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ORIGINAL PAPER

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Copper(II)-catalysed oxidative coupling reaction of 3-hydroxyacetanilide with 3-methyl-2-benzothiazolinone hydrazone for the spectrophotometric determination of traces of copper(II)

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Abstract A spectrophotometric method is developed for the determination of traces of copper(II), based on the catalytic oxidative coupling reaction of 3-hydroxyacetanilide with 3-methyl-2-benzothiazolinone hydrazone in the presence of ammonia and hydrochloric acid. Beer's law is obeyed in the copper(II) concentration range of 0.008–0.16 μg mL^{-1}, and the molar absorptivity at 530 nm is 2.5× 10^5 L mol^{-1} cm^{-1}. The Sandell's sensitivity of the product is 0.000254 μg cm^{-2}. The optimum reaction conditions and other important analytical parameters have been investigated. The proposed method is applied to the analysis of water and soil samples and the results are compared with the literature method.

Keywords Copper(II) · 3-Hydroxyacetanilide · 3-Methyl-2-benzothiazolinone hydrazone · Spectrophotometry

Introduction

The literature concerning the analysis of copper-containing materials is vast. This is due to the widespread interest in copper content in several branches of science such as medicine, biology, industrial chemistry and geology. Copper is widely distributed in nature and various analytical techniques like volumetry [1], potentiometry [2], atomic absorption spectrometry [3], adsorption stripping voltammetry [4] and the use of selective electrodes [5] have been reported for the determination of trace amounts of copper(II). Some catalytic methods for the determination of trace amounts of copper(II) have been reported by several workers using various indicator reactions which have been reviewed [6, 7, 8, 9, 10, 11]. A very recent method for the determination of copper is based on the catalytic redox reaction between methylene blue and ascorbic acid [12]. Most of the methods reported have shortcomings like product instability, the need for extraction, heating and long times for the development of colour, or the addition of too many reagents, which also include oxidizing agents. Another disadvantage is that some of the methods are inapplicable to environment samples.

In view of the above, here we report a sensitive, simple and rapid method for the determination of traces of copper(II). The reaction is based on the catalytic oxidation of 3-hydroxyacetanilide by copper(II), followed by coupling with 3-methyl-2-benzothiazolinone hydrazone in the presence of ammonia and hydrochloric acid to give a pink-coloured product, which is stable for 48 h. The proposed method has been successfully employed for the determination of copper(II) in water and soil samples.

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Experimental

Instrument

A JASCO Model UVIDEC-610 UV-VIS spectrophotometer with 1.0-cm matched cells was used for absorbance measurements.

Reagents and solutions

Copper sulfate pentahydrate (Merck), 3-hydroxyacetanilide (3-HA; Sigma, USA) and 3-methyl-2-benzothiazolinone hydrazone hydrochloride hydrate (MBTH; Sigma, USA) were used without further purification. Ammonia (Merck) and hydrochloric acid (BDH) were used. All other chemicals and solvents used were of analytical reagents grade. Deionized water was used to prepare all solutions and in all experiments.

Stock solution of copper(II) (1 mg mL^{-1}) was prepared by dissolving 0.3929 g of copper(II) salt in water containing 1 mL of conc. sulfuric acid and the solution was diluted to 100 mL. Working solutions of copper(II) were prepared by further dilution of the stock solution. A 0.2% and 0.1% (w/v) solutions of 3-hydroxyacetanilide and 3-methyl-2-benzothiazolinone hydrazone hydrochloride hydrate were prepared by dissolving 200 mg and 100 mg respectively in 100 mL of water. Solutions of 5 mol L^{-1} ammonia and 5 mol L^{-1} hydrochloric acid were used for the experiment.

Standard procedure

A solution containing 0.2–4.0 µg (0.008–0.16 µg mL^{-1}) of copper was transferred into a series of 25-mL calibrated flasks to which 2.5 mL of 3-HA, 2.5 mL of MBTH and 0.5 mL of 5 mol L^{-1} ammonia solution were added; the mixture was shaken for about 20 s for the completion of the reaction. Then, 4 mL of 5 mol L^{-1} hydrochloric acid was added, this was made up to the mark with water and the solution was mixed well. The absorbance of the resulting pink-coloured coupled product was measured at 540 nm against a reagent blank, and the calibration graph was constructed.

