

Liquid-Liquid Extraction and Spectrophotometric Determination of Some Metal Ions with Imine (Schiff Base) Derivative as an Analytical Reagent

Jayashree S. Patil

Department of Chemistry

J. S. M. College, Alibag, Raigad, Maharashtra, India

jayupati25@gmail.com

Abstract: The spectrophotometric method is coupled with solvent extraction technique and used for the determination of Cu(II) using *N,N'*bis(*O*-hydroxy acetophenone) ethylene diimine (HAPED) as an analytical reagent. This reagent is synthesized in the laboratory and characterized by NMR, IR, Mass and elemental analysis for its purity. The reagent forms a light pink coloured stable complex with copper metal, which can be quantitatively extracted into chloroform at pH 3.6. This Cu(II)-HAPED complex in chloroform exhibits intense absorption peak at 405nm. The study of change of colour intensity of Cu(II)-HAPED complex with varying concentration of reagent showed that 2cm³ of 0.1% of reagent is sufficient for full colour development of 100ppm copper solution. The stoichiometric ratio of complex studied by Job's continuous variation method, mole ratio and slope ratio method. The molar absorptivity and Sandell's sensitivity are also calculated. The molar absorptivity is 4012.73 L/mol/cm and Sandell sensitivity is 0.0158 µg/cm². The newly developed method is then applied to various commercial samples successfully and observed to be comparable with earlier known methods. Beer's law is obeyed in the range of 1 to 10 ppm of copper solution giving linear and reproducible graph.

Keywords: Sandell's Sensitivity; Spectrophotometric determination, Imine reagent, Copper(II).

I. INTRODUCTION

The electrical properties of copper are exploited in copper wires and devices such as electromagnets. Extractive methods are highly sensitive but generally lack in simplicity. Spectrophotometry is essentially a trace analytical technique and is one of the most powerful tools in chemical analysis. A wide variety of reagents have been proposed for the spectrophotometric determination of Cu(II). The extractive spectrophotometric analysis enables to separate desired metal ion, which is to be estimated in presence of other metal from samples. In the present work a novel analytical reagent *N,N'*bis(*O*-hydroxy acetophenone) ethylene diimine (HAPED), was used for the extractive spectrophotometric determination of Cu(II). Developed method can be employed for efficient determination of Copper at microgram level. The results of analysis obtained were compared with those obtained by known methods.

II. EXPERIMENTAL WORK

2.1 Instruments

A Shimadzu 2100 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustment.

2.2 Synthesis of Reagent

The reagent was synthesized by *O*-hydroxy acetophenone and ethylene diamine in methanol in 2:1 molar proportions are mixed in Round Bottom Flask. Shake the flask for 10 to 15 minutes. Immediately dark yellow colour solid is obtained which is poured in ice cold water. The solid obtained is separated by filtration and washed with cold water and the product is recrystallised from ethanol. The yield was about 90%. It is then characterized and used for extractive spectrophotometric determination of Cu(II). A stock solution of HAPED

reagent with concentration 0.1% was prepared in methanol. The scheme of reaction is as shown in Figure 1.

2.3 Preparation of Stock Solution

A weighed quantity of Copper Chloride was dissolved in double distilled water containing dilute Hydrochloric acid and then diluted to desired volume by double distilled water. The solution was then standardized by EDTA Method.

2.4 Recommended Procedure

Mix 1 cm³ aqueous solution containing 1-100mg of Copper and 2 cm³ of 0.1% Methanolic solution of HAPED reagent in 25 cm³ beaker. Adjust the pH of the solution to required value with buffer solution make the final volume 10 cm³. Transfer the solution into 125 cm³ separating funnel and equilibrate for 1min with 10 cm³ Chloroform. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 405 nm against reagent blank.

2.5 Preparation of Calibration Plot

The calibration curve was prepared by taking known amount of Copper which is described in the procedure. A graph of absorbance against concentration was prepared Figure 2. The concentration of the unknown Copper solutions is determined from the calibration plot.

2.6 Composition of the Extracted Species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by Mole ratio method and Slope ratio method. These methods show that the composition of Cu(II): HAPED reagent is 1: 2 which is represented in Figure 3.

2.7 Effect of Foreign Ions

The effect of diverse ions on the Copper (II) determination was studied, in presence of a definite amount of a foreign ion. Various cations, anions were investigated in order to find the tolerance limit of these foreign ions in the extraction of Copper (II) presented in Table 2. The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Copper(II). The ions which interfere in the spectrophotometric determination of Copper were masked by using appropriate masking agents presented in Table 3.

2.8 Comparison between Reagents

Various reagents were investigated by the earlier researchers for removal of Copper(II). The proposed reagent N,N'bis(O-hydroxy acetophenone) ethylene diimine (HAPED) is found more superior as that of reported reagents and are presented in Table 5.

III. APPLICATIONS

The present method was applied for determination of amount of Copper(II) in various samples of alloys, commercial mixtures, injection vial, tablets. The results obtained were in well agreement with standard methods shown in Table 4. Every result is average of independent determinations.

