

Simultaneous Solvent Extraction of Metal Ions with Thiacrown Ethers Studied using Inductively Coupled Plasma-Mass Spectrometry

Bahrudin Saad*, Chong Ching Ching, Abdussalam Salhin, Md. Fazlul Bari, Ismail Ab. Rahman, Norita Mohamad and Muhammad Idiris Saleh

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang

* author for correspondence : E-mail: bahrud@usm.my

Abstract : Simultaneous solvent extraction of ten metal ions (Mg^{2+} , V^{4+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+}) with three thiacrown ethers, namely 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) in 1,2-dichloroethane was studied using inductively coupled plasma-mass spectrometry (ICP-MS). Picric acid was used as counter ion. Key extraction parameters such as contact time, pH, ligand and counter ion concentrations were investigated. The three thiacrown ethers show high selectivity towards Ag^+ , followed by Hg^{2+} and Cu^{2+} over the other metal ions studied. Under the optimized conditions, 10 ppm Ag^+ was selectively extracted from 1×10^{-3} M picric acid at pH 5 for 12S4, pH 4 for 15S5 and 18S6 into 1,2-dichloroethane containing 2×10^{-4} M ligand. This procedure was applicable to the selective extraction and determination of Ag^+ from river water sample. The stoichiometry of the extracted complex is also established.

Received : 12.07.04 ; accepted : 13.12.04

Introduction

Solvent extraction, in conjunction with suitable ligands, has been widely used for the pre-concentration and separation of metal ions. Among the various ligands useful for metal ion complexation are the crown ethers and their analogues [1]. Crown ethers have been extensively investigated and are known to be effective for the extraction of hard and soft metal ions with the assistance of an appropriate counter anion [2]. Thiacrown ethers are a class of crown ethers where the donor oxygen atoms on the macrocyclic ring are partially or totally replaced by sulphur atoms. Thiacrown ethers are classified as a soft Lewis bases and are well-known to interact selectively with soft Lewis acids.

Accordingly, most of the past research efforts has focused on thiacrown ether complexation with soft or borderline metal ions³, such as Cu^+ , Cu^{2+} , Ag^+ and Hg^{2+} [4, 5]. Several excellent review articles dealing with the coordination chemistry of 12 to 16-membered thiacrown ethers have been published [6, 7]. Sevdic *et al.* [4, 5] studied the complex formation properties of thiacrown ethers containing four, six and eight sulphur donor atoms with Ag^+ and Hg^{2+} , with picrate and perchlorate serving as counter ions. Complexes of the ratio (metal : ligand) 1 : 1 and 2 : 1 for Hg^{2+} and 1 : 1, 2 : 1 and 3 : 1 for Ag^+ with six sulphur ligand, 1 : 1 for Hg^{2+} and 1 : 1 and 2 : 1 for Ag^+ with four sulphur ligand had also been reported. Ring size effect on the structure of the crown complex has also been discussed. It is further noted that Ag^+ form the most stable complexes with the six-membered sulphur ligand over the eight and four

ones. Solid state complexes of Ni^{2+} , Co^{2+} and third state metal ions such as Cr^{3+} , Co^{3+} and Fe^{3+} with thiacrown ethers (9S3, 10S3, 12S3, 18S6, 24S6) were also reported [8-12]. Due to their excellent selectivity, they readily lend themselves as useful analytical reagents for the determination of Hg^{2+} , Ag^+ and Cu^{2+} [3, 13-14]. Accordingly, extraction of these metal ions with thiacrown ethers have been studied much more widely than extraction with other types of crown ethers [15-17]. Saito *et al.* [3, 18], extensively studied the extraction behaviour of Cu^{2+} with 12 to 16-membered tetrathiacrown ether using tetraphenylborate (TPB) or picrate (Pic) as counter ions. The use of a few thiaethers as chemical sensors have also been reported [19, 20].

Since the introduction of the first commercial instrument in 1983 [21], inductively coupled plasma-mass spectrometry (ICP-MS) has gained prominence as a powerful technique for elemental analysis. ICP-MS offers rapid and simultaneous multi-element analysis, with detection limits ranging from parts per billion to parts per trillion. Other unique capabilities of ICP-MS include, relatively simple spectra and the ability to conduct isotopic analysis [22, 23]. ICP-MS has currently become a universally accepted analytical technique for multi-element determination in diverse fields such as environmental [24], geological [25, 26] industrial [27], biological and clinical [28, 29].

It should be pointed out that, in all previous reports on the extraction using thiacrown ethers, only one metal ion was studied at a time. In the present work, however, the ICP-MS is applied for the

determination of several metal ions (Mg^{2+} , V^{4+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+}) after their simultaneous solvent extraction with three cyclic thiocrown ethers namely 1,4,7,10-tetrathiacyclododecane (**12S4**), 1,4,7,10,13-pentathiacyclopentadecane (**15S5**) and 1,4,7,10,13,16-hexathiacyloctadecane (**18S6**) (**Figure 1**). Picric acid was used as counter anion.

Factors that contribute to the extraction in the studied system such as contact time, the concentration of H^+ , ligand and counter ion concentrations and selectivity amongst the metal ions are investigated.

