Determination of Trace Amounts of Bismuth in Water by Hydride Generation Atomic Absorption Spectrometry after Preconcentration with Thionalide-Loaded Silica Gel

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2-Mercapto-*N*-2-naphthylacetamide (thionalide)-loaded silica gel is used for preconcentration of bismuth(III) in lower concentration than $\mu\text{g l}^{-1}$ from water samples. Bismuth(III) is quantitatively retained on the loaded gel from 0.1–1.0 M (mol l^{-1}) nitric acid or 0.1 M hydrochloric acid solutions in batch experiments. Equilibration is achieved within 2 min. The retention capacity of the gel is $2 \mu\text{mol Bi(III) g}^{-1}$ at 0.25 M nitric acid. The maximum flow velocity for quantitative retention is 2.8 cm min^{-1} . Bismuth retained on the column is completely eluted with 10 ml of 4.0 M hydrochloric acid at flow velocity 1.3 cm min^{-1} . Bismuth in the effluent is determined by atomic absorption spectrometry with hydride generation; the detection limit is 1.0 ng of bismuth.

Keywords Thionalide-loaded silica gel, preconcentration, bismuth(III), water analysis, atomic absorption spectrometry, hydride generation, river water

Bismuth has been industrially utilized as a constituent of many kinds of alloys, semiconductors and contact materials. This element is considered to behave like tin and antimony in hydrosphere. It is thus important to investigate the chemical behavior of this element in natural waters from the standpoint of environmental pollution control. However, the concentrations of bismuth in seawater and rainwater have been reported by Lee¹ to be as low as $0.13\text{--}2.0 \text{ ng kg}^{-1}$ and 3.2 ng kg^{-1} , respectively. On the other hand, the detection limit of the most sensitive method for bismuth analysis, *e.g.*, atomic absorption spectrometry² and atomic fluorescence spectrometry^{3,4} with hydride generation have been reported to be 0.2 ng ml^{-1} and 0.005 ng ml^{-1} , respectively. Therefore, preconcentration is essential for its precise determination from natural water samples.

The present authors have previously reported a preconcentration method of bismuth(III) with 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I) loaded silica gel. But the sorption of the element on the gel was considerably influenced by the chloride ion concentration, so that it was difficult to apply the method to seawater samples.⁵

The thionalide-loaded silica gel, however, revealed efficient sorption of antimony(III) from seawater⁶, and was found to also sorb bismuth(III) even at lower pH values. In the present paper, the method for preconcentration and determination of bismuth(III) by the use of

thionalide-loaded silica gel followed by atomic absorption measurement with hydride generation is described.

Experimental

Reagents

A standard bismuth(III) solution (1000 mg l^{-1}) was prepared by dissolving 1.000 g of bismuth metal (99.99% purity) in 10 ml of (1+1) nitric acid and diluting with (1+10) nitric acid to 1000 ml. 2-Mercapto-*N*-2-naphthylacetamide (thionalide, Tokyo Kasei) and tetrahydrofuran (THF) were of analytical reagent grade. THF was purified by distillation. Acids of analytical reagent grade were used without further purification. Sodium tetrahydroborate (NaBH_4) was reagent for organic synthesis and a 1% aqueous solution (0.3% sodium hydroxide) was freshly prepared each time.

Silica gel (chromatographic grade, Wakogel C-100) was sieved through a nylon sieve (60–80 mesh), soaked with twice its volume of (1+1) hydrochloric acid for 1 d at 90°C , and washed with deionized water until free from chloride. The gel was soaked with twice its volume of (1+2) nitric acid for 1 d at 90°C , washed with deionized water, dried at 110°C for 1 d and stored in a polyethylene bottle kept in a desiccator over silica gel. Deionized water was prepared with a Barnstead "NANOpure" system and was used throughout.

Preparation of thionalide-loaded silica gel (thionalide-SG)

About 100 ml of THF containing 6 g of thionalide was slowly added from a separatory funnel into 50 g of a degassed silica gel, which was previously activated at 110°C for 20 h, and then placed in a suction bottle. After standing for 10 h in a refrigerator at 4°C, the impregnated gel was heated at 40°C under reduced pressure for 4 h to expel the solvent completely. The reagent-loaded gel was added into a certain volume of deionized water and the floated reagent was removed by decantation. Finally, the gel was dried under reduced pressure for 24 h at 40°C, and stored in a polyethylene bottle kept in a desiccator.

