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Determination of Copper by Flame Atomic Absorption Spectrometry After Solid-Phase Extraction

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Abstract: A new solid-phase extraction method was developed for trace analysis of copper. The method is based on the retention of copper as methylthymol blue complex on naphthalene–methyltriocetyl ammonium chloride adsorbent in a column. The adsorbed metal complex was eluted from the column with nitric acid, and its copper content was determined by flame atomic absorption spectrometry. The effect of different variables such as pH, reagent concentration, solution flow rate, and interfering ions on the recovery of the analyte was investigated. The calibration graph was linear in the range $5\text{--}200\text{ ng mL}^{-1}$ of copper in the initial solution with $r = 0.9976$. The $3S_b$ detection limit was 2 ng mL^{-1} , and the relative standard deviation for eight replicate measurements of 25 and 100 ng mL^{-1} of copper was 4.2% and 1.7%, respectively. The method was applied to the determination of copper in river and sewage water samples.

Keywords: Copper, methylthymol blue, naphthalene–methyltriocetyl ammonium chloride adsorbent, river water, sewage water, solid-phase extraction

INTRODUCTION

Copper is a trace element that is considered essential for human health but it is hazardous at high concentrations. Apart from its important role in biological systems, copper finds many applications in industries such as the electrical industry. Copper can be released into the environment by

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both natural sources and industries. In this aspect, reliable and sensitive analytical methods are required for the determination of copper in environmental samples.

Flame atomic absorption spectrometry (FAAS), which is frequently used for the determination of metal ions because of relatively simple equipment, suffers from insufficient sensitivity for direct determination of elements at trace levels. Therefore, an initial preconcentration step in samples such as seawater, natural waters, and rainwater is needed to allow lower limits of detection to be achieved by FAAS measurements. Different methods have been proposed and used for enrichment of copper and other trace elements depending on the nature of sample, concentration, and measurement technique. These include ion exchange,^[1] coprecipitation,^[2] solvent extraction,^[3] membrane filtration,^[4] cloud point extraction,^[5] and solid-phase extraction.^[6-8] However solid-phase extraction has become a preferred method for concentrating the analyte prior to its analysis by FAAS and other techniques. Different solid phases such as silica gel modified by *N*-propylsalicylaldimine,^[9] Amberlite XAD-4 functionalized with *o*-aminobenzoic acid,^[10] Amberlite XAD-2 functionalized with 2-aminoacetylthiophenol,^[11] activated carbon,^[12] green tea leaves,^[13] and naphthalene,^[14] have been used as solid-phase extractants for enrichment of trace metal ions.

In this work, we propose a solid-phase extraction method for the determination of copper with atomic absorption. Copper complex with methylthymol blue can be adsorbed on methyltriocetyl ammonium chloride supported on naphthalene used as an adsorbent column. The copper complex adsorbed on the naphthalene column is eluted with nitric acid solution, and its copper content is determined by flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation

A Philips PU9100X (England) flame atomic absorption spectrometer was used for the determination of copper. It was equipped with a copper hollow cathode lamp and air–acetylene burner. The instrumental parameters were as follows: wavelength 324.8 nm, lamp current 3 mA, bandpass 0.5 nm.

All pH measurements were made by a Metrohm (Switzerland) digital pH meter equipped with a combined glass electrode.

A Shimadzu (Japan) rotary oil vacuum pump type SA18 was also used.

Reagents

All reagents were analytical grade and used as purchased. Double-distilled water was used. The stock solution of 1000 $\mu\text{g mL}^{-1}$ copper was prepared

by dissolving 0.6706 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, Germany) in water, adding 5 mL of nitric acid (Merck; 70%, d = 1.42), and diluting to 250 mL in a volumetric flask. This solution was standardized by iodometric titration.^[15] The required concentration of copper solution was prepared by appropriate dilution of the stock solution. A 1.5 mol L^{-1} nitric acid solution was prepared by diluting 10 mL of HNO_3 (Merck; 70%, d = 1.42) to 100 mL in a volumetric flask.

Buffer solution of $\text{pH} = 9$ was prepared by addition 350 mL of 10% of hydrochloric acid to 50 mL of NH_3 (Merck, 17%, d = 0.88) and diluting to 500 mL. The pH was then adjusted exactly to 9 using a pH meter. A $2.4 \times 10^{-4} \text{ mol L}^{-1}$ of methylthymol blue solution was prepared by dissolving 0.1010 g of methylthymol blue (Merck) in water and diluting to 500 mL in a volumetric flask.

Stock solutions of $1000 \mu\text{g mL}^{-1}$ of interfering cations were prepared using their nitrate salts, and stock solution of $1000 \mu\text{g mL}^{-1}$ of interfering anions were prepared using their sodium or potassium salts.

