CHAPTER TWO
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EXPERIMENTAL

2. INTRODUCTION

The analytical procedures and the physico-chemical techniques employed in the present investigation are described in this chapter. These methods are used to characterise and to study the physical properties of the compound, isolated during the course of the investigation.

2.1 MATERIAL USED

Commercially available chemicals, (Analar or equivalent grade) are used without purification.

2.1.1 METAL COMPOUNDS

i) Magnesium Carbonate, MgCO$_3$, Sarabhai

ii) Calcium Carbonate, CaCO$_3$, (98-100%) M & B.

iii) Strontium Carbonate, SrCO$_3$, Chemco.

iv) Barium Carbonate, BaCO$_3$, Loba-Chemie.

v) Zinc Carbonate, ZnCO$_3$, Loba-Chemie.

vi) Basic Nickel Carbonate, NiCO$_3$.2Ni(OH)$_2$.4H$_2$O, Loba-Chemie.

vii) Sodium Carbonate, Na$_2$CO$_3$, BDH.

viii) Potassium Carbonate, K$_2$CO$_3$, BDH.

ix) Ethylene Diamine Tetracetic Acid-Disodium salt, EDTA, BDH.

x) Potassium Iodate, KIO$_3$, BDH.

xi) Zinc Sulphate Heptahydrate, ZnSO$_4$.7H$_2$O, Qualigen.

xii) Hydrogen Peroxide, H$_2$O$_2$ (30%), E. Merck.
xiii) Nitric Acid, Qualigen.
xiv) Hydrochloric Acid, Qualigen.

2.1.2 HYDRAZINE COMPOUNDS AND NTA
i) Hydrazine Hydrate, $N_2H_4\cdot H_2O$, (99-100%) Qualigen.
ii) Hydrazine Sulphate, $(N_2H_5)_2 SO_4$, Loba Chemie.
iii) Nitrilotriacetic Acid, $H_3[N(CH_2COO)_3]$, Loba-Chemie.

2.1.3 INDICATORS
i) Murexide.
ii) Eriochrome Black - T.

2.2 ANALYTICAL METHODS

Chemical analysis of the metal ion and hydrazine was carried out to fix the composition of product compounds.

2.2.1 ESTIMATION OF METAL

Known amount (approx 0.1g) of the compound was first decomposed$^1$, with 1 cc conc. $HNO_3$ and 3 cc $H_2O_2$, by heating almost to dryness (on a sand bath). The residue was then extracted with 50cc of deionised water. This solution was then used as such for the estimation of metal ion.

A buffer solution with pH = 10 was prepared by using ammonium chloride and ammonium hydroxide.

A standard solution of $0.01 \ M \ EDTA^{2-9}$ was prepared by weighing out the disodium salt of EDTA (3.7225 g per litre of solution) and dissolving it in deionised water. The solution was
standardized by titrating with standard (0.01 M) zinc sulphate solution.

2.2.1.1 MAGNESIUM, CALCIUM AND ZINC ESTIMATION

The solution obtained after the decomposition of the product was maintained at pH = 10 using buffer solution and then titrated against standard 0.01 M EDTA solution using Eriochrome Black - T indicator.

The end point was recorded when the colour of the solution changes from wine red to blue.

\[
1 \text{ ml of 0.01 M EDTA} = 0.0002432 \text{ g of Mg.}
\]
\[
= 0.0004003 \text{ g of Ca.}
\]
\[
= 0.0006538 \text{ g of Zn.}
\]

2.2.1.2 BARIUM ESTIMATION

Volume of the solution, after decomposition, was reduced to 25 cc by boiling and treated with about 10 cc of 2N HCl. 15 cc of hot 2N H₂SO₄ was then added to precipitate Ba²⁺ as BaSO₄. The mixture was digested on a steam bath and filtered hot using Whatman No 40 filter paper. After washing BaSO₄ with warm water, it was dried and ignited in a crucible to weigh as BaSO₄.

\[
233.4 \text{ g of BaSO₄} = 137.33 \text{ g of Ba.}
\]

2.2.1.3 NICKEL ESTIMATION

To the solution containing the nickel ion (2.2.1), after diluting to 75 cc, about 0.05 g of the indicator mixture (murexide + KNO₃) and 10 cc of 1M ammonium chloride was added. The pH of
the mixture was increased to 10, by the addition of concentrated ammonia and then titrated against 0.01 M EDTA until colour changes from yellow to violet \(^2\). \(^3\) (the pH of the solution was further raised to 10 near end point, if required with concentrated ammonia).

2.2.2 ESTIMATION OF HYDRAZINE

Accurately weighed (0.04-0.06 g) compound was taken in a 250 cc reagent bottle. A mixture of 15 cc conc. HCl, 15 cc of deionised water and 5cc of CCl\(_4\) was then added in it. Standard 0.025 M potassium iodate (5.350 g in one liter of the solution) was then added, with constant shaking of the stoppered bottle, until organic layer was just decolourised \(^2\).

\[ 1 \text{ ml of } 0.025 \text{M } \text{KIO}_3 = 0.0008103 \text{ g of } N_2H_4. \]

2.3 PHYSICO-CHEMICAL TECHNIQUES

The Physico-chemical techniques used in the present investigation include flame photometry, infrared spectrometry, magnetic susceptibility measurements, thermogravimetry (TGA), differential thermal analysis (DTA), etc.

