

Preconcentration of Silver(I) with 2-Mercaptobenzothiazole Loaded Silica Gel

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A complexing material, 2-mercaptobenzothiazole loaded silica gel (MBT/SG), was prepared for rapid preconcentration of trace amounts of silver(I) from water samples. Silver(I) was quantitatively retained on the MBT/SG from solution of pH 0–6.3 in batch experiments, while the untreated silica gel captured only 5% of the element in the solution. The retention capacity of the loaded gel was about 8.8 mg Ag g^{-1} ($81.5 \text{ } \mu\text{mol g}^{-1}$) at pH 4.0. The mole ratio of MBT to silver was about 8.3. Silver was quantitatively retained on the MBT/SG column at a high flow velocity (18.8 cm min^{-1}). The silver retained on the column was completely eluted with 10–15 cm^3 of 0.1 mol dm^{-3} nitric acid containing 2% thiourea, and directly determined by one-drop atomic absorption spectrometry. Silver contents of near-shore seawater were determined by the present method.

Keywords 2-Mercaptobenzothiazole loaded-silica gel, preconcentration, silver(I), one-drop atomic absorption spectrometry, seawater

The concentration of silver in environmental samples, such as soil¹, river-water² and seawater³, have been reported as low as $0.3\text{--}1.6 \text{ mg kg}^{-1}$, $0.3 \text{ } \mu\text{g kg}^{-1}$ and $0.01\text{--}4.3 \text{ ng kg}^{-1}$, respectively. Recently, a considerable increase in silver concentration in air has been suggested as a result of rapid development of photographic industries.⁴ On the other hand, it is well known that the toxicity of silver to the organisms of the lower order is very great and comparable to those of cadmium, copper and mercury. Thus the behavior of silver in natural waters is of very interest and important from the standpoint of the environmental pollution control. The detection limit for silver was reported to be $4 \text{ } \mu\text{g dm}^{-3}$ and $2 \text{ } \mu\text{g dm}^{-3}$ by atomic absorption spectrometry with air-hydrogen flame by the use of a silica tube of 60 cm long⁵, and by inductively coupled plasma emission spectrometry⁶, respectively. Therefore, preconcentration is essential for the precise determination of silver in natural waters.

The present authors have reported that *p*-dimethylaminobenzylidenerhodanine loaded silica gel (DMABR/SG) is efficient collector for gold and silver from natural waters.⁷ However, silver retention by DMABR/SG was significantly influenced by iron(III) and the platinum metals. Further, during sample passage, the elution of a certain amount of the reagent from the column was observed. While, 2-mercaptobenzothiazole is very stable and MBT/SG has easily been prepared for the preconcentration of cadmium, copper, lead and zinc⁸, and mercury⁹ by the present authors. MBT can also yield water-insoluble complex

with several metal ions including silver(I) which is formed in rather acidic solution like mercury(II).¹⁰

The present paper describes a rapid and convenient method for preconcentration of silver(I) from natural waters, followed by an one-drop atomic absorption spectrometric determination of the element.

Experimental

Apparatus

A Shimadzu AA-646 atomic absorption spectrometer with Hamamatsu Photonics hollow cathode lamp was used for the determination of silver. The pH of the aqueous solution was measured by a TOA Model IM-20E ion meter with a combined glass electrode. A Shimadzu Model UV-120-02 digital spectrophotometer was used for the determination of MBT. A Taiyo Model SR-11 electric reciprocator was used for batch experiments. A Tokyo Rikakikai Model MP-3 peristaltic pump and a Toyo Model SF-160K balance-operated fraction collector were used for column experiments. The columns were glass tubes (10 mm or 20 mm i.d., 140 mm or 170 mm long) with a coarse sintered glass disc and stopcock at the bottom.

Reagents

2-Mercaptobenzothiazole (Wako Pure Chemical Ind.) was used without further purification. Acetone, ethanol and tetrahydrofuran were purified by distillation. Acids of analytical reagent grade were used

without further purification. A standard silver(I) solution (1000 mg dm^{-3}) was prepared by dissolving 1.5750 g of silver nitrate in deionized water and standardized by titration with a standard sodium chloride solution. Sodium hydroxide was of analytical reagent grade. Deionized water was prepared with a Barnstead "Nanopure" system. Silica gel (Wakogel C-100, chromatographic grade) was sieved through a nylon sieve (60–80 mesh), and was purified as described in the previous paper¹¹, but with nitric acid only.

