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The Rapid Collection of Traces of Silver with Mercury in an Ultrasonic Field

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Previously we reported that microgram quantities of silver deposit quantitatively into numerous mercury globules from 1 to 3 mm in diameter from stirred aqueous solutions, leaving large amounts of such base metals as iron, copper, and lead in the solutions.[1,2] Because mercury is removed by evaporation from the resulting dilute amalgam, this separation method is useful as a preconcentration technique in trace analysis. The procedure, however, is rather time-consuming. The present note will describe a more rapid separation method using a mercury-in-water emulsion in an ultrasonic field. This method has been applied to the atomic absorption spectrometric determination of silver at a low ppm level in lead.

Experimental

Apparatus. A Kaijo Denki model MA-2302 ultrasonic generator (29 kHz, 45 W) with a cylindrical transducer (13 mm diam. × 100 mm) coated with epoxy resin. A Hitachi model 139 spectrophotometer with a model 139-0420 atomic absorption attachment and a model QPD-53 recorder.

Solutions. Ammoniacal sample solutions were prepared by mixing 2 ml of nitric acid, 1.5 ml of hydrochloric acid, and 10 ml of aqueous ammonia and by then diluting to 25 ml with water, or by dissolving 5 g of high-purity copper in 40 ml of 7 M nitric acid, adding 15 ml of hydrochloric acid and 100 ml of aqueous ammonia, and diluting to 200 ml with water.

Standard Procedure. Place 25 ml of water and 34 g of mercury in a 50 ml beaker, immerse an ultrasonic transducer about 2 mm deep in the water, and apply ultrasonics for 30 s to obtain a gray emulsion containing about 150 mg of mercury. Within 3 min add this emulsion to a 100 ml, round-bottomed centrifuge tube containing 25 ml of the sample solution and apply ultrasonics for 30 s as has been described above. Centrifuge for 3 min at 4000 rpm and then discard the supernatant liquid. Add 5 ml of acetone and stir vigorouly with a glass rod for 10 s to effect coalescence into a single mercury droplet (about 3 mm in diameter)

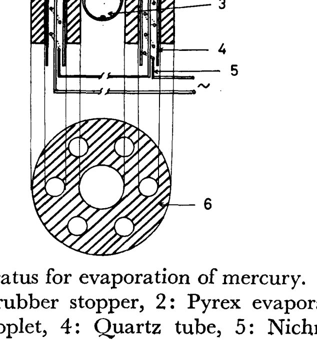

Fig. 1. Apparatus for evaporation of mercury.
1: Silicone rubber stopper, 2: Pyrex evaporation tube, 3: Mercury droplet, 4: Quartz tube, 5: Nichrome wire, 6: Brass block.

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[1] S. Hirano and A. Mizuike, *Bunseki Kagaku*, **8**, 746 (1959).

[2] A. Mizuike, T. Sakamoto, and K. Sugishima, *Mikrochim. Acta* (Wien), **1973**, 291.

with a metallic luster. Discard the acetone, wash the droplet with 2 ml of acetone two or three times, and discard the washings. Transfer the mercury droplet to the bottom of an evaporation tube with a dropping pipet, and then evaporate the mercury at 350 °C (Fig. 1). Cool, and then remove the mercury condensed on the walls of the evaporation tube using a mercury-plated copper wire. Add 1 ml of nitric acid to the evaporation tube to dissolve the residue.

Results and Discussion

Preparation of Mercury-in-Water Emulsions. Mercury-in-water emulsions were prepared with from 7 to 68 g of mercury and 25 ml portions of water with the aid of ultrasonics; the mercury in the emulsion was then separated as a single droplet by centrifugation and by washing with acetone as has been described under *Standard Procedure*, and determined by weighing or EDTA titration. As is shown in Fig. 2, saturation was reached after 20 s of ultrasonic irradiation. The reproducibility for 40 s of ultrasonic irradiation was as follows: 127, 122, 114, 125, and 125 mg of mercury in an emulsion (with 20 g of mercury), and 155, 150, 146, 152, and 138 mg (with 34 g of mercury). The diameter of the mercury droplets was from 1 to 4 μm after 20 s, and the emulsion was stable for about 5 min.

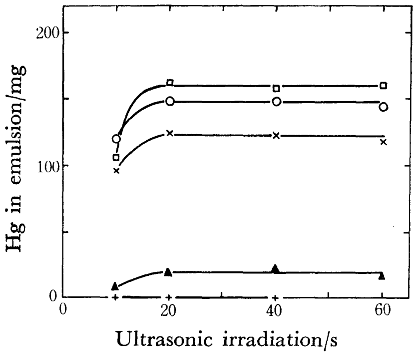

Fig. 2. The quantity of mercury in emulsion as a function of time of ultrasonic irradiation.
Hg used: (□) 68 g, (○) 34 g, (×) 20 g, (▲) 14 g, (+) 7 g.