2.3.1 DENSITY MEASUREMENTS

Pyknometer tube was used to determine the density of the samples. Mass of the displaced CCl\(_4\) by the weighed amount of the solid sample in the tube was determined. By substituting the density of this liquid at ambient temperature, its volume was calculated which corresponds to the volume of the sample. The
required density of the sample was then calculated using the expression \( \rho = \frac{m}{v} \).

\[
\rho_{\text{sample}} = \frac{\text{weight of the sample}}{\text{(weight of the liquid displaced) + (density of the liquid)}}
\]

### 2.3.2 FLAME PHOTOMETRY

Flame photometry is the measurement of the intensity of the emitted radiation by metal ions when sprayed into a flame. Intensity of emitted radiation is proportional to the amount of the ions sprayed. Hence this technique can be used for quantitative estimation of metal ions such as Na\(^+\), K\(^+\), Sr\(^{2+}\), Cu\(^{2+}\) etc. in solution. The solution is sprayed on the flame with the help of the atomizer. ELICO CL 22D flame photometer was used in the present investigation.

### 2.3.3 INFRARED SPECTROPHOTOMETRY

Every molecule will have a number of fundamental vibrational frequencies, each of which may be associated with absorption of radiation of its own frequency. This principle is followed in the infrared spectroscopy and absorption of frequencies is obtained in the form of spectrum, which are sometimes called "the finger prints".

The infrared spectra of solid samples were recorded by dispersing them in Nujol or fluorolube (mull technique) and also in KBr disc (pellet technique).

TOSHNIWAL IR 408 Spectrophotometer was used to record the spectra in the range 4000 - 650 cm\(^{-1}\). Calibration of the
instrument was done with polystyrene with its standard frequencies.

2.3.4 MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Magnetic susceptibility may be defined as the extent to which a substance is susceptible to induced magnetisation. Paramagnetism is a type of magnetic behaviour which is exhibited by substances containing unpaired electrons. These substances are weakly attracted in the magnetic field.

Guoy method is one of the simplest method of measuring the magnetic susceptibility. In this method, the sample in the form of uniform rod is suspended vertically in a strong non-homogeneous magnetic field generated by electromagnets. The force exerted on the rod is measured equivalent to weight difference by a conventional weighing technique.

Mercury tetrathiocyanato cobaltate [HgCo(CNS)$_4$] was used as the calibrant for the tube, which was later on used for the solid samples. All the measurements were made at the ambient temperature. The molar susceptibility $\chi_m$ was first obtained and corrected for the diamagnetism using Pascal constants. From corrected molar susceptibility $\chi_m$, the effective magnetic moment was calculated by relation:

$$\mu_{\text{eff}} = 2.84 \sqrt{\frac{\chi_m}{T}}$$

where $T$ is the temperature in deg. Kelvin.
2.3.5 THERMOANALYTICAL TECHNIQUES

Thermal analysis techniques are those methods in which the changes in the physical and/or chemical properties of a substance is measured as a function of temperature. In these methods, the substance is subjected to a controlled temperature, heating or cooling or constant temperature (isothermal). Most commonly used techniques, thermogravimetry and differential thermal analysis, are employed in the present investigation. Since single thermal analysis technique may not provide sufficient information, it is necessary to have the combination of the two techniques for reliability and complementary data. TG and DTA curves are affected by various factors such as:

i) nature and shape of material used as sample holder,

ii) particle size of the sample,

iii) packing density of the sample,

iv) sample weight and its history,

v) surrounding atmosphere,

vi) sensitivity of the thermocouple.

Heating rate employed for TG/DTA was 5°, 10°, 20° C min⁻¹, in air or nitrogen (20 ml min⁻¹ as flow rate) or argon (same flow rate). About 10 mg of the sample in platinum cups was used for each experiment. Platinum - rhodium thermocouple was used as temperature detectors.
2.3.5.1 THERMOGRAVIMETRY

In thermogravimetry, mass of the sample under investigation is measured as a function of temperature, whilst the sample is subjected to a controlled temperature (heating, cooling or isothermal). The type of weight change observed in the TG and reaction is given in Table 2.1.

The TG experiments were carried out using the instrument SHIMADZU THERMOBALANCE (model TD-30).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Adsorption or Absorption or Oxidation</th>
<th>Desorption or Decomposition or Reduction</th>
<th>Vapourisation or Sublimation or Dehydration</th>
<th>Solid state reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG data</td>
<td>gain</td>
<td>loss</td>
<td>loss</td>
<td>gain or loss</td>
</tr>
</tbody>
</table>

2.3.5.2 DIFFERENTIAL THERMAL ANALYSIS

In DTA, sample and an inert material are simultaneously heated at a controlled heating rate. And the temperature difference between the two is recorded as a function of furnace temperature.

NETZSCH STA-409 Thermal Analyser was used to study the thermoanalytical properties of some of the compounds.
Table 2.2 gives different reactions and the corresponding DTA effect.

TABLE 2.2
The Reactions and the Observed Effects in the DTA

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Adsorption or Absorption</th>
<th>Vapourisation or Sublimation or Dehydration</th>
<th>Decomposition</th>
<th>Oxidative degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal effect</td>
<td>exothermic (+)</td>
<td>endothermic (-)</td>
<td>exo or endo (+) or (-)</td>
<td>endo or exo (+) or (-)</td>
</tr>
</tbody>
</table>

2.3.6 X-RAY POWDER DIFFRACTION

The X-ray powder diffraction patterns were obtained using PHILLIPS X-Ray Diffractometer Mode PW 1840 using Cu radiation with nickel filter.
REFERENCES:
