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# Preconcentration of trace amounts of copper(II) on octadecyl silica membrane disks modified with indane-1,2,3-trione 1,2-dioxime prior to its determination by flame atomic absorption spectrometry

Mehdi Hosseini, Nasser Dalali\* and Saeid Mohammad nejad

## Abstract

**Background:** Oximes are a group of complexing agents with good affinity towards transition metal ions; The major advantages of SPE disks are: faster sample processing due to the high cross sectional area of the disk and decrease in pressure drop, allowing higher sample flow rates; less chance of plugging by particulate matter due to wide bed; reduced channeling and improved mass transfer because of small packing particles.

**Context and purpose:** Indane-1,2,3-trione 1,2-dioxime was used as complexing agent for the preconcentration of trace amounts of Cu(II) ions from aqueous samples by modifying octadecyl silica membrane disks prior to determination by flame atomic absorption spectrometry.

**Results:** The influence of analytical parameters including pH and flow rate of sample solution, amounts of complexing agent, and type and flow rate of eluent for the stripping of Cu(II) from the disks were investigated.

**Main findings:** The proposed method had a linear range of 5.0 to 500 ng mL<sup>-1</sup>. The limit of detection of the method was 0.2 ng mL<sup>-1</sup>, and an enrichment factor of 200 was obtained.

**Conclusion:** The proposed method has been applied to the determination of copper in several aqueous samples with satisfactory results.

**Keywords:** Cu(II), solid phase extraction, octadecyl silica membrane disks, indane-1,2,3-trione 1,2-dioxime, FAAS

## Background

Copper is both vital and toxic for many biological systems [1,2], so its determination in water samples is warranted by the narrow window of concentration between essentiality and toxicity [3,4]. On the other hand, copper is also an important element in geochemistry. It can be easily released from silicates, sulfites, and oxides after some physical and chemical weathering and after transport by water can be accumulated in soils and sediments [5]. Thus, the determination of trace amounts of copper from different matrices is of great importance. The direct determination of the trace metals such as copper in

solid or powder sample solutions with a complicated matrix by atomic spectroscopic methods, such as flame atomic absorption spectrometry (FAAS), is often difficult due to their extremely low concentrations and matrix interferences; therefore, a separation/preconcentration step is required [6,7]. Several procedures such as liquid-liquid extraction, precipitation, cloud point extraction, co-precipitation, solid phase extraction (SPE), etc. are generally used for preconcentration and separation of heavy metals. The above procedures operated in the batch mode are time-consuming and labor-intensive, require large sample/reagent volumes, and suffer from risks of contamination and analyte loss [8,9]. In recent years, different trapped complexing agents on a variety of solid matrices have been successfully used for

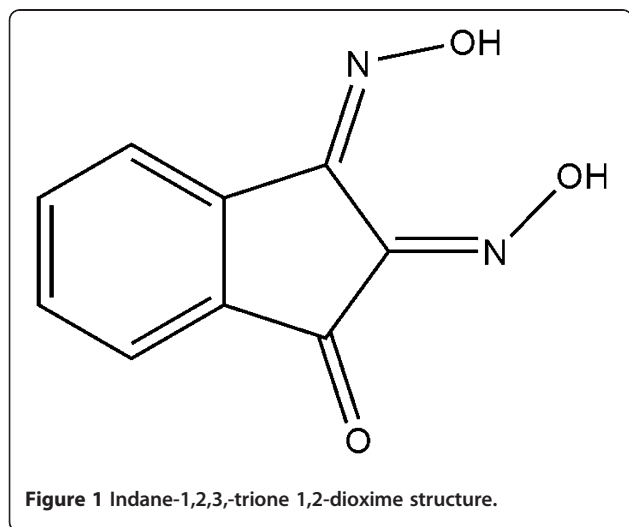
\* Correspondence: Nasser\_zn@yahoo.com  
Phase Separation and FIA Research Lab., Department of Chemistry,  
Faculty of Sciences, University of Zanjan, Zanjan, 45371-38791, Iran

