



Solid phase extraction of amount Cu(II) using C₁₈ disks modified cyclodextrin–chitosan/nano graphene oxide

Ali Moghimi

Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran.

ARTICLE INFO

Article history:

Received: 8 July 2013;

Received in revised form:

20 January 2014;

Accepted: 1 February 2014;

Keywords

Cu(II),
SPE; Octadecyl silica disks,
FAAS,
Cyclodextrin–chitosan/nano graphene
oxide (CCGO).

ABSTRACT

Simple chemical bonding method to synthesize cyclodextrin–chitosan/nano graphene oxide (CCGO) was reported. The adsorption behaviors of Cu(II) in aqueous solution on CCGO were systematically investigated. The procedure is based on the selective formation of Cu(II) at optimum pH by elution with organic eluents and determination by flame atomic absorption spectrometry. The method is based on complex formation on the surface of the ENVI-18 DISK™ disks modified cyclodextrin–chitosan/nano graphene oxide (CCGO) followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, CCGO amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to be about 1000mL providing a preconcentration factor of 600. The maximum capacity of the disks was found to be $398 \pm 3 \mu\text{g}$ for Cu²⁺. The limit of detection of the proposed method is 5ng per 1000mL. The method was applied to the extraction and recovery of copper in different water samples.

© 2014 Elixir All rights reserved

Introduction

Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems¹⁻⁸. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, copper can bind to the cell membrane and hinder the transport process through the cell wall. Copper at nearly 40ng mL⁻¹ is required for normal metabolism of many living organisms^{9, 10}. On the other hand, copper is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of copper is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS)^{11, 12} as well as spectrometric methods^{13, 14}. However, due to the presence of copper in medicinal and environmental samples at low levels, its separation from other elements presents and also the use of a preconcentration step prior to its determination is usually necessary.

Different methods, especially Liquid- Liquid extraction of copper in the presence of various classical¹⁵⁻¹⁹ and macrocyclic²⁰, liquid membrane²⁶, column adsorption of pyrocatechol violet-copper complexes on activated carbon²⁷, ion pairing²⁸, ion pairing²⁹, preconcentration with yeast³⁰, and solid phase extraction using C₁₈ cartridges and disks³¹⁻³³.

Solid phase extraction (SPE) or liquid-solid extraction is popular and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid-liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed³⁴⁻³⁶. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices³⁷⁻⁴⁰. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions⁴¹⁻⁴².

In a recent series of papers,⁴³⁻⁴⁵ we have described the application of metal-DNA conjugates to nucleic acid sequence determination with catalytic signal amplification; the assay relies on the esterase activity of a DNA-linked Cu complex. For optimization of the system and exploration of structure- activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Cu²⁺ in low concentration.

The β-cyclodextrin–chitosan nanoparticles have attracted attentions due to its many excellent properties such as easy separation and high adsorption capacity^{21,22}. In this work, β -cyclodextrin–chitosan/nano graphene oxide materials were prepared via a step procedure route that the carboxyl group of GO chemically reacts with the amine group of magnetic β -cyclodextrin–chitosan with consequent formation of chemical bond between GO and chitosan.

In the present report, we wish to describe a proper concentrative method for assessment of trace levels of copper in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by (CCGO) have not been used for copper isolation and preconcentration, previously of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Cu²⁺ ions from aqueous media using octadecyl silica membrane disks modified by cyclodextrin–chitosan/nano graphene oxide (CCGO) and FAAS determination.

Experimental

Reagents

All acids were of the highest purity available from Merck and were used as received. Methanol and Chlorofom were of HPLC grade from Merck. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and Cu(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany, and High Purity double distilled deionized water was used throughout the experiments.

Tele:

E-mail addresses: alimoghimi@iauvaramin.ac.ir

The stock standard solution of Cu^{2+} was prepared by dissolving 0.1000g of the copper powder in 10mL concentrated nitric acid and diluted to 1000mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution. Chitosan with 80 mesh and average molecular weight of 6.36×10^5 was purchased from Qingdao Baicheng Biochemical Corp. Glutaraldehyde, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), and β -cyclodextrin were Aldrich products. All other reagents used in this study were analytical grade. The synthesis of the CCGO is illustrated in Fig. 1.

