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Analytical method development for extractive spectrophotometric determination of copper (II) using 1, 2 Propanedione,1-phenyl-1-(2-hydroxy-5-bromobenzilidine azine) -2-oxime (PDPHBBAO)

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Abstract

The reagent 1, 2 Propanedione,1-phenyl-1-(2-hydroxy-5-bromobenzilidine azine) -2-oxime (PDPHBBAO) has been synthesized and it was subjected to FTIR, NMR, elemental analysis and Mass Spectroscopy for characterization. This reagent was then applied for extractive spectrophotometric determination of Cu(II). Copper metal forms dark yellow coloured complex, which can be extracted in chloroform at pH 9.6, having absorption maxima at 440 nm. Beer's law is obeyed in the concentration range 1-10.00 µg. The Molar absorptivity and Sandell's sensitivity was calculated on the basis of total Copper(II) taken and found to be 5.9909X 10^3 Lit mol^{-1} cm^{-1} and 10.6 X 10^{-3} µg / cm^2 respectively.

The developed method is highly sensitive, selective, simple, rapid, accurate, and has been satisfactorily applied for the determination of copper in the synthetic mixtures, alloys, beverages, milk samples etc.

Key words: Characterization; Copper; Extractive Spectrophotomertic determination.

1. Introduction

Copper is a biocidal agent that can add to the anti-bacterial and antimicrobial features of a building where germs are reduced[1]. Copper has wide spectrum of applications as in electrical conductor, heat conductor, as a building material, as a component of various alloys, essential trace nutrient, as a co-factor in various enzymes, as a decorative metal art, and as an anti-germ surface.

A wide variety of Chelating agents[2-27] have been reported for the spectrophotometric determination of copper. However these methods suffer from limitations such as critical

pH, low stability of complex, requirement of surfactants or other agents, requirement of heating, and interference from some ions, inconvenient extractant etc. A method, far superior in sensitivity and selectivity to these reported in the literature, is developed for the extractive spectrophotometric determination of copper with PDPHBBAO. A close literature survey indicates that PDPHBBAO has so far not been employed for either co-ordination or analytical studies. The developed method is highly sensitive, selective, simple, rapid, accurate, and has been satisfactorily applied for the determination of copper in the synthetic mixtures, milk samples, beverages industrial waste water etc. The proposed method is free from many limitations.

Experimental

The **PDPHBBAO** was synthesized[28,29,30], characterized[31] and used for extractive spectrophotometric determination of Cu(II) A stock solution (0.5 mg ml^{-1}) of PDPHBBAO was prepared by dissolving 0.05 g of the reagent in 100ml methanol to give 0.005% reagent solution of PDPHBBAO.

Copper (II) Solution

A weighed quantity of Copper Sulphate ($CuSO_4.5\ H_2O$) was dissolved in double distilled water containing dilute sulphuric acid and then diluted to the desired volume using double distilled water. An aliquot of this solution was used for determination of copper by diethyldithiocarbamate

Recommended procedure :

Aqueous solution containing 1-100µg of copper and 1 cm^3 of 0.005 % methanolic solution of PDPHBBAO was mixed in 25 cm^3 beaker. The pH of the solution was adjusted to required value with dilute solution of H_2SO_4 and NaOH. The final aqueous volume was made up to 10 cm^3. The solution was then transferred into 125 cm^3 separating funnel and equilibrated for 1 min with 10 cm^3 chloroform. Allow the two phases to separate and measure the absorbance of the organic extract containing the complex at 440 nm against reagent blank.

Results and Discussion

Condition	Results
Absorption Maxima	440 nm
Solvent	Chloroform
pH range	9.0–10.0.
Equilibration time	*1 min*
Stability of Copper-PDPHBBAO	*15 h*
Beer's range	0.1 to 10.0 µg ml^{-1}
Molar absorptivity $mol^{-1}\ cm^{-1}$	5.9909 X 10^3 lit
Sandell's sensitivity	10.6 X 10^{-3} µg /cm^2
Mole Ratio of Cu : PDPHBBAO	1 : 1

