# 2-Chloro-2'-hydroxy-4'-chloro-5'-methoxychalcone Oxime [CHCMCO] as an Analytical Reagent: Studies on Co (II) Chelate

Jayshree B Rana[1], Nilesh G. Limbachiya[2]

**Abstract:** The ligand 2-Chloro- 2'-hydroxy-4'-chloro-5'methylchalcone oxime (CHCMCO) was developed as a new analytical reagent for the gravimetric and Spectrophotometric analysis of Co (II) ion. In the pH range of 8.0 to 8.5, this reagent gives brown colored complex with Co (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 obeyance of Beer's law was studied and the molar absorptivity was found to be 1.25 x $10^2$ lit.mol$^{-1}$cm$^{-1}$. The reagent and its complex have been characterized by elemental analysis and IR spectra. The magnetic susceptibility measurement of the chelate has been calculated at 4 ampere and 298$^o$ K. The complex is paramagnetic in nature which indicates the presence of one unpaired electron in d-orbitals and confirms the removal of two electrons, one from 3d orbital and one from 4s orbital. Thus 3d and 4s orbitals are involved in the formation of the chelate.

**Key words:** Analytical reagent, Co (II) chelate, 2-Chloro- 2'-hydroxy-4'-chloro-5'methylchalcone oxime (CHCMCO)

---

**Introduction:**

In the current scenario, large numbers 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],[4],[5],[6],[7],[8],[9] etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2-Chloro-2'-hydroxy-4'-chloro-5'methylchalcone oxime (**CHCMCO**) as an analytical reagent for Co (II)

**[1]Head of Department (Humanities and Science), Dr. Babasaheb Bhimrao Ambedkar Government Polytechnic, Union Territory of Dadra & Nagar Haveli Silvassa-396240, India**
**[2] Jamnaben Narottambhai Motiram Patel Science College ,D. C. Patel Navnirman Educational Campus, New City Light Road, Bharthana (Vesu), Surat-395017**
**Corres. author: ranajayshree@gmail.com , n.g.limbachiya@gmail.com**

**Experimental:**

**Instruments:**

Spectrophotometric measurements were done on a "Baush and Laumb" Spectrophotometer working on a Doran's mains unit connected to 220V/50 cycles and "SpectroCoc-20". The IR spectra were recorded on "Perkin-Elmer" IR Spectrophotometer (Model No.377) in KBr pallet. All pH measurements were done on Elico pH meter .Magnetic Susceptibility measurement was carried out on "Gouy" method.

**Stock solution:**

Stock solution of $CoCl_2.6H_2O$ (0.05 M) was prepared by dissolving 2.9741 gm of $CoCl_2.6H_2O$ (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 [10] with EDTA.