The naphthalene adsorbent solution was prepared by dissolving 25 g of naphthalene and 1 g of methyltriocetyl ammonium chloride 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 hr and allowed to stand for 30 min. The supernatant solution of naphthalene coprecipitated with methyltriocetyl ammonium chloride was drained off by decantation and washed twice with water in same way. This adsorbent slurry was stored in a bottle for further use.

Sample Collection

The water samples were collected in polyethylene bottles acidified by adding 5 mL of nitric acid and then kept in the refrigerator before use. The water samples were filtered off using a filter paper (Whatman no. 40) before use.

Recommended Procedure

A funnel-tipped glass tube (50 mm length and 5 mm i.d) with a very fine bore was used as a preconcentration column. It was filled with the adsorbent slurry to a height about 2 cm after slightly pressing the adsorbent in the column with a flat glass rod. One hundred milliliters of the solution containing $5\text{--}200 \text{ ng mL}^{-1}$ of copper, 1 mL of $2.4 \times 10^{-4} \text{ mol L}^{-1}$ methylthymol blue, and 1 mL of ammonium buffer solution ($\text{pH} = 9$) was passed through the column at a solution flow rate of 8 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 2.5 mL of

HNO_3 solution (1.5 mol L^{-1}), and the copper content of the eluent was determined by FAAS. A blank solution was also run under the same condition without adding any copper.

RESULTS AND DISCUSSION

Methylthymol blue (H_6A) forms complex with a number of metal ions.^[16] At high pH values, methylthymol blue is in the form of H_2A^{4-} and forms negative complexes with metal ions. We have recently used methylthymol blue as a ligand for preconcentration of iron on tetraoctyl ammonium bromide–naphthalene adsorbent.^[17] Copper also forms a complex with methylthymol blue. It was found that the negatively charged complex formed is capable of forming an ion pair with methyltriocetyl ammonium ion. Therefore, the retention of copper methylthymol blue complex on a column containing methyltriocetyl ammonium chloride–naphthalene adsorbent was used for enrichment of copper prior to its determination by FAAS.

Effect of Variables

The effect of pH on the retention of copper complex was studied. The pH values of the solutions containing the complex were adjusted in the range 2–10 with the addition of buffers with appropriate pH values, and the recommended procedure was applied. The results showed that the retention of the complex was maximum at pH = 8 to 9 (Fig. 1). Therefore, ammonium chloride–ammonia buffer with pH = 9 was used to maintain this pH.

The influence of methylthymol blue concentration on the retention of the copper complex was also studied. The absorbance was increased up to methylthymol blue concentration of $1.2 \times 10^{-6} \text{ mol L}^{-1}$ in the solution and remained constant above that (Fig. 2). Therefore, a concentration of $2.4 \times 10^{-6} \text{ mol L}^{-1}$ (i.e., 1 mL of $2.4 \times 10^{-4} \text{ mol L}^{-1}$) was added to 100 mL of sample solution to give this concentration was selected for further work.

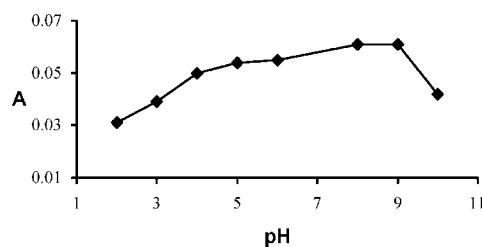


Figure 1. The effect of pH on the retention of complex on the adsorbent. Conditions: 25 mL of 100 ng mL^{-1} of copper, methylthymol blue concentration $2.4 \times 10^{-6} \text{ mol L}^{-1}$.

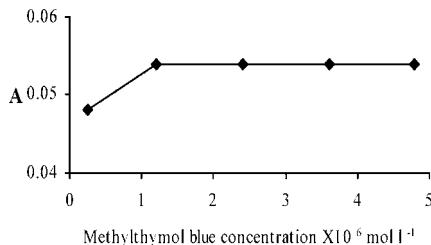


Figure 2. The influence of methylthymol blue concentration on the retention of complex on the adsorbent. Conditions: 25 mL of 100 ng mL^{-1} of copper, $\text{pH} = 9$.

In order to choose a proper eluent for the retained complex, different acids such as nitric, hydrochloric, and sulfuric were examined as eluents. Nitric acid was found to be more effective for the elution of the adsorbed complex than other acids because it gave higher recoveries for the elution of the complex. When using hydrochloric and sulfuric, the amount of copper determined in the eluents by FAAS was only about 50% whereas using nitric acid the recovery was above 90%. Therefore, the effect of nitric acid concentration on the absorption signal of copper was examined. The signal increased as the HNO_3 concentration increased up to 1.5 mol L^{-1} after which it remained constant. Therefore, a nitric acid concentration of 1.5 mol L^{-1} was selected for subsequent studies. Different volumes of the 1.5 mol L^{-1} nitric acid (2–10 mL) were used to strip the complex. High volume is not suitable because it gives a smaller preconcentration factor. Hence, 2.5 mL of nitric acid was chosen for the elution of complex in subsequent studies.

