CHAPTER – 6 SUMMARY & CONCLUSION

Analysis of trace metals in these days has become a necessity rather than desirability in the view of hazardous trends noticed in environment due to chemical pollution. It was known that many analytical methods that are available for the analysis, absorption photometry occupy an important place in view of its elegance and simplicity. Thus UV-Visible spectrophotometry is proved to be a versatile and simple analytical technique with in the reach of many analytical laboratories. The formulation of new spectrophotometric methods requires the designing, synthesis and testing of newer organic compounds for different metal ions. The great progress made in understanding the mechanism of colour forming reactions between metal ions and organic compounds gave a broad basis for synthesis of new chromogenic reagents.

Organic compounds containing different functional groups have been used as chromogenic reagents in the trace metal analysis. Survey of literature reveals that, the carbonyl derivatives and azomethines seems to be very useful in the determination of trace metals. Therefore, such azomethines were synthesized by simple condensation. The multi-dentate ligands such as 2, 4-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (DMBHBH) and 2, 4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH) were synthesized. The compounds were characterized by infrared, NMR, mass and UV-visible spectroscopic studies. The data support the synthesis of ligands and their structures.

The ligands are generally stable in dimethylformamide (DMF) for two days. The ligands are chromogenic for different metal ions. Hence the ligands were used as reagents for the spectrophotometric determination of metal ions. 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) Amount of surfactant required for stability of complex

(g) Beer’s law verification

(h) Optimum concentration range for accurate determination of metal ions (Ringbom’s plots)

(i) Molar absorptivity ($\varepsilon$)

(j) Effect of foreign ions

(k) Composition and stability constant of the complex.

Various physico-chemical and analytical characteristics of Cu (II), Cr (VI) and Cd (II) complexes of DMBHBH reagent; Hg (II) and Pb (II) complexes of DMBIH reagent were summarized in Table 6.1

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

Different $\lambda_{\text{max}}$ is observed for different species in solution. All the metals shows absorbance maximum at zero order is below 400 nm.

(b) **Optimum pH range**

All the metals shows maximum and constant colour development in basic phosphate buffer medium pH range 8.0 to 10.0.

(c) **Amount of reagent required for full colour development**
A 10-fold molar excess of reagent is sufficient for full colour development of Copper (II), Chromium (VI), Cadmium (II), Mercury (II) and Lead (II) with 2,4 – dimethoxy benzaldehyde- 4 – hydroxy benzoyl hydrazone (DMBHBH) and 2,4 - Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH).

(d) Order of addition of reagent

The order of addition of constituents (buffer, metal ion, surfactant and reagent solution) has no adverse effect on the absorbance of the species in all the methods.

(e) Time stability

The colour reactions between metal ions and the reagents are instantaneous and no incubation period is required for full colour development. The metal complexes are stable for more than 2 hrs and are sufficient to record absorbance of several samples.

(f) Amount of surfactant required for stability of complex

Cu (II) and Cd (II) with DMBHBH, 0.5 ml of 5% CTAB was used in the Spectrophotometric determination of Cu (II) and Cd (II). 0.5 ml 5% SDBS was used in the spectrophotometric determination of Cr (VI) with DMBHBH and Pb(II) with DMBIH. But no surfactant was used in the spectrophotometric determination of Hg (II) using DMBIH.

(g) Beer’s law verification

The system obeyed Beer’s law over a wide range of concentration. The values are summarized in Table 6.1.

(h) Optimum concentration range

The data obtained in the Beer’s law verification, Ringbom’s plots are prepared and optimum amount range for the accurate determination of metal ions was determined. The values are presented in Table 6.1.
(i) Molar absorptivity

It is characteristic of a coloured species in solution. It is nothing but slope of calibration plot between absorbance and concentration of metal ions. The reagent DMBHBH was more sensitive ($\varepsilon = 3.8 \times 10^4$ L.Mole$^{-1}$.Cm$^{-1}$) for the spectrophotometric determination of Cu (II).

(j) Effect of foreign ions

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

(k) Composition and stability constant

The reagents DMBHBH and DMBIH gave 1:1 complex with Cu (II), Cr (VI), Cd (II), Hg (II) and Pb (II). The stability constant was calculated using the data obtained in Job’s method. Among the all complexes [Cd (II)-DMBHBH] complex was more stable ($\beta_{1:1} = 8.0101 \times 10^6$). The important analytical properties such as Sandell’s sensitivity and relative standard deviation are incorporated in Table 6.1.

Derivative spectrophotometric analysis

The reagent DMBHBH has been used for first and second order derivative spectrophotometric determination of metal ions such as Cu (II), Cr (VI) and Cd (II), and DMBIH for Hg (II) and Pb (II). The detailed studies were presented in chapter 4 and 5.

