

4-Amino-2,3-dimethyl-1-phenyl-3-pyrazoline 또는 4-(4-Methoxybenzylidenimin)thiophenole을 이용한 활성탄에서의 구리의 예비 농축 및 추출

Mehrorang Ghaedi*, Farshid Ahmadi, Hajir Karimi, and Shiva Gharaghani

Chemistry Department, University of Yasouj, Yasouj 75914-353, Iran

(2005. 4. 29 접수)

Preconcentration and Extraction of Copper on Activated Carbon Using 4-Amino-2, 3-dimethyl-1-phenyl-3-pyrazoline or 4-(4-methoxybenzylidenimin) thiophenole

Mehrorang Ghaedi*, Farshid Ahmadi, Hajir Karimi, and Shiva Gharaghani

Chemistry Department, University of Yasouj, Yasouj 75914-353, Iran

(Received April 29, 2005)

요 약. 불꽃 원자흡수분광법을 사용하여 실제 시료 중의 구리를 예비 농축하고 정량하는데 활성탄 변형법을 사용하였다. 구리 이온을 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline(ADMPP) 또는 4-(4-methoxybenzylidenimin)thiophenole (MBITP)과 착물을 형성시켜 활성탄에 정량적으로 흡착시키고, 고체상에 흡착된 구리를 소량의 질산을 사용하여 정량적으로 용리시켰다. 최대 회수율을 얻는데 있어서 중요한 pH, 운반체의 양, 흐름속도, 활성탄의 양, 용리제의 종류 및 농도와 같은 파라미터의 영향을 조사하였다. 최적 조건에서 ADMPP와 MBITP를 사용하는 이 방법은 $0.05\text{-}1.5\ \mu\text{g mL}^{-1}$ and $0.05\text{-}1.2\ \mu\text{g mL}^{-1}$ 의 구리 농도 범위에서 각각 상관계수 0.9997 및 0.9994의 선형성을 보이며 검출한계는 $1.4\ \text{ng mL}^{-1}$ 였다. 예비 농축의 농축인자는 310에 이르며 돌파부피는 두 리간드에서 모두 1550 mL였다. 이 방법은 방해 이온에 대한 공차한계와 선택성이 좋아서 수돗물, 샘물, 강물 및 폐수와 같은 실제 시료 중의 구리 함량을 정량하는 데 성공적으로 사용되었다.

주제어: 4-Amino-2,3-dimethyl-1-phenyl-3-pyrazoline(ADMPP), 4-(4-Methoxybenzylidenimin)thiophenole(MBITP), Cu(II) 이온, 고체상추출, 활성탄, 원자흡수분광법

ABSTRACT. Activated carbon modified methods were used for the preconcentration and determination of copper in some real samples using the flame atomic absorption spectrometry. The copper ions was adsorbed quantitatively on the activated carbon due to their complexation with 4- amino-2, 3-dimethyl-1-phenyl-3-pyrazoline (ADMPP) or 4-(4- methoxybenzylidenimin) thiophenole (MBITP). The adsorbed copper on solid phase was eluted quantitatively using small amount of nitric acid. The influence of important parameters including pH, amount of carrier, flow rate, amount of activated carbon and type and concentration of eluting agent for obtaining maximum recovery were investigated. The methods based on ADMPP and MBITP at optimum conditions is linear over concentration range of $0.05\text{-}1.5\ \text{ig mL}^{-1}$ and $0.05\text{-}1.2\ \text{ig mL}^{-1}$ of copper with correlation coefficient of 0.9997 and 0.9994 and both detection limit of $1.4\ \text{ng mL}^{-1}$, respectively. The preconcentration leads to enrichment factor of 310 and break through volume of 1550 mL for both ligands. The method has a good tolerance limit of interfering ion and a selectivity that has been successfully applied for the determination of copper content in real sample such as tap, spring, river and waste water.

