[4.1.1] STUDY OF Fe(III) COMPLEX WITH HBCO:

PREPARATION OF STANDARD SOLUTION OF FERRIC CHLORIDE (FeCl₃):

Ferric chloride (anhydrous) (A.R., B.D.H.) 2.0276 g was dissolved in double distilled water, containing a little free acid and was diluted to 250 ml to get 0.05 M stock solution of ferric chloride. This solution was standardised gravimetrically [209]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

Fe(III) was found to form purple coloured ethanol soluble complex in pH range of 2.0 to 4.5. It was not found possible to do gravimetric determination of Fe(III), using the reagent.

ABSORPTION SPECTRA:

To have the absorption spectra, 0.02 M (3.0 ml) of reagent solution and 0.005 M (1.0 ml) of metal ion solution were taken in to 25 ml volumetric flask. The pH of the solution was adjusted within the range where maximum colour develops. The coloured complex was soluble in 70% aqueous ethanol. The solution was made up to the mark. The absorbance values were measured against the reagent blank in the wavelength range 300 nm to 800 nm. Absorption spectras are shown in figure-4.1.1(I).

EFFECT OF pH:

The effect of pH, a series of solutions were prepared by taking 0.005 (1 ml) ferric chloride solution and 0.02 M (3 ml) reagent solution. The pH of the solutions were adjusted to 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 with sodium acetate-hydrochloric acid buffer. The coloured solutions were then diluted to 25 ml. keeping 70% ethanol concentration. The absorbance spectra of each solution was obtained between 300 nm to 800 nm. It was observed that at 500 nm absorbance is maximum at pH 4.0 indicating that maximum complex is formed at this pH. The absorbance values at 500 nm are tabulated in Table-4.1.1 (l) and graph is shown in figure-4.1.1 (l).
TABLE - 4.1.1 (I)

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>0.005 M (1.0 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>0.02 M (3.0 ml)</td>
</tr>
<tr>
<td>Final volume</td>
<td>25 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>500 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>CH₃COONa + HCl</td>
<td>0.138</td>
</tr>
<tr>
<td>2.5</td>
<td>CH₃COONa + HCl</td>
<td>0.141</td>
</tr>
<tr>
<td>3.0</td>
<td>CH₃COONa + HCl</td>
<td>0.156</td>
</tr>
<tr>
<td>3.5</td>
<td>CH₃COONa + HCl</td>
<td>0.166</td>
</tr>
<tr>
<td>4.0</td>
<td>CH₃COONa + HCl</td>
<td>0.254</td>
</tr>
<tr>
<td>4.5</td>
<td>CH₃COONa + HCl</td>
<td>0.186</td>
</tr>
</tbody>
</table>

VERIFICATION OF BEER’S LAW:

In absorption spectra of Fe(III)-HBCO complex there is a shoulder at 500 nm and hence this wavelength was selected for analytical work.

To 10 ml (0.01 M) solution of the reagent HBCO, varying amounts of metal solution (0.002 M) were added and pH was adjusted to 4.0 using (HCl + CH₃COONa) buffer. The content was diluted to 25 ml in volumetric flask, so as to keep ethanol concentration 70% in final solution. The absorbance of these solutions were measured at 500 nm against reagent blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer’s law is obtained up to 11.17 ppm of Fe(III). Standard graph thus obtained may be used for the determination of iron in an unknown solution using HBCO. The results are tabulated in Table-4.1.1 (II) and graph is shown in figure-4.1.1 (II).
TABLE - 4.1.1(II)

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.234</td>
<td>0.060</td>
</tr>
<tr>
<td>1.0</td>
<td>4.468</td>
<td>0.096</td>
</tr>
<tr>
<td>1.5</td>
<td>6.702</td>
<td>0.140</td>
</tr>
<tr>
<td>2.0</td>
<td>8.936</td>
<td>0.188</td>
</tr>
<tr>
<td>2.5</td>
<td>11.170</td>
<td>0.223</td>
</tr>
<tr>
<td>3.0</td>
<td>13.404</td>
<td>0.300</td>
</tr>
<tr>
<td>3.5</td>
<td>15.638</td>
<td>0.391</td>
</tr>
</tbody>
</table>

Molar absorptivity calculated from Beer's law plot was found to be $1.115 \times 10^3 \text{lit.mole}^{-1}.\text{cm}^{-1}$ for Fe(III)-HBCO complex at 500 nm.

**COMPOSITION OF THE COMPLEX:**

The composition of Fe(III)-HBCO complex has been determined on the basis of the results of - (i) Job's method of continuous variation, and (ii) Yoe and Jones mole-ratio method.

(i) **JOB'S METHOD OF CONTINUOUS VARIATION:**

A 0.005 M solution of Fe(III) was prepared by suitable dilution of the standard solution. The solution of the reagent (0.005 M) was prepared in absolute ethanol. The solutions of metal salt and the reagent were mixed in varying proportions as under:

Metal ion solution : 1, 2, 3, ............... , 9, 10, 11 ml
Reagent solution : 11, 10, 9, ............... , 3, 2, 1 ml

pH of the solution was adjusted to 4.0. The content was then made up to 25 ml in volumetric flask. The absorbances of these solutions were measured at 500 nm.
The results are tabulated in Table-4.1.1(III) and the graph is shown in figure-4.1.1(III).

From the graph, it has been found that maximum occurs at 0.50 ratio of metal ion concentration to the metal and ligand concentration indicating the formation of 1:1 (M:L) complex.

### TABLE - 4.1.1 (III)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.083</td>
<td>0.116</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.170</td>
<td>0.235</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.330</td>
<td>0.347</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.420</td>
<td>0.443</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.500</td>
<td>0.505</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.580</td>
<td>0.528</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.670</td>
<td>0.408</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.750</td>
<td>0.254</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.830</td>
<td>0.160</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.920</td>
<td>0.098</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(ii) **YOE AND JONES MOLE-RATIO METHOD:**

In this method, equimolar solutions of the Fe(III) as well as the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution constant (6 ml) while varying the amount (from 1.0 to 9.0 ml) of 0.005 M metal ion solution. pH of these solutions were adjusted to 4.0. The contents was then made up to 25 ml in volumetric flask. Absorbances of these solutions were measured at 500 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.1.1 (IV) and graph is shown in figure-4.1.1 (IV).
It is evident from the graph that, absorbance gradually increases up to the molar composition of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.

**TABLE - 4.1.1 (IV)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>C_m/C_r</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005 M</td>
<td>1</td>
<td>0.140</td>
</tr>
<tr>
<td>Reagent solution</td>
<td>0.005 M (6 ml)</td>
<td>0.227</td>
</tr>
<tr>
<td>pH</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Final volume</td>
<td>25 ml</td>
<td></td>
</tr>
<tr>
<td>Wavelength</td>
<td>500 nm</td>
<td></td>
</tr>
</tbody>
</table>

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB'S METHOD:**

\[
MLn \rightleftharpoons M + nL
\]

\[
C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking n=1, in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{C\alpha^2}
\]

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.
The stability constant is calculated from above equation.

From $K_s$ value, the standard free energy change $\Delta G^o$ at 27°C for the formation reaction of complex has been calculated using the formula,

$$\Delta G^o = -RT\ln K_s$$

The stability constants calculated from above relation are as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_m$</th>
<th>$E_s$</th>
<th>$\alpha$</th>
<th>$K_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job's method</td>
<td>0.552</td>
<td>0.528</td>
<td>0.0434</td>
<td>1.01x10^7</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.675</td>
<td>0.650</td>
<td>0.037</td>
<td>1.40x10^7</td>
</tr>
</tbody>
</table>

Mean $K_s = 1.20x10^7$

$$\Delta G^o = -10.85 \text{ K.cal/mole}$$

DETERMINATION OF IRON IN MEDICINAL SAMPLE (FEFOL):

Contents of one capsule were transferred to an evaporating dish. 5 ml of concentrated HNO$_3$ and 5 ml of distilled water were added and slowly heated on a sand-bath at low temperature. Again 1:1 HNO$_3$ was added and solution was heated to remove all oxides of nitrogen. The contents were dissolved in water and diluted to 100 ml.

2.0 ml aliquot was taken from above solution. 5 ml 0.02 M solution of HBCO and buffer solution of pH 4.0 were added. The contents were diluted to 100 ml. Absorbance of the solution was measured at 500 nm. It was found to be 0.221 (average of three measurements).

RESULTS:

(i) Absorbance of the solution (Average of three measurements) : 0.221
(ii) Concentration of Fe in ppm : 11.0
(iii) Fe found in 2.0 ml diluted solution : 1.1 mg
(iv) Fe found in contents of one capsule : 55.00 mg
(v) Fe reported in one capsule : 55.21 mg
(vi) Error : -0.21 mg
(vii) Percentage error : -0.380%
ABSORPTION SPECTRA OF Fe(III)-HBCO COMPLEX

Fig. 4.1.1 (I)
Beer's Law Plot for Fe(III)-HBCO Complex

Fig. 4.1.1 (II)
Fig. 4.1.1 (III)

Job's Method for Fe(III)-HBCO Complex

$Em = 0.552$

$Es = 0.528$
Mole Ratio Method for Fe(III)-HBCO Complex

Em = 0.675
Es = 0.650

Fig. 4.1.1 (IV)
[4.1.2] STUDY OF Cu(II) COMPLEX:

PREPARATION OF STANDARD SOLUTION OF Cu(II):

Stock solution (0.05 M) of Cu(II) was prepared by dissolving 3.121 g of CuSO$_4$.5H$_2$O in distilled water and little acid and diluted it to 250 ml. This solution was standardised volumetrically using EDTA [210]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2'-HYDROXY-4'-BUTOXYCHALCONE OXIME WITH Cu(II):

0.05 M solution of the reagent in 70% aqueous ethanol was used in all detection and gravimetric and determination.

REACTION WITH Cu(II) AT DIFFERENT pH:

5 ml solution of the reagent was added to 2 ml 0.05 M Cu(II) solution at different pH. The results are tabulated in Table-4.1.2 (I).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Colouration</td>
</tr>
<tr>
<td>2.5</td>
<td>HCl + CH$_3$COOH</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>3.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>4.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>5.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>6.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The brown Cu(II) chelate is insoluble in water, ethanol, benzene but soluble in acetone, carbon tetrachloride, ethyl acetate and chloroform.

GRAVIMETRIC DETERMINATION OF Cu(II) WITH HBCO:

A 0.05 M solution of the reagent in 70% aqueous ethanol was used. Copper sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water and pH of the solution was adjusted between 3.0 to 6.0 using suitable acid buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 ml). A brown precipitate obtained were digested on water-bath for 60 minutes at 60°C. The
precipitate were filtered through a previously weighed sintered glass crucible (G₄) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots at pH 5.0 to evaluate its applicability. The results are given in Table-4.1.2 (II) and Table-4.1.2 (III).

RESULTS:
10 ml solution gave 0.1869 g of Cu(II)-HBCO
Found copper = 31.79 mg
10 ml solution contains = 31.77 mg Cu(II)
Error = + 0.02 mg
= + 0.060%
### TABLE - 4.1.2 (II)

**GRAVIMETRIC DETERMINATION OF Cu(II) USING HBCO**

Cu(II) taken = 31.77 mg  
Drying temperature = 110-115°C  
Salt = CuSO₄·5H₂O

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu(II) complex in g</th>
<th>Cu(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.1861</td>
<td>31.65</td>
<td>-0.11</td>
<td>-0.35</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1860</td>
<td>31.63</td>
<td>-0.14</td>
<td>-0.41</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1862</td>
<td>31.67</td>
<td>-0.10</td>
<td>-0.31</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1863</td>
<td>31.69</td>
<td>-0.08</td>
<td>-0.25</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1865</td>
<td>31.72</td>
<td>-0.05</td>
<td>-0.15</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1864</td>
<td>31.70</td>
<td>-0.07</td>
<td>-0.22</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1867</td>
<td>31.75</td>
<td>-0.02</td>
<td>-0.06</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1866</td>
<td>31.74</td>
<td>-0.03</td>
<td>-0.09</td>
</tr>
<tr>
<td>5.0</td>
<td>0.1869</td>
<td>31.79</td>
<td>+0.02</td>
<td>+0.06</td>
</tr>
<tr>
<td>5.0</td>
<td>0.1870</td>
<td>31.80</td>
<td>+0.03</td>
<td>+0.12</td>
</tr>
<tr>
<td>5.5</td>
<td>0.1873</td>
<td>31.86</td>
<td>+0.09</td>
<td>+0.28</td>
</tr>
<tr>
<td>5.5</td>
<td>0.1872</td>
<td>31.84</td>
<td>+0.07</td>
<td>+0.23</td>
</tr>
<tr>
<td>6.0</td>
<td>0.1876</td>
<td>31.91</td>
<td>+0.14</td>
<td>+0.44</td>
</tr>
<tr>
<td>6.0</td>
<td>0.1875</td>
<td>31.89</td>
<td>+0.12</td>
<td>+0.39</td>
</tr>
</tbody>
</table>

Conversion factor = 0.1700

### TABLE - 4.1.2 (III)

**GRAVIMETRIC DETERMINATION OF Cu(II) IN DIFFERENT ALIQUOTS**

pH = 5.0  
Drying temperature = 110-115°C  
Salt = CuSO₄·5H₂O

<table>
<thead>
<tr>
<th>Cu(II) taken in mg</th>
<th>Cu(II) complex in g</th>
<th>Cu(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.88</td>
<td>0.0933</td>
<td>15.89</td>
<td>-0.01</td>
<td>-0.06</td>
</tr>
<tr>
<td>15.88</td>
<td>0.0932</td>
<td>15.85</td>
<td>-0.03</td>
<td>-0.18</td>
</tr>
<tr>
<td>31.77</td>
<td>0.1867</td>
<td>31.79</td>
<td>+0.02</td>
<td>+0.06</td>
</tr>
<tr>
<td>31.77</td>
<td>0.1865</td>
<td>31.80</td>
<td>+0.03</td>
<td>+0.09</td>
</tr>
<tr>
<td>47.65</td>
<td>0.2801</td>
<td>47.64</td>
<td>-0.01</td>
<td>-0.02</td>
</tr>
<tr>
<td>47.65</td>
<td>0.2800</td>
<td>47.62</td>
<td>-0.03</td>
<td>-0.06</td>
</tr>
</tbody>
</table>
EFFECT OF DIVERSE IONS:

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Ni(II), Zn(II), Ba(II), Cd(II), Mn(II) and Mg(II) do not interfere at this pH but Fe(III) and Pd(II) interfered seriously. Interference of Fe(III) can be removed by masking it with H₃PO₄. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

SPECTROPHOTOMETRIC STUDY OF Cu(II)-HBCO COMPLEX

The Cu(II)-HBCO chelate has been found to be soluble in acetone, carbon tetrachloride, ethyl acetate and chloroform. This enabled to verify the Beer law and its applications for spectrophotometric determination.

ABSORPTION SPECTRA

To take absorption spectra, 5.0 mg of the chelate was dissolved in 25 ml of chloroform and absorption spectra was scanned between 300 to 800 nm.

It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A shoulder is observed at 400 nm and hence all measurements were carried out at 400 nm. The graph is shown in Fig.-4.1.2(I).

VERIFICATION OF BEER’S LAW

To 5 ml of solution (0.01 M) of the reagent HBCO, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using [CH₃COOH + CH₃COONa] buffer. The insoluble complex precipitated was extracted in chloroform using three 5.0 ml, portion of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbance of these solutions were measured at 400 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 63.68 ppm
of Cu(II). The standard graph thus obtained may be used for determination of Cu(II) in an unknown solution using HBCO. The results are tabulated in Table - 4.1.2(IV) and the graph is shown in Fig.-4.1.2 (II).

### TABLE – 4.1.2 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal ion content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.74</td>
<td>0.124</td>
</tr>
<tr>
<td>2</td>
<td>25.47</td>
<td>0.265</td>
</tr>
<tr>
<td>3</td>
<td>38.21</td>
<td>0.385</td>
</tr>
<tr>
<td>4</td>
<td>50.94</td>
<td>0.500</td>
</tr>
<tr>
<td>5</td>
<td>63.68</td>
<td>0.630</td>
</tr>
<tr>
<td>6</td>
<td>76.42</td>
<td>0.725</td>
</tr>
<tr>
<td>7</td>
<td>89.15</td>
<td>0.805</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be $6.30 \times 10^2$ lit.mol$^{-1}$.cm$^{-1}$ for Cu(II)-HBCO complex at 400 nm and Sandell’s sensitivity was found to be 0.1008 $\mu$g/cm$^2$.

