PRECONCENTRATION AND SEPARATION OF TRACE AMOUNTS OF BISMUTH IN HIGH PURITY SILVER WITH HYDROUS LEAD DIOXIDE

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Abstract - A simple method for reconcentration and separation of trace amounts of bismuth(III) in the presence of large amounts of silver(I) was established by filtration through a membrane filter loaded with hydrous lead dioxide(HLD), which adsorbed 5-10 μ g of bismuth(III). Bismuth(III) was not affected by the presence of 5-10 g of silver(I) at pH 1, because the adsorption of silver(I) on the HLD occurred at a pH above 2. This method is applicable to the determination of bismuth in high purity silver.

Key words bismuth, hydrous lead dioxide loaded on membrane filter, preconcentration, differential pulse polarography, high purity silver

We have recently applied hydrous lead dioxide(HLD), freshly produced by hydrolysis of lead tetra-acetate, as a collector for trace amounts of metal ions. The adsorption behavior of some metal ions on HLD has already been reported[1-7]. Previously, we reported that HLD is a superior adsorbent for bismuth(III) in acidic medium and that trace amounts of bismuth(III) can be rapidly and quantitatively collected by filtration through a membrane filter loaded with the HLD, even in the presence of large amounts of aluminum(III)[8]. In this study, we examined the adsorption behavior of silver(I) on HLD and developed a filtration method for preconcentration and separation of trace amounts of Bi(III) in the presence of large amounts of silver(I). The method, in which the collected bismuth(III) was analyzed by differential pulse polarography, was applied to the determination of bismuth in high purity silver.

EXPERIMENTAL

Apparatus A Nippon Jarrell-Ash model AA-855 atomic absorption spectrometer and a PAR model 174A polarographic analyzer were used for the determination of silver(I) and bismuth(III), respectively. The pH meter and incubator used were those employed previously[4,8].

Reagents A stock solution(0.05 M) of lead tetra-acetate in glacial acetic acid was prepared and standardized as reported previously[4,8]. Standard solutions (5×10^{-3} M) of bismuth(III) and silver(I) were prepared by dissolving pure metal(99.99 and 99.999 % purity, respectively) in nitric acid, and adjusted to the final solutions 0.1 M nitric acid. The silver(I) solution(1 M) used for preparation of test solution containing large amounts of silver(I) was prepared by dissolving AgNO_3 of analytical reagent grade in 0.1 M nitric acid, and removal of bismuth(III) impurity in the reagent using HLD. All the other chemicals used were of analytical reagent grade. The water used was made by distilling deionized water containing small amounts of KMnO_4 and NaOH.

Preparation of hydrous lead dioxide(HLD) HLD was prepared by the addition of 10 ml of 0.05 M lead tetra-acetate solution to 100 ml of water, then centrifuging, removing the supernatant liquid, and washing twice with 100 ml portions of water. About 5×10^{-4} mol of HLD (taken as $\text{PbO}_2 \cdot n\text{H}_2\text{O}$) was used for each adsorption test.

Adsorption test for silver(I) ion by a batch method HLD, a known amount of silver(I) and an appropriate buffer solution were placed in a 200 ml Erlenmeyer flask and diluted to 100 ml with water. The pH of the suspension was adjusted with 0.02 M nitric acid-acetic acid, acetic acid-sodium acetate, nitric acid-borate buffers. The suspension was shaken for 1 hr at 30 °C. The HLD was then filtered off with a cellulose nitrate membrane filter (0.45 μ m pore size) and the concentration of silver(I) in the filtrate was determined by a flame atomic

absorption spectrophotometer with an air-acetylene flame. The amount of silver (I) adsorbed was calculated from the difference in its concentration before and after adsorption.

Preparation of HLD loaded filter The suspension containing 5×10^{-4} mol of HLD freshly prepared from the hydrolysis of lead tetra-acetate, as described above, was filtered through a cellulose nitrate membrane filter ($0.45 \mu\text{m}$ pore size), and HLD was retained on the membrane filter. HLD on the membrane filter was washed with two 50 ml portions of water.