IV. RESULT AND DISCUSSION

In this section experimental results of solvent extraction for removal of Cu(II) by using as N,N'bis(O-hydroxy acetophenone) ethylene diimine (HAPED) organic reagent are presented. Effect of various parameters like pH, absorbance wavelength and validity of Beer's Lambert's law. The stability of Copper complex is 36hrs. represented in figure 4. It is observed from this figure that a linear calibration curve was obtained in the range of 1-10 ppm Copper. The best results of solvent extraction were obtained in aqueous phase at pH 3.6 and whereas organic phase containing Chloroform as solvent. The absorption is observed maximum at wavelength 405 nm. The equilibrium is attained within one minute.

4.1 Effect of pH and Absorbance

Various solvents are tried for extraction. Chloroform is found to be the most suitable solvent which is carried maximum extraction which is shown in figure 5. 1 cm³ aqueous solution contain 100 ppm Cu(II) at different pH shaking with 2 cm³ of 0.1% HAPED in Chloroform, after separated a two layers measure the absorbance of organic phase at wavelength of 405nm and pH of 3.6 respectively which is represented in figure 6.

4.2 Shaking Time Effect

1 cm³ aqueous solution contain 100 ppm Cu(II) at pH 3.6 after added 2 cm³ of 0.1% HAPED in Chloroform, shaking for different times (0-60) minutes after separated the layers, measuring the absorbance of organic phase at wavelength of 405nm.

4.3 Mole Ratio Method

Solution of 0.01M HAPED in Chloroform used to extract 0.01M Cu(II) from aqueous solution at optimum conditions, also determine absorbance of organic phase at wavelength of 405nm against Chloroform, figure 3 indicates that the ratio of Cu(II) to complex was 1:2[Cu+2(HAPED)].

V. CONCLUSION

The proposed method is more highly sensitive and selective than the 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.

Sr. No.	Different parameters Studied	Observation
1	Solvent	Chloroform
2	pH	3.6
3	Equilibrium time	1 min.
4	Stoichiometry M:L	1:2
5	95% confidence limit	±0.1532
6	Reagent Conc.	0.1%
7	Volume of Rgt.	2cm ³
8	Average of 7 determination	9.96
9	Stability of the complex	36 hrs.

Table 1

Sr. No.	Interfering ions	Tolerance limit
1	SO ₄ ²⁻ , I ⁻ , Cl ⁻ , BrO ₃ ⁻ , ClO ₃ ⁻ , Br ⁻ , NO ₃ ⁻ , IO ₃ ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , CN ⁻	15
2	Tartarate, Oxalate	11
3	phosphate, Acetate	06
4	Mg(II), Mo(VI), Ce(IV), Ca(II), As(III), Cd(II)	13
5	Co(II), Fe(II), Mn(II), Ni(II)	Interfere strongly

Table 2 Effect of foreign ions

Sr. No.	Interfering Ions	Masking Agents
1	Cd(II)	Thiourea
2	Fe(III)	Sodium Fluoride
3	Co(II)	Sodium Fluoride
4	Ni(II)	DMG
5	EDTA	Boiled with conc.HNO ₃
6	CN ⁻	Boiled with conc.HNO ₃ And formaldehyde

Table-3: Effect of masking agent

Sr. No.	Sample	Standard method	Present method
1	Devardas alloy	72.40µg	72.35µg
2	Cupra-Nickel alloy	81.25µg	82.20µg
3	Cu(100) + Cd(100)	100ppm	99.70ppm
4	Cu(50) + Fe(50) + W(50)	50ppm	50.12ppm

Table 4 Applications

Sr./ Ref. No.	Reagent	Remark
1	2-Hydroxy-1-acetophenone oxime	Extracted in isobutyl methyl ketone
2	2,4 -dihydroxy acetophenone thiosemicarbazone	Beer's Range 0.8-5.5 ppm W ⁶⁺ , Zn ²⁺ interfere
3	2-bromo-2-hydroxy-5-methylacetophenone hydrazone	Beer's Range 0.13-2.75 ppm Ni ⁺² , Co ⁺² interfere
4	3-(O-acetophenyl)-1-methyl triazine-N- oxide	Beer's Range 0.25-4.7 ppm

Table 5 Comparison between reagents

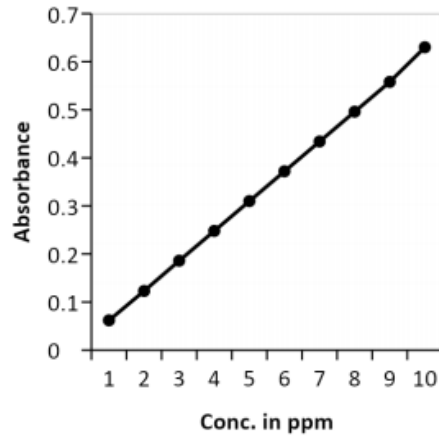


Fig.2 Calibration Plot For Extractive Spectrophotometric Determination of Cu(II) with Chloroform

