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Solid Phase Extraction and Preconcentration of Copper (II) Using a Thia-crown-ether Modified Octadecyl Silica Membrane Disk

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A simple, rapid and cost effective preconcentration method is described for the determination of traces of copper in aqueous samples by flame atomic absorption spectrophotometry. The method is based on sorption of Cu^{2+} ion on octadecyl silica membrane disk modified with 3,6,9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene as a suitable neutral ionophore. The quantitative sorption of copper(II) ions is obtained on modified membrane disks by simply manipulating optimal conditions. The unique feature of the method is the quantitative recovery of analyte from membrane disk using thiourea solution. Effects of the various parameters such as reagent concentrations, sample volume, matrix, etc. on extraction of copper(II) ions have been investigated. Under optimized conditions, the relative standard deviation of the combined method of sample treatment, preconcentration and determination with FAAS ($n = 10$) is generally lower than 5%. The limit of detection ($3s$, $n = 20$) was 5 ng/mL. The method could easily be adopted by any laboratory as the inputs are minimal, inexpensive and easily available. The proposed method has been successfully applied for the determination of trace amount of copper(II) ion in water samples, ore and metallurgy products.

Key Words: Copper, Solid phase extraction, Flame atomic absorption spectrometry, Preconcentration.

INTRODUCTION

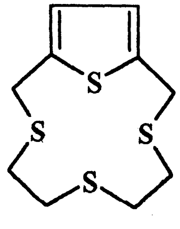
Copper is an essential trace element, which is considered as an abundant micronutrient and as a toxic element, depending on its concentration level[1]. Though, a daily copper intake of 1.52 mg is essential, severe oral intoxications will affect mainly blood and kidneys. Therefore, the determination of trace amounts of copper from different matrices is of great importance. In routine laboratory measurements, copper is measured by flame and furnace atomic absorption spectrometry[2] and spectrophotometric methods[3, 4]. However, the direct determination of trace amounts of copper in complicated materials is usually difficult owing to matrix interferences and/or insufficient detection power. Consequently, a preconcentration and matrix elimination is usually required.

Adsorption, chromatography, coprecipitation, electrolytic deposition, evaporation, liquid-liquid extraction, ion exchange and solid phase extraction were well known as preconcentration of trace metal in analytical chemistry[5]. These preconcentration methods have frequently been joined with instrumental analysis for the determination of ultra trace metal in complex matrix samples[5]. Solid-phase extraction (SPE) using cartridge and disc devices are a widely used sample-preparation technique for the isolation of selected analytes, usually from a mobile phase. SPE was initially developed as a complement or replacement for liquid-liquid extraction (LLE). It is now the most common sampling technique in many areas of chemistry, including environmental, pharmaceutical, clinical, food and industrial chemistry[6–8]. The complexing properties of macrocyclic polythioethers (thiacrown ethers) have been studied and metal complexes with thiacrown ethers have been isolated and characterized[9, 10]. Thiacrown ethers have also been studied as analytical reagents, which are selective for soft metal ions[11, 12]. They have also been used successfully for the selective extraction of some metal ions including Cu^{2+} into organic solvents[13–17]. Recently, some thiacrown ethers and non-crown compounds as neutral modifier or carriers in solid phase extraction and PVC membrane electrode studies of some heavy metal ions[18–22] have been reported.

This paper describes the applications of octadecyl silica (C_{18}) membrane disk modified with 3,6,9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene (TC)[21] for selective extraction and solid phase preconcentration of copper(II) from aqueous and natural samples.

EXPERIMENTAL

All metal salts were of analytical grade and purchased from Merck Chemical Company. The thiacrown TC (Aldrich) was of the highest purity available and used without any further purification except for vacuum drying. Methanol and acetonitrile (both from Merck) were of extra pure grade and used as received. Doubly-distilled deionized water was used throughout.



Thiacrown (TC)

The determinations of copper were performed on a Varian Spectra AA220 atomic absorption spectrometer equipped with a hollow cathode lamp (HCL). The absorbance wavelength was set at 324.8 nm (resonance line) and the spectral bandwidth at 0.5 nm. The determinations of all other cations were carried under recommended conditions for each metal ion. A digital pH meter, Metrohm model 632, equipped with a combined glass calomel electrode was used for the pH adjustments.

Extractions were performed with 47 mm diameter × 0.5 mm thickness 3M Empore^{TM} membrane disks containing octadecyl (C18)-bonded silica (8-μm particle size, 60 Å pore size) distributed by Varian. The disks were used in conjunction with a standard Sartorius 47 mm filtration apparatus.

After placing the membrane disk in the filtration apparatus, it was washed with 10 mL methanol and 10 mL acetonitrile to remove all contaminants arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, it was dried inside an oven at 60°C. Then a solution of 5 mg TS dissolved in 2 mL acetonitrile was introduced into the reservoir of the apparatus and was washed with 25 mL water and then 5 mL methanol and finally dried by passing air through it. In this step, a membrane disk modified by the thiacrown ligand was ready for sample extraction.

