

## Selective Pre-concentration and Solid Phase Extraction of Trace Amounts of Copper(II) in Aqueous Samples Using Octadecyl Silica Membrane Disks

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A new simple and reliable method for rapid and selective extraction and determination of trace levels of  $\text{Cu}^{2+}$  ion is developed. Copper ions are adsorbed quantitatively during passage of aqueous samples through octadecyl silica membrane disks modified with some recently synthesized mixed aza-thioether crowns containing 1,10-phenanthroline subunit. Almost all matrix elements were found to pass through the disk to drain. The retained  $\text{Cu}^{2+}$  ions are then stripped from the disk with a minimal amount of thiosulfate solution as eluent and subsequently measured by atomic absorption spectrometry. The proposed method permitted large enrichment factors of about 200 and higher. The limit of detection of the proposed method is 80 ng  $\text{Cu}^{2+}$  per 1000 mL. The method was applied to the recovery of  $\text{Cu}^{2+}$  ions from different synthetic and water samples.

**Key Words:** Copper, Octadecyl silica membrane disk, Mixed azathioether crowns, 1,10-Phenanthroline.

### INTRODUCTION

The design of highly selective reagents for binding of metal ions is of vital importance to broad areas of analytical chemistry and separation science. Due to the specific metal ion complexing abilities of macrocyclic crown ethers, extensive studies of these ligands and their metal ion complexes have been carried out<sup>1-3</sup>. These types of ligands are capable of selective and efficient transport of alkali and alkaline earth cations across liquid membranes<sup>4,5</sup> and thus, have been widely used in the construction of PVC-based membrane electrodes for these cations<sup>6,7</sup>. However, the complexing ability of crown ethers toward soft heavy metal ions is quite low<sup>1-3</sup>. This problem has been overcome by substitution of some oxygen atoms of crown ethers by sulfur atoms which results in a considerable increase in the stability of such cations as  $\text{Cu}^{2+}$ ,  $\text{Tl}^+$  and  $\text{Hg}^{2+}$  ions in solution while diminishing the stability constants of their alkali and alkaline earth complexes<sup>2,3,8,9</sup>. Thus, in recent years, some sulfur containing crown ethers have been used as neutral carriers in solvent

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extraction<sup>10-13</sup>, liquid-membrane transport<sup>14,15</sup> and PVC-membrane studies of some heavy metal ions<sup>7,16-20</sup>.

The increasing use of copper compounds and copper-containing preparations in industry and medicine, has resulted in an increased copper content of environmental samples<sup>21,22</sup>. Copper also enters the environment in industrial waters because it often occurs as an impurity in copper, zinc, arsenic and antimony ores<sup>23</sup>. Low level exposure to copper compounds is widespread due to the use of soluble copper compounds to disinfect water used for drinking<sup>24</sup>. On the other hand, recent information about the interaction of copper with essential nutrients, especially selenium, copper, vitamin E and vitamin B<sub>12</sub>, have focused attention on its potential toxicity<sup>24,25</sup>.

Due to the very low concentration of most elements, including copper, in environmental samples (*i.e.*, less than 10 µg L<sup>-1</sup>), their separation and sensitive determination urgently necessitate the use of a preconcentration or trace enrichment method<sup>26-28</sup>. The liquid-liquid extraction and separation of copper in the presence of classical<sup>29-31</sup> and macrocyclic ligands<sup>11,32-34</sup> are frequently reported in the literature. However, classical extraction methods are usually time consuming and labour extensive and require relatively large volumes of high-purity solvents. Of additional concern is disposal of the solvents used, which creates a severe environmental problem. Solid-phase extraction (SPE) is an attractive technique that reduces the consumption of and exposure to a solvent, disposal costs and extraction time<sup>35,36</sup>. Recently, SPE disks were successfully utilized for the extraction of several organic<sup>37-39</sup> and inorganic analytes<sup>40-45</sup> from different matrices.

There are a number of literature reports dealing with the preconcentration of copper ions based on SPE, most of which employ chelating groups bound to resins or other polymeric supports<sup>46-48</sup>. The aim of this work was to use aza-thioether crowns containing a 1,10-phenanthroline sub-unit (Fig. 1), as excellent specific modifying agents of the octadecyl silica membrane disks for the highly selective extraction, preconcentration and determination of very low levels of Cu<sup>2+</sup> (µg L<sup>-1</sup>) in aqueous media by atomic absorption spectrometry.

