

Extraction - Spectrofluorimetric Determination of Silver Ion Using Benzothiacrown Ether and Eosin

Masatoshi Oue*

Department of Chemical Engineering, Nara National College of Technology, Yata, Yamato-kōriyama, Nara 639-11, Japan

and Keiichi Kimura and Toshiyuki Shono

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

As benzothiacrown ether exhibited high selectivities for silver ion over several heavy metals on cation extraction, silver ion spectrofluorimetry was carried out by using an ion-pair extraction system with benzothiacrown ether as the ligand and eosin Y as the fluorescent anion. It was possible to determine 2–10 p.p.b. of silver ion, and the method was subject to only low interferences by alkali, alkaline earth and heavy metal ions, except mercury(II) ion. This method was successfully applied to the determination of trace amounts of silver ion in river water.

Keywords: Silver ion determination; spectrofluorimetry; benzothiacrown ether; ion-pair extraction

Crown ethers, which are macrocyclic polyethers, have been widely investigated as ligands in solvent extraction because of their selectivities towards particular metal ions. Ion-pair extraction systems with ternary complex formation between a metal ion, a neutral crown ether and a chromogenic counter anion or with binary complexes of a metal ion and an anionic chromogenic crown ether are useful for the spectrophotometric determination of metal ions.^{1–4}

The spectrofluorimetric determination of K^+ based on ion-pair extraction using a chromogenic counter ion has been attempted using dibenzo-18-crown-6 and anilino-naphthalene sulphonate by Kina *et al.*,⁵ and using 18-crown-6 and eosin by Sanz-Medel *et al.*⁶ Similarly, Pb^{2+} was determined with 18-crown-6 and eosin.⁷ Spectrofluorimetry using crown ethers has also been studied in order to increase the precision of the determination of cations. Nakashima *et al.*⁸ reported the fluorimetry of Li^+ using an Li^+ -selective fluoroionophore, in which a fluorescent group is introduced to a crown ring.⁸ El-Ghamry *et al.*⁹ have determined 100 p.p.b. of silver ion spectrophotometrically by using a ternary complex system of silver ion, ligand and 2,4,5,7-tetrabromofluorescein.

We have already found that benzocrown ethers, in which some oxygen atoms in benzocrown ethers were replaced with sulphur atoms, possess high selectivities for silver ion in cation extraction. In this paper, we report the extraction - spectrofluorimetric determination of trace amounts of silver ion by using benzothiacrown ether as the ligand and eosin as the fluorescent anion. The determination of silver ion in river water is described as a practical application of this extraction - fluorimetric method.

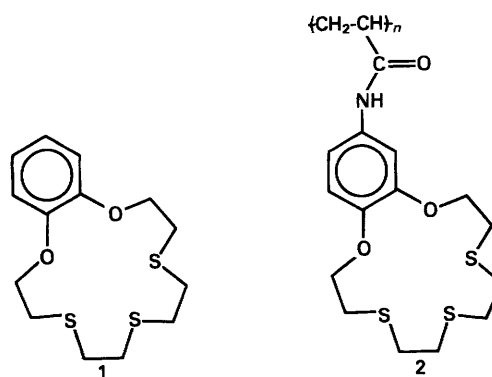
Experimental

Chemicals

All chemicals were of analytical-reagent grade and purchased from Wako Pure Chemicals. De-mineralised, distilled water was used. Chloroform, 1,2-dichloroethane and dichloromethane were distilled before use. The standard solution for fluorescence intensity, I_F , measurements was 5×10^{-5} M quinine sulphate in 0.5 M H_2SO_4 . Eosin Y (2,4,5,7-tetrabromofluorescein, sodium salt) was dissolved in water to give a 9.27×10^{-4} M solution.¹⁰ The metal nitrate concentrations ranged from 9.27×10^{-3} to 9.27×10^{-6} M. For the buffer

solutions, 0.033 and 0.1 M KH_2PO_4 , 0.033 M $Na_2HPO_4 \cdot 12H_2O$, 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ and 0.05 M Na_2CO_3 solutions were prepared. The pH 8.6 buffer was prepared by mixing 3.40 ml of 0.1 M KH_2PO_4 and 6.60 ml of 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ solutions.

Benzothiacrown ether, 2,3-benzo-7,10,13-trithia-1,4-dioxacyclopentadeca-2-ene and the corresponding poly-(benzothiacrown ether)s were synthesised according to previously reported methods.¹¹ The benzothiacrown ether was identified as follows: yield, 65%; colourless crystals; m.p., 98.5–100 °C; IR (KBr), 2900 (CH_2), 1500 (C_6H_6), 1060 cm^{-1} (CO); 1H NMR ($CDCl_3$, δ) 2.8–3.1 (12H, m, CH_2S), 4.2–4.4 (4H, t, CH_2O), 6.9–7.0 (4H, s, aromatic); MS, m/z 316. Analysis calculated for $C_{14}H_{20}S_3O_2$, C 53.13, H 6.37, S 30.39%; found, C 52.99, H 6.33, S 30.22%.