Procedure for soil samples

The soil samples were collected from agricultural land in an air-tight polythene bag, stored at room temperature (27 °C) and analysed within 48 h. A 20-g air-dried soil sample was taken in a 500-mL beaker and 250 mL of 1:10 hydrochloric acid was added. The sample was heated at reflux on a boiling water bath for 3 h, shaking frequently. Hot solution was filtered into 1-L calibrated flask, the residue was washed three times with 10-mL portions of 1:10 hydrochloric acid and diluted to the mark with water. The standard procedure was followed for copper determination.

Procedure for water samples

Tap water samples were collected in polythene bottles from different sources. For the analysis, 1-L water sample was evaporated to 75 mL and transferred along with the washings into a platinum dish. Then, 2 mL of 1:1 sulfuric acid was added to neutralize the alkalinity. A known volume of the neutralized sample was analysed by the standard procedure.

Water sampling and storage

Copper ions tend to be adsorbed on the surface of (glass and metal) sample containers. Therefore, samples were analysed immediately after collection. If storage is necessary, use 0.5 mL of 1:1 hydrochloric acid per 100 mL of sample or acidify to pH 2 with nitric acid to prevent this adsorption.

Literature method

For the validation of the proposed method, the authors selected the method proposed by Haworth and Murnroe [13] as the literature method, which was simple for analysis of copper(II) using the reagent, *N*8-quinolyl-*p*-toluenesulfonamide. The literature method gives a faster rate of colour development for the complex, and the absorbance of the complex is stable for a longer period of time. Most of the common cations and anions did not interfere in this method.

Results and discussion

Spectral characteristics

The proposed method involves the formation of a pink-coloured coupled product with a λ_{max} of 530 nm. The reagent blank had negligible absorption at this wavelength. The absorption spectra of the product and the reagent blank are shown in Fig. 1.

Effect of reagent concentrations

We found that 0.2% of 3-HA and 0.1% of MBTH in the range of 2.0–3.0 mL were necessary to achieve maximum colour intensity. The colour intensity of the product was decreased when the volume of the reagents added was less than the minimum as mentioned above. Hence, 2.5 mL each of 3-HA and MBTH were used for all the subsequent work.

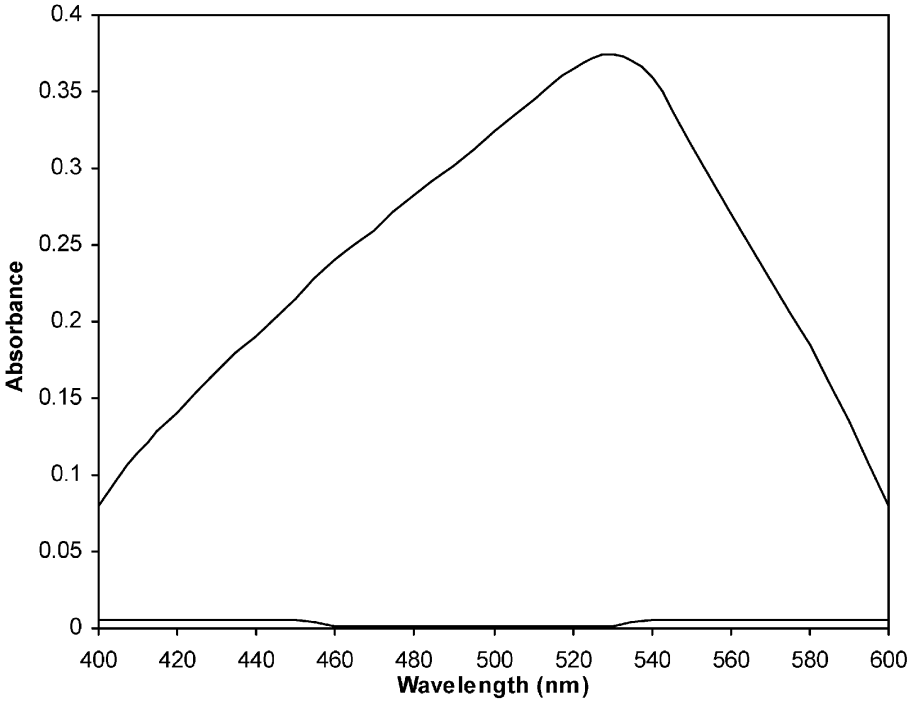


Fig. 1 Absorption spectra of the reaction product (Cu(II) + 3-HA+MBTH) and reagent blank (3-HA+MBTH). Final concentration of copper(II) is 0.08 µg mL^{-1}

