Chapter – II

Experimental Techniques
## Chapter – I

### Experimental Techniques

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In this chapter various analytical, spectral techniques and other experimental techniques carried out in the present research work are discussed in brief.

2.1 Apparatus

Apparatus used for the experimental work were of corning glass. 'A' grade burettes and pipettes were used throughout the work. Burettes, pipettes and volumetric flasks were Standardized using standard analytical methods [1].

2.2 Chemicals

Chemicals of good quality (AR) grade were used throughout the experimental work.

(A) Water: Entire experimental work was carried out using deionized, distilled water in the presence of potassium permanganate and two to three pellets of potassium hydroxide.

(B) Solvents: Methyl alcohol and Ethyl alcohol and chloroform were used for synthesis of Schiff base and their transition metal complexes. The solvents were purified by distilling over dry calcium oxide. All other solvents were used as supplied by reputed manufacturer as they were of AR grade.

(C) Following solvent were used during the experimental work.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Make</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methanol</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>2.</td>
<td>Ethanol</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>3.</td>
<td>chlorofrom</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>5.</td>
<td>Acetone</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>7.</td>
<td>Dimethyl formamide</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>8.</td>
<td>Dimethyl sulfoxide</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
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</tbody>
</table>

(D) Following amines and metal salts were used for the synthesis of Schiff bases and metal complexes
### Experimental Techniques

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Make</th>
<th>Grade</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>4 hydroxychromen-2-one</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>2.</td>
<td>Phosphorus oxychloride</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>4.</td>
<td>Thio semicarbazide</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>5.</td>
<td>2-amino ethanol amine</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>6.</td>
<td>2-amino thio ethanol amine</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>8.</td>
<td>Methyl benzoate</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>9.</td>
<td>Chloro4-methyl benzoate</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>10.</td>
<td>methyl4-methyl benzoate</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>11.</td>
<td>Methoxy4-methyl benzoate</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
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</table>

(E) Following metal salts were used during the experimental work

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Make</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Copper chloride</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>2.</td>
<td>Nickel chloride</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>3.</td>
<td>Zinc chloride</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>5.</td>
<td>Mercuric chloride</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
</tbody>
</table>
(F) Following acid were used during the experimental work

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Make</th>
<th>grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hydrochloric acid</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>2.</td>
<td>Sulphuric acid</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>3.</td>
<td>Nitric acid</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>4.</td>
<td>Glacial acetic acid</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
<tr>
<td>5.</td>
<td>Perchloric acid</td>
<td>S.D.Fine-Chem</td>
<td>AR</td>
</tr>
</tbody>
</table>

### 2.3 INSTRUMENTS USED

#### 2.3.1 BALANCE

An analytical balance manufactured by K-Roy, Varanasi of 0.1 mg sensitivity was used, for samples, weighing up to 100 mg or more. For samples weighing less than 100 mg, a Semi micro balance supplied by Mettler-Toledo AG, Switzerland with Model no. Mettler-200 was used.

#### 2.3.2 pH METER

At various stages in the experimental work, pH measurements were done using pH paper supplied by M/s Merck (Ind) Ltd. For accurate measurement of hydrogen ion concentration, pH meter was used.

Instrument: The instrument was supplied by M/s Elico Pvt. Ltd. Hyderabad, with model no. LI-120.

### 2.4 SOLUTION CONDUCTIVITY

**Principle**

It is one of the recent methods for studying the complexes. The solution conductivity depends on the concentration of solute and the number of charges on ions, which are formed on dissociation in an ionic material [2]. The solution of an electrolyte conducts electric current by migration of ions under the influence of electric field. Hence the ability of any ion to transport charge depends on mobility of ions. Therefore by measuring the solution conductivity...
conductivity one can decide the electrolytic or non-electrolytic nature of the metal complexes.

The electrical conductivity of a solution of an ionic material depends on:

a) The concentration of solute (i.e. number of ions).

b) The number of charges on the species.

c) The mobility of ions.