Apparatus

A Shimadzu AA-646 atomic absorption spectrophotometer was used for the determination of bismuth in the concentration above 1 $\mu\text{g ml}^{-1}$, while for concentrations of the element lower than 1 $\mu\text{g ml}^{-1}$, a Hitachi 170-50 atomic absorption spectrometer was used in conjunction with a Nippon Jarrell-Ash Model XYD-1 continuous hydride generator which was connected with a quartz cell (10 mm i.d., 180 mm long) by Teflon tubing. The cell was heated to about 1000°C with Kanthal alloy wire which surrounded the cell. A Hitachi-Horiba pH meter, M-5, was used to check the pH of the aqueous solution. An Iwaki VS electric shaker, and a Toyo SF-160K fraction collector and Tokyo Rikakikai MP-3 micro pump were used for the batch and column experiments, respectively. A Shimadzu UV-120-02 spectrophotometer was used for determination of thionalide. The column experiments were carried out in a Yamato Kagaku PGV-750 APG-type clean bench (class 100).

Batch experiments

A 20 ml of bismuth(III) solution (0.5 mg l^{-1}), adjusted to desired acidity or pH value, and 0.5 g of thionalide-SG were put into a 50-ml glass stoppered centrifuge tube. The contents were shaken at 200 strokes min^{-1} for 30 min at room temperature. After filtration of the solution through a dry sheet of Toyo No. 5A filter paper, the bismuth concentration of the filtrate was measured by atomic absorption spectrometer and the pH of the solution was also measured.

Column experiments

A glass tube (10 mm i.d., 140 mm long) was filled with a water slurry of 1.0 g of the thionalide-SG and washed with deionized water. A small disc of Toyo No. 5C filter paper was placed on top so that the gel was not disturbed during sample passage. A given volume of sample solution containing bismuth(III) ion was percolated through the column at various flow velocities which were adjusted by the MP-3 pump. After passage of the sample solution, 10 ml of 4 M hydrochloric acid was passed through the column and the effluent was collected by a fraction collector or a measuring flask. The concentration of bismuth was

then measured as described above.

Results and Discussion

Characteristics of thionalide-SG

The amount of thionalide loaded on silica gel was measured as described previously^{6,7} and was found to be 53.8 mg g^{-1} (0.248 mmol g^{-1}) as the average of three determinations. The sorption capacity for bismuth was measured by the breakthrough method by use of 5 $\mu\text{g ml}^{-1}$ Bi(III) solution and 1.0 g of the loaded gel. In 0.25 M nitric acid solution, the capacity of the gel was found to be 0.44 mg Bi(III) g^{-1} (2.1 $\mu\text{mol g}^{-1}$) as the average of three runs. Though the sorption capacity of the gel is smaller than those of organic polymer exchange resins, this has little effect on the preconcentration of micro amounts of bismuth.

Effect of acid concentration and shaking time on retention of bismuth

The retention of bismuth(III) ion from aqueous solutions at various acidities was examined by the batch method, using 0.5 $\mu\text{g ml}^{-1}$ Bi(III) solution. In Fig. 1, the results obtained from nitric acid solution are compared with those obtained from hydrochloric acid medium. In the case of nitric acid medium, bismuth was quantitatively retained on the gel at acidity lower than 1.0 M. In hydrochloric acid medium, retention suddenly began at acidity 2 M, and then reached complete retention at pH 1.0. The quantitative retention occurs at pH higher than 2; a part of bismuth may be sorbed as its oxychloride precipitate, because bismuth(III) gives the precipitate at pH above 1.0. The reduction in sorption with higher hydrochloric acid concentration is explained by formation of bismuth chloride and hydroxychloride complexes, in which the chloride ion should compete with thionalide in complexing to bismuth. The retention of bismuth from 0.25 M nitric acid solution of 5 $\mu\text{g ml}^{-1}$ Bi(III) was

Fig. 1 Effect of acid concentration on retention of Bi(III): (○) nitric acid; (●) hydrochloric acid. Bi (0.5 $\mu\text{g ml}^{-1}$) 20 ml; Thionalide-SG, 0.5 g.