Synthesis of CCGO

β -cyclodextrin–chitosan was prepared following the method of Fan et al.²¹. Nano graphene oxide was prepared from purified natural graphite by the modified Hummers method²³. A GO dispersion was prepared by sonicating GO for 2 h in ultrapure water. 0.1 M EDC and 0.1 M NHS solution was added to the GO dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of GO²⁴. The pH of the resulting solution was maintained at 7.0 using dilute sodium hydroxide. β -cyclodextrin–chitosan (0.1 g), the activated GO solution and 5 mL glutaraldehyde were added into a flask and dispersed in distilled water by ultrasonic dispersion for 10 min. After ultrasonic dispersion, the mixed solutions were stirred at 65 °C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7.0²⁵. Then, the obtained product was collected by the aid of an adsorbent magnet and dried in a vacuum oven at 50 °C. The obtained product was CCGO.²⁸ The application of CCGO is shown in Scheme 1.

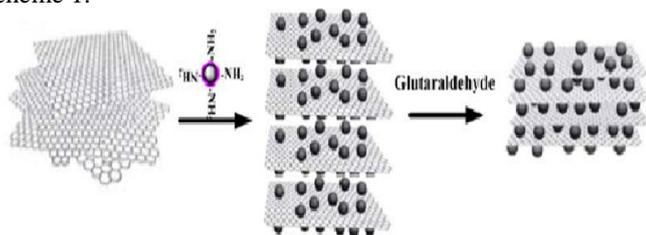


Fig. 1. Schematic of Synthesis and structure of CCGO

Apparatus

Determination of Cu^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1).

CCGO (40 mg) were packed into an SPE ENVI-18 DISK™ disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter \times 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Sample extraction

Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47mm diameter \times 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47mm filtration apparatus connected to water aspirator.⁴⁶

1) *Sample Treatment*: The water samples were filtered through 45 μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol.L⁻¹ HNO_3 overnight and rinsed twice with

deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Cu(II). Then, 5mL of methanol was added to a 90mL portion of each before analysis. The surface of the ENVI-18 DISK™ disks is modified with CCGO and therefore could retain Cu^{2+} ions properly. Instead, 10 mg of CCGO an appropriate volume of an organic solvent (5mL) miscible with water. The most suitable solvent under the experimental conditions was acetone.

2) *Disk cleaning and conditioning*: A disk was placed in the apparatus and was washed with 10mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To insure optimal extraction of the analytes of interest, the disk was again washed with 10mL of methanol, immediately followed by 10mL of water, without letting the surface of the disk dry. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow – rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

3) *Sample addition*: After complete homogenization, accurate volumes of the sample solutions (100mL portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dry (about 5 minute).

4) *Analyte elution* : In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1M HCl in methanol was passed through the disk and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Cu(II) in the eluates were then determined by FAAS using an external calibration graph.

Results and Discussion

Evaluation of the role of the CCGO

Some preliminary experiments were performed for investigation of absence or presence of CCGO on the quantitative extraction of Cu (II). It was concluded that the membrane disk itself does not show any tendency for the retention of Cu(II), but introduction of 100mL portions of aqueous Cu(II) samples containing 10 μg of Cu(II) and 10mg of CCGO leads to satisfactory its retention (Table 2). The latter case is most probably attributed to the existence of a considerable interaction between Cu (II) and the CCGO. It should be mentioned that formation of stable complexes between Cu(II) and CCGO at pH=2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Cu(II) are negligible.

Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Cu(II) on the disks, 5mL of various non organic (each containing 10% V.V⁻¹ methanol) and different organic solvents were tested. The results tabulated in Table 2. As can be seen, the best eluting solvents were found to be 5mL of methanol or ethanol, resulting in quantitative elution of Cu(II) from the disk. It should be emphasized that presence of methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate- disodium hydrogen phosphate, and then solutions passed through the disks.

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Cu(II). Then, percentage recovery at various pH values was determined (Fig. 2). According to the results shown in Fig. 2 up to pH 4.0-4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to the fact that in an acidic solution the protonation of CCGO occurs and there is a weak tendency for retention between Cu(II) and CCGO, whereas at higher values ($\text{pH} > 5$), Cu(II) reacts with hydroxide ions to produce $\text{Cu}(\text{OH})_2$. Therefore, sodium acetate-acetic acid buffer with $\text{pH} = 4.5$ was used for the preconcentration step. Other solvents used for dissolving CCGO were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 2. Meanwhile, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame at higher pH values (> 7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.^{47,48} Cu(II) ions can be retained quantitatively by the modified membrane disk through the pH range from 4.0 to 4.5. However, at lower pH (< 4.0), nitrogen atoms of the CCGO could be protonated and the stability of complex is reduced.