Effect of ammonia and hydrochloric acid

Various concentrations and volumes of ammonia and hydrochloric acid were tried. However, 0.3–0.7 mL of 5 mol L^{-1} ammonia and 3–5 mL of 5 mol L^{-1} hydrochloric acid were necessary to achieve maximum colour intensity. Hence, 0.5 mL of 5 mol L^{-1} ammonia and 4 mL of 5 mol L^{-1} hydrochloric acid were used.

Effect of time and temperature on the coloured product

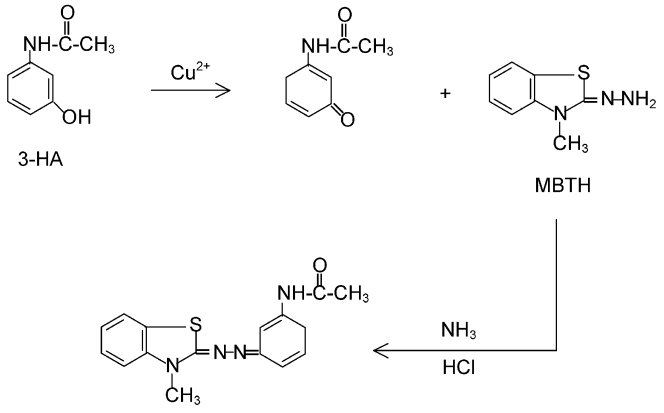
The effect of time on the absorbance of pink product was studied as a function of time for solutions containing different amounts of copper and prepared as described in the standard procedure. The results obtained showed that the maximum absorbance was attained almost instantaneously. In order to obtain maximum sensitivity and constant reading, the absorbance should be measured after 20 s. The colour development is independent of temperature in the range of 20–50 °C, and the coloured product was stable for 48 h; the absorbance varied by not more than 2% over a period of 3 days.

Optical parameters

Beer's law was obeyed over the copper(II) concentration range of 0.008–0.16 μg mL^{-1}. Molar absorptivity, Sandell's sensitivity and other parameters are given in Table 1. The precision and accuracy of the method was studied by analysing the solution containing known amounts of cited reagents within the Beer's law limit. The lower values of relative standard deviation (%) and percentage errors indicated the high accuracy of the method.

Reaction mechanism

The reaction involves catalytic oxidation of 3-hydroxyacetanilide by copper(II) and the oxidized product is then coupled with MBTH in the presence of ammonia solution to give a red precipitate and dilution with hydrochloric acid gives a pink-coloured product (Scheme 1). Under the present experimental conditions, MBTH is not oxidized by copper(II), as the 3-HA has a phenolic group which is prone to oxidation first. Another significant aspect is that ammonia acts as an activator [7] for the catalytic action of copper(II).



Scheme 1 Reaction sequence for the formation of the coupled product

Interference studies

The effect of various cations and anions on the determination of copper(II) was investigated. The tolerance limit was taken as the amount that caused ±2% absorbance error in the determination of 0.08 μg mL^{-1} of copper(II). The results are given in Table 2. Cyanide, EDTA, ferrocyanide and ferricyanide interfere seriously by decolouring the solution. The interference from Fe(III) can be eliminated by the addition of fluoride.

Analytical application

The proposed method is applied to the determination of copper(II) in tap water and soil samples. A comparison of our results with the literature method is given in Table 3. Recovery experiments were performed using the method of addition for synthetic samples only.