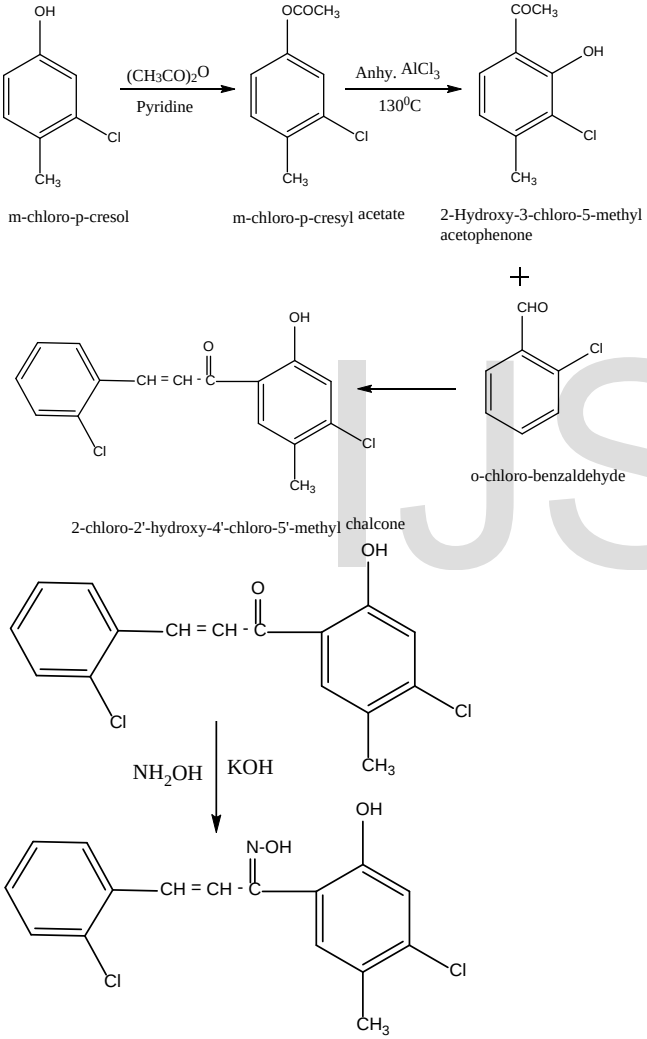
**Synthesis of Reagent [**CHCMCO**] :**

m-chloro-p- cresyl acetate was prepared [11] from m–chloro-p-cresol, glacial acetic acid and pyridine was heated on water bath for 4 hours. The reaction mixture was poured over crushed ice containing hydrochloric acid. The liquid separated was washed with a solution of $NaHCO_3$ and then with water. It was then extracted with ether, dried over anhydrous sodium sulphate; ether was removed and then distilled as colorless liquid at 220$^o$C.

m-chloro-p- cresyl acetate was mixed slowly with anhydrous $AlCl_3$ at room temperature, and then heated at 130$^o$C on an oil bath for 4 hours. The reaction mixture was cooled and decomposed with ice and concentrated hydrochloric acid. 2-hydroxy-4-chloro-5-methyl acetophenone was separated and washed with a solution of $NaHCO_3$ and then with water. The solid separated was collected and crystallized from petroleum ether as colorless needles. The 2-hydroxy-4-chloro-5-methyl acetophenone was converted to 2-chloro-2'hydroxy-4'chloro-5'methylchalcone by its condensation with 2-cholrobenzaldehyde in presence of aqueous KOH for 18 hours at room temperature. The 2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of colorless crystals with m.p.195°C was obtained. Stock

solution of reagent (1%) was prepared by dissolving in 60% aqueous ethanol.

Reaction :




**Gravimetric determination of Co (II):**

Cobalt Chloride 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 - 8.5 using HCl and Borax buffer. A brown precipitate obtained was digested on water-bath for 60 minutes at 60°C-70°C. The precipitate were filtered through a previously weighed sintered glass crucible ($G_4$) and washed with warm water followed by 60% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 105-110°C in hot air oven, cooled and weighed as Co ($C_{32}H_{24}O_4N_2Cl_4$). Duplicate experiments were performed. The results are given in Table 1. 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%.

**TABLE: 1 GRAVIMETRIC DETERMINATION OF Co (II) USING CHCMCO**

pH: 8.0-8.5 Drying temperature: 100-105°C

Salt : $CoCl_2.6H_2O$

| Co(II) taken in g | Co(II) complex in g | Co(II) found in mg | Error in mg |
|---|---|---|---|
| 0.01473 | 0.17296 | 0.014731 | $+1 \times 10^{-6}$ |
| 0.02946 | 0.34600 | 0.029469 | $+9 \times 10^{-6}$ |
| 0.04419 | 0.51885 | 0.044191 | $+1 \times 10^{-6}$ |
| 0.05893 | 0.69200 | 0.058938 | $+8 \times 10^{-6}$ |

Conversion factor = Co (II)/Co (II) complex=0.085171

**Spectrophotometric study of Co (II) - CHCMCO chelate:**

The chelate of Co (II) with the chalcone oxime was extracted in chloroform and the absorption spectra were recorded in the range of 330 to 1000 nm. It was observed that the absorbance of the colored solution of chelate increases continuously towards the shorter wavelength. A band of absorbance curve is observed at 420 nm and hence all measurements were carried out at 420 nm.

**Verification of Beer's law and optimum concentration range :**

A definite amount 0.05 g. of the dried metal chelate was dissolved in 100 mL chloroform. This solution was taken in definite volumes and diluted to 10 mL, thereafter the absorbance of these solutions was measured at 420 nm against chloroform as the blank sample. 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. The standard graph thus obtained was used for the determination of Cobalt in unknown solution using 2-chloro-2'-hydroxy-4'-chloro-5'methylchalcone oxime.

**Stoichiometry of complex:**

Job's method of continuous variation[11] and Yoe and Jones mole ratio method[12] were used to determine the stoichiometry of the Co (II)- CHCMCO 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 stability constant (Ks) found from two methods is 1.849 x $10^9$.