Figure 1 : Chemical structure of thiocrown ethers studied

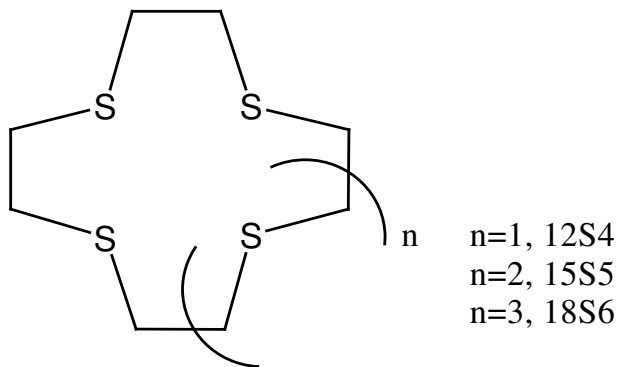


Table 1 : ICP-MS instrumental operating conditions and data acquisition parameters

Condition / parameters	Result
<i>ICP parameters</i>	
R.f. power (W)	1000
Coolant argon flow rate ($L\ min^{-1}$)	15
Auxiliary argon flow rate ($L\ min^{-1}$)	1
Nebulizer argon flow rate ($L\ min^{-1}$)	97
Operating frequency (MHz)	40
Sample introduction system	Cross flow nebulizer
Sample cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Scanning mode	Peak hopping
Pressure (quadrupole analyzer) ICP (Torr)	4.18×10^{-5}
107 Bahruddin Saad et. al Number of replicate	Simultaneous Solvent Extraction of Metal Ions with Thiocrown Ethers Studied using Inductively Coupled Plasma-Mass Spectrometry

Experimental

Apparatus

A Perkin Elmer Elan 6100 inductively coupled plasma-mass spectrometry (ICP-MS) with version 2.0 software was used in the studies. The instrument conditions and general method parameters are listed in **Table 1**. An Orion Ion Analyzer model EA940 was used for pH measurements. A mechanical shaker (Stuart Scientific, UK) was used for extraction. De-

ionized water was produced from Millipore Milli-Q plus.

Chemical and Reagents

Stock solutions (100 ppm) containing mixtures of metals (sulfates of Zn^{2+} , Cd^{2+} , V^{4+} , Ni^{2+} , Cu^{2+} , Mn^{2+} , nitrates of Mg^{2+} , Co^{2+} , Ag^+ and chloride of Hg^{2+} in a final volume of 250 mL were prepared by dissolving appropriate amounts of metal salts in 2% HNO_3 solution.

Thiacrown ethers, 12S4, 15S5 and 18S6 (Aldrich) were used without further purification. Appropriate amounts (0.01 M) of the thiacycrown ether were dissolved in 1,2-dichloroethane (Merck).

A standard solution (0.01 M) of picric acid (BDH) was prepared by dissolving 0.229 g of the dried acid in 100 mL of de-ionized water. A 1 M sodium acetate (Riedel-deHaen) solution was prepared by dissolving 34.02 g of the salt in 250 mL de-ionized water.

For the determination of Ag⁺ in real sample, river water was collected from Waterfall River, Penang, Malaysia. The water was filtered to remove suspended particles.

Liquid-Liquid Extraction

An aliquot sample solution (5 mL) containing a mixture of metal ions (10 ppm each) and picric acid (1 × 10⁻³ M) was placed in 100 mL stoppered conical

flask. The pH was adjusted to the desired value with sodium acetate (1 M). An organic solution (5 mL) containing 2 × 10⁻⁴ M thiacycrown ether in 1,2-dichloroethane was added. The mixture was shaken mechanically for 45 min at room temperature. After shaking, the phases were allowed to settle, separate and metal ions concentration left in the aqueous phase was determined using ICP-MS. The amount of the metal ion extracted into the organic phase was determined by difference.

Distribution Equilibrium of Metal Ion

The distribution equilibrium of metal ion (Mⁿ⁺) from an aqueous picrate (Pic⁻) medium with thiacycrown ether (L) in the present system can be described in general according to Eq. (1). The extraction constant, K_{ex} is defined by Eq. (2).



$$K_{ex} = [MPic_m(L)_n]_{org} / [M^{n+}][Pic^{-}]^m[L]_{org}^n \quad \text{----- (2)}$$

The distribution ratio (D) can be calculated as in Eq. (3).

$$D = [MPic_m(L)_n]_{org} / [M^{n+}] = K_{ex}[Pic^{-}]^m[L]_{org}^n \quad \text{----- (3)}$$

$$\text{Log } D = \text{Log } K_{ex} + m \text{Log}[Pic^{-}] + n \text{Log}[L]_{org} \quad \text{----- (4)}$$

In the presence of two species (M₁Pic_m) and (M₂Pic_m) in the aqueous phase (where M₁ and M₂ refer to different metal ions), then the distribution ratio can be written as

$$D_1 = [M_1Pic_mL_n]_{org} / [M_1Pic_m] + [M_2Pic_m] \quad \text{----- (5)}$$

$$D_2 = [M_2Pic_mL_n]_{org} / [M_1Pic_m] + [M_2Pic_m] \quad \text{----- (6)}$$

The separation factor (β) among the species can be related to the relative extraction constant, K_{ex1} and K_{ex2}, is given by Eq. 7³⁰.