**COMPOSITION OF CHELATE:**

The composition of Cu(II) chelate with the reagent HBCO has been determined on the basis of, (i) Job’s method of continuous variation , and (ii) Yoe and Jones mole-ratio method.

**(i) JOB’S METHOD OF CONTINUOUS VARIATION**

A series of solutions were prepared by mixing the equimolar solution of metal ion and reagent solutions in varying proportion as under:

- Metal ion solution : 1, 2, 3,.................10,11 ml
- Reagent solution : 11, 10, 9,................., 2,1 ml
pH of the solution was adjusted to 5.0 using buffer solution of pH 5.0. The precipitated complex was extracted with three 5.0 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of these solutions were measured against individual blank at 400 nm. The absorbance values were plotted against the ratio of concentration of metal to total concentration of metal and ligand. The results are tabulated in Table-4.1.2(V) and graph is given in Fig -4.1.2(III).

From the graph it has been found that maximum occurs at 0.50 ratio of metal ion concentration to the total metal of and ligand concentration indicating the formation of 1:1 [M: L] complex.

### TABLE – 4.1.2 (V)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>$\frac{C_m}{C_m + C_r}$</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.058</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.142</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.200</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.271</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.340</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.401</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.322</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.258</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.203</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.135</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.070</td>
</tr>
</tbody>
</table>

(ii) **YOE AND JONE’S MOLE-RATIO METHOD**

In this method, equimolar solutions of Cu(II) as well as the reagent (0.005 M) were used. A series of solutions were prepared keeping the concentration of reagent solution (8 ml, 0.005 M) constant, while varying the amount (from 1.0 ml
to 8.0 ml, 0.005 M) of the metal ion solution. pH of the solutions were adjusted to 5.0. The resulting precipitate of complex were extracted with three 5.0 ml portion of chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbances of all solutions were recorded at 400 nm against reagent blank and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.1.2(VI).

It is evident from the Figure-4.1.2 (IV) that absorbance gradually increases up to correct stoichiometry of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.

**TABLE – 4.1.2 (VI)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.070</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.110</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.176</td>
</tr>
<tr>
<td>4</td>
<td>0.500</td>
<td>0.212</td>
</tr>
<tr>
<td>5</td>
<td>0.625</td>
<td>0.289</td>
</tr>
<tr>
<td>6</td>
<td>0.750</td>
<td>0.322</td>
</tr>
<tr>
<td>7</td>
<td>0.875</td>
<td>0.385</td>
</tr>
<tr>
<td>8</td>
<td>1.000</td>
<td>0.412</td>
</tr>
<tr>
<td>9</td>
<td>1.125</td>
<td>0.435</td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that stoichiometry for Cu(II)-HBCO complex is 1:1 [M:L].

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:**

\[
MLn \rightleftharpoons M + nL
\]

\[
C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]
Taking \( n=1 \), in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{C\alpha^2} \quad \text{where,} \quad \alpha = \frac{E_m - E_s}{E_m}
\]

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \( K_s \) value the standard free energy change \( \Delta G^\circ \) at 27\(^\circ\)C for the formation reaction of complex has been calculated using the formula,

\[
\Delta G^\circ = -RT \ln K_s
\]

**TABLE – 4.1.2 (VII)**

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( K_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.420</td>
<td>0.401</td>
<td>0.045</td>
<td>9.434 x 10(^4)</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.435</td>
<td>0.412</td>
<td>0.052</td>
<td>7.011 x 10(^4)</td>
</tr>
</tbody>
</table>

Mean \( K_s = 8.222 \times 10^4 \)

\( \Delta G^\circ = -12.55 \) K.cal/mole
DETERMINATION OF Copper IN BRASS:

Preanalysed sample of brass (0.5523 g) was dissolved in 50% HNO₃ by heating for 30 minutes. The solution is evaporated to a volume of near about 5 ml but not to dryness and the bulk of nitric acid removed. The resulting solution was diluted to 100 ml with doubly distilled water in volumetric flask.

An aliquot of above diluted solution (10 ml) was taken in a clean beaker and copper was determined gravimetrically using 2'-hydroxy-4'-butoxychalcone oxime (HBCO) as per the procedure described previously.

RESULTS:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Wt. of sample taken</td>
<td>0.5523 g</td>
</tr>
<tr>
<td>(2) Wt. of Cu(II)-HBCO complex (Average of three determination)</td>
<td>0.2313 g</td>
</tr>
<tr>
<td>(3) Copper found in 10 ml diluted solution</td>
<td>0.03934 g</td>
</tr>
<tr>
<td>(4) Copper found in brass sample taken</td>
<td>0.3934 g</td>
</tr>
<tr>
<td>(5) % Cu found in brass sample</td>
<td>71.23%</td>
</tr>
<tr>
<td>(6) % Cu reported in brass sample</td>
<td>71.20%</td>
</tr>
<tr>
<td>(7) Absolute Error</td>
<td>- 0.03%</td>
</tr>
<tr>
<td>(8) Percentage error</td>
<td>- 0.042%</td>
</tr>
</tbody>
</table>
ABSORPTION SPECTRA OF Cu(II)-HBCO COMPLEX

Fig. 4.1.2 (I)
Beer’s Law Plot for Cu(II)-HBCO Complex

Absorbance

Concentration in ppm

Fig. 4.1.2 (II)
Job's method for Cu(II)-HBCO complex

Em = 0.420
Es = 0.401

Fig. 4.1.2 (III)
Mole ratio method for Cu(II)-HBCO Complex

Em = 0.435
Es = 0.412

Absorbance vs. Cm/Cr

Fig. 4.1.2 (IV)
PREPARATION OF STANDARD SOLUTION OF Ni(II):

Stock solution (0.05 M) of Ni(II) was prepared by dissolving 3.2838 g of NiSO₄·6H₂O in distilled water and little acid and diluted to 250 ml. This solution was standardised volumetrically using EDTA [211]. Experimental solution of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2'-HYDROXY-4'-BUTOXYCHALCONE OXIME WITH Ni(II):

0.05 M solution of the reagent in 70% aqueous ethanol was used in all detection and gravimetric determination.

REACTION WITH Ni(II) AT DIFFERENT pH:

5 ml solution of the reagent was added to 2 ml 0.05 M Ni(II) solution at different pH. The results are tabulated in Table-4.1.3 (I).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>K₂HPO₄ + KH₂PO₄</td>
<td>Light green colouration</td>
</tr>
<tr>
<td>7.5</td>
<td>K₂HPO₄ + KH₂PO₄</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>8.0</td>
<td>NH₃ + NH₄Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>8.5</td>
<td>NH₃ + NH₄Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>9.0</td>
<td>NH₃ + NH₄Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>9.5</td>
<td>NH₃ + NH₄Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>10.0</td>
<td>NH₃ + NH₄Cl</td>
<td>Light green precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The light green Ni(II) chelate is insoluble in water, ethanol but soluble in acetone, ethyl acetate and chloroform.

GRAVIMETRIC DETERMINATION OF Ni(II) WITH HBCO:

A 0.05 M solution of the reagent in 70% aqueous ethanol was used.

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 \( \text{NH}_3 + \text{NH}_4\text{Cl} \) buffer. A light green precipitate obtained were digested on water-bath for 60 minutes at 60\(^\circ\)C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) 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\(^\circ\)C in hot air oven, cooled and weighed.

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 results are given in Table-4.1.3 (II) and Table-4.1.3 (III).

**RESULTS:**

10 ml solution gave 0.3394 of Ni(II)-HBCO

Found nickel = 29.33 mg

10 ml solution contains = 29.34 mg Ni(II)

Error = - 0.01 mg

= - 0.034%

**TABLE - 4.1.3 (II)**

**GRAVIMETRIC DETERMINATION OF Ni(II) USING HBCO**

Ni(II) taken = 29.34 mg

Drying temperature = 110-115\(^\circ\)C

Salt = NiSO\(_4\).6H\(_2\)O

<table>
<thead>
<tr>
<th>pH</th>
<th>Ni(II) complex in g</th>
<th>Ni(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>0.3372</td>
<td>29.13</td>
<td>-0.21</td>
<td>-0.72</td>
</tr>
<tr>
<td>8.0</td>
<td>0.3376</td>
<td>29.17</td>
<td>-0.17</td>
<td>-0.58</td>
</tr>
<tr>
<td>8.5</td>
<td>0.3385</td>
<td>29.25</td>
<td>-0.09</td>
<td>-0.31</td>
</tr>
<tr>
<td>8.5</td>
<td>0.3384</td>
<td>29.24</td>
<td>-0.10</td>
<td>-0.34</td>
</tr>
<tr>
<td>9.0</td>
<td>0.3394</td>
<td>29.33</td>
<td>-0.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>9.0</td>
<td>0.3393</td>
<td>29.32</td>
<td>-0.02</td>
<td>-0.06</td>
</tr>
<tr>
<td>9.5</td>
<td>0.3396</td>
<td>29.35</td>
<td>+0.01</td>
<td>+0.03</td>
</tr>
<tr>
<td>9.5</td>
<td>0.3398</td>
<td>29.36</td>
<td>+0.02</td>
<td>+0.07</td>
</tr>
<tr>
<td>10.0</td>
<td>0.3402</td>
<td>29.39</td>
<td>+0.05</td>
<td>+0.17</td>
</tr>
<tr>
<td>10.0</td>
<td>0.3406</td>
<td>29.43</td>
<td>+0.09</td>
<td>+0.31</td>
</tr>
</tbody>
</table>

Conversion factor = 0.0864
TABLE - 4.1.3 (III)

GRAVIMETRIC DETERMINATION OF Ni(II) IN DIFFERENT ALIQUOTS

pH = 9.0
Drying temperature = 110-115°C  
Salt = NiSO₄.6H₂O

<table>
<thead>
<tr>
<th>Ni(II) taken in mg</th>
<th>Ni(II) complex in g</th>
<th>Ni(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.28</td>
<td>0.1774</td>
<td>15.33</td>
<td>+0.05</td>
<td>+0.33</td>
</tr>
<tr>
<td>15.28</td>
<td>0.1769</td>
<td>15.29</td>
<td>+0.01</td>
<td>+0.06</td>
</tr>
<tr>
<td>29.33</td>
<td>0.3392</td>
<td>29.31</td>
<td>-0.02</td>
<td>-0.07</td>
</tr>
<tr>
<td>29.33</td>
<td>0.3387</td>
<td>29.27</td>
<td>-0.06</td>
<td>-0.20</td>
</tr>
<tr>
<td>44.62</td>
<td>0.5167</td>
<td>44.65</td>
<td>+0.03</td>
<td>+0.07</td>
</tr>
<tr>
<td>44.62</td>
<td>0.5170</td>
<td>44.67</td>
<td>+0.05</td>
<td>+0.11</td>
</tr>
</tbody>
</table>

EFFECT OF DIVERSE 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 29.33 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.

SPECTROPHOTOMETRIC STUDY OF Ni(II)-HBCO COMPLEX

The Ni(II)-HBCO chelate has been found to be soluble in acetone, ethyl acetate and chloroform. This enabled to verify the Beer law and its applications for spectrophotometric determination.

ABSORPTION SPECTRA

To take absorption spectra, 5.0 mg of the chelate was dissolved in 25 ml of chloroform and absorption spectra was scanned between 300 to 800 nm.

It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 500 nm and hence all measurements were carried out at 500 nm. The graph is shown in Figure-4.1.3(I).
VERIFICATION OF BEER’S LAW

To 5 ml of solution (0.01 M) of the reagent HBCO, 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 absorbances of these solutions were measured at 500 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 117.38 ppm of Ni(II). The standard graph thus obtained may be used for determination of Ni(II) in an unknown solution using HBCO. The results are tabulated in Table-4.1.3(IV) and the graph is shown in Figure-4.1.3(II).

**TABLE – 4.1.3 (IV)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>0.005 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>0.01 M</td>
</tr>
<tr>
<td>pH</td>
<td>9.0</td>
</tr>
<tr>
<td>Final volume of chloroform extract</td>
<td>25.0 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>500 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>23.47</td>
<td>0.063</td>
</tr>
<tr>
<td>4.0</td>
<td>46.95</td>
<td>0.099</td>
</tr>
<tr>
<td>6.0</td>
<td>70.38</td>
<td>0.149</td>
</tr>
<tr>
<td>8.0</td>
<td>93.84</td>
<td>0.203</td>
</tr>
<tr>
<td>10.0</td>
<td>117.38</td>
<td>0.248</td>
</tr>
<tr>
<td>12.0</td>
<td>140.76</td>
<td>0.278</td>
</tr>
<tr>
<td>14.0</td>
<td>164.22</td>
<td>0.298</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be 1.24 x 10² \( \text{lit.mol}^{-1}.\text{cm}^{-1} \) for Ni(II)-HBCO complex at 500 nm and Sandell’s sensitivity was found to be 0.0473 \( \mu \text{g/cm}^2 \).
COMPOSITION OF CHELATE

The composition of Ni(II) chelate with the reagent HBCO has been determined on the basis of, (i) Job’s method of continuous variation, and (ii) Yoe and Jone’s mole-ratio method.

A series of solutions were prepared in a similar way as done for Cu(II)-HBCO complex for both methods and complex was extracted in chloroform. The absorbance values obtained for the two methods are given in Table-4.1.3(V) and Table-4.1.3(VI), respectively and the graphs are shown in Figure-4.1.3(III) and Figure-4.1.3 (IV) respectively.

**TABLE – 4.1.3 (V)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>Cm</th>
<th>Cm +Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.093</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.225</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.261</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.252</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.231</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.178</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.056</td>
<td></td>
</tr>
</tbody>
</table>
TABLE – 4.1.3 (VI)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.070</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.117</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.156</td>
</tr>
<tr>
<td>4</td>
<td>0.500</td>
<td>0.225</td>
</tr>
<tr>
<td>5</td>
<td>0.625</td>
<td>0.240</td>
</tr>
<tr>
<td>6</td>
<td>0.750</td>
<td>0.258</td>
</tr>
<tr>
<td>7</td>
<td>0.875</td>
<td>0.261</td>
</tr>
<tr>
<td>8</td>
<td>1.000</td>
<td>0.265</td>
</tr>
<tr>
<td>9</td>
<td>1.125</td>
<td>0.270</td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that stoichiometry for Ni(II)-HBCO complex is 1:2 [M:L].

EVALUATION OF STABILITY CONSTANT FROM THE MOLE RATIO METHOD AND JOB’S METHOD:

The dissociation of complex can be shown as follows:

\[ ML^n \overset{C(1-\alpha)}{\rightleftharpoons} M + nL \]

\[ C.\alpha \ (nC\alpha)^n \]

\[ K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n} \]

Taking \( n=2 \), in this case the equation reduces to,

\[ K_s = \frac{1-\alpha}{4\alpha^3C^2} \]

where, \( \alpha = \frac{E_m - E_s}{E_m} \)

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.
From mean Ks value, the standard free energy change $\Delta G^0$ at 27°C for the formation reaction of complex has been calculated using the formula.

$$\Delta G^0 = -RT \ln Ks$$

The stability constants calculated from above relation are as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>$Em$</th>
<th>$Es$</th>
<th>$\alpha$</th>
<th>Ks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.280</td>
<td>0.261</td>
<td>0.067</td>
<td>1.21 x 10^9</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.240</td>
<td>0.225</td>
<td>0.062</td>
<td>3.93 x 10^9</td>
</tr>
</tbody>
</table>

Mean Ks = 2.57 x 10^9

$\Delta G^0 = - 56.27 \text{ K.cal/mole}$

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

Exactly weighed german silver (0.6831g) 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'-butoxychalcone 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 is collected in 250 ml beaker for determination of nickel. The chelate was dried to constant weight at 110-115°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 and after cooling, the reagent solution (12 ml, 0.05 M) was added to it and the pH of the solution was adjusted to 9.0 using NH₃-NH₄Cl 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 (G₄) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed. The process was repeated three times.

