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NOTE

2-Hydroxy-3-chloro-5-ethylacetophenone Oxime as an Analytical Reagent for Copper(II)

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2-Hydroxy-3-chloro-5-ethylacetophenone oxime was developed as new analytical reagent for gravimetric estimation of copper and for its separation from other ions. The buff precipitation of copper(II) by the reagent is complete between pH 3.0 to 9.0 and after drying at 110-120 ºC the composition of the precipitation corresponds to $Cu(C_{10}H_{11}O_2NCl)_2$. It is also observed that by proper control of pH and by using suitable masking agents, it is possible to estimate copper in presence of other interfering ions.

Key Words: Analytical reagent, 2-Hydroxy-3-chloro-5-ethylacetophenone oxime, Copper(II).

o-Hydroxy aldoximes[1-3] and ketoximes[4-8] are found to interact with metal ions giving precipitation or colouration due to complex formation. These reagents have been used for spectrophotometric and gravimetric determination of copper and other transition metal ions. In the present work, we report the use of 2-hydroxy-3-chloro-5-ethylacetophenone oxime (HCEAO) as gravimetric and spectrophotometric reagent for Cu(II). The reaction of HCEAO with Cu(II) gives a buff coloured precipitate between the pH range 2.5 to 9.0. Cu(II) (6.5-65 mg) has been determined gravimetrically at pH 3.0-3.5, the error being less than 1 % on the use of Cu(II) calculated. The interference due to several foreign ions has been masked by controlling the pH or by suitable masking agents. The precipitate can be safely dried between 110-120 ºC within a period of 0.5 h .

All the chemicals used were of AR grade. The stock solution of Cu(II) (0.05 M) has been prepared by dissolving the appropriate amount of copper(II) chloride in double distilled water and little hydrochloric acid and was used after standardization with EDTA. An ethanolic solution of ligand (170) was employed and the pH was adjusted using acetate buffer.

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2-Hydroxy-3-chloro-5-ethylacetophenone oxime (HCEAO): *p*-Ethylphenol was chlorinated using sulphuryl chloride. The product was 2-chloro-4-ethylphenol (b.p. 212 ºC)[9] which was acetylated with acetic anhydride to give corresponding phenylacetate (b.p. 232 ºC)[10]. The Fries rearrangement of the ester gave 2-hydroxy-3-chloro-5-ethylacetophenone (HCEAO)[10]. The ketone was condensed with hydroxylamine hydrochloride in presence of sodium acetate to give 2-hydroxy-3-chloro-5-ethylacetophenone oxime (HCEAO). It was recrystallized several times from ethanol, colourless needles (m.p. 118 ºC). (N found = 6.52 %; calculated = 6.57 %).

Determination of Cu(II): A known volume of 0.05 M Cu(II) solution was taken in a beaker and diluted to 150 mL. The required pH was adjusted using acetic acid and sodium acetate buffer.

The buff precipitate so formed was digested for 0.5 h on the water-bath (60-70 ºC) and complete precipitation was checked in supernatant liquid. The precipitate was filtered while hot, through a sintered glass crucible (G-4) and washed with hot water. The precipitate was finally washed with 60 % ethanol and was dried at 110-120 ºC in an oven to constant weight as $Cu(C_{10}H_{11}O_2NCl)_2$.

It has been found that copper can be quantitatively determined in the pH range 3.0-9.0 although the precipitation starts at pH 2.5. The conversion factor (copper/copper complex) is 0.1300. Average results of four reading of the estimations of copper(II) are given in Table-1.

TABLE-1
DETERMINATION OF Cu(II) pH 3.0-3.5

Cu(II) taken (mg)	Wt. of complex (mg)	Cu(II) found (mg)	Error (%)
6.42	49.1	6.38	– 0.54
12.84	99.0	12.87	+ 0.23
16.04	123.6	16.07	+ 0.19
32.09	247.0	32.11	+ 0.06
64.18	493.2	61.12	– 0.08

Effect of pH: To check the effect of pH, absorbance of the organic layer containing Cu(II)-HCEAO complex extracted with chloroform from the aqueous solution of different pH was measured. It was observed that maximum absorbance occurs at pH 3.0-5.0 was selected for the present work.

Effect of foreign ions: The interference of foreign ions were masked employing suitable masking agents or by controlling the pH. Fe(II), Fe(III) and V(IV) were masked by sodium potassium tartarate. Ni(II), Mn(II) and Co(II) are found not to interfere at pH 3.0-3.5. The chloride, sulphate and nitrate ions were washed out by hot water.

Validity of Beer's law: The buff Cu(II) HCEAO complex in $CHCl_3$ obeys Beer's law up to 26.65 ppm of Cu(II). Beyond this concentration the absorbance plot does not show linearity. The average molar absorptivity of the complex obtained from the absorbance data is found to be 7.26×10^2 L mol^{-1} cm^{-2} at 400 nm.

The metal content of the complex was determined by standard analytical method. The elemental analysis gave the results as found (%) C, 49.5; H, 4.40; N, 5.74; Cu, 12.12 : Calculated (%) C, 49.60, H, 4.50; N, 5.78; Cu, 12.23. The composition of the complex corresponds to the molecular formula, $Cu(C_{10}H_{11}O_2NCl)_2$, which is in agreement with the molecular weight determined cryosopically using benzene as solvent. This ratio indicates the monomeric nature of the chelate *i.e.* ML_2 which is further confirmed by Job's continuous variation method[11] and Yoe and Jone's mole ratio method[12]. The copper chelate is extractable in chloroform, benzene and carbon tetrachloride, showing inert nature of the complex.

The magnetic measurement of the complex shows the paramagnetic nature (μ_{eff} BM 1.92). The normal oximes have IR absorption bands at 3300-3150 cm^{-1} (OH *str.*), 1690-1510 cm^{-1} (C=N *str.*) and around 950 cm^{-1} (N-O *str.*). In the present investigations, HCEAO has shown prominent bands at 3075, 1585 and 997 cm^{-1} assignable to intramolecular hydrogen bonded ν(OH), ν(C=N) and ν(N-O *str.*), respectively. The weak band at 3075 cm^{-1} due to intramolecular hydrogen bonded is not observed in the complex. The band due to phenolic C-O vibrations at 1316 cm^{-1} in the ligand is observed at 1389 cm^{-1} in the complex. These observations suggest that *o*-hydroxy group of the reagent has taken part in the bond formation.

The C=N *str.* at 1585 cm^{-1} the free ligand is found at 1535 cm^{-1} in the complex and can be interpreted as a consequence of co-ordination of nitrogen with metal on the basis of above results. Following structure is assigned to the complex.

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