Collection of bismuth(III) by a filtration method Known amounts of bismuth (III) and silver(I) and 10 ml of 5 M nitric acid were placed in a 500 ml Erlenmeyer flask, diluting to 500 ml with water. The sample solution was passed through the HLD loaded filter at a normal flow rate at about 100 ml/min, washing with 150 ml of 0.1 M nitric acid solution. HLD was dissolved with 20 ml of 0.2 M EDTA solution, followed by addition of 2 ml of 1.5 M sodium citrate, 5 ml of 1 M potassium nitrate and 2 ml of 0.25 % acrylamide(polymer). The mixture was adjusted to the pH range of 5.0 to 5.5, diluted to 50 ml with water, and then bismuth(III) in the solution was determined by differential pulse polarography. The amount of bismuth(III) collected was calculated by a standard addition method.

RESULTS AND DISCUSSION

Adsorption behavior of silver(I) The adsorption of silver(I) on HLD from aqueous solution at various pH values was examined by the batch method, using 5×10^{-5} M silver(I) solution. Fig. 1 shows the results and the effect of pH on the adsorption of bismuth(III), for comparison. The adsorption of silver (I) occurred at a pH above 2, and was almost 100 % at a pH above 6, with shaking 1 hr at 30 °C. The adsorption was similar to that of the solution containing divalent metal ions[3].

Effect of silver(I) concentration on the adsorption was investigated at pH 8. There was almost 100 % adsorption, when the concentration of silver(I) was less than 5×10^{-5} M.

Fig. 1 Effect of pH on the adsorption of silver(I) and bismuth(III) on HLD

(○) Ag(I), (●) Bi(III) : 2×10^{-5} M.
Solution volume : 100 ml, shaking time : 1 hr,
temperature : 30 °C.

Effect of the presence of silver(I) on the adsorption of bismuth(III) On the basis of the above results, the effect of the presence of silver(I) on the adsorption of bismuth(III) was studied by the batch method at pH 1. The adsorption of bismuth(III) on HLD from 2×10^{-5} M bismuth(III) solution in the presence of 1×10^{-3} to 1 M silver(I) adjusted to pH 1 was almost 100 %.

Collection of bismuth(III) in the presence of silver(I) by the filtration method The effects of the concentration of bismuth(III) and the flow rate on the collection of bismuth(III) by the filtration method were already described in

previous report[8]. Therefore, the effect of the presence of large amounts of silver(I) on the collection of trace amounts of bismuth(III) was examined. A 500 ml portion of the sample solution containing bismuth(III) and silver(I) adjusted to pH 1 was passed through the HLD loaded filter at a normal flow rate at about 100 ml/min. As shown in Table 1, the collection of trace amounts of bismuth(III) (5-100 μ g) was not affected by the presence of large amounts of silver(I) (5-10 g).

TABLE 1. Collection of bismuth(III) in the presence of silver(I)^{a)}

Ag taken, g	Amount of Bi		Average recovery, %
	Taken, μ g	Found ^{b)} μ g	
5	5.2 ₄	5.1 ₉ $\pm$ 0.1 ₀	99
10	5.2 ₄	5.2 ₄ $\pm$ 0.1 ₀	100
10	10.5	10.4 $\pm$ 0.2	99
10	20.9	20.7 $\pm$ 0.3	99
10	105	105 $\pm$ 1	100

a) Solution volume : 500 ml, flow rate : 100 ml/min.

b) Average and deviation are based on 4-5 runs.

In addition, the effect of other experimental conditions on the collection of bismuth(III) was examined, using a sample solution containing 5 μ g Bi(III) and 5 g Ag(I). The same results as described above were obtained at flow rates from 50 to 300 ml/min, and also obtained from the sample solution adjusted to pH 1.5 or to the acid concentration of 0.5 M nitric acid.