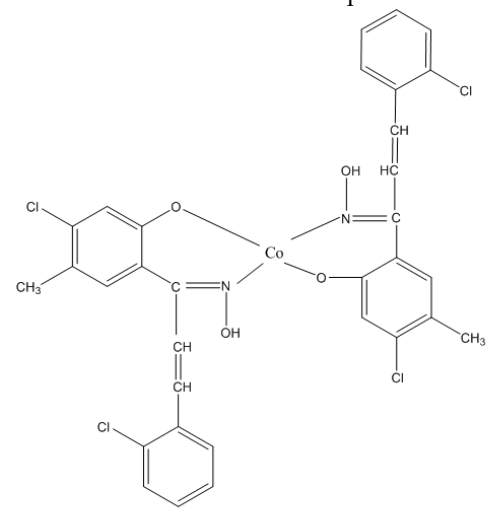
**Magnetic Susceptibility Measurements:**

Gouy method [13] was used to measure the magnetic moment of the crystallized Cu (II)-Chalcone oxime. The calculated (298°K and 4 ampere) effective Magnetic moment ($\mu_{eff}$) was 4.42.

| Name of the Complex | Gram magneticsusceptibility Ā $\chi_g$ x $10^{-6}$ in emu | Molar magnetic susceptibility Ā $\chi_m$ x $10^{-6}$ in emu | Effective magnetic susceptibility Ā $\mu_{eff}$ |
|---|---|---|---|
| Cobalt-2-chloro-2′-hydroxy-4′-chloro-5′-methylchalcone oxime | 11.54 | 8185.6 | 4.42 |

**IR Spectra:**

Examinations of the IR spectra of the chelates show that the band due to O-H phenolic group disappears in the Co (II)-CHCMCO complex. The band due to oximino -OH group in the chelate was observed at 2900 $cm^{-1}$ as compared to the one at 2920 $cm^{-1}$ in the chalcone oxime. The band due to the -C=N stretching which is observed at 1600 $cm^{-1}$ in ligand is shifted to 1590 $cm^{-1}$ in complex. The C-Cl stretching band observed at 750 $cm^{-1}$ remains unaltered in the complex. Co-N band was observed at 550 $cm^{-1}$ and Co-O band was observed at 580 $cm^{-1}$ in the complex.




