Preconcentration of Copper(II) in Water Samples Using Polyurethane Foam/2-(6'-Ethyl-2'-benzothiazolylazo)chromotropic Acid

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In this work, polyurethane foam (PUF) loaded with 2-(6'-ethyl-2'-benzothiazolylazo)chromotropic acid (Ethyl-BTANC) was packed in a minicolumn and it was used in an on-line preconcentration system for cadmium and lead determination. Optimum hydrodynamic and chemical conditions for metal sorption were investigated. The effects of several foreign substances on the adsorption of copper(II) was also reported. The enrichment factor obtained was 37 (Cu) for 180 s preconcentration time. The proposed procedures allowed the determination of metals with detection limits (3σ) of 4.11 $\mu g\ L^{-1}$ (0.10 and 0.52 $\mu g\ g^{-1}$ of solid sample) for copper(II). The precision of the procedures was also calculated: 3.3 (Cu 10 $\mu g\ L^{-1}$). The accuracy of the procedure was checked by analysis of the certified reference materials. copper(II) contents in water samples (sea water and tap water) were determined by applying the proposed procedure.

Key Words: 2-(6'-Ethyl-2'-benzothiazolylazo)chromotropic acid, Preconcentration, Copper(II), Polyurethane foam.

INTRODUCTION

Copper is both vital and toxic for many biological systems[1,2]. Thus, the determination of trace amounts of Cu is becoming increasingly important because of the increased interest in environmental pollution[3]. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of copper in natural waters and wastewaters[4]. Nevertheless, very frequently for the extremely low concentration copper in waters, a direct determination cannot be applied without their previous preconcentration and separation. The most widely used techniques for the separation and preconcentration of trace amounts of Cu are liquid-liquid extraction[4], precipitation[5,6] and chelating resins[7]. The large distribution ratios possible in solvent extraction systems allow the analytical determination of substances present in otherwise non-detectable concentrations.

A proper choice of extractant may lead to an increase in concentration by several orders of magnitude. In other words, a large increase in sensitivity is obtained in

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the analytical method, even when the analyte is analytically detectable in the original sample. Its preconcentration by means of solvent extraction permits use of smaller samples, simplification of the procedure and increased accuracy of the samples. Very often, both separation and preconcentration are required and an advantage of solvent extraction is that both can be obtained in the same step[8]. Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent[9]. For extraction of metal ions, it is preferable that the chelating reagent used has a high distribution coefficient and pH dependence in the system chosen[10-14]. Different methods, especially liquid-liquid extraction of copper in the presence of various classical[15-19] and macrocyclic[20,21] co-extractant ligands has attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time-consuming, labour-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[28,29], 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 (LLE) methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed[34-39]. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices[40-43]. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions[44-46].

In a recent series of papers[47-49], 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 straight forward detection of esterase activity of ligated Cu^{2+} in low concentration. The procedure presented in this work includes a description of an on-line preconcentration procedure using a mini-column packed with a laboratory-made solid sorbent. The sorbent used was polyurethane foam loaded with 2-(6'-ethyl-2'-benzothiazolylazo)chromotropic acid (Ethyl-BTANC), a recently introduced reagent[50]. Optimum conditions, analytical features and selectivity were determined and the proposed procedure was applied to copper(II) determination in several water samples.

EXPERIMENTAL

2-(6'-Ethyl-2'-benzothiazolylazo)chromotropic (Ethyl-BTANC) solution (8.0 × 10⁻⁴ mol L⁻¹) was prepared by dissolving 40 mg of 2-(6'-ethyl-2'-benzothiazolyl-azo)chromotropic acid in 100 mL of ethanol. Polyurethane foam, commercial open cell polyether-type polyurethane foam (all from Merck) was ground in a domestic blender with a large amount of deionized water, as previously described[46]. After-wards, polyurethane foam was filtered off in a vacuum system and it was placed in a stove at 80 ℃ for 1 h. Acetate, borate and ammoniacal buffers[51] were used to adjust the sample pH in the range of 4.7-6.0, 7.0-8.0 and 9.0-10.0, respectively. Deionized water was used for all dilutions. Metal working solutions at microgram per liter level were prepared daily by diluting a corresponding 1000 µg mL⁻¹ solution (Merck, Darmstadt, Germany). The laboratory glassware was kept overnight in a 5 % (v/v) nitric acid solution. The following certified reference biological materials were analyzed: NIST 1570a Spinach Leaves purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

