DEVELOPMENT OF METHOD FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF Cu (II) WITH OF HYDRAZINE CARBOXAMIDE-2-[(2-HYDROXY-1-NAPHTHALENYL) METHYLENE] AS AN ANALYTICAL REAGENT

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ABSTRACT

A spectrophotometric method has been developed for the determination of Cu (II) using Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n-butanol at pH 8.4. The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity calculated were 0.1589×10^4 Lmol^{-1}cm^{-1} and 0.1567 μg/cm^{-2} respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Key words: Copper, Spectrophotometric determination, n-Butanol, Hydrazine carboxamide-2-[(2-Hydroxy-1-Naphthalenyl)methylene]

INTRODUCTION

Copper is one of the most important metals after iron. It plays a vital role in many fields either as metal or its salts such as industry, laboratory, medicine, food, and beverage. Copper and its salts are highly toxic to lower organisms much more than man, however, it is an essential constituent of certain proteins. Recent literature suggests that taste is impaired when copper deficiency is induced[1]. Its toxic effect is main cause of Wilson's disease[2]. In plant physiology it is essential as a component of a number of different plant enzymes[3]. It is one of the most harmful impurities in semiconductor materials[4]. Several compounds are known to react with the metal ions to give coloured complexes and have been employed for

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the quantitative extraction and spectrophotometric determination of metals at trace levels. In continuation to our earlier work[5,6] on the extractive spectrophotometric determination of copper we reported herein the present investigation a novel method for the extractive spectrophotometric determination of copper, which is found to be simple, sensitive, rapid and precise.

EXPERIMENTAL

The reagent Hydrazine carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] was synthesized by the given procedure. The stock solution of Copper (II) was prepared by dissolving a weighed amount of its sulphate in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by diethyldithocarbamate method[7]. Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer with 1 cm quartz cells and digital pH meter with combined glass electode respectively.

Procedure for the extraction

1.0 mL of aqueous solution containing 0.1 mg of Copper metal and 1 mL of reagent were mixed in a 50 mL beaker. The pH of the solution adjusted to 8.4 with 0.2 M boric acid and potassium chloride, keeping the volume 10 mL. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10 mL measuring flask and made up to the mark with organic solvent, if required. After separation of the two phases, the pH of the aqueous phase was measured and the Cu (II) in each phase was determined by diethyldithiocarbamate method[7].

RESULTS AND DISCUSSION

The reagent HCHNM forms greenish yellow coloured complex with Cu (II), which was extracted into organic phase. The extraction of Cu (II) froms an aqueous phase by HCHNM in n-Butanol is studied over a wide range of experimental condition. The results of various studies are discussed below.

Extraction as a function of pH

The extraction of copper with Hydrazine carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] has been studied over the pH range 1-10 and was observed that percentage extraction of Cu (II) is maximum at pH 8.4.

Absorption spectrum

The absorption spectrum of Cu (II): Hydrazine carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] in n-butanol shows the maximum absorption at 398 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 398 nm.

Influence of diluents

The suitability of diluents were investigated using organic solvents such as chloroform, ethyl acetate, isoamyl alcohol, xylene, hexane, diethyl ether, toluene, n-butanol, carbon tetrachloride, MIBK, nitrobenzene, etc. The extraction of Cu (II) was quantitative with HCHNM in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

Effect of salting out agents

The presence of 0.1M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Cu (II): Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] complex extract. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration

Various volumes of 0.1% reagent solution were added to the sample solution containing 50 μg of copper at respective pH values. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 mL. Therefore, 1 mL of 0.1% reagent was chosen for the quantitative determination of the metal.

Effect of equilibration time and stability of the complex

The study of change in absorbance with variation in equilibrium time for extraction of the complex into organic solvent shows that equilibration time of 30 sec. are sufficient for the quantitative extraction of Copper. The study of stability of colour of the Cu (II): HCHNM complex with respect to time shows that the absorbance due to extracted species is stable up to 30 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of copper.

Calibration plot

A calibration plot of absorbance against varying copper concentration and fixed

HCHNM concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of copper (Fig. 1). This shows that the Beer's law is obeyed in this range. The molar absorptivity and sandell sensitivity were calculated to be is 0.1589×10^4 $Lmol^{-1}cm^{-1}$ and 0.1567 $\mu g/cm^{-2}$, respectively.
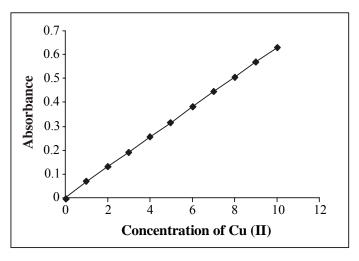

Fig. 1: Calibration plot of Cu (II): HCHNM complex

Nature of extracted species

The composition of extracted species has been determined by Job's continuous variation method, Slope ratio method (Fig. 2) and Mole ratio method. It shows that the composition of Cu (II): HCHNM complex is 1 : 2.
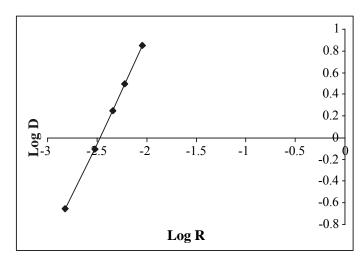

Fig. 2: Slope ratio method for Cu (II): HCHNM complex

Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 50 μg of copper. The ions which show interference in the spectrophotometric determination of copper were overcome by using appropriate masking agents (Table 2).

Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method has been studied by analyzing five solutions each containing 60 μg of copper in the aqueous phase. The average of five determinations were 60.02 and variation from mean at 99% confidence limit was ± 0.2920.

Applications

The proposed method was successfully applied for the determination of copper from various alloys and synthetic mixtures. The results found to be in good agreement with those obtained by the standard known method. (Table 1).

Table 1: Determination of Cu (II) using HCHNM from different samples

Sample	Amount of Cu (II)	
	Standard method	**Present method[b]**
Alloys		
(1) Cupro-Nickel	35.0%	34.98 %
(2) Brass	60.0%	59.97%
(3) Tin Base white	3.5%	3.49%
Synthetic mixture composition[a]		
(1) Cu (10) + Ni (10)	9.99 ppm	9.98 ppm
(2) Cu (55) + Zn (45)	55.0 ppm	54.9 ppm
(3) Cu (100) + Zn (100) + Cd (100)	100 ppm	99.7 ppm

[a]Values given are in microgram amount of the metals.

[b]Avarage of five determinations.

Table 2: Effect of divelent ions and foreign ions

Ion	Tolerated ratio	Ion	Tolerated ratio
Cl^-	1 : 20	Zn^{2+}	1 : 14
Br^-	1 : 18	Ag^+	1 : 17
F^-	1 : 10	K^+	1 : 20
ClO_3^-	1 : 13	Mg^{2+}	1 : 15
BrO_3^-	1 : 16	Ca^{2+}	1 : 10
IO_3^-	1 : 10	Ba^{2+}	1 : 12
SO_3^{2-}	1 : 17	Bi^{2+}	1 : 9
SO_4^{2-}	1 : 10	V^{+5}	1 : 10
NO_2^-	1 : 11	Cr^{3+}	Masked
NO_3^-	1 : 14	Mn^{2+}	Masked
PO_4^{3-}	1 : 20	Ce^{4+}	Masked
$P_2O_7^{2-}$	1 : 19	CN^-	Masked
ClO_4^-	1 : 20	Tartarate	Masked

CONCLUSION

The proposed method is highly sensitive and selective than the other 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 synthetic mixtures and alloys.

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