ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNT OF COPPER IN WATER SAMPLES AFTER PRECONCENTRATION WITH [N-[(S)-3-MERCAPTO-2-METHYLPROPIONYL]-L-PROLINE] ON A NAPHTHALENE

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Abstract

This study presents a new procedure for preconcentration and determination of trace level of copper (II) in water samples. The method is based on the adsorptive enrichment of copper (II) complex with N-[(S)-3-mercapto-2-methylpropionyl-L-proline chelate on naphthalene column. After the preconcentration stage, the analyte was eluted with a HNO_3 solution and determined by flame atomic absorption spectrometry (FAAS). The effect of different variables such as pH, sample volume, amount of chelate, flow rate and eluent solution on the recovery of the analyte was investigated. The effect of some matrix elements, such as Fe, Ni, Na, K, Ca, and Mg, on recovery of copper has also been studied. The calibration graph was linear in the range 25 – 120 µg l^{-1} of copper in the initial solution with r = 0.9994. The limit of detection based on $3S_b$ criterion was 5µg l^{-1} and the relative standard deviation for ten replicate measurements of 50 and 90 µg l^{-1} of copper was 1.7 and 2.1 %, respectively. The accuracy of the method confirmed by analyzing of copper in certified sample material (NBS-Ounce metal 124d). The results demonstrated a good agreement with the certified value. The method was successfully applied for determination of copper in tap and wastewater samples.

Introduction

Metals at trace levels are components of the natural biosphere. Some of them are considered essential but at high concentrations they are toxic and the range between essentiality and toxicity is often very small. In this aspect, reliable and sensitive analytical methods have an important role to evaluate the environmental impact of metal pollutants. Copper occurs in nature as mineral compounds like CuS, CuS_2, $CuFeS_2$, $CuSO_4.5H_2O$ and others. More than 75% of copper that is mined is used in the electrical industries. Other applications include household, metallic blends and pigments.[2] It is an essential element for enzymes, but over a healthy limit it accumulates in the liver, causing dizziness, vomiting, diarrhea, transpiration and, depending on its concentration, can lead to the death.[1] Copper could be determined directly in waters and foods by inductively-coupled plasma atomic emission spectrometry (ICP-AES) or electrothermal atomic absorption spectrometry (ETAAS), which usually have a sufficiently low detection limit. Flame atomic absorption spectrometry (FAAS) is an available in most laboratories and is normally less subject to interferences than ICP-AES or ETAAS, but it requires the use of a preconcentration step in order to reach an appropriate level of sensitivity. Many preconcentration procedures for copper determination have been developed and they involve different analytical techniques and several materials.[3–6] Liquid–liquid extraction by using dithiocarbamate[6] and trioctylmethylammonium chloride[7] as complexing reagents, coprecipitation with magnesium hydroxide as collector,[8] precipitation as rubeanic acid complex and filtration by using membrane filter,[9] and solid phase extraction (SPE)[10–13] are well-known procedures for preconcentration and separation of trace copper.

SPE has found increasing application for the preconcentration of trace copper ions and elimination of matrix interference prior to analysis, because of the availability and easy recovery of the solid phase, and the ease of separation and enrichment using a continuous flow system. In addition it does not usually need an organic solvent, which may be toxic. A variety of solid materials such as activated carbon,[14]silica gel,[15] Amberlite XAD resins,[16] microcrystalline naphthalene[17] and others[18] have been used for the preconcentration of trace amount of copper.

In the present work, copper has been preconcentrated from water and wastewater samples by using [N-[(S)-3-mercapto-2-methylpropionyl]-L-proline] on naphthalene column as the solid phase extractor. Various parameters, i.e. pH, type and volume of eluent, flow rate of sample, volume of sample and interfering ions, have been evaluated. Analytical parameters such as precision and accuracy of the method have also been studied. The

procedure developed has been successfully employed for the determination of trace copper in water and reference material samples.

Experimental

Apparatus and Reagents

A Shimadzu (Tokyo, Japan) flame atomic absorption spectrometer model AA680, with an air-acetylene flame, was used for copper (II) determination. A Metrohm, E-632 pH meter with glass electrode was used to adjust the pH of solutions. The column was manufactured in the laboratory using a glass tubing (50 mm height ×5 mm internal diameter), sealed at the ends with little glass wool plugs to avoid material losses. This column packed with naphthalene adsorbent through which solution containing the metals is passed.

All the reagents used were of analytical reagent grade. Deionized-distilled water was used throughout the experimental work. Copper (II) solutions were prepared by appropriate diluting a 1000 µg l^{-1} copper solution (atomic absorption, Merck) with distilled water. [N-[(S)-3-mercapto-2-methylpropionyl]-L-proline and naphthalene purchased from Fluka (Switzerland) and Merck respectively. Buffer solutions were prepared by standard methods.