By comparison of molar conductivities of complexes with that of known simple ionic materials, the total number of charges on the species formed when the complex dissolves can be deduced. The total number of charges on the species and the number of particles formed from the complex deduced from cryoscopic measurements together can be used to establish the structure of complex [3]. The solution conductivities of the metal complexes in DMSO were measured on digital conductivity bridge at room temperature. The conductivity cell with platinized platinum electrode with a cell constant 1.001 cm\(^{-1}\) was used. The concentration of the solution was around 10\(^{-4}\)M. The molar conductance values were interpreted with the help of data given in the literature [4, 5].

### 2.5 ELEMENTAL ANALYSIS OF LIGANDS, METAL COMPLEXES

The C, H, N analysis of ligands and complexes were carried out by micro combustion method using CHNSO, EA1108, Elemental analyser model-CARLO-ERBA Instruments, Italy, at micro analysis division, National Chemical Laboratory, Pune and Elemental Analyser "PERKINELMER" model No. 2400 at School of Chemical Sciences, North Maharashtra University, Jalgaon. The samples weighing between 1-10 mg were used for the analysis. The molecular stoichiometry of each compound was established on the basis of elemental analysis.

#### 2.5.1 ANALYSIS OF METAL COMPLEXES

The melting point/decomposition temperature of metal complexes was noted.

**Estimation of metal ions**

Atomic absorption and emission spectroscopy are instrumental techniques for determination of elemental analysis [6]. The metal content in complexes were determined by atomic spectra on Perkins Elmer atomic absorption spectrophotometer (Model 2380).

**Procedure for analysis of metal ions by AAS**
All the apparatus used were washed with dilute nitric acid followed by distilled water and dried in oven. The complex under analysis was accurately weighed up to 10 mg in 100 ml beaker. 20 ml perchloric acid was added in the beaker, containing complex and heated till volume was reduced to 10 ml. Further 15-20 ml of perchloric acid was added and heated to dryness. The beaker was cooled and metal in the form of metal chloride was extracted with glass-distilled water and diluted to 250 ml. Using this diluted solution, the percentage of metal ion was calculated using atomic absorption spectrophotometer.

Grams of metal in V ml of solution = \( X \times V / 10^6 \)

Percentage of metal = \( \frac{X \times V \times 100}{10^6 \times W} \)

\( W \) = weight of Complex
\( V \) = Dilution
\( X \) = AAS reading

**Estimation of Chlorides**

Estimation of chlorides was carried out by Volhard's method [7]. 100 mg of test sample of metal complex was dissolved in DMSO and diluted to 50 ml in a standard flask. To a 10 ml aliquot of this solution in a conical flask, 5 ml of 6 M-nitric acid was added. The chloride solution was then treated with a known volume in slight excess (20 ml) of standard 0.01 M-silver nitrate solution. 2-3 ml of pure nitrobenzene and 1 ml of iron (III) indicator were added and contents shaken vigorously to coagulate the precipitate. The residual silver nitrate left unreacted was back titrated with standard 0.01M potassium thiocyanate until a permanent faint reddish-brown coloration appears. A blank titration was performed without the sample solution by following same procedure under similar experimental conditions. The difference in two burette readings was used to find out the volume of 0.01 M AgNO₃ consumed by chloride ion. Finally from the conversion factor (1 ml of 0.01 M AgNO₃ = 0.3545 mg of Cl) and volume of 0.01 M AgNO₃ consumed, the percentage of chloride in respective metal chelates was calculated.
ESTIMATION OF SULPHUR:
Sulphur content in the complexes was estimated after oxidizing it with nitric acid to sulphate. The sulphate was then determined gravimetrically as BaSO₄ [8].

