

2,4-Dihydroxy-5-nitropropiophenone Oxime as a Gravimetric Reagent for Cu(II)

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2,4-Dihydroxy-5-nitropropiophenone oxime (DHNPO) was developed as a new analytical reagent for gravimetric determination of Cu(II). In pH range of 3.0 to 6.0, this reagent gives a buff coloured precipitate with Cu(II). Interference of many cations and anions has been checked. Job's method and mole ratio method revealed that the stoichiometry of the complex is 1 : 2, the Beer law is obeyed upto 7.62 ppm of Cu(II). The molar absorptivity at 520 nm was found to be $9.92 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$. The stability constant of the complex has been calculated from spectrophotometric data. The Cu(II) complex was found to have paramagnetic character. TGA studies were done on the Cu(II) complex. Energy of activation for decomposition step has been calculated using Broide method. The reagent has been successfully applied to the determination of Cu(II) in drain microtech solution.

Key Words: 2,4-Dihydroxy-5-nitropropiophenone Oxime, Gravimetric reagent, Cu(II).

INTRODUCTION

Most of the studies reported on oximes have centred around those derived from aldehydes and ketones, and much less work has been reported on *o*-hydroxy ketoximes¹⁻⁵, phenyl hydrazones, thiosemicarbazones, chalcone oximes etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. In this work, the use of 2,4-dihydroxy-5-nitropropiophenone oxime (DHNPO) as a gravimetric reagent for Cu(II) has been reported. Spectrophotometric methods have been used to confirm the stoichiometry of complex and to determine the stability constants of complex.

EXPERIMENTAL

Spectrophotometric measurements were done on Bausch and Lomb spectrophotometer (Spectronics-20). All the pH measurements were done on Elico pH-meter (LI-10T). The reagent DHNPO was synthesized⁶ and characterized by PMR spectra⁷⁻⁹.

RESULTS AND DISCUSSION

Gravimetric determination of Cu(II): A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Copper sulphate solution (0.05 M, 10 mL) was

taken in a clean beaker and diluted to about 100 mL with distilled water and pH of the solution was adjusted between 4.0 to 5.0 using sodium acetate-acetic acid buffer. The solution was warmed at 60°C and little excess of reagent solution was added (0.05 M, 22 mL). A buff precipitate obtained was digested on water bath for 60 min at 60°C. The precipitate was filtered through a previously weighed sintered glass crucible (G₄) and washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution.

The chelate was dried to constant weight at 110–115°C in a hot air oven, cooled and weighed. The experiment was repeated for different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH to evaluate its applicability. The results are tabulated in Table-1.

TABLE-1

pH	Cu(II) complex (g)	Cu(II) Found (mg)	Error	
			mg	%
3.5	0.2538	31.40	-0.37	-1.16
3.5	0.2542	31.45	-0.32	-1.00
4.0	0.2549	31.53	-0.24	-0.75
4.0	0.2551	31.56	-0.21	-0.66
5.0	0.2576	31.87	+0.10	+0.31
5.0	0.2559	31.66	-0.11	-0.34
5.5	0.2564	31.72	-0.05	-0.15
5.5	0.2571	31.81	+0.04	+0.12
6.0	0.2575	31.86	+0.09	+0.28
6.0	0.2580	31.92	+0.15	+0.47
7.0	0.2552	31.57	-0.20	-0.62
7.0	0.2547	31.51	-0.26	-0.81
8.0	0.2541	31.43	-0.34	-1.07
8.0	0.2539	31.41	-0.36	-1.13
9.0	0.2535	31.36	-0.41	-1.29
9.0	0.2532	31.32	-0.45	-1.41

Conversion factor: 1 g complex = 123.73 mg of Cu(II)

Interference

To study the effect of foreign ions on gravimetric determinations of Cu(II), 810 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.5 and gravimetric estimation was done. It was observed that Sr(II), Ca(II), Zn(II), Ni(II), Mn(II), Ba(II), Mg(II) and Cd(II) do not interfere at this pH, but

Fe(III), Pd(II), Co(II) interfere seriously. Interference of Fe(III) can be removed by masking with H_3PO_4 . Many common anions like chloride, bromide, iodide, nitrite, sulphate were not found to interfere.