Fig. 2 Effect of shaking time on retention of Bi(III).

Table 1 Recovery of bismuth on thionalide-SG column

Bi(III)/ $\mu\text{g l}^{-1}$	Sample vol./ml	Thionalide-SG used/g	Flow vel./ cm min^{-1}	Recovery ^a , %
5.0	25	1.0	1.3	102.0
		1.0	2.8	101.9
		1.0	4.3	74.3
5.0 ^b	100	1.0	2.8	100.3
0.01	1000	1.0	2.8	99.8
0.01 ^c	1000	1.0	2.8	99.3
0.01 ^b	1000	1.0	2.8	27.5

Eluent: 4.0 M HCl.

a. Figures are the average of three determinations.

b. Seawater spiked with Bi(III).

c. River water spiked with Bi(III).

examined after various shaking times. The results showed that above 99.0% of bismuth was sorbed within 30 s, that the quantitative retention was achieved within 2 min, and that the retention was constant for at least 10-min shaking (Fig. 2).

Retention of bismuth on the column

The retention of bismuth from 25 ml of 0.25 M nitric acid solution ($5 \mu\text{g Bi(III) ml}^{-1}$) was examined at various flow velocities by use of 1.0 g of thionalide-SG. The retained bismuth was eluted with 10 ml of 4 M hydrochloric acid and determined by atomic absorption spectrometry with hydride generation. The results proved that the bismuth was quantitatively retained from 25 ml of the solution at flow velocities lower than 2.8 cm min^{-1} . Furthermore, the complete retention was also achieved by passing 100 ml of seawater sample spiked with $0.5 \mu\text{g}$ of bismuth through the same column at a flow velocity of 2.8 cm min^{-1} (Table 1). However, when the bismuth concentration is much lower (10 ng l^{-1}) and the sample volume is larger (1000 ml), the recovery of the element decreased to only 28%. On the other hand, such a lower recovery was never observed in the cases where deionized water or fresh water samples were used under the same conditions. It is therefore assumed that in very low concentration of bismuth, chloride ion considerably hinders the complexation of bismuth with thionalide, but the effect is less extensive than that for

Fig. 3 Elution of bismuth retained on thionalide-SG column by: (O) 6 M HCl; (●) 4 M HCl; (□) 2 M HCl.

the complexation with Bismuthiol I.⁵

The thionalide-SG may satisfactorily be used for the preconcentration of bismuth from the water samples of low chloride concentration, e.g., rain, river and lake waters, but not seawater. Table 1 also shows that preconcentration of bismuth at the sub-ppb level from 10 l of water sample can be achieved within 20 h using a wider column (20 mm i.d.) filled with 4.0 g of the gel.

Elution of bismuth

As can be seen from Fig. 1, bismuth retained on the loaded gel is expected to be eluted with hydrochloric acid of higher acidity than 2.0 M. Thus, 2, 4 and 6 M hydrochloric acids were passed through the column retained $100 \mu\text{g}$ of bismuth at a flow velocity of 1.3 cm min^{-1} . The effluent was collected by a fraction collector, and bismuth in each fraction was determined by atomic absorption spectrometry with hydride generation. From the results shown in Fig. 3, it is evident that 10 ml of 4.0 M hydrochloric acid can completely release bismuth from the column. This effluent can be directly submitted to the following atomic absorption measurement, as will be described later.

Effect of various substances on the retention of bismuth

Several metal ions which might react with thionalide in 0.25 M nitric acid medium, such as antimony(III), copper(II), gold(III), mercury(II), palladium(II), platinum(IV), silver(I) and tin(IV) were investigated for their effect on the preconcentration process. A 100 ml of water sample of $5 \mu\text{g l}^{-1}$ Bi(III) along with one of the other ions in the concentration of $10 \mu\text{g l}^{-1}$ was passed through the column of 1.0 g of the gel. The results are shown in Table 2. At the concentration tested, antimony, gold and platinum somewhat reduced the retention of bismuth, but in the concentration of $5 \mu\text{g l}^{-1}$, they gave little effect. Since there are few natural waters containing these ions in such high concentrations as listed in the table, their influence will be negligible in practice.

