Int. J. Chem. Sci.: 11(1), 2013, 605-613
ISSN 0972-768X
www.sadgurupublications.com

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) WITH [N-(O-METHOXY BENZALDEHYDE)-2-AMINO PHENOL]

RITIKA M. MAKHIJANI and V. D. BARHATE*

V. E. S. College of Arts, Science and Commerce, Sindhi Society, Chembur,
MUMBAI – 400071 (M.S.) INDIA

ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Cu (II) by using N-(o-methoxy benzaldehyde) 2-aminophenol (NOMBAP) as an analytical reagent. NOMBAP has been synthesized and characterized by elemental and spectral analysis. NOMBAP extracts Cu (II) quantitatively (99.78%) into chloroform from an aqueous solution of pH range 5.7-6.8. The chloroform extract shows an intense peak at 440 nm (λ_{max}). Beer's law is obeyed over the Cu (II) concentration range of 0.1-4.0 μg/mL. The Sandell's sensitivity and molar absorptivity for Cu-NOMBAP system is 0.00246 μgcm^{-2} and 25739 L $mole^{-1}$ cm^{-1}, respectively. The composition of extracted species is found to be 1 : 2 (Cu: NOMBAP) by Job's Continuous Variation and Mole Ratio Method. The average of 10 determination of 10 μg of Cu (II) in 10 cm^3 of solution is 10.02 μg, which is varied between 9.964 μg and 10.076 μg at 95% confidence limit and standard deviation is ± 0.079. Interference by various ions has been studied. The proposed method has been successfully applied for determination of Cu (II) in alloy and pharmaceutical samples.

Key words: Extractive spectrophotometry, Copper (II), N (o-methoxy benzaldehyde) 2-aminophenol (NOMBAP), Alloy and pharmaceutical sample.

INTRODUCTION

Copper is a transition element and has a history of use that is 10000 years old. In ancient India, copper was used in holistic medical science. Ancient Egyptians used copper for sterilizing wounds and drinking water, for headache, burns and itching. 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 is an essential element only at very low levels and is

---

*Author for correspondence; E-mail: vasantbarhate@yahoo.co.in 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 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-methoxy benzaldehyde) 2-amino phenol (NOMBAP).

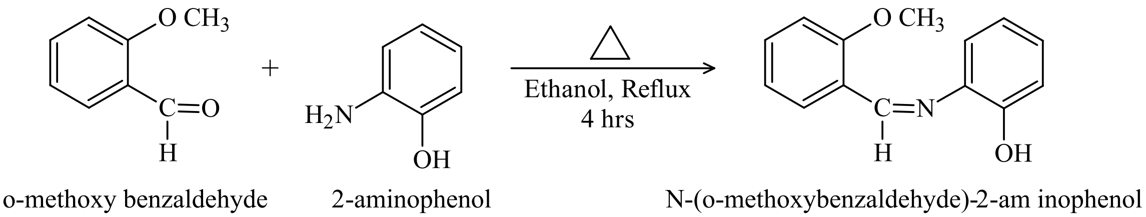
EXPERIMENTAL

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

A stock solution of Cu was prepared by dissolving accurately weighed copper sulphate in water containing sulphuric acid and it was standardized by gravimetrically[13,14]. 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.

General procedure for preparation of N-(o-methoxy benzaldehyde) 2-aminophenol (o-methoxy benzaldehyde) 2-aminophenol (NOMBAP)

The reagent NOMBAP was synthesized by refluxing equimolar amount of ethanolic solution of o-methoxy benzaldehyde with 2-aminophenol for 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80%, m.p.87°-88°C) which was collected by filtration. The resulting NOMBAP was recrystalised using aqueous ethanol as the procedure recommended by Vogel[15].



The product obtained was characterized by elemental and spectral analysis. Its solution was prepared in dimethylformamide (DMF).