Preparation of MBT/SG

About 100 cm^3 of tetrahydrofuran containing 10 g of MBT was slowly added from a separatory funnel into 60 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 60°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 free reagent was removed by decantation. After this procedure was repeated three times, the gel was filtered with a glass filter and dried at 80°C for 20 h under reduced pressure, and stored in a polyethylene bottle standing in a desiccator.

Batch experiments

A 10 cm^3 portion of the silver solution (10 mg dm^{-3}), 5 cm^3 of a solution containing nitric acid and sodium hydroxide solution in various ratios, and 0.5 g of MBT/SG were put into a 50-cm^3 glass stoppered centrifuge tube. The contents were shaken at $300 \text{ strokes min}^{-1}$ for 30 min at room temperature. After filtration of the solution through a dry sheet of Toyo No. 5C filter paper, the silver concentration of the filtrate was measured by one-drop atomic absorption spectrometry, and the percent retention was calculated. At the same time pH of the solution was measured.

Column experiments

A glass column (10 mm i.d. , 140 mm long) was filled with a water slurry of definite amount of the MBT/SG and washed with deionized water. Small discs of Toyo No. 5C filter paper were placed at the bottom and on the top so that the gel was not disturbed during sample passage. A given volume of sample solution containing silver ion was adjusted to a suitable pH and percolated through the column at various flow velocities which were adjusted by the MP-3 pump. The effluents were collected by a fraction collector and the concentration of silver was measured as described above.

In the case of very low concentration of silver, after the column retaining the metal had been washed with a small portion of deionized water, 15 cm^3 of 0.1 mol dm^{-3} nitric acid containing 2% thiourea was passed through the column, and silver eluted was determined.

Determination of the amount of MBT loaded silica gel

One gram of the dried MBT/SG was put into the column tube. A 10 cm^3 of acetone was passed through to elute the reagent completely from the column. The effluent was diluted with ethanol to 200 cm^3 , and after further 10-times dilution, the absorbance was measured at 327 nm using ethanol as a reference.

Results and Discussion

Characteristics of MBT/SG

The amount of MBT retained on silica gel was found to be $114 \pm 6 \text{ mg g}^{-1}$ (0.68 mmol g^{-1}) as the average of three determinations. This suggests that about 8-times loading was achieved compared with the material prepared previously from acetone solution of MBT.¹² Thus, the retention capacity of MBT/SG for silver which was measured by a breakthrough method by use of 0.5 g of MBT/SG was also improved and it was found to be 8.8 mg Ag g^{-1} ($81.5 \text{ } \mu\text{mol g}^{-1}$). This figure, however, indicates that one mol of silver ion reacts with 8.3 mol of MBT. It is known that silver forms a 1:1 metal:ligand complex with MBT¹³, thus, the excess fraction of the reagent seems to be remained unreacted. Perhaps, this may be attributed to the porous structure of the silica gel surface and conglomerated crystallization of MBT on the silica gel which was revealed by a microscopic observation of freshly prepared gel. Most of the surface area of porous silica gel is within the pores, and access to some of these may be restricted by the ligand or silver complex.

Effect of acid concentration and shaking time on retention of silver

Because silver(I) gives its chloride precipitate in hydrochloric acid medium, the experiments were carried out in nitric acid media. The Britton-Robinson's universal buffer solution exhibited an enhancement effect on atomic absorption measurement of silver according to the contents of acetic acid or

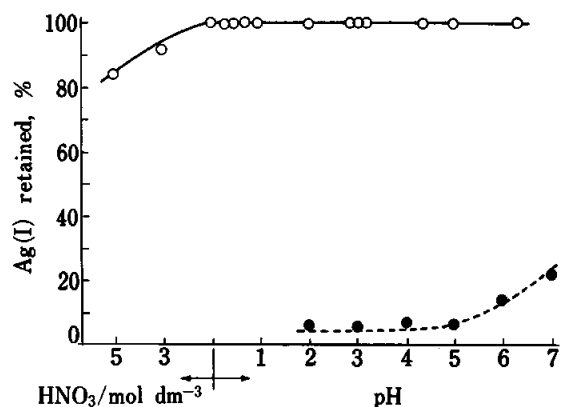


Fig. 1 Effect of nitric acid concentration and pH on retention of silver(I). (○) MBT/SG, (●) untreated silica gel.

phosphoric acid in the solution. Therefore, in the present study the pH of the solution was adjusted with nitric acid and sodium hydroxide solutions.