2.6 MAGNETIC SUSCEPTIBILITY:
The determination of magnetic susceptibility involves measurement of the force exerted by a homogeneous magnetic field on the sample under study. If the force acting on the sample under investigation is known, the magnetic susceptibility of the Compound can be determined, and from this the value of the magnetic moment, can be calculated. Gouy’s method was used for the measurement of magnetic susceptibility of the compounds at room temperature. Gouy’s balance consists of an electromagnet with suitable power supply and a single pan-semi microbalance, E-Mettler-Zurich, Swissmake-H-1640 with maximum capacity 80 mg and a precision ± 0.01 mg. The electromagnets consists of cylindrical poles, 15 cm in diameter tapering at end sat an angle of 450 and ending in circular faces 3.5 cm in diameter. A gap of 4 cm is maintained between the two poles. The magnetic assembly having an electromagnet with capacity up to 7000 oresteds was placed around the tube, with a current of 6 amps fed by a suitable power supply. The specimen tube made up of Pyrex glass, 14 cm in length and 3.5 mm india meter, with a teflon stopper was used to hold the sample. The tube was supported and suspended freely in the magnetic field with the help of clean silver chain in such away that its lower end was located at the center of the pole gap. The empty clean and dry tube was weighed successively when current is off and on with 4 amps and 6 amps. The field strength of the magnet and position of tube with respect to poles remain unchanged during every measurement. The mean of five readings gave the value Wg for the empty tube.

2.6.1 Calibration of the Specimen Tube: -
For accurate measurement of the magnetic moments, the tube constant was determined, using substance of known magnetic susceptibility at room temperature. The standard substance used was mercury tetra thiocyanato cobalt (II), which was prepared by the standard method given in the literature [9]. The measurement of the force developed on the specimen tube was recorded with two independent fillings of the substance. The compound under investigation was filled in glass tube and packed to eliminate any air pockets. The gram susceptibility of the
sample was taken as $16.44 \times 10^{-6}$ CGS units. The tube constant ($\beta$) was determined at room temperature. This value was used for the calculation of magnetic susceptibility of metal complexes.

A typical data of the calibration is as follows –

Weight of empty tube = 10.15365gm.

Weight of empty tube in presence of magnetic field = 10.15125 gm.

Force on the empty tube in presence of magnetic field = 0.0024gm

<table>
<thead>
<tr>
<th>Weight of [HgCo(CN)₂] (g)</th>
<th>Temperature (K)</th>
<th>Force on the sample (g)</th>
<th>$\beta \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19640</td>
<td>298</td>
<td>0.01245</td>
<td>216.69</td>
</tr>
</tbody>
</table>

**Sources of Error:-**

The main source of error in the Gouy’s method for solids arises from the improper packing of the sample. This can be reduced by repeating the measurements on homogeneously repacked samples until relatively constant values of gram susceptibility ($\chi_g$) are obtained. Agreement within 1% is to be considered good.

2.6.2 Measurement of Magnetic Susceptibilities of Metal Complexes:-

The finely powdered substance was filled in the experimental tube upto the reference mark. Proper precautions were taken to ensure tight and uniform packing without any air gap in the sample column. The teflon stopper was tightly fixed on the tube and the tube was suspended between the poles with the help of silver chain suspension from the pan of the balance. The measurements similar to those described earlier were recorded.

From the experimental data the magnetic susceptibility $\chi_g$ of metal complexes were calculated by using the following expression

$$\chi_g = \frac{\beta \, \Delta \omega}{W}$$

$\chi_g$ = Susceptibility per gram of the substance.

$\beta$ = Constant characteristic of the tube (corrected for diamagnetism of Gouy tube)

$\Delta \omega$ = Force exerted by W g of substance

$W$ = Weight of the substance.
The molar susceptibility ($\chi_M$) of complexes were then calculated by the expression.

$$\chi_M = \chi_g \times \text{Molecular Weight}$$

From the values of $\chi_M$, obtained the magnetic moment ($\mu_{\text{eff}}$) of complexes were calculated by the equation: $2.84 \chi_A \cdot T$

Where,

$$\chi_A = \chi_{corr.} = \text{Magnetic susceptibility obtained by subtracting from the molar susceptibility of the metal complex, the diamagnetic susceptibility of the ligand molecule(s) computed by using Pascal’s constants.}$$

$T = \text{Temperature in Kelvin scale.}$

$\mu_{\text{eff}} = \text{Magnetic moment of the metal ion in Bohr magneton (B.M.)}$

The reproducibility of susceptibility measurement of solids was within $\pm 2\%$ presented in table 2.1.
### Table 2.1: Diamagnetic molar susceptibility ($\chi_L$) of the ligand molecules computed from Pascal’s constants

