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Development of method for extractive spectrophotometric determination of Cu(II) with 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone as an analytical reagent

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ABSTRACT

A spectrophotometric method has been developed for the determination of Cu(II) using 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n-butanol at pH 9.2. The method obeys Beer's law over arrange from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity were 0.97×10^4 L $mol^{-1}cm^{-1}$ and 0.26 $\mu g \cdot cm^{-2}$ respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

***Keywords*:** Copper Spectrophotometric determination; n-Butanol; 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazine

1. 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 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 report here in present investigation a novel method for the extractive spectrophotometric determination of copper, which is found to be simple, sensitive rapid and precise.

2. EXPERIMENTAL

The reagent 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone was synthesized by the given procedure. The stock solution of Cu(II) was prepared by dissolving a weighed amount of 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 electrode respectively.

2. 1. Procedure for the extraction

1.0 ml of aqueous solution containing 0.1mg of copper metal and 1 ml of reagent were mixed in a 50 ml beaker. The pH of the solution adjusted to 9.2 with 0.2 M boric acid and potassium chloride, keeping the volume 10 ml. The solution was transferred to 100 ml separating 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 diethyldithocarbamate method [7].

3. RESULTS AND DISCUSSION

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

3. 1. Extraction as a function of pH

The extraction of copper with 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone has been studied over the pH range 1-10 and was observed that percentage extraction of Cu(II) is maximum at pH 9.2

3. 2. Absorption spectrum

The absorption spectrum of Cu(II): 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone in n-butanol shows the maximum absorption at 410 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 360 nm.

3. 3. Influence of diluents

The suitability of diluents was 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 copper (II) was quantitative with HNPH in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

3. 4. 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): 1-Naphthalene Carboxaldehyde -2-hydroxy phenyl hydrazone complex extract. Therefore, no salting out agent was required during the extraction.

3. 5. Effect of reagent concentration

Various volumes of 0.1 % reagent solution were added to the sample solution containing 70 µg of cobalt 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.

3. 6. Effect of equilibration time and stability of the complex

The study of change in absorbance with variation in equilibrium time for extraction of extraction of the complex into organic solvent shows that equilibration time of 1 min is sufficient for the quantitative extraction of Copper. The study of stability of colour of the Cu(II): HNPH complex with respect to time shows that the absorbance due to extracted species is stable up to 72 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.

3. 7. Calibration plot

A calibration plot of absorbance against varying copper concentration and fixed HNPH 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's sensitivity were calculated to be is 0.97×10^4 L $mol^{-1}cm^{-1}$ and 0.26 µg cm^{-2} respectively.

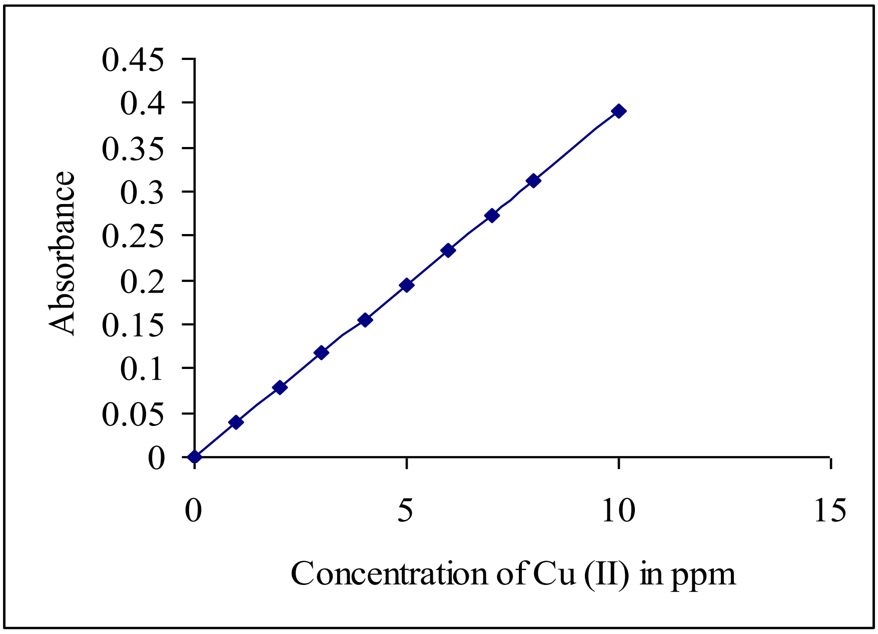

Fig. 1. Calibration plot of Cu(II): HNPH complex.