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 manufac-turers. These characteristics are tabulated in Table-1. The flow system consisted of a four-channel peristaltic pump furnished with silicone tubes to deliver the carrier, eluent and sample solutions and two Rheodyne model 5041 six-port rotary valves (Cotati, USA) to select elution and preconcentration steps.Alaboratory-prepared minicolumn packed with PUF/Ethyl-BTANC (PVC, 3.50 cm length and 0.40 cm i.d.) and capillary tubes of PTFE were also used. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

TABLE-1
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

The mini-column packed with 100 mg of polyurethane foam has the following dimensions: 3.50 cm length and internal diameter of 4.0 mm. An 8.0 × 10⁻⁴ mol L⁻¹ Ethyl-BTANC solution was percolated through the minicolmn at a flow rate of 2.50 mL min⁻¹ for 5 min. After wards, the column was washed with a 10 % (w/v) sodium hydroxide solution until the black-purple effluent became colourless to remove the excess of Ethyl-BTANC. A 5 % (v/v) nitric acid solution and deionized water were used to wash the mini-column before use. Reproducibility of the mini-

columns prepared by this way was monitored by measuring analytical signals obtained for the same sample solution, using different mini-columns.

Synthesis of Ethyl-BTANC: The synthesis of 2-(6'-ethyl-2'-benzothiazolylazo)-chromotropic acid involved diazotization with nitrous acid in acidic media at low temperature and coupling with chromotropic acid in basic media. Ethyl-BTANC was synthesized and characterized according to a previously described procedure[50].

Analysis of real samples: Accuracy of the procedure was evaluated by analysis of certified reference material. Real samples of black tea and spinach leaves were also analyzed. These materials were digested using the following procedure: a portion of 0.2 g of dry sample was precisely weighted into a Teflon cup, 4.0 mL of 1:1 (v/v) nitric acid solution were added and the acid digestion bomb was heated at 150 ºC for 5 h[52]. After cooling at room temperature the bomb was opened carefully in a fume cupboard. The pH of the final digests were adjusted by suitable addition of a 10 % (w/v) sodium hydroxide solution and an appropriate buffer solution and the mixture was finally diluted to 25 mL by double deionized water.

Tap water (Tehran, taken after 10 min operation of the tap), sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed. The only pre-treatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. Natural water samples were filtered before analysis. A volume of 100 mL of the filtrate was taken and the pH was adjusted by addition of buffer solution.

On-line preconcentration system: Preconcentration and determination of copper(II) were performed by using an on-line system previously described for copper(II) analysis in natural waters[53]. The flow system was operated by a time-based mode. In the sorption step, the two six-port valves are in load position. The sample was pumped through the mini-column and metallic ions were retained by PUF/Ethyl-BTANC. After 60 or 180 s, depending on the calibration mode, the valves were then switched to the elute position and a stream of water carried the acid eluent from the loop and column in order to release metal ions directly into the nebulizer of the spectrometer. The column was arranged in the manifold so that the eluent flowed through it, in reverse direction to that of the sample, minimizing thus the dispersion of the analyte. Total elution time is 15 s. Signals were measured as maximum absorbance.

