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Solid Phase Extraction of Amount Cu(II) Using C_{18} Disks Modified Schiff Base-Chitosan Grafted Multiwalled Carbon Nanotubes

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ABSTRACT

A novel and selective method for the fast determination of trace amounts of Cu(II) ions in water samples has been developed. 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^{TM} disks modified Schiff base-chitosan grafted multiwalled carbon nanotubes (S-CS-MWCNTs) 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, S-CS-MWCNTs 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 ± 3 μg for Cu^{2+}. The limit of detection of the proposed method is 5 ng per 1000 mL. The method was applied to the extraction and recovery of copper in different water samples.

Keyword: Cu(II); SPE; Octadecyl slica disks; FAAS; Schiff base-chitosan grafted multiwalled carbon nanotubes (S-CS-MWCNTs).

1. INTRODUCTION

Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [1-8]. 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 40 $ng.mL^{-1}$ 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

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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 present 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 classical [15-19] and macrocylic [20, 21] co-extractant ligands have attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time-consuming, labor-intensive and requires large amounts of high purity solvents for extraction.

Nevertheless, several other techniques for the preconcentration and separation of copper have been proposed including liquid chromatography [22] supercritical fluid extraction [23], flotation [24], aggregate film formation [25], liquid membrane [26], column adsorption of pyrocatechol violet-copper complexes on activated carbon [27], ion pairing [28], ion pairing [29], preconcentration with yeast [30], and solid phase extraction using C_{18} cartridges and disks [31-33].

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 purposed [34-36]. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices [37-40]. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions [41-42].

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 Cu^{2+} in low concentration.

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 (S-CS-MWCNTS) 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 Cu^{2+} ions from aqueous media using octadecyl silica membrane disks modified by Schiff base-chitosan grafted multiwalled carbon nanotubes (S-CS-MWCNTs) and FAAS determination.

2. 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 litium, 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.

The stock standard solution of Cu^{2+} was prepared by dissolving 0.1000 g of the copper powder in 10 mL concentrated nitric acid and diluted to 1000 mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

The synthesis of the S-CS-MWCNTs is illustrated in Figure 1.

Synthesis of S-CS
Purified CS was obtained according to the method reported in the literature [28]. CS (1000 mg) was
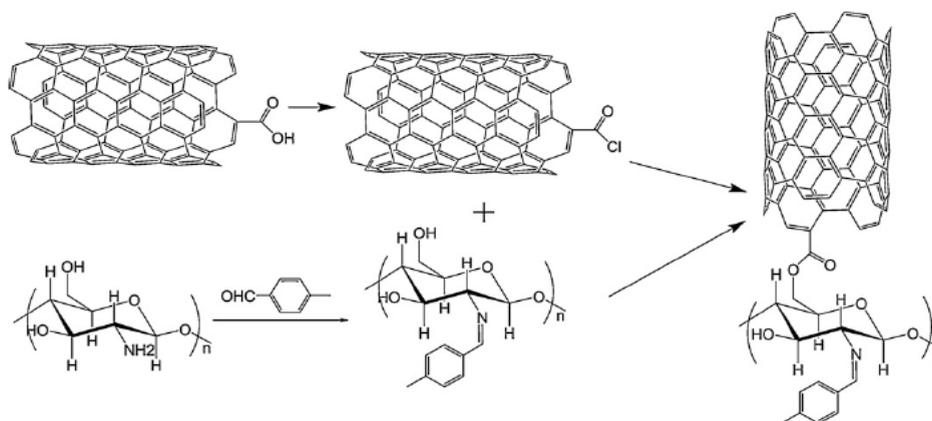
Figure 1: *Schematic of Synthesis and structure of S-CS-MWCNTs.*

dissolved in 80.0 mL of Figure 1.

0.2% (w/w) aqueous acetic acid solution. The solution was allowed to stand overnight, and then 4.0 mL of 4-methylbenzaldehyde in methanol (2:1, v/v) were slowly added. After stirring for 24 h at room temperature, the resulting mixture was washed with ethanol several times, filtered, and dried in a vacuum oven at 40°C for 8 h. The obtained yellow powder was S-CS. [28].