CALCULATIONS AND RESULTS:

(1) For Cu(II):
10 ml solution gave 0.2400 g of Cu(II)-HBCO complex
(Average of three determinations)
Found copper = 0.04082 g
10 ml diluted alloy solution contains 0.04082 g copper
∴ 100 ml diluted alloy solution contains 0.4082 g copper
Percentage of copper found in german silver = 59.76%
(Average of three determinations)
Percentage of copper reported in alloy = 59.00%
Absolute error = +0.76%
Percentage error = +1.288%

(2) For Ni(II):
10 ml solution gave 0.2083 g of Ni(II)-HBCO complex
(Average of three determinations)
Found nickel = 0.0180 g
10 ml diluted alloy solution contains 0.0180 g nickel
∴ 100 ml diluted alloy solution contains 0.180 g nickel
Percentage of nickel found in german silver = 26.35%
(Average of three determinations)
Percentage of nickel reported in alloy = 26.00%
Absolute error = +0.35%
Percentage error = +1.346 %
ABSORPTION SPECTRA OF Ni(II)-HBCO COMPLEX

Fig. 4.1.3 (I)
Beer's Law Plot for Ni(II)-HBCO Complex

Fig. 4.1.3 (II)
Fig. 4.1.3 (III)
Mole Ratio Method for Ni(II)-HBCO Complex

Fig. 4.1.3 (IV)
[ 4.1.4 ] STUDY OF Pd(II) COMPLEX:

PREPARATION OF STANDARD SOLUTION OF Pd(II):

Stock solution (0.01 M) of Pd (II) was prepared by dissolving 0.4435 gm of PdCl$_2$ in little concentrated hydrochloric acid and diluting it to 250 ml with distilled water. The solution was standardised gravimetrically using dimethylglyoxime. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

REACTION OF 2'-HYDROXY-4'-BUTOXYCHALCONE OXIME WITH Pd(II):

0.05 M solution of the reagent in 70 % aqueous ethanol was used in all detection and gravimetric determination.

REACTION WITH Pd (II) AT DIFFERENT pH:

2 ml. of 0.05 M HBCO solution was added to 1 ml of standard 0.01 M Pd(II) solution at different pH. The results are tabulated in Table- 4.1.4 (I)

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>2.5</td>
<td>HCl + CH$_3$COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>3.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>3.5</td>
<td>HCl + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>4.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>4.5</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>5.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>5.5</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>6.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Yellow precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The yellow Pd(II) chelate is insoluble in water, ethanol, carbon tetrachloride and benzene, while it is soluble in ethyl acetate, chloroform and DMF. The solution of the chelate was stable and could be kept for long time without any decomposition.
GRAVIMETRIC DETERMINATION OF Pd(II) WITH HBCO:

A 0.04 M solution of the reagent in 70 % aqueous ethanol was used. Palladium chloride solution (0.01 M, 20 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water and pH of the solution was adjusted between 2.5 to 6.0 using suitable buffer. The solution was warmed to 60°C and a small excess of reagent (0.04 M, 11 ml) was added. A yellow precipitate obtained was digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 70 % aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110 - 115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH to evaluate its applicability. The results are given in Table-4.1.4 (II) and Table-4.1.4 (III).

RESULTS:
20 ml Palladium chloride solution gave 0.1455 g of Pd(II) - HBCO complex.
Found palladium = 21.30 mg
20 ml solution contains = 21.28 mg of Pd (II)
Error = +0.02 mg
= +0.09 %
### TABLE - 4.1.4 (II)

**GRAVIMETRIC DETERMINATION OF Pd(II) USING HIBAO**

Pd(II) taken: 21.28 mg  
Salt: PdCl₂  
Drying temp.: 110-115°C

<table>
<thead>
<tr>
<th>pH</th>
<th>Pd(II) complex in g</th>
<th>Pd(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.1439</td>
<td>21.08</td>
<td>-0.20</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td>0.1441</td>
<td>21.09</td>
<td>-0.19</td>
<td>-0.90</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1443</td>
<td>21.13</td>
<td>-0.15</td>
<td>-0.71</td>
</tr>
<tr>
<td></td>
<td>0.1445</td>
<td>21.15</td>
<td>-0.13</td>
<td>-0.62</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1446</td>
<td>21.17</td>
<td>-0.11</td>
<td>-0.52</td>
</tr>
<tr>
<td></td>
<td>0.1447</td>
<td>21.19</td>
<td>-0.09</td>
<td>-0.42</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1455</td>
<td>21.30</td>
<td>+0.02</td>
<td>+0.09</td>
</tr>
<tr>
<td></td>
<td>0.1457</td>
<td>21.33</td>
<td>+0.05</td>
<td>+0.23</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1458</td>
<td>21.35</td>
<td>+0.07</td>
<td>+0.33</td>
</tr>
<tr>
<td></td>
<td>0.1459</td>
<td>21.36</td>
<td>+0.08</td>
<td>+0.37</td>
</tr>
<tr>
<td>5.0</td>
<td>0.1460</td>
<td>21.38</td>
<td>+0.10</td>
<td>+0.47</td>
</tr>
<tr>
<td></td>
<td>0.1462</td>
<td>21.41</td>
<td>+0.13</td>
<td>+0.61</td>
</tr>
</tbody>
</table>

Conversion factor = 0.1464

### TABLE - 4.1.4 (III)

**GRAVIMETRIC DETERMINATION OF Pd(II) IN DIFFERENT ALIQUOTS**

pH: 4.0  
Salt: PdCl₂  
Drying temp.: 110-115°C

<table>
<thead>
<tr>
<th>Pd(II) taken in mg</th>
<th>Pd(II) complex in gm</th>
<th>Pd(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.64</td>
<td>0.0726</td>
<td>10.63</td>
<td>-0.01</td>
<td>-0.09</td>
</tr>
<tr>
<td>10.64</td>
<td>0.0727</td>
<td>10.66</td>
<td>+0.02</td>
<td>+0.18</td>
</tr>
<tr>
<td>21.28</td>
<td>0.1455</td>
<td>21.30</td>
<td>+0.02</td>
<td>+0.09</td>
</tr>
<tr>
<td>21.28</td>
<td>0.1457</td>
<td>21.33</td>
<td>+0.05</td>
<td>+0.23</td>
</tr>
<tr>
<td>31.92</td>
<td>0.2182</td>
<td>31.95</td>
<td>+0.03</td>
<td>+0.09</td>
</tr>
<tr>
<td>31.92</td>
<td>0.2181</td>
<td>31.93</td>
<td>+0.01</td>
<td>+0.03</td>
</tr>
</tbody>
</table>
EFFECT OF DIVERSE ION:

To study the effect of foreign ions on gravimetric determination of Pd(II), 8-10 mg of various cations were added to solution containing 21.28 mg Pd(II) at pH 4.0 and gravimetric estimations were done. It was observed that Ca(II), Mg(II), Ni(II), Mn(II), Zn(II), Sr(II), Cd(II), Ba(II), K(I) and Na(I) do not interfere at this pH, but Cu(II), Fe(III) and Co(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

SPECTROPHOTOMETRIC STUDY OF Pd (II) - HBCO:

The Pd(II) - HBCO chelate has been found to be soluble in ethyl acetate, chloroform and DMF. This enabled to verify the Beer law and its applications for spectrophotometric determination.

ABSORPTION SPECTRA:

To have the absorption spectra, 5 mg of chelate was dissolved in 25 ml of ethyl acetate and absorption spectra of this solution was recorded in the wavelength range of 350 nm to 600 nm.

It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A shoulder is obtained at 450 nm and hence all the measurements were carried out at 450 nm. The graph is shown in figure-4.1.4 (I).

VERIFICATION OF BEER'S LAW:

It was done in a similar way as in case of Cu(II) and Ni(II) except that the complex was extracted in ethylacetate.

The Pd(II) complex with HBCO obeys Beer's law upto 63.85 ppm of Pd(II) at 450 nm. The Beer law plot obtained can be used for the determination of Pd(II) ion in an unknown solution using HBCO. The results are given in Table-4.1.4 (IV) and graph is shown in figure 4.1.4 (II).
TABLE : 4.1.4 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml.</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>21.28</td>
<td>0.110</td>
</tr>
<tr>
<td>1.5</td>
<td>31.92</td>
<td>0.162</td>
</tr>
<tr>
<td>2.0</td>
<td>42.56</td>
<td>0.217</td>
</tr>
<tr>
<td>2.5</td>
<td>53.20</td>
<td>0.273</td>
</tr>
<tr>
<td>3.0</td>
<td>63.85</td>
<td>0.335</td>
</tr>
<tr>
<td>3.5</td>
<td>74.49</td>
<td>0.364</td>
</tr>
<tr>
<td>4.0</td>
<td>85.12</td>
<td>0.378</td>
</tr>
<tr>
<td>4.5</td>
<td>95.76</td>
<td>0.398</td>
</tr>
</tbody>
</table>

The molar absorptivity from Beer's law plot was found to be $5.58 \times 10^2$ lit.mol$^{-1}$.cm$^{-1}$ for Pd(II) - HBCO complex at 400 nm and Sandell's sensitivity was found to be 0.1907 μg of Pd(II)/cm$^2$.

**COMPOSITION OF CHELATE :**

The composition of Pd(II) chelate with the reagent HBCO has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

The methods were used in a similar way as done for Ni(II) - HBCO complex. The results obtained from the two methods are given in Table- 4.1.4 (V) and Table 4.1.4 (VI) respectively and the graphs are shown in figure- 4.1.4 (III) and figure 4.1.4 (IV) respectively.
**TABLE - 4.1.4 (V)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml.</th>
<th>Reagent solution taken in ml.</th>
<th>( \frac{C_m}{C_m + Cr} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>11.0</td>
<td>0.083</td>
<td>0.052</td>
</tr>
<tr>
<td>2.0</td>
<td>10.0</td>
<td>0.17</td>
<td>0.093</td>
</tr>
<tr>
<td>3.0</td>
<td>9.0</td>
<td>0.25</td>
<td>0.159</td>
</tr>
<tr>
<td>4.0</td>
<td>8.0</td>
<td>0.33</td>
<td>0.185</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>0.42</td>
<td>0.164</td>
</tr>
<tr>
<td>6.0</td>
<td>6.0</td>
<td>0.50</td>
<td>0.146</td>
</tr>
<tr>
<td>7.0</td>
<td>5.0</td>
<td>0.58</td>
<td>0.130</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0</td>
<td>0.67</td>
<td>0.092</td>
</tr>
<tr>
<td>9.0</td>
<td>3.0</td>
<td>0.75</td>
<td>0.08</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>0.83</td>
<td>0.061</td>
</tr>
<tr>
<td>11.0</td>
<td>1.0</td>
<td>0.92</td>
<td>0.038</td>
</tr>
</tbody>
</table>

**TABLE - 4.1.4 (VI)**

<table>
<thead>
<tr>
<th>Metal solution taken in ml.</th>
<th>Cm / Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.17</td>
<td>0.051</td>
</tr>
<tr>
<td>2.0</td>
<td>0.33</td>
<td>0.121</td>
</tr>
<tr>
<td>3.0</td>
<td>0.50</td>
<td>0.173</td>
</tr>
<tr>
<td>4.0</td>
<td>0.66</td>
<td>0.185</td>
</tr>
<tr>
<td>5.0</td>
<td>0.83</td>
<td>0.189</td>
</tr>
<tr>
<td>6.0</td>
<td>1.00</td>
<td>0.191</td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that the stoichiometry for Pd(II) - HBCO complex is 1:2 [M : L].
EVALUATION OF STABILITY CONSTANT FROM THE MOLE RATIO METHOD AND JOB’S METHOD:

The dissociation of complex can be shown as follows:

\[
M[nL] \quad \longrightarrow \quad M + nL
\]

\[
C(1-\alpha) \quad \quad \quad \quad C/\alpha \quad (nC/\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking n=2, in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{4\alpha^3C^2}
\]

where, \( \alpha = \frac{E_m - E_s}{E_m} \)

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean Ks value, the standard free energy change \( \Delta G^0 \) at 27\(^0\)C for the formation reaction of complex has been calculated using the formula.

\[
\Delta G^0 = -RT \ln Ks
\]

The stability constants calculated from above relation are as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( Ks )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s Method</td>
<td>0.199</td>
<td>0.185</td>
<td>0.071</td>
<td>1.04 \times 10^9</td>
</tr>
<tr>
<td>Mole-Ratio Method</td>
<td>0.185</td>
<td>0.173</td>
<td>0.064</td>
<td>3.57 \times 10^9</td>
</tr>
</tbody>
</table>

Mean Ks = 2.30 \times 10^9

\( \Delta G^0 = -49.65 \) K. cal/mole.
ABSORPTION SPECTRA OF Pd(II)-HBCO COMPLEX

Fig. 4.1.4(I)
Beer's Law Plot for Pd(II)-HBCO Complex

Fig. 4.1.4 (II)
Job's Method for Pd(II)-HBCO Complex

Em = 0.199
Es = 0.185

Fig. 4.1.4 (III)
Mole ratio method for Pd(II)-HBCO Complex

Em = 0.185
Es = 0.173

Absorbance vs. Cm/Cr
IR SPECTRA:

IR spectra of ligand HBCO Fig. 4.1(III) and those of Cu(II), Ni(II) and Pd(II) are compared to ascertain the linking of metal with hetero atoms O & N of ligands.

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 Cu(II)-HBCO, Ni(II)-HBCO and Pd(II)-HBCO complexes, while the band due to oximino -OH group at 3446 cm\(^{-1}\) in Cu(II) chelate and at 3472 cm\(^{-1}\) and 3057 cm\(^{-1}\) in Ni(II) complex and Pd(II) complex respectively.

The band due to the O=C=N stretching which is observed at 1596 cm\(^{-1}\) in ligand is shifted to 1582-1585 cm\(^{-1}\) in complexes. This may be due to coordination of metal through nitrogen. This is further supported by slight downward shift of \(\nu\) NO from 1023 cm\(^{-1}\) in the ligand to 970 to 980 cm\(^{-1}\) in copper, nickel and palladium chelates.

Thus, in the chelates, metal is covalently bonded with oxygen and coordinate bonded with nitrogen. The IR spectra of ligand [Fig. 4.1(III)] and complexes are shown in Fig. 4.1(IV), 4.1 (V) and 4.1(VI).

The structure of complex can be given as follows.
IR SPECTRA OF LIGAND HBCO
Fig. 4.1 (III)

IR SPECTRA OF Cu(II)-HBCO COMPLEX
Fig. 4.1 (IV)
IR SPECTRA OF Ni(II)-HBCO COMPLEX
Fig. 4.1 (V)

IR SPECTRA OF Pd(II)-HBCO COMPLEX
Fig. 4.1 (VI)
[4.2.1] STUDY OF Fe(III) COMPLEX WITH HMCO :

PREPARATION OF STANDARD SOLUTION OF FERRIC CHLORIDE (FeCl$_3$):

Ferric chloride (anhydrous) (A.R., B.D.H.) 2.0276 g was dissolved in double distilled water, containing a little free acid and was diluted to 250 ml to get 0.05 M stock solution of ferric chloride. This solution was standardised gravimetrically [209]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

Fe(III) was found to form purple coloured ethanol soluble complex in pH range of 2.0 to 4.5. It was not found possible to do gravimetric determination of Fe(III), using the reagent.

EFFECT OF pH:

The effect of pH, a series of solutions were prepared by taking 0.005 (1 ml) ferric chloride solution and 0.01 M (5 ml) reagent solution. The pH of the solutions were adjusted to 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 with sodium acetate-hydrochloric acid buffer. The coloured solutions were then diluted to 25 ml. keeping 70% ethanol concentration. The absorbance values of each solution were measured between 400 nm to 600 nm. It was observed that at 450 nm and at pH 4.5 absorbance value is found maximum. The absorbance values at 450 nm are tabulated in Table-4.2.1 (I).

**TABLE - 4.2.1 (I)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>:</th>
<th>0.005 M (1.0 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>:</td>
<td>0.01 M (5.0 ml)</td>
</tr>
<tr>
<td>Final volume</td>
<td>:</td>
<td>25 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>:</td>
<td>450 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>CH$_3$COONa + HCl</td>
<td>0.058</td>
</tr>
<tr>
<td>2.5</td>
<td>CH$_3$COONa + HCl</td>
<td>0.081</td>
</tr>
<tr>
<td>3.0</td>
<td>CH$_3$COONa + HCl</td>
<td>0.124</td>
</tr>
<tr>
<td>3.5</td>
<td>CH$_3$COONa + HCl</td>
<td>0.165</td>
</tr>
<tr>
<td>4.0</td>
<td>CH$_3$COONa + HCl</td>
<td>0.214</td>
</tr>
<tr>
<td>4.5</td>
<td>CH$_3$COONa + HCl</td>
<td>0.265</td>
</tr>
</tbody>
</table>
VERIFICATION OF BEER'S LAW:

To 10 ml (0.01 M) solution of the reagent HMCO, varying amounts of metal solution (0.002 M) were added and pH was adjusted to 4.5 using (HCl + CH₃COONa) buffer. The content was diluted to 25 ml in volumetric flask, so as to keep ethanol concentration 70% in final solution. The absorbance of these solutions were measured at 450 nm against reagent blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law is obtained up to 8.93 ppm of Fe(III). Standard graph thus obtained may be used for the determination of iron in an unknown solution using HMCO. The results are tabulated in Table-4.2.1 (II) and graph is shown in figure-4.2.1 (I).