Preparation of naphthalene adsorbent

A solution of naphthalene was prepared by dissolving 25 g of naphthalene (Merck) and 1 g of [N-[(S)-3-mercapto-2-methylpropionyl]-L-proline] in 45 ml of acetone with stirring on a hot-plate at 40°C. This solution was transferred with constant stirring at room temperature into ca. 1000 ml of water. It was stirred for 1-2 h and allowed to stand for 30 min. The supernatant solution of naphthalene co-precipitated with [N-[(S)-3-mercapto-2-methylpropionyl]-L-proline] was drained off by decantation and washed twice with water in same way. The slurry of naphthalene adsorbent in water was stored in a bottle for further use.

General procedure

A funnel tipped glass tube with a very fine bore was used as a preconcentration column. It was filled with the adsorbent slurry to a height of 1.5-2 cm after slightly pressing the adsorbent in the column with a flat glass rod. 120 ml of the solution containing 25 – 120 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 eluted with 2 ml of HNO_3 solution (1.5 mol l^{-1}M, Merck). 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 Discussions

An important parameter in achieving quantitative adsorption and recovery of trace elements on adsorbent is pH. In order to optimize the sorption conditions for the retention of copper on modified naphthalene column, the recovery of copper was determined by applying the general sorption procedure by changing the pH of sample solutions in the range 2-10. As can be seen in figure 1, quantitative recoveries (>95%) were obtained for copper at the wide pH range of 2-8. For subsequent work, pH 6 was selected as the working pH. For real samples lower pH values are preferred because real samples are generally dissolved acids and there is no risk precipitation of sample of components.

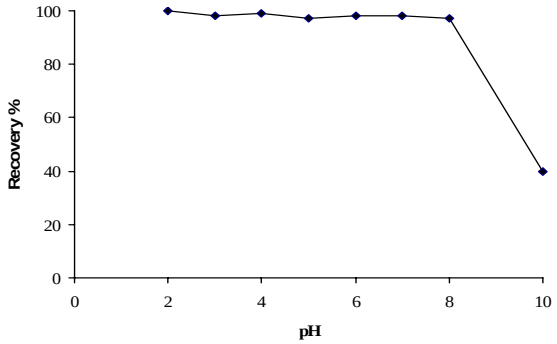
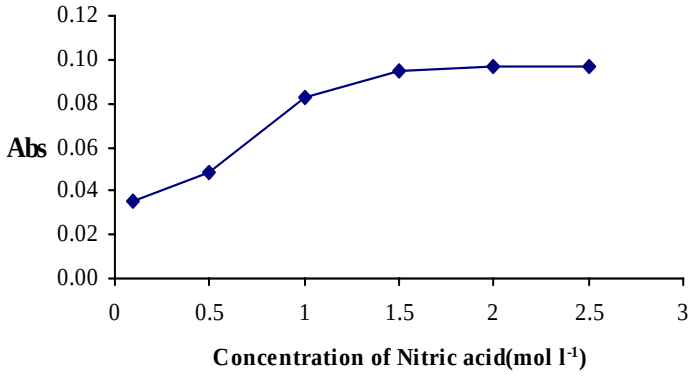


Fig. 1: The effect of pH on the recovery of copper on naphthalene-captopril column Conditions: sample volume 100 ml; amount of copper 50 µg l^{-1}; flow rate 2 ml min^{-1}.

The Influence of flow rates of sample solution on copper retention was investigated over the range 1-8 ml min^{-1} by using constant sample volume of 100 ml at pH = 6. Quantitative retention was obtained between 1 and 2 ml min^{-1}. Copper retention decreased dramatically at flow rate >2 ml min^{-1} owing to very short residence time of the sample in the column, which results in its incomplete retention. Therefore 2 ml min^{-1} was chosen as the flow rate of sample solutions in subsequence experiments

The elution of copper from naphthalene–N-[(S)-3-mercapto-2-methylpropionyl]-L-proline column was studied by using various eluting agents. Since the copper chelate should be is eluted in a small volume of eluent, it is essential to select an eluent in which the complex is highly soluble and also sensitive for AAS measurements. Various solutions such as hydrochloric acid, sulfuric acid and nitric acid solution were examined to obtain quantitative recovery values for copper. The nitric acid was chosen as the eluent owing to its effective elution of the adsorbed complex. The influence of eluent concentration on the recovery of copper from column was studied at concentrations of 0.1-2.5 mol l^{-1}. With the results showed in figure 2. It can be observed that the elution was quantitative for solutions at concentrations equal or higher than 1.5 mol l^{-1}. Therefore a nitric acid concentration of 1.5 mol l^{-1} was selected for subsequent studies. The volume of eluent that can completely strip the retained analytes from the solid phase is an important parameter for obtaining the maximum preconcentration factor. Thus some experiments were carried out in order to choose a proper eluent volume. For this reason the volume of nitric acid was varied from 1 to 5 ml.2 ml of nitric acid was chosen for the elution because it gives good preconcentration factor and more convenient.



