Development of Extractive Spectrophotometric Determination of Copper (II) using N-(o-hydroxy benzylidene) pyridine-2-amine (NOHBPA)

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ABSTRACT

A simple and sensitive extractive spectrophotometric method has been developed for the determination of copper (II) using [N - (o - hydroxy benzylidene) pyridine - 2 - amine] (NOHBPA) as an analytical reagent. NOHBPA has been synthesized and characterized by elemental and spectral analysis. NOHBPA forms reddish brown colour complex of copper (II) and extracts quantitatively (99.40%) into benzene from an aqueous solution of pH range 6.8 - 7.5. The benzene extract shows an intense peak at 540 nm (λ max). The system obeys Beer's law over the Cu (II) concentration range of 0.1 - 14 µg/ml. The sandell's sensitivity and molar absorptivity for Cu - NOHBPA system is 0.0182 μgcm^{-2} and 3494.84 L $mole^{-1}cm^{-1}$ respectively. The composition of extracted species is found to be 1:2 (Cu: NOHBPA) by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method has been successfully employed for the determination of Cu (II) in Pharmaceutical samples.

Key words: Extractive Spectrophotometry, Copper (II), N - (o - hydroxy benzylidene) pyridine - 2 - amine (NOHBPA), Pharmaceutical Samples.
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INTRODUCTION

Copper is technically most important metal after iron. It distributes widely in animal tissues and is also one of the essential element in human body. Therefore, the lack of copper in the body will results in health problems such as anemia, leucopenia and atherosclerosis. Abnormity of copper metabolism in the body will cause some hereditary diseases (e.g., Wilson disease). Copper at only very low level is an essential element and is toxic at higher levels in plants. As far as most

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living organisms are concerned, copper at about 40 ng/ml is needed for their normal metabolism. Hence, it is necessary to seek highly sensitive, accurate, and selective analytical methods for quantitative determination of copper at trace levels.

A solvent extraction is becoming important separation technique in chemistry. It has grown into one of the most promising method in the separation of metal ions at trace level because of its simplicity, rapidity and varsality [1-2]. Solvent extraction as a separation technique with spectrophotometrically using different organic reagent have significant role in pharmaceutical science [3]. Literature survey reveals that various reagents [4-12] are available for the spectrophotometric determination of copper. In the present communication, we describe the extractive spectrophotometric determination of Cu (II) with N - (o - hydroxy benzylidene) pyridine - 2- amine (NOHBPA).

EXPERIMENTAL SECTION

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length was used for absorbance measurement. An ELICO - LI 127 pH meter was employed for pH measurements.

General procedure for preparation of [N - (o - hydroxy benzylidene) pyridine - 2 - amine] (NOHBPA)

The reagent NOHBPA was synthesized by refluxing equimolar amount of ethanolic solution of o - hydroxy benzaldehyde with 2 - amino pyridine for 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80%, m.p.70^0-71^0C) which was collected by filtration. The resulting NOHBPA was recrystalised using aqueous ethanol as the procedure recommended by Vogel [13].

O-HYDROXY BENZALDEHYDE   2-AMINO PYRIDINE   ETHANOL REFLUX

[N- (O - HYDROXY BENZYLIDENE) PYRIDENE - 2 - AMINE]
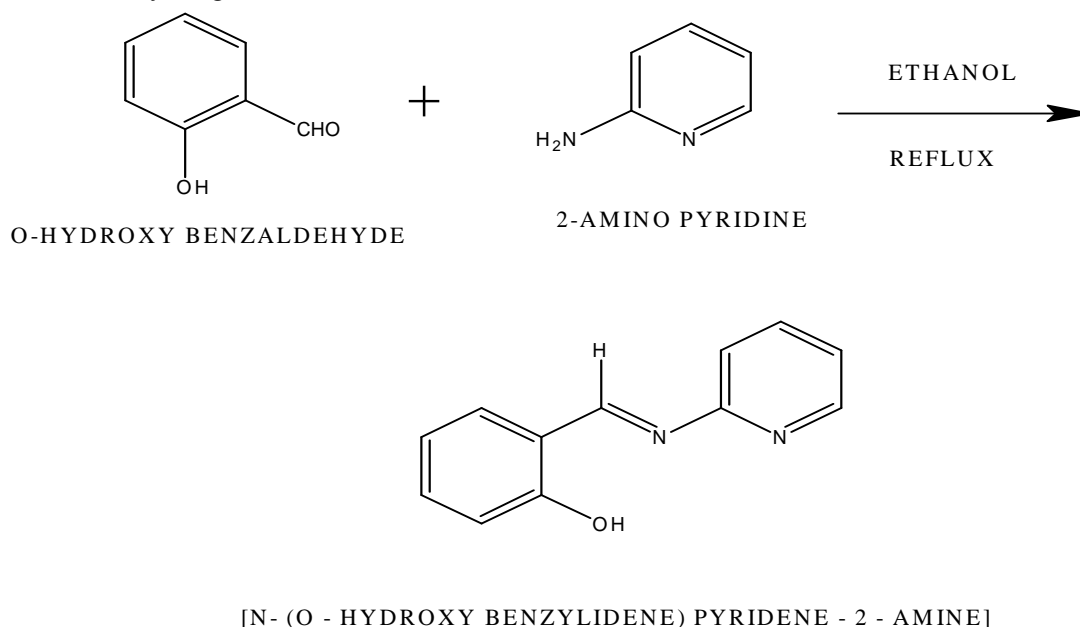
The purity of product was checked by TLC and characterized by elemental and spectral analysis. Its solution was prepared in Dimethylformamide (DMF). A stock solution of Cu (II) was