General Procedure for Extraction - Spectrofluorimetry

An aqueous solution with a total volume of 5 ml was prepared by pipetting 0.1 ml of 9.27×10^{-4} M eosin solution, 1.8 ml of buffer solution, 0.1 ml of 1–20 p.p.m. $AgNO_3$ solution and 3 ml of water into a stoppered flask. After adding 5 ml of a 5×10^{-6} M solution of benzothiacrown ether or poly-(benzothiacrown ether)s (for a crown ring unit) in dichloromethane to the flask, the contents were shaken vigorously and then allowed to stand for a few minutes until the two phases had completely separated. A small portion of organic phase was placed in a 1-cm quartz cell for fluorescence measurement, which was carried out using a Hitachi 885 spectrofluorimeter. The band pass was adjusted to 5 nm for both the excitation and emission waves. The I_F values were measured

* To whom correspondence should be addressed.

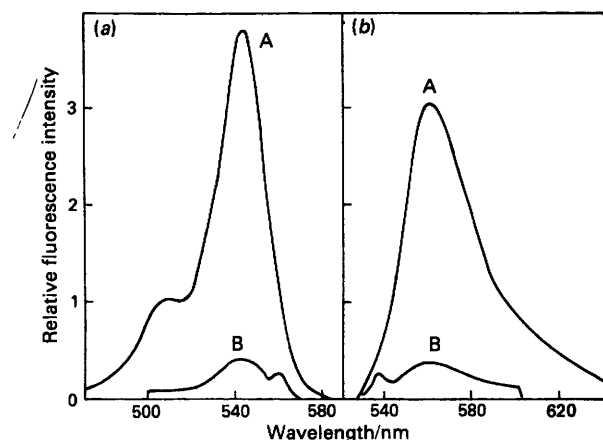


Fig. 1. (a) Excitation and (b) emission spectra for (A) ion-pair complex of benzothiacrown ether and (B) reagent blank

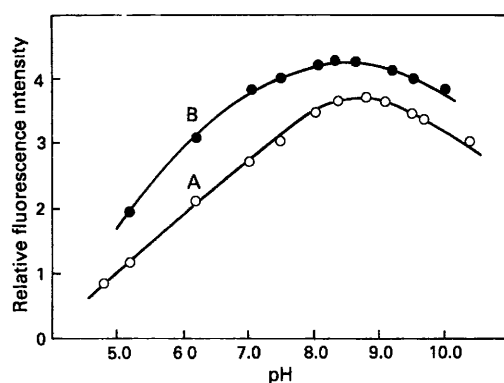


Fig. 2. Relationship between pH and relative fluorescence intensity for (A) benzothiacrown ether and (B) poly(thiacrown ether)s

immediately at an emission wavelength of 558.8 nm with an excitation wavelength of 536.0 nm. A reagent blank solution containing no silver ion was prepared similarly. When examining the effect of foreign ions, the above procedure was also followed, except that an appropriate solution of the foreign ions was additionally added. For the determination of silver ion in river water, 0.1 ml of a Yodo river sample was placed in a stoppered flask and then artificially spiked by adding appropriate amounts of silver ion.

Results and Discussion

Effect of Solvents

Extraction of silver ion was carried out by using benzothiacrown ethers 1 and 2 as the extractant and eosin Y as the fluorescent counter anion. Chloroform, 1,2-dichloroethane and dichloromethane were tested as solvents for the ion-pair extraction and the order of extractability of silver ion was dichloromethane > chloroform > 1,2-dichloroethane. Poor extractability was observed with 1,2-dichloroethane and chloroform showed poor reproducibility at low silver ion concentrations. In contrast, not only the fluorescence intensity of the complex but also that of the reagent blank was high in dichloromethane and the difference between the intensities of the complex and the reagent blank was large and clear. Dichloromethane, therefore, seemed to be the most suitable extraction solvent.

Absorption and Emission Spectra

Representative excitation and emission spectra of the blank and the Ag^+ - benzothiacrown ether - eosin ion-pair complex extracted into the dichloromethane phase from the aqueous phase at pH 8.6 are shown in Fig. 1. When the excitation