$$\beta = K_{ex2} / K_{ex1} = D_2 / D_1 \quad \text{----- (7)}$$

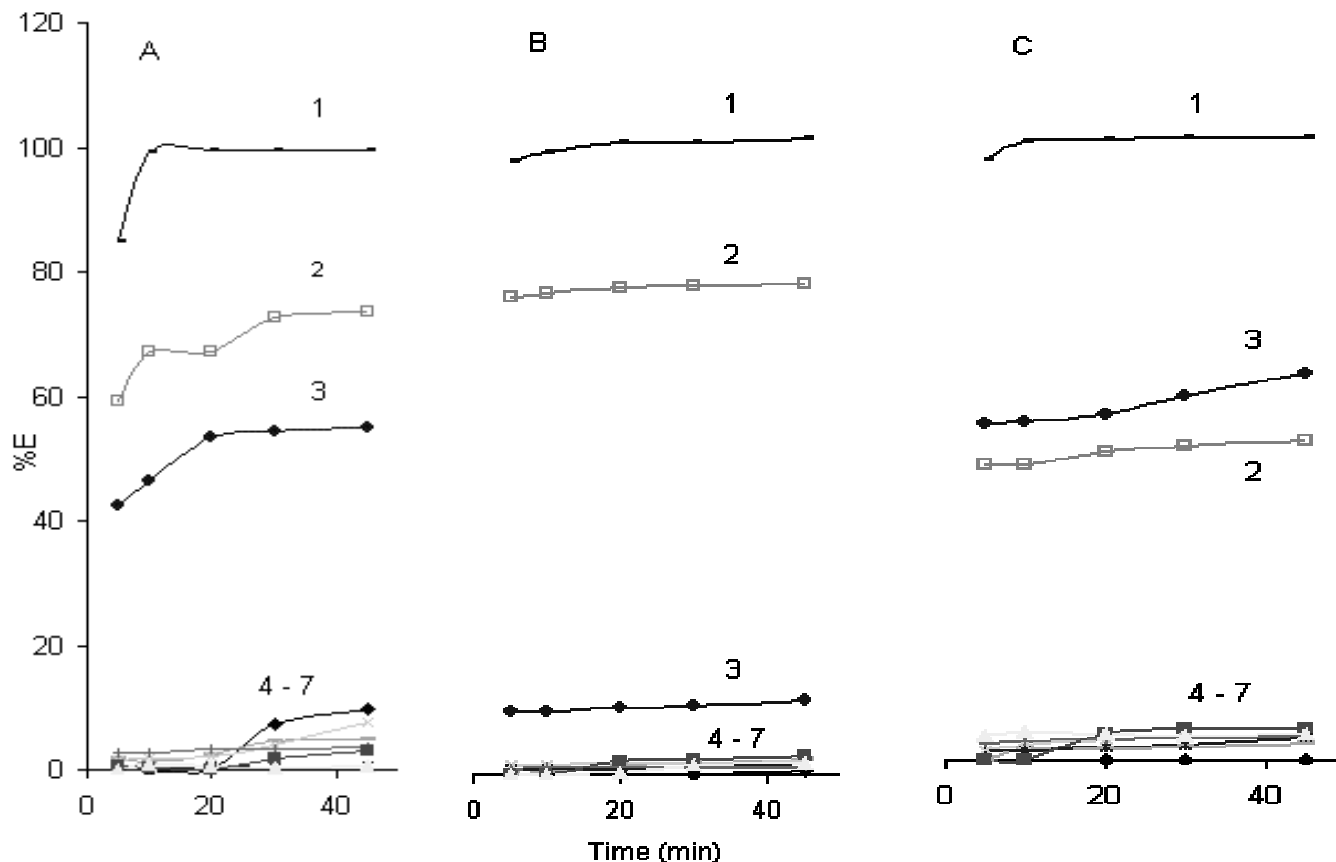


Figure.2.: Effect of equilibrium time on the extraction of metal ions (1= Ag^+ , 2= Hg^{2+} , 3= Cu^{2+} , 4-7= Mg^{2+} , V^{4+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}) with 2×10^{-4} M thiocrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

Result and Discussion

Effect of Contact Time

The solution was shaken on a mechanical shaker from 5 to 45 min. Results show that all the thiocrown ethers undergo a maximum extraction for Ag^+ (**Fig. 2**) after shaking for 10 min or longer, followed by Hg^{2+} and Cu^{2+} . However, once the maximum extraction has been reached, increasing of contact time has no significant effect on the extraction. Therefore, an equilibrium time of 45 min was adopted for subsequent extraction studies to ensure complete extraction. This period of time was also found to be the best by Ikeda and Abe [31] on their solvent extraction of Cu^{2+} with tetrathiacrown ether derivative.

Effect of pH

The effect of pH on the metal extraction by the three ligands is summarized in **Figure 3**. The degree

of extraction is found to increase from pH 2 to pH 4 for Ag^+ and to pH 5 for Hg^{2+} and Cu^{2+} when 12S4 is used as extractant.