Keywords: 4-Amino-2, 3-dimethyl-1-phenyl-3-pyrazoline (ADMPP), 4-(4-Methoxybenzylidenimin) thiophenole (MBITP), Cu (II) ions, Solid Phase Extraction, Activated Carbon, Atomic Absorption Spectrometry

INTRODUCTION

The importance of the determination of trace metal concentration in natural water samples is increasing in contamination monitoring studies. In many cases, the analysis of heavy metals in environmental samples presents a notable difficulty due to both the low levels of metals in the samples and the high complexity of the matrices (1). Copper is a gastrointestinal tract irritant but is generally not harmful to humans at low concentration, however, in concentration less than 1 ppm can be toxic to aquatic plants and some fishes (2). Thus, copper tends to be much more of an environmental hazard than a human hazard. The determination of trace amounts of copper has received considerable attention in many samples especially environmental pollution. Copper is an essential element at trace level, because it can catalysis heme synthesis (3), but intake and congenital inability to excrete extra copper is toxic and lead to Wilson's illness (4). Determination of metal ions at the ng mL^{-1} level generally requires prior separation and/or preconcentration steps in order to improve sensitivity. When preconcentration is carried out, separation of potential interferences, as well as minimization of the matrix effects can also be achieved, besides concentration of the analyte (5).

Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace metals with sufficient sensitivity for most of applications. With traditional method flame atomic absorption spectroscopy (FAAS) with high detection limit of Cu (II) ions, for the determination of traces of this ion in environmental and biological samples with complicated matrix, a preconcentration and extraction step prior to analysis is necessary to simultaneously separate and preconcentrate the Cu (II) ions from matrix elements (6).

The most widely used techniques for the separation and preconcentration of trace amount of copper are transport (7, 8), solvent extraction (9, 10),

co-extraction (11), liquid membrane (12) and solid phase extraction (13-22).

A proper choice of extraction method may lead to an increase in concentration by several orders of magnitude. However, this evaluation can only be accomplished with considering advantages such as, high efficiency, simple on-line operation, rapidity, low sample reagent consumption, relatively simple and compact hardware and freedom from contamination and using organic solvent that are associated with solid phase extraction that enable us to even by a simple, low sensitive AAS content of heavy metals can be evaluated. Therefore, solid phase extraction (SPE) technique has found increasing applications in the enrichment of trace metal ions and elimination of matrix interference prior to AAS analysis.

Solid phase extraction procedures based on sorption of metal complexes on various support, such as silica gel, alumina and activated carbon in the two past century have been widely used for this purpose, among which activated carbon has been widely applied. The reasons for widespread application of the activated carbon as a trace collector for metal ion preconcentration (23-34) are strong interaction and quantitative adsorption of molecules with π electrons on activated carbon (35). Because the activated carbon is a type of hydrophobic adsorbent which adsorbs non-polar or little polar substances in aqueous solutions, metal ions to be preconcentrated need to be transformed corresponding metal chelates (36-38), metal elements (39) or metal hydroxides (40-42). Metal chelates could provide higher selectivity and high enrichment factor for such a separation and preconcentration techniques. The purpose of this work is preconcentration and determination of copper (II) ion content based on activated carbon modified with ADMPP or MBITP.

EXPERIMENTAL

Chemicals. Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, cal-

cium, strontium, barium, silver, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. Activated carbon (gas chromatographic grade, 40-60 mesh from Merck), were soaked in hydrochloric acid for 2 days, it was then washed with water and dried at 110 °C for 1 day. The ligand, 4- amino-2, 3-dimethyl-1-phenyl-3-pyrazoline (ADMPP), was purchased from Merck Company and used as received.

Synthesis of 4-(4-methoxybenzylidenimin) thiophenole. To 0.2 mmol (0.2501 mg) of MBITP in 10 ml methanol, 0.2 mmol (0.2724 mg) of 4-methoxybenzaldehyde was added and reaction mixture was stirred at room temperature. The progress of reaction was monitored by TLC. After 4 hr, the yellowish precipitate (product) was appeared, which was filtered and the precipitate was washed carefully by methanol (twice) and dried under vacuum, that 0.340 mg of product with yield of ~70% was obtained. The compound was identified by IR, ¹HNMR. The MBITP information is as follow:

IR(cm⁻¹, in KBr): 2996(w), 2962(w), 2928(w), 2831(w), 2563(w), 1617(vs), 1600(vs), 1577(vs), 1514(s), 1486(s), 1457(s), 1400(m), 1309(s), 1246(vs), 1195(s), 1161(vs), 1104(m), 1035(s), 967(m), 933(w), 881(m), 842(vs), 819(vs), 807(vs), 867(m), 728(m), 539(m), 568(m).