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prepared by dissolving accurately weighed copper sulphate in water containing dilute sulphuric acid and it was standardized by benzoin-α-oxime method [14]. Working solutions of Cu (II) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

Extractive Spectrophotometric Determination of Cu (II)
To an aliquot of aqueous solution containing 1- 140 µg of Cu (II), 2ml of buffer solution of pH 7.0 and 2 ml of 2% solution of NOHBPA prepared in DMF were added. The volume of solution was made up to 10 ml with distilled water. The solution was then equilibrated for 30 seconds with 10 ml of benzene and the phases were allowed to separate. The benzene extract was collected in a 10 ml standard measuring flask and made up to mark with benzene, if necessary. The absorbance of benzene extract was measured at 540 nm against a reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of Cu (II) present in the sample solution from predetermined calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH or acidity.

Determination of Cu (II) in Pharmaceutical Sample
0.5 - 1.0 gm sample of pharmaceutical product was dissolved in boiling with 10 ml of aquaregia**.** The resulting solution was evaporated to dryness and the residue was dissolved in 10 ml of 6N HCl filter, if required. The resulting solution was then equilibrated twice with 10 ml of di - isopropyl ether to remove Fe (III). The separated aqueous phase was evaporated to dryness, and the residue was dissolved in 100 ml with doubly distilled water. To an aliquot of this solution 1ml was analyzed for Cu (II) by the procedure as described earlier.

RESULTS AND DISCUSSION

Cu (II) could be extracted quantitatively (99.40%) by NOHBPA into benzene from an aqueous solution of pH range 6.8 - 7.5. Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as benzene > ethyl acetate > n-amyl alcohol > toluene > carbon tetrachloride > xylene > chloroform > benzyl alcohol > nitrobenzene > n-butanol. Benzene was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. The benzene extract of Cu: NOHBPA complex showed an intense peak at 540 nm [Fig - I]. The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer's law at this wavelength over a Cu (II) concentration range of 0.1 to 14 µg/ml [Fig - II]. The molar absorptivity of the extracted complex on the basis of Cu (II) content was calculated to be 3494.84 L mol^{-1} cm^{-1}. It was found that 2 ml of 2.0% DMF solution of NOHBPA was sufficient to extract 140 µg of Cu (II). The colour of the Benzene extract was found to be stable at least 24 hrs. at room temperature.

Effect of other ions
Cu (II) (40 µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Cu(II) (40 µg): 10 mg each of Mg(II), Ca(II), V(V), Ni(II), Zn(II), Mo(VI), Ce(IV), Be(II), Ba(II), Bi(III), Li(I), Zr(IV),