A similar trend in pH extraction profile is exhibited for Hg^{2+} and Cu^{2+} when 15S5 and 18S6 are used as extractants, reflecting that the thiocrown ether's extraction efficiency for Hg^{2+} and Cu^{2+} are highly dependant on the ionization of picric acid in the medium. pH 5 is the optimum pH for the extraction of Hg^{2+} and Cu^{2+} with 12S4, and pH 4 is the best for 15S5 and 18S6 systems. The percentage of extraction slightly decreases at pH lower or higher than the optimum pH for the extraction of Hg^{2+} and Cu^{2+} in all the studied systems. This pH profile agree well with the findings of Saito *et al.* [18] on their solvent extraction of Cu^{2+} with 12S4 but do not agree well with the findings of Ikeda and Abe [31], where Cu^{2+} can be extracted quantitatively (100 %E) at pH above 6 when extracted with 12S4 derivative.

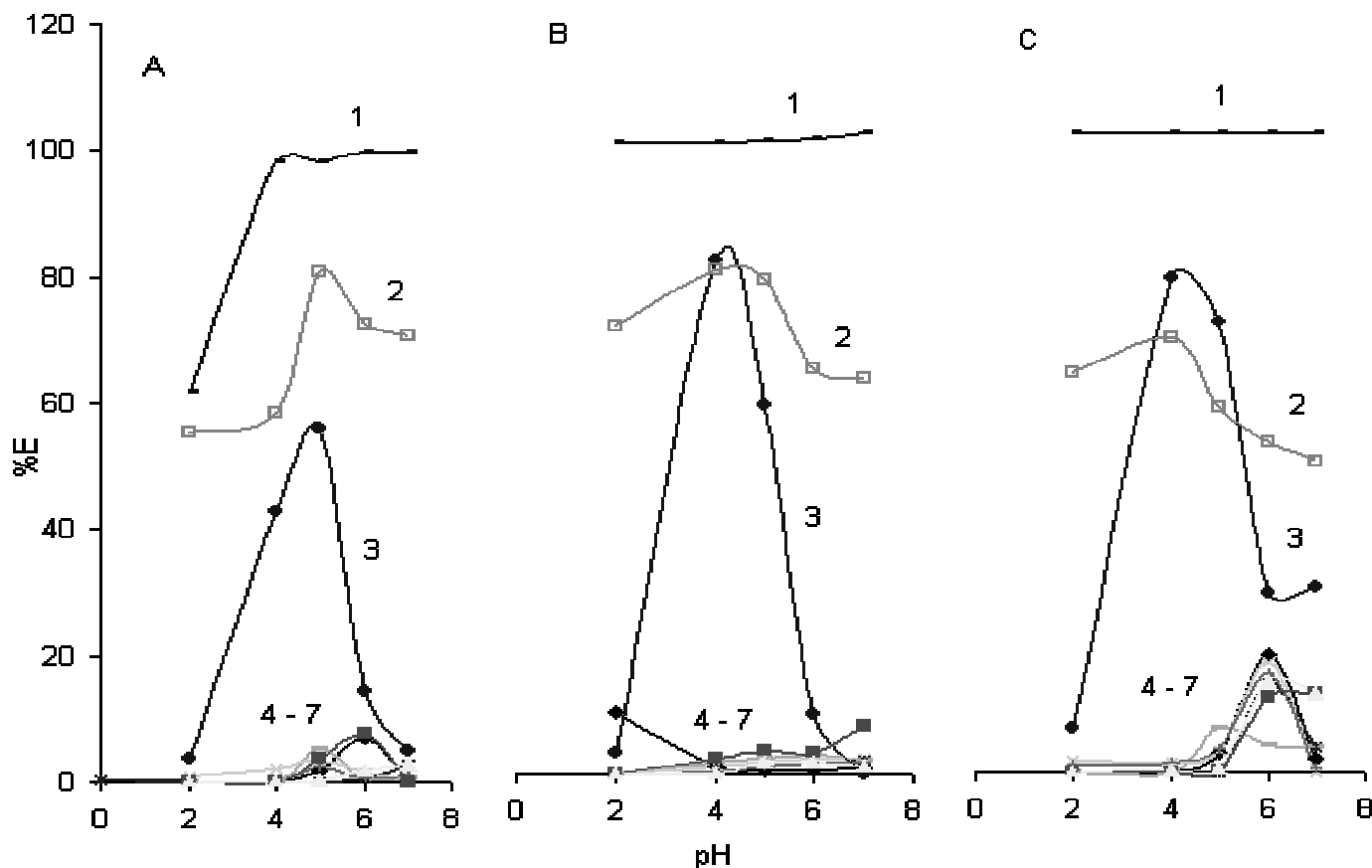


Figure 3 :: Effect of pH on the extraction of metal ions (1= Ag^+ , 2= Hg^{2+} , 3= Cu^{2+} , 4-7= Mg^{2+} , V^{4+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}) with 2×10^{-4} M thiocrown ether (A= 12S4, B= 15S5, C= 18S6). Picrate concentration 1×10^{-3} M.

No noticeable effect of pH on the extraction of Ag^+ with 15S5 and 18S6 was observed. With 12S4, the extraction of Ag^+ is dependent on pH when pH is below 4. Therefore, pH 5 for 12S4 and pH 4 for 15S5 and 18S6 are used in subsequent work.

