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2-HYDROXY-5-CHLOROBENZOPHENONE OXIME [HCBO] AS AN ANALYTICAL REAGENT : STUDIES ON CU(II) CHELATE

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ABSTRACT The ligand 2-Hydroxy-5-chlorobenzophenone oxime (HCBO) was developed as a new analytical reagent for the gravimetric and spectrophotometric analysis of Cu(II) ion. In the pH range of 2.5 to 8.0 this reagent gives buff precipitates with Cu(II). Job's method of continuous variation and Yoe and Jone's mole ratio method revealed the stoichiometry of the complex to be 1:2 [M:L]. The obeyence of Beer's law was studied and the molar absorptivity and Sandell's sensitivity were calculated. The reagent and its complex have been characterized by elemental analysis and IR spectra. The reagent has been used for the determination of Copper content in Brass alloy.

KEYWORDS : Analytical Reagent, Cu(ii) Chelate, 2-hydroxy-5-chlorobenzophenone Oxime(hcbo)

Introduction :

In the current scenario, large number of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes[1-2], phenyl hydrazones, thiosemicarbazones, chalcone oximes[3-12] etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2-Hydroxy-5-chlorobenzophenone oxime [HCBO] as an analytical reagent for Cu(II).

Experimental :

Instruments :

Spectrophotometric measurements were done on a "GENESYS" (Spectronic 20) single beam spectrophotometer and "Shimadzu UV-160A, UV-Visible Spectrophotometer". The IR spectra were recorded on "Perkin-Elmer" FTIR Spectrophotometer (RX-1) in KBr pallet. All pH measurements were done on Equip-Tronic pH meter (Model No.EQ 614).

Stock solution :

Stock solution of $CuSO_4.5H_2O$ (0.05 M) was prepared by dissolving 3.121 gm of $CuSO_4.5H_2O$ (A.R.) in minimum quantity of water and diluted to 250 ml with doubly distilled water. Concentrated sulphuric acid was added in little amount to prevent the hydrolysis of the salt. It was used after standardization[13] with EDTA.

Synthesis of Reagent [HCBO] :

p-chlorophenyl benzoate was prepared from p-chlorophenol. p-chlorophenol (0.1 mol) and benzoylchloride (0.1 mol) were mixed thoroughly and the mixture was heated on boiling water bath for three hrs. It was then poured over crushed ice and kept overnight, the product was treated with diluted NaOH solution. p-chlorophenyl benzoate (0.05 mol) and anhydrous $AlCl_3$ (8.0 g) was taken in round bottom flask and the mixture was heated in oil bath at 120C for four hours. On acidification with HCl, 2-hydroxy-5-chlorobenzophenone was obtained. The 2-hydroxy-5-chlorobenzophenone was converted to oxime by sodium acetate method. 2-hydroxy-5-chlorobenzophenone (3.0 g) was dissolved in minimum quantity of ethanol. Aqueous solution of hydroxylamine hydrochloride (6.0 g) and sodium acetate (5.0 g) were added to it. A little more alcohol was added to get clear solution. The solution was refluxed on a water bath at 75-80C for 6-8 hrs. On crystallization from alcohol pure oxime in the form of white crystals with m.p.114C was obtained. Stock solution of reagent (0.05 M) was prepared by dissolving in 70% aqueous ethanol.

Gravimetric determination of Cu(II) :

Copper sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water. A little excess of reagent solution was added (0.05 M, 22 ml). The pH of the solution was adjusted between 3.0 to 9.0 using suitable acid buffer. A buff precipitate obtained were digested on water-bath for 60 minutes at 60C. The precipitate were filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110C in hot air oven, cooled and weighed as $Cu(C_{13}H_9O_2NCl)$. Duplicate experiments were performed in each case. The results are given in Table 1. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH value to evaluate its applicability. The error in any case did not exceed 1.0%.

Interference from other ions :

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Mg(II), Ca(II), Ni (II), Zn(II), Cd(II) and Al(III) do not interfere at this pH but Pd(II), Co(II) and Fe(III) interfered seriously. Interference of Fe(III) can be removed by masking it with fluoride ion. Many common anions like nitrate, sulphate, chloride, bromide, iodide were not found to interfere.

