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2-Hydroxy-3-iodo-4-*n*-butoxy-5-bromopropiophenone Oxime as An Analytical Reagent for Copper(II)

J.A. DAVE* and S.S. SHAH
Department of Chemistry, Shri U.P. Arts, Smt. M.G. Panchal Science and
V.L. Shah Commerce College, Pilvai-382 850, India
E-mail: jay_phenol@yahoo.com

2-Hydroxy-3-iodo-4-*n*-butoxy-5-bromopropiophenone oxime has been used for the spectrophotometric determination for Cu(II) at pH range of 6 to 9 in chloroform medium. Jobs' method for continuous variation, Yoe and Jones' mole ratio method, the slope ratio method show metal ligand ratio in complex to be 1:2. The stability constant of the complex is found to be 6.29×10^8. The green coloured complex obeys Beer's law in the concentration range 20.96 to 222.39 ppm for Cu(II) ion, while the optimum concentration range from Ringbom plot is found to be 20.96 to 177.82 ppm. The photo-metric sensitivity and molar absorptivity at the 640 nm are found to be 0.031 $\mu g/cm^2$ and 202 l mol^{-1} cm^{-1}, respectively. The standard free energy of formation of complex is -1.219 kcal/mol at 30 ºC. The complex is stable for 2 weeks. The reagent has also been found to give quite satisfactory results for Cu(II) present in alloy like brass and bronze.

Key Words: Analytical reagent, Copper(II), 2-Hydroxy-3-iodo-4-*n*-butoxy-5-bromopropiophenone oxime.

INTRODUCTION

Various phenones, phenone oximes, phenyl hydrozones, chalcone-oximes, *etc.* have been used for the spectrophotometric and gravimetric determination of copper and other transitional metal ions[1-3]. In the present work, the use of 2-hydroxy-3-iodo-4-*n*-butoxy-5-bromopropiophenone oxime (HIBBPO) as photometric reagent for Cu(II) has been described.

EXPERIMENTAL

A 0.1 M stock solution of Cu(II) has been prepared by dissolving copper sulphate (AR) in distilled water containing few drops of HCl. The amount of Cu(II) in this solution was determined following standard procedures[4].

Preparation of 2-hydroxy-3-iodo-4-*n*-butoxy-5-bromopropiophenone oxime (HIBBPO): Respropiophenone was prepared from resorcinol by standard methods[5]. 2-Hydroxy-4-*n*-butoxypropiophenone (HBP)[6], 2-hydroxy-4-*n*-butoxy-5-bromopropiophenone (HBBP)[7] have been prepared subsequently by following standard methods. For the prepareparation of HIBBP from the HBPP, iodination method[8] has been used.

2-Hydroxy-3-iodo-5-bromo-4-*n*-butoxypropiophenone oxime (HIBBPO) has been prepared by refluxing HIBBP with hydroxylamine hydrochloride in the presence of sodium acetate in ethanol medium for 4 h by following standard methods[9,10]. The reagent when recrystallized from ethanol was obtained in the colourless, needle like crystals (m.p. 70 ± 1 ºC), with m.w. 442.087 (calcd. for $C_{13}H_{17}NO_3BrI$ = 442). The reagent is insoluble in water, but soluble in alcohol, acetone, benzene, chloroform and carbon tetrachloride. The elemental analysis and spectral analysis of the compound was confirm its structure.

Preparation of Cu(II)-HBPBIO complex and selection of solvent: When an alcoholic solution of HIBBPO was added to 0.01 M aqueous metal ion solution, greenish precipitates of complex were obtained in the pH range 2.0-10.0. The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non-polar solvents like chloroform, benzene, CCl_4 *etc*. As copper-HIBBPO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of Cu(II).

Spectrophotometric measurements were made with a Systronics UV/Vis spectrophotometer (Model-118) using 10 mm glass cells. All pH measurements were made with Systronic pH meter (model-324).

RESULTS AND DISCUSSION

The pH of the solution has pronounced effect on the reaction between Cu(II) and HIBBPO and the stability of the complex. On the other hand, the absorbance is dependant upon the wavelength used. Both the parameters were therefore controlled to give maximum absorbance.

