

Determination of Silver in Natural Water by Atomic Absorption Spectrometry after Preconcentration with Anion Exchange Resin

Makoto KANKE

Chemistry Laboratory, Faculty of Education

Ehime University

(Received October 8, 1986)

Summary

Silver concentration in natural waters was determined by atomic absorption spectrometry after ion-exchange preconcentration. Silver was adsorbed on anion exchange resin when the sample solutions were adjusted to 0.1M in hydrochloric acid and 0.01M in thiocyanate, respectively. The elution of silver from the column was performed by using 0.4M thiourea solution at 100°C. Silver concentration in sea water collected at the seashore of Matsuyama area was 0.1-0.3 μ g per liter.

Introduction

Because of the low concentration of silver in natural waters, preliminary isolation method has been employed in its determination. Methods used for this purpose include freeze-drying,¹⁾ coprecipitation,²⁻⁴⁾ cocrystallization⁵⁾ and solvent extraction.⁶⁾

Kawabuchi and Reiley⁷⁾ have concentrated silver by anion-exchange (Deacidite FF-IP) from sea water and determined its concentration by neutron activation analysis. Although silver can be determined with much greater absolute sensitivity by this method, more conventional methods of determination have been preferred most of time. The purpose of this work was to establish a routine analytical technique for the determination of silver in natural waters.

In this work it was found that silver can be concentrated on a strongly basic anion-exchange resin from an acidified sea water sample into which ammonium thiocyanate added. The concentration by an anion-exchange followed by atomic absorption spectrometry,

allows ppb levels of silver to be determined successfully.

Experimental

Reagents and Apparatus

Silver stock solution : An appropriate amount of silver nitrate was dissolved in 0.1M nitric acid to give 1.0mg/ml concentration.

Ion-exchange resin : A strong base anion-exchange resin, Dowex 1-X8, Cl-form, 100-200mesh in particle size, was used. The purified resin was stored in a desiccator over a saturated potassium bromide solution.

Hydrochloric acid : Redistilled hydrochloric acid was used.

Thiourea solution : 0.4M solution was prepared by dissolving thiourea in deionized water.

Column : 4.0g of the resin was slurried with water and transferred to a 0.8-cm diam. ion-exchange column. The length of resultant bed was *ca.* 6cm. Prior to use, the column was washed with 50ml of 0.1M hydrochloric acid.

Atomic Absorption Spectrophotometer : Hitachi Model-207 equipped with Hitachi HLA-4S type silver hollow cathode lamp was used. Operating conditions were as follows : lamp current ; 3mA, air flow ; 13-1 min⁻¹, acetylene flow ; 2.5-1 min⁻¹, wave length ; 3281 nm.

Equilibrium study

The distribution coefficient, K_d, for silver on Dowex 1-X8 (Cl-form) was determined by batch equilibrium method as a function of concentration of ammonium thiocyanate, while a concentration of hydrochloric acid kept constant at 0.1M. Exact amount of dried resin (1.0g each) was placed in a glass-stoppered Erlenmeyer flask, to which 100ml of acidified sea water with various concentration of ammonium thiocyanate and 2ml of standard silver solution (Ag 0.2mg) were added. After mechanical shaking for 20 hr at 25°C, the phases were separated by filtration. Silver in the filtrate was determined by atomic absorption spectrometry. K_d values were calculated from the following equation.

$$K_d = \frac{\text{amount of silver in resin phase/g of resin}}{\text{amount of silver in solution phase/ml of solution}}$$

Procedure

A 20-1 sample acidified to 0.1M with respect to hydrochloric acid was percolated through a Millipore Filter (pore size 0.45μm) and the filtrate was adjusted to 0.01M in ammonium thiocyanate. The resultant solution was then passed through an anion-exchange resin column at a flow rate of 2-3ml per min. After the column had been washed with 50ml of water, the adsorbed silver was stripped at 100°C by elution with 60ml of thiourea solution. Silver in the effluent was determined by atomic absorption spectrometry.

Results and Discussion

The distribution coefficient values on the adsorption of silver on Dowex 1-X8 were tabulated in Table 1 as a function of the thiocyanate concentration.