Spectrophotometric study of Cu(II)-DHNPO complex: In absorption spectra of Cu(II) complex in chloroform a shoulder is obtained at 520 nm and hence all spectrophotometric measurements were done at this wavelength. Different aliquots of Cu(II) solution were taken and buffer solution was added to maintain pH = 5.5. The excess of reagent was added to get precipitate of complex. It was extracted with three 5.0 mL portions of chloroform and the combined extracts were diluted to 25 mL. The absorbance was measured at 520 nm. The absorbances were plotted against the concentration of Cu(II). It was found that Beer's law was obeyed up to 7.62 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity were calculated from graph and it was found to be $9.92 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.064 \mu\text{g of Cu(II)/cm}^2$ respectively.

Job's methods¹⁰ and mole ratio method¹¹ were used to determine the stoichiometry of the complex. It was found to be 1 : 2 (M : L). This is in agreement with the stoichiometry determined from gravimetry. The stability constants were calculated using the formula:

$$K_a = \frac{1 - \alpha}{4\alpha^3 C^2}$$

where α = degree of ionization given by $\frac{E_m - E_s}{E_m}$

C = concentration of complex

E_m = maximum absorbance found from the graph

E_s = absorbance at the stoichiometric molar ratio of the metal reagent in complex

The average stability constant found from two methods is 5.44×10^9 and ΔG^0 for complex formation at 27°C is -13.27 KCal/mol.

Thermogravimetric analysis: TGA of the Cu(II) chelate was done on Universal V₁-12E-TA thermal analysis system. It was found that there is no loss in weight up to 200°C indicating that the chelate can be safely dried without decomposition at 110°C. Loss in weight above 200°C is due to decomposition of chelate and loss of ligand molecules. Weight of final residue corresponds to CuO in accordance with the formula $(C_9H_9O_5N_2)_2Cu$. The observed loss and weight of residue agree well with the loss and weight expected as per formula of chelate in which M : L ratio is 1 : 2 in the complex.

Broido's method¹² was applied to TGA thermograms of Cu(II)-DHNPO complex obtained with heating rate 10°C/min. Activation energy E_a was found to be 20.13 kcal/mol.

Magnetic susceptibility measurement: The magnetic measurements of complex at room temperature were carried out on Gouy balance as per the method suggested by Prasad *et al.*¹³ The magnetic moment of solid Cu(II)-DHNPO complex was determined, which indicates the paramagnetic character. Values of magnetic moments at 4 A and 6 A are 1.86 BM and 1.87 BM respectively.

Effective magnetic moment value of Cu(II)-DHNPO complex indicates the presence of one unpaired electron.

IR Spectra

IR (cm^{-1}) spectrum (KBr) of the ligand and its complex shows the following bands:

TABLE-2
IR (cm^{-1}) BANDS OF Cu(II)-DHNPO COMPLEX

Compound	$\nu(\text{OH})$	$\nu(\text{CH})$ Aliphatic	$\nu(\text{CH})$ Aromatic	$\nu(\text{C}=\text{N})$	$\nu(\text{NO})$
DHNPO	3399	2860	2990	1583	993
Cu(II)-DHNPO	–	2860	2990	1540	930

Examination of the IR spectra of the chelate shows that the band due to O—H stretching of 2-hydroxy group disappears in the Cu(II)-DHNPO chelate. This indicates that during chelate formation the hydrogen of 2-hydroxy group is lost and oxygen forms covalent bond with metal. The band due to the C=N stretching which is observed at 1583 cm^{-1} in ligand is shifted to 1540 cm^{-1} in chelate. This may be due to coordination of metal through nitrogen. This is also supported by slight downward shift of $\nu(\text{NO})$.

Determination of copper in drained microetch solution (persulphate base)

Gujarat Narmada Valley Fertilizers Corporation Limited (GNFC), Bharuch has a plant to manufacture printed circuit boards. In this plant they get microetch solution (persulphate base) which has approximately 2% copper. This solution was procured to check the applicability of the reagent DHNPO to determine copper.

The sample was analyzed by conventional titrimetric method, which showed 2.166% copper content. To determine copper in the solution, 10 mL solution was diluted to 100 mL with distilled water. 10 mL of this diluted solution was taken to a gravimetric procedure using DHNPO. The experiment was repeated three times. The results are tabulated in Table-3.

TABLE-3

Expt. No.	Weight of Cu(II)-DHNPO chelate in g	Weight of Cu(II) found in mg	% of copper in sample solution	% Error
1.	0.1745	21.59	2.16	-0.32
2.	0.1740	21.52	2.15	-0.64
3.	0.1742	21.55	2.15	-0.50

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