



2'-HYDROXY-4'-METHOXYCHALCONE OXIME [HMCO] AS A GRAVIMETRIC AND SPECTROPHOTOMETRIC REAGENT FOR THE DETERMINATION OF Ni(II)

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ABSTRACT The ligand 2'-Hydroxy-4'-methoxychalcone oxime (HMCO) was developed as a gravimetric and spectrophotometric reagent for the determination of Ni(II). In the pH range of 7.0 to 10.0 this reagent gives light green complex with Ni(II). Job's method of continuous variation and Yoe and Jones mole ratio method revealed the stoichiometry of the complex to be 1:2 [M:L]. The obeyance 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 Nickel content in German silver alloy.

KEYWORDS : Analytical reagent, Ni(II) chelate, 2'-Hydroxy-4'-methoxychalcone oxime (HMCO)

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^{3-15, 21-22} etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2'-Hydroxy-4'-methoxychalcone oxime [HMCO] as an analytical reagent for Ni(II).

EXPERIMENTAL :

Instruments :

Spectrophotometric measurements were done on a "Milton Roy" (Spectronic 20D+) Spectrophotometer and "Abotta make UV-1100, UV-Visible Spectrophotometer". The IR spectra were recorded on "Perkin-Elmer" FTIR Spectrophotometer (RX-1) in KBr pallet. The NMR spectra were recorded on "Bruker Avance II 400 NMR Spectrometer. All pH measurements were done on Equip-Tronic pH meter (Model No.EQ 614).

Stock solution :

Stock solution of Ni(II) (0.05 M) was prepared by dissolving 3.2838 g of NiSO₄.6H₂O (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 standardization¹⁶ with EDTA.

Synthesis of Reagent [HMCO] :

Resacetophenone was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride according to the method of R. Robinson and R. C. Shah¹⁷. Resacetophenone was treated with methyl iodide and anhydrous potassium carbonate in acetone on a water bath at 65-70°C for six hours. On acidification with dilute HCl, 2-hydroxy-4-methoxyacetophenone was obtained. The 2-hydroxy-4-methoxyacetophenone was converted to chalcone by its condensation with benzaldehyde in presence of aqueous KOH for 24 hours at room temperature. The 2'-hydroxy-4'-methoxychalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of light yellow crystals with m.p.85°C 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 8.0 to 10.0 using NH₃ + NH₄Cl buffer. A light green precipitate obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G₁) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110°C in hot air oven, cooled and weighed as Ni(C₁₆H₁₅O₃N)₂. 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 29.34 mg Ni(II) at pH 9.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Na(I), K(I), Mg(II), Ba(II), Pd(II), Cd(II) do not interfere at this pH but Mn(II) and Cu(II) interfered seriously. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

TABLE - 1
GRAVIMETRIC DETERMINATION OF Ni(II) USING HMCO

Ni(II) taken = 29.34 mg
Drying temperature = 110-115°C
Salt = NiSO₄.6H₂O

pH	Ni(II) complex in g	Ni(II) found in mg	Error	
			in mg	%
8.0	0.2964	29.13	-0.21	-0.72
8.0	0.2968	29.17	-0.17	-0.58
8.5	0.2977	29.26	-0.08	-0.20
8.5	0.2980	29.29	-0.05	-0.17
9.0	0.2986	29.35	+0.01	+0.03
9.0	0.2988	29.37	+0.03	+0.10
9.5	0.2990	29.39	+0.05	+0.17
9.5	0.2991	29.40	+0.06	+0.20
10.0	0.2994	29.43	+0.09	+0.31
10.0	0.2995	29.44	+0.10	+0.34

Conversion factor = 0.0983

SPECTROPHOTOMETRIC STUDY OF Ni(II)-HMCO CHELATE :

The Ni(II)-HMCO chelate has been found to be soluble in acetone, ethyl acetate and chloroform. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 440 nm and hence all measurements were carried out at 440 nm.