RESULTS AND DISCUSSION

Elution: Desorption of the metals was studied using solutions of eluents at several concentrations. Copper(II) (10 µg L^{-1}) solutions were used. Best results were obtained when used hydrochloric acid solutions at concentrations equal or higher than 1.0 mol L^{-1}. These results are shown in Fig. 1. Similar results were found for nitric acid. Organic solvents, such as acetone or ethanol, were also tested as eluents, associated to acid solutions. However, the use of these solvents did not

result in any significant increase in analytical signal. In posterior experiments, a 1.0 mol L^{-1} hydrochloric acid solution was used in the elution of copper(II) from mini-column. Amount of eluent necessary for a quantitative dessorption of metals from mini-column was studied, varying the eluent loop. According results shown in Fig. 2 elution is complete for eluent loops upper 80 μL. It was used an eluent loop of 100 μL for copper(II).
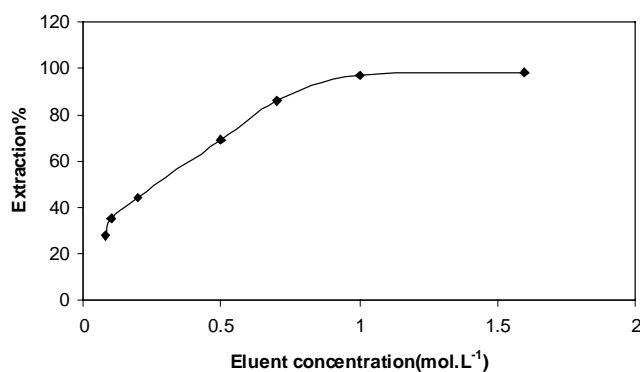

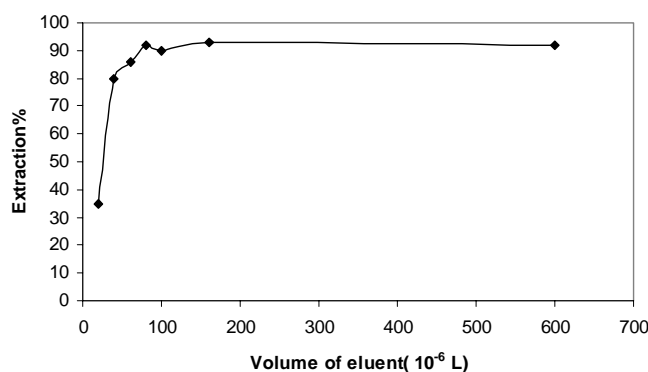Fig. 1. Effect of eluent concentration on the preconcentration of copper(II)

Fig. 2. Effect of eluent amount on the preconcentration of copper(II)

Sorption studies: Sorption in the mini-column is based in the formation of chelates between Ethyl-BTANC and cations. Therefore, the pH of the metal solution is an important parameter to study in this system because the formation of the complex species is strongly dependent of hydronium (or hydroxide) ions concentration in the media. The pH of copper(II) (10 μg L^{-1}) solutions was adjusted with acetate, borate and ammoniacal buffers. Analytical signals reached a maximum in pH value of 3.0, according to the results shown in Fig. 3. These results are in good agreement with pH range favourable for Cu(II)/Ethyl-BTANC complex[50]. Borate pH 3.0 was employed for pH adjusting of copper(II) solutions, in further experiments. Studies about sorption capacity of PUF/Ethyl-BTANC were performed by

using 100 mL of Cu(II) 10 mg L^{-1} solutions. The pH of these solutions was adjusted as in the anterior paragraph. Buffered metal solutions were added to plastic flasks containing 100 mg of the sorbent and the systems were kept under agitation in a mechanical shaker for 4 h.
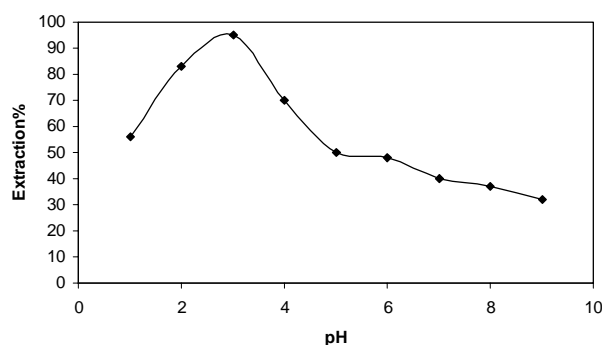