¹HNMR (CDCl₃): (8.37 ppm, s, 1H), (7.52 ppm, d, 2H), (7-7.2 ppm, dd, 4H), (6.79 ppm, d, 2H), (3.71 ppm, s, 3H), (2.9 ppm, s, 1H).

Pretreatment of natural water samples. Waste water samples were collected from four different stations in the Ghachsaran Iran, spring water Cheshme Mishi, Sisakht, Iran, Cheshmeh Gol, Yasouj, Iran and Beshar River Yasouj Iran.

Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 mm. The organic content of the water samples were oxidized in the presence of 1% H₂O₂ and addition of concentrated nitric acid. The samples were filtered through a filter paper. After acidification to 1% with concentrated nitric acid, they

were stored in polyethylene bottles. For the preconcentration procedure, 800 ml of water samples were heated until their volume take 250 mL. After adjustment of desired pH by addition of appropriate amount of dilute sodium hydroxide or nitric acid to phosphate buffer, SPE experiment has been carried out. The retained Cu (II) ions on modified activated carbon were eluted with 5 mL of 6 mol L⁻¹ HNO₃. The effluent was sent to FAAS for evaluation of Cu (II) ions content.

Apparatus. The metal ion content determination were carried out on a Perkin-Elmer 603 atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector with a hallow cathode lamp at wavelengths of 324.8 nm (copper resonance line) and the air-acetylene flame were adjusted according to standard recommendations. The AAS determinations of all other cations were performed under the recommended conditions for each metal. A Metrohm 691 pH/Ion meter has been used for pH adjustment. A UV-Vis 160 spectrophotometer (Shimadzu) has been applied for evaluating the amount of ligand loaded on activated carbon. Extractions were performed with solid phase suspended in tube that a piece of glass wool put in the end to inhibit loss of solid phase and sample were passed throughout to preconcentrate and separate the Cu (II) ions.

Preparation of the solid phase. Ligand loaded activated carbon was prepared by dissolving a weighed amount of 4- amino-2, 3-dimethyl-1-phenyl-3-pyrazoline (ADMPP) or 4-(4- methoxybenzylidenimin) thiophenole (MBITP) in 0.005 mol L⁻¹ NaOH to the required amount of activated carbon. After 18 hr, the solutions were filtered through the filter paper and activated carbons were washed with distilled water until the filter out was no longer alkaline. Finally, the mixtures were dried at 70 °C overnight. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 35 mg 4- amino-2, 3-dimethyl-1-phenyl-3-pyrazoline (ADMPP) or 50 mg 4-(4- methoxybenzylidenimin) thiophenole (MBITP) per 500 mg of AC.

Measurement of the amount of ligand loaded on the AC. 0.5 g AC was placed in a 10 mL vial and 5 mL of 5 mmol L⁻¹ NaOH containing weighed amount of ligands were added and shaken. After 18 hr while shaking, a portion of the supernatant liquids was diluted to the appropriate volume and the absorbance of the solutions was measured using UV-Vis Shimadzu at maximum wavelengths. Results show that both ligands at these quantities quantitatively adsorbed on activated carbon.

Preconcentration. The pH of standard water solutions containing 0.03-2.0 µg mL⁻¹ of copper was adjusted to the desired pH value by addition of appropriate amount of dilute sodium hydroxide or nitric acid to phosphate buffer or acetate buffer. The sample was passed through the ligand loaded activated carbon column with flow rate lower than 6 mL min⁻¹. The concentration of copper was determined in the final solutions by flame AAS.

Loading capacity. To investigate the loading capacity, 100 mL of 5.0 µg mL⁻¹ of copper solution at pH 5.0 were passed through the solid phase columns containing 35 mg 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline (ADMPP) or 50 mg 4-(4-methoxybenzylideneimin) thiophenole (MBITP) per 500 mg of AC. After loading and elution by nitric acid as stripping agent, effluent was sent into the FAAS to measure the metal ions content and sample solution was evaluated by AAS for un-retained copper content.

RESULTS AND DISCUSSION

The influence of effective analytical parameters such as pH, amount of ADMPP or MBITP, flow rate, amount of activated carbon and type and concentration of eluting agent using the univariate method on Cu (II) ions recovery must be studied. The optimum values or range of parameters with using this value for a solution of 250 mL 0.3 µg mL⁻¹ Cu (II) ions were studied.