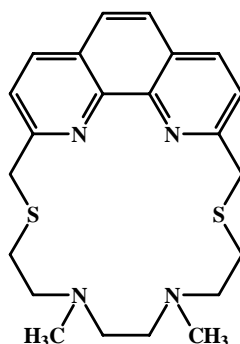


Fig. 1. Structure of ligand (L)

## EXPERIMENTAL

Analytical grade nitrate salts of copper, sodium potassium, cesium, magnesium calcium, strontium, manganese, cobalt, nickel, copper, zinc, lead, cadmium and lanthanum and potassium iodide and sodium thiosulfate (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over  $P_2O_5$ . All acids were of the highest purity available from Merck and used as received. Methanol and acetonitrile (both from Merck) were of extra pure grade and used as received. The macrocycle, aza-thioether crowns containing 1,10-phenanthroline sub unit (L) was synthesized and purified as described elsewhere<sup>49,50</sup>.

Determination of copper and other cations used were carried out with a Perkin-Elmer 603 atomic absorption spectrometer under recommended conditions for each metal ion. The pH measurements were made using a corning 250 pH/mV meter with a combined glass-calomel electrode. Extractions were performed with 47 mm diameter  $\times$  0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8  $\mu$ m particle, 60-A pore size, 3 M Co., St. Paul, MN) with a standard Millipore 47 mm filtration apparatus.

**Sample extraction:** After placing the membrane disk in a filtration apparatus, it was washed with 10 mL methanol and 10 mL acetonitrile to remove all contaminants from the manufacturing process and environment. After drying the disk by passing air through it for several min, solution of 5 mg ligand dissolved in 5 mL acetonitrile was introduced to the reservoir of the apparatus and slowly drawn through the disk by applying a slight vacuum until the ligand completely penetrate membrane. The solvent was then evaporated at 50 °C in an oven for 15 min. The general procedure for the extraction of copper ions on the modified membrane disk was as follows. The modified disk was first washed with 2 mL methanol followed by washing with 25 mL water. This step pre-wets the surface of the disk prior to the extraction of  $Cu^{2+}$  from water. It is noteworthy that the surface of the disk should not become dry from the time methanol was added until the extraction of copper ion from water was completed. Then 25-2000 mL of the sample solutions containing 10  $\mu$ g amounts of  $Cu^{2+}$  was passed through the membrane at a flow rate of 20 mL  $min^{-1}$ . With this procedure, all  $Cu^{2+}$  ions in water are quantitatively adsorbed on the modified disk and at the same time all of the ions were then eluted from the disk by 10 mL of 2.0 M  $Na_2S_2O_4$  solution at a flow rate of 5 mL  $min^{-1}$ , collected in a 10 mL volumetric flask and diluted to the mark with water (if necessary). The copper concentration was finally determined by atomic absorption spectrometry.

## RESULTS AND DISCUSSION

Complexing agents containing sulfur and nitrogen coordination sites are known to generate a great affinity toward  $d^9$  transition metal ions<sup>1,2</sup> such as  $Cu^{2+}$ . Different thiacycrown ether derivatives have been used successfully as suitable neutral ligand for the selective complexation of  $Cu^{2+}$  ion in liquid-liquid extraction<sup>10-13</sup> and ion

transport experiments<sup>14,15</sup>. In this work, it is observed that some mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit (L) can act as excellent modifiers for selective complexation and SPE of low levels of Cu<sup>2+</sup> ions.

The presence of rigid heterocyclic molecules such as 1,10-phenanthroline as part of a macrocyclic ligand has been shown to stabilize low-valent metal complexes as well as to have a marked influence on the coordination geometry at the metal center<sup>50-52</sup>.

Some preliminary experiments were carried out in order to investigate the quantitative retention of Cu<sup>2+</sup> ions by the octadecyl silica membrane disks in the absence and presence of macrocyclic ligand. It was found that the membrane disk itself show very low tendency for the extraction of copper ions (*i.e.*, some 12 %), the disks modified by macrocyclic ligand are capable to retain Cu<sup>2+</sup> ions in the sample solution quantitatively (the test solution contained 10 µg Cu<sup>2+</sup> in 25 mL water). The optimal amount of the ligand which must be adsorbed on the octadecyl silica membrane disks for the quantitative recovery of 10-50 µg copper ion from aqueous sample solutions was found to be *ca.* 5 mg or more. The use of less than 5 mg of the ligand, however, resulted in considerable decrease in the recovery of Cu<sup>2+</sup> ions. It is noteworthy that the low relative standard deviation of 1 and lower obtained for the modification of the membrane disks with different crown ether derivatives clearly revealed that the procedure as given in sample extraction result in the event distribution of the ligands over membrane disks.