The %E values for the other metal ions, (Mg^{2+} , V^{4+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+}) are below 8% ($\text{Log } D < -1$) for both 12S4 and 15S5 and slightly more than 15% ($\text{Log } D < -0.8$) for 18S6. This implies that these metal ions were very poorly extracted under the studied conditions. Therefore, due to the favourable extraction characteristics of these ligands towards Ag^+ , Hg^{2+} and Cu^{2+} , no further experiments are carried out involving the other metal ions.

Effect of Ligand Concentration

The influence of 12S4, 15S5 and 18S6 concentration was studied by extracting the metal ions with different amount of ligands, which varied from 2×10^{-5} to 6×10^{-4} M. The extraction was

carried out at the respective optimum pH (5 for 12S4 and 4 for both 15S5 and 18S6). Overall results show that the extraction was optimum when the ligand concentration $\geq 2 \times 10^{-4}$ M. **Figure 4** shows the effect of 12S4, 15S5 and 18S6 concentration on the distribution ratio ($\text{Log } D$) for Ag^+ , Hg^{2+} and Cu^{2+} using 1×10^{-3} M picrate concentration. A good linear dependence on ligand concentration with a normal slopes of 0.5 for Ag^+ and Hg^{2+} , 2 for Cu^{2+} with 12S4, 1.5 for Ag^+ , 2 for Hg^{2+} , 1.4 for Cu^{2+} with 15S5 and 1.5 for Ag^+ , 0.4 for Hg^{2+} and 1.0 for Cu^{2+} with 18S6. This dependence confirms the general applicability of Eq. 3 in describing the extraction process. These results indicated that ligand 12S4 form complexes of ratios (ligand:metal) of 1:2 with Ag^+ and Hg^{2+} and 2:1 with Cu^{2+} , ligand 15S5 form complexes of ratios of 3:2 with Ag^+ and Cu^{2+} and 2:1 with Hg^{2+} , and ligand 18S6 form complexes of ratios of 3:2 with Ag^+ , 1:2 with Hg^{2+} and 1:1 with Cu^{2+} in the presence of picrate anion.