The general procedure for the extraction of Cu^{2+} ions on the membrane disk was performed as follows: The modified disk was first washed with 2 mL methanol followed by washing with 25 mL water. This step prewets the surface of the disk prior to the extraction of Cu^{2+} ions from water. It is practically important to wet the surface of the disk with methanol while the extraction of copper(II) ions is under way. Then 500 or 1000 mL of the sample solution containing 5 μg amount of Cu^{2+} was passed through the membrane at a flow rate of 40–45 mL/min. With this procedure, Cu^{2+} ions in water samples were quantitatively absorbed on the modified disk and consequently eluted by three 5 mL portions of 0.4 M thiourea solution at a flow rate of 20 mL/min. Each portion was collected in a 5 mL volumetric flask and diluted to the mark with water (as necessary) and the amount of copper(II) was then determined by atomic absorption spectrometry.

Samples of waste water and river water were collected from the Sarcheshme (near the copper mine the Sarcheshme) and Karoun river. Recovery experiments were also conducted by spiking the samples with appropriate amounts of copper and their copper content determined by this method.

Procedure for determination of copper in human hair: Hair samples were washed with acetone and distilled water to remove the surface contamination and dryashed in a muffle furnace at 450°C. The residue was dissolved in nitric acid and evaporated to dryness at low heating rate. The residue was dissolved in 20 mL of water and filtered. The clear solution was quantitatively transferred into a 50 mL volumetric flask and diluted to mark with water. Working solutions were prepared by taking a suitable aliquot of the sample and its copper content extracted by this method and determined by FAAS.

RESULTS AND DISCUSSION

Due to its water insolubility as well as its tendency to form a selective and stable complex with Cu^{2+}, thiacrown (TC) was employed in this work as a proper ligand for selective SPE of copper from aqueous solutions. Thus, some preliminary experiments were carried out to investigate the quantitative retention of Cu^{2+} by the octadecyl silica membrane disks in the absence and presence of TC. It was found that while the membrane disk itself does not show any tendency for the extraction of copper ions, a membrane disk modified with TC is capable of retaining Cu^{2+} in the sample solutions quantitatively. The optimum amount of ligand that must be adsorbed on the C_{18} membrane disks for the quantitative recovery of 1–50 μg copper from aqueous sample solutions was found to be *ca.* 5 mg or more.

The effects of several experimental parameters on the preconcentration and determination of Cu^{2+} were studied by spiking 50 mL of distilled water with 5.0 μg of copper and using the procedure described in the general procedure. These parameters comprise the nature and concentration of eluent, pH of sample and eluent, sample and eluent flow rate, and sample volume.

Choice of eluent: From the various eluents used, the highest recovery was achieved with thiourea solution. Incomplete stripping of Cu^{2+} ions was observed for all the other solutions (Table-1). From the data given in Table-1 it is immediately obvious that the concentration of thiourea solution which gave the highest stripping was 0.4 M or higher.

TABLE-1
PER CENT RECOVERY OF COPPER FROM THE MODIFIED MEMBRANE DISK AS A FUNCTION OF STRIPPING SOLUTIONS AND VOLUME OF ELUENT*

Stripping agent	Percentage recovery		
	1st 5 mL	2nd 5 mL	Total
KSCN	9	3	12
$Na_2S_2O_3$	25	30	55
1,10-Ortophenantroline	50	28	78
EDTA	65	25	90
Thiourea (0.05M)	32	22	54
Thiourea (0.1 M)	50	35	85
Thiourea (0.2 M)	55	38	93
Thiourea (0.4 M)	65	35	100
Thiourea (0.5 M)	70	30	100

*Initial samples contained 5 μg Cu^{2+} ion in 100 mL water

Effect of flow rate and pH : The effect of flow rates of sample and stripping solutions from the modified membrane disk on the retention and recovery of Cu^{2+} ion was studied. It was found that, in the range of 10 to 50 mL min^{-1}, the retention of copper by the membrane disk is not very much affected by the sample solution flow rate considerably. The effect of the eluent flow rate on recovery was also investigated and the maximum recovery was achieved for flow rates between 20–25 mL min^{-1}. At higher flow rates, quantitative stripping of copper needed larger volumes of 0.4 M thiourea solution.

The influence of the pH of test solutions on the recovery of 5 μg Cu^{2+} from 500 mL solution was studied in the pH range 1.0–8.0. The pH was adjusted by using 1 M HCl or 0.1 M NaOH. The results (Fig. 1) indicate that the Cu^{2+} ion can be retained quantitatively in the pH range 4.0–7.0. The pronounced decrease in Cu^{2+} recovery in solutions of pH < 4.0 is due to the protonation of thiacrown ether in acid solution. Higher pH values (> 8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks and hydrolysis of Cu^{2+} ions.

