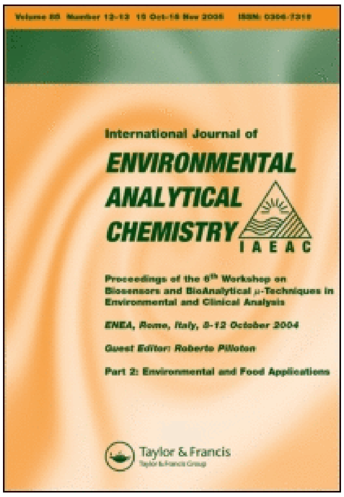

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DETERMINATION OF SILVER IN WATER BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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A precise method to determine Ag in natural water using flame atomic absorption spectrometry is described. This method consists of the precipitation of Ag with Fe^{3+} and Na_2S, and the separation of Ag into methylisobutylketone (MIBK) using sodium N,N-diethyl-dithiocarbamate (DDTC) as a complexing agent after redissolving the Ag in the precipitate. Silver in the MIBK is determined by direct aspiration into a flame atomic absorption spectrophotometer.

The amounts of Fe^{3+} and Na_2S that should be added and the appropriate pH for Ag precipitation were investigated. The results showed that more amounts of both Fe^{3+} and Na_2S were needed for Lake Kasumigaura water than for distilled water to recover all the Ag added to the water samples. The detection limit ($S/N = 2$) for the method was 0.005 μg Ag L^{-1}.

Using the method, Ag concentrations in some water samples taken from rivers, lakes and ponds were determined. The Ag concentrations ranged from < 0.005 to 0.210 μg L^{-1}, which were lower than the value reported by Bowen[1].

KEY WORDS: Flame atomic absorption spectrometry, preconcentration, silver, water

INTRODUCTION

Silver has been found to be toxic to aquatic living things. Davies *et al.*[2] found that only 0.17 μg Ag L^{-1} in water was effective on rainbow trout (*Salmo gairdneri*) based on mortality data of an 18-month experiment, and Okamura *et al.*[3] reported the EC_{50} (50% effective concentration) of Ag for the alga (*Chlorella ellipsoidea*) is 14 μg L^{-1} that was a smaller value than that of Cu, Cd, Cr, Ni or Co.

Ward *et al.*[4], Jones *et al.*[5], or Jones[6] reported the Ag pollution in river waters caused by mining activity. The Ag pollution may also occur by photographic processing industry. For example, Wang *et al.*[7] reported that Ag concentrations in the photographic finishing waste waters ranged from 0.019 to 2.120 mg L^{-1} even after the Ag recovery process.

The reported Ag concentrations in natural fresh water samples were compiled by Bowen[1] as 0.3 μg L^{-1} ranging from 0.01 to 3.5 μg L^{-1}. These values were widely distributed because an adequate method for determining below 1 μg L^{-1} of Ag in natural water had not been established.

For the determination of Ag in natural water, furnace atomic absorption spectrometry was generally used[4–6,8]. Jones[5] reported that the Ag detection limit of the furnace atomic absorption spectrometry was 7 pg, and to determine a lower amount, a multiple injection method had to be used. Sheaffer *et al.*[8] used an enlarged furnace for multiple injection.

They also reported that the organic solvent extraction method was not adaptable for the furnace atomic absorption spectrometry.

We believe that flame atomic absorption spectrometry is more preferable than furnace atomic absorption spectrometry for precise determination of Ag in water samples.

Therefore, we used flame atomic absorption spectrometry with preconcentration by precipitation and an organic solvent extraction method.

EXPERIMENTAL

Apparatus

A Shimadzu model AA610S atomic absorption spectrophotometer was used with a Hamamatsu Photonics Ag hollow-cathode lamp and a Shimadzu model U-125 recorder. The instrumental and operating conditions were those recommended by the manufactures. An air-C_2H_2 flame was used.

Reagents

Silver standard solution in 1 M HNO_3 was prepared from Silver Standard Solution (1 mg mL^{-1}. Kanto Chemical Co.Inc.). Fe^{3+} (0.1%) solution was prepared from ferric chloride ($FeCl_3 \cdot 6\ H_2O$, Wako Pure Chemical Industries, Ltd.) and sodium sulfide (0.1%) solution was prepared from sodium sulfide ($Na_2S \cdot 9\ H_2O$, Wako Pure Chemical Industries, Ltd.) in distilled water.