**TABLE - 4.2.1 (II)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>:</th>
<th>0.002 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>:</td>
<td>0.01 M (10 ml)</td>
</tr>
<tr>
<td>pH</td>
<td>:</td>
<td>4.5</td>
</tr>
<tr>
<td>Final volume</td>
<td>:</td>
<td>25 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>:</td>
<td>450 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.234</td>
<td>0.102</td>
</tr>
<tr>
<td>1.0</td>
<td>4.468</td>
<td>0.172</td>
</tr>
<tr>
<td>1.5</td>
<td>6.702</td>
<td>0.236</td>
</tr>
<tr>
<td>2.0</td>
<td>8.936</td>
<td>0.348</td>
</tr>
<tr>
<td>2.5</td>
<td>11.170</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Molar absorptivity calculated from Beer's law plot was found to be 2.175x10³ lit.mole⁻¹.cm⁻¹ for Fe(III)-HMCO complex at 450 nm.
COMPOSITION OF THE COMPLEX:

The composition of Fe(III)-HMCO complex has been determined on the basis of the results of - (i) Job’s method of continuous variation, and (ii) Yoe and Jones mole-ratio method.

(i) JOB’S METHOD OF CONTINUOUS VARIATION:

A 0.005 M solution of Fe(III) was prepared by suitable dilution of the standard solution. The solution of the reagent (0.005 M) was prepared in absolute ethanol. The solutions of metal salt and the reagent were mixed in varying proportions as under:

Metal ion solution : 1, 2, 3, ................., 9, 10, 11 ml
Reagent solution : 11, 10, 9, ................., 3, 2, 1 ml

pH of the solution was adjusted to 4.5. The content was then made up to 25 ml in volumetric flask. The absorbances of these solutions were measured at 450 nm. The results are tabulated in Table-4.2.1(III) and the graph is shown in figure-4.2.1(II).

From the graph, it has been found that maximum occurs at 0.50 ratio of metal ion concentration to the metal and ligand concentration indicating the formation of 1:1 (M:L) complex.
### TABLE - 4.2.1 (III)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.083</td>
<td>0.150</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.170</td>
<td>0.225</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.250</td>
<td>0.321</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.330</td>
<td>0.450</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.420</td>
<td>0.651</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.500</td>
<td>0.692</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.580</td>
<td>0.611</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.670</td>
<td>0.555</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.750</td>
<td>0.475</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.830</td>
<td>0.425</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.920</td>
<td>0.376</td>
</tr>
</tbody>
</table>

(ii) **YOE AND JONES MOLE-RATIO METHOD:**

In this method, equimolar solutions of the Fe(III) as well as the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution constant (6 ml) while varying the amount (from 1.0 to 7.0 ml) of 0.005 M metal ion solution. pH of these solutions were adjusted to 4.5. The contents was then made up to 25 ml in volumetric flask. Absorbances of these solutions were measured at 450 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.2.1 (IV) and graph is shown in figure-4.2.1 (III).

It is evident from the graph that, absorbance gradually increases up to the molar composition of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.
TABLE - 4.2.1 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reagent solution</td>
<td>0.005 M (6 ml)</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Final volume</td>
<td>25 ml</td>
<td></td>
</tr>
<tr>
<td>Wavelength</td>
<td>450 nm</td>
<td></td>
</tr>
</tbody>
</table>

**Metal ion solution taken in ml | Cm/Cr | Absorbance**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
<td>0.174</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>0.368</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.523</td>
</tr>
<tr>
<td>4</td>
<td>0.67</td>
<td>0.642</td>
</tr>
<tr>
<td>5</td>
<td>0.83</td>
<td>0.800</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.950</td>
</tr>
<tr>
<td>7</td>
<td>1.17</td>
<td>0.970</td>
</tr>
</tbody>
</table>

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:**

\[
MLn \rightleftharpoons M + nL
\]

\[
C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking \(n=1\), in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{C\alpha^2}
\]

where, \(E_m = \) maximum absorbance obtained at the intersect of the two lines.

\(E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

The stability constant is calculated from above equation.
From $K_s$ value, the standard free energy change $\Delta G^\circ$ at 27°C for the formation reaction of complex has been calculated using the formula,

$$\Delta G^\circ = -RT\ln K_s$$

The stability constants calculated from above relation are as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_m$</th>
<th>$E_s$</th>
<th>$\alpha$</th>
<th>$K_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job's method</td>
<td>0.710</td>
<td>0.692</td>
<td>0.025</td>
<td>3.12x10^5</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.970</td>
<td>0.950</td>
<td>0.020</td>
<td>4.90x10^5</td>
</tr>
</tbody>
</table>

Mean $K_s = 4.01x10^5$

$\Delta G^\circ = -7.69$ K.cal/mole

**DETERMINATION OF IRON IN MEDICINAL SAMPLE (FEFOL CAPSULE):**

Contents of one capsule were transferred to an evaporating dish. 5 ml of concentrated HNO$_3$ and 5 ml of distilled water were added and slowly heated on a sand-bath at low temperature. Again 1:1 HNO$_3$ was added and solution was heated to remove all oxides of nitrogen. The contents were dissolved in water and diluted to 100 ml.

1.0 ml aliquot was taken from above solution. 5 ml 0.02 M solution of HMCO and buffer solution of pH 4.5 were added. The contents were diluted to 100 ml. Absorbance of the solution was measured at 450 nm. It was found to be 0.193 (average of three measurements).

**RESULTS:**

(i) Absorbance of the solution (Average of three : 0.193 measurements)

(ii) Concentration of Fe in ppm : 5.5

(iii) Fe found in 1.0 ml diluted solution : 0.550

(iv) Fe found in contents of one capsule : 55.00 mg

(v) Fe reported in one capsule (150.0 mg anhydrous FeSO$_4$) : 55.21 mg

(vi) Error : -0.21 mg

(vii) Percentage error : -0.380 %
Beer's law plot for Fe(III)-HMCO

Absorbance

Concentration in ppm

5.5 ppm

0.193

Fig.4.2.1(I)
Fig. 4.2.1 (II)

Job's method for Fe(III)-HMCO

$E_m = 0.710$
$E_s = 0.692$
Mole-ratio method for Fe(III)-HMCO

Em = 0.970
Es = 0.950

Fig.4.2.1(III)
[4.2.2] STUDY OF Cu(II) COMPLEX WITH HMCO:

PREPARATION OF STANDARD SOLUTION OF Cu(II):

Stock solution (0.05 M) of Cu(II) was prepared by dissolving 3.121 g of CuSO$_4$·5H$_2$O in distilled water and little acid and diluted it to 250 ml. This solution was standardised volumetrically using EDTA [210]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2'-HYDROXY-4'-METHOXYCHALCONE OXIME WITH Cu(II):

0.05 M solution of the reagent in 70% aqueous ethanol was used in all detection and gravimetric and determination.

REACTION WITH Cu(II) AT DIFFERENT pH:

5 ml solution of the reagent was added to 2 ml 0.05 M Cu(II) solution at different pH. The results are tabulated in Table-4.2.2 (I).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Colouration</td>
</tr>
<tr>
<td>2.5</td>
<td>HCl + CH$_3$COOH</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>3.0</td>
<td>HCl + CH$_3$COOH</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>4.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>5.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
<tr>
<td>6.0</td>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>Brown precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The brown Cu(II) chelate is insoluble in water, ethanol, benzene but soluble in acetone, carbon tetrachloride, ethyl acetate and chloroform.

GRAVIMETRIC DETERMINATION OF Cu(II) WITH HMCO:

A 0.05 M solution of the reagent in 70% aqueous ethanol was used. Copper sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water and pH of the solution was adjusted
between 3.0 to 6.0 using suitable acid buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 ml). A brown precipitate obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G₄) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots at pH 5.0 to evaluate its applicability. The results are given in Table-4.2.2 (II) and Table-4.2.2 (III).

RESULTS:
10 ml solution gave 0.3014 g of Cu(II)-HMCO

Found copper = 31.79 mg

10 ml solution contains = 31.77 mg Cu(II)

Error = + 0.02 mg

= + 0.060%

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu(II) complex in g</th>
<th>Cu(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.3000</td>
<td>31.65</td>
<td>-0.12</td>
<td>-0.37</td>
</tr>
<tr>
<td>3.0</td>
<td>0.2999</td>
<td>31.64</td>
<td>-0.13</td>
<td>-0.40</td>
</tr>
<tr>
<td>3.5</td>
<td>0.3002</td>
<td>31.67</td>
<td>-0.10</td>
<td>-0.31</td>
</tr>
<tr>
<td>3.5</td>
<td>0.3004</td>
<td>31.69</td>
<td>-0.08</td>
<td>-0.25</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3005</td>
<td>31.70</td>
<td>-0.07</td>
<td>-0.18</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3007</td>
<td>31.72</td>
<td>-0.05</td>
<td>-0.15</td>
</tr>
<tr>
<td>4.5</td>
<td>0.3010</td>
<td>31.75</td>
<td>-0.02</td>
<td>-0.06</td>
</tr>
<tr>
<td>4.5</td>
<td>0.3012</td>
<td>31.76</td>
<td>-0.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>5.0</td>
<td>0.3014</td>
<td>31.79</td>
<td>+0.02</td>
<td>+0.06</td>
</tr>
<tr>
<td>5.0</td>
<td>0.3015</td>
<td>31.80</td>
<td>+0.03</td>
<td>+0.12</td>
</tr>
<tr>
<td>5.5</td>
<td>0.3020</td>
<td>31.86</td>
<td>+0.09</td>
<td>+0.28</td>
</tr>
<tr>
<td>5.5</td>
<td>0.3018</td>
<td>31.83</td>
<td>+0.06</td>
<td>+0.18</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3025</td>
<td>31.91</td>
<td>+0.14</td>
<td>+0.44</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3022</td>
<td>31.88</td>
<td>+0.11</td>
<td>+0.34</td>
</tr>
</tbody>
</table>

Conversion factor = 0.1055

TABLE - 4.2.2 (II)

GRAVIMETRIC DETERMINATION OF Cu(II) USING HMCO

Cu(II) taken = 31.77 mg

Drying temperature = 110-115°C

Salt = CuSO₄·5H₂O
TABLE - 4.2.2 (III)

GRAVIMETRIC DETERMINATION OF Cu(II) IN DIFFERENT ALIQUOTS

pH = 5.0

<table>
<thead>
<tr>
<th>Cu(II) taken in mg</th>
<th>Cu(II) complex in g</th>
<th>Cu(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.89</td>
<td>0.1506</td>
<td>15.88</td>
<td>-0.01</td>
<td>-0.06</td>
</tr>
<tr>
<td>15.89</td>
<td>0.1505</td>
<td>15.87</td>
<td>-0.02</td>
<td>-0.12</td>
</tr>
<tr>
<td>31.77</td>
<td>0.3014</td>
<td>31.79</td>
<td>+0.02</td>
<td>+0.06</td>
</tr>
<tr>
<td>31.77</td>
<td>0.3015</td>
<td>31.80</td>
<td>+0.03</td>
<td>+0.09</td>
</tr>
<tr>
<td>47.65</td>
<td>0.4519</td>
<td>47.67</td>
<td>+0.02</td>
<td>+0.04</td>
</tr>
<tr>
<td>47.65</td>
<td>0.4518</td>
<td>47.66</td>
<td>+0.01</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

EFFECT OF DIVERSE IONS:

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Ni(II), Zn(II), Ba(II), Cd(II), Mn(II) and Mg(II) do not interfere at this pH but Fe(III) and Pd(II) interfered seriously. Interference of Fe(III) can be removed by masking it with H₃PO₄. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

SPECTROPHOTOMETRIC STUDY OF Cu(II)-HMCO COMPLEX

The Cu(II)-HMCO chelate has been found to be soluble in acetone, carbon tetrachloride, ethyl acetate and chloroform. This enabled to verify the Beer law and its applications for spectrophotometric determination.

ABSORPTION SPECTRA

To take absorption spectra, 5.0 mg of the chelate was dissolved in 25 ml of chloroform and absorption spectra was scanned between 300 to 500 nm.

It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A shoulder is observed
at 400 nm and hence all measurements were carried out at 400 nm. The graph is shown in Fig.-4.2.2(I).

**VERIFICATION OF BEER’S LAW**

To 5 ml of solution (0.01 M) of the reagent HMCO, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using [CH$_3$COOH + CH$_3$COONa] buffer. The insoluble complex precipitated was extracted in chloroform using three 5.0 ml, portion of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbance of these solutions were measured at 400 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 38.12 ppm of Cu(II). The standard graph thus obtained may be used for determination of Cu(II) in an unknown solution using HMCO. The results are tabulated in Table - 4.2.2 (IV) and the graph is shown in Fig.-4.2.2 (II).

**TABLE – 4.2.2 (IV)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>: 0.005 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>: 0.01 M (5 ml) constant</td>
</tr>
<tr>
<td>pH</td>
<td>: 5.0</td>
</tr>
<tr>
<td>Final volume of chloroform extract</td>
<td>: 25.0 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>: 400 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal ion content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12.70</td>
<td>0.200</td>
</tr>
<tr>
<td>1.5</td>
<td>19.00</td>
<td>0.272</td>
</tr>
<tr>
<td>2.0</td>
<td>25.41</td>
<td>0.364</td>
</tr>
<tr>
<td>2.5</td>
<td>31.77</td>
<td>0.452</td>
</tr>
<tr>
<td>3.0</td>
<td>38.12</td>
<td>0.521</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be $6.716 \times 10^2$ lit.mol$^{-1}$.cm$^{-1}$ for Cu(II)-HMCO complex at 400 nm and Sandell’s sensitivity was found to be 0.0946 $\mu$g/cm$^2$. 
COMPOSITION OF CHELATE:

The composition of Cu(II) chelate with the reagent HMCO has been determined on the basis of, (i) Job’s method of continuous variation , and (ii) Yoe and Jones mole-ratio method.

(i) JOB’S METHOD OF CONTINUOUS VARIATION

A series of solutions were prepared by mixing the equimolar solution of metal ion and reagent solutions in varying proportion as under:

Metal ion solution : 1, 2, 3,..................10,11 ml
Reagent solution : 11, 10, 9,.................., 2,1 ml

pH of the solution was adjusted to 5.0 using buffer solution of pH 5.0. The precipitated complex was extracted with three 5.0 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of these solutions were measured against individual blank at 400 nm. The absorbance values were plotted against the ratio of concentration of metal to total concentration of metal and ligand. The results are tabulated in Table-4.2.2(V) and graph is given in Fig -4.2.2(III).

From the graph it has been found that maximum occurs at 0.333 ratio of metal ion concentration to the total metal of and ligand concentration indicating the formation of 1:2 [M: L] complex.
TABLE – 4.2.2 (V)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.260</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.548</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.654</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.661</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.643</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.500</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.451</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.290</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.238</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.165</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.114</td>
</tr>
</tbody>
</table>

(ii) YOE AND JONE’S MOLE-RATIO METHOD

In this method, equimolar solutions of Cu(II) as well as the reagent (0.005 M) were used. A series of solutions were prepared keeping the concentration of reagent solution (8 ml, 0.005 M) constant, while varying the amount (from 1.0 ml to 7.0 ml, 0.005 M) of the metal ion solution. pH of the solutions were adjusted to 5.0. The resulting precipitate of complex were extracted with three 5.0 ml portion of chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbances of all solutions were recorded at 400 nm against reagent blank and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.2.2(VI).

It is evident from the Figure-4.2.2(IV) that absorbance gradually increases up to correct stoichiometry of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.
TABLE – 4.2.2 (VI)

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>0.250</td>
<td>0.321</td>
<td></td>
</tr>
<tr>
<td>0.375</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>0.642</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>0.700</td>
<td></td>
</tr>
<tr>
<td>0.750</td>
<td>0.710</td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>0.715</td>
<td></td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that stoichiometry for Cu(II)-HMCO complex is 1:2 [M:L].

EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:

\[
MLn \rightleftharpoons M + nL \\
C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking n=2 in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \text{where,} \quad \alpha = \frac{E_m - E_s}{E_m}
\]

where, \( E_m \) = maximum absorbance obtained at the intersect of the two lines.