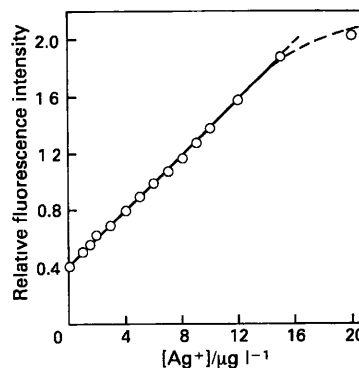


Fig. 3. Calibration graph for the fluorimetric determination of silver ion

spectrum was measured from 220 nm at a fixed emission wavelength of 558.8 nm, only one absorption peak appeared, at 536.0 nm. The emission peak was at 558.8 nm when the excitation wavelength was fixed at 536.0 nm. The reagent blank spectrum based on eosin extracted into the dichloromethane phase without complex formation was similar to the spectrum of the ion-pair complex. As the I_F of the reagent blank was not zero, the detection limit in this spectrofluorimetric determination depends on the I_F difference between the ion-pair complex and the reagent blank. It seems necessary to prepare the eosin Y solution freshly each day in order to obtain large differences in I_F and a high reproducibility.^{12,13} If not, the I_F of the ion-pair complex was not always reproducible in the extraction of the Ag^+ - eosin complex.⁸ The I_F values for the poly(benzothiacrown ether)s system were slightly higher than those for the monomeric benzothiacrown ether (1), but large differences in I_F were not observed when equimolar concentrations of the crown ring unit were employed.

Effect of pH

The pH of the aqueous phase is an important factor for the ion-pair extraction. It has been reported that fluorescein in an aqueous phase undergoes the pH-dependent formation of four ionic types, that is, cationic, electrically neutral, mono-anionic and dianionic,^{14,15} and that the cationic form of fluorescein appears at *ca.* pH 1 and the dianionic form at pH 12. Eosin, which is tetrabrominated fluorescein, is also expected to assume different forms at different aqueous phase pH. The relationship between pH and I_F is shown in Fig. 2. For each of the pH ranges 5.0–8.0, 8.0–9.0 and 9.0–11.0 buffer solutions were used. The I_F versus pH graphs in the pH range 5.0–11.0, at which eosin is considered to be neutral or monoanionic, exhibit a reversed U-shape with a maximum at pH 8.0–9.0 for both benzothiacrown ether and the polymeric analogue.

Calibration Graph

Linearity of the calibration graph was studied at pH 8.6 [0.1 M KH_2PO_4 - 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (34 + 66)]. Below 100 p.p.b. of silver ion the calibration graph showed good linearity and above this level I_F hardly increased with increasing concentration of silver ion. More detailed examination of the measurement concentration range showed that the detection limit of silver ion is 1 p.p.b. and that between 2 and 15 p.p.b. the calibration graph possesses good linearity (Fig. 3). The linear calibration graph did not pass through the origin, because eosin was distributed into the organic phase from the aqueous phase even without any silver ion present in the aqueous phase.

The concentration ratio of eosin to silver ion was adjusted to 10–100, as in the extraction method described previously.¹¹ At

Table 1. Effect of other cations on the determination of silver ion

Cation	Molar ratio (M ⁺ : Ag ⁺)*	Apparent recovery, %
Li ⁺	1000 : 1	102.7
Na ⁺	1000 : 1	100.0
K ⁺	1000 : 1	100.0
NH ₄ ⁺	1000 : 1	100.4
Mg ²⁺	1000 : 1	99.7
Ca ²⁺	1000 : 1	97.5
Ba ²⁺	1000 : 1	101.1
Cr ³⁺	1000 : 1	101.7
Mn ²⁺	1000 : 1	95.7
Fe ³⁺	1000 : 1	103.3
Co ²⁺	1000 : 1	97.1
Ni ²⁺	1000 : 1	109.2
	500 : 1	104.2
Cu ²⁺	1000 : 1	110.4
	500 : 1	103.8
Zn ²⁺	1000 : 1	112.6
	500 : 1	103.9
Cd ²⁺	1000 : 1	113.5
	500 : 1	102.7
Hg ²⁺	500 : 1	130.4
	100 : 1	120.3
	10 : 1	100.6
Pb ²⁺	1000 : 1	98.3

* Constant silver ion concentration, 10.0 p.p.b.

eosin to Ag⁺ ratios below 10 or over 100, poor stability and reproducibility of the fluorescence were observed. The concentration ratio of benzothiacrown ether to silver ion was 5, as described previously.¹¹

Extractions were performed in two ways, viz., a mixture of aqueous and organic phases was shaken for 40 min at 25.0 ± 0.1 °C, or shaken vigorously for a few minutes at room temperature. Both methods gave almost the same cation extractability and I_F values in the organic phase, so for a fast extraction the latter method was adopted.

Effect of Foreign Ions

Thiacrown ethers generally possess affinity for silver ions. Benzothiacrown ethers, in which some oxygen atoms have been replaced by sulphur atoms, also exhibit high extractabilities for silver ion and mercury(II) ion.¹¹ We examined whether spectrofluorimetry of silver ions using benzothiacrown ethers suffered interference from co-existing alkali and alkaline earth metal ions and heavy metal ions. The results are shown in Table 1. In the system with benzothiacrown ether, which showed a similar extraction behaviour to the poly-(benzothiacrown ether)s, even 1000-fold excesses of alkali and alkaline earth metal and some heavy metal ions do not seem to interfere significantly.