Collection of Silver. A mercury-in-water emulsion (25 ml) was added to 25 ml of a sample solution containing from 5 to 10 μg of ^{110m}Ag-labeled silver; the silver was then collected as has been described under *Standard Procedure* except that the quantity of mercury and the collecting time were changed, and the gamma activity of the mercury droplet was measured. The results are summarized in Fig. 3. A silver recovery of greater than 96% was attained with from 125 to 150 mg of mercury between 20 and 40 s. In the case of nitric acid solutions, the silver recovery then decreased with the time because of the dissolution of mercury in the solutions, as is shown in Fig. 4. The dissolved mercury was determined by EDTA titration after the removal of the mercury droplets by means of a centrifuge.

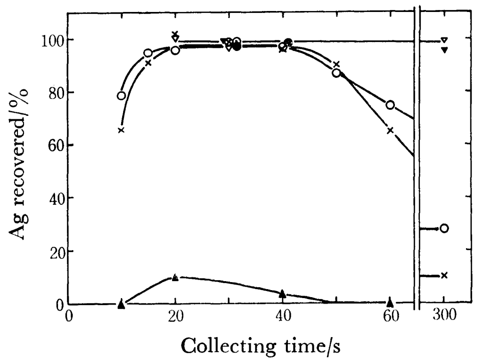

Fig. 3. Collection of silver with mercury.

Hg in emulsion (mg)	Sample solution
(○) 150	0.2 M nitric acid
(●) 150	0.2 M nitric acid solution containing 1 g of Pb
(⊙) 150	0.2 M nitric acid solution containing 1 g of Cu
(×) 125	0.2 M nitric acid
(▲) 20	0.2 M nitric acid
(▽) 150	Ammoniacal solution
(▼) 150	Ammoniacal solution containing 0.5 g of Cu

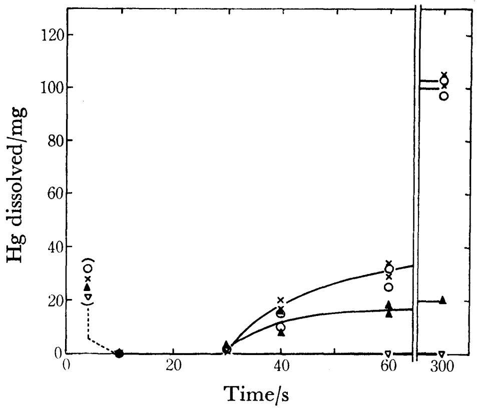

Fig. 4. Dissolution of mercury.

Hg in emulsion (mg)	Sample solution
(○) 150	0.2 M nitric acid
(×) 125	0.2 M nitric acid
(▲) 20	0.2 M nitric acid
(▽) 150	Ammoniacal solution

Separation of Silver from Matrix Elements. Table 1 shows that ppm quantities of silver in lead and copper matrices can be separated with recoveries of greater than 96% and concentration factors of greater than 10^5 by the standard procedure. In this experiment, both the silver recovery and the quantity of the matrix elements accompanying the silver were measured after the removal of the mercury by evaporation.

The proposed method may also be applied to the separation of traces of gold or palladium from copper and other base metals in ammoniacal or nitric acid solutions.

Table 1. SEPARATION OF SILVER FROM MATRIX ELEMENTS IN 0.1 M NITRIC ACID SOLUTIONS[a]

Matrix element present (g)	Ag recovered (%)	Matrix element accompanying Ag[b] (μg)
Pb 0.50	96, 100	—
Pb 1.00	98, 100	3, 5
Cu 1.00	96, 102	0.7, 1.3

a) ^{110m}Ag-labeled Ag present 3-10 μg,
b) Determined by square-wave polarography.

Determination of Traces of Silver in Lead. A 5 g lead sample was dissolved in 15 ml of 7 M nitric acid. The solution was then evaporated to dryness, and the residue was dissolved in 50 ml of 0.5 M nitric acid. A 1/10 or 1/5 aliquot was taken and diluted to 25 ml with 0.12 M nitric acid or water (final acidity, 0.2 M). The silver in the solution was separated by the standard procedure, and the residue in the evaporation tube was dissolved in 1 ml of 7 M nitric acid. The solution was then evaporated to dryness, and the residue was dissolved in 0.80 ml of 2 M nitric acid and then in 1.20 ml of acetone. The silver in the solution was then determined by atomic absorption spectrometry at 328.1 nm.[2] The analytical results are shown in Table 2. The time required for a determination was about 2 hr.

TABLE 2. DETERMINATION OF SILVER IN LEAD

Sample	Aliquot taken	Ag found[b] (μg)	Ag in sample (ppm)
High-purity lead, 5.00 g	1/10	1.8	3.6
	1/10	1.9	3.8
	1/5	3.5	3.5
	1/5[a]	8.4	3.4
			Av. 3.6

a) 5.0 μg of Ag was added before the separation.

b) A blank value was not detected (<0.2 μg).