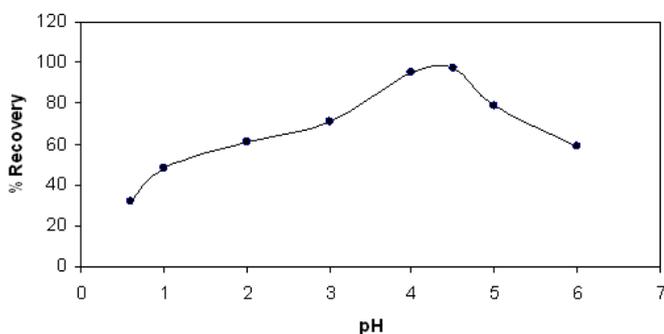


Fig. 2. Influence of sample pH on the percentage recovery of Cu(II)

Effect amount of counter anion

In order to investigate the effect of counter ion on the recovery of Cu^{2+} ions by the modified disks, different counter anions were tested (Table 4). It is immediately obvious that the nature of the counter anion strongly influences the retention of copper ions by the disk. The results revealed that the CCGO behaves in a pH range of 4.0-4.5^{28,27} so that the copper ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Cu(II) ions. The influence of the concentration of sodium acetate ion on copper recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Cu^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ion-pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

The influence of flow-rate

One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 $\text{mL}\cdot\text{min}^{-1}$, the retention of Cu(II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 3). Thus, the

flow-rate was maintained at $89\text{mL}\cdot\text{min}^{-1}$ throughout the experiment.

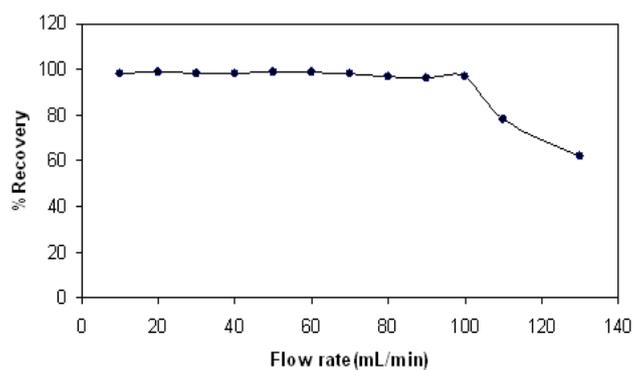


Fig. 3. The effect of the flow-rate on extraction percent of Cu(II)

Quantity of the CCGO

The optimum amount of CCGO for the quantitative extraction of Cu(II) was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in Table 5. The experimental results revealed that the extraction of Cu(II) was quantitative using a sample solution containing more than 10 mg CCGO. Hence, subsequent extractions were performed with 15 mg of CCGO.

Disk efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISKTM disk could perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic eluents practically decrease the number of times a disk could be used to 10 replicates. These observations are represented in Fig. 4.

Analytical Performance

When solutions of $10\mu\text{g}$ copper in 10, 50, 100, 600, 1000, 2000, 2500 and 3000 mL solutions under optimal experimental conditions were passed through the disks, the Cu(II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500 mL, providing a concentration factor of > 600 . The limit of detection (LOD) of the method for the determination of Cu(II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5 mL of methanol) is 5 ng per 1000 mL.

The capacity of modified disks (5 mg CCGO) was determined by passing 50 mL portions of sample solutions containing 8 mg of copper and 0.1 M sodium acetate-acetic acid buffer with pH 4.0-4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was $398 \pm 3\mu\text{g}$ of Cu^{2+} on the disk.

In order to investigate the selective separation and determination of Cu^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50 mL) containing $10\mu\text{g}$ Cu^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 6. The results show that the Cu(II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100 mg of various ions.

