

SHORT COMMUNICATION

MICROWAVE ASSISTED SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COPPER USING LEUCOCRYSTAL VIOLET

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ABSTRACT. A sensitive spectrophotometric method has been developed for the trace determination of copper using leucocrystal violet as chromogenic reagent. The proposed method is based on the reaction of copper(II) with potassium iodide in acid medium to liberate iodine, which oxidizes leucocrystal violet to crystal violet dye having absorption maximum at 590 nm. The reaction between copper and potassium iodide is accelerated by irradiating the mixture with microwave energy for 15 s at 480 W. Beer's law is obeyed in the concentration range 0.004 – 0.04 µg mL⁻¹. The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit were found to be 1.47×10^6 L mol⁻¹ cm⁻¹, 4.3×10^{-6} µg mL⁻², 0.001 µg mL⁻¹, 0.0043 µg mL⁻¹, respectively. The optimum conditions and other analytical parameters were evaluated. The effect of interfering ions on the determination is described. The proposed method has been successfully applied for the determination of copper in environmental samples like tap water, agricultural run off water, plant materials and pharmaceutical samples.

KEY WORDS: Spectrophotometry, Copper determination, Leucocrystal violet

INTRODUCTION

Copper is widely distributed and has diverse functions in plants and animals. It is an essential trace metal for animals and man because it is required for the formation of erythrocytes and hemoglobin [1, 2] as well as oxidative enzymes [3]. It is widely used in the form of wire, rods, cooking utensils. It is also used in anti fouling paints, in insecticides, as rot-proofing agent for fabrics and forms alloys [4]. Inhalation of dusts, fumes and mists of copper salts results in congestion of nasal septum [5]. Copper metal fumes or salts cause salivation, nausea, vomiting, gastric pain etc. Contact with skin causes itching eczema. In chronic exposure, liver, kidney and spleen may be injured and may develop anemia [5]. Toxicity of dissolved copper(II) is considered less than mercury but greater than cadmium, silver, lead and zinc [6]. A limit of 0.1 mg m⁻³ for copper fume has been tentatively suggested. The Public Health Service for drinking water standard is 1 mg dm⁻³ or 1 ppm [5]. As a pollutant, copper is of particular concern, because of its high degree of toxicity to aquatic organism. In view of this, simple and sensitive methods are required for the trace determination of copper.

Several methods like AAS [7], ICP-AES [7], flow injection catalytic photometric method [8, 9], adsorptive cathodic stripping voltammetry [10], derivative potentiometric stripping analysis [11] and spectrophotometric methods [12-15] are reported in literature for the determination of copper(II). Spectrophotometric methods for the determination of copper are far more convenient and economical to other methods. However, the reported spectrophotometric methods suffer

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from certain drawbacks, such as few are extractive, less sensitive, time consuming while few others suffer from narrow range of determination. In the present work, a sensitive spectrophotometric method to determine copper(II) with leucocrystal violet (LCV) is proposed, based on the well-known reaction, that is, liberation of iodine by copper(II) from potassium iodide in acidic medium. Heating in a microwave oven accelerates this reaction, which enables the trace determination of copper. The liberated iodine oxidizes leucocrystal violet to crystal violet dye, which is measured at 590 nm. The experimental variables affecting color formation and the possible interference of foreign ions were studied. The optimum conditions established are incorporated in the recommended procedure, which was applied to determine copper(II) in tap water, agricultural run off water, plant materials and pharmaceutical samples.

EXPERIMENTAL

Instruments

A Systronics (India) 109 spectrophotometer with 1 cm matched quartz cells, a Systronics (India) 331 pH meter and a domestic LG (India) microwave oven were used.

Reagents

All chemicals used were of analytical reagent grade and double distilled water was used throughout the experiment. A stock solution containing 1 mg mL⁻¹ copper was prepared by dissolving 3.929 mg of copper sulfate (BDH, India) in distilled water and volume made up to 1 L. Working standards were prepared by appropriate dilution of the stock solution. Potassium iodide (Merck, India): 2 % aqueous solution. Leucocrystal violet (Eastmann Kodak Co.): 250 mg of leucocrystal violet was dissolved in 200 mL distilled water containing 3 mL 85 % phosphoric acid (Merck, India) and the volume was made up to 1 L with distilled water and was stored in amber colored bottle away from sunlight. Hydrochloric acid (BDH, India): 2 M aqueous solution. Sodium hydroxide (LOBA Chemie, India): 0.1 M aqueous solution.