The effect of solution flow rate on the retention of the copper methylthymol blue complex was examined under optimum conditions by using a pump. The solution was passed through the column with solution flow rates adjusted in the range of $1\text{--}8 \text{ mL min}^{-1}$ (Fig. 3). It was found that the solution flow rate did not have much effect on the retention. Therefore, a solution flow rate of 8 mL min^{-1} was selected as the working solution flow rate to decrease the analysis time.

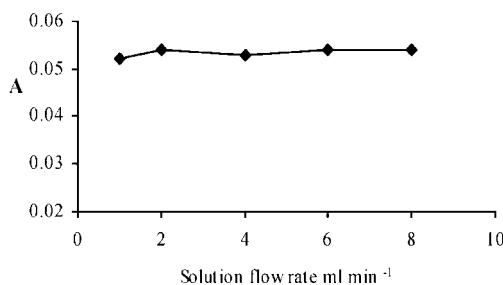


Figure 3. The effect of solution flow rate on the retention of complex on the adsorbent. Conditions: 25 mL of 100 ng mL^{-1} of copper, methylthymol blue concentration $2.4 \times 10^{-6} \text{ mol L}^{-1}$, $\text{pH} = 9$.

In order to determine the volume of the applicable sample solution, the volume of the aqueous phase varied from 10 to 150 mL, all containing the same amounts of copper so that the final solution after preconcentration step would have the same concentration. It was found that the absorbance of the solution was constant when up to 100 mL of the sample solution was used. At the higher volumes, the recovery was decreased. Therefore, a preconcentration factor 40 can be achieved when using 100 mL of the sample and eluting the column with 2.5 mL of nitric acid.

Analytical Performance

The calibration graph was linear in the range of 5–200 ng mL⁻¹ of copper in the initial solution. The equation of the line is $A = 0.0018C + 0.0127$, where C is concentration of copper in ng mL⁻¹ in the initial solution (0.2–8 µg mL⁻¹ in the final solution after preconcentration factor of 40) with $r = 0.9976$. The limit of detection based on the equation $LOD = KS_b/m$ ($K = 3$, m is the slope of the calibration curve, and S_b is standard deviation of 10 blank measurements) was 2 ng mL⁻¹. The relative standard deviation for eight replicate measurements of 25 and 100 ng mL⁻¹ of copper was 4.2% and 1.7%, respectively.

Effect of Interfering Ions

Solutions containing 100 ng mL⁻¹ of copper and different concentration of interfering ions were prepared, and the general procedure was applied. The tolerance limit was defined as the amount of foreign ion causing a change in the absorbance of less than 4%. Table 1 shows the results. As can be seen, a good selectivity is achieved. The interference of Fe²⁺, Fe³⁺ can be overcome by the addition of oxalate solution. Oxalate forms complexes with Fe²⁺, Fe³⁺ and removes their interference.

Table 1. The effect of interfering ions on determination of 100 ng mL⁻¹ of copper

Foreign ions	Tolerance ratio (foreign ion/copper)
Mg ²⁺ , Na ⁺ , Co ²⁺ , Ba ²⁺ , Ca ²⁺ , Zn ²⁺ NH ₄ ⁺ , K ⁺ , Br ⁻ , PO ₄ ³⁻ , Cl ⁻ , CN ⁻ , CO ₃ ²⁻ SO ₄ ²⁻ , Cr ³⁺ , Mo(VI), NO ₃ ⁻ , NO ₂ ⁻	1000
Sn ²⁺ , Hg ²⁺ , Cd ²⁺ , Pb ²⁺	100
Fe ²⁺ , Fe ³⁺	10 ^a

^aThe interference of Fe²⁺, Fe³⁺ can be completely overcome by the addition of oxalate solution.

Table 2. Determination of copper in river and sewage water samples (n = 5)

Copper added (ng mL ⁻¹)	Copper found ^a (ng mL ⁻¹)	Recovery (%)
River water		
0.0	6.8 ± 0.6	—
25.0	32.4 ± 1.4	101.8
100.0	106.0 ± 3.6	99.2
Sewage water		
0.0	40.4 ± 1.1	—
25.0	65.2 ± 2.3	99.7
100.0	139.3 ± 4.1	99.2

^a $x \pm ts/\sqrt{n}$ at 95% confidence.

Application

The proposed method was applied to the preconcentration and determination of copper content of river and sewage water samples. The results reported in Table 2 show that good recoveries are obtained by analyzing copper spiked to the water samples.

CONCLUSIONS

The proposed preconcentration procedure is simple and selective for the determination of trace amounts of copper. The detection limit achieved is better than some of the previously reported methods^[4,5,8] and allows the determination of copper at ng mL⁻¹ by flame atomic absorption spectrometry to be carried out. Although some of the other methods are more sensitive, they use a high sample volume, which is more time consuming.^[11] The method was applied to the determination of copper in river and sewage water samples with good recoveries.

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