Absorbance measurements of the reagent in chloroform show maxima at 227, 262 and 318 nm with negligible absorbance beyond 400 nm. The absorbance measurements of Cu(II)-HBBIPO complex show a maxima at 390-410 nm and shoulder or plateau in the range 630-650 nm. As the interference due to the reagent appeared to be negligible a wavelength of 640 nm was selected for the present work.

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 2.0 to 10.0 were prepared, using sodium acetate, HCl and/or ammonium hydroxide. To above buffer solutions, 3 mL of 0.005 M Cu(II) solution and 10 mL 0.005 HIBBPO solution in chloroform were added. After shaking the mixture for 2 min. The absorbance of extracted green coloured complex was measured at 640 nm again a blank. From the results given in Fig. 1, it may be generalized that maximum absorbance takes place at pH range 6.0 to 9.0. Hence, a pH of 7.0 and wavelength of 640 nm have been selected for the present work.

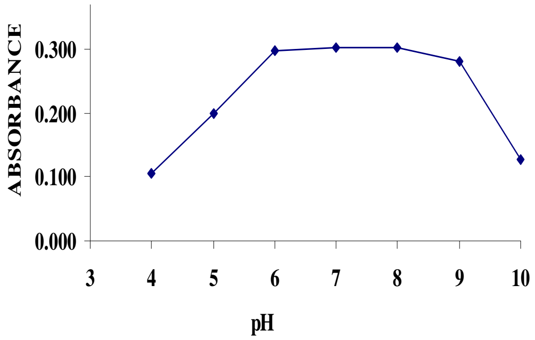

Fig. 1. Effect of pH

Reproducibility: Absorbance measurements of a set of six extracted complex solution prepared in a similar way and containing the same concentrations of all the reagents show that the reproducibility of measurements are quite good with a standard deviation of 3.22 Units, *i.e.*, 0.81 %.

Effect of time and temperature: To determine the effect of time and temperature on the intensity of colour and the stability of the Cu(II)-HIBBPO complex, absorbance was measured at room temperature (30 ºC) at regular intervals of time up to 2 weeks and also at temperatures of 30 to 55 ºC. The results show that complex is stable (1 % deviation) for two weeks and up to 50 ºC.

Stoichiometry and stability constant of the complex: The method of Vosbourgh and Cooper[11] showed that one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method[12], the slope ratio method[13] and Job's method of continuous variation[14] were employed (Fig. 2-4). All the three methods show a 1:2 metal:ligand ratio in the complex.

The IR spectra of reagent and complex revealed that the -OH (stretch) bond of 3385 cm^{-1} for the reagent disappears when the complex is formed *i.e.*, the complex formation takes place through the N of oximino group and O- of the 2-hydroxy group. Based on above data the Cu(II)-HIBBPO complex can be assigned the following structure.

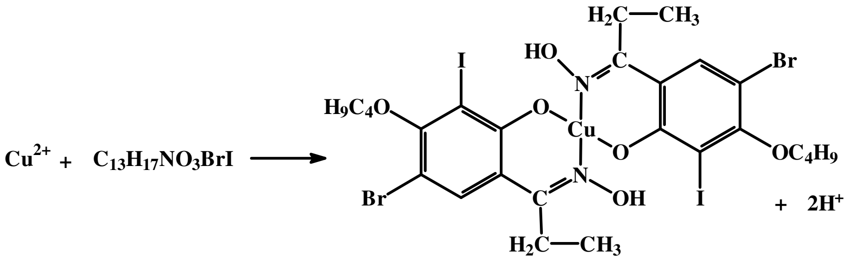

Fig. 2. Job's method of continuous variation; Set-I: 0.01 M Cu(II) and 0.01 M HIBBPO, Set-II: 0.02 M Cu(II) and 0.02 M HIBBPO