Procedure for the extraction and separation of Cu (II)

An aliquot of aqueous solution containing 500 μg of Cu (II) and 2 mL of 2% solution of NOMBAP prepared in DMF 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 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 one 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[14]. The extraction was carried out with different solvents to find out the best extracting solvent. On the basis of copper content in aqueous and organic phase extraction coefficient and percentage extraction was calculated.

Procedure for the extractive spectrophotometric determination of Copper (II)

To an aliquot of aqueous solution containing 1-40 μg of Cu (II), 2 mL of buffer solution of pH 6.0 and 2 mL of 2% solution of NOMBAP prepared in DMF were added. The volume of solution was made up to 10 mL with distilled water. The solution was then equilibrated for one minute with 10 mL of chloroform and the phases were allowed to separate. The chloroform extract was collected in a 10 mL standard measuring flask and made up to mark with chloroform, if necessary. The absorbance of chloroform extract was measured at 440 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 g sample of Al alloy 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 dilute 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.

Procedure for the determination of Copper (II) in pharmaceutical sample

0.5-1.0 g 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 5 mL of diluted HCl filter, if required. The resulting solution was then diluted to 100 mL with distilled water. 1 mL aliquot of this solution was analyzed for Cu (II) by the procedure as described earlier using 1 mL of 0.5 M solution of Tri ethanol amine to mask Fe (III).

RESULTS AND DISCUSSION

Copper (II) could be extracted quantitatively (99.40%) by NOMBAP into chloroform from an aqueous solution of pH range 5.7-6.8 (Fig. 1). Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as chloroform > ethyl acetate > carbon tetrachloride > n-amyl alcohol > benzene > toluene > > nitrobenzene > benzyl alcohol > n-butanol > xylene (Fig. 2). Chloroform was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. The chloroform extract of Cu: NOMBAP complex showed an intense peak at 440 nm (Fig. 3). 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 4.0 µg/mL (Fig. 4). The molar absorptivity of the extracted complex on the basis of Cu (II) content was calculated to be 25739 L mol^{-1} cm^{-1}. It was found that 2 mL of 2.0% DMF solution of NOMBAP was sufficient to extract 40 µg of Cu (II). The colour of the Chloroform extract was found to be stable at least 24 hrs. at room temperature.

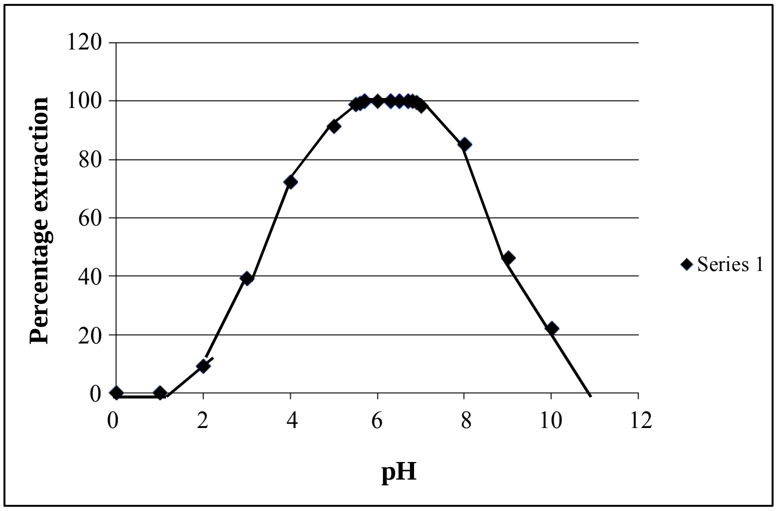


Fig. 1: Effect of pH on Extraction of Cu(II)