STRUCTURE OF Co(II)-2-CHLORO-2'-HYDROXY-4'-CHLORO-5'-METHOXYCHALCONE OXIME COMPLEX

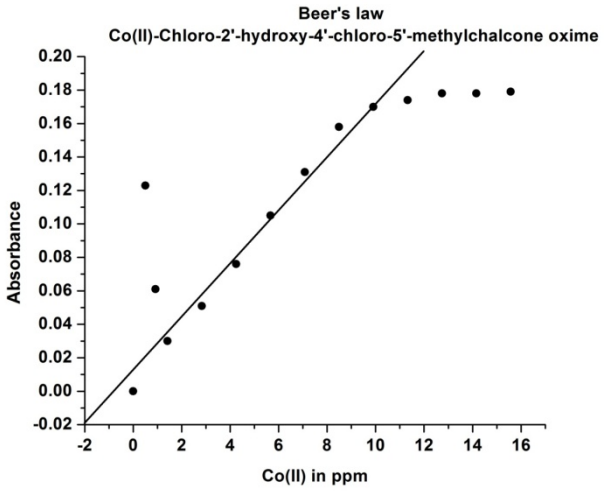



**Fig-1: Beer's law plot for Co (II)-CHCMCO complex**

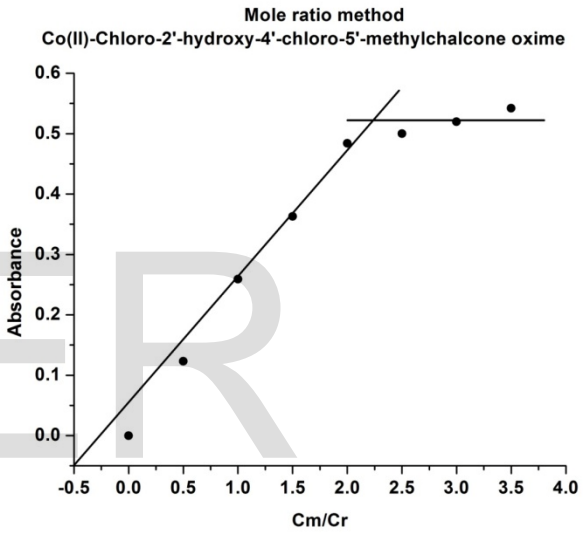



**Fig -2: Yoe and Jones mole ratio method for Co (II)-CHCMCO complex**

Plots of Yoe and Jones mole ratio method for determination of M: L ratio

0.002 M Co (II), 0.002 M CHCMCO; pH = 6.0-6.5; $\lambda_{max}$= 420 nm.

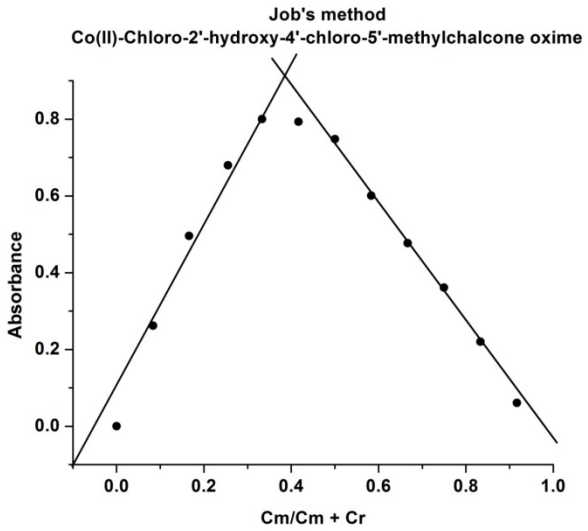



**Fig-3: Job's method for Co (II)-CHCMCO complex**
Plots of Job's method of continuous variation for determination of M:L ratio
0.002 M Co(II), 0.002 M CHCMCO; pH = 6.0-6.5; $\lambda_{max}$= 420 nm.

## Conclusion:

2-chloro-2'-hydroxy-4'-chloro-5'methylchalcone oxime (CHCMCO) is suitable reagent for the gravimetric and Spectrophotometric determination of Co (II). The complex is paramagnetic in nature which indicates the presence of one unpaired electron in d-orbitals and confirms the removal of two electrons, one from 3d orbital and one from 4s orbital. Thus 3d and 4s orbitals are involved in the formation of the chelate.

## Reference :

1. K. K. Desai, N. D. Naik and H.B. Naik, *J .Indian Chem. Soc*., 50, 81 (1973)
2. Trivedi P.C and Haldar B.C., *J. Indian Chem. Soc*., 54, 414 (1977) & *J. Inst Chemist (India)*, 53, 285, (1981)
3. S. K. Shingadia and K. K. Desai, "2-Hydroxy-5-methylbenzophenone Oxime (HMBO) as an Analytical reagent for Gravimetric Determination of Cu (II)" *E-journal of Chemistry*, Vol.4, No.1, 97-102 (2007)
4. Miss Krishna Purohit and K. K. Desai, "2-Hydroxy-4-Methoxybenzophenone Oxime as an Analytical Reagent for Copper (II)" *E-journal of Chemistry*, Vol.2, No.2, 161-164 (2005)
5. J. J .Desai, P. G. Desai and A. G. Mehta, Asian J. Chem., 11(2), 519 (1999)
6. Nitinkumar B Patel, Yashpalsinh Solanki and A.B. Patel, "2,4-dihydroxy-5-bromo-α-phenylacetophenone Thiosemicarbazone (DHB- α-PAT) as Analytical Reagent: Studies on Cu (II) Chelate ", *Oriental Journal of Chemistry*, Vol.29, No. (1),257, 2013
7. Nilesh G Limbachiya and K. K. Desai, "2'-Hydroxy-4'-Butoxychalcone Oxime (HBCO) as an Analytical Reagent: Studies on Cu(II) Chelate", *International Journal of ChemTech Research, V*ol.6. No.1, 786, (2014)
8. Nilesh G Limbachiya & A.G. Mehta., "2'-Hydroxy-4'-Methoxychalcone Oxime (HMCO) as A Gravimetric and Spectrophotometric Reagent for The Determination of Cu(II)" *Indian Journal of Applied Research,* Vol 4., Issue-6,(2014)
9. Anila Desai and H B Naik, "2-Hydroxy-4-n- propoxyacetophenone oxime as a Gravimetric Reagent for V(V) and Mn(II)", *J.Inst. Chemists (India),* Vol. 62, July, 1990
10. Vogel A. I., "A Text-Book of Quantitative Inorganic Analysis", Longmans Green and Co., 1961.
11. R. Robinson and R. C. Shah; J. Chem. Soc., 1994 (1934).
12. Job P., Ann. Chem., 1928, 9, 113.
13. Yoe and Jones A. L., Ind. Eng. Chem. and Edn., 1944, 16, 111.
14. Gouy., Comp.Rend., 109,935(1839) and Job.O., Ann (10), 9,113 (1928);(II),6,97 (1936), Compt. Rend., 180, 928 (1925)