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Research Article

Determination of copper in various environmental samples using 4-dimethyl amino benzyl thiourea following solid phase extraction

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Abstract: The author successfully synthesized 4-dimethyl amino benzyl thiourea and it gives a yellow colored complex with copper metal solution in sodium acetate-acetic acid buffer of pH 5.5. Maximum absorption is found at 390 nm. Various factors such as pH, reagent concentration and choice of the solvent, foreign ions effects were studied. This method is successfully applied for the determination of copper in various environmental samples.

Keywords: 4-dimethyl amino benzyl thiourea, copper metal, water samples, milk samples, spectrophotometry, etc.

INTRODUCTION

Copper is one of the important and essential nutrients for human health as well as for the growth of animals and plants¹⁻⁴. Although copper is an essential micronutrient and is required by the body in very small amounts, excess copper in the human body can cause stomach and intestinal distress such as nausea, vomiting, diarrhea, and stomach cramps. Copper is required for normal metabolic processes. Copper combines with certain proteins to produce enzymes that act as catalysts to help a number of body functions. The lowest level at which these adverse effects occur has not been well defined. People with Wilson's disease, a rare genetic disorder, are more sensitive to the effects of copper. Copper is also a commonly occurring element in natural waters. Most copper contamination

in drinking water happens in the water delivery system, as a result of corrosion of the copper pipes or fittings⁵⁻⁹.

Shishehborea *et al.*¹⁰ developed a spectrophotometric determination of trace copper after preconcentration with 1,5-Diphenylcarbazone on microcrystalline naphthalene. Turkoglu and soylak¹¹ proposed a spectrophotometric determination of copper in natural waters and pharmaceutical samples with Chloro(phenyl) glyoxime. Nabivanets *et al.*¹² used a new selective reagent, potassium dodecahydro-1,2-dicarbaundecaborate, for the extraction-photometric determination of copper in water and other materials. Felkel and Spinelli¹³ reported that propylene carbonate simultaneously extracts the neocuproine- copper chelate and the TPTZ-iron chelate. Smith and Manahan¹⁴ used a complexing antioxidant buffer for the determination of copper in tap water at different concentrations. Nonova and Stoyanov¹⁵ reported an extraction-spectrophotometric determination of copper (II) with 4-(2-pyridylazo) resorcinol and a long-chain quaternary ammonium salt. QuanMin *et al.*¹⁶ developed a new method of using phenolphthalein loaded with 1-(2-pyridylazo)-2-naphthol (PAN) as solid phase extractant to separate and enrich trace copper in diverse water samples. An indirect spectrophotometric determination of sodium ceftriaxone with n-propyl alcohol-ammonium sulfate-water system by extraction flotation of copper (II) was proposed by Zhao *et al.*¹⁷.

A simple spectrophotometric method for the determination of copper in industrial, environmental, biological and soil samples using 2,5-dimercapto-1,3,4-thiadiazole has been reported by Ahmed *et al.*¹⁸. Spectrophotometric determination of zinc and copper using a liquid waveguide capillary cell by Pascoa and his coworkers¹⁹ and it was successfully applied to natural water samples. To improve the performance analytically a rapid synergistic cloud point extraction of trace amounts of copper in various samples using spectrophotometry²⁰. Copperdithiocarbamate is used as a reagent for simultaneous determination of copper and zinc in environmental samples was developed by Uddain *et al.*²¹. In the present work, a novel reagent 4-dimethyl amino benzyl thiourea in the laboratory has been used for the determination of copper in various environmental samples.

EXPERIMENTAL

Synthesis of 4-dimethyl amino benzyl thiourea reagent, different analytical instruments used for measurements are discussed. Chemicals and reagents used are of analytical grade and procured from Sigma-Aldrich Company. Double distilled water has been used throughout the experiment.

Synthesis of 4-dimethyl amino benzyl thiourea: 4-dimethyl amino benzaldehyde was dissolved in 40% methanol and thiourea dissolved in water and the mixture was refluxed at room temperature for 3 h and the flask was kept in ice cold condition for two days. Light yellow color crystals were obtained and these crystals were washed with double distilled water and recrystallized from methanol. The melting point of the product is 162° C.

RESULTS AND DISCUSSION

4-dimethyl amino benzyl thiourea gives a yellow colored complex with copper metal solution in sodium acetate-acetic acid buffer of pH 5.5. Maximum absorption is found at 390 nm and is stable for six hours. The conditions for effective extraction were established after studying the effects of various factors such as pH, reagent concentration, choice of the solvent, foreign ions effects. This method is successfully applied for the determination of copper in various environmental samples.

Absorption spectrum: The absorption spectrum for 4-dimethyl amino benzyl thiourea- copper complex in water is shown in **Figure 1**. A reagent blank was used as a reference. Absorption maximum is found at 390 nm.