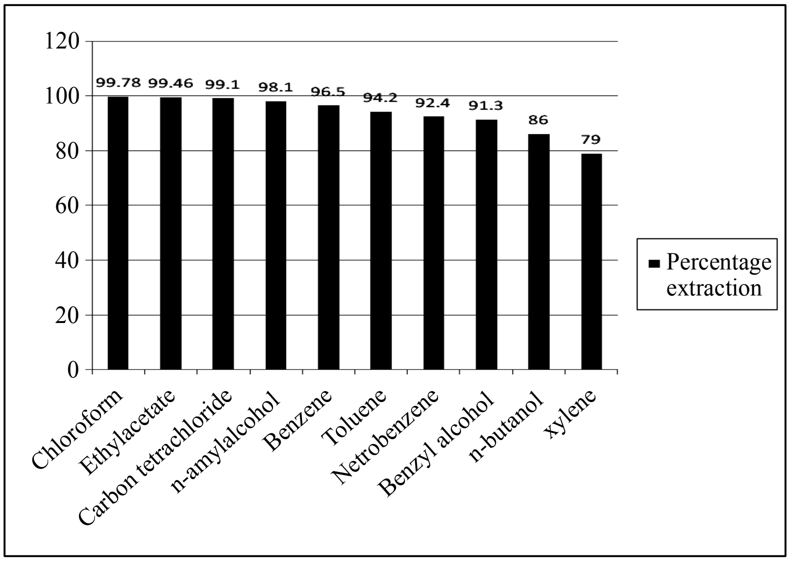


Fig. 2: Percentage Extraction of Cu(II) into various Solvents

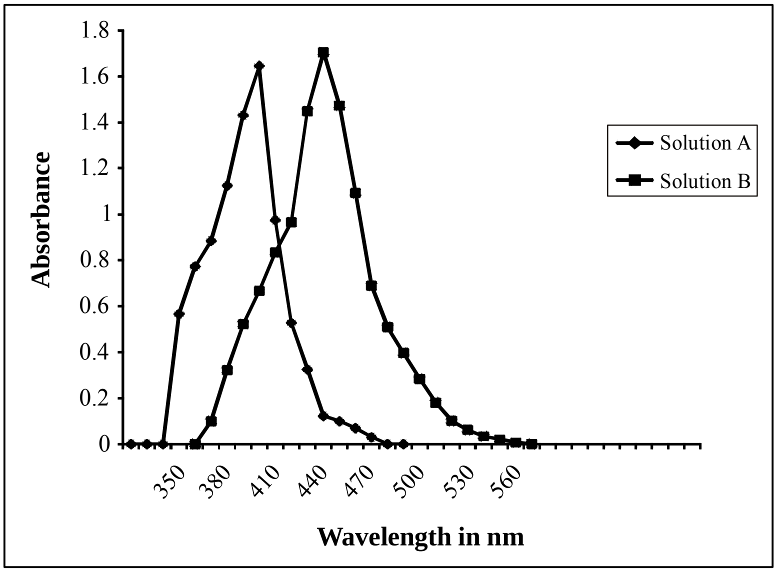


Fig. 3: Absorbance spectra of NOMBAP and Cu: NOMBAP

Solution A: Absorbance spectra of NOMBAP

Solution B: Absorbance spectra of Cu - NOMBAP complex

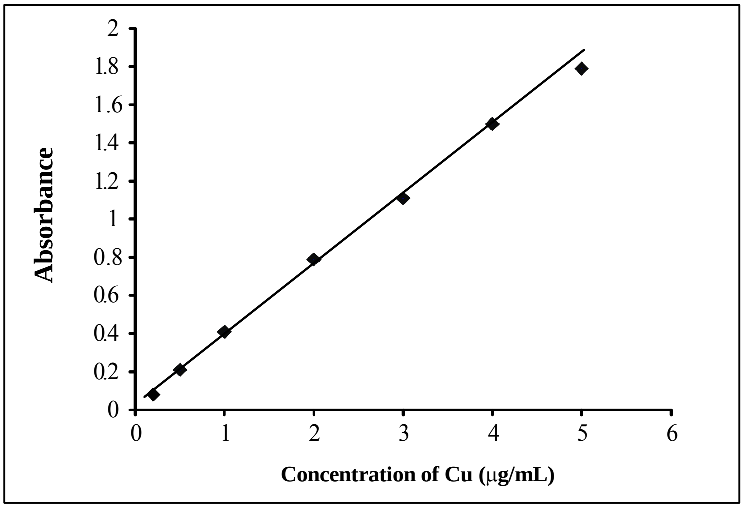


Fig. 4: Calibration curve for Cu (II)

