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Original Research Paper

Chemistry

2-HYDROXY-5-CHLOROBENZOPHENONE OXIME [HCBO] AS A GRAVIMETRIC AND SPECTROPHOTOMETRIC REAGENT FOR THE DETERMINATION OF NI(II)"

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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 Ni(II) ion. In the pH range of 6.0 to 10.0 this reagent gives light green precipitates with Ni(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 and Nickel content in German Silver.

KEYWORDS : Analytical reagent, Ni(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[3-14] 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 Ni(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 $NiSO_4.7H_2O$ (0.05 M) was prepared by dissolving 3.511 gm of $NiSO_4.7H_2O$ (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[15] 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 Ni(II) :

Nickel 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 6.0 to 10.0 using suitable basic buffer. A light green 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 $Ni(C_{13}H_9O_2NCl)$. 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 Ni(II), 8-10 mg of various cations were added to a solution containing 29.64 mg Ni(II) at pH 8.5 and gravimetric estimations were done. It was observed that Mg(II), Zn(II) and Cd(II) do not interfere at this pH but Mn(II), Co(II), Cu(II) and Fe(III) interfered seriously. Interference of Fe(III) can be removed by masking it with fluoride ion. Many common anions like nitrite, nitrate, sulphate, chloride, bromide, iodide were not found to interfere.

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

Ni(II) taken = 29.64 mg

Drying temperature = 110-115°C Salt = $NiSO_4.7H_2O$

pH	Cu(II) complex in mg	Cu(II) found in mg	Error	
			in mg	%
6.0	275.35	29.30	-0.34	-1.15
	275.38	29.30	-0.34	-1.15
6.5	276.51	29.42	-0.22	-0.74
	276.62	29.43	-0.21	-0.74
7.0	276.85	29.46	-0.18	-0.61
	276.89	29.46	-0.18	-0.61
7.5	277.15	29.49	-0.15	-0.51
	277.23	29.50	-0.14	-0.47
8.0	277.59	29.54	-0.10	-0.34
	277.65	29.54	-0.10	-0.34
8.5	278.95	29.68	+0.04	+0.14
	278.87	29.67	+0.03	+0.10
9.0	278.22	29.60	-0.04	-0.13
	278.12	29.59	-0.05	-0.17
9.5	277.85	29.56	-0.08	-0.26
	277.90	29.57	-0.07	-0.24
10.0	277.25	29.50	-0.14	-0.47
10.0	277.15	29.49	-0.15	-0.51

Conversion factor = 0.1064

Spectrophotometric study of Ni(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 600 nm and hence all measurements were carried out at 600 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 Ni(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using [$NH_3 + NH_4Cl$] 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 600 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 46.97 ppm of Ni(II). The molar absorptivity of the Ni(II)-HCBO complex was found to be 3.00 x 10^2 lit.mol^{-1}.cm^{-1} and the Sandell's sensitivity is found to be 0.196 µg/cm^2 at 600 nm.

Stoichiometry of complex :

Job's method of continuous variation[16] and Yoe and Jones mole ratio method[17] were used to determine the stoichiometry of the Ni(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 4.42 x 10^8. The Gibb's free energy change for complex formation reaction at 30C was found to be -11.865 K.cal/mole.

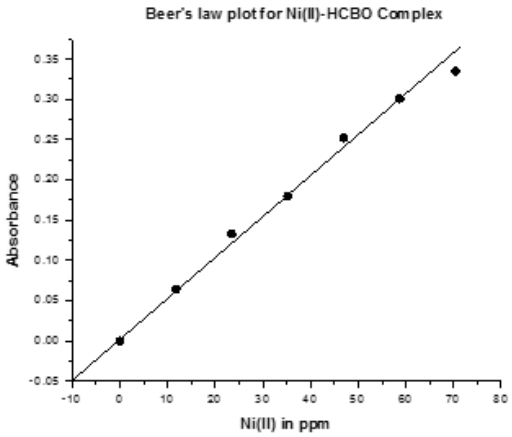

Figure 1 : Beer's law plot for Ni(II)-HCBO complex

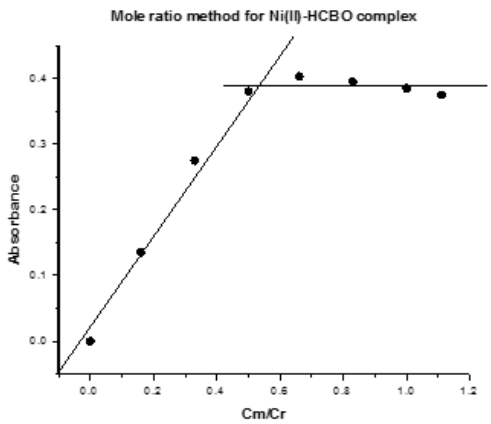

Figure -2. Yoe and Jones mole ratio method for Ni(II)-HCBO complex Plots of Yoe and Jones mole ratio method for determination of M:L ratio 0.005 M Ni(II), 0.005 M HCBO; pH = 5.0; λmax= 600 nm.

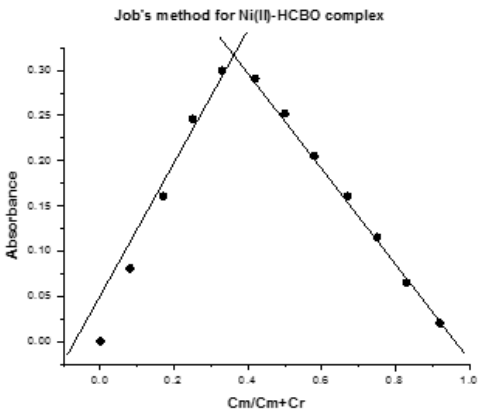

Figure -3. Job's method for Ni(II)-HCBO complex Plots of Job's method of continuous variation for determination of M:L ratio 0.005 M Ni(II), 0.005 M HCBO; pH = 5.0; λmax= 600 nm.

Gravimetric estimation of Cu(II) and Ni(II) in German silver using HCBO :

Preanalysed sample of german silver (0.9565 g) was dissolved in 50% HNO3 by heating for 30 minutes. The solution is heated to dissolve the alloy. Excess nitric acid was boiled off and 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) and the nickel was also determined gravimetrically as per the procedure described previously.

Results : Estimation of copper :

1.	10 ml solution gave 0.4730 g of Cu(II)-HCBO complex (Average of three determinations) Found copper	= 0.0540 g
2.	10 ml diluted alloy solution contains	= 0.0540 g
3.	100 ml diluted alloy solution contains	= 0.540 g
4.	Percentage of copper found in german silver	= 56.46%
5.	Percentage of copper reported in german silver	= 56.00 %
6.	Percentage error	= +0.82 %

Estimation of nickel :

1.	10 ml solution gave 0.1701 g of Ni(II)-HCBO complex (Average of three determinations) Found nickel	= 0.01809 g
2.	10 ml diluted alloy solution contains	= 0.01809 g
3.	100 ml diluted alloy solution contains	= 0.1809 g
4.	Percentage of nickel found in german silver	= 18.91%
5.	Percentage of nickel reported in german silver	= 19.00 %
6.	Percentage error	= -0.47 %

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