Procedure

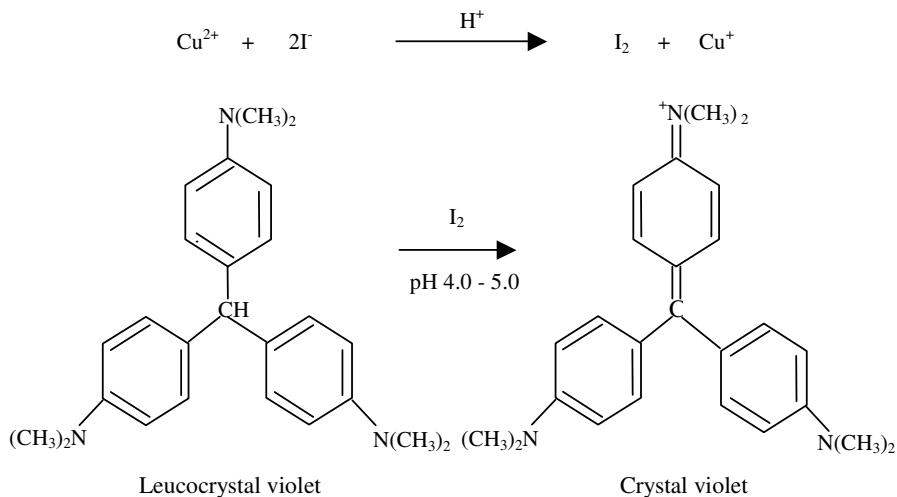
To an aliquot containing 0.1 to 1.0 µg of copper(II), 2 mL of 2 % potassium iodide and 2 mL of 2 M hydrochloric acid were added and was heated in the center of microwave oven at medium power (480 W) for 15 s in a covered graduated 25 mL beaker for liberation of iodine. To this 1 mL of 0.125 % (w/v) solution of LCV was added followed by addition of ~15 mL of 0.1 M sodium hydroxide solution with shaking till slight turbidity. The content was then kept in a water bath at 75 °C for 2 min, when a violet colored dye was formed. The volume was made up to 25 mL and kept for 15 min for full color development. The absorbance was measured at 590 nm against the reagent blank.

RESULTS AND DISCUSSION

Spectral characteristics

The crystal violet dye shows a maximum absorbance at 590 nm against reagent blank and the reaction system is represented in Scheme 1. The reagent blank showed negligible absorbance at this wavelength. Beer's law was obeyed over the concentration range 0.004–0.04 µg mL⁻¹ of

copper(II) with a good correlation coefficient ($r = 0.9994$) and an intercept of 0.0168. The slope of the calibration curve leads to a molar absorptivity of $1.47 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$. The Sandell's sensitivity [18], detection limit ($D_L = 3.3 \sigma/m$) and quantitation limit ($Q_L = 10 \sigma/m$), where σ = standard deviation of the reagent blank and m = slope of calibration curve [19] were found to be $4.3 \times 10^{-5} \mu\text{g cm}^{-2}$, $0.001 \mu\text{g mL}^{-1}$ and $0.0043 \mu\text{g mL}^{-1}$, respectively.



Scheme 1. Reaction between KI-Cu(II) system with LCV.

Effect of variables

It was found that under optimum conditions 2 mL of 2 % potassium iodide, 2 mL of 2.0 M hydrochloric acid and 1 mL of 0.125 % (w/v) solution of LCV were required for full color development. At higher concentration of reagents, absorbance remained unchanged. The most suitable pH range was found to be 4.5 ± 0.5 for which ~ 15 mL of 0.1 M sodium hydroxide was required. Below pH 4.0 no color was observed and above pH 5.0 solution becomes turbid. For maximum liberation of iodine, prolonged heating at 100°C was required. Using a microwave oven eliminated this. Suitable range for heating was medium power (480 W) for 15 s. For final color development, after adding LCV, the contents required heating on a water bath at 75°C for 2 min. The maximum absorbance was obtained after 15 min and the color was stable for more than 24 h. The reproducibility of the method was checked by seven replicate analyses of 0.4 μg per 25 mL of copper solution. The standard deviation and relative standard deviation were found to be ± 0.005 and 1.25 %, respectively. The effects of various foreign ions that are likely to interfere in the determination were studied (Table 1). Most of the ions do not interfere. Selenium causes interference, which can be masked by DMG, ethanolic solution [20]. Fe³⁺ also interferes, which can be masked by sodium fluoride. When present above tolerance limit, iron and selenium gave higher absorbance values.