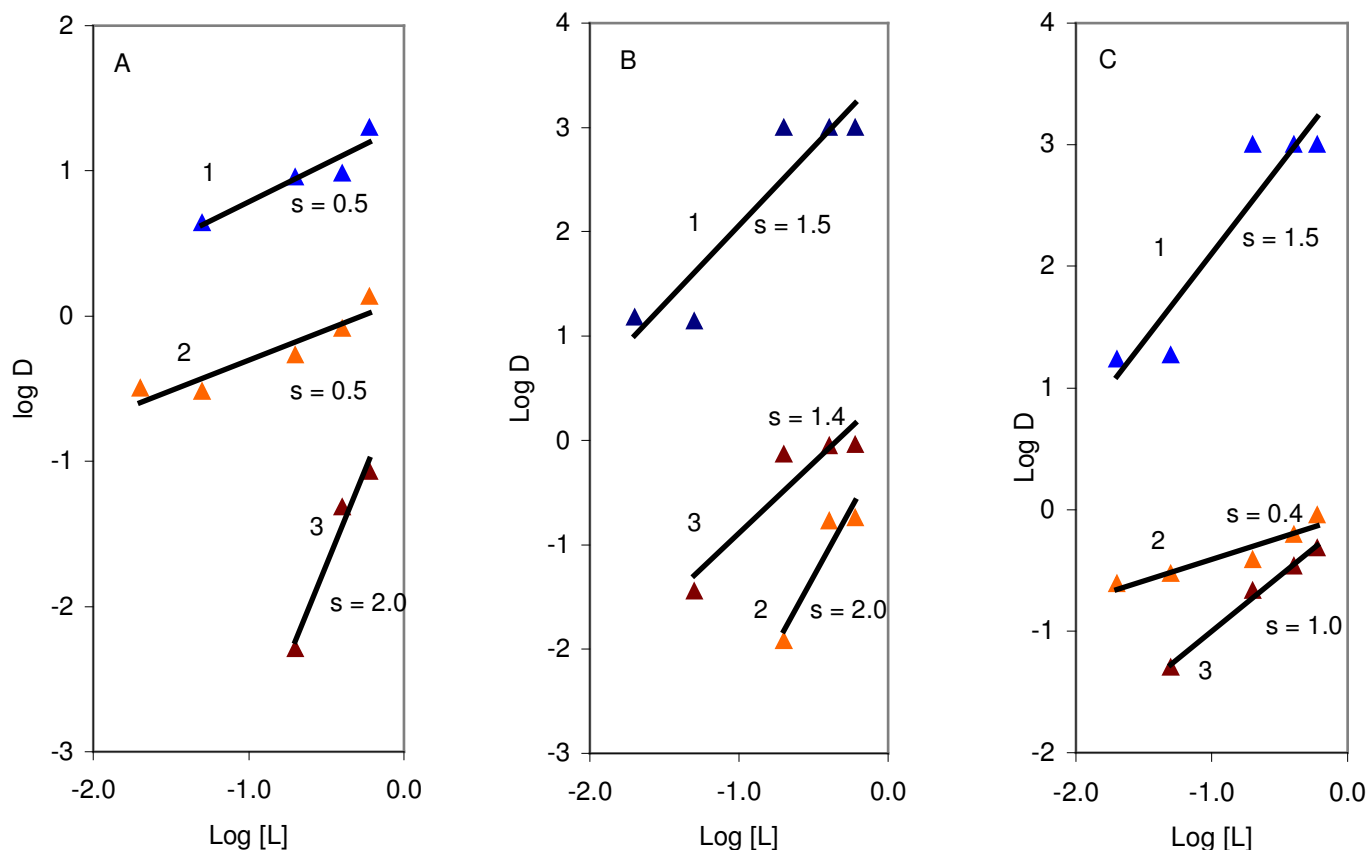


Figure 4 : Effect of thiocrown ether (A= 12S4, B= 15S5, C= 18S6) concentration on the distribution ratio of metal ions (1= Ag^+ , 2= Hg^{2+} , 3= Cu^{2+}) from picrate medium (1×10^{-3} M), pH (A= 5, B & C= 4), s = slope.

The formation of sandwich and club-sandwich complexes involving more than one metal or ligand for crown ether complexes has been reported [32]. Therefore, 2×10^{-4} M of thiocrown ethers was adopted as a suitable concentration for subsequent extraction study.

Effect of Picrate Concentration

A study of picrate ion concentration varied from 5×10^{-5} to 1.4×10^{-3} M was examined under constant ligand concentration (2×10^{-4} M) and pH 5 for 12S4 and pH 4 for both 15S5 and 18S6. **Figure 5** shows the effect of picrate concentration on the distribution ratios of Ag^+ , Hg^{2+} and Cu^{2+} . The log D values linearly increase with increase in the picrate concentration for all cases. The slopes of the logarithmic plot of D vs. picrate concentration were found equal to 0.5 for Ag^+ , 0.4 Hg^{2+} and 1 for Cu^{2+}

with 12S4, 0.7 for Ag^+ , 0.2 for Hg^{2+} and 0.5 for Cu^{2+} with 15S5 and 1.5 for Ag^+ , 0.4 for Hg^{2+} and 0.6 for Cu^{2+} with 18S6. These results indicate that one mole picrate is associated with two moles of Ag^+ and Hg^{2+} ions, one mole for Cu^{2+} when extracted with 12S4 from picrate medium. However, 0.7 moles of picrate are needed for the extraction of one mole Ag^+ with both 15S5 and 1.5 for 18S6 ligands, while 0.5 mole of picrate is necessary for the extraction of Cu^{2+} with 15S5 and 0.4 mole of picrate is needed for the extraction of Hg^{2+} with 18S6. Slope of 0.7 for the extraction of Ag^+ with 15S5 indicate that two types of reactions are involved simultaneously, i.e. complex of 1:1 (picrate: Ag^+) and 1:2 (picrate: Ag^+). The formation of such reactions was also observed in the complexation behaviour between lanthanum and ligand based on phosphinic acid [33].