The DDTC and methylisobutylketone (MIBK) used were of analytical reagent grade, and the other reagents were of special (GR) grade.

Water samples

Distilled water, Lake Kasumigaura water, and Seimei River water were used. The natural water samples were taken using a polyethylene bucket equipped with a nylon rope, and transferred to a 10 L polyethylene tank, then acidified to 0.1 M HNO_3 immediately after sampling. The water sample was passed through a Toyo No. 5A filter paper (pore size 20–25 μm) to remove sediment.

Examination for Ag determination method

The concentration of Ag in natural water was so small that it should be preconcentrated for determination. For this purpose, several methods were reported such as freeze drying[9], cation exchange resin sorption[10], and coprecipitation[11,12]. Although the last method is easy and needs no special apparatus, an appropriate inorganic precipitant that could successfully adsorb Ag was not known. Zirconium oxide that is generally applied for precipitation of trace metals could not recover sufficient Ag[12]. Although Ag was reported to have a strong affinity to Fe oxide[13] or Mn oxide[14], these oxides could recover less than 10% of added Ag in our experiment.

We found that the precipitation of Fe oxide could collect Ag almost 100% by addition of Na_2S. Therefore, we investigated a method to preconcentrate Ag using Fe^{3+} and Na_2S.

For 1 L of water sample, the proper amounts of $FeCl_3$ solution and Na_2S solution were added, then NH_4OH solution was added to raise pH. The Ag in the solution should be precipitated with Fe oxide. The precipitate was gathered on a Toyo No. 5B filter paper (pore size 8 μm) and was redissolved with HCl, and made up to 50 mL with distilled water.

The Ag in the solution was able to extract to MIBK using DDTC as a complexing agent. The method was the same as in the former paper[15]. For 50 mL of the solution in a 100 mL beaker, 5 mL of 10% EDTA · 4Na solution was added while stirring with a magnetic stirrer, then its pH was adjusted to 9.5 using conc. NH_4OH solution, followed by the addition of 5 mL of 2% DDTC solution. It was transferred to a 200 mL squib separating funnel, 5 mL of MIBK was added, and shaken thoroughly for 3 minutes by a shaker. Then the MIBK phase was separated into a 10 mL stoppered test tube and the Ag concentration was determined using atomic absorption spectrometry by direct aspiration of the MIBK phase into flame. The determination of Ag using the DDTC-MIBK extraction method was shown to be unaffected by the presence of various ions extracted from uncontaminated or contaminated soils[15].

To determine the appropriate condition for the method, the amount of Fe^{3+} and Na_2S, and pH for precipitation were investigated.

RESULTS AND DISCUSSION

The amount of Fe added

In the proposed method, the amount of Fe was varied to investigate the effect on the recovery of Ag. The amount of Na_2S was fixed to 3 mg and the pH for precipitation was fixed to 9.

For each 1 L of distilled water and Lake Kasumigaura water, 0.5 μg of Ag was added as $AgNO_3$ solution in advance. The results are shown in Figure 1. For distilled water, the added Ag was almost perfectly recovered by the addition of 0.05 mg or more Fe^{3+}, but for Lake Kasumigaura water, more than 1.0 mg of Fe^{3+} had to be added for 100% recovery. It is assumed that impurities such as organic matter in the lake water interfered with the coprecipitation of Ag. From these results, the amount of Fe^{3+} added was determined to be 5 mg.

The amount of Na_2S added

The amount of Na_2S added was varied to investigate the effect on the recovery of Ag. The amount of Fe^{3+} was fixed to 5 mg and the pH for precipitation was fixed to 9. The results are shown in Figure 2. For distilled water, the recovery was almost 100% by the addition of 0.005 mg or more Na_2S, and for the Lake Kasumigaura water 1 mg had to be added for 100% recovery. The difference among these two samples also occurred probably due to the interference of impurities in the lake water as mentioned above.

On the other hand, when Na_2S was not added, only 15% of Ag was recovered for distilled water whereas 85% was recovered for the lake water. This might be caused by something like colloidal matter in the lake water that had the same role as Na_2S. From these results, the amount of Na_2S added was determined to be 2 mg.