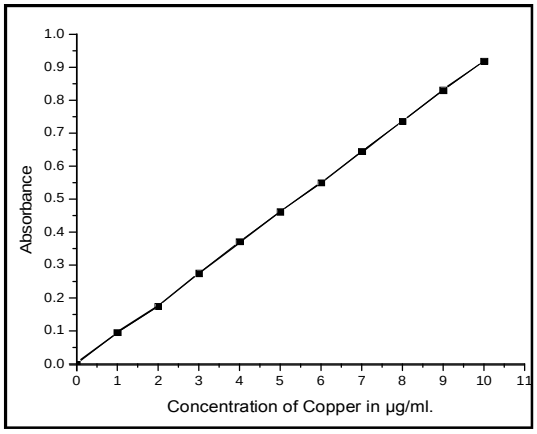

Fig. 1. Calibration Plot

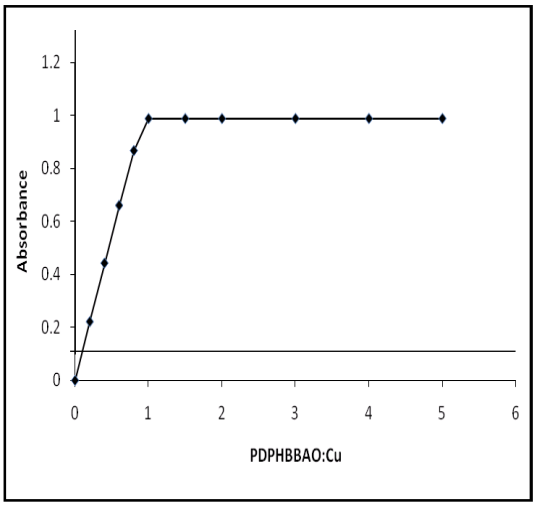

Fig. 2. Mole Ratio Plot

Precision and accuracy in the determination of copper

Concentration copper (µg)		SD	% RSD
Taken	Found[a]		
0.50	0.501	0.0028	0.56
0.75	0.750	0.0033	0.44
1.00	0.998	0.0050	0.51
1.25	1.250	0.0047	0.38
1.50	1.502	0.0052	0.35

[a] Average of five determinations

Effect of foreign ions :

Different amounts of diverse ions were added to 5.0 µg copper and were extracted according to the present procedure. The tolerance limit of an ion was taken as the maximum amount (mg) causing an error not greater than ± 2% in the absorbance value of the organic extract. Most of the ions associated with copper do not interfere, except Ag^+. The interference from large amounts of Ag^+ can be overcome by masking it with iodide. The results are shown in Table 2.

Table 2 Effect of foreign ions

Anion added	Amount added in mg.	Cation added	Amount added in mg.
Chloride	20	Ca	2
Fluoride	10	Sr	2
Bromide	20	Ba	2
Iodide	10	Mo	5
Bromate	10	Mn	5
Iodate	10	Mg	10
Chlorate	10	V	5
Chromate	15	Rh	1
Dichromate	15	Tl	5
Carbonate	10	U	5
Phosphate	05	Th	2
Urea	20	Li	5
Thiourea	10	Ce	2
Acetate	20	Zr	2
Thiosulphate	05	Cd	2
Oxalate	10	Al	2
Nitrate	10	Hg	5
Nitrite	10	As	5
Sulphate	20	Zn	5

Applications

The present method was applied for determination of amount of copper (II) in various samples as alloys, synthetic mixtures, milk samples, beverages as Beer and Wine, and industrial waste water.. The results are shown in Table 3.

Table 3. Applications

	Sample	Amount of Cu (II)	
		Standard method	**Present method**
Copper alloys.	Cupronickel	35.0%	34.8 ± 0.03%
	Brass	60%	59.90 ± 0.05%
	Devarda's Alloy	47.9 %	47.9± 0.07 %
	Tin Base White Metal	3.5 %	3.55±0.09 %
Milk Samples2.	Raw Milk	$4.8X10^{-2}$	$4.7X10^{-2} \pm 0.07X10^{-2}$
	Chocó Milk	$7.5X10^{-2}$	$7.3X10^{-2} \pm 0.08X10^{-2}$
Synthetic mixture.	Cu(55)+Zn (45)	55 ppm	54.9~0.07Ppm
	Cu (100) + Zn(100)+Cd (100)	100 ppm	98.5 ± 0.05Ppm
Beverages.	Beer (Bottle)	6.6 µg	6.5 ± 0.07 µg
	Wine (Bottle)	8.7 µg	8.6 ± 0.08 µg
	Industrial Waste Water at Ulhasnagar Creek	3.6 ppm	3.4 ± 0.05 ppm

Every result is average of three independent determinations.

Conclusion

The results obtained show that the newly developed method in which the reagent PDPHBBAO was used, can be effectively used for quantitative extraction and estimation of Cu (II) from aqueous media. The proposed method is quick and requires less volume of organic solvent. The results show good agreement with the standard methods. The method is very precise, faster and simpler than other methods.

The proposed method is more highly sensitive and selective than the reported methods for the extractive spectrophotometric determination of microgram amounts of copper. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of copper at trace level in alloys, synthetic mixtures, milk samples, beverages as Beer and Wine, and industrial waste water.

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