

DEVELOPMENT OF EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) USING [N - (O - HYDROXY BENZYLIDENE) - 4 - METHYLANILINE] (NOHBMA) AS AN ANALYTICAL REAGENT

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Received: 22 December 2013, Revised and Accepted: 03 January 2014

ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Cu (II) by using [N-(o-Hydroxy benzylidene)-4-methyl aniline](NOHBMA) as an analytical reagent. NOHBMA has been synthesized and characterized by elemental and spectral analysis. NOHBMA extracts Cu (II) quantitatively (99.64 %) into n-amyl alcohol from an aqueous solution of pH range 5.8 - 6.8. The n-amyl alcohol extract shows an intense peak at 510 nm (λ max). Beer's law is obeyed over the Cu (II) concentration range of 1.0 - 20.0 $\mu\text{g/ml}$. The sandell's sensitivity and molar absorptivity for Cu - NOHBMA system is $0.07142 \mu\text{gcm}^{-2}$ and $890 \text{ L mole}^{-1}\text{cm}^{-1}$ respectively. The composition of extracted species is found to be 1:2 (Cu:NOHBMA) by Job's Continuous Variation and Mole Ratio Method. The average of 10 determination of 100 μg of Cu (II) in 10cm^3 of solution is 100.2 μg which is varied between 100.05 μg and 100.36 μg at 95% confidence limit and standard deviation is ± 0.155 . Interference by various ions has been studied. The proposed method has been successfully applied for determination of Cu (II) in alloy sample.

Keywords: Extractive Spectrophotometry, Copper (II), [N-(o-Hydroxy benzylidene)-4-methyl aniline] (NOHBMA) and alloy Sample.

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 result in health problems such as anemia, leucopenia and atherosclerosis. Abnormality of copper metabolism in the body will cause some hereditary diseases (e.g., Wilson disease). Copper at only very low levels is an essential element and is toxic at higher levels in plants. As far as most 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 versatility [1-2]. Solvent extraction as a separation technique with spectrophotometrically using different organic reagent have significant role in pharmaceutical science³. 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) - 4 - methyl aniline] (NOHBMA).

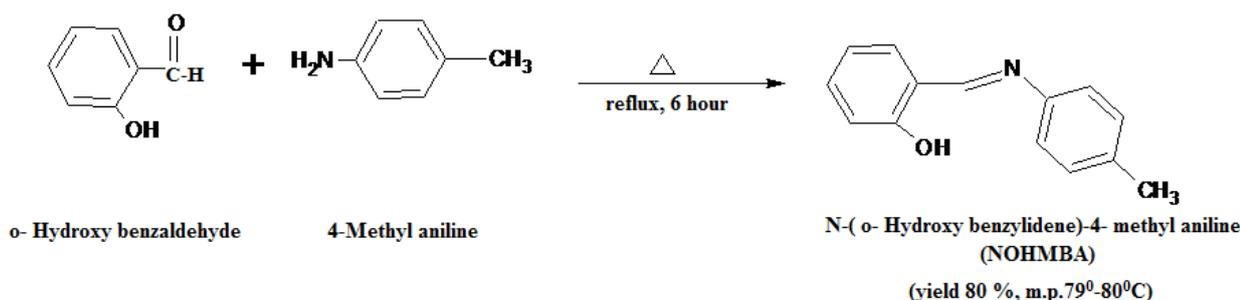
EXPERIMENTAL

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) - 4 - methyl aniline] (NOHBMA)

The reagent NOHBMA was synthesized by refluxing equimolar amount of ethanolic solution of salicylaldehyde with p-toluidine for 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80.00%, m.p. 79°C - 80°C) which was collected by filtration. The resulting NOHBMA was recrystallised using aqueous ethanol. [13]

The purity of product was checked by TLC and characterized by elemental and spectral analysis. Its solution was prepared in alcohol. A stock solution of Cu was prepared by dissolving accurately weighed copper sulphate in water containing sulphuric acid and it was standardized by gravimetrically [15]. 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.



Procedure for the extraction and separation of copper (II)

An aliquot of aqueous solution containing 500 μg of Cu (II) and 2 ml of 1% solution of NOHBMA prepared in alcohol were mixed in 25 ml beaker. The pH of solution was adjusted to the desired value with dilute solution of HCl/NaOH, keeping the total volume to 10 ml with

distilled water. The resulting solution was then transferred into 125 ml separatory funnel. The beaker was then washed twice with 5 ml portion of organic solvent and each washing was added to the solution in the separatory funnel. The two phases were equilibrated for 1 minute and allowed to separate. After the separation of two phases, pH of the equilibrated aqueous phase was measured and

copper content in each phase was estimated by Diethyldithiocarbamate method [16]. The extraction was carried out with different solvents to find out the best extracting solvent.