Determination of copper in tap water

In tap water, amount of copper was found to be negligible. Applicability of the method was checked by adding known amount of copper to water samples. The percent recovery was found to be 98 – 99 % (Table 2).

Table 1. Effect of diverse ions (concentration of copper: 0.4 µg per 25 mL).

Foreign species	Tolerance limit ($\mu\text{g mL}^{-1}$) ^a
PO_4^{3-} , SO_4^{2-} , CO_3^{2-}	2000
Sn^{4+} , Co^{3+}	1500
As^{5+}	1100
H_2O_2 , NO_2^-	100
VO_4^{3-} , $\text{Cr}_2\text{O}_7^{2-}$	40
Se^{2+}	30
Fe^{3+}	10

^aTolerance limit may vary the absorbance values by $\pm 2\%$.

Table 2. Determination of copper in tap water.

Tap water ^a	Copper added (μg)	Copper found ^b (μg)		Recovery (%)	
		Present method	Reported method [18]	Present method	Reported method [18]
Sample 1	2	1.96 ± 0.01	1.98 ± 0.01	98.0	99.0
Sample 2	4	3.96 ± 0.03	3.94 ± 0.05	99.0	98.5
Sample 3	6	5.93 ± 0.04	5.89 ± 0.03	98.9	98.2

^aVolume of sample: 10 mL. ^bMean of three determinations.

Determination in agricultural run off water

Run off water samples from agricultural fields, where Bordeaux mixture (copper sulfate, lime and water in the ratio 1:1:5) was sprayed, was analyzed by the present and reported method using sodium diethyl dithiocarbamate [16]. The results are given in Table 3.

Table 3. Determination of copper in agricultural run off water.

Run off water ^a	Copper found (μg)	
	Present method	Reported method [18]
Sample 1	5.3 ± 0.3	5.4 ± 0.2
Sample 2	6.2 ± 0.3	6.2 ± 0.4
Sample 3	5.8 ± 0.2	5.9 ± 0.3

^aVolume of sample: 10 mL.

Determination of copper in plant materials

The proposed method was applied for the determination of copper in plant material like potato and papaya. The samples were dried in a muffle furnace at 500 °C for 8 h in porcelain crucible. Dried sample (0.5 g) was weighed and brought into solution by dry ash method [17]. The results show that the proposed method can be applied for the determination of copper in potato and papaya. The results (Table 4) are compared with reported method [16].

Determination of copper in pharmaceutical samples

A multivitamin tablet (Supradyn tablet, Nicholas Piramal Ltd., India) containing copper was dissolved in aqua regia and was heated on a sand bath and evaporated to dryness. The residue was dissolved in water and again evaporated to dryness. The residue was dissolved in 5 mL of dilute hydrochloric acid and the volume made up to the mark with distilled water in a 100 mL standard flask. A suitable aliquot of diluted solution was taken and analyzed for copper according to the proposed method. Iron(III) can be effectively removed from solution by

precipitation with 1-2 mL of saturated solution of sodium fluoride. The precipitate was filtered off before addition of potassium iodide. The results are summarized in Table 4.

Table 4. Determination of copper in plant material and pharmaceutical samples.

Sample ^a	Copper found ^b	
	Present method	Reported method [18]
Potato	0.45 ± 0.03	0.48 ± 0.02
Papaya	3.5 ± 0.4	3.6 ± 0.5
Multivitamin tablet ^c (Supradyn)	3.36 ± 0.02	3.35 ± 0.03

^aAmount of sample = 0.500 g. ^bCopper found in potato (mg), papaya (µg) in 0.5 g sample and tablet (mg per tablet). ^cCertified value of copper in tablet (Supradyn, Nicholas Piramal Ltd., India): 3.39 mg per tablet.

CONCLUSIONS

For the first time, the reaction between copper and potassium iodide was carried out in a microwave oven and leucocrystal violet has been used as a chromogenic reagent for the spectrophotometric determination of copper. The proposed method offers advantages of high sensitivity and does not require extraction into toxic organic solvents. The proposed method was successfully applied to the determination of copper in water samples, plant materials and pharmaceutical samples.

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