



http://www.e-journals.net



ISSN: 0973-4945; CODEN ECJHAO

E-Journal of Chemistry

2011, 8(1), 435-442

Cloud Point Extraction and Determination of Silver Ion in Real Sample using Bis((1*H*-benzo[*d*]imidazol-2-yl)methyl)sulfane

FARSHID AHMADI^{§*}, KHODABAKHSH NIKNAM[#], EBRAHIM NIKNAM[§],
SAEID DELAVARI[§] and AZADEH KHANMOHAMMADI

[§]Chemistry Department
Gachsaran Azad University, Gachsaran, Iran

[#]Chemistry Department
Persian Gulf University, Bushehr, Iran
Young Researchers Club
Gachsaran Azad University, Gachsaran, Iran
ahmadi@iaug.ac.ir

Received 15 January 2010; Accepted March 2010

Abstract: Bis((1*H*-benzo[*d*]imidazol-2-yl)methyl)sulfane (BHIS) was used as a complexing agent in cloud point extraction for the first time and applied for selective pre-concentration of trace amounts of silver. The method is based on the extraction of silver at pH 8.0 by using non-ionic surfactant T-X114 and bis((1*H*-benzo[*d*]imidazol-2-yl)methyl)sulfane as a chelating agent. The adopted concentrations for BHIS, Triton X-114 and HNO₃, bath temperature, centrifuge rate and time were optimized. Detection limits (3SDb/m) of 1.7 along with enrichment factor of 39 for silver ion was achieved. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated. The proposed method was successfully applied to the ultra-trace determination of silver in real samples.

Keywords: Bis((1*H*-benzo[*d*]imidazol-2-yl)methyl)sulfane, Silver ion, Cloud point extraction, Flame atomic absorption spectrometry.

Introduction

The increasing use of silver compounds and silver containing preparations in industry and medicine has resulted in an increased silver content of environmental samples^{1,2}. Silver also

enters the environment in industrial waters because it often occurs as an impurity in copper, zinc, arsenic and antimony ores³. Low level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect water used for drinking⁴. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, vitamins E and B12, has focused attention on its potential toxicity^{4,5}.

Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace metals with sufficient sensitivity for most of applications. However, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrix effects. Pre-concentration and separation can solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS)⁶. There are many methods of pre-concentration and separation such as liquid-liquid extraction (LLE)^{7,8}, ion-exchange techniques^{9,10}, co-precipitation^{11,12}, sorption on the various adsorbents such as activated carbon^{8,9}, Amberlite XAD resins^{13,14} and other sorbents^{15,16}.

Micelles and other organized amphiphilic assembles are increasingly utilized in analytical chemistry especially in separation and pre-concentration procedures. Their unique micro-heterogeneous structures capable of selective interaction with different solute molecules can strongly modify solubility, chemical equilibrium, kinetics and the spectroscopic properties of analytes and reagents^{17,22}. Separation procedures based on the peculiar properties of aqueous non-ionic and zwitterionic surfactant solution have also been proposed as an alternative to the use of traditional organic solvents. Aqueous solutions of almost all non-ionic surfactants become turbid when heated to a temperature known as the cloud point. Above this temperature, the isotropic micellar solution separates into two transparent liquid phases: a surfactant-rich phase of very small volume composed mostly of the surfactant plus a small amount of water, and an aqueous phase, in equilibrium with the former, which contains a surfactant concentration close to its critical micellar concentration, is the base of cloud point extraction (CPE). The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient and of lower toxicity to the environment than those extractions that use organic solvents. The CPE phenomenon has been used for the extraction and pre-concentration of metal cations after the formation of sparingly water-soluble complexes. CPE has been shown to be an effective sample pre-concentration technique for improving sensitivity and selectivity prior to atomic spectrometry²³⁻²⁸.

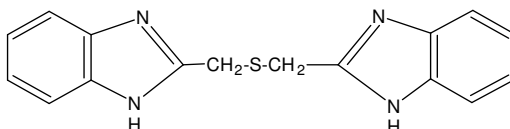
In the present work, we report on the results obtained from applying the CPE for the extraction of silver from real sample and its determination by atomic absorption spectrometric.