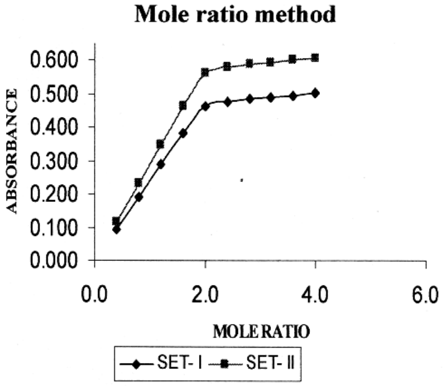

Fig. 3. Yoe and Jones mole ratio method; Set-I: 0.0025 M Cu(II) and 0.01 M HIBBPO, Set-II: 0.003 M Cu(II) and 0.012 M HIBBPO

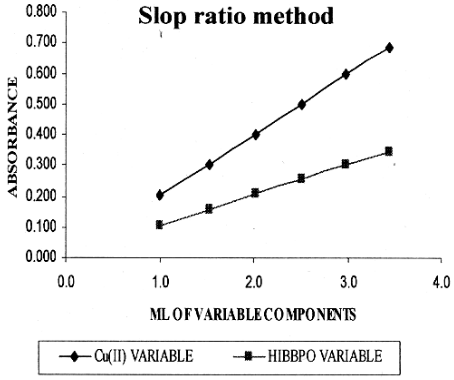

Fig. 4. Slope ratio method; 10 mL 0.01 M HIBBPO; 0.01 Cu(II) (variable) 10 mL 0.01 M Cu(II): 0.01 HIBBPO (variable)

The value of the stability constants calculated from the job's method as well as from the mole ratio method are given in Table-1. From the table the average value of stability constant may be taken as 6.29×10^8. The standard free energy of formation of the complex, ΔGº, is -1.219 kcal/mol at 30 ºC.

TABLE-1
STABILITY CONSTANT OF Cu(II)-HBPBIO COMPLEX AT 30 ºC

Method employed	Em	Es	α	K_{stab} (n=1)
Mole ratio method				
Set-I	0.505	0.485	0.03960	6.18×10^8
Set-II	0.606	0.585	0.03465	6.44×10^8
Job's Method				
Set-I	0.403	0.385	0.04467	6.70×10^8
Set-II	0.787	0.764	0.29220	6.08×10^8
Mean K_{stab}				6.29×10^8

Conformity to Beer's law and the optimum concentration range: Beer's law is obeyed between the range 20.96 to 222.39 ppm of Cu(II). At higher concentrations negative deviations occur. The optimum concentration range for determination of Cu(II) in solution, as deduced from the Ringbom plot[15], is found to be 20.96 to 177.82 ppm. The molar absorptivity (ε) of the complex is 202 mol^{-1} cm^{-1} and the photometric sensitivity as per Sandell's definition[16] is found to be 0.031 $\mu g/cm^2$ at 640 nm.

Effect of diverse ions: The interference due to the presence of other ions on the determination copper ions as Cu(II)-HBPBIO complex has also been studied. A difference of more than 2 % in the absorbance value has been considered as interference. According to this criterion, the tolerance limits of various ions, expressed in ppm, for a solution containing 15.88 ppm (Cu(II)) are as follows.

1000 ppm: F^-, Cl^-, Br^-, I^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Tartrate, Citrate, SCN^-.
50 ppm: Zn^{2+}, Sr^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Bi^{2+}.
5 ppm: Mo^{6+}, U^{2+}, Sn^{2+}, Ti^{2+}, V^{5+}, Fe^{3+}.

Determination of copper from various samples: To determine the usefulness of the reagent in estimation of copper from various samples containing copper were taken and estimated by HIBBPO. For this purpose, the alloy samples containing copper metal were dissolved in 1:1 nitric acid by heating on a sand bath. The resulting solution for suitable aliquot of given sample solution was made up to 100 mL with distilled water in a volumetric flask. 2 mL of this diluted solution was pipeted out and its spectrophotomatic determation was carried out by the proposed method. The result are given in Table-2.

TABLE-2
ANALYSIS OF COPPER IN VARIOUS SAMPLES

Sample	Copper content (%)		Relative error (%)
	Reported/found using standard method	Found using proposed method	
Brass	72.50	73.08 73.12 73.12 Average 73.10	0.82
Bronze	92.06	93.64 93.50 93.27 Average 93.47	1.53

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