Table 1 Distribution coefficient of silver

Thiocyanate Concentration (M)	0.0	0.01	0.1	0.5
Log (Kd)	2.77	3.09	3.07	2.89

These data suggested that maximum adsorption of silver by the anion-exchange resin was achieved when the sea water was made up to 0.1M with hydrochloric acid and 0.01M with ammonium thiocyanate. However, distribution coefficient, Kd, seemed to somewhat lower to apply to concentration of silver from large volume of sea water. Then the distribution of silver in the column was further investigated. The test was performed as follows: A 20-1 of artificial sample spiked with silver was passed through the column. The resin bed was then divided carefully into 1cm height fractions and silver in each fraction was determined following elution with 0.4M thiourea solution. The results were shown in Fig. 1. The top fraction of the column had the highest silver concentration. Based on this fact, it was assumed that although Kd values were low, this technique could be applicable to concentration of silver from sea water.

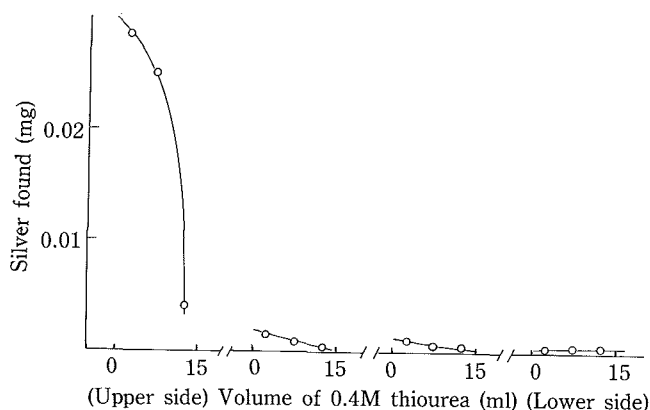


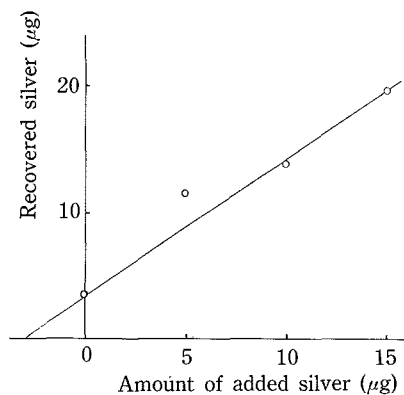
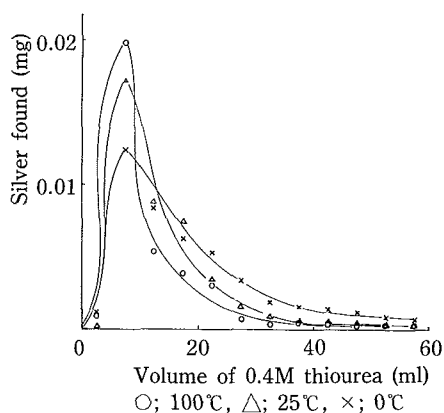
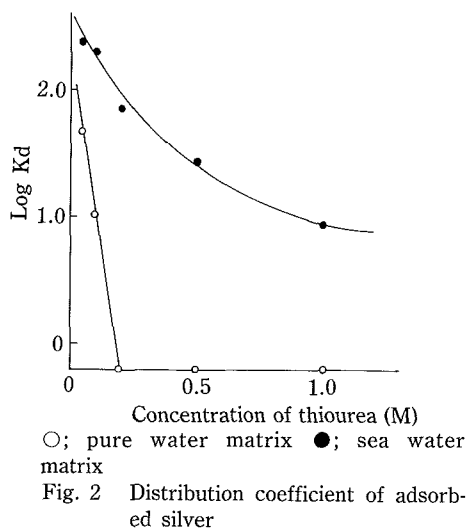
Fig. 1 Adsorption profile of silver on the column