Effect of activated carbon amounts on extraction recovery

Support has a significant role in an extraction

process. It must not only adsorb ligand completely but also not competes with ligand for adsorbing metal ions and therefore has reversible elution step. Therefore, the effect of amount of activated carbon required for complete sorption and reversible desorption of 75 µg copper ions were studied and results are given in Table 1. As can be seen, the sorption were quantitative with increasing amount of activated carbon until 500 mg and further addition lead to decrease in the extraction efficiency and probability due to irreversible adsorption of metal ion on activated carbon. So 500 mg of activated carbon were used for further studies. At lower amount of activated carbon, complexation is responsible for adsorption and at higher content of activated carbon the Cu (II) ions adsorbed on activated carbon.

Effect of pH on recovery

The sorbents contain phenolic groups or aminopyrazoline group, which are weakly acid, so that they are not available to form chelate complexes at low pH. The dependence of the extractability of Cu (II) ion on the pH was studied by adsorption/desorption evaluation of copper content in 250 mL solution of 0.3 µg mL⁻¹ at pH value ranging from 2.0-9.0 using solid phase comprises of appropriate amount of ligands on 500 mg activated carbon. The results, which are presented in Fig. 1, show that in the pH range of 3.1-6.5 and 3.2-6.8 for ADMPP and MBITP, respectively, the extraction recovery is independent of pH. The observed decrease in analytical signal at higher pHs was probably caused by competition with copper hydrolysis products, which

Table 1. Effect of activated carbon amount on copper (II) ion recovery

AC (mg)	Recovery %	
	ADMPP	MBITP
100	68.3	63.9
200	83.9	88.8
300	94.4	95.2
400	97.6	99.3
500	99.8	99.8
600	93.8	99.7
700	87.3	95.8

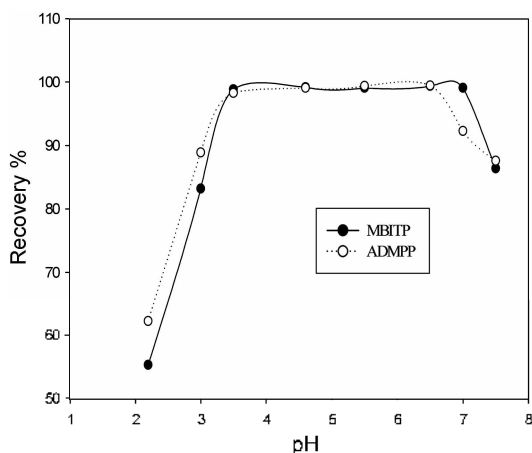


Fig. 1. Effect of pH on recovery of Cu (II) ion pre-concentration. Conditions: 250 ml of $0.3 \mu\text{g mL}^{-1}$ Cu (II) ion at flow rate of 6 mL min^{-1} at various pH; solid phase 0.5 g AC, and 35 mg ADMPP or 50 mg MBITP; eluent, $5 \text{ mL } 6 \text{ mol L}^{-1} \text{ HNO}_3$.

reduce the adsorption efficiency of copper on solid phase. At lower pH, hydrogen ions compete with Cu (II) ions to N and S sites in ligand while the efficiency of extraction has been reduced due to the hydroxide precipitation in basic media. All further experiments were carried out in buffer solutions at pH 5.5.

Effect of sorbents amount on Cu (II) ion recovery

To investigate the role of sorbents amount on the extractability of Cu (II) ion, the proposed procedures was applied to 250 mL of $0.3 \mu\text{g mL}^{-1}$ Cu (II) ion, changing only the ligands mass loaded on constant amount of activated carbon (500 mg). The results are described in Fig. 2. It was found that the extraction efficiency increased with the chelating mass for both ligands, reaching a maximum and constant value over 35 and 50 mg for ADMPP and MBITP.

Flow rate has a great effect on the extraction efficiency. Therefore, different flow rate was examined and results are presented in Table 2. The results display that up to 6 mL min^{-1} efficiency of extraction increase and further addition gradually decreased the extraction efficiency. So 6 mL min^{-1} was used for further studies.