Synthesis of acyl-chloride-modified MWCNTs (MWCNTs-COCl)

MWCNTs-COOH (80 mg) was dispersed in 40.0 mL of thionyl chloride. The suspension was stirred for 24 h at 70°C. The residue was separated by filtration, washed with N,N-dimethylformamide (DMF), and dried under a vacuum at 80°C for 8 h to obtain MWCNTs-COCl.

Synthesis of S-CS-grafted MWCNTs-COOH

MWCNTs-COCl (50 mg) and S-CS (400 mg) were added in 30.0 mL of DMF. The mixture was stirred at 100°C for 48 h under a nitrogen atmosphere and filtered through a 0.22 µm microporous membrane. To remove the physically adsorbed compounds, the residue was washed with 0.2% acetic acid, ethanol, and DDW. The S-CS-MWCNTs adsorbent was obtained after drying overnight in an oven at 40°C. [27].

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 hallow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1).

S-CS-MWCNTs (40 mg) were packed into an SPE ENVI-18 DISK^{TM} disk. Solid phase extractions were carried out by glassy membrane disks, ENVI-18 DISK^{TM} 47 mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A° 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).

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	324.8 nm
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}

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Sample extraction

Extraction were performed with glassy membrane disks, ENVI-18 DISK[TM] 47 mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 A° pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47 mm 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, 5 mL of methanol was added to a 90 mL portion of each before analysis. The surface of the ENVI-18 DISK[TM] disks is modified with S-CS-MWCNTS and therefore could retain Cu^{2+} ions properly. Instead, 10 mg of S-CS-MWCNTS is mixed with appropriate volume of an organic solvent (5 mL) 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 10 mL 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 10 mL of methanol, immediately followed by 10 mL 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 (100 mL 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 minutes).

4) Analyte elution: In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1 M 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 was then determined by FAAS using an external calibration graph.

3. RESULTS AND DISCUSSION

Evaluation of the role of the S-CS-MWCNTs
Some preliminary experiments were performed the investigation of absence or presence of S-CS-MWCNTS 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 100 mL portions of aqueous Cu(II) samples containing 10μg of Cu(II) and 10 mg of S-CS-MWCNTS leads to satisfactory retention (Table 2). The latter case is most probably attributed to the existence of a considerable interaction between Cu(II) and the S-CS-MWC-NTS. It should be mentioned that formation of stable complexes between Cu(II) and S-CS-MWC-NTS 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.

Table 2: The effect of presence of S-CS-MWCNTS on extraction percent of Cu(II)[a].

S-CS-MWCNTS	pH	Extraction percent of Cu(II)
Absence	2-6	0.03(7.6)[b]
Presence	2-6	98.9(2.5) to 65(2.3)

[a] Initial samples contained 10 μg of Cu(II) in 100 mL of water.
[b] Values in parentheses are RSDS based on five individual replicate analyses.

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 5 mL 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 acceate-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
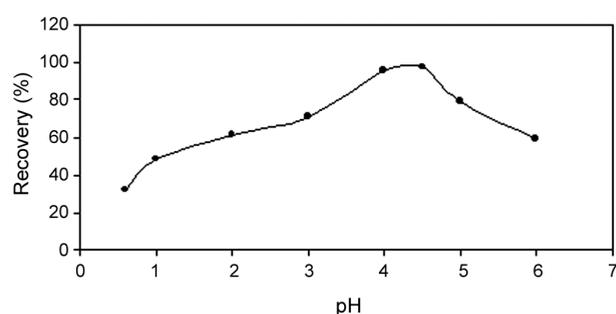

Figure 2: *Influence of sample pH on the percentage recovery of Cu (II).*

Cu(II). Then, percentage recovery at various pH values was determined (Figure 2). According to the results shown in Figure 2 up to pH 4.0-4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of S-CS-MWCNTS occurs and there is a weak tendency for retention between Cu(II) and S-CS-MWCNTS, whereas at higher values (pH>5), Cu(II) reacts with hydroxide ions to produce $Cu(OH)_2$. Therefore, sodium acceate-acetic acid

Table 3: *Effect of different eluting solvents on Percentage recovery of Cu (II) adsorbed on the disk* [a].