Effect of coexisting substances The effect of coexisting substances on the procedure was examined. A 500 ml sample solution containing 5 μ g Bi(III) and 5 g or 10 g Ag(I) along with one of the other ions in the concentration of 200 μ g or 500 μ g was passed through the HLD loaded filter. As shown in Table 2, the presence of other coexisting substances, which are usually contained in high purity silver, did not interfere with the collection of bismuth(III).

TABLE 2. Effect of foreign ions on the recovery of bismuth(III) in the presence of large amounts of silver(I)^{a)}

Foreign ions		Ag taken, μ g	Recovery ^{b)} %
Ions	Added, μ g		
Fe(III)	200	5.4	99 $\pm$ 3
	500	10.8	99 $\pm$ 2
Cu(II)	200	5.4	100 $\pm$ 2
	500	10.8	99 $\pm$ 2
Pb(II)	200	5.4	98 $\pm$ 2
	500	10.8	99 $\pm$ 2
Zn(II)	200	5.4	100 $\pm$ 2
	500	10.8	99 $\pm$ 2
Sn(IV)	200	5.4	100 $\pm$ 2
	500	10.8	99 $\pm$ 2

a) Bi(III) taken : 5.2₄ μ g, solution volume : 500 ml, flow rate : 100 ml/min.

b) Average and deviation are based on 4-5 runs.

The following conclusions were drawn:

① HLD loaded on the membrane filter is recommended as a collector for the preconcentration of bismuth (III), owing to its excellent collecting ability. The trace amount of bismuth was rapidly and quantitatively collected by the simple filtration method using the membrane filter loaded with HLD, even in the presence of a large amount of silver. ② The variation of the experimental conditions, such as the acid concentration of the sample solution and the flow rate on the filtration procedure, had little effect on the collection of bismuth(III). ③ The presence of other coexisting substances, which are usually contained in high purity silver, did not interfere with the collection of bismuth(III). ④ The present method, which involves the collection of bismuth(III) with the HLD loaded filter and then the determination of its by differential pulse polarography, can be successfully applied to the determination of trace amounts of bismuth in a high purity silver sample.

Application to the determination of bismuth in high purity silver

The present method was applied to a high pure silver sample (99.99 and 99.999 % purity). The sample of shot high purity silver (5 g or 10 g) was dissolved in 20 ml or 40 ml of (1+1) nitric acid, respectively, by warming the solution

on a hot plate. The resulting solution was diluted to 500 ml with water, and treated according to the proposed method. The results are shown in Table 3. The determination limit was 0.1 ppm, when 5 g sample was used. In conclusion, trace amounts of bismuth in high purity silver can be determined easily using the proposed method.

TABLE 3. Results of the determination of bismuth in high purity silver^{a)}

Sample	Taken, g	Added, μ g	Bi		Bi	
			Found ^{b)}	μ g	content ^{c)}	ppm
99.999 %	5	0		< 0.3	< 0.1	(n=5) ^{e)}
	5	5.1 ₇	5.2 ₆	$\pm 0.1_6$	< 0.1	(n=5) ^{e)}
	10	0		< 0.3	< 0.1	(n=4) ^{e)}
99.99 %	5	0	2.1 ₆	$\pm 0.1_8$	0.4 ₃	(n=6) ^{e)}
	5	5.1 ₇	7.3 ₈	$\pm 0.1_6$	0.4 ₄	(n=5) ^{e)}
	10	0	4.2 ₆	$\pm 0.1_8$	0.4 ₃	(n=7) ^{e)}
	10	0	4.2	$\pm 0.6^d)$	0.4 ₂	(n=5) ^{e)}

a)HLD : 5×10^{-4} mol, solution volume : 500 ml, flow rate : 100 ml/min.

b)Average $\pm$ standard deviation. c)Average. d)From the AAS method[9].

e)Number of measurements.

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