Effect of other ions

Copper (II) (20 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) (20 μg): 10 mg each of Li (I), Be (II), Mg (II), Ca (II), Sr (II), Ba (II), Sn (II), Bi (III), Mo (VI), W (VI), Ce (IV), Th (IV) and Zr (IV). 2 mg each of Pb (II), Cd (II) and Zn (II). 1 mg each of Pd (II), Pt (IV) and Hg (II). 0.1 mg of Co (III). 20 mg each of chloride, bromide, fluoride, sulphate, nitrate, thiocyanate, phosphates, acetate, tartarate and thiourea. Interference by the various ions were removed by using appropriate masking agent (Table 1).

Table 1: Masking agent to suppress the interference by other ions

S. No.	Interferring ions	Amount added in mg	Masking agent added 1 mL of 0.5 M solution	Absorbance
1	Fe (II) & Fe (III)	10	Tri ethanol amine	0.81
2	Ru (III) and Rh (III)	10	Thiourea	0.81
3	Ag (I)	10	Potassium thiocyanate	0.81
4	Mn (II)	10	Thiocyanate	0.81
5	Cr (III)	10	Tri ethanol amine	0.81
6	V (V)	10	Tri ethanol amine	0.81
7	Ni (II)	10	5-sulphosalicylic acid	0.81
8	Oxalate	10	Sodium molybdate	0.81

Composition of the extracted complex

The composition of the extracted complex was found to be 1 : 2 (Cu: NOMBAP) by Job's continuous variation (Fig. 5) and Mole ratio methods (Fig. 6).