<table>
<thead>
<tr>
<th>NO.</th>
<th>Name of Ligand and molecular formula</th>
<th>Symbol</th>
<th>$\chi_L \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)hydrazinecarboxamide</td>
<td>L₁</td>
<td>248.72</td>
</tr>
<tr>
<td>2.</td>
<td>2-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)hydrazinecarbothioamide</td>
<td>L₂</td>
<td>269.50</td>
</tr>
<tr>
<td>3.</td>
<td>1) 4-hydroxy-3-((1-(2-hydroxyethylimino)ethyl)-2H-chromen-2-one (L₃)</td>
<td>L₃</td>
<td>266.28</td>
</tr>
<tr>
<td>4.</td>
<td>4-hydroxy-3-((1-(2-mercaptoethylimino)ethyl)-2H-chromen-2-one</td>
<td>L₄</td>
<td>287.06</td>
</tr>
<tr>
<td>5.</td>
<td>N’-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)benzohydrazide</td>
<td>L₅</td>
<td>335.22</td>
</tr>
<tr>
<td>6.</td>
<td>N’-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)-4-methylbenzohydrazide</td>
<td>L₆</td>
<td>370.80</td>
</tr>
<tr>
<td>7.</td>
<td>N’-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)-4-chlorobenzohydrazide</td>
<td>L₇</td>
<td>329.36</td>
</tr>
<tr>
<td>8.</td>
<td>N’-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyldiene)-4-methoxybenzohydrazide</td>
<td>L₈</td>
<td>368.16</td>
</tr>
</tbody>
</table>
2.7 ELECTRON ABSORPTION SPECTROSCOPY

The electronic spectra give an insight into the geometry of the molecule. The absorption of ultraviolet (UV) or visible light results in a change in the energy if electrons of the absorbing molecule. The electronic spectrum consists of bands containing several absorption lines. Each band corresponds to a definite change in the electronic energy, and individual lines within the band are due to definite transitions. The structure of metal complexes can be predicted from interpretation of their electronic absorption spectra and comparing them with the electronic absorption spectra of corresponding ligands. The complexes can be identified by their characteristic absorption, which is based on the position of maxima and minima in the absorption spectra along with the molar extinction coefficient value. In the spectra of transition metal ions, bands corresponding basically are of three types [10],
I) Bands due to d-d transitions.
II) Charge transfer bands.
III) Bands due to electron transfer within the ligand. (a) Spin selection rule:
  “Transitions of an electron does not change its spin ($\Delta S = \pm 0$)”
(b) Laporte’s selection rule:
  “The transitions which involve a change in the subsidiary quantum number $\Delta l = \pm 1$ are Laporte allowed.”

In transition metal complexes, bands are weak because all d-d transitions are Laporte forbidden but there is slight relaxation in the Laporte rule because of there is some mixing of $s$ and $p$ orbitals may occur during formation of complexes [11].

The spectrum of a coloured solution may be measured quite easily using a spectrophotometer.

A beam of monochromatic light obtained using a prism and a narrow slit is passed through the solution and on to a photoelectric cell. The amount of light absorbed at any particular frequency can be read off, or a whole frequency range can be scanned, and the absorbance $A$ plotted as a graph on a paper chart recorder.

The complexes were sparingly soluble in DMSO.
The synthesized Schiff base were soluble in methanol and their complexes with Cu (II), Ni (II), Zn (III), Cd (II), and Hg (II) were soluble in DMSO. Therefore their solution spectra in this solvent were recorded on SHIMADZU-UV-1601 UV/visible double beam spectrophotometer in the region 200-800 nm using quartz tubes of 1 cm path length at Ayurvedic College Nanded.