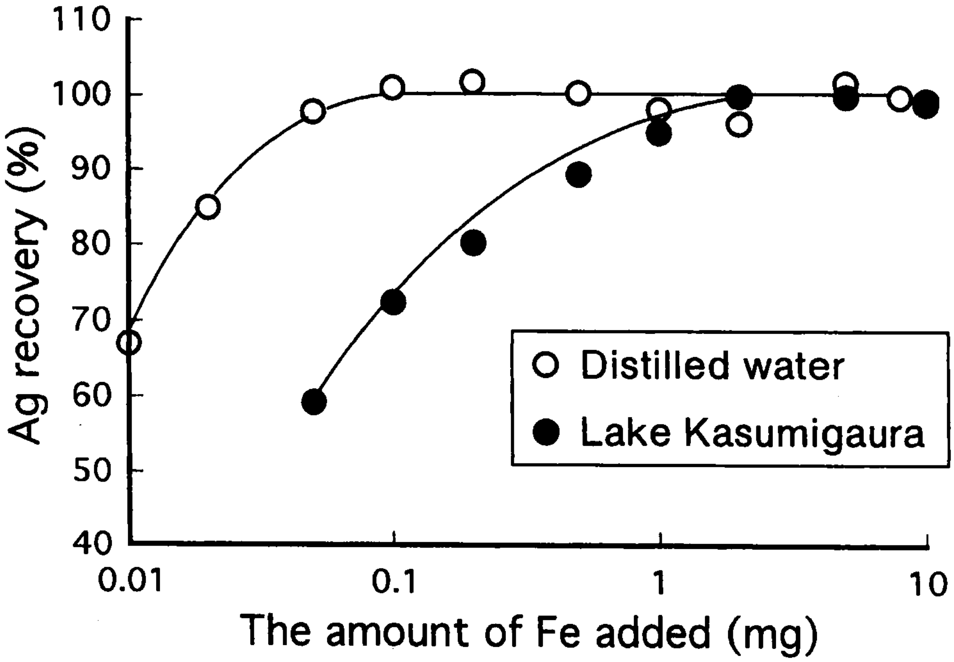

Figure 1 The effect of the amount of Fe^{3+} added on the recovery of Ag.

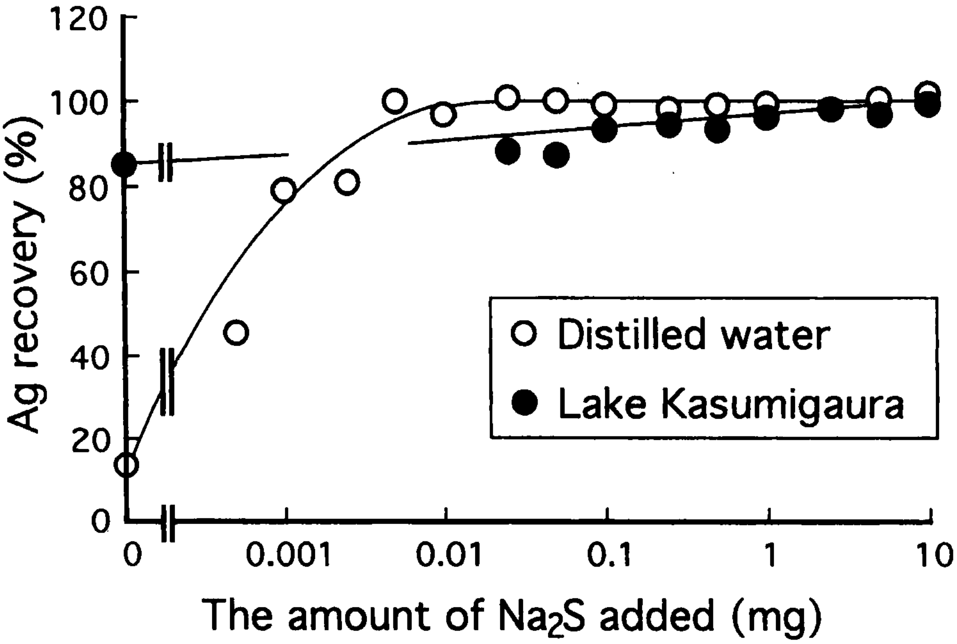

Figure 2 The effect of the amount of Na_2S added on the recovery of Ag.

The effect of pH

The effect of pH for precipitation was investigated. For distilled water containing 0.5 μg of Ag, 5 mg Fe^{3+} and 2 mg Na_2S were added and the pH for precipitation is arranged from 6 to 9. The Ag was almost perfectly recovered in the pH between 7 and 9 as shown in Figure 3. Then the pH for precipitation was determined to be 8 to 9.

