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# Solid Phase Extraction of Copper(II) by Modified Octadecyl Silica Membrane Disks with 3-{2-[2-(2-Hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one Oxime

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A simple, selective and rapid method for determining trace amounts of copper(II) ions in various types of water samples using atomic absorption spectrophotometry was investigated. Copper(II) ions from water samples were preconcentrated by solid phase extraction using octadecyl silica membrane disks modified with 3-{2-[2-(2-hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one oxime, (H<sub>2</sub>mdo). The experimental conditions were optimized by changing several parameters such as volume of eluting solvent, the effect of pH, eluent flow rates, the amount of H<sub>2</sub>mdo, breakthrough the volume, limit of detection and maximum capacity of the disks for Cu<sup>2+</sup> recovery. The method was applied to the recovery of Cu(II) ions from seven different water samples and an international certified reference sample (SLRS-4), the method was also quantitative.

**Key Words:** Copper, solid phase extraction, ultratrace elements, silica membrane.

## Introduction

Although copper(II) ions are extremely important for several biological processes, their levels in some situations are indications of a problem or disease in many living systems or environments<sup>1-3</sup>. While trace copper ions promote rancidity and off-flavors in nutrients, copper accumulation in the liver is a characteristics of Wilson's disease, producing neurological and psychiatric defects<sup>4</sup>. Therefore, various works have been conducted to design a powerful method for determining trace copper ions in environmental and biological samples. The two most widely used methods are atomic absorption spectrometry<sup>5</sup> and other

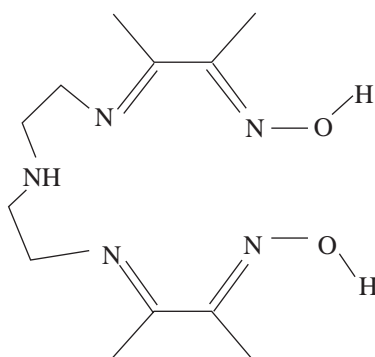
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spectrophotometric methods<sup>6</sup>. However, a preconcentration step is generally necessary in order to increase their sensitivities for most samples.

Recently, several matrices immobilized with organic ligands have been developed to the separation and preconcentration of metals from environmental samples<sup>7–13</sup>. Solid phase extraction (SPE) using metal specific ligand-modified-octadecyl (C<sub>18</sub>) bonded silica cartridges has provided sensitive and selective pre-concentrations for the spectrophotometric detection of copper ions<sup>12–16</sup>. In recent years, SPE disks and cartridges have been successfully used for the determination of copper ions in various environmental samples<sup>11–15</sup>.

Schiff base and oxime compounds have been extensively studied because of their biological and structural importance<sup>17–19</sup> and especially their specific and selective reactions with metal ions. Therefore, these compounds are able to form stable complexes with several transition metal ions<sup>20,21</sup>, among which the resulting Cu<sup>2+</sup> complexes are among the most stable<sup>17</sup>. Recently, H<sub>2</sub>mdo ligand (Fig. 1) was successfully applied to the direct determination of copper ions in pharmaceutical and biological samples<sup>22</sup>.



**Figure 1.** 3-{2-[2-(2-hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one oxime, (H<sub>2</sub>mdo).

This article reports an investigation for the separation and preconcentration of copper ions by SPE using octadecyl silica membrane disks immobilized with 3-{2-[2-(2-hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one oxime, (H<sub>2</sub>mdo). In order to optimize the experimental conditions, several parameters such as the volume of eluting solvent, the pH effect, eluent flow rates, the amount of H<sub>2</sub>mdo and breakthrough volume, limit of detection, maximum capacity of disks for Cu<sup>2+</sup> recovery and the recovery of Cu(II) ions from seven different water samples and SLRS-4 have been analyzed.