\( E_s \) = absorbance at the stoichiometric molar ratio of the metal to ligand in complex.
From mean $K_s$ value the standard free energy change $\Delta G^\circ$ at $27^\circ C$ for the formation reaction of complex has been calculated using the formula,

$$\Delta G^\circ = -RT \ln K_s$$

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_m$</th>
<th>$E_s$</th>
<th>$\alpha$</th>
<th>$K_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.750</td>
<td>0.654</td>
<td>0.128</td>
<td>$1.624 \times 10^8$</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.700</td>
<td>0.642</td>
<td>0.082</td>
<td>$6.506 \times 10^8$</td>
</tr>
</tbody>
</table>

Mean $K_s = 4.065 \times 10^8$
$\Delta G^\circ = -11.81$ K.cal/mole

DETERMINATION OF COPPER IN BRASS:

Preanalysed sample of brass (0.5523 g) was dissolved in 50% HNO$_3$ by heating for 30 minutes. The solution is evaporated to a volume of near about 5 ml but not to dryness and the bulk of nitric acid removed. The resulting solution was diluted to 100 ml with doubly distilled water in volumetric flask.

An aliquot of above diluted solution (10 ml) was taken in a clean beaker and copper was determined gravimetrically using 2'-hydroxy-4'-methoxychalcone oxime (HMCO) as per the procedure described previously.

RESULTS:

(1) Wt. of sample taken : 0.5523 g
(2) Wt. of Cu(II)-HMCO complex 
   (Average of three determination) : 0.3842 g
(3) Copper found in 10 ml diluted solution : 0.04058 g
(4) Copper found in brass sample taken : 0.4058 g
(5) % Cu found in brass sample : 73.47%
(6) % Cu reported in brass sample : 73.40%
(7) Absolute Error : -0.07%
(8) Percentage error : -0.095%
FIG. 4.2.2(I)

ABSORPTION SPECTRA OF Cu(II)-HMCO COMPLEX
Beer's law plot for Cu(II)-HMCO

Fig. 4.2.2(II)
Job's method for Cu(II)-HMCO

$Em = 0.750$
$Es = 0.654$

Fig. 4.2.2(III)
Mole-ratio method for Cu(II)-HMCO

Em = 0.700
Es = 0.642

Fig. 4.2.2(IV)
[4.2.3] STUDY OF Ni(II) COMPLEX WITH HMCO:

PREPARATION OF STANDARD SOLUTION OF Ni(II):

Stock solution (0.05 M) of Ni(II) was prepared by dissolving 3.2838 g of NiSO\(_4\).6H\(_2\)O in distilled water and little acid and diluted to 250 ml. This solution was standardised volumetrically using EDTA [211]. Experimental solution of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2’-HYDROXY-4’-METHOXYCHALCONE OXIME WITH Ni(II):

0.05 M solution of the reagent in 70% aqueous ethanol was used in all detection and gravimetric determination.

REACTION WITH Ni(II) AT DIFFERENT pH:

5 ml solution of the reagent was added to 2 ml 0.05 M Ni(II) solution at different pH. The results are tabulated in Table-4.2.3 (I).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>K(_2)HPO(_4) + KH(_2)PO(_4)</td>
<td>Light green colouration</td>
</tr>
<tr>
<td>7.5</td>
<td>K(_2)HPO(_4) + KH(_2)PO(_4)</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>8.0</td>
<td>NH(_3) + NH(_4)Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>8.5</td>
<td>NH(_3) + NH(_4)Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>9.0</td>
<td>NH(_3) + NH(_4)Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>9.5</td>
<td>NH(_3) + NH(_4)Cl</td>
<td>Light green precipitate</td>
</tr>
<tr>
<td>10.0</td>
<td>NH(_3) + NH(_4)Cl</td>
<td>Light green precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The light green Ni(II) chelate is insoluble in water, ethanol but soluble in acetone, ethyl acetate and chloroform.
GRAVIMETRIC DETERMINATION OF Ni(II) WITH HMCO:

A 0.05 M solution of the reagent in 70% aqueous ethanol was used. 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 (G₄) 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.

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 results are given in Table-4.2.3 (II) and Table-4.2.3 (III).

RESULTS:

10 ml solution gave 0.2986 of Ni(II)-HMCO

Found nickel = 29.35 mg

10 ml solution contains = 29.34 mg Ni(II)

Error = + 0.01 mg

= + 0.034%
TABLE - 4.2.3 (II)

GRAVIMETRIC DETERMINATION OF Ni(II) USING HMCO

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

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

Conversion factor = 0.0983

TABLE - 4.2.3 (III)

GRAVIMETRIC DETERMINATION OF Ni(II) IN DIFFERENT ALIQUOTS

pH = 9.0
Drying temperature = 110-115°C
Salt = NiSO₄.6H₂O

<table>
<thead>
<tr>
<th>Ni(II) taken in mg</th>
<th>Ni(II) complex in g</th>
<th>Ni(II) found in mg</th>
<th>Error in mg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.68</td>
<td>0.1495</td>
<td>14.69</td>
<td>+0.01</td>
<td>+0.06</td>
</tr>
<tr>
<td>14.68</td>
<td>0.1498</td>
<td>14.72</td>
<td>+0.04</td>
<td>+0.27</td>
</tr>
<tr>
<td>29.36</td>
<td>0.2986</td>
<td>29.35</td>
<td>-0.01</td>
<td>-0.03</td>
</tr>
<tr>
<td>29.36</td>
<td>0.2984</td>
<td>29.33</td>
<td>-0.03</td>
<td>-0.10</td>
</tr>
<tr>
<td>44.04</td>
<td>0.4483</td>
<td>44.06</td>
<td>+0.02</td>
<td>+0.04</td>
</tr>
<tr>
<td>44.04</td>
<td>0.4486</td>
<td>44.09</td>
<td>+0.05</td>
<td>+0.11</td>
</tr>
</tbody>
</table>

EFFECT OF DIVERSE 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.

**SPECTROPHOTOMETRIC STUDY OF Ni(II)-HMCO COMPLEX**

The Ni(II)-HMCO chelate has been found to be soluble in acetone, ethyl acetate and chloroform. This enabled to verify the Beer law and its applications for spectrophotometric determination.

**ABSORPTION SPECTRA**

To take absorption spectra, 5.0 mg of the chelate was dissolved in 25 ml of chloroform and absorption spectra was scanned between 350 to 500 nm.

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. The graph is shown in Figure-4.2.3(I).

**VERIFICATION OF BEER’S LAW**

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 results are tabulated in Table-4.2.3(IV) and the graph is shown in Figure-4.2.3(II).
TABLE – 4.2.3 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>23.47</td>
<td>0.241</td>
</tr>
<tr>
<td>4.0</td>
<td>46.95</td>
<td>0.472</td>
</tr>
<tr>
<td>6.0</td>
<td>70.38</td>
<td>0.693</td>
</tr>
<tr>
<td>8.0</td>
<td>93.84</td>
<td>0.906</td>
</tr>
<tr>
<td>10.0</td>
<td>117.38</td>
<td>1.213</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be $5.662 \times 10^2$ lit.mol$^{-1}$.cm$^{-1}$ for Ni(II)-HMCO complex at 440 nm and Sandell’s sensitivity was found to be 0.0103 µg/cm$^2$.

COMPOSITION OF CHELATE

The composition of Ni(II) chelate with the reagent HMCO has been determined on the basis of, (i) Job’s method of continuous variation, and (ii) Yoe and Jone’s mole-ratio method.

A series of solutions were prepared in a similar way as done for Cu(II)-HMCO complex for both methods and complex was extracted in chloroform. The absorbance values obtained for the two methods are given in Table-4.2.3(V) and Table-4.2.3(VI), respectively and the graphs are shown in Figure-4.2.3(III) and Figure-4.2.3(IV) respectively.
**TABLE – 4.2.3 (V)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>Cm</th>
<th>Cm +Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.235</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.318</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.421</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.631</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.592</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.562</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.496</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.347</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.261</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.184</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.102</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE – 4.2.3 (VI)**

<table>
<thead>
<tr>
<th>Metal ion solution taken In ml</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.074</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.154</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.212</td>
</tr>
<tr>
<td>4</td>
<td>0.500</td>
<td>0.297</td>
</tr>
<tr>
<td>5</td>
<td>0.625</td>
<td>0.321</td>
</tr>
<tr>
<td>6</td>
<td>0.750</td>
<td>0.325</td>
</tr>
<tr>
<td>7</td>
<td>0.875</td>
<td>0.325</td>
</tr>
</tbody>
</table>
It is seen from the results of both the methods that stoichiometry for Ni(II)-HMCO complex is 1:2 [M:L].

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE RATIO METHOD AND JOB’S METHOD:**

The dissociation of complex can be shown as follows:

\[
MLn \underset{\text{C}(1-\alpha)}{\rightleftharpoons} M + nL \quad \text{C.} \alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking \(n=2\), in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \text{where,} \quad \alpha = \frac{E_m-E_s}{E_m}
\]

where, \(E_m\) = maximum absorbance obtained at the intersect of the two lines.

\(E_s\) = absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \(K_s\) value, the standard free energy change \(\Delta G^0\) at 27°C for the formation reaction of complex has been calculated using the formula.

\[
\Delta G^0 = -RT \ln K_s
\]

The stability constants calculated from above relation are as follows:

**TABLE – 4.2.3 (VII)**

<table>
<thead>
<tr>
<th>Method</th>
<th>(E_m)</th>
<th>(E_s)</th>
<th>(\alpha)</th>
<th>(K_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.700</td>
<td>0.631</td>
<td>0.098</td>
<td>3.744 x (10^6)</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.321</td>
<td>0.297</td>
<td>0.074</td>
<td>8.929 x (10^8)</td>
</tr>
</tbody>
</table>

Mean \(K_s\) = 6.336 x \(10^8\)

\(\Delta G^0 = -12.20\ \text{K.cal/mole}\)
GRAVIMETRIC ESTIMATION OF Cu(II) AND Ni(II) IN GERMAN SILVER USING HMCO:

Exactly weighed german silver (0.6831g) 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 (G₄) 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 110-115°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 (12 ml, 0.05 M) was added to it and the pH of the solution was adjusted to 9.0 using NH₃-NH₄Cl 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 (G₄) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed. The determinations were done three times, taking 10.0 ml aliquot solution everytime.
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
∴ 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
∴ 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%
ABSORPTION SPECTRA OF Ni(II)-HMCO COMPLEX

Fig. 4.2.3(I)
Fig. 4.2.3 (II)

Beer's law plot for Ni(II)-HMCO
Fig. 4.2.3 (III)

Job's method for Ni(II)-HMCO

Em = 0.700
Es = 0.631
Mole-ratio method for Ni(II)-HMCO

$E_m = 0.321$

$E_s = 0.297$

Fig. 4.2.3 (IV)
PREPARATION OF STANDARD SOLUTION OF Pd(II):

Stock solution (0.01 M) of Pd (II) was prepared by dissolving 0.4435 gm of PdCl₂ in little concentrated hydrochloric acid and diluting it to 250 ml with distilled water. The solution was standardised gravimetrically using dimethyl glyoxime. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

REACTION OF 2'-HYDROXY-4'-METHOXYPHALCONE OXIME WITH Pd(II):

0.05 M solution of the reagent in 70 % aqueous ethanol was used in all detection and gravimetric determination.

REACTION WITH Pd (II) AT DIFFERENT pH:

2 ml. of 0.05 M HMCO solution was added to 1 ml of standard 0.01 M Pd(II) solution at different pH. The results are tabulated in Table- 4.2.4 (I)

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>HCl + CH₃COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>2.5</td>
<td>HCl + CH₃COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>3.0</td>
<td>HCl + CH₃COOH</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>3.5</td>
<td>HCl + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>4.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>4.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>5.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>5.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
<tr>
<td>6.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>Yellow precipitate</td>
</tr>
</tbody>
</table>

SOLUBILITY OF CHELATE:

The yellow Pd(II) chelate is insoluble in water, ethanol, carbon tetrachloride and benzene, while it is soluble in ethyl acetate, chloroform and DMF. The
solution of the chelate was stable and could be kept for long time without any decomposition.

**GRAVIMETRIC DETERMINATION OF Pd(II) WITH HMCO**:

A 0.04 M solution of the reagent in 70 % aqueous ethanol was used.

Palladium chloride solution (0.01 M, 20 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water and pH of the solution was adjusted between 3.0 to 5.0 using suitable buffer. The solution was warmed to 60°C and a small excess of reagent (0.04 M, 11 ml) was added. A yellow precipitate obtained was digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 70 % aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110 - 115°C in hot air oven, cooled and weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH to evaluate its applicability. The results are given in Table-4.2.4 (II) and Table-4.2.4 (III).

**RESULTS**:

20 ml Palladium chloride solution gave 0.1290 g of Pd(II) - HMCO complex.

Found palladium = 21.29 mg

20 ml solution contains = 21.28 mg of Pd (II)

Error = +0.01 mg

= +0.04 %
TABLE - 4.2.4 (II)

GRAVIMETRIC DETERMINATION OF Pd(II) USING HIBAO

<table>
<thead>
<tr>
<th>pH</th>
<th>Pd(II) complex in g</th>
<th>Pd(II) found in mg</th>
<th>Error in mg</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.1279</td>
<td>21.11</td>
<td>-0.17</td>
<td>-0.80</td>
</tr>
<tr>
<td></td>
<td>0.1280</td>
<td>21.13</td>
<td>-0.15</td>
<td>-0.70</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1281</td>
<td>21.14</td>
<td>-0.14</td>
<td>-0.66</td>
</tr>
<tr>
<td></td>
<td>0.1282</td>
<td>21.16</td>
<td>-0.12</td>
<td>-0.56</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1290</td>
<td>21.29</td>
<td>+0.01</td>
<td>+0.04</td>
</tr>
<tr>
<td></td>
<td>0.1291</td>
<td>21.31</td>
<td>+0.03</td>
<td>+0.14</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1293</td>
<td>21.34</td>
<td>+0.06</td>
<td>+0.28</td>
</tr>
<tr>
<td></td>
<td>0.1294</td>
<td>21.36</td>
<td>+0.08</td>
<td>+0.37</td>
</tr>
<tr>
<td>5.0</td>
<td>0.1296</td>
<td>21.39</td>
<td>+0.11</td>
<td>+0.51</td>
</tr>
<tr>
<td></td>
<td>0.1297</td>
<td>21.41</td>
<td>+0.13</td>
<td>+0.61</td>
</tr>
</tbody>
</table>

Conversion factor = 0.1651

TABLE - 4.2.4 (III)

GRAVIMETRIC DETERMINATION OF Pd(II) IN DIFFERENT ALIQUOTS

<table>
<thead>
<tr>
<th>pH</th>
<th>Pd(II) taken in mg</th>
<th>Pd(II) complex in gm</th>
<th>Pd(II) found in mg</th>
<th>Error in mg</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.65</td>
<td>0.0645</td>
<td>10.64</td>
<td>-0.01</td>
<td>-0.09</td>
<td></td>
</tr>
<tr>
<td>10.65</td>
<td>0.0646</td>
<td>10.66</td>
<td>+0.02</td>
<td>+0.18</td>
<td></td>
</tr>
<tr>
<td>21.30</td>
<td>0.1292</td>
<td>21.33</td>
<td>+0.03</td>
<td>+0.14</td>
<td></td>
</tr>
<tr>
<td>21.30</td>
<td>0.1294</td>
<td>21.36</td>
<td>+0.06</td>
<td>+0.28</td>
<td></td>
</tr>
<tr>
<td>31.95</td>
<td>0.1937</td>
<td>31.97</td>
<td>+0.02</td>
<td>+0.06</td>
<td></td>
</tr>
<tr>
<td>31.95</td>
<td>0.1936</td>
<td>31.96</td>
<td>+0.01</td>
<td>+0.03</td>
<td></td>
</tr>
</tbody>
</table>

EFFECT OF DIVERSE ION :

To study the effect of foreign ions on gravimetric determination of Pd(II), 8-10 mg of various cations were added to solution containing 21.28 mg Pd(II) at
pH 4.0 and gravimetric estimations were done. It was observed that Ca(II), Mg(II), Ni(II), Mn(II), Zn(II), Sr(II), Cd(II), Ba(II), K(I) and Na(I) do not interfere at this pH, but Cu(II), Fe(III) and Co(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

**SPECTROPHOTOMETRIC STUDY OF Pd (II) - HMCO:**

The Pd(II) - HMCO chelate has been found to be soluble in ethyl acetate, chloroform and DMF. This enabled to verify the Beer law and its applications for spectrophotometric determination.