the preconcentration, separation, and sensitive determination of trace metal ions [10]. Among those preconcentration/separation methods, SPE is an attractive technique that reduces consumption and exposure to solvent, disposal costs, and extraction time [11]. Recently, SPE columns were successfully utilized for the extraction of several organic [12] and inorganic analytes [13]. The nature and the properties of the sorbent materials used in SPE as a solid phase are of prime importance for effective retention of metals or organic analytes [14]. The main requirements of a sorbent material are the following: fast and quantitative adsorption/elution, regeneration ability, high capacity, accessibility, and chemical and mechanical resistibility to endure harsh conditions. Various packing materials (sorbent) have been used for the preconcentration of heavy metal ions such as multi-walled carbon nanotubes [15], microcrystalline naphthalene [16], polyurethane foam [17], silica gel [18], styrene-divinylbenzene [19,20], chitosan [21], styrene-divinylbenzene, and other sorbents [22]. In the present study, a rapid and efficient method for the selective extraction and preconcentration of copper(II) in aqueous media by octadecyl silica membrane disks modified with synthesized oxime, indane-1,2,3-trione 1,2-dioxime Figure 1, is used, prior to its determination by flame atomic absorption spectrometry was proposed.

## Experimental

### Apparatus

A Varian model SpectrAA-220 flame atomic absorption spectrometer (Mulgrave, Vic., Australia) equipped with a deuterium background corrector was used for the determination of metal ions. A copper hollow cathode lamp was used as light source and was operated at 15 mA. The wavelength was set at a resonance line of 324.7 nm,



and the spectral band pass was at 0.2 nm. A time constant of 0.2 s was used for the peak height evaluation. The air flow rate was set at 8.6 L min<sup>-1</sup>; acetylene flow rate, at 0.8 L min<sup>-1</sup>. The determinations of all other cations were carried out under recommended conditions by the manufacture for each metal ion. A digital pH meter, Metrohm model 692 (Metrohm AG, Herisau, Switzerland), equipped with a combined glass calomel electrode was used for the pH adjustments.

### Reagents

All chemicals were of analytical reagent grade and provided by Merck (Darmstadt, Germany). A 1,000-mg L<sup>-1</sup> Cu(II) solution was prepared by dissolving 1,000 g of the metal in a small volume of concentrated nitric acid and diluted to 1.0 L with 1% (v/v) nitric acid. Working standard solutions containing 2.5 to 50 ng mL<sup>-1</sup> of copper were prepared by appropriate dilution. Indane-1,2,3-trione 1,2-dioxime was synthesized according to literature [23-27].

### General procedure

Extractions were performed using 47 mm in diameter by 0.5 mm in thickness 3M Empore™ (3M, St. Paul, MN, USA) membrane disks containing octadecyl-bonded silica (8-μm particle sizes, 60-nm pore size) distributed by Varian (Varian Medical Systems, Palo Alto, CA, USA). The disks were used in conjunction with a standard Sartorius 47-mm filtration apparatus (Sartorius AG, Goettingen, Germany). 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 from the environment. After drying the disk by passing air through it for several minutes, a solution of 7.5 mg ligand dissolved in 10 mL ethanol was introduced onto the disk and was washed with 25 mL of water. Finally, the disk was washed with 25 mL of water and 10 mL methanol and dried by passing air through it. Then, the modified membrane disk was ready for sample extraction. The general procedure for the extraction of Cu(II) ions on the membrane disk was performed as follows. The modified disk was first washed with 4 mL methanol followed by washing with 25 mL of water. It is important to note that the surface of the disk was not left to become dry from the time methanol was added until the extraction of Cu(II) ions from water was completed. Then, 500 mL of the sample solutions containing microgram amounts of Cu(II) was passed through the membrane at a flow rate of 20 to 30 mL min<sup>-1</sup>. With this procedure, all Cu(II) ions in water samples are quantitatively adsorbed on the modified disk. The extracted copper was eluted from the disk using two 5-mL portions of 0.1 mol L<sup>-1</sup> ethylenediaminetetraacetic acid