F1g. 2: Effect of nitric acid as the eluent on the recovery of copper Conditions: Copper concentration, 50 µg l^{-1}, volume of the sample 100 ml, Flow rate, 2 ml min^{-1}

The effect of sample volume on the retention of copper ion was investigated by passing 10, 25, 50, 100, 120 and 150 ml volume solution through the column at a constant flow rate of 2 ml min^{-1}. It was found that the analyte could be recovered quantitatively when up to 120 ml of the sample solution was used. At higher volumes the recoveries is decreased. Therefore a preconcentration factor of 60 can be achieved when using 120 ml of the sample and eluting the column with 2 ml of 1.5 mol l^{-1} nitric acid.

The amount of N-[(S)-3-mercapto-2-methylpropionyl]-L-proline loaded on naphthalene was optimized and the results showed that a loading 1 g of N-[(S)-3-mercapto-2-methylpropionyl]-L-proline on 25 g of naphthalene gave highest absorbance for copper ion. The height of adsorbent packing was optimized and it was found that up to 14 µg of copper is quantitatively adsorbed using an adsorbent height of 2 cm in a funnel-tipped glass tube.

Interference study

Analytical FAAS is a well established and very specific technique and low sensitive to interferences. Then, the potential interferences effects occurring in this procedure are mainly related to the extraction during the preconcentration step applied to the target samples, and this effect should be particularly relevant with respect to the consumption of the analytical reagent. Considering the samples of interest, and the most probable metal

ions reported the effect of potential interfering ions on the determination of copper was investigated. For this study, different amounts of ionic species tested were added to a 100 ml of 50 µg l^{-1} solution of copper and the general procedure was followed. The results were summarized in table 1. The tolerate amounts of each ion were the concentration values tested that caused less than 4% the absorbance alteration. The ions normally present in water do not interfere under the experimental conditions used.

Table 1: The effect of foreign ions on determination of copper

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

Analytical Parameters

The proposed procedure can be applied to the preconcentration of copper within the range from 25 to 120 µg l^{-1}, in a solution volume of 10 to 120 ml. The calibration graph was linear in this range with an equation of A= 1.40 × 10^{-3}C + 0.028 where C is concentration of copper in µg l^{-1} of the initial solution (120 ml). The limit of detection was 5 µg l^{-1} obtained by the equation LOD = KS_b/m (K=3, m is the slope of the calibration curve and S_b is the standard deviation of ten replicate readings of the reagent blank performed under the general procedure). The precision of the preconcentration method, calculated as the relative standard deviation in sample solutions containing 50 and 90 µgl^{-1} of copper was 1.7% and 2.1%, respectively, both calculated by ten measurements. The accuracy of the proposed preconcentration methodology was evaluated by means of copper determination in certified sample material (NBS-Ounce metal 124d). The result obtained was in good agreement with the certified value.

Determination of copper in water samples

In order to show the validity of the method in various and complicated matrices, copper were determined in spiked tap and wastewater samples. The results for the determination of Cu in various spiked samples (tap water and wastewater) are given in TABLES 2 and 3. All the results found were in the range of 95% confidence limits. These results clearly prove the validity of the method described in this technique.

Table 2: Determination of copper in tap water (n=5)

Sample No.	Amount of Copper µg l^{-1} Spiked	Amount of Copper µg l^{-1} Found[a]	Recovery %
1	0	14 ± 1.2	-----
2	45	61 ± 2.7	103.3
3	80	96 ± 3.1	102.1

[a] $x \pm ts/\sqrt{n}$ at 95 % confidence

Table 3: Determination of copper in wastewater samples (n=5)

Sample No.	Amount of Copper µg l^{-1} Spiked	Amount of Copper µg l^{-1} Found[a]	Recovery %
Sample1[b]	0	70 ± 3.4	-----
	15	88 ± 4.8	103.5
	40	113 ± 4.2	102.7
Sample 2[b]			
	0	96 ± 3.6	-----
	35	134 ± 4.1	102.3

[a] $x \pm ts/\sqrt{n}$ at 95 % confidence
[b] waste water effluent from Machine Tool Factory

Conclusion

The proposed procedure provides a simple, accurate and precise method for the preconcentration and determination of copper in water samples. The selectivity was excellent, making it possible to determine copper in the presence of concentrations of iron, zinc, lead, sodium and calcium ions. The detection limit achieved was satisfactory for the sample studied. This adsorbent was chosen because of it has high surface and it simply prepared by mixing naphthalene and [N-[(S)-3-mercapto-2-methylpropionyl]-L-proline] in acetone. In addition this method is sensitive, low cost, mainly if more sophisticated techniques such as ICP-OES or GFAAS are not available. The proposed procedure can be successfully applied for the determination of copper in industrial and water samples with good recoveries.

Acknowledgement

The financial support of this work by Semnan University Research Council is greatly acknowledged.

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