## Experimental

### Reagents

Methanol, dimethylsulfoxide, hydrochloric acid, acetic acid, nitric acid, sulfuric acid and all other chemicals used were of analytical reagent grade (BDH and Merck). The 3-{2-[2-(2-hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one oxime, (H<sub>2</sub>mdo) was prepared according to a previous report<sup>23</sup>. Deionized water was used throughout the experiments. The standard stock solution of copper(II) (1000 ppm) was prepared by dissolving 1.0000 g of copper wire (99.98% ) with 2 mL of concentrated nitric acid and diluting to 1000 mL in a calibrated volumetric flask with water. All solutions were prepared by appropriate dilution of the stock solution with water.

## Apparatus

The copper determinations were carried out on a ATI Unicam 929 model atomic absorption spectrophotometer with a hollow cathode lamp and a wavelength of 324.8 nm using an air-acetylene flame. An Orion 601/A pH meter was also used for measurements. Extraction was performed with 47 mm diameter × 0.5 mm thick Empore membrane disks containing octadecyl-bonded silica (8- $\mu$ m particle, 60-Å pore size, 3M Co., St. Paul, MN, USA) with a standard Schott-Duran 47-mm filtration apparatus connecting to a water aspirator. The typical composition of the disks was 90% w/w octadecyl-bonded silica and 10% PTFE fibers.

## Procedure

The washing, wetting and conditioning procedures were performed as recommended by the supplier (3M Co.). After the washing and drying steps, the disk was immersed in a solution of 5 mg H<sub>2</sub>mdo dissolved in 2 mL of the DMSO and a slight vacuum was slowly applied through the disk until the ligand penetrated the membrane completely. Finally, the membrane disk modified by H<sub>2</sub>mdo was washed and air-dried for copper extraction.

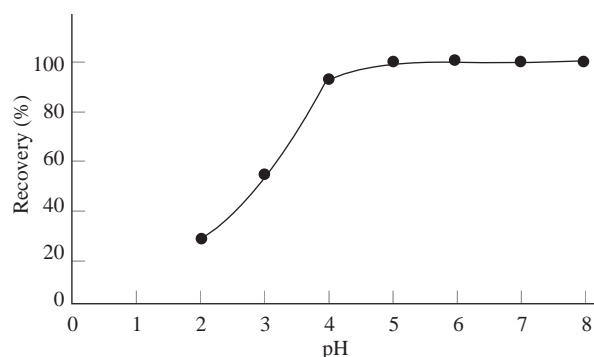
The general procedure for the extraction of Cu<sup>2+</sup> ions on the modified membrane disk was as follows: the modified disk was prewetted with 1 mL of methanol followed by washing with 25 mL of water prior to the extraction of Cu<sup>2+</sup> ions from the sample. Five hundred milliliters sample solution containing 10  $\mu$ g Cu<sup>2+</sup> having a pH value between 6.0 and 6.5 was passed through the membrane at a flow rate of 20 mL/min. The extracted copper was removed from membrane disks using 5 mL of 1 M nitric acid by applying a slight vacuum on standard Schott-Duran 47-mm filtration apparatus. Copper containing fractions were combined in a 10 mL calibrated flask and diluted to the mark with 1 M nitric acid. At the same time, a standard Cu<sup>2+</sup> solution was also prepared in 1 M nitric acid.

## Results and discussion

In this study, H<sub>2</sub>mdo ligand was used as a modifier for the SPE and H<sub>2</sub>mdo-modified membrane disks used for Cu<sup>2+</sup> preconcentration from water samples and determination by AAS. The preliminary experiments were performed to investigate whether unmodified and H<sub>2</sub>mdo-modified octadecyl silica membrane disks have any affinity to quantitatively retain copper ions. It was observed that the unmodified disks retained only 10% of copper ions from the sample solution. The membrane disk modified by H<sub>2</sub>mdo is, however, quantitatively able to retain Cu<sup>2+</sup> ions from the sample solution.

