Kurze Mitteilungen

Separation of Antimony from Sea Water by Flotation

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Abtrennung von Antimon aus Meerwasser durch Flotation

In previous papers [5–10], a flotation technique [2–4] in which the precipitate of iron(III) hydroxide is floated with the aid of a surfactant and small air bubbles was used for the preconcentration of arsenic(III,V) [5,6], selenium(IV) [7], tin(II,IV) [8], bismuth(III) [9] in water and sea water, and antimony(III,V) [10] in water.

DeCarlo et al. [1] reported a method for the simultaneous separation of germanium, arsenic, antimony, and selenium from an acidic aqueous solution.

However, to the best of the authors' knowledge, the flotation separation of low ppb levels of antimony in natural sea water has not been reported previously.

This paper describes the application of the above-mentioned separation technique [5–10] for the preconcentration of submicrogram amounts of antimony in natural sea water. The precipitate is readily separated from the mother liquor and then dissolved in dilute hydrochloric acid for the atomic absorption spectrophotometry by generation of stibine using sodium borohydride as a reductant.

The pH-effect was examined for the coprecipitation of antimony using 1,000 ml of solution containing 0.8 μg of antimony(III,V) and 10 mg of iron(III). Hydrochloric acid and aqueous ammonia solution were used to adjust the pH to values within the range of 3.4–10.1. Quantitative recoveries of antimony(III,V) were obtained in the pH-range of 3.4–7.0 [10]. At pH-values above 7.5, the efficiency of coprecipitation decreased considerably. When the mixed surfactant (sodium dodecyl sulphate and sodium oleate) 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.

To investigate the applicability of this method to the separation of antimony in natural sea water, recoveries of known amounts of antimony(III) added to the natural sea water sample were examined by the procedure described here. The analyses were carried out with 1,000 ml aliquots of clear, uncontaminated sea water, filtered through 0.45 μm Millipore filters after the addition of 10 ml of hydrochloric acid immediately after collection. Recoveries of antimony added to the natural sea water sample were about 63% when 10 mg of iron(III) were used. When 20 mg of iron(III) were added to 1,000 ml of the sample solution, recoveries of antimony were about 82% at levels of 0.3 and 0.6 μg of antimony added to natural sea water (Table 1). These recoveries of antimony were quantitatively lower than those obtained when the same procedure was used for the separation of arsenic(III,V) [6], selenium(IV) [7], tin(II,IV) [8], and bismuth(III) [9]. The antimony concentration in the natural coastal sea water sample was lower: 0.15 μg l^{-1}.

Experimental. Apparatus and reagents were almost the same as those described previously [9,10].

Procedure. Place 1,000 ml of acidified sea water sample in a 1,000 ml beaker and add 4 ml of iron(III) solution (5 mg ml^{-1}). Adjust the pH to 4.0 ± 0.2 with aqueous ammonia solution to precipitate iron(III) hydroxide, while stirring magnetically for 15 min. Add 4 ml of mixed surfactant solution [0.5 mg ml^{-1} for each of sodium dodecyl sulphate and sodium oleate in 99.5% (v/v) ethanol] into the beaker. Transfer the contents of the beaker to a flotation cell and wash the residue in the beaker into the cell by using three small portions of water. Pass air at a flow rate of 50 ml min^{-1} from the lower end of the cell for about 2 min, in order to obtain complete mixing and flotation of the precipitate. While the air was passing through at a flow rate of about 10 ml min^{-1}, most of the mother liquor was drained by the side arm by opening the cock of the drain pipe. After closing the cock, suck off the residual mother liquor through the sintered-glass disk. Wash down the precipitate adhering to the wall of the cell by spraying with water, then wash the precipitate with 30 ml of water. Add 4 ml of 6 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 disk with water, add the washings to the flask and dilute to 9 ml with water. Add 0.5 ml of potassium iodide solution (20% w/v) into the flask prior to analysis and dilute to 10 ml with water.

The procedure for the atomic absorption spectrophotometric determination of antimony after the separation was almost the same as those for the determination of bismuth [9] and antimony [10]. Construct a calibration curve using 2.4 M hydrochloric acid solutions containing 2 mg ml^{-1} of iron(III), 1% of potassium iodide and 0–0.10 μg ml^{-1} of antimony(III); this curve is linear within the above range of antimony. The atomic absorption equipment 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 61 min^{-1}; spectral bandwidth 1 nm.

