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Application of Naphthalene-captopril Column for Pre-concentration and Determination of Trace Amount of Copper(II) in Waste Water Samples by Flame Atomic Absorption Spectrometry

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A sensitive and selective pre-concentration method for the determination of copper(II) by flame atomic absorption spectrometry has been developed. Copper forms a complex with captopril. This complex is retained by naphthalene-captopril adsorbent in a column with a height of *ca.* 2.5 cm. The adsorbed metal complex is then eluted from the column with nitric acid and its copper content is determined by flame atomic absorption spectrometry. The effect of different variables such as pH, reagent concentration, flow rate and interfering ions on the recovery of the analyte was investigated. The calibration graph was linear in the range 75-350 $\mu g\ L^{-1}$ of copper in the initial solution. Detection limits (3σ, $n = 10$) of 23 $\mu g\ L^{-1}$ and relative standard deviation 2.4 and 1.6 % at 200 and 300 $\mu g\ L^{-1}$ level were obtained. This procedure was successfully applied to the determination of copper in waste water samples. Analytical recoveries of copper added to samples were 98-103 %.

Key Words: Pre-concentration, Copper, Captopril, Flame atomic absorption spectrometry.

INTRODUCTION

Copper is both vital and toxic for many biological systems. Thus the determination of trace amounts of Cu is becoming increasingly important because of the increased interest in environmental pollution. Flame atomic absorption spectrometry, ion selective electrode (ISE)[1] and spectrophotometric methods[2-5] are the most common methods for determination of copper, but their sensitivity is usually insufficient for the low concentrations in environmental samples and some of them suffer from either selectivity and also analyses are time consuming. Therefore a pre-concentration and matrix elimination step is usually required.

The most widely used techniques for the separation and pre-concentration of trace amounts of copper are liquid-liquid extraction[6,7], precipitation, cation exchange resins and solid phase extraction[8-13]. Solid-phase extraction is an attractive technique that reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation[14]. The basic principle behind the solid-phase extraction involves passing the water sample through a cartridge or a column containing an adsorbent that retains the analytes. After the sample has been passed through the column, the analytes are eluted from the adsorbent using a suitable solvent and analytes were determined by proportional methods.

In the present studies, the use of naphthalene-captopril as a sorbent in pre-concentration system to determine copper trace levels by flame atomic absorption spectrometry is proposed. The procedure was based on the chemical sorption of copper(II) ions onto a column packed with naphthalene-captopril, followed by 2 mL of 1.5 mol L^{-1} nitric acid elution and determination by flame atomic absorption spectrometry. The effect of some variables such as pH, reagent concentration, flow rate and interfering ions on the recovery of the analyte was studied. The proposed procedure was applied for determination of copper in some water samples with satisfactory accuracy.

EXPERIMENTAL

All chemicals were of analytical reagent grade and deionized water was used throughout. A copper stock solution (1000 mg L^{-1}) was prepared From $Cu(NO_3)_2{\cdot}3H_2O$ (Merck). Copper working standard solutions were prepared daily by several dilutions of the stock standard solution with deionized water. Interference studies were carried out by using the chloride or nitrate salts of the metal cations. A 1.5 M nitric acid solution was prepared by diluting 10 mL of HNO_3 (Merck) to 100 mL in a volumetric flask. Buffer solutions were prepared by standard procedure.

Preparation of the sorbent: The naphthalene adsorbent solution was prepared by dissolving 25 g of naphthalene and 1 g of captopril in 45 mL of acetone on a hot-plate stirrer at 40°C. This solution was transferred to 1000 mL of water while stirring the solution at room temperature. It was stirred for 1-2 h and allowed to stand for 0.5 h. The supernatant solution of naphthalene coprecipitated with captopril was drained off by decantation and washed twice with water in same way. This adsorbent slurry was stored in a bottle for further use.

An atomic absorption spectrometer Shimadzu AA680 (Tokyo-Japan) was used for atomic absorption measurements. Operating conditions were: analytical line 324.7 nm, slit width 0.2 nm, lamp current 5 mA, fuel gas (acetylene) flow rate 2 L min^{-1}, air flow rate 5.0 L min^{-1} and integration time 3 s. The pre-concentration column was a funnel-tipped glass tube of 50 mm length and 5 mm internal diameter, packed with an adsorbent. A Metrohm E-632 pH meter with a glass combination electrode was used throughout this study.

General procedure: A funnel tipped glass tube (50 mm length and 5 mm i.d) with a very fine bore was used as a pre-concentration column. It was filled with the adsorbent slurry to a height of 2-2.5 cm after slightly pressing the adsorbent in the column with a flat glass rod. 100 mL of the solution containing 75-350 μg L^{-1} of copper was passed through the column at a flow rate of 2 mL min^{-1}. The column packing was then washed with a small volume of water and the naphthalene material was pushed down with a flat glass rod to eliminate the excess water attached to naphthalene. The metal complex was washed with 2 mL of HNO_3 solution (1.5 M). The eluents were collected and copper determined by FAAS. A blank solution was also run under the same condition without adding any copper.