**ABSORPTION SPECTRA:**

To have the absorption spectra, 5 mg of chelate was dissolved in 25 ml of ethyl acetate and absorption spectra of this solution was recorded in the wavelength range of 350 nm to 500 nm.

It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A shoulder is obtained at 420 nm and hence all the measurements were carried out at 420 nm. The graph is shown in figure-4.2.4 (I).

**VERIFICATION OF BEER’S LAW:**

It was done in a similar way as in case of Cu(II) and Ni(II) except that the complex was extracted in ethylacetate.

The Pd(II) complex with HMCO obeys Beer’s law upto 74.49 ppm of Pd(II) at 420 nm. The Beer law plot obtained can be used for the determination of Pd(II) ion in an unknown solution using HMCO. The results are given in Table-4.2.4 (IV) and graph is shown in figure 4.2.4 (II).
TABLE : 4.2.4 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml.</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>21.28</td>
<td>0.126</td>
</tr>
<tr>
<td>1.5</td>
<td>31.92</td>
<td>0.200</td>
</tr>
<tr>
<td>2.0</td>
<td>42.56</td>
<td>0.252</td>
</tr>
<tr>
<td>2.5</td>
<td>53.20</td>
<td>0.376</td>
</tr>
<tr>
<td>3.0</td>
<td>63.85</td>
<td>0.403</td>
</tr>
<tr>
<td>3.5</td>
<td>74.49</td>
<td>0.481</td>
</tr>
</tbody>
</table>

The molar absorptivity from Beer's law plot was found to be $6.716 \times 10^2$ \text{lit.mol}^{-1}.\text{cm}^{-1}$ for Pd(II) - HMCO complex at 420 nm and Sandell's sensitivity was found to be 0.1584 \text{μg} of Pd(II)/cm$^2$.

COMPOSITION OF CHELATE :

The composition of Pd(II) chelate with the reagent HMCO has been determined on the basis of (i) Job's method of continuous variation, and (ii) Yoe and Jones mole ratio method.

The methods were used in a similar way as done for Ni(II) - HMCO complex. The results obtained from the two methods are given in Table- 4.2.4 (V) and Table 4.2.4 (VI) respectively and the graphs are shown in figure- 4.2.4 (III) and figure 4.2.4 (IV) respectively.
**TABLE - 4.2.4 (V)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml.</th>
<th>Reagent solution taken in ml.</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>11.0</td>
<td>0.083</td>
<td>0.110</td>
</tr>
<tr>
<td>2.0</td>
<td>10.0</td>
<td>0.17</td>
<td>0.162</td>
</tr>
<tr>
<td>3.0</td>
<td>9.0</td>
<td>0.25</td>
<td>0.248</td>
</tr>
<tr>
<td>4.0</td>
<td>8.0</td>
<td>0.33</td>
<td>0.332</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>0.42</td>
<td>0.302</td>
</tr>
<tr>
<td>6.0</td>
<td>6.0</td>
<td>0.50</td>
<td>0.269</td>
</tr>
<tr>
<td>7.0</td>
<td>5.0</td>
<td>0.58</td>
<td>0.249</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0</td>
<td>0.67</td>
<td>0.221</td>
</tr>
<tr>
<td>9.0</td>
<td>3.0</td>
<td>0.75</td>
<td>0.194</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>0.83</td>
<td>0.187</td>
</tr>
<tr>
<td>11.0</td>
<td>1.0</td>
<td>0.92</td>
<td>0.168</td>
</tr>
</tbody>
</table>

**TABLE - 4.2.4 (VI)**

<table>
<thead>
<tr>
<th>Metal solution taken in ml.</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.16</td>
<td>0.051</td>
</tr>
<tr>
<td>2.0</td>
<td>0.33</td>
<td>0.084</td>
</tr>
<tr>
<td>3.0</td>
<td>0.50</td>
<td>0.125</td>
</tr>
<tr>
<td>4.0</td>
<td>0.66</td>
<td>0.130</td>
</tr>
<tr>
<td>5.0</td>
<td>0.83</td>
<td>0.133</td>
</tr>
<tr>
<td>6.0</td>
<td>1.00</td>
<td>0.135</td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that the stoichiometry for Pd(II) - HMCO complex is 1:2 [M : L].
EVALUATION OF STABILITY CONSTANT FROM THE MOLE RATIO METHOD 
AND JOB’S METHOD :

The dissociation of complex can be shown as follows:

\[ \text{MLn} \xlongequal{\text{K}_s} \text{M} + \text{nL} \]

\[ C(1-\alpha) \quad \text{C}_\alpha (nC_\alpha)^n \]

\[ K_s = \frac{C(1-\alpha)}{C_\alpha(nC_\alpha)^n} \]

Taking \( n=2 \), in this case the equation reduces to,

\[ K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \text{where,} \quad \alpha = \frac{E_m-E_s}{E_m} \]

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \( K_s \) value, the standard free energy change \( \Delta G^0 \) at 27\(^0\)C for the formation reaction of complex has been calculated using the formula.

\[ \Delta G^0 = -RT \ln Ks \]

The stability constants calculated from above relation are as follows :

**TABLE - 4.2.4 (VII)**

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( Ks )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s Method</td>
<td>0.350</td>
<td>0.332</td>
<td>0.051</td>
<td>2.796 x 10(^9)</td>
</tr>
<tr>
<td>Mole-Ratio Method</td>
<td>0.130</td>
<td>0.125</td>
<td>0.038</td>
<td>6.851 x 10(^9)</td>
</tr>
</tbody>
</table>

Mean \( K_s = 4.823 \times 10^9 \)

\[ \Delta G^0 = -13.29 \text{ K. cal/mole.} \]
ABSORPTION SPECTRA OF Pd(II)-HMCO COMPLEX

Fig. 4.2.4 (I)
Fig. 4.2.4 (II)

Beer's law plot for Pd(II)-HMCO

Absorbance vs. Concentration in ppm
Fig. 4.2.4 (III)

Job's method for Pd(II)-HMCO

Em = 0.350
Es = 0.332
Fig. 4.2.4 (IV)

Mole-ratio method for Pd(II)-HMCO

Em = 0.130
Es = 0.125
IR SPECTRA:

IR spectra of ligand HMCO Fig. 4.2(III) and those of Cu(II), Ni(II) and Pd(II) are compared to ascertain the linking of metal with hetero atoms O & N of ligands.

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 Cu(II)-HMCO, Ni(II)-HMCO and Pd(II)-HMCO complexes, while the band due to oximino -OH group at 3429 cm\(^{-1}\) in Cu(II) chelate and at 3430 cm\(^{-1}\) and 3064 cm\(^{-1}\) in Ni(II) complex, and Pd(II) complex respectively.

The band due to the -C=N stretching which is observed at 1548 cm\(^{-1}\) in ligand is shifted to 1507-1608 cm\(^{-1}\) in complexes. This may be due to coordination of metal through nitrogen. This is further supported by slight downward shift of \(\nu\) NO from 1029 cm\(^{-1}\) in the ligand to 959 to 982 cm\(^{-1}\) in copper, nickel and palladium chelates.

Thus, in the chelates, metal is covalently bonded with oxygen and coordinate bonded with nitrogen. The IR spectra of ligand Fig.4.2(III) and complexes are shown in Fig. 4.2 (IV), 4.2(V) and 4.2(VI).

The structure of complex can be given as follows.

\[ \text{M}^{+2} = \text{Cu(II), Ni(II), Pd(II)} \]
IR SPECTRA OF LIGAND HMCO
Fig. 4.2 (III)

IR SPECTRA OF Cu(II)-HMCO COMPLEX
Fig. 4.2 (IV)
IR SPECTRA OF Ni(II)-HMCO COMPLEX

Fig. 4.2 (V)

IR SPECTRA OF Pd(II)-HMCO COMPLEX

Fig. 4.2 (VI)
THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF Cu(II)-HMCO, Ni(II)-HMCO AND Pd(II)-HMCO COMPLEX:

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

Thermogravimetric analysis of copper 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 50^0C to 850^0C in a programmed manner at the heating rate of 10^0C/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 8.660 mg
2. Temperature at which decomposition started 150^0C
3. Total % weight loss obtained between 100^0C to 800^0C 86.00 %
4. Total % weight loss expected due to loss of ligand molecules as per formula \((C_{16}H_{15}O_{3}N)_{2}Cu\) 85.19%
5. Weight of CuO residue observed 1.213 mg
6. Weight of CuO residue expected according to formula \((C_{16}H_{15}O_{3}N)_{2}Cu\) 1.144 mg

From the result of TGA, it is seen that the complex is stable upto temperature 150^0C and so it can be dried safely without decomposition at 100-150^0C. The loss in weight in the temperature range 150^0C to 800^0C 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.
THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF Ni(II)-HMCO COMPLEX:

Thermogravimetric analysis of nickel chelate was done in a similar way as in copper chelate in the temperature range 50\(^0\)C to 850\(^0\)C with a heating rate of 10\(^0\)C/min. The results obtained are as follows:

1. The weight of chelate taken 8.765 mg
2. Temperature at which decomposition started 200\(^0\)C
3. Total % weight loss obtained between 200\(^0\)C to 800\(^0\)C 89.25 %
4. Total % weight loss expected due to loss of ligand molecules as per formula \((C_{16}H_{15}O_3N)_2Ni\)
   90.16%
5. Weight of NiO residue observed 1.118 mg
6. Weight of NiO residue expected according to formula \((C_{16}H_{15}O_3N)_2Ni\)
   1.097 mg

From the result of TGA, it is seen that the complex is stable upto temperature 180\(^0\)C and so it can be dried safely without decomposition at 100-180\(^0\)C. The loss in weight in the temperature range 200\(^0\)C to 800\(^0\)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.
THERMOGRAVIMETRIC ANALYSIS (TGA) STUDY OF Pd(II)-HMCO COMPLEX:

Thermogravimetric analysis of palladium chelate was done in a similar way as in copper chelate in the temperature range 50$^\circ$C to 850$^\circ$C with a heating rate of 10$^\circ$C/min. The results obtained are as follows:

1. The weight of chelate taken 8.209 mg
2. Temperature at which decomposition started 200$^\circ$C
3. Total % weight loss obtained between 200$^\circ$C to 850$^\circ$C 81.00 %
4. Total % weight loss expected due to loss of ligand molecules as per formula $(C_{16}H_{15}O_3N)_{2}Pd$ 81.05%
5. Weight of Pd residue observed 1.560 mg
6. Weight of Pd residue expected according to formula $(C_{16}H_{15}O_3N)_{2}Pd$ 1.350 mg

From the result of TGA, it is seen that the complex is stable upto temperature 150$^\circ$C and so it can be dried safely without decomposition at 100-180$^\circ$C. The loss in weight in the temperature range 200$^\circ$C to 850$^\circ$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.

In case of palladium complex residue is of palladium metal. The weight of residue observed agrees well with weight of residue expected as per the stoichiometry (1:2) (M:L).
EVALUATION OF E (ACTIVATION ENERGY) BASED ON SINGLE HEATING RATE METHOD:

Dynamic TGA thermograms obtained at a heating rate of 10°C/min have been analysed in terms of the graphical method proposed by Broido.

METHOD OF BROIDO:

**TABLE - I**

APPLICATION OF BROIDO’S METHOD TO TGA - THERMOGRAMS OF Cu(II)-HMCO OBTAINED AT 10°C/min

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>% Weight</th>
<th>Y=(Wt-Wα) (W0-Wα)</th>
<th>1/Y</th>
<th>Inln((1/y)</th>
<th>Temp °k</th>
<th>(1/T*1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>92.9275</td>
<td>0.9178</td>
<td>1.0896</td>
<td>2.4554</td>
<td>423</td>
<td>2.3641</td>
</tr>
<tr>
<td>160</td>
<td>91.0683</td>
<td>0.8961</td>
<td>1.1159</td>
<td>2.2103</td>
<td>433</td>
<td>2.3095</td>
</tr>
<tr>
<td>170</td>
<td>89.3576</td>
<td>0.8762</td>
<td>1.1412</td>
<td>2.0241</td>
<td>443</td>
<td>2.2573</td>
</tr>
<tr>
<td>180</td>
<td>87.6168</td>
<td>0.8560</td>
<td>1.1682</td>
<td>1.8612</td>
<td>453</td>
<td>2.2075</td>
</tr>
<tr>
<td>190</td>
<td>85.599</td>
<td>0.8325</td>
<td>1.2012</td>
<td>1.6967</td>
<td>463</td>
<td>2.1598</td>
</tr>
<tr>
<td>200</td>
<td>82.1634</td>
<td>0.7926</td>
<td>1.2617</td>
<td>1.4590</td>
<td>473</td>
<td>2.1142</td>
</tr>
<tr>
<td>210</td>
<td>77.0109</td>
<td>0.7327</td>
<td>1.3649</td>
<td>1.1677</td>
<td>483</td>
<td>2.0704</td>
</tr>
<tr>
<td>220</td>
<td>72.0826</td>
<td>0.6754</td>
<td>1.4807</td>
<td>0.9352</td>
<td>493</td>
<td>2.0284</td>
</tr>
<tr>
<td>230</td>
<td>68.6089</td>
<td>0.6350</td>
<td>1.5749</td>
<td>0.7892</td>
<td>503</td>
<td>1.9881</td>
</tr>
<tr>
<td>240</td>
<td>65.7567</td>
<td>0.6018</td>
<td>1.6617</td>
<td>0.6776</td>
<td>513</td>
<td>1.9493</td>
</tr>
<tr>
<td>250</td>
<td>63.0459</td>
<td>0.5703</td>
<td>1.7536</td>
<td>0.5769</td>
<td>523</td>
<td>1.9120</td>
</tr>
<tr>
<td>260</td>
<td>60.33</td>
<td>0.5387</td>
<td>1.8564</td>
<td>0.4803</td>
<td>533</td>
<td>1.8762</td>
</tr>
<tr>
<td>270</td>
<td>57.7185</td>
<td>0.5083</td>
<td>1.9673</td>
<td>0.3906</td>
<td>543</td>
<td>1.8416</td>
</tr>
<tr>
<td>280</td>
<td>55.3422</td>
<td>0.4807</td>
<td>2.0804</td>
<td>0.3112</td>
<td>553</td>
<td>1.8083</td>
</tr>
<tr>
<td>290</td>
<td>53.186</td>
<td>0.4556</td>
<td>2.1949</td>
<td>0.2406</td>
<td>563</td>
<td>1.7762</td>
</tr>
<tr>
<td>300</td>
<td>51.2152</td>
<td>0.4327</td>
<td>2.3111</td>
<td>0.1771</td>
<td>573</td>
<td>1.7452</td>
</tr>
<tr>
<td>310</td>
<td>49.2744</td>
<td>0.4101</td>
<td>2.4383</td>
<td>0.1151</td>
<td>583</td>
<td>1.7153</td>
</tr>
<tr>
<td>320</td>
<td>47.3243</td>
<td>0.3874</td>
<td>2.5810</td>
<td>0.0532</td>
<td>593</td>
<td>1.6863</td>
</tr>
<tr>
<td>330</td>
<td>45.2798</td>
<td>0.3637</td>
<td>2.7498</td>
<td>0.0114</td>
<td>603</td>
<td>1.6584</td>
</tr>
<tr>
<td>340</td>
<td>43.3608</td>
<td>0.3414</td>
<td>2.9295</td>
<td>0.0722</td>
<td>613</td>
<td>1.6313</td>
</tr>
<tr>
<td>350</td>
<td>41.6029</td>
<td>0.3209</td>
<td>3.1161</td>
<td>0.1280</td>
<td>623</td>
<td>1.6051</td>
</tr>
<tr>
<td>360</td>
<td>40.3176</td>
<td>0.3060</td>
<td>3.2684</td>
<td>0.1691</td>
<td>633</td>
<td>1.5798</td>
</tr>
<tr>
<td>370</td>
<td>39.5146</td>
<td>0.2966</td>
<td>3.3713</td>
<td>0.1950</td>
<td>643</td>
<td>1.5552</td>
</tr>
<tr>
<td>380</td>
<td>38.9199</td>
<td>0.2897</td>
<td>3.4517</td>
<td>0.2142</td>
<td>653</td>
<td>1.5314</td>
</tr>
<tr>
<td>390</td>
<td>38.4652</td>
<td>0.2844</td>
<td>3.5159</td>
<td>0.2290</td>
<td>663</td>
<td>1.5083</td>
</tr>
<tr>
<td>400</td>
<td>38.0599</td>
<td>0.2797</td>
<td>3.5752</td>
<td>0.2422</td>
<td>673</td>
<td>1.4859</td>
</tr>
</tbody>
</table>
A plot of \( \ln(1/Y) \) Vs \( 1/T \times 1000K^{-1} \) yield a straight line. From the slope of the graph, energy of activation "E" for the decomposition stage is calculated, the value of "E" are given in Table-II.