### The effect of pH

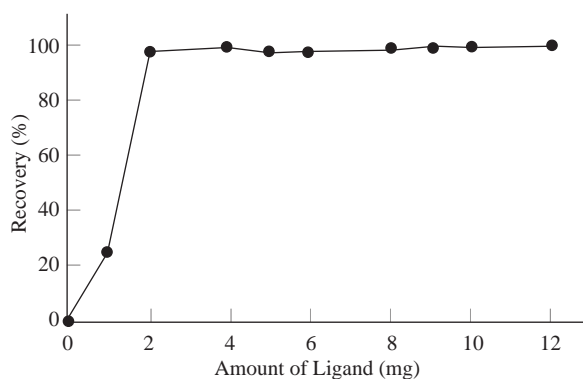
The effect of pH on the SPE of copper ions was studied in the range 2-8. The pH was adjusted by using 0.1 M of either nitric acid or sodium hydroxide solutions. The recovery percentage depended on the pH of the solution, which was nearly constant in the pH range of 5-8 (Fig. 2). These results indicate that Cu<sup>2+</sup> ions can be quantitatively retained by the membrane disk in the pH range 5-8. Higher pH values (>8) were not tested because of the possibility of the hydrolysis of octadecyl-silica in the disks<sup>21</sup>.



**Figure 2.** Effect of pH of sample solution on extraction efficiency of Cu(II) ions.

### Effects of amount of ligand and flow rate

In order to investigate the amount of H<sub>2</sub>mdo on the quantitative recovery of Cu<sup>2+</sup> by the membrane disk, Cu<sup>2+</sup> ion extraction was conducted by varying the amount of ligand from 0 to 12 mg (Fig. 3). It was found that the extraction of copper by ligand modified disks was quantitative in the presence of 2-12 mg ligand. Therefore, 5 mg of the ligand was used for all the subsequent experiments.



**Figure 3.** Effect of amount of H<sub>2</sub>mdo on extraction efficiency of Cu(II) ions.

The most ideal flow rates of the copper containing water samples through the membrane disks have been observed in the range 5-40 mL/min, whereas quantitative removal of the copper complex from the H<sub>2</sub>mdo-modified disk by using 5 mL of 1 M nitric acid was achieved in a flow range of 1-10 mL/min.

### Choice of eluent for the removal of retained Cu<sup>2+</sup> ions

Several acids of varying concentration have been applied to select a proper elution reagent for the retained Cu<sup>2+</sup> extracted from 10 µg copper containing 100 mL water by the disk modified with 5 mg of H<sub>2</sub>mdo (Table 1). It was found that 15 mL of 1 M acid can quantitatively remove copper ions. However, a lower volume (5 mL) and concentration (1 M) of nitric acid can be used to completely eluate Cu<sup>2+</sup> ions from the membrane disk. Thus, 8 mL of 1 M nitric acid was used for all subsequent experiments.

### Maximum capacity of modified disks

The performance of the H<sub>2</sub>mdo-modified disks to retain copper ions was investigated by using excess amounts of copper in water samples. One thousand milliliter portions of an aqueous solution containing 1000 µg copper

were passed through the modified disks with 5 mg H<sub>2</sub>mdo at pH 6.0-6.5. Maximum copper content retained on the modified disks was determined spectroscopically as  $305 \pm 5 \mu\text{g}$  of Cu<sup>2+</sup> by AAS.

**Table 1.** Percent recovery of Cu(II) from the modified membrane disk using different stripping acid solutions<sup>a</sup>.

Stripping acid solutions,(M)	Volume (mL)			
	2	5	10	15
	Recovery (%)			
HNO <sub>3</sub> (0.1 )	15.0 (1.2) <sup>b</sup>	44.1 (1.4)	61.0 (1.8)	96.0 (1.5)
HCl (0.1)	15.2 (1.4)	50.2 (1.3)	59.9 (1.6)	84.8 (1.4)
H <sub>2</sub> SO <sub>4</sub> (0.1)	11.6 (2.2)	40.6 (1.6)	60.2 (1.5)	84.8 (1.9)
CH <sub>3</sub> COOH (0.1)	14.4 (2.5)	49.8 (1.4)	64.4 (1.3)	89.6 (1.3)
HNO <sub>3</sub> (1)	26.3 (1.9)	99.3 (1.0)	99.5 (1.5)	99.6 (0.9)
HCl (1)	23.3 (2.1)	82.4 (1.1)	97.0 (1.7)	97.9 (0.8)
H <sub>2</sub> SO <sub>4</sub> (1)	24.8 (1.8)	78.3 (1.1)	81.1 (1.5)	89.9 (1.2)
CH <sub>3</sub> COOH (1)	24.3 (0.9)	64.4 (1.9)	76.5 (1.2)	85.9 (2.2)
HNO <sub>3</sub> (3)	49.5 (0.9)	98.5 (1.1)	99.8 (1.4)	99.8 (1.1)
HCl (3)	45.5 (0.8)	82.5 (1.2)	99.7 (0.9)	99.8 (1.7)
H <sub>2</sub> SO <sub>4</sub> (3)	51.0 (1.1)	79.5 (1.3)	99.3 (1.3)	99.9 (1.5)
CH <sub>3</sub> COOH (3)	47.5 (1.3)	74.0 (1.0)	90.5 (1.3)	97.8 (1.8)