Experimental

A Shimadzu AA-680 atomic absorption/flame emission spectrometer equipped with deuterium background correction was used with silver hollow-cathode lamps as radiation sources. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in methanol containing 2.0 M nitric acid. A 691 pH /Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. A MP4 centrifuge (International Equipment Company, USA) was used to accelerate the phase separation.

Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water was used for all dilutions. A 0.5% (w/v) Triton X-114 from Merck Company was prepared by dissolving 0.5 g of Triton X-114 in 100 mL volumetric flask with stirring. Stock standard solution of silver at a concentration of 1000 µg/mL was obtained from Spectrosol. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A solution of 2.0×10^{-3} M bis((1*H*-benzo[*d*]imidazol-2-yl)methyl)sulfane²⁹ (Scheme 1) in Triton X-114 was prepared from the commercially available product. Merck sample of nitric acid and methanol were used.



Scheme 1. Bis((1*H*-benzo[*d*]imidazol-2-yl) methyl)sulfane

Procedure

For CPE, an aliquot of 15 mL of a solution containing silver ion, 0.07% Triton X-114 and 0.07 mM of BHIS was adjusted to pH 8.0 with HCl. The mixture was kept for 20 min in the thermostatic bath maintained at 50 °C. The phase separation was accelerated by centrifuging at 4000 rpm for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 500 µL of 2.0 M HNO₃ in methanol and then the silver ion content was readily evaluated by FAAS.

Preparation of real samples

Water samples

Analysis of water samples for determination of silver ion content was performed as following: 200 mL of sample was poured in a beaker and 8 mL concentrated HNO₃ and 3 mL of H₂O₂ of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the CPE were performed according to general described procedure³⁰.

Blood sample

Homogenized blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO₃ and 2 mL HClO₄ 70% was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. In all of real and synthetic sample amount of silver ion was found by standard addition method¹⁷.

Results and discussion

Adsorption spectra

Figure 1 shows the absorption spectra for the individual silver complex in surfactant-rich phase against reagent blank. The silver complexes of BHIS are insoluble in water but are easily dissolved in micelles such as Triton X-114.

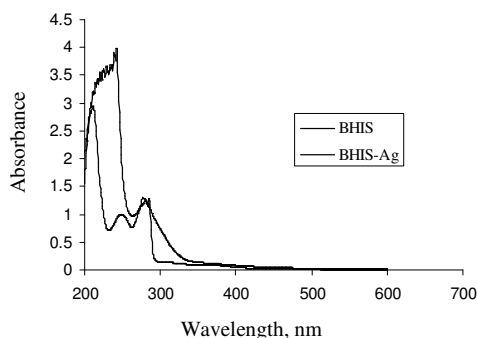


Figure 1. Absorption spectra of BHIS-Ag complex.

Conditions: 0.07% (w/v) Triton X-114, 0.07 mM BHIS and $0.05 \mu\text{g mL}^{-1}$ silver ion

Effect of pH

The separation of silver ion by cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase; thus obtaining the desired pre-concentration. CPE of silver was performed in different pH solutions. Figure 2 shows the effect of pH on the absorbance of silver ion. As can be seen, at pH 8.0 maximum absorbance was obtained. Hence, pH 8.0 was chosen as the working pH.

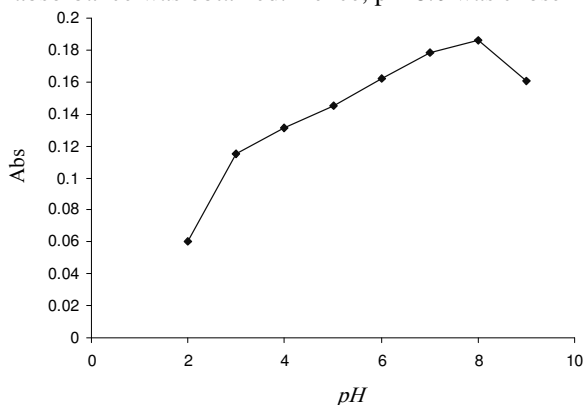


Figure 2. Effect of pH on the absorbances of silver ion pH

Condition: 15 mL $0.05 \mu\text{g mL}^{-1}$ silver ion at various pH, 0.07% (w/v) Triton X-114, 0.067 mM BHIS, 2.0 M KCl, eluting solution 500 μL of 2.0 M HNO_3 in methanol

