dissolving 1.371 g of potassium antimony tartrate hemihydrate in water and then diluting the mixture to 500 cm^3 with water. An antimony(V) stock solution (0.1 mg Sb cm^{-3}) was prepared from the antimony(III) solution by oxidation with a minimum amount of potassium permanganate. A mixed surfactant solution (0.5 mg cm^{-3} for each surfactant) was prepared by dissolving sodium dodecyl sulfate and sodium oleate in 99.5% (v/v) ethanol, with magnetic stirring for sodium oleate. A potassium iodide solution (20% w/v) was prepared by dissolving in water.

Procedure for the Flotation Step. One thousand cm^3 of acidified water is placed in a 1000-cm^3 beaker, and 2 cm^3 of an iron(III) solution (5 mg cm^{-3}) is added. The pH of the solution is adjusted to 4.0±0.2 with an aqueous ammonia solution to precipitate iron(III) hydroxide, and the mixture is stirred for 15 min. After adding 2 cm^3 of the surfactant solution to the beaker, the contents of the beaker are transferred to a flotation cell. Air is passed through at a flow rate of 50 cm^3 min^{-1} from the lower end of the cell for about 2 min to obtain a complete mixing and flotation of the precipitate. Most of the mother liquor is drained from the side arm by opening the cock of the drain pipe. After closing the cock, the residual mother liquor is sucked off through the sintered-glass disk, and the precipitate is washed with 30 cm^3 of water. Four cm^3 of 6 mol dm^{-3} hydrochloric acid is added to the cell to dissolve the precipitate, the filtrate is collected by suction in a 10-cm^3 calibrated flask, the sintered-glass disk is washed with water, the washings are added to the flask, and the mixture is diluted to 9 cm^3 with water. The potassium iodide solution (0.5 cm^3) is added to the flask prior to analysis, and the mixture is diluted to 10 cm^3 with water.

Procedure for the Determination of Antimony. The procedure is similar to that for the determination of tin.[8] A calibration curve is constructed using 2.4 mol dm^{-3} hydrochloric acid solutions containing 1.0 mg cm^{-3} of iron(III), 1.0% of potassium iodide, and 0—0.10 μg cm^{-3} of antimony(III); this curve is linear within the above range of antimony. The detection limit of antimony was found to be 0.4 ng cm^{-3}.

The atomic-absorption apparatus was operated under the following conditions: wavelength, 217.6 nm; lamp current, 12 mA; gas-flow rates, nitrogen 1.0, hydrogen 1.0, and auxiliary nitrogen 6 dm^3 min^{-1}; spectral bandwidth, 1 nm.

Results and Discussion

The effect of the pH of a 1000-cm^3 solution containing 0.8 μg of antimony(III,V) on the coprecipitation of antimony was investigated. As Fig. 1 shows, satisfactory recoveries of antimony(III,V) were obtained in the pH range of 3.4—7.0. At pH values above 7.5, the efficiency of coprecipitation decreased considerably. When the mixed surfactant solution was used, the surface-foam layer supporting the precipitate of iron(III) hydroxide was stable within the pH range of 3.4—10.1; the pH of 4.0±0.2 was, therefore, used throughout the work.

The presence of up to at least 2.5 mg cm^{-3} of iron(III) added as a collector did not affect the stibine generation in the presence of potassium iodide.

Table 1 shows the permissible amounts of foreign

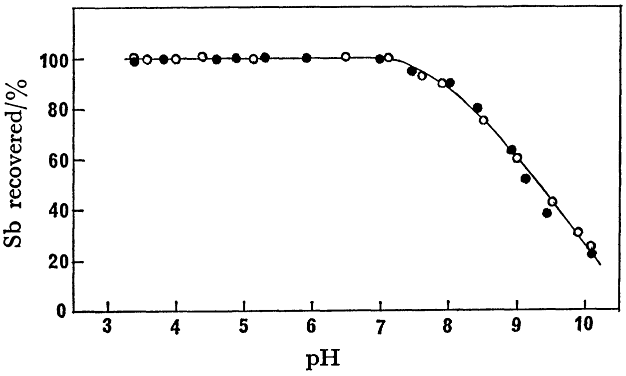

Fig. 1. Coprecipitation of antimony with iron(III) hydroxide as a function of pH.
Solution containing 0.8 μg of Sb and 10 mg of Fe(III), sample volume: 1000 cm^3, ●: Sb(III), ○: Sb(V).

