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NOTE

2-Hydroxy-4-Isopropoxy-5-Bromoacetophenone Oxime as an Analytical Reagent for Cu(II)

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2-Hydroxy-4-isopropoxy-5-bromoacetophenone oxime (HIBAO) was developed as a new analytical reagent for the gravimetric estimation of Cu(II). In pH range 3.5–8.0 the reagent gives a brown coloured precipitate with Cu(II). Spectrophotometric methods revealed that the stoichiometry of the complex is 1 : 2 (metal : ligand). Beer's law is obeyed up to 76.42 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity at 400 nm were found to be 6.32×10^2 L mol^{-1} cm^{-1} and 0.108 $\mu g/cm^2$ respectively. The stability constant cf Cu(II)-HIBAO complex is found to be 4.25×10^9. Gibb's free energy change for complex formation reaction was found to be –13.18 kcal/mol. The reagent can be used for the analysis of brass.

Key Words: Gravimetric estimation, Cu(II), 2-Hydroxy-4-isopropoxy-5-bromoacetophenone oxime.

Many organic reagents like *o*-hydroxy ketoximes[1–4], thiosemicarbazones[5] and chalcone oximes[6] have been used for gravimetric or spectrophotometric determination of transition metal ions. The present work describes the use of 2-hydroxy-4-isopropoxy-5-bromoacetophenone oxime (HIBAO) as gravimetric and spectrophotometric reagent for Cu(II). Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constant of the complex.

Spectrophotometric measurements were done on Bausch and Lomb single beam spectrophotometer (Spectronic-20) and Shimadzu UV-160, UV-Vis Spectrophotometer. All pH measurements were done on Equiptronic pH-meter (Model No. EQ614).

Preparation of Reagent: Bromination of 2,4-dihydroxyacetophenone using bromine in acetic acid at 20°C gave 2,4-dihydroxy-5-bromoacetophenone. 2-Hydroxy-4-isopropoxy-5-bromoacetophenone was prepared from 2,4-dihydroxy-5-bromoacetophenone, K_2CO_3 and isopropyl bromide. Its oxime was prepared by sodium acetate method. It was crystallized from ethanol (m.p. 198°C) (nitrogen, found: 4.83%, calcd: 4.86%).

Stock solution: Stock solution of Cu(II) (0.05 M) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ in distilled water and was used after standardization with

EDTA. Stock solution of 2-hydroxy-4-isopropoxy-5-bromoacetophenone oxime (HIBAO) (0.05 M) was prepared by dissolving the oxime in 70% aqueous ethanol.

Gravimetric procedure: An aliquot of Cu(II) was diluted to 100 mL with distilled water, warmed and the pH of the solution was adjusted in the range 3.5–8.0 with suitable buffer. Then 0.05 M solution of HIBAO in ethanol was added till precipitation was completed. The brown 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 70% aqueous ethanol to remove any reagent which might have precipitated on dilution. The precipitates were dried at 110°C and weighed.

Gravimetric Determination of Copper: To establish the applicability of the reagent for gravimetric estimation of Cu(II), the metal ion was determined in the pH range 3.5–8.0, the maximum error being ±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 ±0.25% (Table-1).

TABLE-1
RESULTS OF GRAVIMETRIC ESTIMATION OF COPPER(II) AT pH 5

Copper taken (mg)	Cu(II)-HIBAO complex obtained (mg)	Copper found (mg)	Error	
			mg	%
15.89	0.1592	15.86	–0.03	–0.18
31.77	0.3190	31.78	+0.01	+0.03
47.66	0.4783	47.64	–0.02	–0.04
63.56	0.6383	63.57	+0.01	+0.01

Effect of diverse ions: In gravimetric determination of copper (31.77 mg) at pH 5, it was found that Ca^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Zn^{2+}, Ba^{2+} and common anions chloride, bromide, nitrate, sulfate, nitrate, thiosulphate did not interfere. At this pH, Pd(II), Co(II) and Fe(III) interfere seriously.

Spectrophotometric Studies: For taking the absorption spectra, 5 mg chelate was dissolved in 25 mL methyl isobutyl ketone (MIBK) and the absorbance was measured in the range 350–800 nm. It was observed that the absorbance of the solution increased continuously towards the shorter wavelength. The absorption spectrum showed a shoulder at 400 nm and hence all measurements were carried out at 400 nm.

The Cu(II)-HIBAO complex is insoluble in ethanol and methanol. It is soluble in solvents like methylisobutylketone (MIBK) and DMF; hence, the complex was extracted in MIBK. For this purpose a suitable aliquot of Cu(II) solution was taken and pH was adjusted to 5 with ($CH_3COOH + CH_3COONa$) buffer and HIBAO solution was added. The complex thus precipitated was extracted with three 5-mL portions of MIBK and the volume of MIBK extract was made up to 25 mL. The absorbance of MIBK extract was measured against solvent blank.

Validity of Beer's Law: The Cu(II)-HIBAO complex in MIBK obeys Beer's law up to 76.42 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 6.32×10^2 L mol^{-1} cm^{-1} at 400 nm. The photometric sensitivity as per Sandell's definition is 0.108 $\mu g/cm^2$ of Cu(II) at 400 nm.

Stoichiometry and Stability Constant of Complex: The stoichiometry of Cu(II)-HIBAO complex was determined by (i) Job's method of continuous variation and (ii) Yoe and Jones mole-ratio method. Both the methods gave the metal : ligand ratio of 1 : 2. Stability constant calculated using data of above methods is 4.25×10^9. From K_s value, Gibb's free energy change for complex formation reaction was calculated and its value was found –13.18 kcal/mol at 27°C.

Determination of Copper in Brass: Exactly 0.5589 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 at pH 4.0 as described previously. Zn(II) and other trace metals did not interfere at this pH. The experiment was repeated three times. Cu (found): 70.42%, Cu (reported) 70.69%.

The same reagent has been used for the complexation of other transition metal ions,

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