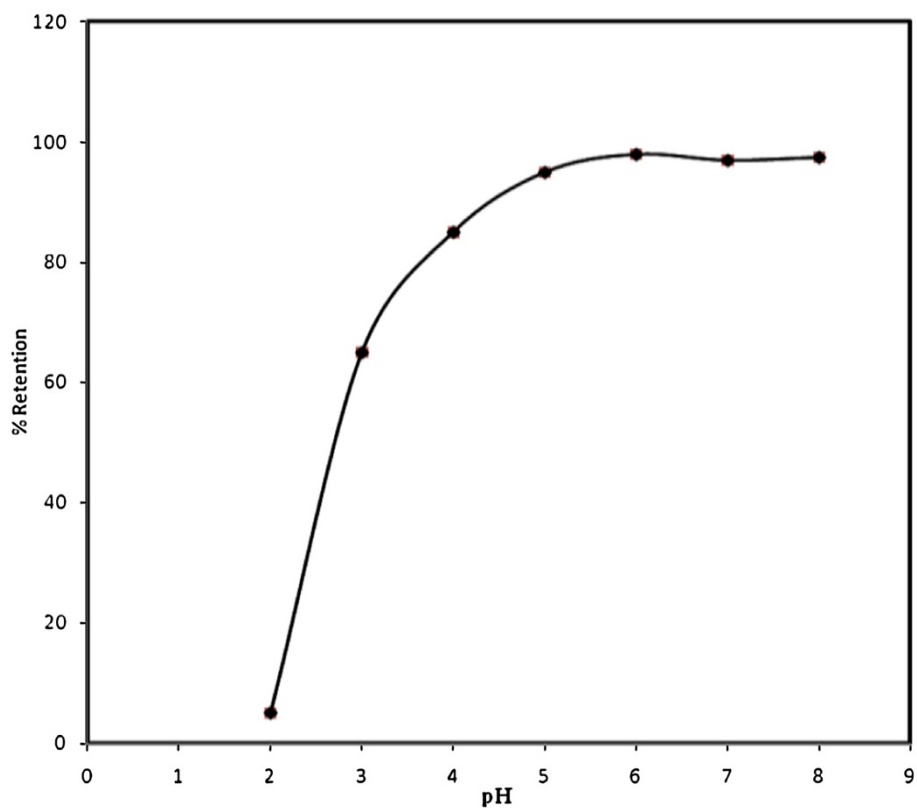
(EDTA) solutions at a flow rate of 5 mL min<sup>-1</sup>. Each portion was collected in a 5-mL volumetric flask and was diluted to the mark (if necessary) with distilled water. The amounts of Cu(II) were then determined by FAAS.

### Results and discussion

Considering the stability trend as well as the high lipophilicity of some oximes (as a complexing agent), we investigated the use of indane-1,2,3-trione 1,2-dioxime as a suitable modifier for selective extraction and preconcentration of Cu(II) ions on octadecyl silica membrane disks. Some preliminary experiments were carried out in order to investigate the quantitative retention of Cu(II) ions by the membrane disk in the absence and presence of the ligand. It was found that, while the membrane disk itself does not show any tendency for the extraction of copper ions, the modified disks are capable to quantitatively retain Cu(II) ions in the aqueous sample solution (the test solutions used contained 10 µg Cu(II) in 500 mL of distilled water). The optimum amount of the indane-1,2,3-trione 1,2-dioxime necessary for the quantitative extraction of Cu(II) was 7.5 mg.

**Table 1 Copper's percentage recovery from modified membrane disk as function of stripping solutions and eluent volume**

Stripping solution	Percentage recovery volume (mL)				
	First (5 mL)	Second (5 mL)	Third (5 mL)	Fourth (5 mL)	Total
HCl (0.01 M)	28	20	5	-	53
HCl (0.05 M)	60	8.6	1.2	-	69.8
HCl (0.1 M)	72.8	11	2.5	1.5	87.8
HCl (0.5 M)	75	11.5	1.4	1.7	89.6
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.01 M)	22.5	19.8	2	1.2	45.5
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.05 M)	18	5.5	1.7	1	26.2
EDTA (0.005 M)	61	14	6.8	3.5	85.3
EDTA (0.01 M)	84	16	-	-	100
EDTA (0.1 M)	85.4	12.6	2.1	-	100.1
HNO <sub>3</sub> (0.01 M)	51	8.5	1.2	-	60.7
HNO <sub>3</sub> (0.05 M)	60	11	-	-	71
HNO <sub>3</sub> (0.1 M)	64.4	14	2.5	-	80.9



**Figure 2 Effect of pH on retention of Cu<sup>2+</sup> ion.** Conditions, 200 mL of sample solutions containing 10 µg Cu(II) with a 35-mL min<sup>-1</sup> flow rate were passed. The volume of stripping solution (0.1 mol L<sup>-1</sup> EDTA) was 10 mL and passed through the disk with a 5-mL min<sup>-1</sup> flow rate.