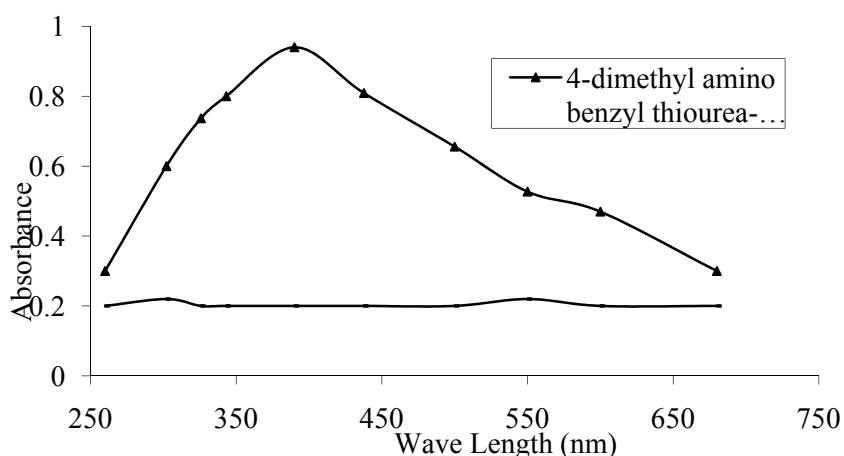


Figure.1. Absorption spectrum for 4-dimethyl amino benzyl thiourea-copper complex

Effect of pH: The influence of pH on the extraction of copper complex is studied in the range of 2–8, using sodium acetate, HCl, and KOH for pH adjustment. Figure.2 shows that copper-4-dimethyl amino benzyl thiourea complex gives maximum absorbance at pH 5.5. In further study, a buffer solution of pH 5.5 was used.

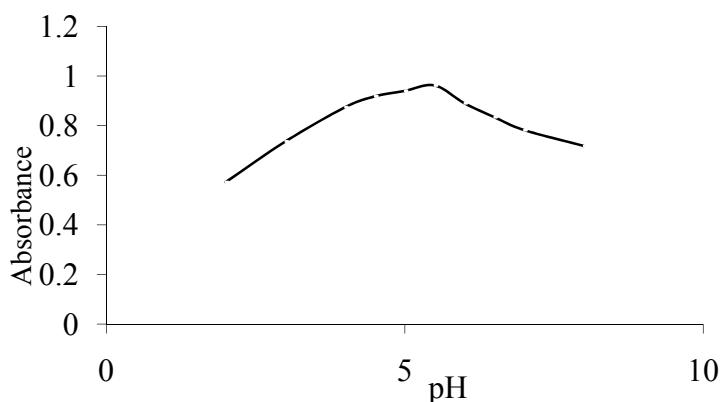


Figure.2. Variation of absorbance with pH for 4-dimethyl amino benzyl thiourea-copper complex

Effect of reagent concentration: The effect of 4-dimethyl amino benzyl thiourea reagent concentration has been studied by taking constant 2 mL of copper solution and 3.0 mL of pH 5.5 buffer solution. The reagent concentration was varied between $1 \mu\text{g mL}^{-1}$ and $10 \mu\text{g mL}^{-1}$ to obtain maximum color formation. Maximum color development of the complex and maximum absorbance is observed at $6 \mu\text{g mL}^{-1}$. Hence a $6 \mu\text{g mL}^{-1}$ of the reagent is maintained for all further studies.

Effect of diverse ions: Effect of foreign ions on the complexation of copper has been evaluated by measuring the absorbance of solution containing $10 \mu\text{g}$ of copper (II) in 25 mL of distilled water. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of copper. The results are summarized in **Table 1**. The formation of the Cu (II)- complex was not influenced by alkaline, earth alkaline ions, some transition metal ions, or other anions. The concentrations of Cr^{3+} , Co^{2+} and Ni^{2+} , in real samples were found to be within tolerable limits. Therefore the procedure could be applied to these samples.

Table-1: Tolerance limit of foreign ions on copper ($10 \mu\text{g L}^{-1}$) determination by proposed method

Substance	Maximum tolerable ion amount ($\mu\text{g L}^{-1}$)
K^{+2}	1
Mg^{2+}	0.5
Ca^{2+}	0.5
Cl^{-}	0.2
Al^{3+}	0.08
Cd^{2+}	0.05
Co^{2+}	0.05
Zn^{2+}	0.05
Ni^{2+}	0.04
Na^{+}	0.2
SO_4^{2-}	0.05
Cr^{3+}	0.15
Fe^{3+}	0.3
NO_3^-	0.1
Pb^{2+}	0.01

Stability of the color reaction: The absorbance values of 4-dimethyl amino benzyl thiourea –copper complex were noted at different intervals of time at 390 nm. It was observed that the absorbance remained constant upto 6 hours. Thereby this indicates that the coloured complex is stable for at least 6 hours.