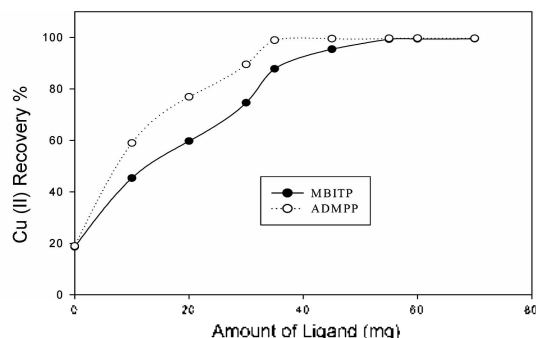


Fig. 2. Effect of ADMPP or MBITP concentration on Cu (II) ion pre-concentration. Conditions: 250 ml of $0.3 \mu\text{g mL}^{-1}$ Cu (II) ion at flow rate of 6 mL min^{-1} at pH 5.5; solid phase, 0.5 g AC, different amount of ADMPP or MBITP; eluent, $5 \text{ mL } 6 \text{ mol L}^{-1} \text{ HNO}_3$.

Table 2. Effect of flow rate on copper (II) ion recovery

Flow rate (mL min^{-1})	Recovery %	
	ADMPP	MBITP
2	99.6	99.8
4	99.6	99.7
6	99.5	99.6
8	98.8	98.4

Effect of type and concentration of eluting agent on recovery

In order to choose the most effective eluent for the quantitative stripping of the retained Cu (II) ions by the modified columns, after the extraction of copper content in 250 ml $0.3 \mu\text{g mL}^{-1}$, the Cu (II) ions were stripped with different acids or histidine with various concentrations as eluting agents. As it is immediately obvious from Table 3, every acid

Table 3. Effect of type and concentration of eluent on recovery

Eluent (mol L^{-1})	Recovery %	
	ADMPP	MBITP
6.0 HCl	38.6	35.9
6.0 HNO ₃	99.6	99.7
6.0 H ₂ SO ₄	96.8	97.4
0.2 Histidine	70.1	67.3
3 HNO ₃	58.7	55.8
4 HNO ₃	87.1	89.3
5 HNO ₃	92.6	94.9
7 HNO ₃	99.6	99.6

a)The number is in mol L^{-1}

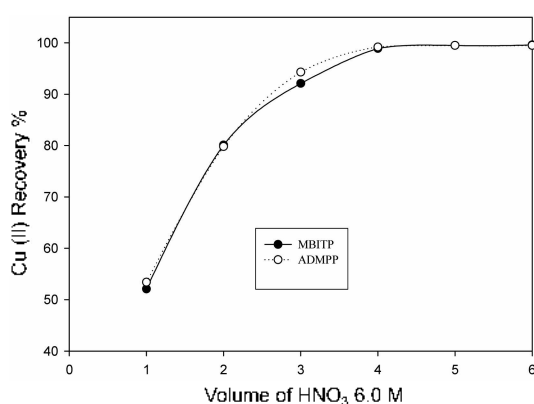


Fig. 3. Effect of HNO₃ volume on Cu (II) ion preconcentration, Conditions: 250 ml of 0.3 μg mL⁻¹ Cu (II) ion at flow rate of 6 ml min⁻¹ at pH 5.5; solid phase, 0.5 g AC, and 35 mg ADMPP or 50 mg MBITP; eluent, various volume of 6 mol L⁻¹ HNO₃.

except nitric acid with concentration lower than 6.0 mol L⁻¹ has low efficiency for copper desorption, <60%, but, when nitric acid 6.0 mol L⁻¹ has been used, high recovery for Cu (II) ions will be obtained. Therefore, 6.0 mol L⁻¹ HNO₃ were selected for subsequent experiments.

In preliminary test, it was found that 6 mol L⁻¹ of nitric acid was an effective eluent for the quantitative stripping of the retained Cu (II) ions. Various volume of 6.0 mol L⁻¹ nitric acid were used to elute the adsorbed Cu (II) ions and the results are summarized in Fig. 3. Because the application of a smaller volume of eluent contributes to obtaining a higher preconcentration factor and a lower blank value in the subsequent FAAS measurements, 5 mL of 6 mol L⁻¹ of nitric acid were adopted as the eluent throughout the experiments.

Examination of reproducibility

In order to investigate reproducibility of method at optimum condition six experiments for each sorbents were carried out and results are shown in Table 4. Results indicate the high repeatability of proposed method for Cu (II) ions recovery. As can be seen, the recovery of Cu (II) ions for SPE method based on ADMPP and MBITP are 99.0±0.6 and 98.8±0.5, respectively. The results of repeatability

Table 4. Investigation of reproducibility

No	Recovery %	
	ADMPP	MBITP
1	98.9	98.7
2	98.5	99.1
3	99.7	99.5
4	99.1	99.0
5	98.4	98.6
6	99.6	98.0
Mean	99.0	98.8
RSD	0.6	0.5

(six measurements) as RDS for 0.3 μg mL⁻¹ Cu (II) ions are 0.5% and 0.6% respectively.

Interferences

Analytical preconcentration/separation procedures for Cu (II) ions in the presence of common interfering ions were examined. The recovery percent can be strongly affected by the matrix constituents of the sample. This is known as matrix effect. Before the application of the preconcentration method for the determination of Cu (II) ion in real samples, the influences of some alkaline and alkaline earth ions and transition metal ions on the recovery of the Cu (II) ion were also investigated. The results are given in Table 5. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5% related to the preconcentration and determination of Cu (II) ions. Cu (II) ions were quantitatively recovered at large amounts for alkaline and earth alkaline ions and other transition metal ions. In the

Table 5. Investigation of tolerance limit of interfering ion

Interfering ion	[Interfering ion]/[Cu (II)]	
	MBITP	ADMPP
Ag (I)	550	1000
Hg (II)	500	1000
Cd (II)	1000	1000
Ni (II), Co (II)	1000	1000
Zn (II)	1000	1000
Fe (II), Fe (III)	1000	1000
K ⁺	1000	1000
Ba (II)	1000	1000
Mg (II)	1000	1000
Pb (II)	1000	1000

case of MBITP as ligand interference of Hg^{2+} and Ag^+ ions agree well with the view that soft coordination sites of sulfur offer great affinity toward Ag and especially Hg^{2+} as soft transition metal ions (43).

Calibration graphs and precisions

The calibration curve was obtained by using 250 mL $0.03-2.0 \mu g mL^{-1}$ Cu (II) ion solutions at optimum values of effective variable of both methods. The eluting solution was sent to AAS for evaluating Cu (II) ion content. The calibration curves were linear for copper in the range of 0.05-1.5 and 0.05-1.2 $\mu g mL^{-1}$ based on ADMPP and MBITP, respectively. Relative standard deviations of measurements (six measurements) were found to be 0.6% and 0.5% for $0.3 \mu g mL^{-1}$ of Cu (II) ions at MBITP and ADMPP, respectively. Detection limits for the copper (II) ion for both ligand is $1.4 ng mL^{-1}$.

Accuracy and applications

To ensure that the methods are valid and have reasonable accuracy and precision, recovery of the Cu (II) ions in tap, spring, river and wastewater samples were determined and results are shown in Table 6. Results confirmed with reference standard addition method express that reproducible and quantitative recovery for copper (II) can be obtained.

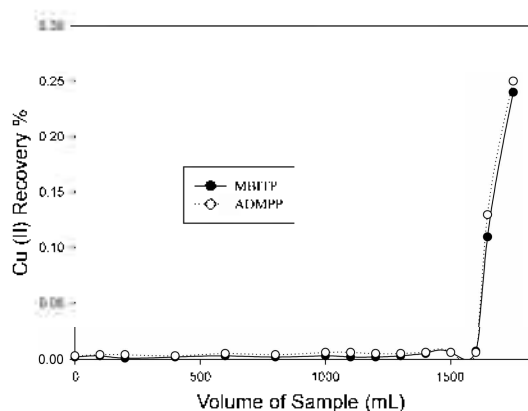


Fig. 4. Investigation of Loading Capacity, Conditions: different volume of $0.3 \mu g mL^{-1}$ Cu (II) ion at flow rate of $6 mL min^{-1}$ in pH 5.5: 0.5 g AC, and 35 mg ADMPP or 50 mg MBITP; eluent, 5 ml of $6 mol L^{-1} HNO_3$.