VERIFICATION OF BEER'S LAW AND OPTIMUM CONCENTRATION RANGE :

To 5 ml of solution (0.01 M) of the reagent HMCO, varying amount of the Ni(II) solution (0.005 M) was added and the pH was adjusted to 9.0, using [NH₃ + NH₄Cl] buffer. The insoluble complex precipitated 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 absorbance of these solutions were measured at 440 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 93.84 ppm of Ni(II). The standard graph thus obtained may be used for determination of Ni(II) in an unknown solution using HMCO. The molar absorptivity from Beer's law plot was found to be 5.662 x 10² lit.mol⁻¹.cm⁻¹ for Ni(II)-HMCO complex at 440 nm and Sandell's

sensitivity was found to be $0.0103 \mu\text{g}/\text{cm}^2$.

STOICHIOMETRY OF COMPLEX:

Job's method of continuous variation¹⁸ and Yoe and Jones mole ratio method¹⁹ were used to determine the stoichiometry of the Ni(II)-HMCO 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 6.336×10^8 . The Gibb's free energy change for complex formation reaction at 30°C was found to be $-12.20 \text{ K.cal/mole}$.

IR SPECTRA:

Examination of the IR spectra of the chelates show that the band due to intramolecular hydrogen bonded O-H stretching of 2-hydroxy group disappears in the Ni(II)-HMCO while the band due to oximino -OH group at 3430 cm^{-1} in Ni(II) complex.

The band due to the -C=N stretching which is observed at 1548 cm^{-1} in ligand is shifted to $1507\text{-}1608 \text{ cm}^{-1}$ in complexes. This may be due to coordination of metal through nitrogen. This is further supported by slight downward shift of NO from 1029 cm^{-1} in the ligand to 959 to 982 cm^{-1} in nickel chelate. Thus, in the chelate, metal is covalently bonded with oxygen and coordinate bonded with nitrogen.

GRAVIMETRIC ESTIMATION OF Cu(II) AND Ni(II) IN GERMAN SILVER USING HMCO:

Exactly weighed german silver (0.6831 g) was transferred to a 250 ml beaker. 50 ml 1:1 nitric acid was put in it. The solution was heated to dissolve the alloy. Excess nitric acid was boiled off and the solution was diluted to 100 ml with distilled water.

DETERMINATION OF COPPER(II):

10 ml german silver solution (as prepared above) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was carefully adjusted to 5.0 using sodium acetate-hydrochloric acid buffer. The solution was warmed at 60°C and small excess of reagent 2'-hydroxy-4'-methoxychalcone oxime was added (0.05 M , 12 ml). A brown precipitate obtained were digested on a water-bath for 60 minutes. 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 the excess reagent. All the filtrate was collected in 250 ml beaker for determination of nickel. The chelate was dried to constant weight at $110\text{-}115^\circ\text{C}$ in hot air oven, cooled and weighed. The experiment was repeated three times.

DETERMINATION OF NICKEL(II):

The filtrate obtained after filtering the copper complex was concentrated to 120 ml and after cooling, the reagent solution (0.05 M) was added to it and the pH of the solution was adjusted to 9.0 using $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer. A light green precipitate obtained were digested on water-bath for 60 minutes. 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 $110\text{-}115^\circ\text{C}$ in hot air oven, cooled and weighed. The determinations were done three times, taking 10.0 ml aliquot solution every time.

