CHAPTER 11

SUMMARY AND CONCLUSIONS
Oxime-Hydrazones viz. diacetylmonoxime benzoylhydrazone (DMBH), diacetylmonoxime isonicotinoylhydrazone (DMIH) and benzil-α-monoxime isonicotinoylhydrazone (BMIH) have been synthesized. Survey of literature reveals that these oxime hydrazones are not used much for the spectrophotometric determination of metal ions. Spectral methods (IR, NMR and Mass) are employed for the characterization of ligands. The data support the synthesis of ligands and their structures (I-III).

\[
\begin{align*}
&\text{O} \quad \text{H} \\
&\text{R} \quad \text{N} \\
&\text{N} \\
&\text{R} \quad \text{C} \quad \text{O} \\
&\text{N} \\
&\text{H} \\
&\text{X} \quad \text{C} \\
\end{align*}
\]

\[
R = \text{CH}_3, \quad X = \text{CH}; \quad \text{DMBH (I)}
\]

\[
R = \text{CH}_3, \quad X = \text{N}; \quad \text{DMIH (II)}
\]

\[
R = \text{C}_6\text{H}_5, \quad X = \text{N}; \quad \text{BMIH (III)}
\]

The ligands are generally stable in dimethylformamide (DMF) for two days. The ligands are chromogenic for different metal ions. Hence these ligands are used as reagents for the spectrophotometric determination of lead(II), cadmium(II), nickel(II) and copper(II). The colour reactions are investigated in detail with a view to develop spectrophotometric methods for the determination of metal ions in aqueous medium. During the process various parameters have been investigated. They include (a) absorbance maximum ($\lambda_{\text{max}}$), (b) optimum pH range, (c) amount of reagent required for
full colour development, (d) order of addition of reagents, (e) time stability, 
(f) verification of Beer's law, (g) optimum concentration range for accurate 
determination of metal ion (Ringbom plot), (h) molar absorptivity, (i) effect of 
foreign ions (cations and anions) and (j) composition and stability constant. 
Various physico-chemical and analytical characteristics of Pb(II), Cd(II), Ni(II) 
and Cu(II) complexes of DMBH, DMIH and BMIH are summarized in 
Table 11.1.

(a) **Absorbance maximum** ($\lambda_{\text{max}}$)

Different $\lambda_{\text{max}}$ values are observed for different species in solution. The 
Ni-BMIH species is having absorbance maximum at 398 nm while for 
Cu-DMBH, it is only 346 nm.

(b) **Optimum pH range**

Cu-DMBH complex shows maximum and constant absorbance in the 
$pH$ range 8.0-11.0, which is sufficiently wide for the spectrophotometric 
determination of metal ion. However, certain systems show maximum and 
constant absorbance over a narrow range, e.g., Cd-DMIH system ($pH$, 8.75 - 
9.25).

(c) **Reagent required for full colour development**

A 10-fold molar excess of reagent is generally sufficient for full colour 
development in most of the methods.

(d) **Order of addition of reagents**

Order of addition of reagents has no adverse effect on the absorbance of 
the species in all the methods.
### TABLE 11.1
A detailed account of physico-chemical and analytical properties of metal complexes

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</thead>
<tbody>
<tr>
<td>Absorbance maximum ($\lambda_{max}$)</td>
<td>372</td>
<td>374</td>
<td>348</td>
<td>346</td>
<td>364</td>
<td>362</td>
<td>366</td>
<td>398</td>
<td>346</td>
<td>346</td>
<td>346</td>
</tr>
<tr>
<td>Optimum pH range</td>
<td>10.0-12.0</td>
<td>10.00-11.0</td>
<td>9.0-9.5</td>
<td>8.75-9.25</td>
<td>8.25-8.75</td>
<td>8.0-10.0</td>
<td>8.0-8.5</td>
<td>8.0-9.0</td>
<td>8.0-11.0</td>
<td>8.0-9.0</td>
<td>8.0-9.0</td>
</tr>
<tr>
<td>Molar absorptivity x10^4 (L mol⁻¹ cm⁻¹)</td>
<td>1.25</td>
<td>1.25</td>
<td>1.6</td>
<td>2.0</td>
<td>2.5</td>
<td>2.125</td>
<td>1.75</td>
<td>1.45</td>
<td>1.36</td>
<td>1.12</td>
<td>1.19</td>
</tr>
<tr>
<td>Sandell’s sensitivity (µg of metal ion cm⁻³)</td>
<td>0.0166</td>
<td>0.0166</td>
<td>0.00712</td>
<td>0.00562</td>
<td>0.00450</td>
<td>0.00276</td>
<td>0.00335</td>
<td>0.004055</td>
<td>0.00468</td>
<td>0.00565</td>
<td>0.00534</td>
</tr>
<tr>
<td>Beer’s law validity range (µg/ml)</td>
<td>0.83-7.46</td>
<td>0.83-6.630</td>
<td>0.225-4.950</td>
<td>0.225-5.40</td>
<td>0.45-4.5</td>
<td>0.117-2.580</td>
<td>0.235-2.350</td>
<td>0.117-2.820</td>
<td>0.254-2.032</td>
<td>0.51-2.29</td>
<td>1.016-5.081</td>
</tr>
<tr>
<td>Optimum concentration range (µg/ml)</td>
<td>2.5-6.6</td>
<td>2.5-6.6</td>
<td>0.45-4.50</td>
<td>0.90-4.95</td>
<td>0.9-4.0</td>
<td>0.47-2.11</td>
<td>0.47-1.88</td>
<td>0.235-2.350</td>
<td>0.51-2.28</td>
<td>0.762-2.030</td>
<td>1.5-4.5</td>
</tr>
<tr>
<td>Composition (M:L) of complex in solution</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:2</td>
<td>1:1</td>
<td>1:2</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
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<tr>
<td>Stability constant (P) of the complex</td>
<td>7.12x10⁵</td>
<td>17.4x10⁴</td>
<td>3.76x10⁴</td>
<td>2.88x10⁹</td>
<td>1.17x10⁹</td>
<td>4.5x10⁹</td>
<td>7.8x10¹⁰</td>
<td>1.5x10⁶</td>
<td>3.0x10³</td>
<td>2.7x10⁴</td>
<td>1.10x10⁶</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.0025</td>
<td>0.003</td>
<td>0.002</td>
<td>0.005</td>
<td>0.006</td>
<td>0.006</td>
<td>0.0021</td>
<td>0.004</td>
<td>0.003</td>
<td>0.0013</td>
<td>0.003</td>
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<tr>
<td>Relative standard deviation (RSD)</td>
<td>1.0%</td>
<td>1.2%</td>
<td>0.6%</td>
<td>1.3%</td>
<td>1.2%</td>
<td>1.4%</td>
<td>0.57%</td>
<td>1.2%</td>
<td>1.2%</td>
<td>0.5%</td>
<td>1.2%</td>
</tr>
</tbody>
</table>
(e) Time stability