Table 1. Recovery of antimony added to natural sea water[a]

Antimony (μg)			Mean recovery (%)
Added[b]	Found[c]	Recovered	
None	0.120 ± 0.004		
0.300	0.370 ± 0.012	0.250	83
0.600	0.605 ± 0.016	0.485	81

[a] This sample was taken at 34° 25′ N, 133° 54′ E (Shibukawa, Okayama Prefecture, Japan); volume of sample, 1,000 ml; Fe(III), 20 mg
[b] Added as Sb(III)
[c] Mean value ± S.D. of four measurements

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Cerium(IV)-Iron(II) Back-Titrimetric Determination of the Composition of Ternary Uranium Oxides

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Bestimmung der Zusammensetzung ternärer Uranoxide durch Cer(IV)/Eisen(II)-Rücktitration

The composition of ternary uranium oxides which is generally expressed as $M_yU_{1-y}O_{2+x}$ (M: alkali metals, alkaline earth metals or rare earth elements) can be obtained if the amount of total uranium is determined as well as uranium(IV) for a known weight of the compound. However, reports concerning it [1, 2] are meagre. We report here a modified method for the composition of ternary uranium oxides where the total uranium is determined by a pipetting technique of reduction with zinc amalgam after dissolution in sulphuric acid containing excess cerium(IV) and uranium(IV) is determined by the back-titration method of Dharwadkar and Chandrasekharaiah [3].

Two separate procedures are necessary for a sample, which will be designated as procedure 1 and 2 hereafter. *Procedure 1* is essentially the same as that of Dharwadkar and Chandrasekharaiah [3]. In a small glass crucible, 10−30 mg of the sample is weighed out and the sample powder is transferred to a titration vessel (50 ml beaker). 5 ml of cerium(IV) sulphate solution (0.07−0.08 M in 1.5 M H_2SO_4), standardized with stoichiometric UO_2 are pipetted into the beaker and several ml of 3 M H_2SO_4 are added. The beaker is warmed on a steam bath at 60−80°C until dissolution of the sample is completed. To the solution, one drop (ca. 0.06 ml) of ferroin indicator (0.006 M) is added, and the excess cerium(IV) is titrated against standard iron(II) ammonium sulphate solution (0.05 M in 1.5 M H_2SO_4) from a calibrated 10 ml micro-burette swirling the solution with magnetic stirrer. *Procedure 2* is the same as procedure 1 until dissolution. Then, the solution is transferred into a 20 ml glass bottle containing a few ml of zinc amalgam [4]. This is done by using a fine-nozzled pipette of which the end is connected to a syringe with gum tube. The bottle should have a cap with polyethylene packing so as to prevent the leakage of solution on shaking. After the cap is tightened, the bottle is shaken vigorously for about 1 min. Then, the solution is transferred back to the beaker by the same pipette. Several milliliter of 1.5 M H_2SO_4 are introduced into the bottle followed by shaking, and the solution is added to the solution of the reduced uranium by the pipette. This washing procedure is repeated twice. Subsequently, oxygen is passed through the solution from a fine nozzle of glass tubing at a rate of ca. 0.5 ml·s^{-1} for 15 min to oxidize any traces of over-reduced uranium(III) to uranium(IV). 5 ml of the cerium(IV) sulphate solution are pipetted into the beaker, and the remaining cerium(IV) is titrated against iron(II) after the addition of one drop of the ferroin solution.

Table 1. Determination of x and y values of $Sr_yU_{1-y}O_{2+x}$

No.	Pro-cedure	Sample weight (mg)	Iron(II) solution (ml)	x Value	y Value
	1	19.877[a]	4.970[a]		
1	2	20.435	3.921[b]	−0.0371	0.3008
2	2	21.780	3.743[b]	−0.0357	0.3000
3	2	18.855	4.127[b]	−0.0357	0.3000
4	2	18.865	4.134[b]	−0.0443	0.3052
5	2	18.850	4.133[b]	−0.0413	0.3033

Average of x values: −0.039
Average of y values: 0.302

Composition of the sample: $x = -0.036 \pm 0.001$, $y = 0.300 \pm 0.001$
Concentrations of the standard solutions: $Ce(IV) = 0.06269 \pm 0.0001$ M, $Fe(II) = 0.04753 \pm 0.0001$ M
[a] Averaged values of three determinations
[b] Corrected for blank, 0.053 ml

Applicability of the present method was examined for a solid solution, $Sr_yU_{1-y}O_{2+x}$, having a known composition [5, 6]. Table 1 shows the x and y values of this test sample. These values were obtained with no knowledge other than that the component elements were strontium, uranium and oxygen, and that the valencies of strontium and oxygen were +2 and −2, respectively. The average of five determinations gave $x = -0.039$ and $y = 0.302$, which are in good agreement with the known composition of $x = -0.036 \pm 0.001$ and $y = 0.300 \pm 0.001$. It is reasonable to estimate that the volume error in titration is less than 0.006 ml, which leads to accuracies for x and y values of ± 0.006 and ± 0.004, respectively. Direct calculation of standard deviation in Table 1 exhibits smaller errors.

The present method may be useful because: (1) Oxides were dissolved more rapidly in the presence of excess cerium (IV), even for total uranium determinations. (2) Instead of the usual separatory funnel, reduction was carried out in a liquid-tight small glass bottle. The solution was transferred in and out of the bottle using a fine-nozzled pipette. (3) Back-titration for total uranium. The sharp end-point enables us to determine the composition of small amounts of ternary uranium oxides (10−30 mg for each determination). (4) Higher accuracies of $\Delta x = \pm 0.006$ and $\Delta y = \pm 0.004$.

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