Table 1 . The operational conditions of flame for determination of copper

Slit width	0.7 nm
Operation current of HI-HCL	15 mA
Resonance fine	324.8nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min ⁻¹
Acetylene flow	1.7 mL.min ⁻¹

Table 2. The effect of presence of CCGO on extraction percent of Cu(II)^a

CCGO	pH	Extraction percent of Cu(II)
Absence	2-6	0.03(7.3) ^b
Presence	2-6	98.9(2.5) to 63(2.2)

^a Initial samples contained 10µg of Cu(II) in 100mL of water.^b Values in parentheses are RSD_s based on five individual replicate analyses.**Table 3. Effect of different eluting solvents on Percentage recovery of Cu(II) adsorbed on the disk ^a**

Stripping solution	% Recovery		
	2ml	5ml	10ml
Methanol	82.3(2.6) ^b	92.5(2.7)	98.7(2.0)
Acidified methanol ^c	54.5(2.3)	83.5(2.6)	83.8(2.9)
Ammoniacal methanol ^d	53.4 (2.5)	87.5(2.6)	86.3(2.8)
Ethanol	82.5(1.3)	99.6(1.5)	99.0(2.3)
Acetonitril	36.6(4.3)	46.5(5.5)	69.5(2.9)
Formic acid(1M)10% V.V ⁻¹ mthanol	55.2(1.2)	68.3(2.0)	71.5(2.8)
Hydrochloric acid(1M)10% V.V ⁻¹ mthanol	54.3(1.9)	92.0(2.6)	91.6(2.0)
Hydrochloric acid(1M)10% V.V ⁻¹ mthanol	55.6(2.5)	65.3 (2.5)	97.7(1.6)
Nitric acid(2M)10% V.V ⁻¹ mthanol	59.8(1.9)	85.9(2.3)	85.4(2.0)
Nitric acid(1M)10% V.V ⁻¹ mthanol	64.0(2.5)	85.8(2.1)	87.7(1.6)
Ethanol	85.1(2.8)	95.7(2.0)	97.7(2.2)

^a Initial samples contained 10 µg of each copper in 100 mL water.^b Values in parentheses are RSDs based on five individual replicate analysis.^c Acidified solvents obtained by addition of 0.1M HCl.^d Ammoniacal solvents obtained by addition of 0.1M NH₃**Table 4. Percent recovery of copper from the modified membrane disk in the presence of 0.01 M of different counter anions^a**

counter anion	%Recovery
Cl ⁻	13.8
Br ⁻	23.9
ClO ₄ ⁻	35.0
SCN ⁻	45.8
Picrate	76.9
Acetate	98.7

^a Initial samples contained 10µg of Cu(II) in 100mL of water.**Table 5. Influence of the CCGO amount on the recovery of Cu(II) ions ^a**

CCGO amount (mg)	Recovery(%) of Cu(II)
2	34.25(2.6) ^b
5	44.46(2.0)
8	83.20(2.6)
10	95.5(2.5)
15	98.5(2.5)
20	98.6(2.8)

^a Initial samples contained 10 µg of each copper in 100 mL water.^b Values in parentheses are RSDs based on five individual replicate analysis**Table 6. Separation of copper from binary mixtures ^a**

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Cu ²⁺ ion
Na ⁺	92.4	1.15(2.4) ^b	98.5(2.7)
K ⁺	92.5	1.36(2.3)	98.0(2.2)
Mg ²⁺	24.5	0.70(2.6)	98.5(1.7)
Ca ²⁺	26.3	2.65(3.0)	98.5(1.8)
Sr ²⁺	2.45	2.85(2.1)	98.4(2.0)
Ba ²⁺	3.66	3.16(2.1)	98.7(2.3)
Mn ²⁺	2.66	1.75(2.2)	96.3(2.3)
Co ²⁺	2.17	6.44(2.3)	93.0(1.9)
Ni ²⁺	1.64	2.43(2.4)	93.7(2.4)
Zn ²⁺	2.76	4.97(2.1)	97.6(2.4)
Cd ²⁺	2.77	2.96(2.4)	97.2(2.7)
Pb ²⁺	1.74	2.74(1.9)	97.7(2.7)
Hg ²⁺	1.67	2.71(2.1)	97.7(2.7)
Ag ⁺	2.6i	3.47(2.9)	97.6(2.3)
UO ²⁺	2.76	2.74(2.1)	98.3(2.7)

^aInitial samples contained 10µg Cu²⁺ and different amounts of various ions in 100 mL water(0.1 M acetate ion).^bValues in parentheses are RSDs based on five individual replicate analysis.

Table 7. Recovery of copper added to 1000mL of different water samples (containing 0.1M acetate at pH= 4.0-4.5)

Sample	Cu ²⁺ added (µg)	Cu ²⁺ determined (ng.mL ⁻¹)	ICP-AES
Tap water	0.0	1.72(2.8) ^a	ND
	10.0	11.93(2.0)	11.8
Snow water	0.0	4.85(2.5)	ND
	10.0	14.94(2.6)	14.5
Rain water	0.0	2.65(2.3)	ND
	10.0	12.85(2.4)	12.9
Sea Water	0.0	12.96(2.3)	12.8
	10.0	22.50(2.5)	23.0

^a Values in parentheses are %RSDs based on five individual replicate analysis

^b Not detected.