Table 1 Optical Characteristics and precision data

Parameters/characteristics	Product
Colour	Pink
λ_{max} (nm)	530
Stability (h)	48
Beer's law range (μg mL^{-1})	0.008–0.16
Molar absorptivity (L mol^{-1} cm^{-1})	2.5×10^5
Sandell's sensitivity (μg cm^{-2})	0.000254
Regression equation (*Y*)[a]	
Slope (a)	2.763
Intercept (b)	0.0225
Correlation coefficient (*r*)[b]	0.9924
Relative standard deviation (%)[b]	0.5524
Range of error (95% confidence level)	±0.7667
Detection limit (μg mL^{-1})	0.003

[a]y=ax+b, where x is the concentration of copper(II) in μg mL^{-1}
[b]n=5

Table 2 Effect of foreign ions on the determination of 0.08 μg mL^{-1} of copper(II)

Foreign ions	Tolerance limit (μg mL^{-1})
Na^+, NH_4^+, SO_4^{2-}, Cl^-, tartarate, Ca^{2+}, Mg^{2+}, NO_3^-, PO_4^{3-}	600
F^-, Mg^{2+}, CO_3^{2-}, Ba^{2+}	400
Fe^{2+}, SO_3^{2-}, CH_3COO^-	100
Pb^{2+}, Sn^{2+}, I^-, Mn^{2+}, Fe^{3+}[a]	40
Co^{2+}, Hg^{2+}, Cd^{2+}, $C_2O_4^{2-}$, S^{2-}	20

[a]Can be masked up to 40 μg mL^{-1} by the addition of 1% sodium fluoride solution

Table 3 Determination of copper (II) in various samples

Sample	Copper (II) added ($\mu g\ mL^{-1}$)	Proposed method		Literature method [13]	
		Copper (II) found[a] ($\mu g\ mL^{-1}$)	Mean recovery (%)	Copper (II) found* ($\mu g\ mL^{-1}$)	Mean recovery (%)
Synthetic sample	0.01	0.01	100	Not found	–
	0.06	0.058	96.7	0.057	95.0
	0.08	0.079	98.8	0.08	100.0
	0.12	0.116	96.7	0.115	95.8
Tap water	–	0.01	–	Not found	–
	–	0.10	–	0.09	–
	–	0.14	–	0.14	–
Soil sample	–	0.146	–	0.146	–
	–	0.152	–	0.154	–
	–	0.158	–	0.155	–

[a]Average of five determinations

Table 4 Comparison of spectrophotometric methods for the determination of copper(II)

Sl. No.	Reagent	λmax (nm)	Molar absorptivity ($L\ mol^{-1}\ cm^{-1}$)	Sandell's sensitivity ($\mu g\ cm^{-2}$)	Application	Ref.
1	1-(3-Chlorophenyl)-3-hydroxy-3-methyltriazen	415	0.925×10^3	0.0686	No application	[14]
2	Phenanthrene-9,10-quinone monoximate	470	6.3×10^4	0.001	Wastewater, wine and fly ash	[15]
3	1-Phenyl-4,4,6-trimethyl-1*H*,4*H*-pyrimidine-2-thiol	400	1.3×10^4	0.0048	No application	[16]
4	4-hydroxy-3-[(2-hydroxy-3,5-dinitrophenyl)azol-naphthalene-2,7-disulphonic acid	550	2.1×10^4	Not given	Rock sample	[17]
5	2-Methyl-3-chloro-5-hydroxy-4-naphthoquinone	520	0.62×10^4	0.5124	No application	[18]
6	*S*,*S*′-Bis(2-aminophenyl)oxalate	504	0.536×10^4	Not given	Pharmaceutical formulations, environmental and foodstuff samples	[19]
7	9-Phenyl-2,3,7-trihydroxy-6-fluorone	595	0.67×10^4	Not given	Blood serum	[20]
8	3-Methyl-2-benzothiazolinone hydrazone hydrate + 3-hydroxyacetanilide	540	2.5×10^5	0.00254	Water and soil samples	Present work

Conclusions

The present method is simple, rapid and highly sensitive for the determination of copper(II). Extraction or heating is not necessary. This fact makes it easy for the metal ion determination, because a tedious and expensive prior solvent extraction step, which generally uses toxic organic solvents, is not required. A number of associated elements do not interfere in the determination. The method is well suited for the analysis of environmental samples. A comparison of the analytical performances with those of literature methods is given in Table 4.

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