**Table 2 Separation of copper ion from binary mixtures**

Diverse ion	Amount taken (mg)	Percentage diverse ion <sup>a</sup>	Percentage recovery of Cu(II) ion	Percentage RSD (N=6)
Ni <sup>2+</sup>	1.0	-	98.7	1.1
K <sup>+</sup>	1,000.0	-	101.2	0.4
Na <sup>+</sup>	1,000.0	-	100.0	2.5
Cd <sup>2+</sup>	1.0	5.4	99.8	1.2
Co <sup>2+</sup>	1.0	3.3	99.8	0.4
Zn <sup>2+</sup>	1.0	-	98.9	0.8
Cr <sup>3+</sup>	5.0	2.0	102.0	2.0
Mn <sup>2+</sup>	5.0	2.8	99.4	0.7
Ca <sup>2+</sup>	200.0	2.3	99.6	0.6
Pb <sup>2+</sup>	2.0	3.6	100.1	1.0

<sup>a</sup>Adsorbed by the disk. Conditions: sample solutions with a 35-mL min<sup>-1</sup> flow rate were passed. The volume of stripping solution (0.1 mol L<sup>-1</sup> EDTA) was 10 mL and passed through the disk with a 5-mL min<sup>-1</sup> flow rate. The pH of the sample solution was about 6.0. Initial samples contained 10 µg Cu(II) and different amounts of diverse ions in 200 mL of water.

#### Effect of the sample and eluent flow rates

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of Cu(II) ion was investigated by passing 200 mL sample solutions containing 10 µg Cu(II) followed by stripping of the retained copper ion with 10 mL of 0.1 mol L<sup>-1</sup> EDTA. It was found that, in the range of 10 to 40 mL min<sup>-1</sup>, the retention of copper by the membrane disk is not affected the sample solution flow rate considerably. On the other hand, quantitative stripping of the retained copper ions from the disk was achieved in a flow rate range of 1.0 to 15 mL min<sup>-1</sup>, using 10 mL of 0.1 mol L<sup>-1</sup> EDTA. The results showed that the recovery of copper from the disk was quantitative to 5 mL min<sup>-1</sup>. At higher flow rates (up to 5 mL min<sup>-1</sup>), quantitative stripping of copper needed larger volumes of EDTA solution.

**Table 3 Characteristics of different SPE methods**

Sorbent	Ions	Method	Eluent	CF <sup>a</sup>	LOD(ng mL <sup>-1</sup> )	Reference
2,6-Dichlorophenyl-3,3-bis(indolyl) methane loaded Amberlite XAD-16	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup>	FAAS	HNO <sub>3</sub> (4M)	225	1.9 (for Cu)	[28]
MWNTs	Cu <sup>2+</sup>	FAAS	HNO <sub>3</sub> (2 M)	60	1.46	[29]
2-(2-Quinoloni)-azo)-4-methyl-1,3-dihydroxid benzene loaded MCI GEL CHP 20Y resin	Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Ag <sup>+</sup>	GAAS	HNO <sub>3</sub> (1 M)	-	1.2 (for Cu)	[30]
4-(Phenyl(iazenyl)benzene-1,3-diamine (PDBDM)	Cu <sup>2+</sup>	FAAS	HNO <sub>3</sub> (1 M)	30	0.6	[31]
Ammonium pyrrolidine dithiocarbamate (APDC) loaded PTFE column	Cu <sup>2+</sup>	FAAS	Isobutyl methyl ketone	340	0.05	[32]
Indane-1,2,3-trione 1,2-dioxime loaded silica octa decyl disk memberane	Cu <sup>2+</sup>	FAAS	EDTA (0.1 M)	200	0.2	This work

<sup>a</sup>Concentration factor.

**Table 4 Recovery of copper from real samples by the modified disk**

Sample	Cu(II) added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	Percentage RSD (N=6)
Urine	0.0020.0	224.2245.1	0.51.5
Tap water	0.0010.0	6.016.7	0.50.7
Waste water	0.0015.0	68.682.5	1.51.1

Conditions, 50-mL sample solutions with a 35-mL min<sup>-1</sup> flow rate were passed. Volume of the stripping solution (0.1 mol L<sup>-1</sup> EDTA) was 10 mL and passed through the disk with a 5-mL min<sup>-1</sup> flow rate. The pH of the sample solution was about 6.0.

#### Effect of sample solution pH

The influence of the pH of test solutions on the retention of 10 µg Cu(II) in 100-mL solutions was studied at a pH range of 2.0 to 8.0. The pH was adjusted using 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH. The results shown in Figure 2 indicate that the Cu(II) ion can be retained quantitatively at a pH range of 5.0 to 7.0. The pronounced decrease in the Cu(II) retention in solutions of pH < 5 is due to the possible protonation of carrier ligand in acid solution. However, higher pH values (>8) were not tested because of the hydrolysis of Cu(II) and possibility of the hydrolysis of octadecyl silica on the disks.