Colour reactions between metal ions are instantaneous and hence no incubation period is required for full colour development. The complexes are stable for a period (more than 30 minutes) which is sufficient to record absorbance of several samples.

(f) Verification of Beer’s law

The systems obey’s Beer’s law over a wide range of concentration (see Table 11.1).

(g) Optimum concentration range

Using the data obtained in the verification of Beer’s law, Ringbom plots are prepared and the optimum concentration range for the accurate determination of metal ion is determined. The values are summarized in Table 11.1.

(h) Molar absorptivity

It is very characteristic of a coloured species in solution. It is nothing but the slope of calibration plot between absorbance and concentration of metal ion. The reagent, BMIH is more sensitive \((2.5 \times 10^4 \text{ L. mol}^{-1} \text{ cm}^{-1})\) for the spectrophotometric determination of cadmium(II).

(i) Effect of foreign ions

The effect of foreign ions have been investigated. Many anions and cations do not interfere in the determination of metal ions.

The important analytical properties such as Sandell’s sensitivity, standard deviation, relative standard deviation are incorporated in Table 11.1.
(j) **Composition and stability constant**

Most of the reagents gave 1:1 complexes. The stability constants have been calculated using the data obtained in Job's method. Among 1:1 complexes, Pb-DMIH complex is most stable ($\beta = 1.74 \times 10^7$) while in 1:2 complexes Ni-DMIH has high stability constant ($\beta_2 = 7.8 \times 10^{10}$).

**Derivative spectrophotometric analysis**

Nickel(II) and copper(II) have been determined using (DMBH, DMIH, BMIH) first and second order derivative spectrophotometry. First order derivative spectrophotometric technique is employed for the simultaneous determination of Ni(II) and Cu(II) using the present ligands.

**Applications**

The present methods are applied for the determination of metal ions in different samples. They include water, synthetic alloy samples, industrial effluents, tobacco samples etc.

**Conclusions**

Survey of literature in the analytical chemistry of hydrazones and oximes revealed that new type of reagents viz. oxime-hydrazones (I-III) are not exploited for the spectrophotometric determination of lead(II), cadmium(II), nickel(II) and copper(II).

Based on the lacuna identified in the literature, new oxime-hydroxazones (I-III) have been synthesized and characterized by employing different spectral methods. The spectral data are consistent with the structures proposed for the reagents. The reagents gave intense colours with different metal ions. Hence the reagents are potential for the spectrophotometric determination of metal ions.
Lead(II), cadmium(II), nickel(II) and [copper(II)] metal ions are known inorganic metal pollutants. With this in mind the author has developed spectrophotometric methods for the determination of these metal ions using DMBH, DMIH and BMIH ligands in aqueous medium.

The colour reactions are instantaneous and methods do not involve heating of the reaction mixture. The reagents gave colour reactions with metal ions in basic medium. Tolerance limit values for certain metal ions are small. Triethanolamine, thioglycolic acid, fluoride etc., are used as masking agents to improve the selectivity of different methods.

Derivative spectrophotometric techniques are advantageously employed for the determination of Ni(II) and Cu(II). The tolerance limit values are more for most of the foreign ions in derivative methods. First order derivative spectrophotometry is employed for the simultaneous determination of Ni(II) and Cu(II).

The methods are applied for the determination of metal ions in appropriate samples. Satisfactory results are obtained in the analysis.

The present methods are simple, sensitive, reasonably selective and rapid without the need for heating or extraction. The reagents are very easy to synthesize and purify. The most favourable characteristic of present reagents is that they gave water soluble complexes which facilitate to determine the metal ions in aqueous medium.