Sensitivity and molar absorptivity: The molar absorptivity of the complex was calculated and reported as $2.3 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and the Sandell's sensitivity of the complex was found to be $2.4283 \times 10^{-3} \mu\text{g cm}^{-2}$.

Solid Phase Extraction: Experiments were carried out in order to investigate the retention of reagent-metal complex on the glass column containing stop cock. It was determined that the reagent-metal complex was retained on the column quantitatively when it passed as an aqueous solution by taking 75 mg of reagent and 50 mg of metal in 100 mL.

GENERAL PROCEDURE

Known aliquots of the sample was poured into a 100 mL beaker and to this add 5 mL of pH 5.5 buffer solution, 3 mL of reagent solution and 2 mL of metal solution. This mixture was diluted to a volume of 50 mL and mixed well. After 10 min, the solution was passed through the column at a flow rate of 2.5 mL min^{-1} . After the enrichment was finished, the retained complex was eluted from the column with 6 mL of n-butanol at a flow rate of 1.5 mL min^{-1} . The absorbance of the eluent was measured at 390 nm against reagent blank prepared by using same procedure without metal solution.

APPLICATIONS

The procedure developed for the determination of copper was successfully applied to determine the content of copper in various water and industrial effluent samples.

Application of method to natural water samples: The proposed procedure was applied for the preconcentration and determination of copper metal ion in natural water samples. The natural water samples were collected in and around Tirupati, India. Analysis of copper in natural water samples was carried out as described in general procedure. The results are presented in **Table 2**.

Table- 2: Determination of copper in various water samples

Sample	Cu added ($\mu\text{g mL}^{-1}$)	Proposed method ($\mu\text{g mL}^{-1}$)	
		Found ^a	Recovery (%) ^a
Polluted water ^b	-	0.16 ± 0.02	-
Natural water ^c	0.3	0.28 ± 0.04	93.33
	1.0	0.99 ± 0.03	99.00
Bore well water ^d	-	1.0 ± 0.04	-
Drinking water ^e	0.3	1.26 ± 0.06	96.92
	0.6	1.58 ± 0.02	98.75

a) Mean ± standard deviation (n=6), b) Collected from near Gajulamanyam Industrial area, A.P., India

c) Collected from Swarnamukhi river, Srikalahasti, A.P, India. d) Collected from in and around Tirupati,

e) Collected from municipal water supply, Tirupati.

Application of method to various milk samples for copper determination: Take 100 mL of milk sample into a platinum capsule. Evaporate to dryness, char, and ignite the residue at 450°C to a white carbon free ash. Dissolve the residue in 5 to 10 mL of 10% hydrochloric acid. In cases of incomplete solubility, heat the sample on a steam bath to dissolve the residue completely. Transfer the solution quantitatively to a 50 mL separatory funnel; add 1 mL of 4N tartaric acid, 3 mL of freshly prepared reagent solution, followed by 5 mL chloroform. Add a sufficient amount of 4 N sodium hydroxide to make the medium alkaline. Shake the separatory funnel vigorously to extract all of the Cu(II)- reagent complex formed in the aqueous layer. Transfer the chloroform layer to a 10 mL standard flask. Continue the extraction with 3 and 2 mL volumes of chloroform, respectively. Fill the flask to the mark, and measure the absorbance of the solution against a similarly prepared reagent²² blank at 390 nm. The results are shown in **Table 3**.

Table-3: Determination of copper content in various milk samples

Sample	Amount of Copper founda ($\mu\text{g mL}^{-1}$)		C.V(%)
	Standard Reagent	Synthesized Reagent ^e	
Heritage Milk ^b	0.62	0.58±0.02	3.4
Dodla Milk ^b	0.86	0.85±0.04	4.7
Sangam Milk ^b	0.54	0.52±0.02	3.8
Local Buffalo Milk ^c	1.0	0.98±0.03	3.0
Local Cow Milk ^d	1.6	1.59±0.05	3.1
Balaji Milk ^b	0.48	0.46±0.02	4.3

a) Mean±S.D, b) collected from local markets, c) Jersi Buffalo milk collected from Tirupati, d) Regional Cow milk collected from chandragiri. e) Leuco Methylene Green reagent procured from local market

CONCLUSIONS

It is noted from the literature that there is much scope for development of new reagents for the extractive spectrophotometric determination of copper in various environmental samples. The proposed method is highly sensitive when compared to the reported methods for the extraction-spectrophotometric determination of copper. This method offers advantages like reliability and reproducibility, in addition to its simplicity, instant color development and less interference. The selectivity of this method is improved by using masking. This method was successfully applied for the determination of copper in various samples.

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