TABLE 1. PERMISSIBLE AMOUNTS OF FOREIGN IONS FOR THE DETERMINATION OF ANTIMONY[a)]

Ion	Limit [Ion]/[Sb]		Ion	Limit [Ion]/[Sb]		Ion	Limit [Ion]/[Sb]	
Na^+	10000	b)	Zn^{2+}	1000	b)	Se^{4+}	1000	b)
K^+	10000		Mn^{2+}	1000		Se^{6+}	1000	
Ca^{2+}	10000		Al^{3+}	1000		PO_4^{3-}	1000	
Mg^{2+}	10000		Cr^{3+}	1000		Ni^{2+}	800	
Cl^-	10000		Cr^{6+}	1000		Te^{4+}	200	
NO_3^-	10000		Mo^{6+}	1000		Bi^{3+}	100	
SO_4^{2-}	10000		Pb^{2+}	1000		(+) As^{3+}	30	
SiO_3^{2-}	10000		Hg^{2+}	1000		(+) As^{5+}	30	
Sr^{2+}	1000		Co^{2+}	1000		(+) Sn^{4+}	10	
Ba^{2+}	1000		V^{5+}	1000				
Cd^{2+}	1000		Cu^{2+}	1000				

a) Solution containing 1.0 μg of Sb(III) and 10 mg of Fe(III); sample volume, 1000 cm^3. b) Maximum concentrations tested. (+): the amounts which give a 10% positive error.

TABLE 2. RECOVERY OF ANTIMONY ADDED TO NATURAL SURFACE-WATER SAMPLES[a)]

Sample	Antimony added μg	Antimony[b)] found μg	Antimony recovered μg	Mean recovery %
Tap water[c)]	None	0.046±0.004		
	0.300	0.343±0.007	0.297	99
	0.600	0.635±0.012	0.589	98
River water[d)]	None	0.028±0.003		
	0.300	0.309±0.008	0.281	94
	0.600	0.592±0.013	0.564	94

a) Volume of sample, 1000 cm^3. b) The mean value of four measurements. c) Laboratory tap water. d) This sample was taken from the Takahashi River, Okayama Prefecture.

ions within a 10% negative or positive error for the determination of 1.0 μg of antimony(III) in 1000-cm^3 solutions. As can be seen in Table 1, most foreign ions hardly interfere at all with the determination of antimony(III). In the procedure described here, the addition of potassium iodide overcame suppressive effects by copper(II) and selenium(IV), but did not show much effect on the negative interference by nickel(II). However, when coprecipitation at pH 4 was used, the depressive effect by nickel(II) was found to be largely eliminated in comparison with that which occurs when antimony is directly determined. That is, when the proposed method was used, the value of the permissible amount of nickel(II) increased from 4 to 800 (Ni/Sb in weight) compared with the value permissible in a direct determination. Hydride-forming elements, such as tin(IV), arsenic(III,V), bismuth(III), and tellurium(IV), are coprecipitated with iron(III) hydroxide in the same way as antimony and exert a relatively great effect on the generation of stibine.

The solutions (1000 cm^3) containing 0.2—20.0 μg of antimony(III) were analyzed by the procedure described above. The recoveries of the antimony that had been added were greater than 94% in all instances. No blank value was detected throughout the analytical process. The proposed conditions, therefore, appear to be optimal for 1000-cm^3 volumes of a solution containing up to 20 μg of antimony(III). The relative standard deviations of ten-times-repeated analyses of the solutions containing 0.4 and 0.8 μg of antimony(III) per 1000 cm^3 were 2.7 and 2.4% respectively.

In order to investigate the applicability of this method to surface water, the recoveries of known amounts of antimony(III) added to natural surface water samples were examined by the above procedure. The analyses were carried out on 1000-cm^3 aliquots of clear, uncontaminated tap and river waters which had been filtered through 0.45 μm Millipore filters after the addition of hydrochloric acid immediately after sampling. Table 2 indicates that the analytical process gave a satisfactory recovery of antimony from surface waters. The antimony concentrations in the tap and river water samples were low: 0.046 and 0.028 μg dm^{-3} respectively.

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