Procedure for the extractive spectrophotometric determination of copper (II)

To an aliquot of aqueous solution containing 10- 200 μg of Cu (II), 3ml of buffer solution of sodium acetate and acetic acid of pH 6.0 and 2 ml of 1% solution of NOHBMA prepared in alcohol were added. The volume of solution was made up to 10 ml with distilled water. The solution was then equilibrated for 1 minute with 10 ml of n-amyl alcohol and the phases were allowed to separate. The n-amyl alcohol extract was collected in a 10 ml standard measuring flask and made up to mark with n-amyl alcohol, if necessary. The absorbance of n-amyl alcohol extract was measured at 510 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.

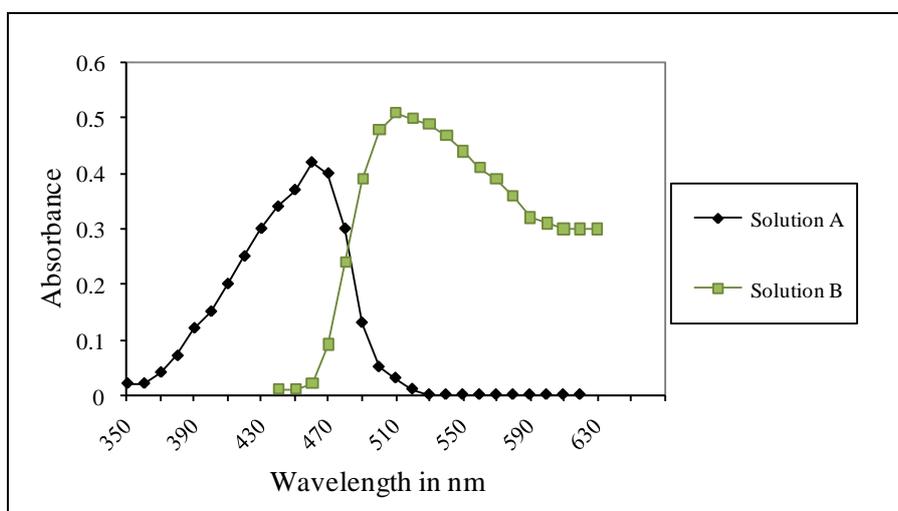
Procedure for the determination of copper (II) in alloy sample

0.1 - 0.2 gm sample of Al alloy 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 1M HCl filter, if required. The resulting solution was diluted to 250 ml of distilled water. 1ml aliquot of this solution was analyzed for Cu (II) by the procedure as described earlier.

RESULTS AND DISCUSSION

Cu (II) could be extracted quantitatively (99.64%) by NOHBMA into n-amyl alcohol from an aqueous solution of pH range 5.8-6.8 . Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as n-Amyl alcohol > Iso-propyl alcohol > n-Butanol > Chloroform > Nitrobenzene > Carbon tetrachloride > Xylene > Ethyl acetate. n-Amyl alcohol was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. The n-Amyl alcohol extract of Cu: NOHBMA complex showed an intense peak at 510 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 1.0 to 20.0 $\mu\text{g}/\text{ml}$ [Fig - II]. The molar absorptivity of the extracted complex on the basis of Cu(II) content was calculated to be 890 $\text{L mol}^{-1}\text{cm}^{-1}$. It was found that 2 ml of 1.0% alcohol solution of NOHBMA was sufficient to extract 50 μg of Cu (II). The colour of the n-Amyl alcohol extract was found to be stable at least 24 hrs. at room temperature



Solution A: Absorbance spectra of NOHBMA

Solution B: Absorbance spectra of Cu:NOHBMA complex

Fig. I

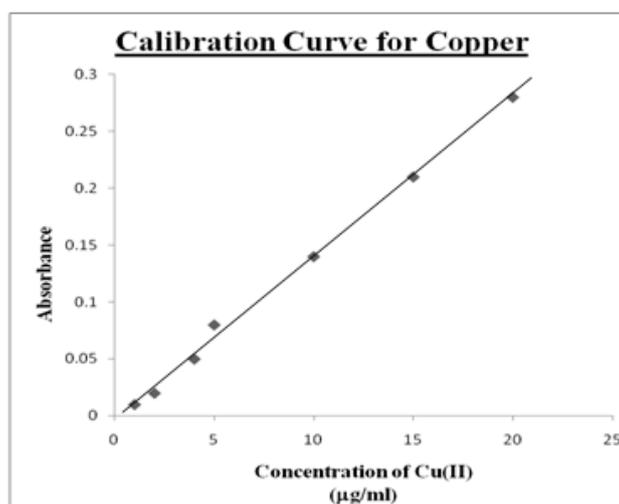


Fig. II

Effect of other ion

Cu(II) (20 μ g) 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) (20 μ g):