RESULTS AND DISCUSSION

Effect of pH: The copper solution was adjusted to a fixed pH between (2-10) and passed through a column at a flow rate of 2 mL min^{-1}. Then the copper complex was eluted from column and its copper ion was determined by flame atomic absorption spectrometry. Results gave the same percentage recoveries in various pH. Therefore copper has been quantitatively retained in the pH range of 2-10.

Effect of sample flow rate: The influence of the sample loading flow rate on the pre-concentration of copper was studied. For this reason a volume of 10 mL of a solution containing the analyte was passed into column at flow rates of 1-8 mL min^{-1} by using a pump. As shown in Fig. 1 the maximum recovery of copper was achieved at the flow rates of 1 and 2 mL min^{-1}. Therefore a flow rate of 2 mL min^{-1} was found to be suitable for optimum loading of the analyte and was used for further studies.

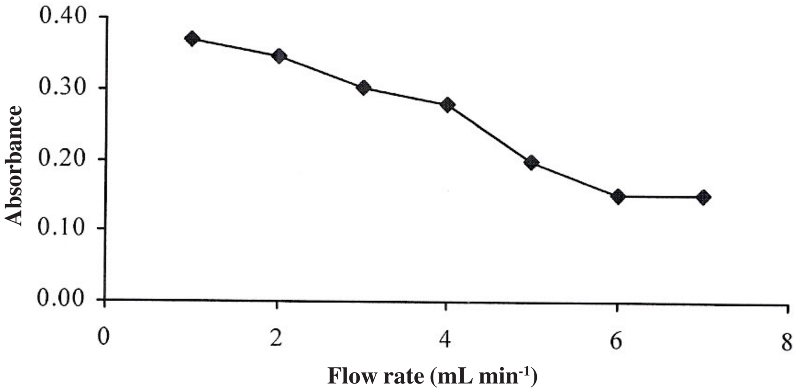

Fig. 1. Effect of sample flow rate on the recovery of copper(II)
Conditions: $[Cu^{2+}]$ = 250 μg L^{-1}, volume of the sample = 10 mL and pH = 7

Effect of type and volume of eluent: The elution efficiencies of hydrochloric acid and nitric acid were compared at different concentrations. The data show that the nitric acid was more effective than hydrochloric acid solution and then it was chosen as the eluent. The effect of eluent concentration on the recovery of copper (25 mL of 200 µg L^{-1}) was examined. The recovery increased as the HNO_3 concentration increased up to 1.5 M after which it remained constant. Therefore a nitric acid concentration of 1.5 M was selected for subsequent studies (Fig. 2). The volume of the nitric acid was varied ftom 1 to 5 mL. 5 mL would not be suitable because it gives a smaller pre concentration factor. 2 mL of nitric acid was chosen for the elution of complex for more convenience.

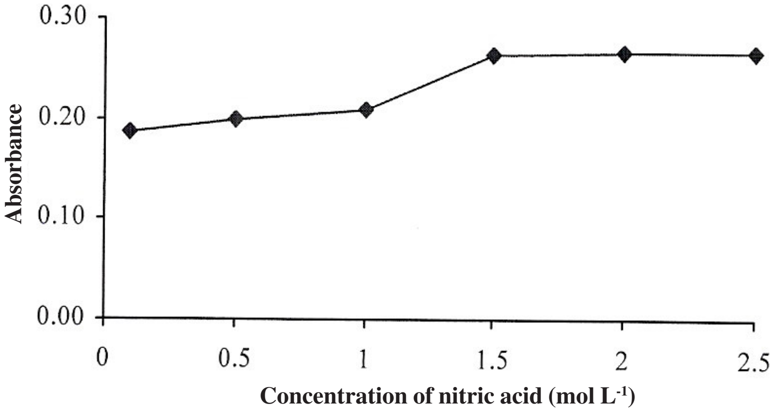

Fig. 2. Effect of nitric acid as the eluent on the recovery of copper
Conditions: [Cu^{2+}] = 200 µg L^{-1}, volume of the sample = 25 mL,
pH = 7 and flow rate = 2 mL/min

Effect of sample volume: The enrichment factor was studied by recommended procedure using increasing volume of metal ion solution. Recoveries (> 95 %) were obtained for sample volumes of less than 120 mL and at the higher volumes the recoveries were decreased. Therefore a pre-concentration factor of 60 can be achieved when using 120 mL of the sample and eluting the column with 2 mL of nitric acid.

Characteristics of the method: Calibration graph was obtained by plotting the absorbance value for copper *vs.* analyte concentration. The linear equation and coefficient calculated were $A = 0.004\ C + 0.018$ and $r = 0.9995$, where C is concentration of copper as µg L^{-1}. The proposed procedure can be applied to pre-concentration of copper in the range of 75-350 µg L^{-1} contained in a solution of 10-120 mL by elute with 2 mL of HNO_3 1.5 M solution. The relative standard deviation (RSD) for eight replicate of 200 and 300 µg L^{-1} was 2.4 and 1.6 %. The detection limit for the proposed procedure was 23 µg L^{-1}.