Proposed method for the determination of Ag in water

As a result of the investigation, we proposed a method for the determination of Ag in water as follows.

For 1 L of water sample, 5 mL of 0.1% $FeCl_3$ solution and 2 mL of 0.1% Na_2S solution were added. Stirring with a magnetic stirrer, conc. NH_4OH solution was added to raise pH between 8 and 9 for precipitation. The precipitate was gathered on a Toyo No. 5B filter paper (pore size 8 μm) and was redissolved with 4 mL conc. HCl, then washed into a 100 mL beaker with 0.1 M HCl. The filtrate was made up to 50 mL with distilled water.

The Ag concentration in the solution is extracted to MIBK and determined by atomic absorption spectrometry as shown in the former section.

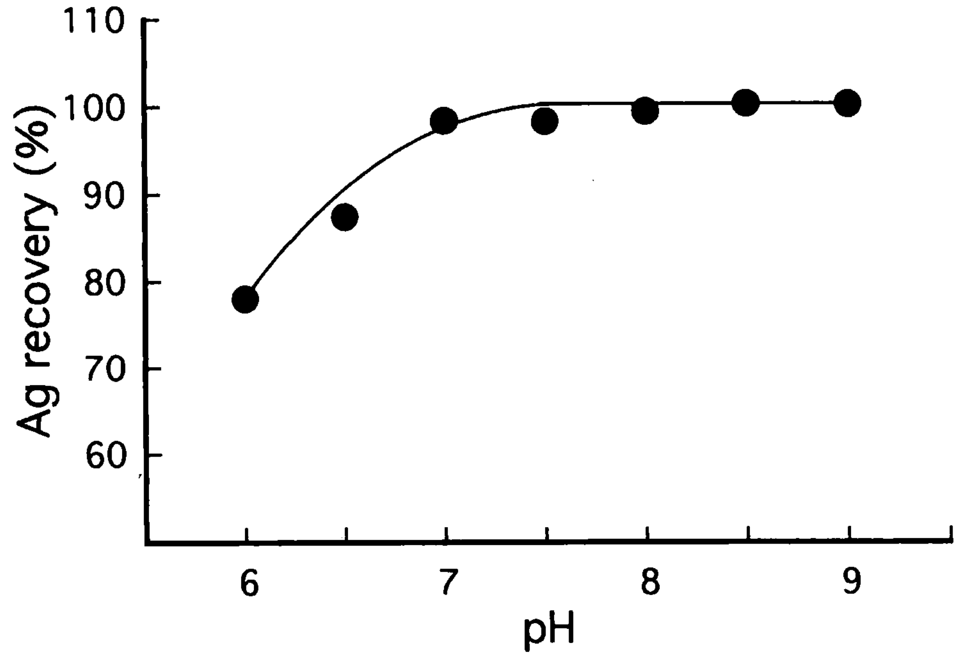

Figure 3 The effect of pH on the recovery of Ag.

Recovery of Ag, precision and detection limit

The recoveries of Ag added to distilled water, Lake Kasumigaura water, and Seimei River water are shown in Table 1. In this experiment, 0, 0.1 or 0.5 μg Ag was added to each 1 L of water as 0.1 mg L^{-1} $AgNO_3$ solution. Nearly all the Ag added was recovered.

The relative standard deviation were 8.9% for Lake Kasumigaura water (0.023 μgAg L^{-1}) and 1.3% for Seimei River water (0.210 μgAg L^{-1}).

The detection limit (S/N = 2; the Ag concentration for the signal peak of Ag twice as large as the noise) by this method was 1 μg L^{-1} for the MIBK phase, which corresponded to 0.005 μg L^{-1} for the water sample.

Determination of Ag in rivers, lakes and ponds

By using this method, Ag concentrations of 11 water samples taken from rivers, lakes and ponds were determined.

Water samples were taken at the Lake Kasumigaura and the nearby rivers, lakes, and ponds from October to December, 1994. The sampling points are shown in Figure 4. The river water were sampled from bridges by using a polyethylene bucket equipped with a nylon rope. The lake and pond waters were sampled by the same method as river water if there was a suitable bridge, and if not, sampled from shore with care not to mix with sediment. The water was transferred to a 10 L polyethylene tank, and acidified to 0.1 M HNO_3 immediately. Then the water was filtered by a Toyo No. 5A filter paper. The container used for water sampling were all washed carefully by 1 M HCl, 1 M HNO_3, and then distilled water.