Effect of Triton X-114 concentration

The non-ionic surfactant Triton X-114 was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost. Also, the high density of the surfactant-rich phase, facilitates phase separation by centrifugation. Additionally the cloud point (23–62 °C) of Triton X-114 permits its use in the extraction and/or pre-concentration of a large number of molecules and chelate^{31–33}. The variation in absorbance within the Triton X-114 range 0.017–0.17% (w/v) was examined. Figure 3 highlights the differences observed in the signals at different surfactant concentrations. A concentration of 0.07% (w/v) was chosen as optimum concentration for the determination of silver ion. At lower concentrations, the absorbance of silver ion is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.

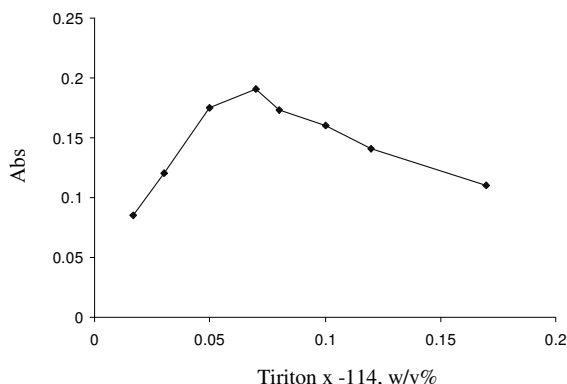


Figure 3 Effect of Triton X-114 concentration on the absorbances of silver ion
 Condition: 15 mL $0.05 \mu\text{g mL}^{-1}$ silver ion at various Triton X-114, 0.067 mM BHIS, pH=8.0, 2.0 M KCl, eluting solution 500 μL of 2.0 M HNO_3 in methanol

Effect of BHIS concentration

The effect of concentration of the chelating agent on the analytical responses was examined and the results are shown in Figure 4. Major improvement on the responses was obtained as the chelating agent concentration increased up to certain values, which are sufficient for total complexation and the extraction. A concentration of 0.07 mM (1.0 mL from 2.0×10^{-3} M solution) was chosen as the optimum concentration of the chelating agent for CPE of metal ions. The concentrations above this value have no significant effect on the performance of the system. The slight difference in the behaviour of BHIS with silver ion is probably due to different chelate formation constants.

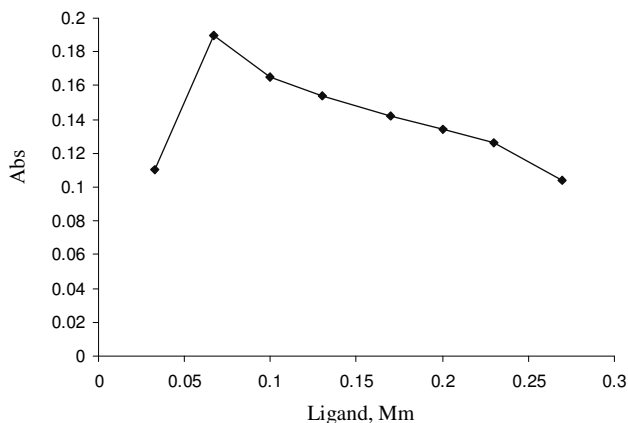


Figure 4. Effect of BHIS concentration on the absorbances of silver ion
 Condition: 15 mL $0.05 \mu\text{g mL}^{-1}$ silver ion at various AMTD, 0.1% (w/v) Triton X-114, pH=8.0, 2.0 M KCl, eluting solution 500 μL of 2.0 M HNO_3 in methanol

Effects of added electrolyte

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction

efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase²². In this way, 2.0 M KCl concentration was used in all further experiments.

Effect of methanol

Since the surfactant-rich phase obtained after the cloud point pre-concentration contains a high concentration of Triton X-114 and at the same time, the volume obtained is rather small (500 μL), methanol containing 2.0 mol L^{-1} HNO_3 was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (500 μL) with respect to the silver ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 500 μL volume of methanol was therefore used throughout the remaining experiments.