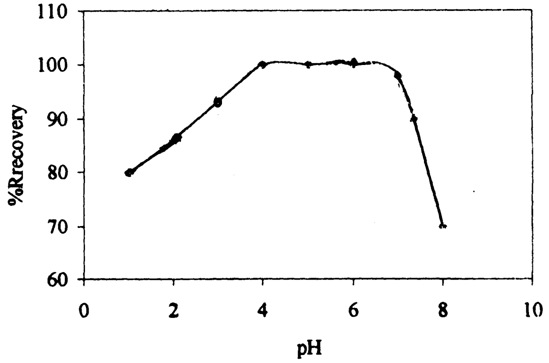


Fig. 1. Effect of pH of sample on the extraction of Cu^{2+} ion. (Initial sample contained 5 μg Cu^{2+})

Analytical performance: The maximum capacity of the membrane disk modified by 5.0 mg of TC was determined by passing 10 mL portions of an aqueous solution containing 5 μg copper, followed by the determination of the retained Cu^{2+} ions using AAS. The maximum capacity of the disk was found to be 100 μg of copper ion on the disk.

The reuse of a modified disk was tested for its ability to perform the SPE for more than one sample. It was found that the use of the same disk modified with 5 mg TC for at least ten times resulted no change in the recovery of Cu^{2+} ion. However, for the SPE of trace amounts of copper from real samples, it is recommended to use a new modified disk for every sample to protect the samples from possible contamination.

The repeatability of extraction of copper ion with membrane disk modified with 5 mg TC was investigated and the percentage of metal ion (5 μg Cu^{2+} in 100 mL water) obtained from ten replicate experiments at optimum conditions was found to be 99.97 ± 0.07%.

The break through volume of sample solution was tested by dissolving 5 μg of copper(II) ion in 50, 100, 500, 1000, 1500 and 2000 mL water and the recommended procedure was followed under optimum conditions. The Cu^{2+} ions were quantitatively retained from 1500 mL or smaller volumes. Thus, the break-through volume and the preconcentration factor for the proposed SPE method were 1500 and 150 mL, respectively.

In order to study the selective separation and determination of copper ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solutions (100 mL) containing 5.0 μg Cu^{2+} and mg amounts of other cations was taken and the proposed procedure was followed. The results are summarized in Table-2. The results show that the modified membrane disk, even in the presence of up to about 5 mg of diverse ions retain the copper(II) ions in the binary mixtures almost completely.

TABLE-2
EFFECT OF DIVERSE IONS*

No.	Ions	Remarks
1.	Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, K^+, Na^+, Mg^{2+}	No interference at 1000 fold level
2.	Ag^+, Hg^{2+}, Pb^{2+}	No interference at 500 fold level

*Initial samples contained 5.0 μg Cu^{2+} and different amounts of diverse ions in 100 mL water

In order to test the accuracy and applicability of the proposed method to the analysis of the real samples, with different matrices, it was applied to the separation and recovery of Cu^{2+} ions from a synthetic sample. The result, as the average of five separate determinations, is shown in Table-3. In view of the application of the method to the determination of copper in water, standard solutions containing Cu^{2+} were added to tap water, river water and spring water. The results are summarized in Table-3 and show that, in all cases, the copper recovery is almost quantitative. In addition, the proposed method was also used for separation and determination of copper from some real samples (Table 3). As seen, the recoveries of copper from each sample were about 97–102%.

TABLE-3
DETERMINATION AND RECOVERY OF COPPER IN WATER SAMPLES AND HUMAN HAIR*

Sample	Added (μg/L)	Found (AAS) (μg/L)	Found (this work)	Recovery (%)
Synthetic sample 1 (Zn^{2+}, Co^{2+} and Ni^{2+}, 2 mg of each cation and 5 μg of Cu^{2+})			5.102 (0.005)	102.0
Synthetic sample 2 (Mg^{2+}, Pb^{2+} and Hg^{2+}, 500 μg of each cation 5 μg of Cu^{2+})			5.103(0.005)	102.1
River water	4.7		4.80(0.02)	102.1
Rain water	2.1		2.05(0.01)	97.6
Tap water	3.5		3.57(0.03)	102.0
Sarcheshme water		2.02	2.10 (0.04)	—
Human hair		14.2 (μg/g)	14.1 (μg/g) (0.1)	—

*Values in parentheses are RSDs based on five replicate analyses.

Conclusion

The proposed method has the following advantages: the method is selective for separate and determination of Cu^{2+} from other metal ions associated, even in much higher concentrations. The method can be successfully applied to the separation and determination of copper in real samples such as water and human hair samples. The method is rapid, the time taken for the separation and analysis of copper in 1 L water sample is at most 25 min and it is a simple method for the separation of copper.

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