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

Jayshree B Rana¹, Nilesh G. Limbachiya²

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 Jane's mole ratio method revealed the stoichiometry of the complex to be 1:2 [M: L]. The obeance of Beer's law was studied and the molar absorptivity was found to be 1.25 x 10² 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° 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)

Stock solution of CoCl₂.6H₂O (0.05 M) was prepared by dissolving 2.9741 gm of CoCl₂.6H₂O (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 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 NaHCO₃ 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°C.
m-chloro-p- cresyl acetate was mixed slowly with anhydrous AlCl₃ at room temperature, and then heated at 130°C on an oil bath for 4 hours. The reaction mixture was poured over crushed ice containing hydrochloric acid. The liquid separated was washed with a solution of NaHCO₃ 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°C.

m-chloro-p- cresyl acetate was mixed slowly with anhydrous AlCl₃ at room temperature, and then heated at 130°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 NaHCO₃ 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-chlorobenzaldehyde 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:

\[
\begin{align*}
\text{m-chloro-p-cresol} & \rightarrow \text{m-chloro-p-cresyl acetate} \\
\text{Pyridine} \quad & \quad \text{Anhy. AlCl}_3 \quad & \quad 130^\circ C \\
\text{Cl} \quad & \quad \text{Cl} \\
\text{CH}_3 \quad & \quad \text{CH}_3
\end{align*}
\]

2-Hydroxy-3-chloro-5-methyl acetophenone

TABLE 1  GRAVIMETRIC DETERMINATION OF Co (II) USING CHCMCO

<table>
<thead>
<tr>
<th>Co(II) taken in g</th>
<th>Co(II) complex in g</th>
<th>Co(II) found in mg</th>
<th>Error in mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01473</td>
<td>0.17296</td>
<td>0.01473</td>
<td>+1 x 10^{-6}</td>
</tr>
<tr>
<td>0.02946</td>
<td>0.34600</td>
<td>0.02946</td>
<td>+9 x 10^{-6}</td>
</tr>
<tr>
<td>0.04419</td>
<td>0.51885</td>
<td>0.04419</td>
<td>+1 x 10^{-6}</td>
</tr>
<tr>
<td>0.05893</td>
<td>0.69200</td>
<td>0.05893</td>
<td>+8 x 10^{-6}</td>
</tr>
</tbody>
</table>

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\textsuperscript{11} and Yoe and Jones mole ratio method\textsuperscript{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 (Kₚ) found from two methods is 1.849 x 10⁹.

**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 (µₑffective) was 4.42.

<table>
<thead>
<tr>
<th>Name of the Complex</th>
<th>Gram magnetic susceptibility Å</th>
<th>Molar magnetic susceptibility Å</th>
<th>Effective magnetic susceptibility Å µₑffective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt-2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone oxime</td>
<td>11.54</td>
<td>8185.6</td>
<td>4.42</td>
</tr>
</tbody>
</table>

**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.

**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; λ_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:
14. Gouy., Comp.Rend., 109,935(1839) and Job.O., Ann (10), 9,113 (1928);(II),6,97 (1936), Compt. Rend., 180, 928 (1925)