Effect of other experimental factors

Optimal incubation time and equilibration temperature are necessary to complete reactions, and to achieve easy phase separation and pre-concentration as efficient as possible. Providing that the complexation reaction has been completed under certain conditions, relevant data show that, for equilibration times of some minutes up to a few days, extraction efficiency increases very slightly and the phase-volume ratio decreases a little³¹. On the other hand, it appears that the phase volume ratio of all non-ionic surfactants decrease as the equilibration temperature increase. The greatest analyte pre-concentration factors are thus expected under conditions where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant. The results showed that an equilibration temperature of 50 $^\circ\text{C}$ and an equilibration time of 15 min are adequate to obtain quantitative extraction of two ions. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5-25 min. A centrifugation time of 15 min at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative.

Analytical figures of merit

A calibration curve was constructed by pre-concentrating 15 mL of sample standard solutions with Triton X-114. Table 1 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for silver was linear from 2 to 400 ng mL^{-1} . The enhancement factor of about 39 obtained by pre-concentrating a 10 mL of sample volume can be considered highly satisfactory compared with other CPE methodologies. The limit of detection was sufficiently low.

Table 1. Specification of method at optimum conditions for silver ion (n=6)

Linear range, ng L^{-1}	2-400
Detection limit, ng mL^{-1}	1.9
RSD %	1.5
Enhancement factor	3.9

Effect of foreign ions

The influences of some alkaline and alkaline-earth ions and transition metal ions on the copper ion recovery of the analyte ion were investigated by the presented CPE procedure. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the pre-concentration and determination of metal ions. metal ions were quantitatively recovered in the presence of large amounts of alkaline and alkaline earth ions and some transition metal ions. The matrix ion contents in the final solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

Table 1. Effects of the matrix ions on the recoveries of the examined silver ion (N=6)

Ion	Added As	Tolerance Limit, mg L ⁻¹
Cl ⁻ , K ⁺ , Na ⁺	KCl, NaCl	1000
Mg ²⁺ , Ca ²⁺	Chloride salts	1000
Cu ²⁺	Nitrate salts	1000
HCO ₃ ⁻	NaHCO ₃	1000
SCN ⁻	KSCN	1000
PO ₄ ³⁻	Na ₃ PO ₄	650
Fe ²⁺ , Mn ²⁺	Nitrate salts	750
CO ₃ ²⁻	Na ₂ CO ₃	750
Cr ³⁺	Nitrate salts	450
Cd ²⁺ , Ba ²⁺	Nitrate salts	550
Hg ²⁺	Nitrate salts	50
Cu ²⁺ , Fe ³⁺ , Al ³⁺ , Zn ²⁺	Nitrate salts	250
Co ²⁺ , Ni ²⁺ , Pb ²⁺	Nitrate salts	600

Determination of silver in real samples

In order to validate the proposed methodology, the developed procedure was applied to the determination silver ion in real samples. For this purpose, 15 mL of each of the samples were pre-concentrated with 0.07% (w/v) Triton X-114 and BHIS concentration of 0.07 mM, following the proposed procedure. The results are shown in Table 3.

Table 3. Recovery of trace silver from water and blood sample after application of presented CPE procedure (N=6)

sample	Added, ng L ⁻¹	Founded, ng L ⁻¹	RSD %	Recovery %
Tap water	0	4.5	1.3	-
	15	20.1	1.5	103
River water	0	9.5	1.2	-
	15	23.8	1.6	95.3
Wastewater (Hospital)	0	76	1.1	-
	15	91.1	1.5	100.7
	0	2.3	1.4	-
Blood	15	17.1	1.6	98

Conclusion

The combined advantages of the cloud point methodology and the use of bis((1*H*-benzo [*d*]imidazol-2yl)methyl)sulfane as a ligand for silver were utilized for the determination of silver in real samples. The method is fairly selective, leading to an effective separation and

constitutes an inexpensive alternative to other pre-concentration methods. The method gives a low limit of detection, good R.S.D and solvent-free extraction of the element from its initial matrix following a single step extraction procedure without interferences.