The recovery of silver(I) ion from an aqueous solution at various pH values was examined by the batch method. The results are illustrated in Fig. 1 along with that obtained using untreated silica gel. Silver(I) was quantitatively retained on MBT/SG at pH 0–6.3, while the retention tended to reduce in higher acidic solution. In nitric acid of higher concentration than 6 mol dm⁻³ MBT was dissolved out of the material. The retention of silver from a solution of pH 4.0 was examined after various shaking times. The results showed that the silver was quantitatively retained within 2 min, and the retention was constant for at least 10-min shaking.

Retention of silver on the column

The operating retention capacity of the MBT/SG was expected to be related to the concentration of silver and to the flow velocity of the water sample. A sample solution containing 1 mg dm⁻³ silver and adjusted to 0.1 mol dm⁻³ with nitric acid was passed through the column filled with 0.3 g or 1.0 g of MBT/SG which made the column bed 10 mm or 30 mm long, respectively. The results are shown in Fig. 2. It is clear that silver(I) was quantitatively retained on the column even at a high flow velocity (18.8 cm min⁻¹) with the latter column, while it reduced to 97% retention at a flow velocity of 9.4 cm min⁻¹ with the

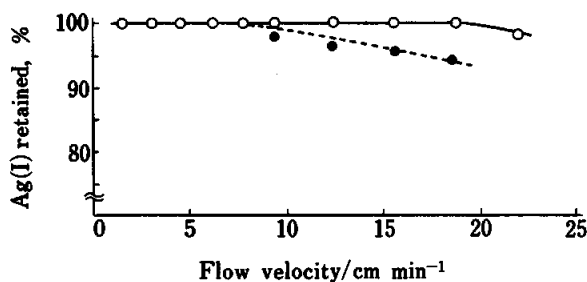


Fig. 2 Effect of flow velocity on retention of silver(I) on MBT/SG column. (O) MBT/SG: 1 g, (●) MBT/SG: 0.3 g.

Table 1 Recovery of silver on MBT/SG column

Ag(I)/ μg dm ⁻³	Sample volume/ dm ³	MBT/SG used/g	Flow velocity/ cm min ⁻¹	Recovery, ^a %
100	1.0	5.0	18.8	99.8
10	2.0	5.0	18.8	101
5	1.0	5.0	18.8	100
2.5	2.0	5.0	18.8	102
0.5	1.0	5.0	18.8	100
0.25	2.0	5.0	18.8	100
0.1	10.0	15	9.6	100

a. Eluent, 0.1 mol dm⁻³ nitric acid containing 2% thiourea.

former column. Therefore, when wider and longer column is used, more quick sample passage should be achieved for complete retention of silver. Table 1 shows the recovery of the element for various concentration of silver and sample volume used. The metal contents were measured after elution with 15 ml of 0.1 mol dm⁻³ nitric acid containing 2% thiourea. The quantitative retention was obtained for silver in the range 0.25–100 μg dm⁻³ from 1.0 or 2.0 dm⁻³ of the water sample at flow velocity of 18.8 cm min⁻¹, while in the concentration of 0.1 μg dm⁻³, it was attained at flow velocity of 9.6 cm min⁻¹ using the column of 20 mm i.d. and 15 g of MBT/SG from 10 dm³ of the water sample.

Elution of silver

Several kinds of reagent, such as nitric acid, thiourea and nitric acid containing thiourea were investigated for the elution of silver. Nitric acid or thiourea alone had no effect at all, but nitric acid containing thiourea was found to be most adequate for the elution. It is seen from the results shown in Fig. 3 that 0.1 mol dm⁻³ nitric acid containing 1 or 2% thiourea was most effective, but the elution efficiency was slightly decreased with the increase in acid concentration. Ten to 15 cm³ of the eluting solution was sufficient to the complete elution at a flow velocity of 1.0 cm min⁻¹.