Application of this method is illustrated for Cu(II)-HMCO in Table-I and the relevant plot is shown in Fig.(I).

In a similar way, the other two complexes were analysed and energy of activation of different stage of decomposition were determined.

**TABLE - II**

ACTIVATION ENERGY "E" (K. cal/mole\(^{-1}\)) EVALUATED ACCORDING TO THE METHOD OF BROIDO FOR THERMAL DECOMPOSITION OF CHELATES

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Decomposition stage</th>
<th>Activation Energy &quot;E&quot; (K. cal/mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)-HMCO</td>
<td>I</td>
<td>3.012</td>
</tr>
<tr>
<td>Ni(II)-HMCO</td>
<td>I</td>
<td>5.039</td>
</tr>
<tr>
<td>Ni(II)-HMCO</td>
<td>II</td>
<td>8.097</td>
</tr>
<tr>
<td>Pd(II)-HMCO</td>
<td>I</td>
<td>2.610</td>
</tr>
<tr>
<td>Pd(II)-HMCO</td>
<td>II</td>
<td>8.087</td>
</tr>
</tbody>
</table>
Fig. (I) TG Curve of Cu(II)-HMCO Complex

Method of Broido : Cu(II)-HMCO Complex

\[ y = -1.516x + 2.339 \]
Fig. (II) TG Curve of Ni(II)-HMCO Complex

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

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

\[ y = -1.314x + 1.004 \]

Method of Broido: Pd(II)-HMCO Complex (Step-II)

\[ y = -4.070x + 4.727 \]
[4.3.1] STUDY OF Fe(III) COMPLEX WITH HMAT:

PREPARATION OF STANDARD SOLUTION OF FERRIC CHLORIDE (FeCl₃):

Ferric chloride (anhydrous) (A.R., B.D.H.) 2.0276 g was dissolved in double distilled water, containing a little free acid and was diluted to 250 ml to get 0.05 M stock solution of ferric chloride. This solution was standardised gravimetrically [209]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

Fe(III) was found to form purple coloured ethanol soluble complex in pH range of 2.0 to 4.5.

EFFECT OF pH:

The effect of pH, a series of solutions were prepared by taking 0.005 M (1 ml) ferric chloride solution and 0.02 M (3 ml) reagent solution. The pH of the solutions were adjusted to 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 with sodium acetate-hydrochloric acid buffer. The coloured solutions were then diluted to 25 ml. keeping 70% ethanol concentration. The absorbance values of each solution were measured between 400 nm to 500 nm against reagent blank. It was observed that at 440 nm and at pH 4.5 absorbance value is found maximum. The absorbance values at 440 nm are tabulated in Table-4.3.1(I).

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>CH₃COONa + HCl</td>
<td>0.698</td>
</tr>
<tr>
<td>3.0</td>
<td>CH₃COONa + HCl</td>
<td>0.700</td>
</tr>
<tr>
<td>3.5</td>
<td>CH₃COONa + HCl</td>
<td>0.792</td>
</tr>
<tr>
<td>4.0</td>
<td>CH₃COONa + HCl</td>
<td>0.863</td>
</tr>
<tr>
<td>4.5</td>
<td>CH₃COONa + HCl</td>
<td>0.953</td>
</tr>
<tr>
<td>5.0</td>
<td>CH₃COONa + HCl</td>
<td>0.590</td>
</tr>
</tbody>
</table>
VERIFICATION OF BEER’S LAW:

To 6 ml (0.01 M) solution of the reagent HMAT, varying amounts of metal solution (0.001 M) were added and pH was adjusted to 4.5 using (HCl + CH₃COONa) buffer. The content was diluted to 25 ml in volumetric flask, so as to keep ethanol concentration 70% in final solution. The absorbance of these solutions were measured at 440 nm against reagent blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer’s law is obtained up to 8.93 ppm of Fe(III). Standard graph thus obtained may be used for the determination of iron in an unknown solution using HMAT. The results are tabulated in Table-4.3.1 (II) and graph is shown in figure-4.3.1 (I).

<table>
<thead>
<tr>
<th>Table - 4.3.1 (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ion solution : 0.001 M</td>
</tr>
<tr>
<td>Reagent solution : 0.01 M (6 ml)</td>
</tr>
<tr>
<td>pH : 4.5</td>
</tr>
<tr>
<td>Final volume : 25 ml</td>
</tr>
<tr>
<td>Wavelength : 440 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.233</td>
<td>0.192</td>
</tr>
<tr>
<td>2.0</td>
<td>4.467</td>
<td>0.332</td>
</tr>
<tr>
<td>3.0</td>
<td>6.702</td>
<td>0.558</td>
</tr>
<tr>
<td>4.0</td>
<td>8.934</td>
<td>0.776</td>
</tr>
<tr>
<td>5.0</td>
<td>11.170</td>
<td>0.890</td>
</tr>
<tr>
<td>6.0</td>
<td>13.40</td>
<td>0.902</td>
</tr>
</tbody>
</table>

Molar absorptivity calculated from Beer's law plot was found to be \(4.910 \times 10^3\) \text{lit} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\ for Fe(III)-HMAT complex at 440 nm, and Sandell's sensitivity was found to be 0.011 \(\mu\text{g/cm}^2\).
COMPOSITION OF THE COMPLEX:

The composition of Fe(III)-HMAT complex has been determined on the basis of the results of - (i) Job’s method of continuous variation, and (ii) Yoe and Jones mole-ratio method.

(i) JOB’S METHOD OF CONTINUOUS VARIATION:

A 0.001 M solution of Fe(III) was prepared by suitable dilution of the standard solution. The solution of the reagent (0.001 M) was prepared in absolute ethanol. The solutions of metal salt and the reagent were mixed in varying proportions as under:

- Metal ion solution : 1, 2, 3, ................., 9, 10, 11 ml
- Reagent solution : 11, 10, 9, ................., 3, 2, 1 ml

pH of the solution was adjusted to 4.5. The content was then made up to 25 ml in volumetric flask so as to keep ethanol concentration 70%. The absorbance of these solutions were measured at 440 nm against reagent blank. The results are tabulated in Table-4.3.1 (III) and the graph is shown in figure-4.3.1 (II).

From the graph, it has been found that maximum occurs at 0.50 ratio of metal ion concentration to the metal and ligand concentration indicating the formation of 1:1 (M:L) complex.
TABLE - 4.3.1 (III)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>$\frac{C_m}{C_m + C_r}$</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.083</td>
<td>0.131</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.170</td>
<td>0.290</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.250</td>
<td>0.423</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.330</td>
<td>0.579</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.420</td>
<td>0.752</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.500</td>
<td>0.850</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.580</td>
<td>0.771</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.670</td>
<td>0.603</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.750</td>
<td>0.443</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.830</td>
<td>0.312</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.920</td>
<td>0.136</td>
</tr>
</tbody>
</table>

(ii) YOE AND JONES MOLE-RATIO METHOD:

In this method, equimolar solutions of the Fe(III) as well as the reagent (0.001 M) were used. A series of solutions were prepared, keeping the reagent solution constant (6 ml) while varying the amount (from 1.0 to 9.0 ml) of 0.001 M metal ion solution. pH of these solutions were adjusted to 4.5. The contents was then made up to 25 ml in volumetric flask. Absorbances of these solutions were measured at 440 nm against reagent blank and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.3.1 (IV) and graph is shown in figure-4.3.1 (III).

It is evident from the graph that, absorbance gradually increases up to the molar composition of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.
EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:

\[
\text{MLn} \rightleftharpoons \text{M} + \text{nL}
\]

\[
C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n}
\]

Taking \(n=1\), in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{C\alpha^2} \quad \text{where,} \quad \alpha = \frac{E_m - E_s}{E_m}
\]

where, \(E_m = \) maximum absorbance obtained at the intersect of the two lines.

\(E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

The stability constant is calculated from above equation.
From $K_s$ value, the standard free energy change $\Delta G^\circ$ at 27°C for the formation reaction of complex has been calculated using the formula,

$$\Delta G^\circ = -RT \ln K_s$$

The stability constants calculated from above relation are as follows:

**TABLE - 4.3.1 (V)**

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_m$</th>
<th>$E_s$</th>
<th>$\alpha$</th>
<th>$K_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job's method</td>
<td>0.910</td>
<td>0.850</td>
<td>0.065</td>
<td>1.106 x 10^6</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.435</td>
<td>0.412</td>
<td>0.052</td>
<td>1.752 x 10^6</td>
</tr>
</tbody>
</table>

Mean $K_s = 1.429 \times 10^6$

$\Delta G^\circ = -8.44 \text{ K.cal/mole}$

**DETERMINATION OF IRON IN MEDICINAL SAMPLE (FEFOL CAPSULE):**

"FEFOL" is a formulation containing anhydrous FeSO$_4$ and folic acid.

Contents of one capsule were transferred to an evaporating dish. 5 ml of concentrated HNO$_3$ and 5 ml of distilled water were added and slowly heated on a sand-bath at low temperature. Again 1:1 HNO$_3$ was added and solution was heated to remove all oxides of nitrogen. The contents were dissolved in water and diluted to 100 ml.

1.0 ml aliquot was taken from above solution. 5 ml 0.02 M solution of HMAT and buffer solution of pH 4.5 were added. The contents were diluted to 100 ml. Absorbance of the solution was measured at 440 nm against reagent blank. It was found to be 0.410 (average of three measurements).
RESULTS:

(i) Absorbance of the solution (Average of three measurements) : 0.410
(ii) Concentration of Fe in ppm : 5.0
(iii) Fe found in 1.0 ml diluted solution : 0.50 mg
(iv) Fe found in contents of one capsule : 50.00 mg
(v) Fe reported in one capsule (150.0 mg anhydrous FeSO₄) : 55.21 mg
(vi) Error : +5.21
(vii) Percentage error : +9.43
Beer's law plot for Fe(III)-HMAT

Fig. 4.3.1 (I)
Fig. 4.3.1 (II)

Job's method for Fe(III)-HMAT

Em = 0.910
Es = 0.850
Mole-ratio method for Fe(III)-HMAT Complex

Em = 0.435
Es = 0.412

Fig. 4.3.1 (III)
[4.3.2] STUDY OF Cu(II) COMPLEX WITH HMAT:

PREPARATION OF STANDARD SOLUTION OF Cu(II):

Stock solution (0.05 M) of Cu(II) was prepared by dissolving 3.121 g of CuSO₄·5H₂O in distilled water and little acid and diluted it to 250 ml. This solution was standardised volumetrically using EDTA [210]. Experimental solutions of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2-HYDROXY-4-METHOXYACETOPHENONE THIOSEMICARBAZONE WITH Cu(II):

Cu(II) was found to give yellowish green coloured complex with HMAT. Solution of HMAT in 50% ethanol with suitable concentration was used in different methods.

EFFECT OF pH:

The effect of pH, a series of solutions were prepared by taking 1.0 ml of (0.005 M) copper sulphate solution and 5.0 ml (0.01 M) reagent solution. The pH of solutions were adjusted to 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5 with suitable buffer. The solutions were then transferred to 25 ml volumetric flask and diluted to the mark with required amount of ethanol and doubly distilled water to maintain 50% ethanol concentration. The absorbance values of each solution were measured between 400 nm to 600 nm against reagent blank. It was observed that at 520 nm and at pH 4.5 absorbance value is found maximum. The absorbance values at different pH at 520 nm are tabulated in Table :4.3.2(I).
TABLE - 4.3.2 (I)

**ABSORBANCE DATA OF Cu(II)-HMAT COMPLEX AT DIFFERENT pH**

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.687</td>
</tr>
<tr>
<td>4.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.712</td>
</tr>
<tr>
<td>5.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.339</td>
</tr>
<tr>
<td>5.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.377</td>
</tr>
<tr>
<td>6.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.355</td>
</tr>
<tr>
<td>6.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.398</td>
</tr>
</tbody>
</table>

It was seen from the above observation that maximum complex formation occurs at pH 4.5 and therefore in all subsequent experiments, this pH was maintained.

**EFFECT OF SOLVENT AND TIME :**

Since the complex is easily soluble in 50% aqueous ethanol, the concentration of ethanol was kept around 50% in all final solutions prepared for absorbance measurements of Cu(II)-HMAT complex. The colour of complex was found to be stable upto 6 hours.

**VERIFICATION OF BEER’S LAW**

To 5 ml of solution (0.01 M) of the reagent HMAT, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 4.5, using [CH₃COOH + CH₃COONa] buffer and the contents were diluted to the mark with ethanol and doubly distilled water, to make the final concentration of ethanol 50%. The absorbance of these solutions were measured at 520 nm against reagent 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 31.77 ppm of Cu(II). The standard graph thus
obtained may be used for determination of Cu(II) in an unknown solution using HMAT. The results are tabulated in Table - 4.3.2(II) and the graph is shown in Fig.-4.3.2 (I).

**TABLE – 4.3.2 (II)**

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>:</th>
<th>0.005 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>:</td>
<td>0.01 M (5 ml) constant</td>
</tr>
<tr>
<td>pH</td>
<td>:</td>
<td>4.5</td>
</tr>
<tr>
<td>Final volume of chloroform extract</td>
<td>:</td>
<td>25.0 ml</td>
</tr>
<tr>
<td>Wavelength</td>
<td>:</td>
<td>520 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal ion content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12.70</td>
<td>0.225</td>
</tr>
<tr>
<td>1.5</td>
<td>19.06</td>
<td>0.357</td>
</tr>
<tr>
<td>2.0</td>
<td>25.41</td>
<td>0.468</td>
</tr>
<tr>
<td>2.5</td>
<td>31.77</td>
<td>0.621</td>
</tr>
<tr>
<td>3.0</td>
<td>38.12</td>
<td>0.812</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be $1.242 \times 10^3 \text{lit.mol}^{-1}.\text{cm}^{-1}$ for Cu(II)-HMAT complex at 520 nm and Sandell’s sensitivity was found to be $0.0511 \mu g/cm^2$.

**COMPOSITION OF CHELATE:**

The composition of Cu(II) chelate with the reagent HMAT has been determined on the basis of, (i) Job’s method of continuous variation, and (ii) Yoe and Jones mole-ratio method.

(i) **JOB’S METHOD OF CONTINUOUS VARIATION**

A series of solutions were prepared by mixing the equimolar solution of metal ion and reagent solutions in varying proportion as under:

<table>
<thead>
<tr>
<th>Metal ion solution</th>
<th>:</th>
<th>1, 2, 3,.................10,11 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent solution</td>
<td>:</td>
<td>11, 10, 9,..................., 2,1 ml</td>
</tr>
</tbody>
</table>
pH of the solution was adjusted to 4.5 using buffer solution of pH 4.5. These solutions were then diluted up to the mark with ethanol and double distilled water so as to keep the concentration of ethanol in final volumes 50%. The absorbance of these solutions were measured against individual blank at 520 nm. The absorbance values were plotted against the ratio of concentration of metal to total concentration of metal and ligand. The results are tabulated in Table-4.3.2(III) and graph is given in Fig -4.3.2(II).

From the graph it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total metal of and ligand concentration indicating the formation of 1:2 [M: L] complex.

**TABLE – 4.3.2 (III)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.047</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.101</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.143</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.164</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.154</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.123</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.109</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.091</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.069</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.051</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.039</td>
</tr>
</tbody>
</table>

(ii) **YOE AND JONE’S MOLE-RATIO METHOD**

In this method, equimolar solutions of Cu(II) as well as the reagent (0.001 M) were used. A series of solutions were prepared keeping the concentration of reagent solution (8 ml, 0.001 M) constant, while varying the amount (from 1.0 ml
to 7.0 ml, 0.001 M) of the metal ion solution. pH of the solutions were adjusted to 4.5. These solutions were then diluted upto the mark with ethanol and double distilled water so as to keep the concentration of ethanol in final volumes 50%. Absorbances of all solutions were recorded at 520 nm against reagent blank and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-4.3.2(IV) and graph is given in Fig -4.3.2(III).

It is evident from the Figure-4.3.2 (III) that absorbance gradually increases up to correct stoichiometry of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

**TABLE – 4.3.2 (IV)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Cm/Cr</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.046</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.096</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.126</td>
</tr>
<tr>
<td>4</td>
<td>0.500</td>
<td>0.181</td>
</tr>
<tr>
<td>5</td>
<td>0.625</td>
<td>0.195</td>
</tr>
<tr>
<td>6</td>
<td>0.750</td>
<td>0.200</td>
</tr>
<tr>
<td>7</td>
<td>0.875</td>
<td>0.205</td>
</tr>
</tbody>
</table>

It is seen from the results of both the methods that stoichiometry for Cu(II)-HMAT complex is 1:2 [M:L].

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:**

\[
MLn \rightleftharpoons M + nL
\]

\[
C(1-\alpha) \quad C\alpha \quad (nC\alpha)^n
\]

\[
K_s = \frac{C(1-\alpha)}{C\alpha (nC\alpha)^n}
\]
Taking \( n=2 \), in this case the equation reduces to,

\[
K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \text{where,} \quad \alpha = \frac{E_m - E_s}{E_m}
\]

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \( K_s \) value the standard free energy change \( \Delta G^o \) at 27\(^0\)C for the formation reaction of complex has been calculated using the formula,

\[
\Delta G^o = -RT \ln K_s
\]

**TABLE – 4.3.2 (V)**

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( K_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.179</td>
<td>0.164</td>
<td>0.083</td>
<td>1.063 \times 10^{11}</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.200</td>
<td>0.181</td>
<td>0.095</td>
<td>1.055 \times 10^{11}</td>
</tr>
</tbody>
</table>

Mean \( K_s = 1.329 \times 10^{11} \)

\( \Delta G^o = -15.26 \) K.cal/mole
Beer's law plot for Cu(II)-HMAT Complex

Fig. 4.3.2 (I)
Em = 0.179
Es = 0.164

Fig. 4.3.2 (II)
Mole-ratio method for Cu(II)-HMAT Complex

Em = 0.200
Es = 0.181

Fig. 4.3.2 (III)
[4.3.3] STUDY OF Ni(II) COMPLEX WITH HMAT:

PREPARATION OF STANDARD SOLUTION OF Ni(II):

Stock solution (0.05 M) of Ni(II) was prepared by dissolving 3.2838 g of NiSO₄·6H₂O in distilled water and little acid and diluted to 250 ml. This solution was standardised volumetrically using EDTA [211]. Experimental solution of required concentrations were prepared by appropriate dilution of the above stock solution.

REACTION OF 2-HYDROXY-4-METHOXYACETOPHENONE THIOSEMICARBAZONE WITH Ni(II):

Ni(II) was found to give green coloured complex with HMAT. Solution of HMAT in 50% ethanol with suitable concentration was used in different methods.

EFFECT OF pH:

The effect of pH on the complex formation was studied by preparing the solutions of different pH in a similar way as done for Cu(II)-HMAT complex. The absorbance values of each solution were measured between 400 nm to 500 nm against reagent blank. It was observed that at 460 nm and at pH 8.5 absorbance value is found maximum. The results are tabulated in Table: 4.3.3(I).

**TABLE - 4.3.3 (I)**

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>Borax + Hydrochloric acid</td>
<td>0.197</td>
</tr>
<tr>
<td>7.5</td>
<td>Borax + Hydrochloric acid</td>
<td>0.331</td>
</tr>
<tr>
<td>8.0</td>
<td>Borax + Hydrochloric acid</td>
<td>0.457</td>
</tr>
<tr>
<td>8.5</td>
<td>Borax + Hydrochloric acid</td>
<td>0.484</td>
</tr>
<tr>
<td>9.0</td>
<td>Ammonia + Ammonium chloride</td>
<td>0.424</td>
</tr>
<tr>
<td>9.5</td>
<td>Ammonia + Ammonium chloride</td>
<td>0.410</td>
</tr>
<tr>
<td>10.0</td>
<td>Ammonia + Ammonium chloride</td>
<td>0.318</td>
</tr>
</tbody>
</table>

ABSORBANCE DATA OF Ni(II)-HMAT COMPLEX AT DIFFERENT pH

Ni(II) solution: 0.001 (1.0 ml)
Reagent solution: 0.01 M (5.0 ml)
Total volume: 25 ml
Wavelength: 460 nm
It was seen from the above observation that maximum complex formation occurs at pH 8.5 and therefore in all subsequent experiments, this pH was maintained.

**EFFECT OF SOLVENT AND TIME:**

Since the complex is easily soluble in 50% aqueous ethanol, the concentration of ethanol was kept around 50% in all final solutions prepared for absorbance measurements of Ni(II)-HMAT complex. The colour of complex was found to be stable upto 6 hours.

**VERIFICATION OF BEER’S LAW**

To 5 ml of solution (0.01 M) of the reagent HMAT, varying amount of the Ni(II) solution (0.001 M) was added and the pH was adjusted to 8.5, using [NH₃ + NH₄Cl] buffer and the contents were diluted to the mark with ethanol and doubly distilled water, to make the final concentration of ethanol 50%. The absorbance of these solutions were measured at 460 nm against reagent 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 18.77 ppm of Ni(II). The standard graph thus obtained may be used for determination of Ni(II) in an unknown solution using HMAT. The results are tabulated in Table - 4.3.3(II) and the graph is shown in Fig.-4.3.3(I).
TABLE – 4.3.3 (II)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal ion content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.347</td>
<td>0.058</td>
</tr>
<tr>
<td>2.0</td>
<td>4.694</td>
<td>0.102</td>
</tr>
<tr>
<td>3.0</td>
<td>7.041</td>
<td>0.148</td>
</tr>
<tr>
<td>4.0</td>
<td>9.388</td>
<td>0.205</td>
</tr>
<tr>
<td>5.0</td>
<td>11.735</td>
<td>0.242</td>
</tr>
<tr>
<td>6.0</td>
<td>14.083</td>
<td>0.301</td>
</tr>
<tr>
<td>7.0</td>
<td>16.429</td>
<td>0.356</td>
</tr>
<tr>
<td>8.0</td>
<td>18.776</td>
<td>0.410</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer’s law plot was found to be $1.281 \times 10^3$ \text{lit.mol}^{-1}.\text{cm}^{-1} for Ni(II)-HMAT complex at 460 nm and Sandell’s sensitivity was found to be 0.0458 \text{µg/cm}^2.

COMPOSITION OF CHELATE:

The composition of Ni(II) chelate with the reagent HMAT has been determined on the basis of, (i) Job’s method of continuous variation, and (ii) Yoe and Jones mole-ratio method.

(i) JOB’S METHOD OF CONTINUOUS VARIATION

A series of solutions were prepared in a similar way as done for Cu(II)-HMAT complex. The results obtained are given in Table 4.3.3(III) and the graph is shown in Fig.4.3.3(II)

From the graph it has been found that maximum occurs at 0.33 ratio of metal ion concentration to the total metal of and ligand concentration indicating the formation of 1:2 [M: L] complex.
### TABLE – 4.3.3 (III)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>C_m/C_m + C_r</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.125</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.310</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.442</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.624</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.590</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.512</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.477</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.425</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.381</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.325</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.262</td>
</tr>
</tbody>
</table>

### TABLE – 4.3.3 (IV)

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>C_m/C_r</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.114</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>0.232</td>
</tr>
<tr>
<td>3</td>
<td>0.375</td>
<td>0.351</td>
</tr>
<tr>
<td>4</td>
<td>0.500</td>
<td>0.490</td>
</tr>
<tr>
<td>5</td>
<td>0.625</td>
<td>0.500</td>
</tr>
<tr>
<td>6</td>
<td>0.750</td>
<td>0.520</td>
</tr>
</tbody>
</table>
It is evident from the Figure 4.3.3(III) that absorbance gradually increases up to correct stoichiometry of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

It is seen from the results of both the methods that stoichiometry for Ni(II)-HMAT complex is 1:2 [M:L].

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:**

\[ MLn \rightleftharpoons M + nL \]

\[ C(1-\alpha) \quad C.\alpha \quad (nC\alpha)^n \]

\[ K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n} \]

Taking \( n = 2 \), in this case the equation reduces to,

\[ K_s = \frac{1-\alpha}{4\alpha^3C^2} \quad \text{where,} \quad \alpha = \frac{E_m - E_s}{E_m} \]

where, \( E_m = \) maximum absorbance obtained at the intersect of the two lines.

\( E_s = \) absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \( K_s \) value the standard free energy change \( \Delta G^o \) at 27°C for the formation reaction of complex has been calculated using the formula,

\[ \Delta G^o = -RT \ln K_s \]

**TABLE – 4.3.3 (V)**

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( K_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.658</td>
<td>0.624</td>
<td>0.051</td>
<td>1.788 \times 10^{11}</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.520</td>
<td>0.490</td>
<td>0.057</td>
<td>1.273 \times 10^{11}</td>
</tr>
</tbody>
</table>

Mean \( K_s = 1.5305 \times 10^{11} \)

\( \Delta G^o = - 15.34 \) K.cal/mole
Fig. 4.3.3 (II)

Job's method for Ni(II)-HMAT Complex

Em = 0.658
Es = 0.624
Mole-ratio method for Ni(II)-HMAT Complex

Em = 0.520
Es = 0.490

Fig. 4.3.3 (III)
STUDY OF Pd(II) COMPLEX WITH HMAT:

PREPARATION OF STANDARD SOLUTION OF Pd(II):

Stock solution (0.01 M) of Pd (II) was prepared by dissolving 0.4435 gm of PdCl₂ in little concentrated hydrochloric acid and diluting it to 250 ml with distilled water. The solution was standardised gravimetrically using dimethyl glyoxime. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

REACTION OF 2-HYDROXY-4-METHOXYACETOPHENONE THIOSEMICARBAZONE WITH Pd(II):

Pd(II) was found to give yellow coloured complex with HMAT. Solution of HMAT in 50% ethanol with suitable concentration was used in different methods.

EFFECT OF pH:

The effect of pH on the complex formation was studied by preparing the solutions of different pH in a similar way as done for Cu(II)-HMAT complex. The absorbance values of each solution were measured between 400 nm to 500 nm against reagent blank. It was observed that at 460 nm and at pH 4.5 absorbance value is found maximum. The absorbance values at 460 nm are tabulated in Table: 4.3.4(I).
TABLE - 4.3.4 (I)

ABSORBANCE DATA OF Pd(II)-HMAT COMPLEX AT DIFFERENT pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>HCl + CH₃COOH</td>
<td>0.016</td>
</tr>
<tr>
<td>3.5</td>
<td>HCl + CH₃COOH</td>
<td>0.249</td>
</tr>
<tr>
<td>4.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.145</td>
</tr>
<tr>
<td>4.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.313</td>
</tr>
<tr>
<td>5.0</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.285</td>
</tr>
<tr>
<td>5.5</td>
<td>CH₃COOH + CH₃COONa</td>
<td>0.194</td>
</tr>
</tbody>
</table>

It was seen from the above observation that maximum complex formation occurs at pH 4.5 and therefore in all subsequent experiments, this pH was maintained.

EFFECT OF SOLVENT AND TIME:

Since the complex is easily soluble in 50% aqueous ethanol, the concentration of ethanol was kept around 50% in all final solutions prepared for absorbance measurements of Pd(II)-HMAT complex. The colour of complex was found to be stable upto 6 hours.

VERIFICATION OF BEER’S LAW

To 5 ml of solution (0.01 M) of the reagent HMAT, varying amount of the Pd(II) solution (0.005 M) was added and the pH was adjusted to 4.5, using [CH₃COOH + CH₃COONa] buffer and the contents were diluted to the mark with ethanol and doubly distilled water, to make the final concentration of ethanol 50%. The absorbance of these solutions were measured at 460 nm against reagent 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 63.85 ppm of Pd(II). The standard graph thus obtained may be used for determination of Pd(II) in an unknown solution using HMAT. The results are tabulated in Table - 4.3.4(II) and the graph is shown in Fig.-4.3.4 (I).

**TABLE – 4.3.4 (II)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Metal ion content in ppm</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>21.284</td>
<td>0.316</td>
</tr>
<tr>
<td>1.5</td>
<td>31.926</td>
<td>0.403</td>
</tr>
<tr>
<td>2.0</td>
<td>42.568</td>
<td>0.640</td>
</tr>
<tr>
<td>2.5</td>
<td>53.210</td>
<td>0.773</td>
</tr>
<tr>
<td>3.0</td>
<td>63.852</td>
<td>0.983</td>
</tr>
<tr>
<td>3.5</td>
<td>74.494</td>
<td>1.086</td>
</tr>
</tbody>
</table>

Molar absorptivity from Beer's law plot was found to be $1.683 \times 10^3$ lit.mol$^{-1}$.cm$^{-1}$ for Pd(II)-HMAT complex at 460 nm and Sandell’s sensitivity was found to be 0.063 µg/cm$^2$.

**COMPOSITION OF CHELATE:**

The composition of Pd(II) chelate with the reagent HMAT has been determined on the basis of, (i) Job’s method of continuous variation , and (ii) Yoe and Jones mole-ratio method.

(i) **JOB’S METHOD OF CONTINUOUS VARIATION**

A series of solutions were prepared in a similar way as done for Cu(II)-HMAT complex. The results obtained are given in Table 4.3.4(III) and the graph is shown in Fig. 4.3.4(II).
From the graph it has been found that maximum occurs at 0.50 ratio of metal ion concentration to the total metal of and ligand concentration indicating the formation of 1:1 [M: L] complex.

**TABLE – 4.3.4 (III)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>Reagent solution taken in ml</th>
<th>( \frac{C_m}{C_m + C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.08</td>
<td>0.056</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.17</td>
<td>0.150</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.25</td>
<td>0.227</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.33</td>
<td>0.322</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.42</td>
<td>0.481</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.50</td>
<td>0.502</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.58</td>
<td>0.478</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.67</td>
<td>0.396</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>0.75</td>
<td>0.327</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.83</td>
<td>0.272</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.92</td>
<td>0.171</td>
</tr>
</tbody>
</table>

**TABLE – 4.3.4 (IV)**

<table>
<thead>
<tr>
<th>Metal ion solution taken in ml</th>
<th>( \frac{C_m}{C_r} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
<td>0.058</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>0.115</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.155</td>
</tr>
<tr>
<td>4</td>
<td>0.67</td>
<td>0.212</td>
</tr>
<tr>
<td>5</td>
<td>0.83</td>
<td>0.274</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.310</td>
</tr>
<tr>
<td>7</td>
<td>1.16</td>
<td>0.350</td>
</tr>
<tr>
<td>8</td>
<td>1.33</td>
<td>0.353</td>
</tr>
</tbody>
</table>
It is evident from the Figure 4.3.4(III) that absorbance gradually increases up to correct stoichiometry of metal to the reagent and after that it becomes constant indicating 1:1 stoichiometry of the complex.

It is seen from the results of both the methods that stoichiometry for Pd(II)-HMAT complex is 1:1 [M:L].

**EVALUATION OF STABILITY CONSTANT FROM THE MOLE-RATIO METHOD AND JOB’S METHOD:**

\[ MLn \rightleftharpoons M + nL \]

\[ C(1-\alpha) \]

\[ C.\alpha \]

\[ (nC\alpha)^n \]

\[ K_s = \frac{C(1-\alpha)}{C\alpha(nC\alpha)^n} \]

Taking \( n=1 \), in this case the equation reduces to,

\[ K_s = \frac{1-\alpha}{C\alpha^2} \]

where, \( \alpha = \frac{E_m-E_s}{E_m} \)

where, \( E_m \) = maximum absorbance obtained at the intersect of the two lines.

\( E_s \) = absorbance at the stoichiometric molar ratio of the metal to ligand in complex.

From mean \( K_s \) value the standard free energy change \( \Delta G^0 \) at 27°C for the formation reaction of complex has been calculated using the formula,

\[ \Delta G^0 = -RT \ln K_s \]

**TABLE – 4.3.4 (V)**

<table>
<thead>
<tr>
<th>Method</th>
<th>( E_m )</th>
<th>( E_s )</th>
<th>( \alpha )</th>
<th>( K_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job’s method</td>
<td>0.555</td>
<td>0.502</td>
<td>0.0954</td>
<td>8.278 x 10^4</td>
</tr>
<tr>
<td>Mole-ratio method</td>
<td>0.350</td>
<td>0.310</td>
<td>0.114</td>
<td>6.820 x 10^4</td>
</tr>
</tbody>
</table>

\[ \text{Mean } K_s = 7.549 \times 10^4 \]

\[ \Delta G^0 = -6.69 \text{ K.cal/mole} \]
Beer's law plot for Pd(II)-HMAT Complex

Fig. 4.3.4 (I)
Fig. 4.3.4 (II)
Mole ratio method for Pd(II)-HMAT Complex

Absorbance

Cm/Cr

Em = 0.350
Es = 0.310

Fig. 4.3.4 (III)