Table : 1 GRAVIMETRIC DETERMINATION OF Cu(II) USING HCBO

Cu(II) taken = 32.09 mg

Drying temperature = 110-115°C
Salt = $CuSO_4.5H_2O$

pH	Cu(II) complex in mg	Cu(II) found in mg	Error	
			in mg	%
3.0	278.15	31.74	-0.35	-1.10
3.0	278.2	31.74	-0.35	-1.08
3.5	278.85	31.82	-0.27	-0.85
3.5	278.76	31.81	-0.28	-0.88
4.0	281.60	32.13	+0.04	+0.13
4.0	281.56	32.13	+0.04	+0.11
4.5	281.91	32.17	+0.08	+0.24
4.5	281.95	32.17	+0.08	+0.25
5.0	281.98	32.17	+0.08	+0.26
5.0	281.97	32.17	+0.08	+0.26
5.5	283.32	32.33	+0.24	+0.74
5.5	283.25	32.32	+0.23	+0.71
6.0	283.75	32.38	+0.29	+0.89
6.0	283.95	32.40	+0.31	+0.86
6.5	284.20	32.42	+0.33	+1.02
6.5	284.12	32.43	+0.34	+1.05

Conversion factor = 0.1141

Spectrophotometric study of Cu(II)-HCBO chelate :

5 mg of chelate was extracted in 25 ml of chloroform and the absorption spectra was recorded in the range of 300 to 800 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 620 nm and hence all measurements were carried out at 620 nm.

Verification of Beer's law and optimum concentration range :

To 5 ml of solution (0.01 M) of the reagent HCBO, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using [$CH_3COOH + CH_3COONa$] buffer. The insoluble complex was extracted in chloroform using three 5.0 ml, portions of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbances of these solutions were measured at 620 nm against chloroform as blank. Absorbance values were plotted against metal concentration expressed in ppm. A straight line passing through the origin, indicating obeyance of Beer's law is obtained up to 31.11 ppm of Cu(II). The molar absorptivity of the Cu(II)-HCBO complex was found to be 5.77 x 10^2 lit.mol^{-1}.cm^{-1} and the Sandell's sensitivity is found to be 0.11 µg/cm^2 at 620 nm.

Stoichiometry of complex :

Job's method of continuous variation[14] and Yoe and Jones mole ratio method[15] were used to determine the stoichiometry of the Cu(II)-HCBO complex. From both the methods, it was found to be 1:2 [M:L] ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from two methods is 8.42 x 10^8. The Gibb's free energy change for complex formation reaction at 30C was found to be -9.21 K.cal/mole.

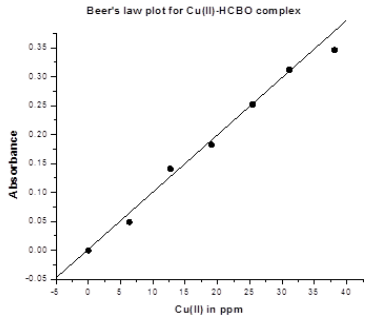

Figure 1 : Beer's law plot for Cu(II)-HCBO complex

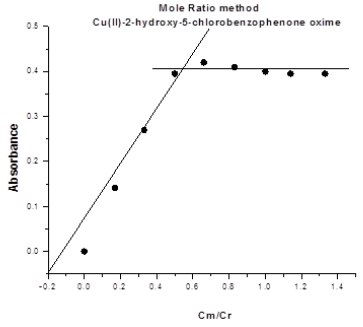

Figure -2. Yoe and Jones mole ratio method for Cu(II)-HCBO complex Plots of Yoe and Jones mole ratio method for determination of M:L ratio 0.005 M Cu(II), 0.005 M HCBO; pH = 5.0; lmax= 620 nm.

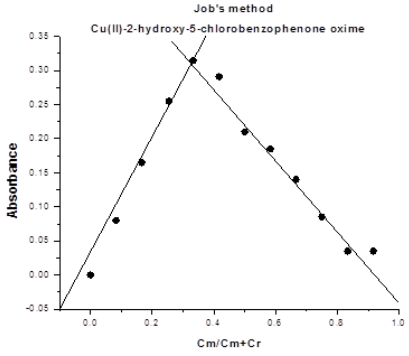

Figure -3. Job's method for Cu(II)-HCBO complex Plots of Job's method of continuous variation for determination of M:L ratio 0.005 M Cu(II), 0.005 M HCBO; pH = 5.0; = 620 nm.

Gravimetric estimation of Cu(II) in Brass alloy using HCBO :

Preanalysed sample of brass (0.5310 g) was dissolved in 50% HNO_3 by heating for 30 minutes. The solution is evaporated to a volume of near about 5 ml but not to dryness and the bulk of nitric acid removed. The resulting solution was diluted to 100 ml with doubly distilled water in volumetric flask.

An aliquot of above diluted solution (10 ml) was taken in a clean beaker and copper was determined gravimetrically using 2-hydroxy-5-chlorobenzophenone oxime (HCBO) as per the procedure described previously.

Results : Estimation of copper :

1.	Weight of Cu(II)-HCBO complex	= 0.3314 gm
2.	Copper found in 10 ml diluted solution (Average of three determinations)	= 0.0378 gm
3.	Copper found in brass alloy sample	= 0.378 gm
4.	Percentage of copper found in brass alloy sample	= 71.19%
5.	Percentage of copper reported in brass alloy sample	= 70.50 %
6.	Percentage error	= +0.98 %

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