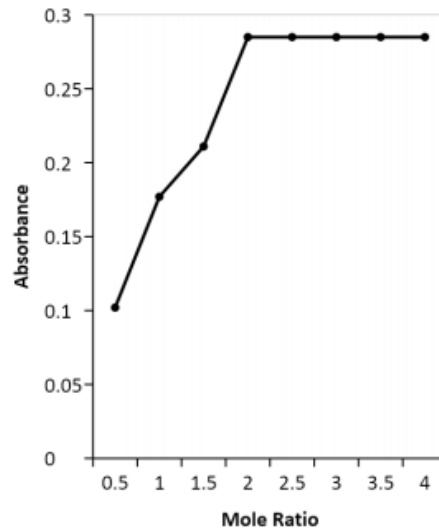


Fig.3 Composition Of The Extracted Cu(II) : HAPED Species By Mole Ratio Method

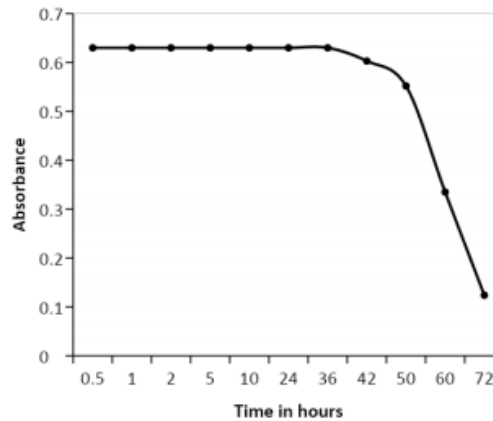


Fig.4 Effect Of The Stability On Absorbance Of Cu(II) : HAPED complex

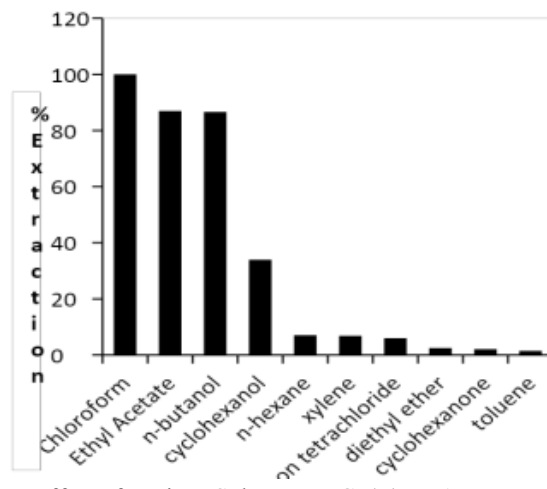


Fig. 5 Effect of Various Solvents on Cu(II) : HAPED complex

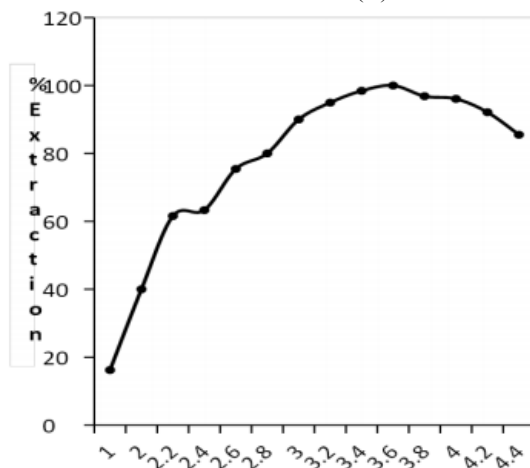


Fig.6 Effect of pH on the Extraction of Cu(II) : HAPED complex.

REFERENCES

- [1]. Desai, A. and Naik, H.B.; J. Inst. Chem. 62, 165 (1990).
- [2]. National Research Council. Copper. In: Recommended Dietary Allowances. Washington, D.C.: Food Nutrition Board, NRC/NAS, 151 (1980).
- [3]. Janwadker S.P, Lokhande R.S., Pitale S.M., Kulkarni S.W. & Patil S.K., Int. J. Chemtech, Research, 2011,3(4), 1765-1768.
- [4]. Rickwood, P. C. American Mineralogist 66: 885. (1981).
- [5]. Vogel A.I., "Text Book of qualitative Inorganic Analysis, Longmann Green and Co. Ltd. London (1961)
- [6]. Ahluwalia, V.K. Bhagat, P. Agarwal, R. Chandra, Intermediates for organic synthesis, I.K. International Pvt. Ltd., 2005.
- [7]. Vogel, A.I. Textbook of organic synthesis, 3rd edition ; ELBS, London, 1957. 8.
- [8]. Desai, B.D. and Desai, K.K.; Asian. J. Chem., 13(1), 366, (2001).
- [9]. Lokhande, R.S.; Poman, S.V. and Kapadi, U. R.; Asian J. Chem., 13, 1222 (2001).
- [10]. Rao, D.M.; Reddy, K.H.; Reddy, D.V. and Shrikrishnadevaraya; Ind. J. Chem. 28A, Sec A (1989).