The MBT/SG, once used in column operation, could be re-used at least ten times.

Effect of various ions and organic substances

Recovery of silver from a seawater sample to which the silver standard was added, was found to be complete by the use of MBT/SG column. Therefore, major elements in seawater, such as sodium, potassium, magnesium, calcium, chloride and sulfate ions have no influence on the retention of silver.

Several metal ions which might react with MBT,

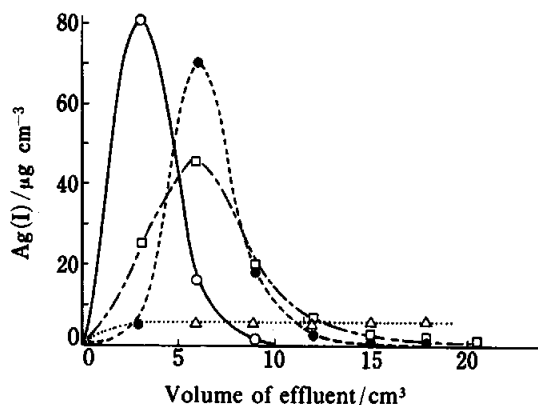


Fig. 3 Elution of silver retained on MBT/SG column by: (O) 0.1 mol dm⁻³ HNO₃ (2% thiourea), (●) 0.1 mol dm⁻³ HNO₃ (1% thiourea), (□) 0.2 mol dm⁻³ HNO₃ (1% thiourea), (Δ) 1% thiourea.

such as bismuth(III), cadmium(II), copper(II), iron(III), lead(II), mercury(II) and zinc(II), were investigated for their effect on the preconcentration or recovery process. A 1 dm³ of water sample of 5 µg dm⁻³ Ag(I) as well as one of the other ions in the concentration range 10–10000 µg dm⁻³ was passed through the column containing 5 g of MBT/SG. The results are shown in Table 2. At the concentration listed in the table, no metal ions interfered with the retention of silver. The same results were obtained for the water sample containing all the ions listed above and for seawater sample. Therefore, in practice, the interference of these ions may be neglected on treatment of natural waters.

The effect of some organic substances was also examined. The results are shown in Table 3. Thiosulfate and thiocyanate ions somewhat hindered retention of silver. However, in natural waters, especially seawater, these organic ligands are rarely found in such high concentration and therefore,

Table 2 Permissible concentration of foreign ions for recovery of silver(I)^a

Ion	Permissible concentration/µg dm ⁻³
Bi(III)	10
Cd(II)	10
Cu(II)	100
Fe(III)	10000
Hg(II)	1000
Pb(II)	10
Zn(II)	1000

a. Ag(I) concentration: 5 µg dm⁻³.
Sample volume, 1000 cm³; flow velocity: 18.8 cm min⁻¹.

Table 3 Effect of organic ligands for recovery of silver(I)^a

Ligand	Concentration/ mmol dm ⁻³	Recovery of Ag(I), %
Citrate	0.1	100
	0.1	96
Tartrate	0.01	100
	0.1	98
Cysteine	0.01	100
	0.1	100
EDTA	0.1	86
	0.01	98
	0.005	100
Thiocyanate	0.1	84
	0.01	93
	0.002	100

a. Ag(I) concentration, 5 µg dm⁻³.
Sample volume, 1000 cm³; flow velocity, 18.8 cm min⁻¹.

influence of these substances will be negligible in practice.

Analysis of seawater for silver

The present method was applied to seawater sample which was collected from surface of near-shore at the western bank of Kanazawa Harbor on 15th of February, 1986. It was immediately acidified by adding 5 cm³ of nitric acid to each 1 dm³ of the sample.

The sample was brought to the laboratory and filtered with a glass filter and passed through the column containing 5 g of MBT/SG at a flow velocity of 15 cm min⁻¹. The sample amounts used were 1 and 5 dm³. The effluent was made to 20 cm³ and silver content was measured by one-drop atomic absorption spectrometry. In each case, 1.8 µg dm⁻³ was found as silver content which indicates that this area might be considerably polluted with silver.

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