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Pd(II), Pt(IV), Sn(II), Th(IV), W(VI), Rh(III) and 1mg of Cr(III), Fe(II) and Fe(III); 20 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, carbonate, sulphate, thiocyanate, phosphates, acetate, tartarate, persulphate and thiosulphate and 1mg of oxalate and citrate Interference by the various ions were removed by using appropriate masking agent (Table - I).
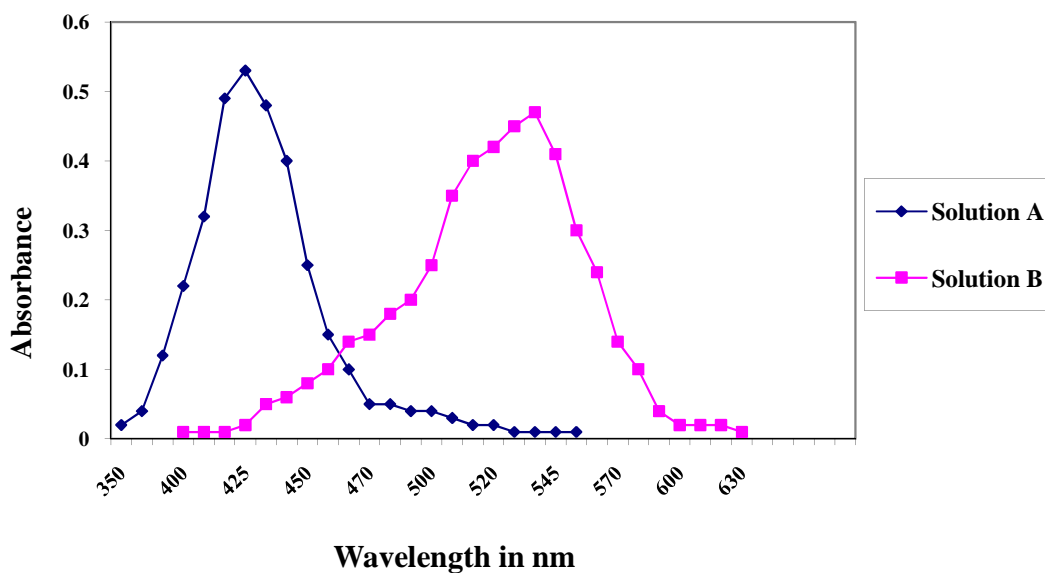

Fig – I: Solution A: Absorbance spectra of NOHBPA, Solution B: Absorbance spectra of Cu - NOHBPA complex
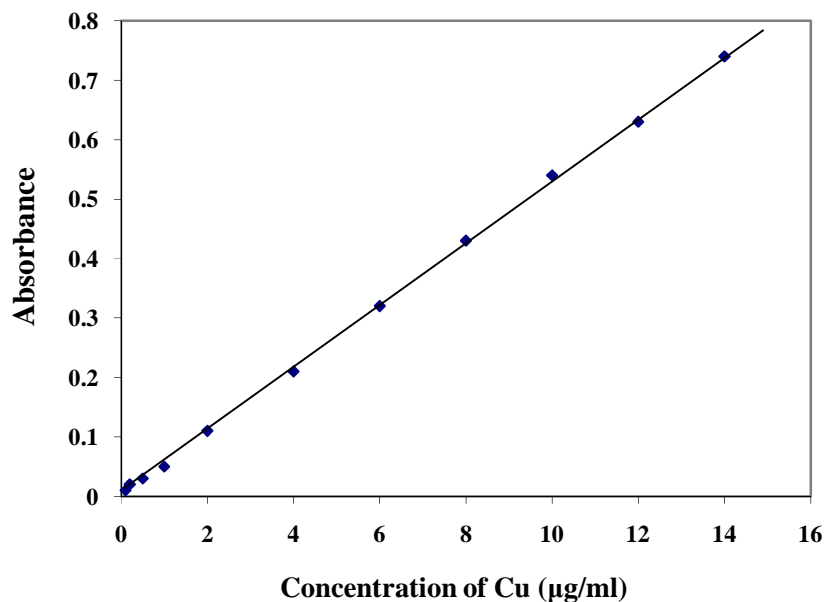
Fig - II   Calibration Curve for Cu (II)

162

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Table - I

Interfering ion	Amount added in mg	Masking agent 2ml of 0.5M solution
Ag(I), Cd(II), Ru(III) and EDTA	10	Thiourea
Hg(II)	10	Potassium Iodide
Mn(II)	10	Thiocyanate
Pb(II)	10	Sodium Thiosulphate

Composition of the Extracted Complex

The composition of the extracted complex [15-17] was found to be 1:2 (Cu: NOHBPA) by Job's continuous variation [Fig - III] and Mole ratio methods. [Fig - IV]

Fig - III   Job's Continuous Variation Method

Mole fraction of Cu (II)
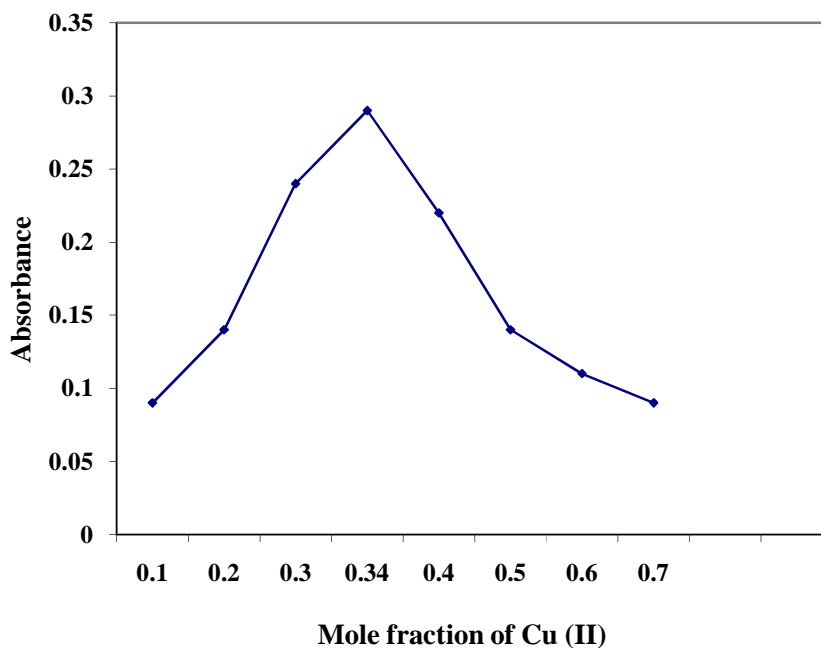
Precision, Accuracy, Sensitivity and Applications of Method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Cu (II) following the recommended procedure. The average of 10 determination of 40 µg of Cu (II) in 10 cm^3 solutions was 40.2 µg, which is varied between 40.76 and 39.64 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ±0.789 and 0.0182 µgcm^{-2} respectively. The proposed method has been successfully applied for the determination of Cu (II) in pharmaceutical samples [18-19].

The results of the analysis of the samples were comparable with those obtained by the diethyl-dithiocarbamate method [20] for Cu (II) (Table - II).
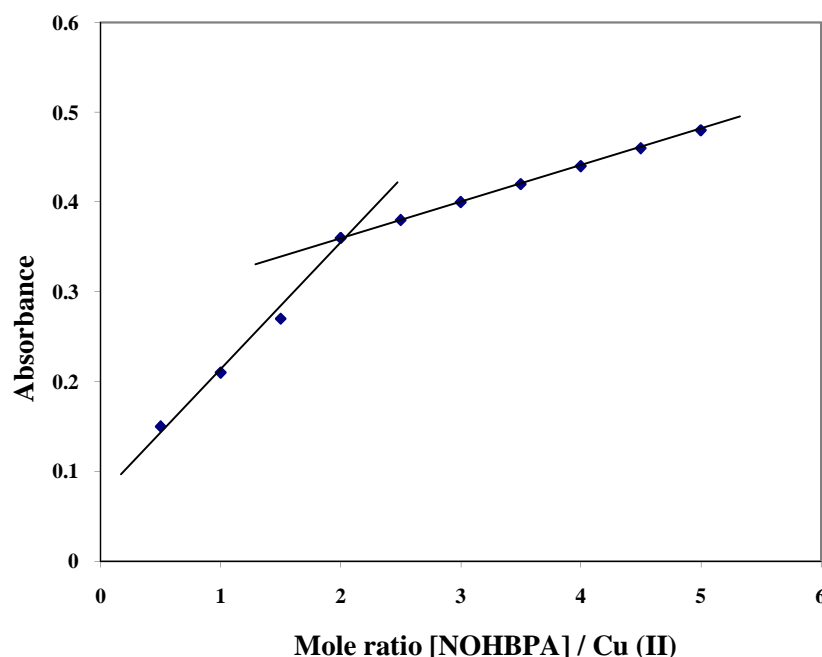
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Fig - IV   Mole Ratio Method

Table – II: Determination of Cu (II) in Pharmaceutical Samples

Sample	Cu (II) found (mg) * Present method	Diethyl – dithiocarbamate method (mg)	Reported value (mg)
Supradyne Tablet	3.30	3.35	3.39
Revital Capsule	0.45	0.50	0.50

*Average of three determinations

Acknowledgement

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