Varying volumes of different stripping agents including 3 M solutions of hydrochloric acid, hydrobromic acid and nitric acid as well as 2 M solutions of potassium iodide and sodium thiosulfate were examined in order to choose a proper eluent for the retained Cu<sup>2+</sup> ions, after the extraction of 10 µg copper from 25 mL water by the modified disks. The results are summarized in Table-1. It is obvious that, among 5 different stripping agents examined, thiosulfate is the most promising one. The influence of varying concentration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ion on the recovery of copper was also investigated in the range of 0.5-2.0 M. The results revealed that 10 mL of 2.0 M thiosulfate solution can accomplish the quantitative elution of copper from the modified membrane disk.

The extraction ability of the octadecyl silica membrane disks was found to be considerably dependent on the structure of the ligand used for their modification. Table-2 shows that, under similar experimental conditions, the efficiency of the extraction of copper ion by the membrane disks modified with macrocyclic ligand decreased. This could be mainly due to the increased stability of the Cu<sup>2+</sup> ion complex with ligand, in comparison with the corresponding complexes with macrocyclic ligand. The spectrofluorometric studies in acetonitrile solution revealed that the macrocyclic ligand (water insoluble compounds) can form fairly stable 2:1 ligand-to-Cu<sup>2+</sup> complexes in solution, the stability of which varied in the order L (log β<sub>2s</sub> = 8.9), supporting the aforementioned conclusion.

TABLE-1  
PER CENT RECOVERY OF COPPER FROM THE MEMBRANE DISKS MODIFIED  
WITH MACROCYCLIC LIGAND AS A FUNCTION OF STRIPPING  
SOLUTIONS AND VOLUME OF ELUENT

Stripping solution	Recovery (%) <sup>a</sup>			
	Volume (mL)			
	5	10	15	25
HCl (3 M)	67.0 (2.0)	96.0 (1.0)	100.0 (1.0)	100.0 (2.0)
HBr (3 M)	78.0 (1.0)	95.0 (1.0)	98.3 (1.5)	98.9 (1.8)
HNO <sub>3</sub> (3 M)	2.9 (1.0)	14.8 (1.8)	21.0 (1.4)	29.3 (0.9)
KI (2 M)	74.0 (1.0)	92.0 (2.0)	98.9 (1.0)	99.2 (1.3)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (2 M)	98.8 (1.8)	99.2 (1.6)	100.0 (2.0)	100.0 (1.9)

Initial samples contained 10 µg Cu<sup>2+</sup> in 25 mL water.

<sup>a</sup>Values in parentheses are RSD based on 3 replicate analyses.

TABLE-2  
EFFECT OF THE LIGAND STRUCTURE ON THE RECOVERY OF 10 µg Cu<sup>2+</sup>  
IN 500 mL WATER FROM THE MEMBRANE DISKS MODIFIED WITH  
MACROCYCLIC LIGAND

Ligand	L
Recovery (%) <sup>a</sup>	99.7 (1.2)

<sup>a</sup>Values in parentheses are RSD based on 3 replicate analyses.

The influence of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of copper ions was investigated by passing 500 mL sample solutions containing 10 µg Cu<sup>2+</sup> followed by stripping with 10 mL of a 2 M thiosulfate solution. It was found that in the range of 5-25 mL min<sup>-1</sup>, the retention of copper by the modified disk is not affected by the sample solution flow rate considerably. Similar results for the extraction of both organic materials and metal ions by SPE have already been reported<sup>37-45</sup>. On the other hand, quantitative stripping of the retained copper ions from the modified disk was achieved in a flow rate range of 1-10 mL min<sup>-1</sup> using 10-15 mL of 2 M thiosulfate solution. However, at higher flow rates, quantitative stripping of copper ions needed larger volumes of a 2 M thiosulfate solution. It is interesting to note that the stability constant of the copper-thiosulfate complex (*i.e.*, log β<sub>3</sub> = 14.1 in water) is much higher than that of the copper crown ether complex, so that it can easily release the retained copper ions from the modified disks.

The effect of the pH of test solutions on the recovery of 10 µg Cu<sup>2+</sup> from 500 mL solutions was investigated in the range of 2.0-8.0. The pH was adjusted by using 0.1 M of either nitric acid or sodium hydroxide solutions. The results indicated that the Cu<sup>2+</sup> ions can be retained quantitatively by the modified disks in the pH range 3.5-8.0. A pronounced decrease in the recovery of Cu<sup>2+</sup> was observed at pH < 3.5, most probably due to the possible decomposition of thiosulfate ion in acid solution<sup>33</sup>, on one hand and possible protonation of the ligand, on the other. However, higher pH values (> 8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks<sup>41</sup>.

When solutions containing 10 µg of copper in 25, 50, 100, 250, 500, 1000, 1500 and 2000 mL water were passed through the modified disks, the Cu<sup>2+</sup> was quantitatively retained in all cases. Thus, the break-through volume for the method should be greater than 2000 mL.