10 mg each of Li(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Sn(II), Zn(II), Ni(II), CO(II), Cr(III), Al(III), Mo(VI), W(VI), Ce(VI), Th(IV) and Zr(IV), 2 mg each of Pb(II), Cd(II), 1 mg each of Pd(II), Ru(III),

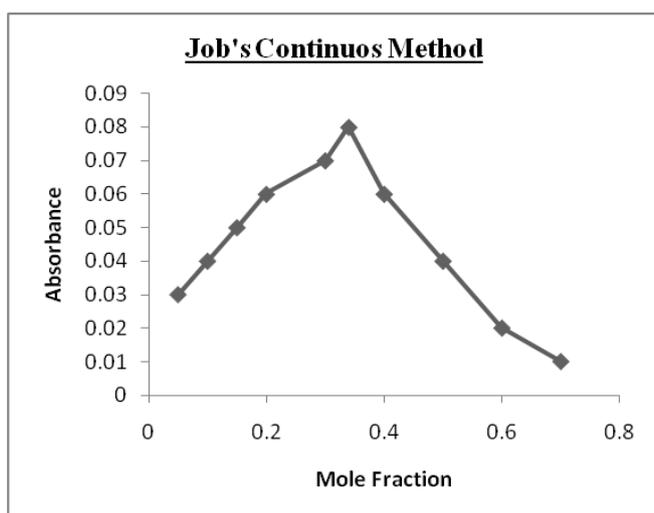
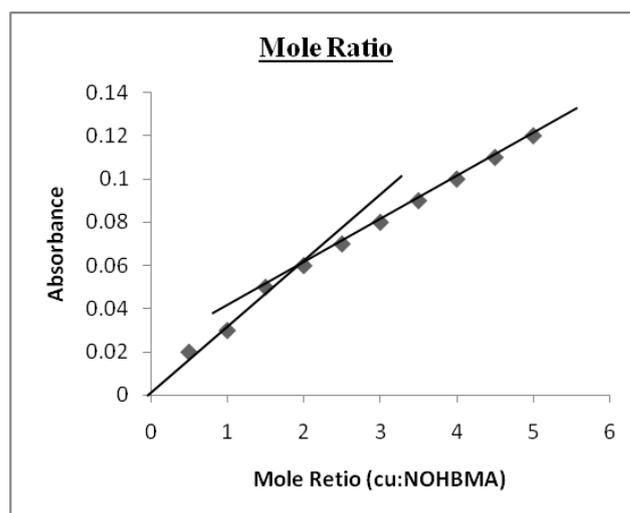
Rh(III), Pt(IV). 20 mg each of chloride, bromide, Fluoride, sulphate, nitrate, nitrite, phosphate, acetate. Interference by the various ions were removed by using appropriate masking agent (Table - I).

Composition of the extracted complex

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

Table 1

Sr. No.	Interfering ions	Amount added in Mg	Masking agent added 1ml of 0.5 M solution
1.	Fe(II) and Fe(III)	10	Sodium fluoride
2.	V(V)	10	Sodium Fluoride

**Fig. III****Fig. IV****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 10 μ g/ml of Cu (II) in 10 cm^3 solutions was 100.2 μ g, which is varied between 100.045 and 100.355 at 95% confidence limit. Standard

deviation and Sandell's sensitivity of the extracted species is found to be ± 0.155 and $0.07142 \mu\text{g cm}^{-2}$ respectively. The proposed method has been applied for the determination of Cu (II) in Al alloy.

The results of the analysis of the samples were comparable with those obtained by the diethyl- dithiocarbamate method[16] for Cu (II) (Table - II).

Table II: Determination of copper (II) in AL-Alloy sample

Commercial Samples	Copper (II) found (%)	
	Present method*	Diethyl - dithiocarbamate method[16]
Al-alloy	8.03	7.99

*Average of three determinations

CONCLUSION

The extractive spectrophotometric determination of Cu (II) was successfully carried out. The reagent NOHBMA formed complex with copper (II) which were easily extracted into organic solvent. The method is simple and reliable. Experimental conditions for maximum extraction was determined and applied for the analysis of alloy samples.

ACKNOWLEDGEMENTS

Authors are thankful to the Principal, Dr. (Mrs.) J. K. Phadnis, V.E. S. College of Arts, Science and Commerce, Sindhi Society, Chembur, Mumbai - 71 for providing necessary research facilities.

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