2.8 INFRA-RED SPECTROSCOPY

Infrared radiation refers to that part of electromagnetic spectrum, which is in between visible, and microwave region. Every chemical compound has its own characteristic IR spectrum. In organic chemistry, Infrared spectrum provides information about functional groups of molecule and also useful for identification of molecule. In coordination chemistry, it provides the information about site of bonding to metal ion and which groups involved in coordination. The IR spectrums of the complexes were compared with that of the free ligand. The characteristic absorption bands of the free ligands are shifted and new vibrational bands are appeared on complexation [12]. IR absorption occurs not only with organic molecules but also with covalently bonded metal complexes, which are generally active in the longer wavelength IR region. The inorganic complexes derived from organic chelating groups have a tendency to absorb in the IR region 400-660 cm⁻¹ which is of greatest practical value in the study of metal complexes. This vibration -rotational band occurring at particular frequency or wavelength depends on the relative mass of the atom, the force constants of the bands, and the geometry of the atoms. The presentation of band position is by either wave number or wavelength. The wave number unit is generally used because it is directly proportional to the energy of vibration. Wavelength is reported as micrometers (10⁻⁶ meters) and wave number as reciprocal of centimeters (cm⁻¹). Wave number (υ) is reciprocally related to wavelength (υ= C/λ). Infrared spectra of the ligands and metal complexes were taken as KBr pellets on Shimadzu spectrometer and some Infrared spectra were recorded as KBr pellets on FTIR-4100 spectrophotometer at IICT, Hyderabad, NCL Pune, on Perkin Elmer at Chandigarh and C.F.C. Shivaji University.
Kolhapur and. From the spectra, the characteristic groups were assigned to the different frequencies in the synthesized ligands as well as comparative in complexes the coordination modes of ligands to the central metal ions and donor atoms were find out [13,14].

2.9 NUCLEAR MAGNETIC RESONANCE SPECTROMETER (NMR)

Any spinning charge creates a magnetic field, there is a magnetic moment associated with the angular momentum. It is this property of matter that is exploited in nuclear magnetic resonance (NMR) spectroscopy.

The NMR spectroscopy is related to magnetic $^1$H and $^{13}$C nuclei are commonly known as proton magnetic resonance ($^1$HNMR) and carbon magnetic resonance ($^{13}$CMR) respectively [15].

The difference in peak positions due to difference in electron density from some standard is known as chemical shift. The number of signals obtained for a molecule gives us the information about the number of the sets of equivalent protons.

The electronic environment of protons decides the position of signals. The positions of signals in NMR spectrum give the information about the types of protons.

The intensity of signal indicates how many protons of each kind are present in molecule.

The splitting of signals arises between the nuclei of neighboring atoms known as spin-spin splitting which shows about the environment of a proton with respective to the neighbor protons.

The distance between adjacent peaks of a multiplet is known as the coupling constant. It is expressed in hertz. Coupling constant is independent of the applied magnetic field.

Similarly $^{13}$CNMR spectrum gives information about the carbon skeleton. $^1$HNMR spectra of ligands were recorded at IICT Hyderabad in CD$_3$OD and some in DMSO solvent using TMS as an internal standard and $^{13}$CNMR of selected ligands were recorded at IICT Hyderabad in DMSO.
2.10 MASS SPECTROSCOPY:

Mass spectrometry (MS) is an analytical method in which free gaseous ions are produced and subsequently subjected to magnetic and electric fields in a high vacuum for analysis of mass/charge ratios. Although initially developed predominantly for physicochemical investigations, mass spectrometry has found broad application since the 1950s in the analysis of more complex organic and small biochemical molecules [16].

John Fenn and Kuichi Tanaka award of the 2002 Nobel prizes in chemistry to two scientists pioneering the development of electrospray-ionization and laser desorption mass spectrometry [17].

A mass spectrometer has three basic components: something to volatilize and ionize the molecule into a beam of charged particles; something to focus the beam so that particles of the same mass: charge ratios are separated from all others; and something to detect the particles.

All spectrometers in common use operate in a high vacuum and usually use positive ions.

The history of the development of liquid chromatography mass spectrometry (LCMS) from its beginnings in the early 1970s till the 1990s has been briefly outlined by Niessen [18].

In the mass spectrometer, molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions.

Each kind of ion has a particular ratio of mass to charge. Signal is obtained for each value of \( m/e \) obtained. The intensity of each signal reflects the relative abundance of the ion producing the signal. The largest peak is called the base peak.

A plot showing the relative intensities of signals at the various \( m/e \) values is called a mass spectrum and is highly characteristic of a particular compound. A mass spectrum helps to establish the structure of a new compound and give an exact mass molecular weight.

