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Preconcentration of Copper with Solid Phase Extraction and its Determination by Flame Atomic Absorption Spectrometry

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Abstract: A new method for the solid phase extraction (SPE) and determination of copper ions at low levels is presented. Extraction percent and the effects of some factors were evaluated. The detection limit was in the range of $2.26 \mu\text{g} \cdot \text{L}^{-1}$. This procedure has been successfully applied to determination of copper in water samples.

Keywords: Copper ions, Solid phase extraction, Modified carbon

Introduction

Determination of copper is usually carried out by atomic absorption spectrometry^{1,2} as well as spectrophotometric methods^{3,4}. Preconcentration step prior to determination of copper ions is usually necessary, because of low levels of copper in environmental samples. Liquid-liquid extraction of copper has been used elsewhere^{5,6}. Nevertheless, several techniques for the preconcentration or determination of copper have been proposed including spectrophotometry⁷, SPE using C18 cartridge⁸, modified microcrystalline naphthalene⁹, modified silica gel¹⁰ and 4-phenylenediamine propyl silica xerogel¹¹ as sorbents, FIA with spectrophotometric determination¹², and differential pulse adsorption stripping voltammetry¹³. Disadvantages of these methods are: using toxic solvents^{8,9}, small preconcentration factor¹⁰, and existing of interfering ions^{7,10,12,13}.

SPE has received much attention in recent years. This technique reduces consumption of and exposure to solvent, disposal costs, and extraction time^{14,15}. Recently, modified activated carbon (AC) have been used as SPE sorbent^{16,17,18}.

Many methods based on different SPE sorbents have been applied to the preconcentration of copper. Okutani *et al.*¹⁹ applied chitosan as adsorbent. There was interference effect on the determination of copper. In other research by Okutani *et al.*²⁰ AC was used as a sorbent. There were interfering ions with the determination of copper. Knezevic *et al.*²¹ used chelating ion exchanger. In this study the recovery wasn't complete. Granados *et al.*²² applied adsorbent of Lewatit. There were interfering ions in this procedure. Cellulose nitrate was used by Soyak *et al.*²³ In this research sorbent acted as a filter. Tokman *et al.*²⁴ applied modified silica gel. Cesur¹⁸ used modified AC. This study was laborious and toxic compounds were applied.

The ligands derived from salicylaldehyde can form very stable chelates with transition metal ions^{25,26}. There are a few papers on the use of these substances in preparing solid phases²⁷⁻³¹. Application of AC as adsorbent and use of a new Schiff base is another way for preconcentration of copper ions. In this paper, application of modified AC with 5 - ((4 - heptyloxyphenyl) azo) -N - (4-butyloxyphenyl)-salicylaldimine (HPBS) (Figure 1) as a new sorbent for preconcentration of Cu(II) ions are explained.

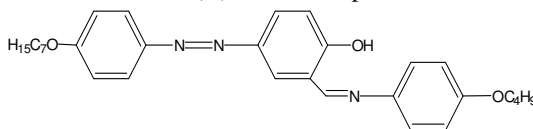


Figure 1. Structure of HPBS.

Experimental

Reagents

All reagents and substances were of the highest purity available from Fluka. AC was purchased from Merck. HPBS was synthesized as described elsewhere³².

The stock standard solution of Cu(II) was prepared by dissolving 3.9292 g of the $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ in water and diluted to one liter. A HPBS solution (0.6% w/v) was prepared by dissolving 0.3 g of HPBS in 50 mL chloroform.

Instrumentation

The determination of Cu(II) was performed on a Perkin Elmer Analyst 300 atomic absorption spectrometer. Spectrophotometric measurements were carried out with a Camspec M350 spectrophotometer. A Metrohm model 691 digital pH meter was used for the pH measurements.

Preparation of the modified AC

The AC was first pounded in a porcelain mortar and sieved with 40-mesh sieve, then was stirred with concentrated HCl for 1h, and was allowed to stand for 2h. After filtration, the AC was washed with water, and then dried at 120°C for 1h. Then, 20 g of purified AC was put into a 1000 mL stoppered bottle and 50 mL of 0.6% w/v HPBS solution was added to bottle and stirred for 1h by mechanical shaker. After filtration, the modified AC was dried at 60°C for 1h. Then 0.1 g of the sorbent was packed into a polypropylene column (10 mm i.d., and 50 mm height).

Procedure

The preconcentration of Cu(II) ions on the modified AC was as follows: A 50-250 mL of the sample solution containing 100 μg Cu(II), buffered at pH=6, was passed through the column at a flow rate of 0.5 mL \cdot min⁻¹ by suction. After the sorption, the column was washed with 10 mL of water, and the extracted copper was then eluted from the adsorbent using 10 mL of 4 M of HNO_3 containing 20% w/v of acetone. The copper concentration was determined by FAAS.

The water samples were first passed through a filter, then enough buffer was added to achieve the pH=6. The copper ions were extracted from the thus treated aliquot and quantified as described above.

Results and Discussion

HPBS is a Schiff base. The results of IR spectrum have showed that the OH group of HPBS has deprotonated and coordinated to the copper ions, and C=N group of ligand coordinated to the copper ions via N atom. Also, elemental analysis results showed that the ligand coordinated to Cu(II) in 2:1 ratio³². It is suggested square planar form for this kind of compounds³³. Also, HPBS could be adsorbed onto AC, due to producing a strong π - π interaction¹⁷.

Capacity of AC for HPBS

Into a series of stoppered bottles, 5 to 33 mL of a 0.03% w/v solution of HPBS was transferred and each one mixed with 0.1 g of AC. After 1h, the mixtures were filtered and the absorbances of the filtrates were measured spectrophotometrically. From the results (Figure 2), for further experiments AC loaded with 1.5% w/v of HPBS.

Influence of pH

The effect of the pH of sample containing $2 \mu\text{g}\cdot\text{mL}^{-1}$ was studied in the pH range of 1-12. The results showed that Maximum retention of Cu(II) by sorbent were at pH 6. In an acidic solution the protonation of HPBS occurs and there is a weak tendency for reaction between Cu(II) and HPBS, but at higher pHs (pH>6) Cu(OH)₂ is formed. Thus, buffer with pH 6 was used for the sorption step (Figure 3).

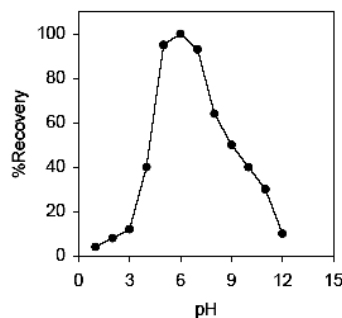
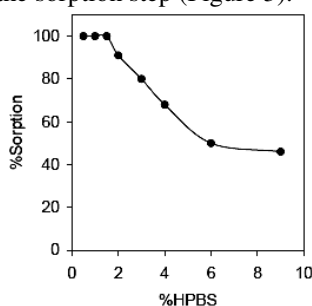


Figure 2. Capacity of AC for the adsorption of HPBS. **Figure 3.** Effect of pH on the recovery.

Effect of different eluents

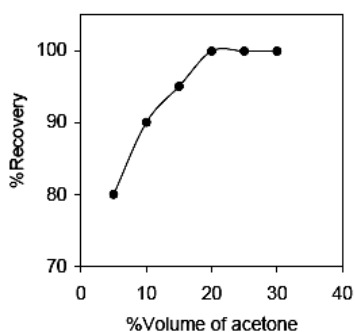
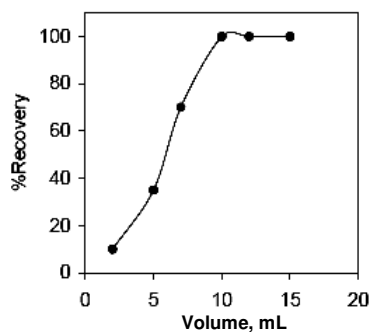
After the adsorption step, the copper ions were eluted with different eluents. From the data given in Table 1 and Figures of 4 and 5, it is obvious that the best eluent is 10 mL of 4 M HNO₃ containing 20% v/v acetone.