Investigation of break through volume, enrichment factor and loading capacity

For investigation of enrichment factor and break through volume, various volumes (mL) of $0.3 \mu g mL^{-1}$ of copper (II) ion were passed through column and then the effluents were sent to AAS for evaluating copper (II) ion content. The results are shown in Fig. 4 display that adsorbed copper (II) ion on activated carbon modified using ADMPP and MBITP can be eluted by 5 mL of $6.0 mol L^{-1}$ nitric acid lead to enrichment factors of 310. Similar experiment

Table 6. Recovery of trace copper from different spiked water samples after preconcentration on activated carbon modified with MBITP or ADMPP

Element ^a	MBITP				ADMPP			
	Added	Founded	RSD %	Recovery %	Added	Founded	RSD %	Recovery %
Tap Water	0	B. L. ^b	---	---	0	B. L. ^b	---	---
	50	53.4	1.3	107	50	52.4	1.4	104.8
	200	204.6	0.9	102.3	200	203.1	1.4	101.6
River Water	0	63.9	1.3	---	0	61.4	2.6	---
	50	115.1	0.9	102.4	50	110.7	2.0	98.6
Waste Water	0	87.9	1.8	---	0	85.6	2.4	---
	50	139.0	1.1	102.2	50	136.4	1.8	101.6
Cheshmeh Mishi	0	B. L. ^b	1.7	---	0	B. L. ^b	1.3	---
	50	52.3	1.0	104.6	50	54.2	0.9	108.4
	100	103.4	0.8	103.4	100	103.3	0.7	103.3
Cheshmeh Gol	0	B. L. ^b	1.5	---	0	B. L. ^b	1.2	---
	50	53.4	0.9	106.8	50	52.7	1.0	105.4
	100	102.8	0.7	102.8	100	103.5	0.8	103.5

a) All values are for 3 measurements vs. $\mu g L^{-1}$ b) Below Linear Range

for investigation of loading capacity was carried out. The result of Fig. 4 shows that until 1550 mL Cu (II) ions (0.93 mg g^{-1}) adsorbed quantitatively on activated carbon. The high capacity of modified columns permitted large sample volumes to be pre-concentrated without degradation of the analytical performance.

CONCLUSIONS

It was shown that modified AC methods with unique advantages such as no need to organic harmful solvent, low consumption of material, easy and simple operation, low cost, high precision, accuracy, sensitivity and selectivity in addition to its high tolerance limit of common interfering is a powerful alternative for successful determination of Cu (II) ion content especially water samples with complicated matrix and low concentration.

The method has high efficiency (<98%), low limit of detection, and high pre-concentration factor (310) with relatively wide applicable pH range without hydroxide formation and high stability of prepared sorbents with acid that suitable to elute the retained ion with small amount $6 \text{ mol L}^{-1} \text{ HNO}_3$.

Acknowledgements. The authors gratefully acknowledge the support of this work by the University of Yasouj Research Council.