Thiocyanatocomplex of silver adsorbed on the column can be stripped easily by elution with thiourea solution of moderate concentrations since thiourea forms a strong cationic complex with silver. As the other eluting agents, soft bases such as cyanide, thiosulfate, and o-phenanthroline appear to be effective because silver is generally classified as a soft acid. Based on this prediction, the Kd values of silver were measured by the batch equilibrium method in the thiocyanate-thiosulfate system and the thiocyanate-o-phenanthroline system. The thiocyanate-cyanide system was eliminated because of the high toxicity of cyanide in the presence of acid. On the other hand, both reagents gave fairly high Kd values against expectation. In order to confirm the effectiveness of thiourea as an eluting agent, the Kd values of silver for the resin were measured again in the thiocyanate-thiourea system. The result obtained was shown in Fig. 2. The Kd values decrease as increasing

the concentration of thiourea. In other words, higher thiourea concentrations are apparently favorable in desorption of silver from the resin. However, from a practical point of view, 0.4M thiourea solution was considered to be the most practical concentration in elution of silver. Based on these observations, it was concluded to concentrate silver from sea water that a sample should be adjusted to 0.1M with hydrochloric acid and 0.01M with ammonium thiocyanate, and subsequently silver was recovered with 0.4M thiourea solution. The elution profile curves of the silver are shown in Fig. 3. Although fairly tailing occurred when the silver was eluted at low temperature with 0.4M thiourea solution, raising the temperature to 100°C reduced the tailing. Subsequent elutions were carried out under these conditions. As trace of silver was found in the used reagents, a correction was made by a reagent blank for the measured values of silver.

The adsorption of thiocyanatocomplex of silver and subsequent elution with thiourea were not selective to isolate silver from sea water. Gold, copper (II), platinum (IV), palladium (II), mercury (II), zinc (II) and cobalt (II) were also adsorbed by the ion exchange resin and eluted to any appreciable with 0.4M thiourea solution. Among these elements, the concentration and the elution of copper and zinc were also confirmed in this work by atomic absorption spectrometry. Fortunately, as these elements did not interfere particularly with the determination of silver, further studies were not proceeded. This procedure was used in all subsequent work.

In order to evaluate the overall recovery of silver from sea water, additional test was carried out with 20-1 of the deionized water. Adding 0.2mg of silver, an overall recovery of



80% (6 determinations, RSD 4.4%) was obtained. Therefore, the results obtained in the atomic absorption spectrometry should be corrected for the losses of silver.

The results of the determination of silver in two sea water and one river water samples are given in Table 2.

Table 2 Concentration of silver in natural waters

	Sample 1	Sample 2	Sample 3
Sample	Sea water	Sea water	River water
Sampling date	10/11/83	25/1/84	13/12/83
Sampling place	Hōjō	Shimonada	Deai
Ag concentration ($\mu\text{g/l}$)	0.14	0.28	0.38

The values were obtained by the standard addition method as shown in Fig. 4. The silver contents are close to the range of reference value.¹⁰⁾

Acknowledgment

The author thanks Mrs. K. Yoshioka and Miss K. Yarikōchi for thier assistance in this study.

References

- 1) D.F.Schutz and K.K.Turekian, *Geochim. Cosmochim. Acta*, **29**, 259 (1965).
- 2) F.Haber, *Z. Angew. Chem.*, **40**, 303 (1927).
- 3) W.A.P.Black and R.L.Mitchell, *J. Mar. Biol. Assoc. (U.K.)*, **30**, 575 (1952).
- 4) R. Fukai and L. Huynh-Ngoc, *J. Oceanogr. Soc. Jpn.*, **27**, 91 (1971).
- 5) M.G.Lai and H.V.Weiss, *Anal. Chem.*, **34**, 1012 (1962).
- 6) A.Preston, D.F.Jeffries, J.W.R.Dutton and A.K.Steele, *Environ. Pollut.*, **3**, 64 (1972).
- 7) K.Kawabuchi and J.P.Riley, *Anal. Chim. Acta*, **65**, 271 (1973).
- 8) K.B.Yatsimirskii and V.P.Vasilev, "Instability Constants of Complex Compounds", D.Van Nostrand (1966), p.125.
- 9) The Chemical Society, "Stability Constants Supplement No.1", The Chemical Society (1971), p.238.
- 10) J.P.Reiley and R.Chester, "Introduction to Marine Chemistry", Academic Press (1971), p.65.