Fig. 3. Effect of pH on the preconcentration of copper(II)

Solid phase was separated by filtration and the metal contents in the liquids remaining were determined by FAAS. The sorption capacity calculated was 32.2 µmol g^{-1} of PUF/Ethyl-BTANC, for copper(II). The lifetime of the mini-column was monitored by measuring the analytical signal of 10 µg L^{-1} Cu(II) at the end of each day of work and counting the number of preconcentration cycles. Mini-column shown good reproducibility for about 450 cycles.

Hydrodynamic variables: The influence of the sample flow rate in the sorption of Cu(II) ions on a PUF/Ethyl-BTANC mini-column was studied in the range of 1.5-15.0 mL min^{-1}. This study was made by pumping 5.0 mL of the solution containing Cu(II) into the system at various flow rates. The absorbance was linear up to 8.0 mL min^{-1}, implying that the complexation is complete and the contact time is sufficient. Above this value the analytical signal decreased because metal ions probably could not equilibrate properly with the resin due to increasing in the velocity of the ions, that reduces the residence times. In posterior experiments, the flow rate was kept constant at 7.0 mL min^{-1}. In on-line system, the carrier (water) flow rate controls the velocity of desorption. The effect of carrier flow rate was studied in the range of 2.0-7.0 mL min^{-1}. Best results were found within the range of 3.0-7.0 mL min^{-1} for both metals. A flow rate of 5.0 mL min^{-1} was selected in the subsequent studies, in order to match carrier and aspiration flow rates.

Selectivity: In order to investigate whether the described procedure suffers from interference, the effect of co-existing ions on the determination of 10 µg L^{-1} Cu(II) by the proposed method was studied. Any deviation $> \pm 5$ % from the absorbance value of Cu(II) solution was taken as an interference. The results are given in Table-2. The interfering substances examined were found not to impair the quality of the analytical signal when the chemical and hydrodynamic variables were maintained at the optimum levels.

TABLE-2
SEPARATION OF COPPER FROM BINARY MIXTURES FOR THE ONLINE
SYSTEM USING POLYURETHANE FOAM/ETHYL-BTANC
MINICOLUMN FOR COPPER(II) (10 μg L^{-1})

Recovery of Cu^{2+} (%)	Diverse found ion (%)	Amount taken (mg)	Diverse ion
98.8 (1.9)^b	NA^a	2.1	Na$^+$
98.2 (1.4)	NA	1.6	Mg^{2+}
99.0 (1.1)	NA	1.7	Ca^{2+}
97.9 (1.9)	2.5 (1.1)	2.0	Sr^{2+}
98.9 (1.3)	NA	1.4	Ba^{2+}
99.0 (1.7)	NA	2.0	Co^{2+}
98.5 (1.7)	NA	1.9	Ni^{2+}
96.4 (1.6)	NA	1.8	Pb^{2+}
97.3 (1.5)	NA	2.0	Zn^{2+}
99.2 (1.8)	NA	1.2	Cd^{2+}
98.0 (2.9)	NA	1.3	Hg^{2+}

^{a}No adsorption; ^{b}Values in parentheses are RSDs based on three replicate analyses.