Stripping solution	Recovery (%)		
	2 mL	5 mL	10 mL
Methanol	82.3(2.6)[b]	92.5(2.6)	98.5(2.0)
Acidified methanol [c]	54.5(2.3)	83.2(2.2)	83.4(2.9)
Ammoniacal methanol [d]	53.4 (2.5)	87.5(2.6)	86.3(2.8)
Ethanol	82.5(1.7)	99.61.5)	99.8(2.3)
Acetonitril	36.6(4.8)	46.5(5.5)	69.0(2.9)
Formic acid (1M)10% V.V^{-1} mthanol	55.6(1.2)	68.3(2.0)	71.5(2.8)
Hydrochloric acid (1M)10% V.V^{-1} mthanol	52.7(1.9)	92.0(2.6)	91.2(2.0)
Hydrochloric acid (1M)10% V.V^{-1} mthanol	51.6(2.5)	65.3 (2.5)	97.3(1.6)
Nitric acid (2M)10% V.V^{-1} mthanol	52.8(1.9)	85.2(2.3)	85.4(2.0)
Nitric acid (1M)10% V.V^{-1} mthanol	64.0(2.5)	85.2(2.1)	87.9(1.6)
Ethanol	85.1(2.8)	95.8(2.0)	97.0(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 0.1 M HCl.
[d] Ammoniacal solvents obtained by addition of 0.1 M NH_3.

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buffer with pH=4.5 was used for the precon-centration step. Other solvents used for dissolving S-CS-MWCNTS were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Figure 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 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 S-CS-MWCNTS could be protonated and the stability of complex is reduced.

Effect amount of counter anion

In order to investigate the effect of counter ion on the recovery 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 S-CS-MWCNTS behaves in pH range 4.0-4.5 [28, 27] so that the copper ions are retained as ion pair complexes by the membrane disks. As it is 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 it is seen, the percent recovery

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^-	15.8
Br^-	20.9
ClO_4^-	35.0
SCN^-	47.8
Picrate	74.9
Acetate	98.0

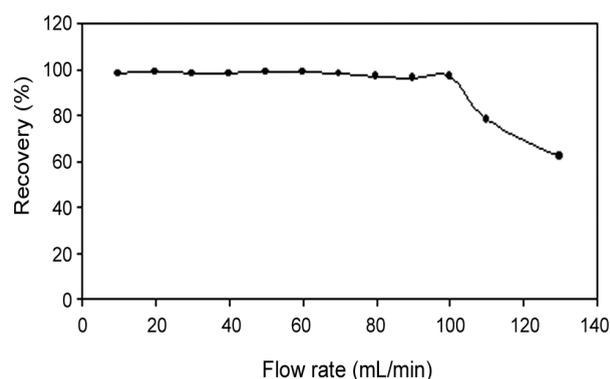[a] Initial samples contained 10 μg of Cu(II) in 100 mL of water.

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

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 ions-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 $mL.min^{-1}$, the retention of Cu(II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Figure 3). Thus, the flow-rate was maintained at 89 $mL.min^{-1}$ throughout the experiment.

Quantity of the S-CS-MWCNTS

The optimum amount of S-CS-MWCNTS 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 S-CS-MWCNTS. Hence, subsequent extractions were performed with 15 mg of S-CS-MWCNTS.

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Table 5: Influence of the S-CS-MWCNTS amount on the recovery of Cu(II) ions [a].

S-CS-MWCNTS amount (mg)	Recovery(%) of Cu(II)
2	32.20(2.5)[b]
5	45.40(2.0)
8	83.20(2.8)
10	95.7(2.8)
15	98.5(2.9)
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.

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 DISK[TM] 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 time a disk could be used to 10 replicates. These observations are represented in Figure 4.

Analytical Performance

When solutions of 10 μg 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 1000mL.

