

NOTE

2-Hydroxy-4-Ethoxy-5-Bromopropiophenone Oxime as an Analytical Reagent for Cu(II)

B.D. DESAI and K.K. DESAI*

Department of Chemistry, South Gujarat University, Surat-395 007, India

2-Hydroxy-4-ethoxy-5-bromopropiophenone oxime (HEBPO) was developed as a new analytical reagent for the gravimetric estimation of Cu(II). In pH range 3 to 8 the reagent gives a buff coloured precipitate with Cu^{2+} . Job's method and Yoe Jones' mole ratio method revealed that the stoichiometry of the complex is 1 : 2 metal : ligand. The Beer law is obeyed up to 101.90 ppm of Cu^{2+} . The molar absorptivity and the Sandell's sensitivity at 420 nm were found to be $1.725 \times 10^2 \text{ Lit mol}^{-1} \text{ cm}^{-1}$ and $0.368 \mu\text{g/cm}^2$ respectively. The stability constant of Cu(II)-HEBPO complex is found to be 3.154×10^8 . Gibb's free energy change for complex formation reaction was found to be $-11.624 \text{ kcal/mole}$. The reagent can be used for the analysis of brass.

Many organic reagents like *o*-hydroxy ketoximes¹⁻⁴, thiosemicarbazones⁵ and chalcone oximes⁶ have been used for gravimetric or spectrophotometric determination of transition metal ions. In this work the use of 2-hydroxy-4-ethoxy-5-bromopropiophenone oxime (HEBPO) as gravimetric and spectrophotometric reagent for copper is reported. Spectrophotometric methods have been used to confirm the stoichiometry of complex and to determine the stability constant of complex.

Spectrophotometric measurements were done on Bausch and Lomb Spectronics-20 spectrophotometer. All pH measurements were done on Elico pH meter LI-10T.

Bromination of 2-hydroxy-4-ethoxy propiophenone⁴ by bromine in acetic acid at 20°C gives 2-hydroxy-4-ethoxy-5-bromopropiophenone. Its oxime was prepared by sodium acetate method. It was crystallised from ethanol (m.p. $136 \pm 1^\circ\text{C}$). The reagent is soluble in ethanol, methanol and acetone.

Stock Solution: Stock solution of Cu(II) (0.05 M) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and was used after standardisation with EDTA. Stock solution of 2-hydroxy-4-ethoxy-5-bromopropiophenone oxime (HEBPO) (0.05 M) was prepared by dissolving the oxime in 70% aqueous ethanol.

Gravimetric Procedure: An aliquot of Cu(II) solution was diluted to 100 mL with distilled water, warmed and the pH of solution was adjusted in the range of 3 to 8 with suitable buffer. Then 0.05 M solution of HEBPO in ethanol was

added till precipitation was complete. The buff precipitate was digested on a water bath at 60°C for 1 h and filtered through a previously weighed sintered glass crucible (G-4). The precipitate was washed with hot water and then finally with ethanol to remove any reagent which might have precipitated on dilution. The precipitate were dried at 110°C and weighed.

Spectrophotometric Procedure

The Cu(II)-HEBPO complex is insoluble in ethanol and methanol. It is soluble in solvents like chloroform, dioxane; hence the complex was extracted in chloroform. For this purpose a suitable aliquot of Cu(II) solution was taken and pH was adjusted to 5 with (CH₃COOH + CH₃COONa) buffer and a HEBPO solution was added. The complex thus precipitated was extracted with three 5 mL portions of chloroform and the volume of chloroform extract was made up to 25 mL. The absorbance of chloroform extract was measured against solvent blank.

Gravimetric Determination of Copper: To establish the applicability of the reagent for gravimetric estimation of Cu(II), the metal ion was determined in pH range 3 to 8, the error being maximum 1%. Estimations were done at pH 5 using different aliquots of Cu(II). In all cases, the error in Cu(II) content did not exceed ±0.5% (Table-1).

TABLE-1
EFFECT OF Cu(II) CONCENTRATION ON GRAVIMETRIC ESTIMATION
OF COPPER AT pH 5

Copper taken (mg)	Cu(II) HEBPO complex obtained (mg)	Copper found (mg)	Error	
			(mg)	%
15.89	158.8	15.83	-0.06	-0.37
31.77	318.8	31.78	+0.01	+0.03
47.67	478.1	47.66	-0.01	-0.02

Effect of Diverse Ions: In gravimetric determination of copper (31.77 mg) at pH 5, it was found that Ca²⁺, Ba²⁺, Sr²⁺, Al³⁺, Zn²⁺, Be²⁺ and common anions chloride, bromide, nitrate, sulfate, nitrite, thiosulphate did not interfere. Fe³⁺ interferes but its interference can be removed by masking Fe³⁺ with NaF.

Spectrophotometric Determination of Copper: For taking the absorption spectra, 5 mg chelate was dissolved in 25 mL chloroform and the absorbance was measured in the range of 350–600 nm. It was observed that the absorbance of solution increases continuously towards the shorter wavelength. The absorbance spectrum shows a shoulder band at 420 nm and hence all measurements were carried out at 420 nm.

Validity of Beer's Law: The Cu(II)-HEBPO complex in chloroform obeys Beer's law up to 101.90 ppm of Cu(II). Beyond this concentration the absorbance plot shows a negative deviation from linearity. The molar absorptivity of the complex obtained from absorbance data is found to be 1.725×10^2 lit. mol⁻¹cm⁻¹ at 420 nm. The photometric sensitivity as per Sandell's definition is 0.368 µg/cm² of Cu(II) at 420 nm.

Stoichiometry and Stability Constant of Complex: The stoichiometry of Cu(II)-HEBPO complex was determined by (i) Job's method of continuous variation and (ii) Yoe Jones mole ratio method. Both the methods gave the metal : ligand ratio of 1 : 2. Stability constant calculated using data of above methods is 3.154×10^8 . From K_s value, Gibb's free energy change for complex formation reaction was calculated and its value is -11.624 kcal/mole at 27°C .

Determination of Copper in Brass: Exactly 0.3148 g of brass was taken and dissolved in nitric acid (1 : 1). The excess nitric acid was boiled off and the solution was diluted to 100 mL with distilled water. 10 mL aliquot was taken and Cu(II) was determined gravimetrically as described previously. The experiment was repeated three times. Analysis %: Cu (found) 70.84; Cu (reported) 70.48.

The same reagent is being studied for the complexation of other transition metal ions.

ACKNOWLEDGEMENT

The authors are thankful to the Head, Chemistry Department, South Gujarat University, Surat for providing facilities to carry out the work.

REFERENCES

1. K.K. Desai, N.D. Naik and H.B. Naik, *J. Indian Chem. Soc.*, **54**, 414 (1977).
2. A.B. Bhatt and K.K. Desai, *J. Inst. Chemists (India)*, **61**, 5 (1989).
3. D. Vijaykumar, R.C. Hussain and N. Appalaraju, *J. Indian Chem. Soc.*, **67**, 786 (1990).
4. K.K. Desai and H.B. Naik, *Indian J. Chem.*, **25A**, 297 (1986).
5. M.J. Desai and K.K. Desai, *Asian J. Chem.*, **11**, 1313 (1999).
6. J.J. Desai, P.G. Desai and A.G. Mehta, *Asian J. Chem.*, **11**, 519 (1999).

(Received: 18 September 2000; Accepted: 16 November 2000) AJC-2188