However, copper, zinc, cadmium and nickel ions interfered severely at 1000-fold concentrations over silver ion, but at a 500-fold concentration it was possible to obtain apparent recoveries within 105% of the true value. Mercury(II) ion interfered seriously, probably because the affinity of the thiacrown ether for the mercury(II) ion is as great as that for the silver ion. The apparent recovery with the silver - mercury ion system is higher than those with the systems with other heavy metals.

Determination of Silver Ion in River Water Samples

River water samples collected from the upper stream of the Yodo river, Osaka City, were first filtered to remove insoluble solids such as wood chips. In neither the unconcentrated sample nor a 100-fold concentrated sample could any silver ion be detected by atomic absorption spectrometry. The main foreign metal ions present in the sample were Zn 60, Pb <10,

Table 2. Determination of silver ion in river water samples

Sample No.	Ag ⁺ concentration, p.p.b.		Relative standard deviation, %
	Actual	Found*	
1	2.0	1.9 ± 0.1	4.3
2	4.0	4.1 ± 0.1	2.0
3	10.0	9.8 ± 0.2	2.0
4	20.0	16.6 ± 0.2	1.0

* n = 4.

Cu <10, Fe 400, Cd <10, Mn 50 and Cr <10 p.p.b. The river water sample was therefore spiked with p.p.b. levels of silver ion. This level also could not be detected by atomic absorption spectrometry, but we found that the silver ion concentration could be measured by extraction - spectrofluorimetry with the benzothiacrown ether - eosin system. The results are shown in Table 2.

Four artificial river sample waters prepared here contained 2.0, 4.0, 10.0 and 20.0 p.p.b. of silver ion. The standard deviation and accuracy were best for the samples containing 2.0 or 4.0 p.p.b. of silver. In the sample that contained 20.0 p.p.b. of silver ion, a lower value (16.6 p.p.b.) was determined, probably because of some concentration quenching. A determination range of 1.0–10.0 p.p.b. may be suitable for this method.

In the determination of silver ion by this extraction - spectrofluorimetric method, lower concentrations of silver ion can be determined than by atomic absorption spectrometry without pre-treatment. Hence this method seems promising for the determination of trace amounts of silver ion in aqueous solution.

Conclusion

The selectivities of benzothiacrown ether for silver ion over alkali and alkaline earth metal ions and heavy metal ions were excellent, except for mercury(II) ion. The determination range of Ag⁺ was 2–10 p.p.b., which is lower than the levels that can be determined by other silver ion determination methods. Trace amounts of Ag⁺ in river water samples were successfully determined by this extraction - spectrofluorimetric method.

References

1. Szaeapaniak, W., and Juskowiak, B., *Anal. Chim. Acta*, 1982, **140**, 261.
2. Takagi, M., Nakamura, H., Sanui, Y., Ueno, K., *Anal. Chim. Acta*, 1981, **126**, 185.
3. Löhr, H.-G., and Vogtle, F., *Acc. Chem. Res.*, 1985, **18**, 65.
4. Sekido, E., and Chayama, K., *Nippon Kagaku Kaishi*, 1986, 907.
5. Kina, K., Shiraishi, K., and Ishibashi, N., *Bunseki Kagaku*, 1978, **27**, 291.
6. Sanz-Medel, A., Gomis, D. B., and Alvarez, J. R. G., *Talanta*, 1981, **28**, 425.
7. Sanz-Medel, A., Gomis, D. B., Fuente, E., and Jimeno, S. A., *Talanta*, 1984, **31**, 515.
8. Nakashima, K., Nakatsuji, S., Akiyama, S., Tanigawa, I., Kaneda, T., and Misumi, S., *Talanta*, 1984, **31**, 749.
9. El-Ghamry, M. T., and Frei, R. W., *Anal. Chem.*, 1986, **40**, 1986.
10. The Society of Dyers and Colourists, "Colour Index," Third Edition, Volume 4, Lund Humphries, London, 1971, p. 4426.
11. Oue, M., Ishigaki, A., Matsui, Y., Kimura, K., and Shono, T., *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**, 2033.
12. Elmgren, H., *J. Polym. Sci., Polym. Lett. Ed.*, 1980, **18**, 815.
13. Markuszewski, R., and Diehl, H., *Talanta*, 1980, **27**, 937.
14. Martin, E., Pardo, A., Guijarro, M. S., and Fernandez-Alonso, J. I., *J. Mol. Struct.*, 1986, **142**, 197.
15. Zanker, V., and Peter, W., *Chem. Ber.*, 1958, **91**, 572.

Paper A7/378

Received September 4th, 1987

Accepted October 12th, 1987