<sup>a</sup> Initial samples contained 10  $\mu\text{g}$  Cu<sup>2+</sup> and different amounts of diverse ions in 100 mL water.

<sup>b</sup> Values in parentheses are RSD based on four replicated analyses.

## Breakthrough volume

The breakthrough volumes of tap, snow, river, rain, spring, mineral and seawater sample solutions were investigated by dissolving 5  $\mu\text{g}$  of copper in 100, 250, 500, 750, 1000, 1250 or 1500 mL of water under optimal experimental conditions. The results clearly indicate that the breakthrough volume of the applied method should be greater than 1500 mL for all the samples except seawater, which is 1000 mL.

## Effect of diverse ions

Selective separation and determination of Cu<sup>2+</sup> in the presence of foreign ions were investigated in order to find out the tolerance limit of the method. An aqueous 500 mL solution containing 10  $\mu\text{g}$  Cu<sup>2+</sup> and milligram amounts of other ions were taken and the above procedure was followed. The results as summarized in Table 2 clearly indicate that 10  $\mu\text{g}$  of Cu(II) ions in the binary mixtures are retained quantitatively by the H<sub>2</sub>mdo-modified membrane disk. Most of the tested ions do not interfere with the determination of copper. The method is applicable in the presence of 10-15 mg of foreign cations, whereas the tolerance limit is extremely high for foreign anions.

## Precision and accuracy

The precision of the method was checked by taking 10 replicate measurements on 10 determinations with blank solutions. The relative standard deviation (10 determinations with blank solutions, 95% confidence level) is  $\pm 0.55\%$ . The limit of detection (LOD) is  $0.17 \mu\text{g/L}$ , the limit of quantification (LOQ) is  $0.57 \mu\text{g/L}$ , and the LOD/LOQ ratio is 0.29, thus indicating the robustness of the procedure. The accuracy of the method was checked by using an international certified reference sample (SLRS-4). The method was applied

to the separation and recovery of  $\text{Cu}^{2+}$  ions from real samples to assess its applicability. Seven different water samples (tap, snow, river, rain, spring, mineral and sea (water) not less than 1000 mL in volume were analyzed. The copper(II) ions added were quantitatively recovered from the water samples (Table 3).

**Table 2.** Determination of copper from binary mixtures<sup>a</sup>.

Foreign ion	Tolerance limit of ion (interfering ion/mg)	Recovery (%)
$\text{Ni}^{+2}$	0.3	95.3(2.2) <sup>b</sup>
$\text{Mn}^{+2}$	20	95.8 (1.3)
$\text{Co}^{+2}$	20	95.2(2.1)
$\text{Cr}^{+3}$	15	95.4(1.5)
$\text{Fe}^{+2}$	15	95.7(0.7)
$\text{Pb}^{+2}$	25	95.8(0.4)
$\text{Hg}^{+2}$	20	95.2(1.6)
$\text{Cd}^{+2}$	20	95.2(2.1)
$\text{Sr}^{+2}$	30	95.0(0.6)
$\text{Mg}^{+2}$	100	99.0(1.2)
$\text{Ca}^{+2}$	100	99.0(1.4)
$\text{Sn}^{+4}$	20	95.3(0.8)
$\text{Ag}^{+}$	20	95.3(0.8)
$\text{Na}^{+}$	200	99.4(0.4)
$\text{Cl}^{-}$	200	99.1(1.1)
$\text{SO}_4^{-2}$	150	98.8(1.2)
$\text{NO}_3^{-}$	200	98.6(0.9)
$\text{CH}_3\text{COO}^{-}$	120	98.8(1.1)
$\text{PO}_4^{-3}$	400	98.5(0.9)
$\text{Na}_2\text{H}_2\text{Y}$	0.3	95.0(1.3)