Effect of diverse ions: The influence of foreign ions that might be adsorbed on naphthalene modified with captopril was investigated in order to identify potential interferences. The results show in Table-1 that the tolerance limits of the investigated electrolytes or cations are very high. The reported tolerance limit is defined as the ion concentration causing a relative error < ± 5 %. It is evident, a very good selectivity is achieved.

TABLE-1
EFFECT OF DIVERSE IONS ON DETERMINATION OF 150 μg L^{-1} OF COPPER(II)

Diverse ions	Tolerance ratio (Foreign ion conc./copper conc.)
Na^+, Co^{2+}, Ag^+, Li^+, Hg^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Bi^{3+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Ba^{2+}, W^{6+}, K^+, Br^-, SCN^-, $S_2O_8^{2-}$, PO_4^{3-}, Cl^-, NO_3^-, CO_3^{2-}, NO_2^-, Se^{2+}, SO_4^{2-}	1000
V(IV), V(V), Cr^{3+}, Sn^{2+}, Al^{3+}	500

Application of the proposed method: The proposed procedure was applied to the determination of copper(II) in waste water samples. The analyte was previously enrichment in pre-concentration procedure and its copper contents were determined by flame atomic absorption spectrometry. A 100 mL volume of sample solutions was treated under the general procedure. The sample was spiked with various amounts of analytes and the recoveries obtained from all analytes were in the 98-103 % range (Tables 2 and 3) which is satisfactory values for environmental samples.

TABLE-2
DETERMINATION OF COPPER IN WASTE WATER SAMPLES, VOLUME OF SAMPLE: 100 mL (n = 8)

Sample	Copper		
	Added/μg L^{-1}	Found[a]/μg L^{-1}	Recovery (%)
Sample 1[b]	–	96 ± 3.6	–
	35	134 ± 4.1	102.3
	80	179 ± 2.8	101.7
Sample 2[b]	–	150 ± 3.2	–
	50	196 ± 2.1	98.0
	100	253 ± 3.1	101.2

[a] $x \pm ts/\sqrt{n}$ at 95 % confidence, [b] Waste water from electroplating industry.

TABLE-3
DETERMINATION OF COPPER IN WATER EFFLUENT FROM MACHINE TOOL FACTORY, VOLUME OF SAMPLE: 100 mL (n = 8)

Sample	Copper		
	Added/µg L^{-1}	Found[a]/µg L^{-1}	Recovery (%)
Sample 1	0	85 ± 3.4	–
	150	241 ± 4.8	102.5
	250	345 ± 5.2	103.0

[a] x ± ts/√n at 95 % confidence.

Conclusion

A simple analytical technique flame atomic absorption spectrometry has been used to determine copper concentration in water samples after pre-concentration step by naphthalene captopril column. The naphthalene column is simply prepared by mixing naphthalene and captopril in acetone and applied to the pre-concentration of copper. The method was demonstrated to be both precise and accurate and was successfully aplied to the analysis of copper in wastewater samples.

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REFERENCES

1. R. Say, E. Birlik, A. Ersoz, F. Yilmaz, T. Gedikbey and A. Denizli, *Anal. Chim. Acta*, **480**, 251 (2003).
2. A.M.G. Rodriguez, A.G. de Torres, J.M.C. Pavon and C.B. Ojeda, *Talanta*, **47**, 463 (1998).
3. J. Di, Y. Wu and Y. Ma, *Spectrochim. Acta*, **61A**, 937 (2005).
4. D.M. Magni, A.C. Olivieri and A.L. Bonivardi, *Anal. Chim. Acta*, **528**, 275 (2005).
5. M.I. Toral, P. Richter and C. Rodriguez, *Talanta*, **45**, 147 (1997).
6. M.C.T. Diniza, O.F. Filhob and J.J.R. Rohwedder, *Anal. Chim. Acta*, **525**, 281 (2004).
7. S. Nohut, S. Karabocek, S. Guner and Y. Gok, *J. Pharm. Biomed. Anal.*, **20**, 309 (1999).
8. A. Ali, X. Yin, H. Shen, Y. Gu and X. Ye, *Anal. Chim. Acta*, **392**, 283 (1999).
9. S.V.M. De Moraes, J.L. Brasil, C.D. Milcharek, L.C. Martins, M.T. Laranjo, M.R. Gallas, E.V. Benvenutti and E.C. Lima, *Spectrochim. Acta*, **62A**, 398 (2005).
10. V.A. Lemos and P.X. Baliza, *Talanta*, **67**, 564 (2005).
11. P.S. Roldan, L. Ilton, C.F. Cilene and P.M. Padilh, *Fuel*, **84**, 305 (2005).
12. E.L. Da Silva, A.O. Martins, A. Valentini, V.T. De Favere and E. Carasek, *Talanta*, **64**, 181 (2004).
13. S.L.C. Ferreira, J.R. Ferreira, A.F. Dantas, V.A. Lemos, N.M.L. Araujo and A.C.S. Costa, *Talanta*, **50**, 1253 (2000).
14. R. Majors, *LC-GC*, **4**, 972 (1986).

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