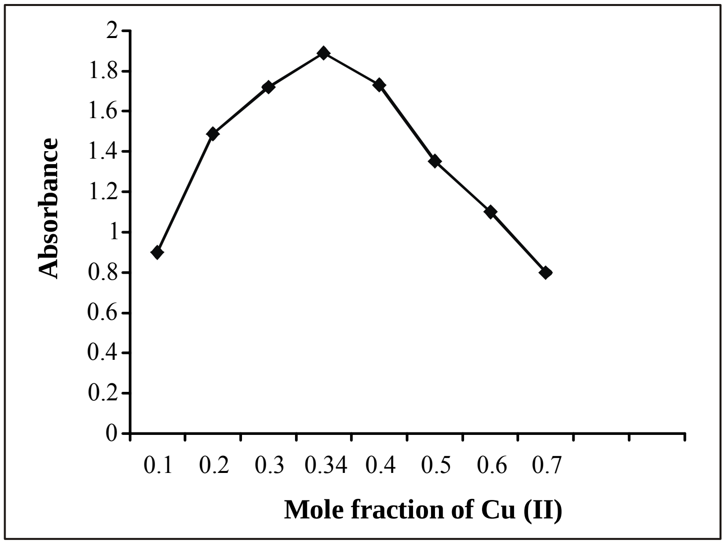


Fig. 5: Job's continuous variation method

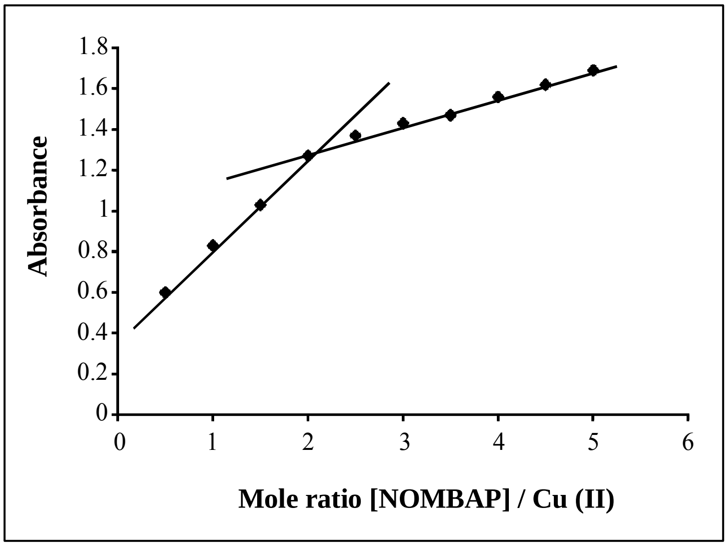


Fig. 6: Mole ratio method

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 µg of Cu (II) in 10 cm^3 solutions was 10.02 µg, which is varied between 9.964 and 10.076 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ± 0.079 and 0.00246 μgcm^{-2}, respectively. The proposed method has been applied for the determination of Cu (II) in Al alloy and pharmaceutical samples.

The results of the analysis of the samples were comparable with those obtained by the diethyl dithiocarbamate method[14] for Cu (II) (Table 2).

Table 2: Determination of Cu (II) in Al alloy and pharmaceutical Samples

Sample	Cu (II) found (mg) present method*	Diethyl-dithiocarbamate[14] method (mg)	Reported value (mg)
Al-alloy	8.02	8.01	7.98
Revital capsule	0.48	0.50	0.50

*Average of three determinations

ACKNOWLEDGEMENT

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

REFERENCES

1. S. M. Khopkar and R. A. Chalmers, Solvent Extraction of Metals, Van Nostrad Reinhold Co., London (1970).
2. F. Feig, Chemistry of Specific, Selective and Sensitive Reactions, English Ed. By Oesper R. E. Academic Press, New York (1949) p. 209.
3. K. A. Mirzaeva, M. S. Akhmedove, A. Ramazanov and S. A. Akhmedove, Extraction and Spectrophotometric Determination of Dimedrol and Papavarine in Pharmaceutical Dosage Forms, J. Analytical Chem., **59(1)**, 215-218 (2004).

4. R. B. Singh, B. S. Garg and R. P. Singh, Talanta, **26**, 525-526 (1979).

5. K. N. Vidhate, M. K. Lande, B. R. Arbad, Extractive Spectrophotometric Simultaneous Determination of Ru (III), J. Indian Chem. Soc., **86(1)**, 109-112 (2009).

6. B. K. Pala and M. Sahedur Rahmand, Spectrophotometric Study of Ruthenium (III) using 2-Pyridyl Thioquanaldemide (PTQA), Talanta, **48(5)**, 1075-1084 (1999).

7. S. H. Gaikwad, D. S. Bange and M. A. Anuse, Development of New Spectrophotometric Method for the Determination of Ru (III) using 1, 3-bis (hydroxymethyl) benzimideazole-2-thione [BHMBT], Shivaji University Kolhapur; Revue Roumaine de Chime, **49(7)**, 1510-1514 (2004).

8. R. E. Peterson and M. E. Boiler, Anal, Chem., **27**, 1195-1197 (1955).

9. H. A. Mahajan and M. R. Patil, Chim Anal., **37**, 239-242 (1992).

10. B. Maria and E. Świcicka, Talanta, **43(3)**, 471-478 (1996).

11. A. M. Khambekar and A. D. Sawant, J. Indian Chem. Soc., **36A (5)**, 459-460 (1997).

12. R. Nath, S. C. Nantial and H. Singh, Labdev Part - A, **12(2)**, 53-58 (1974).

13. A. I. Vogel, Text Book of Quantitative Inorganic Analysis, Longman Green and Co. Ltd., London (1978).

14. E. B. Sandell, Colorimetric Determination of Traces of Metals; 3rd Edn. Interscience, N.Y. (1965) p. 414.

15. A. I. Vogel, Practical Organic Chemistry 5th Ed. Longman Group Limited, London (1989).

Revised : 01.02.2013 *Accepted : 04.02.2013*