Applications

The present investigations were applied for the determination of metal ions in different samples. They include Real samples, water samples, commercial samples, biological samples and synthetic alloys samples.
Table 6.1: A detail account of physico-chemical and analytical properties of metal complexes
Using DMBHBH and DMBIH

<table>
<thead>
<tr>
<th>CHARACTERISTICS</th>
<th>Cu (II) - DMBHBH</th>
<th>Cr (VI) - DMBHBH</th>
<th>Cd (II) - DMBHBH</th>
<th>Hg (II) – DMBIH</th>
<th>Pb (II) – DMBIH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Absorbance (Zero order) ($\lambda_{\text{max}}$)</td>
<td>384</td>
<td>379</td>
<td>387</td>
<td>390</td>
<td>396</td>
</tr>
<tr>
<td>Optimum pH range</td>
<td>9.0-11.0</td>
<td>8.0-10.0</td>
<td>7.0-9.0</td>
<td>7.0-9.0</td>
<td>8.0-10.0</td>
</tr>
<tr>
<td>Colour of the Complex</td>
<td>Orange</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
</tr>
<tr>
<td>First derivative ($\lambda_{\text{max}}$)</td>
<td>440</td>
<td>440</td>
<td>428</td>
<td>450</td>
<td>425</td>
</tr>
<tr>
<td>Second derivative ($\lambda_{\text{max}}$)</td>
<td>455</td>
<td>450</td>
<td>440</td>
<td>465</td>
<td>445</td>
</tr>
<tr>
<td>Molar absorptivity ($\varepsilon$) L.mol$^{-1}$.cm$^{-1}$</td>
<td>3.8 x 10$^4$</td>
<td>2.1739 x 10$^4$</td>
<td>3.6864 x 10$^4$</td>
<td>2.8 x 10$^4$</td>
<td>3.1372 x 10$^4$</td>
</tr>
<tr>
<td>Sandell’s sensitivity (µg.cm$^{-2}$)</td>
<td>0.005847</td>
<td>0.008</td>
<td>0.003</td>
<td>0.00571</td>
<td>0.005</td>
</tr>
<tr>
<td>Beer’s law validity range (µg/mL)</td>
<td>0.1588-1.9063</td>
<td>0.1299-1.5598</td>
<td>0.4877-5.8524</td>
<td>0.5014-6.0177</td>
<td>0.4596-5.5152</td>
</tr>
<tr>
<td>Optimum concentration range (µg/mL)</td>
<td>0.3177-1.5886</td>
<td>0.2599-1.2999</td>
<td>0.9754-4.877</td>
<td>1.0029-5.0147</td>
<td>0.9192-4.596</td>
</tr>
<tr>
<td>Composition (M:L)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Stability constant ($\beta$)</td>
<td>1.1502 x 10$^6$</td>
<td>1.8888 x 10$^6$</td>
<td>8.0101 x 10$^6$</td>
<td>4.5653 x 10$^6$</td>
<td>3.57 x 10$^6$</td>
</tr>
<tr>
<td>R.S.D (%)</td>
<td>0.3</td>
<td>0.02</td>
<td>0.03</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Among all organic reagents, hydrazones are very potential reagents for the spectrophotometric determination of metal ions in micro gram quantities. The survey of literature in the analytical chemistry of hydrazones revealed that 2,4-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (DMBHBH) and 2,4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH) are not exploited much for the spectrophotometric determination of metal ions.

Based on the lacuna identified in the literature, new hydrazones viz. 2,4-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (DMBHBH) and 2,4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH) were 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.

Copper (II) is a biologically important metal where as Cr (VI) is transition metal. They were also used in alloys. Cd (II) , Hg(II) and Pb (II) were most pollutant metals in environment. with this in mind the author has developed direct and derivative spectrophotometric methods for the determination of above metal ions using DMBHBH and DMBIH ligands in aqueous medium.

The colour reactions are instantaneous and methods do not involve heating of the reaction mixture or pre-extraction of the components. The reagents gave colour reactions with metal ions in basic medium. Tolerance limit values for certain metal ions are small. Fluoride, phosphate, cyanide, ascorbic acid and thiourea etc., are used as masking agents to improve the selectivity of different methods.
Derivative spectrophotometric techniques are advantageously employed for the determination of Copper (II), Chromium (VI), Cadmium (II), Mercury (II) and Lead (II) metal ions. The tolerance limit values are more for the most of foreign ions in derivative methods.

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 need of heating or extraction. The reagents are very easy to synthesize and purify with available chemicals. The most favorable characteristic of present reagents is that they gave water soluble complexes which facilitate to determine the metal ions in aqueous medium. Further, the surfactants used are sensitized and stabilizes the metal-reagent complexes.