The results are shown in Table 2. The Ag concentration of river waters ranged from 0.005 to 0.210 μg L^{-1}, and of lake and pond waters from < 0.005 to 0.023 μg L^{-1}. The Seimei R. No. 2 sample contained 0.210 μg L^{-1} that was an extremely higher value than all other points and attained a level effective to rainbow trout shown by Davies *et al.*[2]. The Ag contamination might have occurred by the photographic waste water excreted from the hospital nearby. The Ag concentrations in the lake and pond water samples were lower than those in river water samples. These Ag concentrations were much less than the mean value shown by Bowen[1].

Table 1 Recoveries of Ag added to waters.

Water	*Ag added** *(μg L^{-1})*	*Ag found* *(μg^{-1})*	*Recovery*	
			(μg L^{-1})	*(%)*
Distilled water	0.000	0.000	–	–
	0.100	0.097	0.097	97.0
	0.500	0.498	0.498	99.6
Lake Kasumigaura	0.000	0.023	–	–
	0.100	0.126	0.103	103.0
	0.500	0.519	0.496	99.2
Seimei River	0.000	0.210	–	–
	0.100	0.313	0.103	103.0
	0.500	0.708	0.498	99.6

* 0, 1 or 5 mL $AgNO_3$ solution (0.1 mg Ag L^{-1}) was added to each 1 L water.

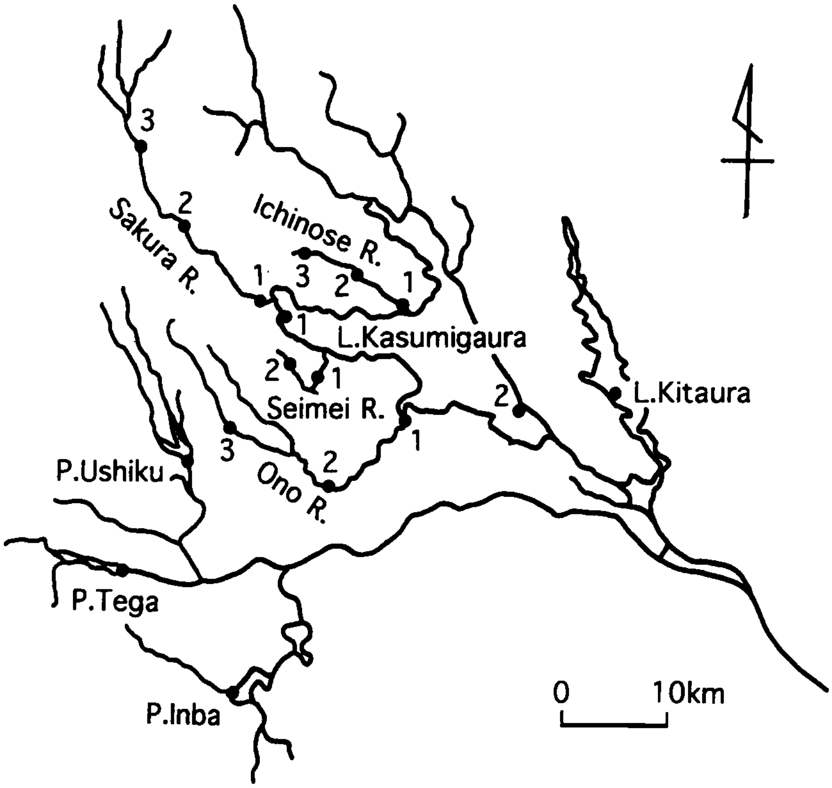

Figure 4 Sampling location in rivers, lakes and ponds.

Table 2 Ag contents in the water samples taken from rivers, lakes and ponds.

Water	*No.*	*Ag content* $(\mu g\ g^{-1})$
Seimei R.	1	0.012 ± 0.001
	2	0.210 ± 0.003
Ono R.	1	0.012 ± 0.003
	2	0.024 ± 0.001
	3	0.005 ± 0.001
Sakura R.	1	0.016 ± 0.001
	2	0.035 ± 0.002
	3	0.026 ± 0.002
Ichinose R.	1	0.008 ± 0.001
	2	0.006 ± 0.001
	3	0.014 ± 0.002
Lake Kasumigaura	1	0.023 ± 0.002
	2	0.008 ± 0.001
Lake Kitaura		< 0.005
Pond Inba		0.010 ± 0.002
Pond Tega		0.006 ± 0.001
Pond Ushiku		< 0.005

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