#### Capacity of modified membrane disk

The maximum capacity of the modified membrane disk was determined by passing 10-mL portions of an aqueous solution containing 5 µg of copper, followed by the determination of Cu(II) ions using FAAS. The maximum capacity of the disk was found to be 150 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 modified disk for at least eight times resulted in no change in the recovery of the Cu(II) 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 contaminations.

### Eluent type and concentration of elution solution

In order to choose a proper eluent for the retained Cu (II) ions, after the extraction of 10 µg of copper from 100 mL of water by the modified disks, the copper ions were stripped with four 5-mL portions of various potential stripping agents. The results are summarized in Table 1. It is obvious that, among different stripping agents examined, EDTA is the most promising one. The effect of varying concentrations of EDTA on the recovery of copper ion was also studied, and the results are included in Table 1. Subsequent quantitative elution of copper was carried out with 0.1 M EDTA solution.

### Analytical figures of merit

The measurement of breakthrough volume is important in solid-phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 10 µg of copper in 100, 250, 500, 1,000, and 2,000 mL of distilled water, and the proposed procedure was followed. In all cases, the extraction by the modified membrane disk was found to be quantitative. Thus, the breakthrough volume for the proposed SPE method should be greater than 2,000 mL. Hence, by considering the final elution volume of 10 mL and the breakthrough volume of 2,000 mL, a preconcentration factor of 200 was easily achievable.

The linear dynamic range of the proposed method for Cu(II) was found in a wide concentration range of 5.0 to 500 ng mL<sup>-1</sup>.

The limit of detection (LOD) of the proposed method for the determination of copper was studied under optimal experimental conditions. The LOD based on 3σ of the blank is 0.2 ng mL<sup>-1</sup>.

The reproducibility of the proposed method for the extraction and determination of 10 µg of copper from 500 ml of water was also studied. The results obtained on six replicate measurements revealed a relative standard deviation (RSD) of 2%.

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 (500 mL) containing 10 µg of Cu(II) and amounts in milligrams 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, retains the Cu(II) ions in the binary mixtures almost completely. In Table 3, the figures of merit of this and other selected SPE methods, which use FAAS or electrothermal atomic absorption spectrometry (ETAAS) as determination method, are summarized for comparative purposes. With FAAS determination, the LOD and the preconcentration factor of the

proposed method are lower than those obtained with other sorbent materials and are comparable to the method using ETAAS. However, it should be taken in account that the proposed SPE-FAAS method consists of simpler apparatus with easier manipulation of the system, much lower equipment, and running costs.

In order to test the accuracy and applicability of the proposed method to the analysis of the real samples with different matrixes, it was applied to the separation and recovery of Cu(II) ions from different samples as tap water, waste water, and urine. The results are summarized in Table 4 and show that, in all cases, the copper recovery is almost quantitative.

### Conclusion

Results presented in this work well demonstrate the tremendous possibilities offered by the solid-phase extraction of trace amounts of Cu<sup>2+</sup> in real samples using octadecyl-bonded silica membrane disks modified by a synthesized oxime, indane-1,2,3-trione 1,2-dioxime, and its determination by flame atomic absorption spectrometry. The method developed is a precise and accurate alternative to conventional procedures for determining copper in real samples. In conclusion, the developed SPE method has been successfully used on a routine basis and allows the quantitation in real samples.

### Competing interest

The method developed is a precise and accurate alternative to conventional procedures for determining copper in real samples.

### Acknowledgement

The authors are grateful for the financial support of the Scientific Research Projects' unit of the University of Zanjan.

### Authors' contributions

MA and SM carried out the experimental works under supervision of ND. ND compiled and drafted the manuscript.

### Author's information

N. Dalali is the associate professor in Applied Analytical Chemistry of Zanjan University. M. Hosseini is MSc. Analytical chemistry and the PhD scholar Analytical chemistry; S. Mohammadnejad is the MSc. Analytical Chemistry, (both from Zanjan University).

Received: 16 May 2011 Accepted: 20 June 2012

Published: 20 June 2012

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doi:10.1186/2228-5547-3-7

**Cite this article as:** Hosseini *et al.*: Preconcentration of trace amounts of copper(II) on octadecyl silica membrane disks modified with indane-1,2,3-trione 1,2-dioxime and its determination by flame atomic absorption spectrometry. *International Journal of Industrial Chemistry* 2012 3:7.

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