<sup>a</sup> Initial samples contained 10  $\mu\text{g}$   $\text{Cu}^{2+}$  and different amounts of diverse ions in 500 mL water.

<sup>b</sup> Values in parentheses are RSD based on four replicated analyses.

## Conclusion

The ligand used in this study could be obtained at high yields by a very simple procedure of mixing initial reagents in ethanol for no more than 1 h. However, it might decompose in solution if kept more than a couple of days at room temperature. Therefore, it should be prepared when it is needed and used fresh or kept below 4 °C in a colored bottle. The proposed SPE possesses the following advantages: the method is rapid when compared with the previously reported procedures for the separation and determination of copper<sup>22,24–26</sup>; the time taken for the separation and determination of copper in a 500 mL sample is at the most 20 min. Moreover, it is a simple, highly sensitive, selective and reproducible method for the separation of  $\text{Cu}^{2+}$  and can be successfully applied to the separation and determination of copper from water samples (Table 4). The reproducibility of the procedure is at most 2%.

**Table 3.** Recovery of copper(II) added to 1000 mL of different water samples.

Water sample	Cu(II) added ( $\mu\text{g}$ )	Cu(II) determined ( $\mu\text{g/L}$ ), $\bar{x} \pm S$
SLRS-4( $1.81 \pm 0.08 \mu\text{g/L Cu}$ )	0	$1.98 \pm 0.15$
	10	$12.01 \pm 0.21$
Snow	0	$3.22 \pm 0.15$
	10	$13.15 \pm 0.2$
Rain	0	$4.66 \pm 0.2$
	10	$14.44 \pm 0.16$
Tap	0	$2.17 \pm 0.15$
	10	$12.28 \pm 0.18$
River	0	$24.33 \pm 0.21$
	10	$34.46 \pm 0.14$
Sea	0	$1.12 \pm 0.15$
	10	$11.03 \pm 0.14$
Aytaç(akyudum)/spring water(Sakarya-Turkey)	0	$2.64 \pm 0.13$
	10	$12.49 \pm 0.12$
Çaldağ mineral water/ Giresun-Turkey	0	$3.50 \pm 0.9$
	10	$14.10 \pm 0.15$

**Table 4.** Comparison of characteristic features of various procedures for the separation and determination of copper(II).

Complexing Agent	Support	Elements Studied	Water	Technique	LOD ng/mL	References
8-Hydroxyquinoline	Silica	Cu, Bi, Cd, Pb, Zn, In	Sea	ASV	-	7
8-Hydroxyquinoline	Cellulose	Cu	Synthetic solutions	AAS	0.3	8
Ammonium tetramethylene- dithiocarbamate	XAD-4	Cu, Cd, Mn, Co, Pb, Ni, Fe	River	AAS	-	9
1-(2-Pyridylazo)-2- naphthol	Dowex- 50W	Cu	Spiked	Spectro- photometer	1	10
2,2'-[1,2-ethanediyl bis(1- nitriloethylidyne)] bis(1-naphthalene)	Disk	Cu	Water samples	AAS	4	11
Neocuproine	Disk	Cu	Water samples	Spectro- photometer	0.12	12
11- hydroxynaphthacene- 5,12-quinone	Disk	Cu	Water samples	FAAS	0.2	15
H <sub>2</sub> mdo <sup>a</sup>	Disk	Cu	Water samples	AAS	0.17	Present method

<sup>a</sup>3-{2-[2-(2-hydroxyimino-1-methyl-propylideneamino)-ethylamino]-ethyl-imino}-butan-2-one oxime



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