Meanwhile, retention of other cations by the disk is very low and they can be separated effectively from the Cu²⁺ ion. It is interesting to note that, in other experiments, we found that in the presence of high enough concentrations of NH₂OH.HCl as a suitable reducing agent (> 0.5M)⁴⁸.

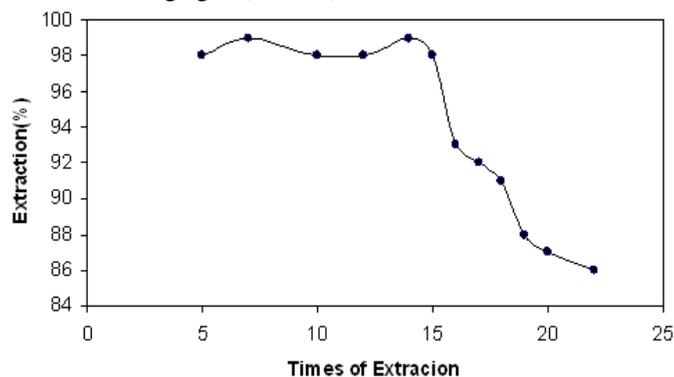


Fig. 4. Influence of eluent (5mL of methanol) type on disk efficiency

Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2012), Snow water (Tehran, 16 February, 2012) and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 7). As can be seen from Table 4 the added copper ions can be quantitatively recovered from the water samples used. As is seen, the recovered copper ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICP-AES.

Conclusion

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Cu(II) in water samples using Octadecyl Silica membrane disks modified by (CCGO) and its determination by FAAS. The method developed was simple, reliable, and precise for determining copper in water. Also, the proposed method was free of interference compared to conventional procedures to determine copper.⁴⁹⁻⁵² The method can be successfully applied to the separation and determination of copper in binary mixtures.

Acknowledgements

The author wishes to thank the Chemistry Department of Varamin (Pishva) branch Islamic Azad University and East Tehran branch Islamic Azad University for financial support.

References

- 1- H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979, pp.132-135.
- 2- L.E. Brand, W.G. Sunda, R.R.L. Guillard, *J. Exp. Mar. Biol. Ecol.* 96(1986)225.
- 3- H.H. Taylor, J.M. Anstiss, *Mar. Freshwat. Res.* 50(1999)907.

- 4- F.M.M. Morel, R.J.M. Hudson, N.M. Price, *Limnol. Oceanogr.* 36(1991)1742.
- 5- A.S. Gordan, *Mar. Chem.* 38(1992)1.
- 6- J.W. Moffett, L.E. Brand, P.L. Croot, K.A. Barbeau, *Limnol. Oceanogr.* 42(1997)789.
- 7- P.L. Croot, J.W. Moffett, L.E. Brand, *Limnol. Oceanogr.* 45(2000)619.
- 8- M. Wood, H.K. Wang, *Environ. Sci. Technol.* 17(1983)582A.
- 9- N.N. Greenwood, A. Eamshaw, *Chemistry of Elements*, Pergamon Press, New York, 1984.
- 10- C.A. Burtis, E.R. Ashwood, *Tietz Textbook of Clinical Chemistry*, third ed., Macmillan, New York, 1999.
- 11- B. Wetz, *Atomic Absorption Spectroscopy*, VCH, Amsterdam, 1985.
- 12- A.D. Eaton, L.S. Clesceri, A.E. Greenberg, *Standard Methods for the examination of water and waste water*, 19th ed., American Public Health Association, Washington, DC, 1995.
- 13- F.J. Welcher, E. Boschmann, *Organic Reagents for Copper*, Krieger Huntington, New York, 1979.
- 14- Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood, London, 1986.
- 15- O.P. Bharagava, *Talanta* 16(1969)743.
- 16- A.A. Schilt, W.C. Hoyle, *Anal. Chem.* 41(1964)344.
- 17- L.G. Borchart, J.P. Butler, *Anal. Chem.* 29(1957)414.
- 18- R. Chaisuksant, W.P. Ayuthaya, K. Grudpan, *Talanta* 53(2000)579.
- 19- D. Kara, M. Alkan, *Microchem. J.* 71(2002)29.
- 20- K. Saito, S. Murakami, A. Muromatsu, E. Sekido, *Anal. Chim. Acta* 294(1994)329.
- 21- L. Fan, C.N. Luo, M. Sun, X.J. Li, *Colloids Surf. Biointerfaces* 95(2012)42-49.
- 22- Y.J. Guo, S.J. Guo, Y.M. Zhai, S.J. Dong, E.K. Wang, *ACS Nano* 4(2010)4001-4010.
- 23- P. Ramesh, S. Bhagyalakshmi, S. Sampath, *J. Colloid Interface Sci.* 274(2004)95-102.
- 24- D. Depan, B. Girase, J.S. Shah, R.D.K. Misra, *Acta Biomater.* 7(2011)3432-3445.
- 25- L. Fan, C.N. Luo, M. Sun, X.J. Li, *Bioresour. Technol.* 114(2012)703-706.
- 26- M. Endo, K. Suzuki, S. Abe, *Anal. Chim. Acta* 364(1998)13.
- 27- D. Bingye, C. Meirong, F. Guozhen, L. Bing, D. Xv, P. Mingfei, W. Shuo *Journal of Hazardous Materials* 219-220(2012)103.
- 28- Leilei L., Lulu F., Min S., Huamin Q., Xiangjun L., Huimin D., Chuannan L. *Colloids and Surfaces B: Biointerfaces* 107(2013)76.
- 29- Y. Akama, M. Ito, S. Tanaka, *Talanta* 52(2000)645.
- 30- K. Ohta, H. Tanahasi, T. Suzuki, S. Kaneco, *Talanta* 53(2001)715.
- 31- V. Cuculic, M. Mlakar, M. Branica, *Anal. Chim. Acta* 339(1997)181.