3. 8. Nature of extracted species

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

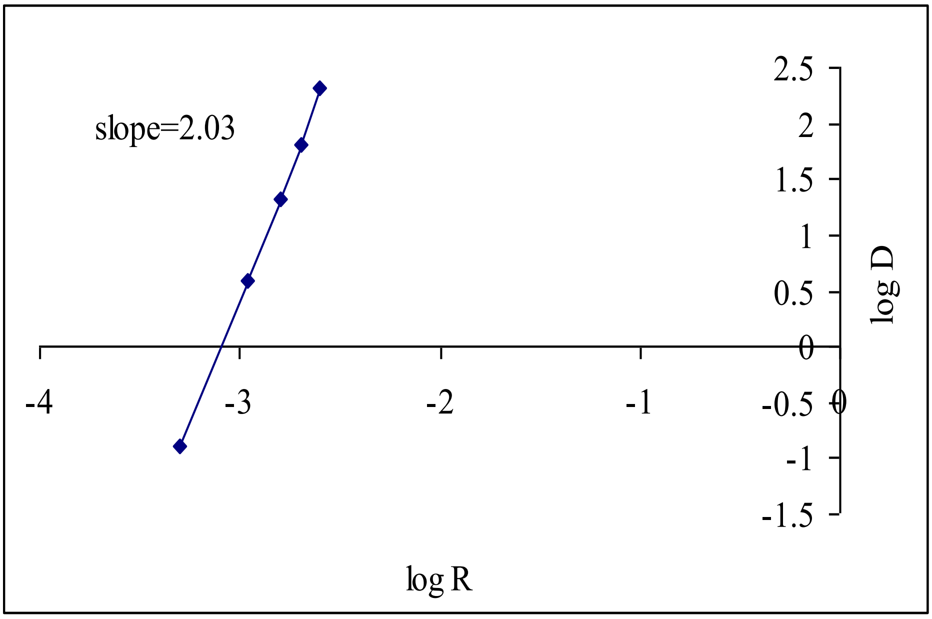

Fig. 2. Slope ratio method for Cu(II) : HNPH complex.

3. 9. Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 30 µg of copper. The ions which show interference in the spectrophotometric determination of copper were overcome by using appropriate masking agents (Table 2).

3. 10.Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing five solutions each containing 60 µg of Copper in aqueous phase. The average of five determinations was 59.96 and variation from mean at 99 % confidence limit was ± 0.27.

3. 11. Applications

Various commercial samples and synthetic mixtures containing Cu(II) were prepared and analyzed according to the recommended procedure and the results were compared to those obtained by standard method. The proposed method facilitates separation of copper (II) from synthetic mixtures. These metal ions do not extract and remain quantitatively in the aqueous phase under the optimum extraction conditions of copper (II) with HNPH system facilitating separation of bivalent cobalt quantitatively by the proposed method. The results found to be in good agreement with those obtained by the standard known method (Table 1) [7].

Table 1. Determination of Cu(II) using HNPH from different samples.

Sr. No	Sample	Amount of Cu(II)	
		Standard method	Present method
I	Copper alloys		
1	Cupronickel	35.0 %	34.9 %
2	Brass	60.0 %	59.8 %
3	Devadra's alloy	47.9 %	47.5 %
4	Monel metal	63.0 %	62.8 %
II	Pharmaceutical Samples		
1	Suparadyn(Nicholas Piramal)	6.7 mg	6.5 mg
2	Multivitamin Capsule (Mayers Organic Ltd.)	5.0 mg	4.8 mg
III	Synthetic mixture		
1	Cu (55) + Zn (45)	55 ppm	54.9 ppm
2	Cu (100) + Zn (100) + Cd (100)	100 ppm	99.8 ppm
IV	Beverages		
1	Beer (Bottle)	5.49 %	5.48 %
2	Wine (Bottle)	3.70 %	3.65 %

Table 2. Effect of divalent 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

4. CONCLUSION

The results obtained show that HNPH in n-Butanol can be effectively used for quantitative extraction from aqueous media. The proposed method is found to be quantitative as compared to other standard methods. The equilibrium time required is very little, i.e. only 1 min and the complex is stable for 72 hrs. The results show good agreement with the standard method. The method is very fast, accurate and precise. The 2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone was used for the first time for extraction of Cu(II) from various binary mixtures.

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