Analytical performance

When solutions of 50 μg copper in 50, 100, 200, and 250 mL solutions were passed through the sorbent under optimum conditions, the Cu(II) was quantitatively retained in all cases. Therefore, the breakthrough volume for the method must be greater than 250 mL, providing a concentration factor of 25. This preconcentration factor was superior to the reported papers^{21,24}. The detection limit³⁵⁻³⁷ of (DL) of the method is $2.26 \mu\text{g}\cdot\text{L}^{-1}$. The presented method has been achieved better DL relative to elsewhere^{28,22}. The CV of the method was 1.4%. The repeatability of the method surpassed those in the previous reports^{10,19-23,34}.

Table 1. %Recovery of Cu(II) from the sorbent using 10 mL of different eluents.

Eluent Concentration, M	%Recovery			
	1.0	2.0	3.0	4.0
NaOH	7	9	9	13
NH ₃	13	15	15	17
HCl	14	17	18	18
H ₂ SO ₄	19	19	19	19
HClO ₄	20	22	23	25
HNO ₃	40	50	58	77
HNO ₃ +Acetone ^a	60	82	94	100

^a 20% v/v acetone in HNO₃.**Figure 4.** Effect of %volume of acetone in the eluent**Figure 5.** Effect of volume of eluent*Effect of foreign ions*

The effect of other ions was studied by adding a given amount of the desired ion to 50 mL aliquot of solution containing 50 µg Cu(II). The results (Table 2) show that the Cu(II) ions in binary mixtures are retained completely by the adsorbent.

Table 2. Effect of foreign ions^a.

	Amount taken, mg	%Recovery of Cu(II)
Na(I)	12.0	100
K(I)	12.0	100
Ca(II)	12.0	100
Mg(II)	12.0	100
Fe(III)	1.0	100
Al(III)	1.0	99
Cr(III)	1.0	100
Ba(II)	1.0	100
Zn(II)	0.8	100
Mn(II)	0.8	98
Co(II)	0.8	97
Ni(II)	0.8	98
Bi(III)	0.05	99
Pb(II)	0.05	100
Cd(II)	0.05	99
Hg(II)	0.05	98

^a Initial samples contained 50 µg Cu(II) ion in 50 mL water

Analysis of water samples

Tap water of Ardabil city, river water of Borjloo and one synthetic sample were analyzed. For demonstrating the accuracy of the developed method, it was compared with the standard method² for determination of Cu(II). Results (Table 3) show that, the added copper ions can be quantitatively recovered from the samples.

Table 3. Recovery of copper added to 250 mL of different water samples.

Sample	Cu(II) added $\mu\text{g} \cdot \text{mL}^{-1}$	Cu(II) found $\mu\text{g} \cdot \text{mL}^{-1}$	Cu(II) found ^a $\mu\text{g} \cdot \text{mL}^{-1}$
Tap water	0.000	0.000	0.000
	0.080	0.080(0.908) ^b	0.079(0.734)
River water (1)	0.000	0.100(1.200)	0.102(0.568)
	0.080	0.180(1.001)	0.181(0.845)
River water (2)	0.000	0.102(0.787)	0.103(0.559)
	0.080	0.182(0.337)	0.180(1.154)
Synthetic sample [Na ⁺ , Ca ²⁺ , Al ³⁺ , Ba ²⁺ , Co ²⁺ , Bi ³⁺ , Cd ²⁺ , 0.2 mg of each cation]	0.000	0.000	0.000
	0.080	0.082(1.019)	0.082(1.414)

^aCu(II) found by standard method. ^bValues in parentheses are CVs based on three replicate analysis.

Conclusions

Results of this work show powerful ability of SPE using modified AC with HPBS. The method was simple, and low cost. Also, the presented method was free of interference. The method successfully applied to the preconcentration and determination of copper in binary mixtures.

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