The capacity of modified disks (5 mg S-CS-MWCNTS) was determined by passing 50 mL portions of sample solutions containing 8 mg of
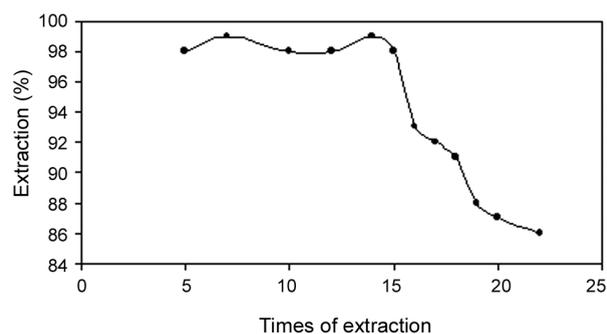
Figure 4: Influence of eluent (5 mL of methanol) type on disk efficiency.

copper and 0.1 M sodium acceate-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±3 μg 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 μg 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 100mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can be separate effectively from the Cu^{2+} ion. It is interesting to note that, in other experiments, we found that in the presence of high enough concentrations $NH_2OH.HCl$ as a suitable reducing agent (>0.5 M) [48].

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 it can be seen from Table 4 the added

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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	1.32(2.3)	98.0(2.2)
Mg^{2+}	24.5	0.70(2.2)	98.5(1.7)
Ca^{2+}	26.3	2.25(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(2.8)
Co^{2+}	2.15	6.40(2.3)	98.0(1.9)
Ni^{2+}	1.64	2.23(2.4)	98.5(2.4)
Zn^{2+}	2.76	4.97(2.1)	98.6(2.4)
Cd^{2+}	2.57	2.90(2.0)	98.2(2.8)
Pb^{2+}	1.54	2.70(1.9)	97.8(2.5)
Hg^{2+}	1.65	2.81(2.1)	97.7(2.8)
Ag^+	2.6i	3.45(2.9)	98.6(2.3)
UO^{2+}	2.86	2.80(2.1)	98.3(2.7)

[a] Initial samples contained 10 μg Cu^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).
[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table 7: *Recovery of copper added to 1000 mL of different water samples (containing 0.1Macetate 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(2.7)	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	22.70(2.5)	23.0

[a] Values in parentheses are %RSDs based on five individual replicate analysis
[b] Not detected.

copper ions can be quantitatively recovered from the water samples used. As it is seen, the recovered copper ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

4. CONCLUSIONS

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 (S-CS-MWCNTS) 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.

ACKNOWLEDGEMENT

REFERENCES

1. H.J.M. Bowen, 1979. Enviromental Chemistery of the Elements, Academic Press, New York.

2. Brand L.E., Sunda W.G, Guillard R.R.L., *J. Exp. Mar. Biol. Ecol.*, **96**(1986), 225.

3. Taylor H.H., Anstiss J.M., *Mar. Freshwat. Res.*, **50**(1999), 907.

4. Morel F.M.M., Hudson R.J.M., Price N.M., *Limnol. Oceanogr.*, **36**(1991), 1742.

5. Gordan A.S., *Mar.Chem,*. **38**(1992), 1.

6. Moffett J.W., Brand L.E., Croot P.L., Barbeau K.A., *Limnol. Oceanoger.,* **42**(1997), 789.

7. Croot P.L., Moffett J.W., *Brand L.E., Limnol. Oceanogr.,* **45**(2000), 619.

8. Wood M., Wang H.K., *Environ. Sci. Technol.,* **17**(1983), 582A.

9. N.N. Greemwood and A. Eamshow, 1984. Chemistery of Elements, Pergamon Press, New York.

10. C.A. Burtis and E.R. Ashwood, 1999. Tiets Textbook of Clinical Chemistery, third ed., Macmillan, New York.

11. B. Wetz, 1985. Atomic Absorption Spectroscopy, VCH, Amsterdam.

12. A.D. Eaton, L.S. Clesceri and A.E. Greenberg, 1995. Standard Methods for the examination of water and waste water, 19 th ed, American Public Health Association, Washington, DC.