The effect of some organic ligands was also examin-

Table 2 Effect of diverse ions and ligands on the recovery of bismuth(III)

Ion or ligand	Concentration/ $\mu\text{g l}^{-1}$	Recovery of Bi(III) ^a %
Ag(I)	10	99.0
Au(III)	10	94.2
Cu(II)	10	98.2
Hg(II)	10	100
Pd(II)	10	97.5
Pt (IV)	10	92.0
Sb(III)	10	86.4
	5	101.0
Sn(IV)	10	98.2
EDTA	10^{-10} M	94.0
	10^{-11} M	100.0
Citrate	10^{-3} M	99.2
Tartrate	10^{-7} M	93.0
	10^{-8} M	101.2

Bi(III) added: $5 \mu\text{g l}^{-1}$. Sample volume: 100 ml.

a. Figures are the average of three determinations.

ed. The results are shown in Table 2. Even in very low concentration, EDTA and tartrate considerably hindered retention of bismuth. These results may be attributed to the high stability of their complexes of the element. However, in natural waters, these substances, particularly EDTA, rarely exist in the level listed and therefore, influence of these substances will be negligibly small.

Atomic absorption spectrometry with hydride generation for bismuth

The effluent containing bismuth eluted from the gel column (4.0 M hydrochloric acid) was made up to 20 ml with deionized water. This solution and alkaline sodium tetrahydroborate solution were continuously introduced into the hydride generator. The experimental conditions chosen in the present study are summarized in Table 3. The generated bismuth trihydride was trapped in a U-tube containing fine glass beads and dipped in a liquid nitrogen bath. After the carrier gas was passed through for 3 min, the tube was transferred in a mantle heater to expel the hydride into an AAS cell. Under the conditions, the detection limit was 1.0 ng and the calibration curve was straight in the concentration range of 0.1–2.0 ng ml⁻¹.

Analysis of water samples for bismuth

The present method was applied to river water samples. The samples were collected from the Sai river and the Tatsumi canal, which originates from the Sai river, and the Asano river, Kanazawa City. The samples were brought to the laboratory and filtered through a millipore filter (0.45 μm pore) and acidified by adding 18 ml of nitric acid to each 1 l of the sample. The analytical data are summarized in Table 4. The bismuth concentration of the Tatsumi canal was fairly

Table 3 Optical operating conditions for hydride generation AAS of bismuth

AAS	
Wavelength	223.5 nm
Lamp current	10 mA
Slit width	1.1 mm
Gain	2.0
Hydride generation	
Sample solution acidity	4.0 M HCl
Sample solution flow rate	20.0 ml min ⁻¹
NaBH ₄ solution concentration	1.0% (w/v) in 0.5% (w/v) NaOH
NaBH ₄ solution flow rate	12.0 ml min ⁻¹
Acid solution concentration	2.0 M HCl
Acid solution flow rate	12.0 ml min ⁻¹
Carrier gas (I) flow rate	0.1 l min ⁻¹
Carrier gas (II) flow rate	0.5 l min ⁻¹

Table 4 Determination of Bi in samples of river water

Location	Sample volume/ml	Bi contents/ ng l ⁻¹
Sai river ^a (Kanazawa)	1000	2.4
Tatsumi canal ^b (Kanazawa)	1500	3.4
Asano river ^b (Kanazawa)	1500	n.d.

a. 4.0 g of thionalide-SG was used (column: 20 mm i.d.).

b. 1.0 g of thionalide-SG was used (column: 10 mm i.d.).

consistent with that for the Sai river, while no bismuth could be detected in the sample from the Asano river. Because the determination limit under the present conditions is 0.1 ng ml⁻¹, the bismuth content in the sample from the Asano river may be estimated as lower than 1.0 ng l⁻¹.

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