Analytical features: Calibration graphs were run under the optimum conditions of the on-line preconcentration system for FAAS determination of copper and lead. Analytical characteristics of the procedure are given in Table-3. The data are shown for 60 and 180 s preconcentration time. Calibration graphs obtained for each metal by direct aspiration were A = 4.32 × 10^{-3} + 3.52 × 10^{-4} C (Cu 10-1000 μg L^{-1}) for Cu(II), where A is the absorbance and C is the metal concentration in solution. The enrichment factors were calculated as the ratio of slopes of linear section of the calibration graphs before and after preconcentration[54] for 60 (Cu: 20) and 180 s (Cu: 37). In order to determinate the transfer phase factor, 25mL of a 10 μg L^{-1} Cu(II) solution was percolated by the column under optimum conditions. The desorption was carried out with 1.00 mL of 1.00 mol L^{-1} hydrochloric acid solution and the metal was measured by FAAS. The transfer phase factor of the column is defined

TABLE-3
ANALYTICAL CHARACTERISTICS OF THE ON-LINE COPPER AND LEAD
PRECONCENTRATION SYSTEM USING POLYURETHANE FOAM/ETHYL-BTANC
MINICOLUMN (A: ABSORBANCE C: METAL CONCENTRATION, μg L^{-1})

Pb(II)	Cu(II)	Element
180	60	Preconcentration time (s)
37	20	Enrichment factor
12	17	Concentration efficiency (min^{-1})
	0.95	Transfer phase factor
0.57	0.35	Consumptive index (mL)
19	51	Sample frequency (h^{-1})
	100	Eluent consumption (μL)
4.11	8.58	Limit of detection (μg L^{-1})
3.30	2.90	Precision (%)
A = 4.32×10^{-3} + 3.52×10^{-4} C	A = -2.15×10^{-3} + 8.28×10^{-4} C	Calibration function

as the ratio between the analyte mass in original sample and that in the concentrate[55]. Other parameters used for evaluating preconcentration systems, such as concentration efficiency (CE) and consumptive index (CI)[55] were also determined. The detection limits were calculated as three times the standard deviation of the signals obtained from 15 sample blanks. The precision of the procedures were calculated as the relative standard deviation in 10 μg L^{-1} Cu(II)solutions (n = 7).

To evaluate the accuracy of the present method, two certified reference materials were analyzed: NIST 1570a Spinach. According to Table-4, the determined concentrations of Cu(II) in these materials by developed procedure are in good agreement with the certified values. Confidence intervals are at 95 % level. These results indicate the applicability of the developed preconcentration system for interference-free determination of trace Cu(II)in the biological samples analyzed.

TABLE-4
METAL DETERMINATION IN CERTIFIED REFERENCE
MATERIALS BY PROPOSED METHODOLOGY* (n=3)

Sample	Lead amount (μg g^{-1})	
	Found	Certified
NIST 1570a Spinach leaves	3.95 ± 0.2	3.90 ± 0.1

NIST = National Institute of Standards & Technology, USA; *Confidence interval 95 %.

Determination of copper and lead in real samples: The proposed analytical procedure was applied to the determination of Cu in black tea and spinach leaves. The results are described in Tables 4 and 5. Recoveries (R) of spike were quantitative. 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), sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table-5). As can be seen from Table-5 the added copper ions can be quantitatively recovered from the water samples used.

TABLE-5
RESULTS OBTAINED FOR DETERMINATION OF
COPPER IN WATER SAMPLES (n = 4)

Sample	Cu^{2+} added (μg)	Cu^{2+} determined (ng mL^{-1})
Tap water	0.0	1.88 (0.9)^a
	10.0	12.20 (1.3)
Sea water	0.0	13.56 (1.7)
	10.0	23.98 (1.8)

^{a}Values in parentheses are RSDs based on five individual replicate analysis.

Conclusion

Using polyurethane foam loaded with Ethyl-BTANC as solid sorbent, a new method for the determination of copper was successfully established. This is an alternative procedure for the preconcentration of copper as a prior step to their

determination by flame atomic absorption spectrometry. The determination involves a fast, easy and effective procedure for the preconcentration of the metals. The on-line preconcentration system is very economical and simple in apparatus and manipulation. No severe sources of interference for the technique were observed from various tested water samples. The high tolerance to interference, allied to presented advantages is very interesting for routine laboratories in trace element analysis.

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