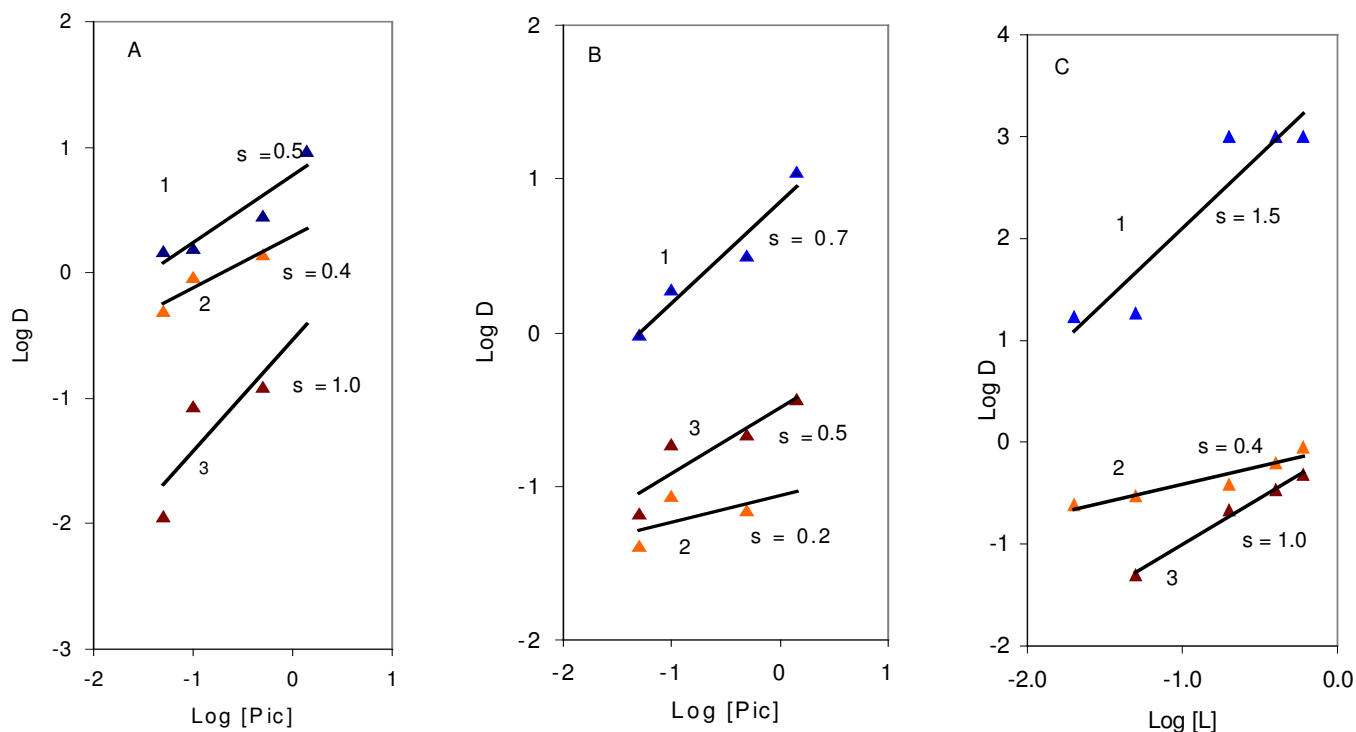


Figure 5 : Effect of picric acid concentration on the distribution ratio of metal ions (1= Ag^+ , 2= Hg^{2+} , 3= Cu^{2+}) with (2×10^{-4} M) thiocrown ether (A= 12S4, B= 15S5, C= 18S6), pH (A= 5, B & C= 4), s= slope.

Separation

Under the optimum extraction system of 2×10^{-4} M ligand and 1×10^{-3} M picrate as a counter anion, the percentage extraction (%E) of the studied metal ions with 12S4, 15S5 and 18S6 is in the order $\text{Ag}^+ \gg \text{Hg}^{2+} > \text{Cu}^{2+}$, $\text{Ag}^+ \gg \text{Cu}^{2+} > \text{Hg}^{2+}$ and $\text{Ag}^+ \gg \text{Hg}^{2+} > \text{Cu}^{2+}$ respectively. The separation factor of metal ions are summarized in Table 2. The table shows that all the thiocrown ethers are very selective towards Ag^+ .

These results further show that 15S5 is the best ligand for the extraction and separation of Ag^+ or Cu^{2+} in the presence of Hg^{2+} ($\beta = 8.32 \times 10^3$ and 16.48 respectively), while 12S4 was found to be the best ligand for a selective separation of Ag^+ or Hg^{2+} in the presence of Cu^{2+} ($\beta = 1.78 \times 10^3$ and 105.26 respectively). Poor selectivity of 18S6 among Hg^{2+} and Cu^{2+} have also been observed.

Table 2 : Separation factor (β) of metal ions by different ligands

Metal	β		
	12S4	15S5	18S6
Ag / Hg	16.93	8.32×10^3	256.88
Ag / Cu	1.78×10^3	135.32	460.96
Hg / Ag	5.90×10^{-2}	1.20×10^{-4}	3.89×10^{-3}
Hg / Cu	105.26	1.60×10^{-2}	1.79
Cu / Ag	5.61×10^{-4}	7.39×10^{-3}	2.17×10^{-3}
Cu / Hg	9.50×10^{-3}	16.48	0.56

Isolation of Ag⁺ in river water sample

The usefulness of the ligand in the isolation and preconcentration of traces of Ag⁺ in real water sample such as river water sample was demonstrated using the proposed extraction procedure. The importance of separation of analytes from the matrix before subjected to instrumental methods of analysis has been highlighted [34]. In our studies, firstly, the water was directly analyzed with ICP-MS to determine the metal ions content. The main metal ions found in the river water are Mg²⁺ (194 ppb), Zn²⁺ (3 ppb), Mn²⁺ (2 ppb) and Ca²⁺ (2001 ppb), but Ag⁺ was not detected in the sample. The data are average of three determinations mainly carried out from different spots. Next, various concentration of Ag⁺ (5, 10, 20, 40 ppm) was spiked respectively to the samples. The extraction results of these spiked samples are summarized in Table 3.

Overall results proved that all of the three thiocrown ethers show significant extraction (> 90%) of Ag⁺ in the river water sample. Up to 10 ppm of Ag⁺ was extracted quantitatively (100% E) by 15S5 and 18S6. However, the percentage of extraction slightly decreased when the spiked Ag⁺ level was increased.

ligands towards metal ions in a mixture. This extraction-ICP-MS method was successfully applied for the separation of Ag⁺ in river water sample. The immobilization of these ligands for analytical applications under batch and flow conditions are actively being pursued in our laboratories.

Acknowledgement

Financial support of the work from the Government of Malaysia through a Fundamental Research Grant Scheme is gratefully acknowledged.

References

1. G. Gokel (1991) Crown Ethers and Cryptands. *The Royal Society of Chemistry, Cambridge*, **190**.
2. F. C. J. M. Veggel, W. Verboom and D. N. Reinhoudt (1994) *Chem. Rev.*, **94**, 279.
3. K. Saito, S. Murakami, A. Muromatsu and E. Sekido (1994) *Anal. Chim. Acta*, **294**, 329.
4. D. Sevdic, L. Fekete and H. Meider (1980) *J. Inorg. Nucl. Chem.*, **42**, 885.
5. D. Sevdic and H. Meider (1981) *J. Inorg. Nucl. Chem.*, **43**, 153.