- 32- A.Moghimi, M.S.Tehrani, S.Waqif Husain, *Material Science Research India* 3(1a) (2006)27.
- 33- M.S.Tehrani, A.Moghimi, S.Waqif Husain, *Material Science Research India* 3(2) (2005)135.
- 34- E.M.Thurman,M.S.Mills,*Solid-Phase Extraction, Principles and Practice*, Wiley, New York, 1998.
- 35- J.Pawliszyn, *Solid-Phase Microextraction, Theory and Practice*, Wiley-VCH, New York, 1997.
- 36- R.M. Izatt, J.S. Bradshaw, R.L. Bruening, *Pure Appl. Chem.* 68(1996)1237.
- 37- D.F.Hagen, C.G.Markell, G.A. Schmitt, *Anal.Chim. Acta* 236(1990)157.
- 38- C.J.Krueger, J.A. Fild, *Anal.Chem.* 67(1995)3363.
- 39- K.Z.Taylor, D.S.Waddell, E.J.Reiner,*Anal. Chem.* 67 (1995)1186.
- 40- Y.Yamini, M.Ashraf-Khorassani, J.High Resolut. *Chromatogr.*17(1994)634.
- 41- M.Shamsipur, A.R.Ghiasvand, Y.Yamini, *Anal.Chem.* 71 (1999) 4892.
- 42- M.Shamsipur, A.R.Ghiasvand, H. Sharghi, *Int. J. Environ. Anal.Chem.* 82(2001)23.
- 43- Brunner, J.;Mokhir, A.;Kramer, R.*J.Am.Chem.Soc.* 125 (2003)12410.
- 44- Zelder, F.H.;Brunner, J.; Kramer, R. *Chem. Commun.*2004, 902.
- 45- Boll, I.; Kramer, R.; Brunner, J.; Mokhir, A. *J.Am.Chem. Soc.* 27(2005)7849.
- 46- MOGHIMI, A.; *Oriental Journal of Chemistry* 2006,22(3),527.
- 47- Nayebi, P.; MOGHIMI, A.; *Oriental Journal of Chemistry* 2006,22(3),507.
- 48- MOGHIMI, A.; "*Chinese Journal of Chemistry*" 2007,25, 640.
- 49- MOGHIMI, A.; "*Chinese Journal of Chemistry*" 2007,25,10, 1536.
- 50- Moghimi, A.; Ghamamy S. "*Environmental chemistry an Indian journal*"2007,Vol.2, Issues 3.
- 51- Choi,Y.S.; Choi,H.S.*Bull. Korean Chem. Soc.*24(2003)222.
- 52- Saber Tehrani, M.; Rastegar,F.; Parchehbaf, A.;Rezvani, Z.; *Chinese Journal of Chemistry* 23(2005)1437.