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Determination of Silver in Sea Water after Flotation with 2-Mercaptobenzothiazole

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Synopsis. Nanogram quantities of silver in 3000 ml of acidified sea water were quantitatively coprecipitated with 2-mercaptobenzothiazole. The precipitate was then floated with the aid of small nitrogen bubbles, and the silver determined by atomic-absorption spectrophotometry after wet oxidation. The silver concentration was 0.09 μg per liter.

Since the silver content of sea water is low (reported values: 0.0—2.9 μg per liter),[1,2] it must be concentrated from a large volume of sample before atomic-absorption spectrophotometric determination. Traces of silver ions in aqueous solutions can be collected on the precipitate formed by adding an acetone solution of 2-mercaptobenzothiazole,[3] but filtration of this amorphous precipitate is difficult. Centrifugation also is not applicable because of incomplete sedimentation. In the present work, the flotation technique[4] was successfully applied. The precipitate is readily separated from the main liquor without surfactants, and then the silver in it is determined by atomic-absorption spectrophotometry. Commercial 2-mercaptobenzothiazole contained appreciable amounts of silver, but it was easily purified by the amalgamation method.[5]

Experimental

Apparatus. A Nippon Jarrell-Ash model AA-1 Mark II atomic-absorption spectrophotometer with an SA-61 slit burner and a Hitachi model QPD53 recorder, and a Fujitsu well-type NaI(Tl) scintillation counter were employed. The flotation cell consisted of a 120 mm i.d. × 700 mm or 45 mm i.d. × 250 mm glass tubing tapered at the lower end with a sintered-glass disc (No. 4, 110 mm or 40 mm diam.) near the lower end.

Reagents. A 2-mercaptobenzothiazole solution (40 mg/ml) was prepared and purified as follows: 4 g of 2-mercaptobenzothiazole was dissolved in 90 ml of acetone in a 200-ml tall beaker, 2 ml of mercury was added, and the solution was stirred vigorously for 10 min with a magnetic stirrer. The mercury was separated by centrifugation, another 2 ml of mercury was added to the solution, and the above treatment was repeated once more. The solution was diluted to 100 ml with acetone. Standard silver solutions were prepared from silver nitrate. Water was purified by distillation and ion-exchange. All reagents used were of reagent grade. ^{110m}Ag was used as a tracer.

Recommended Procedure. Place 3000 ml of sea water (acidified to 0.1 M with nitric acid) in a 5000-ml beaker, and add 50 ml of 2-mercaptobenzothiazole solution in small portions while stirring with a magnetic stirrer. Stir the solution vigorously for 30 min. Transfer the contents of the beaker (excluding the stirring bar) to a flotation cell (120 mm i.d. × 700 mm), and wash the beaker with 50 ml of 1 M nitric acid. Pass nitrogen from the lower end of the cell for 1—2 min to effect complete agitation followed by flotation of the precipitate with small bubbles (*ca.* 0.1 mm diam.). Suck off the main liquor through the sintered-glass disc, and wash the precipitate with two 100-ml portions of 1 M nitric acid followed by two 100-ml portions of water (to remove the nitric acid). Discard the filtrate and washing solutions. Add 50 ml of acetone to the cell to dissolve the precipitate, collect the filtrate by suction in a 200-ml beaker, and wash the sintered-glass disc with 20 ml of acetone. Evaporate the solution to dryness on a water bath, cautiously add 20 ml of 13.8 M nitric acid, heat gently to dissolve the residue, and evaporate to 5 ml. Transfer the solution to a 50-ml beaker, and wash the 200-ml beaker with 15-ml of 13.8 M nitric acid. Evaporate the solution to near dryness and cool. Add 4 ml of 30% hydrogen peroxide in small portions (the residue becomes colorless) and evaporate to near dryness. Wash the walls of the beaker with 3 ml of 30% hydrogen peroxide and evaporate again to near dryness. Dissolve the residue in 3 ml of 13.8 M nitric acid, transfer the solution to a 5-ml volumetric flask, wash the beaker with water, and dilute to the mark. Determine the silver in the solution by atomic-absorption spectrophotometry under the following operating conditions: wavelength 328.1 nm, lamp current 10 mA, air 8.0 l/min, acetylene 2.5 l/min, slit-widths 0.10 (entrance) and 0.15 mm (exit). Construct a calibration curve by taking 1 ml of standard silver solutions containing 0—5.0 μg of silver and 3 ml of 13.8 M nitric acid in a 5-ml volumetric flask and diluting to the mark with water. Run a blank through the whole procedure using 3000 ml of 0.5 M nitric acid.