Table 3 : %E of Ag⁺ from spiked river water sample

Ag ⁺ spiked (ppm)	%E		
	12S5	15S5	18S6
5	95.8 (0.5)	100 (0.1)	100 (0.1)
10	93.8 (0.8)	100 (0.1)	100 (0.1)
20	91.4 (0.3)	98.0 (0.3)	98.7 (0.3)
40	90.2 (0.6)	97.7 (0.5)	97.8 (0.9)

• n = 3

Conclusion

A simultaneous solvent extraction system having excellent selectivity towards Ag⁺ has been developed using the thiocrown ethers (12S4, 15S5 and 18S6) as macrocyclic neutral ligands and picrate as counter anion. The selectivity trend of these ligands are found to be the best for Ag⁺, followed by Hg²⁺ and Cu²⁺. However, negligible extraction was observed for other studied metal ions. On the whole, the results obtained are in agreement with those obtained by single-element analysis but we believe the present approach give more realistic information about the selectivity behaviour of these kind of macrocyclic

6. A. J. Blake, R. O. Gould, A. J. Hloder, T. I. Hyde and M. Schroder (1989) *Polyhedron*, **4**, 513.
7. M. Munakata, L. P. Wu, T. K. Sowa and M. Maekawa (1995) *J. Chem. Soc. Dalton Trans*, **3215**.
8. J. R. Hartman, E. J. Hints and S. R. Cooper (1984) *J. Chem. Soc. Chem. Commun.*, **386**.
9. G. J. Grant, K. E. Rogers, W. N. Setzer and D. G. Van Dorveer (1995) *Inorg. Chim. Acta*, **234**, 35.
10. H. J. Kuppers and K. Wieghardt (1989) *Polyhedron*, **8**, 1770.

11. H. J. Kuppers, A. Neves, C. Pomp, D. Ventur, K. Weighardt, B. Nuber and J. Weiss, (1986) *Inorg. Chem.*, **25**, 2400.
12. A. J. Blake, A. J. Helder and M. Schroder (1989) *J. Chem. Soc. Chem. Commun.*, **1433**.
13. B. Saad and S.M. Sultan (1995) *Talanta*, **42**, 1349.
14. M. Oue, K. Kimura and T. Shono (1988) *Analyst*, **113**, 551.
15. K. Saito, I. Taninaka, S. Murakami and A. Muromatsu (1998) *Talanta*, **46**, 1187.
16. K. Saito, I. Taninaka, S. Murakami and A. Muromatsu (1994) *Anal. Chim. Acta*, **299**, 137.
17. Y. Qin and J. Yang (1994) *Anal. Chim. Acta*, **286**, 265.
18. K. Saito, Y. Masuda and E. Sekido (1983) *Anal. Chim. Acta*, **151**, 447.
19. M. H. Moashhadizadeh and M. Shamsipur (1999) *Anal. Chim. Acta*, **381**, 111.
20. M. Shamsipur and M.H. Moashhadizadeh (2001) *Talanta*, **53**, 1065.
21. J. W. Olesik (2000) *Inorganic Mass Spectrometry Fundamentals and Application. Marcel Dekker, New York*, **63**.
22. J. S. Becker and H. S. Dietze (1998) *Spectrochimica Acta, Part B: Atomic Spectroscopy*, **53**, 1475.
23. J. A. Caruso and M. M. Bayon (2003) *Ecotoxicology & Environmental Safety*, **56**, 148.
24. S. Hirarta, T. Kajiya, N. Takano, M. Aihara, K. Honda, O. Shikino and E. Nakayama (2003) *Anal. Chim. Acta*, **499**, 157.
25. J. Enzweiler and P. J. Potts (1995) *Analyst*, **120**, 1394.
26. M. P. Field and R. M. Sherrell (1998) *Anal. Chem.*, **70**, 4480.
27. S. Laly, K. Nakagawa, T. Arimura and T. Kimijima (1996) *Spectrochimica Acta Part B: Atomic Spectroscopy*, **51**, 1393.
28. T. Wang, J. Wu, R. Hartman, X. Jia and R. S. Egan (2000) *Journal of Pharmaceutical & Biomedical Analysis*, **23**, 867.
29. D. E. Nixon and T. P. Moyer (1996) *Spectrochimica Acta Part B: Atomic Spectroscopy*, **51**, 13.
30. J. Rydberg, G. Musikan and G. R. Khoppin (1992) *Principles and Practices of Solvent Extraction, Marcel Dekker, New York*.
31. K. Ikeda and S. Abe (1998) *Anal. Chim. Acta*, **363**, 165.
32. K.L. Cheng, K. Ueno and T. Imamura (1982) *CRC Handbook of Organic Analytical Reagents, CRC Press, Boca Raton, Florida*, **127**.
33. M.I. Saleh, M.F. Bari, and B. Saad (2002) *Hydrometallurgy*, **63**, 75.
34. P.K. Jal, S. Patel and B.K. Mishra (2004) *Talanta*, **62**, 1005.