The maximum capacity of the membrane disk modified by 5 mg L<sup>-1</sup> was determined by passing 1000 mL portions of an aqueous solution containing 1000 µg copper at pH 5.0, followed by the determination of retained metal ions using atomic absorption spectrometry.

The maximum capacity of the membrane disk was found to be 945 ± 5 µg of Cu<sup>2+</sup> ion on the disk. Consequently, by considering the final elution volume of 5.0 mL of 2 M thiosulfate and the break through volume of 2000 mL, an enrichment factor of 400 was easily achievable. The limit of detection (LOD) of the method for the determination of copper was studied under the optimal experimental conditions. The LOD obtained from 3σ of blank<sup>53</sup> is 80 ng per 1000 mL. The relative standard deviation for the 10 replicate recoveries of 100 µg Cu<sup>2+</sup> from 500 mL aqueous solutions was found to be ± 1.6 %. The selective separation and determination of copper ion was investigated by the recovery of 10 µg Cu<sup>2+</sup> in the presence of excess amounts of diverse ions in 500 mL water following the recommended procedure. The results are summarized in Table-3. The results clearly indicate that 10 µg of copper ions in the binary mixtures are retained almost quantitatively, even in the presence of 10 mg of diverse ions. Meanwhile, the retention of other cations by the modified disk is quite low and most of them can be separated almost completely from the Cu<sup>2+</sup> ion.

TABLE-3  
SEPARATION OF COPPER FROM BINARY MIXTURES

Diverse ion	Amount taken (mg)	Found (%)	Recovery of Cu <sup>2+</sup> ion (%)
Na <sup>+</sup>	8	NAPD <sup>a</sup>	100.0 (1.2) <sup>b</sup>
K <sup>+</sup>	8	NAPD	100.6 (1.6)
Cs <sup>+</sup>	8	NAPD	99.6 (2.7)
Tl <sup>+</sup>	5	2.4 (1.3)	97.5 (1.9)
Mg <sup>2+</sup>	12	NAPD	99.8 (2.6)
Ca <sup>2+</sup>	12	NAPD	99.5 (1.6)
Sr <sup>2+</sup>	11	0.9 (1.9)	99.1 (1.0)
Mn <sup>2+</sup>	11	NAPD	99.3 (1.2)
Ni <sup>2+</sup>	5	1.8 (1.4)	98.9 (2.3)
Hg <sup>2+</sup>	5	3.1 (2.6)	98.0 (3.2)
Zn <sup>2+</sup>	5	3.2 (1.7)	97.8 (1.3)
Cd <sup>2+</sup>	7	2.6 (1.6)	98.3 (1.8)
Pb <sup>2+</sup>	6	1.2 (1.9)	98.7 (1.2)
Fe <sup>3+</sup>	4	2.3 (1.4)	98.4 (1.2)
La <sup>3+</sup>	4	2.4 (1.5)	98.6 (1.4)

Initial samples contained 10 µg Cu<sup>2+</sup> and different amounts of diverse ion in 500 mL water.

<sup>a</sup>No adsorption, passes through disk.

<sup>b</sup>Values in parentheses are RSD based on 3 replicate analyses.

The applicability of the method to real samples was examined by its use in separation and recovery of Cu<sup>2+</sup> ions from 500 mL of 5 different synthetic and water samples, tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2006), snow water (Saveh, 6 February, 2006) and the results are summarized in Table-4. It is obvious, the copper ions added can be quantitatively recovered from the synthetic and water matrices.

TABLE 4  
RECOVERY OF 10 µg COPPER SPIKED TO 500 mL SOLUTION OF  
SYNTHETIC AND WATER SAMPLES

Sample	Recovery (%) <sup>a</sup>
Synthetic sample 1 (Pb <sup>2+</sup> , Ni <sup>2+</sup> and Cu <sup>2+</sup> , 3 mg each)	98.6 (1.4)
Synthetic sample 2 (Ca <sup>2+</sup> , Zn <sup>2+</sup> and Cd <sup>2+</sup> , 4 mg each)	99.6 (2.3)
Synthetic sample 3 (Sr <sup>2+</sup> , 3 mg, La <sup>3+</sup> , 2 mg)	98.1 (2.0)
Rain water	98.5 (2.2)
Tap water	99.6 (2.8)
Snow water	98.5 (2.4)

<sup>a</sup> Values in parentheses are RSD based on 3 replicate analyses.

## Conclusion

The proposed solid phase extraction procedure based on octadecyl silica membrane disks modified with a novel mixed aza-thioether crown containing a 1,10-phenanthroline sub-unit is simple, highly sensitive, selective, reproducible and rapid, when compared with the previously reported SPE methods<sup>46-48</sup>. The method can be successfully applied to the separation, preconcentration and determination of copper in real samples.

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