References

1. Kolthoff I M and Eiving P J, (Eds.), *Treatise on Analytical Chemistry*, Part II, vol. 5, Interscience, New York, 1966.
2. Renner H, *Ulmans Encyklopedie der Technischen-Chemie*, Vol. 21, 4th Ed., Verlag Chemie, Weinheim, 1982.
3. Soager R, *Metallic Raw Materials Dictionary*, Bank Tobel, Zurich, 1984.
4. Environmental Protection Agency (EPA), *Ambient Water Quality Criteria for Silver*, EPA 4405-80-071, Office of Water Regulations, Washington, DC, 1980.
5. Meian E, (Ed.), *Metals and Their Compounds in the Environment*, VCH, New York, 1991.
6. Chen J and Teo K C, *Analytica Chimica Acta*, 2001, **450(1-2)**, 215-222.
7. Malvankar P L and Shined V M, *Analyst*, 1991, **116(10)**, 1081-1084.
8. More P S and Sawant A.D, *Anal Lett.*, 1994, **27(9)**, 1737 -1748.
9. Bae S Y, Zeng X and Murray G M, *JAAS*, 1998, **10**, 1177-1181.
10. Prakash N, Csanady G, Michaelis M.R.A and Knapp G, *Microchimica Acta*, 1989, **99(3)**, 257-265.
11. Vircaus M, Rone V, Paine A and Vircava D, *Anal Chim Acta*, 1994, **299(2)**, 291-298.
12. Elci L, Sahin U and Oztas S, *Talanta.*, 1997, **44(6)**, 1017-1023.
13. Gucer S and Yaman M, *J Anal At Spectrom.*, 1992, **7(2)**, 179-182
14. Soylak M, Narin I and Dogan M, *Anal Lett.*, 1997, **30**, 2801-2808
15. Soylak M and Elc L, *Int J Environ Anal Chem.*, 1997, **66**, 51-59
16. Soylak M, Sahin U and Elc L, *Anal Chim Acta.*, 1996, **322**, 111-115
17. Ghaedi M, *Spectrochimica Acta Part A*, 2007, **66**, 295- 299-301
18. Ghaedi M, Asadpour E and Vafaie A, *Spectrochim Acta A*, 2006, **63**, 182-88.
19. Quina F H and Hinze W L, *Eng Chem Res.*, 1999, **38(11)**, 4150-4168
20. Pramauro E and Prevot A B, *Pure Appl Chem.*, 1995, **67**, 551-556.
21. Stalikas C D, *Trends Anal Chem.*, 2002, **21**, 343-355.
22. Manzoori J L and Bavili-Tabrizi A, *Anal Chem.*, 2002, **470**, 215. - 221.
23. Kulichenko S A, Doroschuk V O and Lelyushok S.O, *Talanta.*, 2003, **59(4)**, 767- 773.
24. Manzoori J L and Bavili-Tabrizi A, *Microchem J.*, 2002, **72**, 1-7
25. Silva M A M, Frescura V L A, Aguilera F J N and Curtius A.J, *J Anal At Spectrom.*, 1998, **13**, 1369- 1373.
26. Silva M A M, Frescura V L A, Curtius A J, *Spectrochim Acta.*, 2000, **55B**, 803- 813.
27. Tarly C R T and Arruda M A .Z, *Anal Sci.*, 2004, **20**, 961- 966.
28. Ahmadi F, Khanmohammadi A, Heydari S, Mirzazadeh M and Malekpour E, *Jordan J Chem.*, 2008, **3(1)**, 77-7
29. Niknam K, Zolfigol M A and Sadabadi T, *J Iran Chem Soc.*, 2007, **4**,199-204
30. Ghaedi M, Ahmadi F, Karimi H and Gharaghani S, *J Korean Chem Soc.*, 2006, **50(1)**, 23-31.
31. Laespada M E F, Perez Pavón J L and Moreno Cordero B, *Analyst*, 1993, **118**, 209-214.
32. Frankewich R P and Hinze W L, *Anal Chem.*, 1994, **66**, 944-952.
33. Ghaedi M, Shokrollahi A, Ahmadi F, Rajabi H.R and Soylak M, *J Hazardous Materials*, 2008 **150**, 533-540.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