Tracer Experiments. The recovery of silver from 3000 or 100 ml of artificial sea water[6] or diluted nitric acid was examined radiochemically. For the 3000-ml samples, the gamma-activity of a 2-ml aliquot of the final 5-ml solution obtained by the recommended procedure was measured. For 100-ml samples, the separation of silver was carried out as follows. A hundred ml of artificial sea water or diluted nitric acid containing 0.05 μg of labeled silver was placed in a 200-ml beaker, 2.5 ml of 2-mercaptobenzothiazole solution was added, and the solution was stirred for 30 min. The contents of he beaker were transferred to a flotation cell (45 mm i.d. × 250 mm), the beaker was washed with 10 ml of water, and nitrogen was passed for 15 s. The main liquor was sucked off and discarded. Six ml of acetone was added to the cell to dissolve the precipitate, the filtrate was collected in a 10-ml volumetric flask, and diluted to the mark with acetone. The gamma-activity of a 2-ml aliquot was measured.

Results and Discussion

Purification of 2-Mercaptobenzothiazole. 2-Mercaptobenzothiazole is a readily available and inexpensive reagent, but containing 0.15—0.30 ppm of silver. Tracer experiments showed that more than 95% of silver was removed by the amalgamation method (80% removed by a single treatment). Silver in 50 ml of purified 2-mercaptobenzothiazole solution was less than 0.1 μg (from atomic-absorption spectro-

photometry).

Reaction Conditions. Tracer experiments were carried out on 100-ml samples to determine the optimal acidity for the separation of silver. The results are shown in Fig. 1. Silver, 0.05 μg, was recovered in yields greater than 95% from artificial sea water acidified to 0.04—1.5 M with nitric acid and from 0.3—1.5 M nitric acid. The low recoveries in nitric acid below 0.2 M were due to the passage of the precipitate through the sintered-glass disc (resulting from incomplete coagulation).

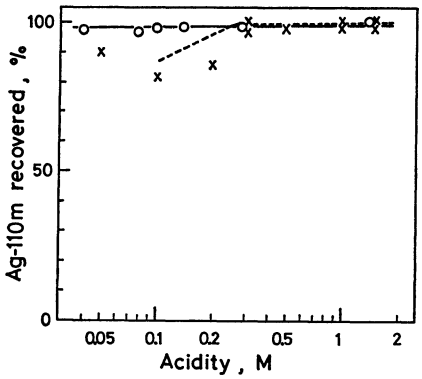

Fig. 1. Effect of acidity on silver recovery.
Solution volume: 100 ml; Ag: 0.05 μg; 2-mercaptobenzothiazole solution: 2.5 ml.
—○—: Artificial sea water, --×--: Diluted nitric acid.

Table 1. Determination of silver in sea water

Sample	Ag found (μg)	Ag in sample (μg/l)
1	0.30	0.10
2	0.28	0.09
3	0.28	0.09
4[a)]	0.30	0.10
5[b)]	0.57	0.09
6[c)]	0.72	0.07
		Av. 0.09

Solution volume: 3000 ml; Salinity: 35.16 ‰; Location: 22°01′N, 152°00′E.
a) An acidic sample was filtered through a Millipore filter HA (0.45 μm). b) 0.30 μg of silver was added. c) 0.50 μg of silver was added.

From 3000 ml of artificial sea water (acidified to 0.1 M with nitric acid) and 0.5 M nitric acid, 0.05—5 μg of labeled silver was separated by the recommended procedure with the following recoveries: 96, 97% for 0.05 μg of silver, 96, 96, 96, 97, 97% for 1 μg, 97, 98% for 5 μg (in artificial sea water); 95, 95% for 0.05 μg, and 96% for 5 μg (in 0.5 M nitric acid).

Atomic-Absorption Measurements. The calibration curve was linear up to at least 5 μg of silver with a maximum deviation of 0.05 μg, and passed through the origin. The lower limit of determination was 0.1 μg. Fifty mg each of sodium, magnesium, potassium, and strontium, and 2.5 mg of calcium did not interfere with the determination of silver. The residue from evaporation of the final 5-ml solution weighed 25—35 mg, and the calcium in it was less than 1 mg (determined by EDTA titration).

Determination of Silver in Sea Water. The analyses were carried out on 3000-ml aliquots of a sample of surface sea water acidified to 0.1 M with nitric acid immediately after collection. The results are shown in Table 1. The blank through the whole procedure was less than 0.1 μg of silver. The time required for a determination was about 4 hr.

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