13. F.J. Welcher and E. Boschmann, 1979. Organic Reagents for Copper, Krieger Huntington, New York.

14. Z. Marczenko, 1986. Separation and Spectrophotometric Determination of Elements, Ellis Horwood, London.

15. Bharagava O.P., *Talanta*, **16**(1969), 743.

16. Schilt A.A., Hoyle W.C., *Anal. Chem.,* **41**(1964), 344.

17. Borchart L.G., Butler J.P., *Anal. Chem.,* **29**(1957), 414.

18. Chaisuksant R., Ayuthaya W.P., Grudpan K., *Talanta*, **53**(2000), 579.

19. Kara D., Alkan M., *J. Microchem.,* **71**(2002), 29.

20. Saito K., Murakami S., Muromatsu A., Sekido E., *Anal .Chim. Acta*, **294**(1994), 329.

21. Ikeda K., Abe S., Anl. Chim. Acta*, 363(1998), 165.*

22. Igarashi S., Ide N., Takagai Y., *Anal. Chim. Acta*, **424**(2000), 263.

23. Liu J., Wang W., Li G., *Talanta*, **53**(2001), 1149.

24. Anthemidis A.N., Zachariadis G.A., Stratis J.A., *Talanta*, **54**(2001), 935.

25. Zenedelovska D., Pavlovska G., Cundeva K., Stafilov T., *Talanta*, **54**(2001), 139.

26. Endo M., Suziki K., Abe S., *Anal. Chim. Acta*, **364**(1998), 13.

27. Bingye D., Meirong C., Guozhen F., Bing L., Xv D., Mingfei P., Shuo W., *Journal of Hazardous Materials*, **103**(2012), 219- 220.

28. Wu Z.G., Feng W., Feng Y.Y., Liu Q., Xu X.H., Fujii A., Ozaki M., Preparation and characerization of chitosan-grafted multiwalled carbon nanotubes and their electrochemical properties, *Carbon*, **45**(2007), 1212-1218.

29. Akama Y., Ito M., Tanaka S., *Talanta*, **52**(2000), 645.

30. Ohta K., Tanahasi H., Suzuki T., Kaneco S., *Talanta*, **53**(2001), 715.

31. Cuculic V., Mlakar M., Branica M., *Anal. Chim. Acta*, **339**(1997), 181.

32. Moghimi A., Tehrani M.S., Waqif Husain S., *Material Science Research India 3*, (**1a**) (2006),

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 2 (2012), 105-114

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27.

33. Tehrani M.S., Moghimi A., Waqif Husain S., *Material Science Research India 3*, (**2**) (2005), 135.

34. E.M. Thurman and M.S. Mills, 1998. Solid-Phase Extraction, Principles and Practice, Wiley, New York.

35. J. Pawliszyn, 1997. Solid-Phase Microextraction, Theory and Practice, Wiley-VCH, New York.

36. Izatt R.M., Bradshaw J.S., Bruening R.L., *Pure Appl. Chem.*, **68**(1996), 1237.

37. Hagen D.F., Markell C.G., Schmitt G.A., *Anal.Chim. Acta*, **236**(1990), 157.

38. Krueger C.J., Fild J.A., *Anal. Chem.*, **67**(1995), 3363.

39. Taylor K.Z., Waddell D.S., Reiner E.J., *Anal. Chem.*, **67**(1995), 1186.

40. Yamini Y., Ashraf-Khorassani M., High Resolut J., *Chromatogr*, **17**(1994), 634.

41. Shamsipur M., Ghiasvand A.R., Yamini Y., *Anal. Chem.*, **71**(1999), 4892.

42. Shamsipur M., Ghiasvand A.R., Sharghi H., *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*, **22**(3) (2006), 527.

47. Nayebi P., Moghimi A., *Oriental Journal of Chemistry*, **22**(3) (2006), 507.

48. Moghimi A., *Chinese Journal of Chemistry*, **25**(2007), 640.

49. Moghimi A., *Chinese Journal of Chemistry*, **25**(10) (2007), 1536.

50. Moghimi A., Ghammamy S., *Environmental Chemistry an Indian Journal*, **2**(3) (2007), 51.

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.