CALCULATIONS AND RESULTS:

(1) For Cu(II):

10 ml solution gave 0.3690 g of Cu(II)-HMCO complex
(Average of three determinations)
Found copper = 0.03897 g
10 ml diluted alloy solution contains 0.03897 g copper

\therefore 100 ml diluted alloy solution contains 0.3897 g copper
Percentage of copper found in german silver = 57.04%
(Average of three determinations)
Percentage of copper reported in alloy = 56.00%
Absolute error = $+1.04\%$
Percentage error = $+1.857\%$

(2) For Ni(II):

10 ml solution gave 0.1821 g of Ni(II)-HMCO complex
(Average of three determinations)
Found nickel = 0.01791 g
10 ml diluted alloy solution contains 0.01791 g nickel

\therefore 100 ml diluted alloy solution contains 0.1791 g nickel

Percentage of nickel found in german silver = 26.21%

(Average of three determinations)

Percentage of nickel reported in alloy = 26.00%

Absolute error = $+0.21\%$

Percentage error = $+0.807\%$

THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF Ni(II)-HMCO COMPLEX:

Thermogravimetric analysis of nickel chelate was done on "Perkin Elmer, Pyris 1 TGA". A definite quantity of chelate was taken in an alumina crucible and was put on a hanger of microbalance and the crucible was kept in a furnace. The temperature of the furnace was raised from 50°C to 850°C in a programmed manner at the heating rate of $10^\circ\text{C}/\text{min}$. The atmosphere in the furnace was of static air. The temperature scale of thermobalance was calibrated using the standards supplied by Perkin Elmer Company. The graph of weight of chelate as a function of temperature was recorded automatically. The instrument had also facility to compute the percentage weight loss, in different stages. The weight of final residue obtained was recorded on the microbalance. The results obtained are as follows:

1.	The weight of chelate taken	8.765 mg
2.	Temperature at which decomposition started	200°C
3.	Total % weight loss obtained between 200°C to 800°C	89.25 %
4.	Total % weight loss expected due to loss of ligand molecules as per formula $(\text{C}_{16}\text{H}_{15}\text{O}_3\text{N})_2\text{Ni}$	90.16%
5.	Weight of NiO residue observed	1.118 mg
6.	Weight of NiO residue expected according to formula $(\text{C}_{16}\text{H}_{15}\text{O}_3\text{N})_2\text{Ni}$	1.097 mg

From the result of TGA, it is seen that the complex is stable upto temperature 180°C and so it can be dried safely without decomposition at $100\text{-}180^\circ\text{C}$. The loss in weight in the temperature range 200°C to 800°C is due to the removal of organic ligand molecule. The observed loss agrees well with the loss expected as per formula of the chelate in which M:L ratio is 1:2. The weight of residue agrees with the weight of residue expected as per the given formula. This confirms the metal:ligand ratio 1:2 which is also established from the results of gravimetric analysis, elemental analysis and spectrophotometric methods.

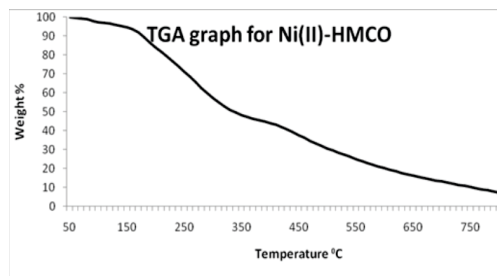


Fig.(I) TG Curve of Ni(II)-HMCO Complex

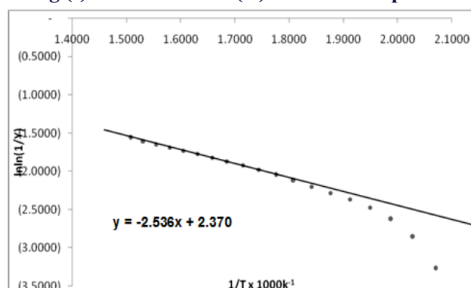


Fig.(II) Method of Broido : Ni(II)-HMCO Complex (Step-I)

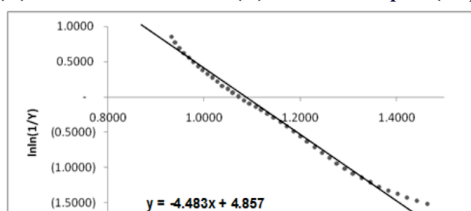


Fig.(II) Method of Broido : Ni(II)-HMCO Complex (Step-II)

$$y=-4.483x + 4.857$$

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