REFERENCES

- Davydova, S. L. *Crit. Rev. Anal. Chem.* **1999**, *28*, 377.
- Choi, Y. S.; Choi, H. S. *Bull. Korean Chem. Soc.* **2003**, *24*, 222.
- Reddy, B. K.; Kumar, J. R.; Reddy, K. J.; Sarma, L. S.; Reddy, A. V. *Anal. Sci.* **2003**, *19*, 423.
- Metal ions in biological system vol 13 copper proteins*, Marcel Dekker New York 1981 pp 349 or N.N. Greenwood and A. Ernschaw, *Chemistry of Element*, Pergamon, New York, 1984, 339.
- Fang, Z. *Flow Injection Separation and Preconcentration*: VHC Weinheim, 1993.
- Narin, I.; Soylak, M.; Latif, E.; Mehmet, D. *Talanta* **2000**, *52*, 1041.
- Cleij, M. C.; Scrimin, P.; Tecilla, P.; Tonellato, U. J. *Org. Chem.* **1997**, *62*, 5592.
- Safavi, A.; Rastegarzadeh, S. *Talanta* **1995**, *42*, 2039.
- Kara, D.; Alkan, M. *Microchem. J.* **2002**, *71*, 29.
- Sandhibigraha, S. A.; Bhaskara Sarma, P. V. R. *Hydro-metallurgy* **1997**, *45*, 211.
- Mendiguchi, C.; Moreno, C.; Vargas, M. G. *Anal. Chim. Acta* **2002**, *460*, 35.
- Shamsipur, M.; Avanes, A.; Sharghi, H.; Aghapour, G. *Talanta* **2001**, *54*, 863.
- Shamsipur, M.; Ghiasvand, A. R.; Sharghi, H.; Naeimi, H. *Anal. Chim. Acta*, **2000**, *408*, 271.
- Anthemidis, A. N.; Zachariadis, G. A.; Stratis, J. A. *Talanta* **2001**, *54*, 935.
- Kim, J. S.; Yi, J. *J. Chem. Technol. Biotechnol.* **2000**, *75*, 359.
- Taher, M. A.; Mobarakeh, S. Z. M.; Mohadesi, A. R. *Turk. J. Chem.* **2005**, *29*, 17.
- Yamini, Y.; Tamaddon, A. *Talanta* **1999**, *49*, 119.
- Say, R.; Birlik, E.; Ersöz, A.; Yılmaz, F.; Gedikbey, T.; Denizli, A. *Anal. Chim. Acta* **2003**, *480*, 251.
- Hostenl, E.; Welz, B. *Anal. Chim. Acta* **1999**, *392*, 55.
- Park, C.; Kim, H. S.; Cha, K.W. *Bull. Korean Chem. Soc.* **1999**, *20*, 352.
- Hosing, Y.; Liu, Z. S.; Huang, S. D. *Spectrochim. Acta. Part B.* **1997**, *52B(6)*, 755.
- Cesur, H.; Bati, B. *Anal. Lett.* **2000**, *33(3)*, 489-501.
- Soylak, M.; Narin, I.; Dogan, M. *Anal. Lett.* **1997**, *30*, 2801.
- Sakai, Y.; Tomura, T.; Ohshita, K.; Koshimizu, S. *J. Radioanal. Nucl. Chem.* **1998**, *230*, 261.
- Ensafi, A. A.; Khayamian, T.; Karbasi, M. H. *Anal. Sci.* **2003**, *19*, 953.
- Chakrapani, G.; Murty, D. S. R.; Mohanta, P. L.; Rangaswamy, R. *J. Geochem. Explor.* **1998**, *63*, 145.
- Bagheri, H.; Saraji, M.; Naderi, M. *Analyst.* **2000**, *125(9)*, 1649.
- Yaman, M. *Chem. Anal. (Warsaw)* **1997**, *42(1)*, 79.
- Xingguang, S.; Meijia, W.; Yihua, Z.; Jiahua, Z.; Hanqi, Z.; Qinhan, J. *Talanta* **2003**, *59*, 989.
- Uzawa, A.; Narukawa, T.; Okutani, T. *Anal. Sci.* **1998**, *14*, 395.
- Soylak, M.; Doan, M. *Anal. Lett.* **1996**, *29(4)*, 635.
- Aydemir, T.; Guecer, S. *Chem. Anal. (Warsaw)*, **1996**, *41*, 829.
- Yaman, M. *J. Anal. At. Spectrom.* **1999**, *14*, 275.
- Cesur, H.; Macit, M.; Bati, B. *Anal. Lett.* **2000**, *33*, 1991.
- Zhang, H.; Yuan, X.; Zhao, X.; Jin, Q. *Talanta* **1997**, *44*, 1615.
- Hutchinson, D. J.; Schilt, A.A. *Anal. Chim. Acta* **1983**, *154*, 159.
- Santelli, R. E.; Gallego, M.; Valcarcel, M. *Talanta* **1994**,

41. 817.
38. Gallego, M.; Valcarcel, M.; de Pena, Y. P. *J. Anal. At. Spectrom.* **1994**, *9*, 691.
39. Hall, E. M.; Pelchat, J. C.; *J. Anal. At. Spectrom.* **1993**, *8*, 1059.
40. Koshima, H.; Onishi, H. *Talanta* **1980**, *27*, 795.
41. Koshima, H.; Onishi, H. *Talanta* **1986**, *33*, 391.
42. Kimura, M.; Egana, S. *Talanta* **1982**, *29*, 329.
43. Casabó, J.; Flor, T.; Romero, M. I.; Teixidor, F.; Pérez-Jiménez, C. *Anal. Chim. Acta* **1994**, *294*, 207.
-