Electrospray ionization (ESI) is a technique used in mass spectrometry to produce ions. Mass spectrometry using ESI is called electrospray ionization mass spectrometry.
(ESI-MS) or, less commonly, electrospray mass spectrometry (ES-MS). The ions observed by mass spectrometry may be quasi molecular ions created by the addition of a proton (a hydrogen ion) and denoted \([M + H]^+\), or of another cation such as sodium ion, \([M + Na]^+\), or the removal of a proton, \([M − H]^-\). Multiply-charged ions such as \([M + nH]^{n+}\) are often observed. In the present investigation mass spectral studies is carried out using electrospray mass spectrometry (ES-MS).

2.11 ELECTRON SPIN RESONANCE\(^{17}\) (ESR) MEASUREMENT:

The ESR spectra of the Cu(II) complexes were recorded on a JEOL Electron Spin Resonance Spectrometer at room temperature. ESR spectrometers have three general working units viz., a source, a means of propagating energy from the source onto a sample and detection system.

In the present investigation JEOL spectrometer model JES-FEIX was employed for ESR measurements of pyrazolone with transition metal ions. The JEOL spectrometer model JES-FE1X has the following main parts (1) Spectrometer (2) Microwave unit (3) Cavity resonator and (4) Electromagnet and excitation power supply.

The spectrometer part consists of magnetic field control unit, 100 KHz/80 Hz modulation unit, oscilloscope and recorder. The microwave unit consists of a Gunn diode oscillator and the magic T is housed with a pre-amplifier, an Automatic Frequency Control (AFC) circuit and a Gunn oscillator power supply.

The cavity resonator part has Ultraviolet ray irradiation aperture, a cooling device, a 100 KHz modulation coil, sample tube holder, variable temperature attachments and so on.

The electromagnet and its excitation power supply along with the Hall element, the linear field sweep unit, the detector, the modulation coil at 80 Hz etc., form another important part of the instrument [19]. The sample is placed in the cavity resonator, and adjusted to be at the middle of the poles of the electromagnet, which produces a wide range of magnetic field H. Then the sample
is subjected to a microwave magnetic field of constant frequency and which is perpendicular to H. The magnitude of H is changed by varying the electromagnet excitation current and when the resonance condition is fulfilled, part of the microwave energy is absorbed into the sample, with the result, the cavity resonator Q value changes. This Q variation is detected, amplified and recorded. When the magnetic field is varied while the frequency is kept constant an absorption signal is observed.

In addition, if an alternating magnetic field having the same direction as H and with an amplitude smaller than the absorption signal width is applied to H (i.e., magnetic field modulation) and H is varied, the detector output at each point on the absorption signal will form a sinusoidal wave having the same period as the alternating field and an amplitude in proportion to the gradient of the absorption line. This sinusoidal wave is amplified by a selective amplifier and phase detected throughout the absorption signal width. Thus a differential curve is derived from the absorption curve.

Since the crystal noise output is inversely proportional to the modulation frequency, the amplitude of a high frequency magnetic field modulation enables high sensitivity ESR measurements to be carried out. 100KHz/80 Hz modulation unit amplifies the ESR signal.

The oscilloscope screen (133 mm) provides a facility for mode check and observation of ESR signal. The DyT type recorder records the ESR signal on a chart of width 250 X 360 mm.

2.12: X-RAY DIFFRACTION STUDIES:

The X–ray diffraction is a powerful method to understand the structure of the compound. X–ray method, can determine the structure and symmetry properties of complexes. It gives information of inter atomic distance, bond angles and electronic arrangement in a complex. X-ray diffraction patterns [20] of the selected metal complexes in powder form were recorded on Philips PW 1050/70 X-ray diffraction machine attached with X-ray Diffractometer which is equipped with Cu-Ka target tube (\(A = 1.54056^\circ\text{A}\)) at C.F.C Kolhapur. The diffraction pattern was recorded at a scanning
rate of 2°/min and at a chart speed of 2 cm/min using the scale 1°=1cm. All calculations were performed by using computerized software program *Powder-X* developed by Cheng Dang and calculate parameter *h, k, and l.*
REFERENCES:


