CHAPTER II

METHODS OF ANALYSIS AND MEASUREMENTS
Chromium:

The chromium complexes were generally analysed in three different ways:

(i) The complexes were decomposed by digesting with dilute aqueous ammonia and ammonium chloride in presence of air. The precipitated hydrated chromium(III) oxide was filtered, washed, calcined and finally weighed as $\text{Cr}_2\text{O}_3$.96.

(ii) The compounds were decomposed with a few drops of concentrated nitric acid in a tared silica crucible. The mass was then ignited and finally weighed as $\text{Cr}_2\text{O}_3$.

(iii) The difficultly decomposable compounds were fused with sodium hydroxide in a nickel crucible and the organic ligands like, 2,2'-dipyridyl, 1,10-phenanthroline, pyridine etc. were driven off by cautious heating. The residue was, then, transferred to a beaker and oxidised with a few grains of sodium peroxide in an aqueous medium. The excess peroxide was then decomposed by boiling. The resultant chromium (VI) was determined by the addition of known excess of iron (II) and back titrated with standard potassium dichromate solution under the usual conditions.

Potassium:

The chromium complexes containing potassium were decomposed by digesting with ammonium hydroxide and ammonium chloride. The chromium (III) hydroxide was removed by filtration and the filtrate was evaporated with a few drops of concentrated sulfuric acid to a small volume. It was then transferred to a tared platinum crucible, evaporated completely, the sulfuric acid driven off and the residue was heated to a
dull redness. Any pyrosulfate formed by the pyrolysis of the bisulfate was decomposed by the addition of a small quantity of pure solid ammonium carbonate. It was reignited and finally weighed as anhydrous potassium sulfate.

Chlorine, Bromine and Iodine:

The compounds were decomposed by digestion with very dilute aqueous sodium hydroxide and chromium(III) hydroxide was removed by filtration. The halides present in the complexes were then precipitated in the filtrate and washing as the silver salt under usual conditions and were determined gravimetrically.

Nitrogen:

The nitrogen content of all the complexes were determined in the laboratory by Duma’s method in a semi-micro scale.

Mercury:

Mercury was determined in the complexes in two different ways:

(i) The easily decomposable compounds were taken in aqueous suspension and hydrogen sulphide gas was passed through them. Mercuric sulphide was quantitatively precipitated and was filtered in a sintered bed crucible, washed thoroughly with cold water and then successively with aqueous ethanol and carbon disulfide (to remove traces of sulfur). It was finally dried at 110° and weighed as HgS.

(ii) The mercury compound containing thiocyanate was oxidised by digesting with concentrated nitric acid. On completion of the decomposition, the solution was diluted to a known volume in a volumetric flask. To an aliquot of the diluted solution, known volume of
standard sodium chloride solution was added and the excess chloride was back titrated with standardised mercury(II) nitrate solution using diphenyl carbazone and bromophenol blue indicator. Sulfur:

The chromium complexes containing sulfur was determined in two ways:

(i) When the element was present as $SO_4^{2-}$ in soluble compounds, it was dissolved in known volume of water, acidified (0.1N) with hydrochloric acid and $BaSO_4$ was precipitated from hot solution with hot aqueous barium chloride. The precipitate was filtered through a tared sintered glass crucible, washed with water, dried at 120°C and weighed.

(ii) In other cases, the compounds were digested with concentrated nitric acid for several hours to ensure complete decomposition (e.g. of thiocyanate). The solution was then evaporated just to dryness. The mass was extracted with water and the resulting sulfate was determined gravimetrically as barium sulfate.

Oxalate:

The oxalato complexes were digested with dilute aqueous sodium hydroxide and the precipitated chromium(III) hydroxide was filtered off. The filtrate was acidified with dilute hydrochloric acid, heated to 70-80°C, and a slight excess of calcium chloride solution was added. It was made just ammonical and digested on a water bath for an hour. The precipitated calcium oxalate was filtered, washed with cold water till free from chloride and then dissolved in
The oxalate was finally determined titrimetrically with standard potassium permanganate solution as usual.

**Tetrafluoborate:**

The chromium complexes containing tetrafluoborate anion were all soluble in water. An aqueous solution of the weighed quantity of the complex was passed through a column of Dowex-50 resin (in the hydrogen form). The liberated free fluoboric acid was collected in a known excess of standard sodium hydroxide solution and the excess alkali was back titrated with standard sulfuric acid. The quantity of fluoboric acid present was then calculated.

**Tetrafluoberyllate:**

The quantity of fluoberyllate contained in the chromium complex was determined gravimetrically as insoluble barium fluoberyllate just like barium sulfate.

**Phosphorous:**

The compound containing phosphorous was evaporated on water-bath with concentrated nitric acid for several times and diluted with 50 ml of water. 15 ml of concentrated nitric acid was added to it followed by the addition of 10 ml of concentrated ammonia. The solution was boiled and 10 ml 15% ammonium molybdate reagent was added dropwise immediately with constant stirring. It was left for half an hour and the precipitate was filtered, washed with 5% ammonium nitrate solution and finally with water till free from acid. It was dissolved in a known volume of standard caustic soda and the excess base was back titrated in the presence of 5 ml of neutralised formaldehyde, using phenolphthalein indicator. One mole of phosphorous is equivalent
to 26 moles of caustic soda solution.

Perchlorate:

The chromium complex containing perchlorate anion was soluble in water. An aqueous solution of the weighed quantity of the complex was passed through a column of Dowex-50 resin (in the hydrogen form). The liberated free perchloric acid was collected in a known excess of standard sodium hydroxide solution and the excess alkali was back titrated with standard sulfuric acid. The quantity of perchloric acid present was then calculated.

Physical Measurements

Magnetic susceptibility:

The magnetic susceptibility of the compounds were measured in a Guoy balance. The field strength of the magnet under the experimental condition was determined by measuring the pull due to standard samples of copper sulfate pentahydrate and chrome alum. The average field strength at the centre of the pole pieces was found to be $9.1 \times 10^3$ Oe. Diamagnetic correction for the constituent atoms and ions were made from the values given by Lewis and Wilkins (vide Table 2.1). The molar magnetic susceptibility $\chi_M$ were calculated from the following expression,

$$\chi_M = \frac{2 \times l \times g \times w \times M}{W \times H^2}$$

where $l$ = length of the sample column in cm
$g$ = acceleration due to gravity (981 cm per sec$^2$)
$w$ = increase in weight of the sample due to the magnetic field in mg
$M$ = formula weight of the sample
maximum field strength at one end of the sample column placed at the centre of the pole pieces.

the sample in absence of the field in gm.

The effective magnetic moment, $\mu_{\text{eff}}$, was calculated in Bohr Magnetons from the relation,

$$\mu_{\text{eff}} = 2.84 \left( \chi'_M \times T \right)^{1/2}$$

where $\chi'_M$ = molar susceptibility corrected for the diamagnetism of the constituents in the molecule.

$T$ = the absolute temperature.

Electronic spectra:

The electronic spectra of the compounds were recorded on a Hilger's UVISPEK and VARION 634 spectrophotometer in matched silica cells of one cm path length.

I.R. and Raman spectra:

The infrared spectra were recorded on Beckmann IR 20, Pye and Unicam SP 1025, and Perkin Elmer instruments. The Raman spectrum was recorded on a SPEX 1401 with photon counting and 90° collection as powdered solids in 2 mm o.d. capillaries. Excitation was by He/Ne 632.8 nm laser (40 mw).

pH measurements:

pH measurements were done with an Expanded Scale pH meter of Electronic Corporation of India.

Conductance:

Conductance measurements of the solution were done with a Philips RCL bridge (PP 9030) using dip-type cell having the cell...
factor of 1.525 cm.

**Pyrolysis studies:**

Pyrolytic decompositions of the solid compounds were studied with the help of a manual thermobalance constructed in the laboratory. The balance was sensitive to 0.1 mg. A linear heating rate of 5°C per minute was maintained within a temperature range of 40°C-800°C with the help of an electronic programme controller driven by the temperature recording galvanometer. 100 mg of the sample was used in each experiment.

**Polarography:**

Polarographic experiments were carried out with a Cambridge pen recording polarograph. The capillary characteristics of the dropping mercury electrode were:

(i) the outflow velocity of mercury, \( m = 1.575 \text{ mg sec}^{-1} \)

(ii) the drop time, \( t_1 = 2.790 \text{ sec at the height of the mercury column } h = 60 \text{ cms and at a potential of } -1.50 \text{ V against the saturated calomel electrode (S.C.E.)} \)

**Polarimetry:**

The optical rotation measurement was done with the help of a Perkin Elmer (Model 241) polarimeter.
### TABLE 2.1

Diamagnetic Corrections for Several Constituents

(The given values x 10^6 cgsu/g.atom)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Value (x 10^6)</th>
<th>Ion</th>
<th>Correction (x 10^6 cgsu/g.atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-dipyridal</td>
<td>105.00</td>
<td>Cl^-</td>
<td>23.40</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>128.00</td>
<td>Br^-</td>
<td>34.60</td>
</tr>
<tr>
<td>Pyridine</td>
<td>55.43</td>
<td>I^-</td>
<td>50.60</td>
</tr>
<tr>
<td>H</td>
<td>2.93</td>
<td>NO_3^-</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>14.36</td>
<td>CN^-</td>
<td>13.00</td>
</tr>
<tr>
<td>NO</td>
<td>10.20</td>
<td>SCN^-</td>
<td>31.00</td>
</tr>
<tr>
<td>C_2O_4^-</td>
<td>25.44</td>
<td>K^+</td>
<td>14.90</td>
</tr>
<tr>
<td>SO_4^2-</td>
<td>40.10</td>
<td>Hg^{2+}</td>
<td></td>
</tr>
<tr>
<td>H_2O</td>
<td>13.00</td>
<td>ClO_4^-</td>
<td></td>
</tr>
<tr>
<td>OH^-</td>
<td>12.00</td>
<td>NH_4^+</td>
<td>13.30</td>
</tr>
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