3.1 Introduction

Instrumentation is an important part of every chemical analysis. New methodology and instrumentation is applied with the goal of providing information on the nature and composition of matter [1]. It becomes a requirement to employ several instrumental techniques to obtain the information about an analytical problem. Analytical chemistry allows the determination of a compound’s structure, either partially or totally, in samples of differing complexity. Finally, part of the role of analytical chemistry is to provide an interpretation of the results obtained. From a more applied point of view, analytical chemistry is the basis of chemical analysis, which corresponds to the study of the methods and their diverse techniques designed to solve the concrete problems of analysis. Further, there are two terms associated with chemical analysis, a procedure and a protocol. A procedure is a set of written directions telling us how to apply a method to a particular sample, including information on obtaining samples, handling interferents, and validating results. A method may have several procedures as each analyst or agency adapts it to a specific need. A protocol is a set of stringent guidelines specifying a procedure that must be followed if an agency is to accept the results. Protocols are common when the result of an analysis supports or defines public policy. Some of the instruments used in the thesis are X-ray diffraction, Transmission electron microscopy (TEM), Photoluminescence spectroscopy, TL spectroscopy and FT-IR spectroscopy.

3.2 X-ray diffraction

X-rays were discovered by the German Physicist Rontgen, he found that unlike
ordinary light X-rays were invisible, but they travelled in straight lines and affected photographic film in the same way as light. In 1912, the exact nature of x-rays was established and in the same year, the phenomenon of X-ray diffraction by crystals was discovered. X-ray diffraction (XRD) is an analytical technique looking at X-ray scattering from crystalline materials. Each material produces a unique X-ray "fingerprint" of X-ray intensity versus scattering angle that is characteristic of its crystalline atomic structure. In X-ray diffraction, the diffraction effects are observed when an electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the wavelength of the radiation [2]. The interatomic distance in the crystals and molecules amount to 0.15-0.4 nm which correspond to the wavelength of X-rays in the electromagnetic spectrum.

The X-ray diffraction occurs with the condition satisfying the Bragg’s law. The Bragg’s law can be derived as follows: Three X-rays beams shown in Fig. 3.1, are reflected, let us consider two rays out of the three.

![X-ray Diffraction Diagram](image)

**Fig.3.1** Derivation of Bragg’s law for X-ray diffraction
The two parallel incident rays 1 and 2 make an angle ($\theta$) with these planes. A reflected beam of maximum intensity will result if the waves represented by 1` and 2` are in phase. The difference in path length between 1 to 1` and 2 to 2` must then be an integral number of wavelengths, $\lambda$. We can express this relationship mathematically in Bragg’s law as:

$$2d \sin \theta = n \lambda.$$  \hspace{1cm} (1)

The process of reflection is described here in terms of incident and reflected (or diffracted) rays, each making an angle $\theta$ with a fixed crystal plane. Reflections occur from planes set at angle $\theta$ with respect to the incident beam and generates a reflected beam at an angle $2\theta$ from the incident beam. The possible d-spacing defined by the indices h, k, l are determined by the shape of the unit cell.

Rewriting Bragg’s law we get:

$$\sin \theta = \lambda/2d$$ \hspace{1cm} (2)

Therefore the possible $2\theta$ values where we can have reflections are determined by the unit cell dimensions. However, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located. Planes going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities.

From the diffraction peaks corresponding to ‘$2\theta$’ values, one can find the phase of the material by comparing the literature of Power Diffraction File (Joint Committee on Powder Diffraction Standards, Swathmore, USA). Knowing the $d$-spacing and
corresponding \( hkl \) planes, it is possible to calculate the lattice parameters of the materials.

The average crystal size can be calculated using Scherrer equation:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]  

(3)

Where \( d \) is the mean size of the crystallite, \( k \) is the shape factor and its value is taken as 0.9 for dimensionless shape factor, \( \lambda \) is the X-ray wavelength, \( \beta \) is the line broadening at half the maximum intensity (FWHM) in radians and \( \theta \) is the Bragg angle [3].

### 3.3 Transmission electron microscopy (TEM)

When electrons are accelerated up to high energy levels (few hundreds keV) and focused on a material, they can scatter or backscatter elastically or in elastically, or produce many interactions, source of different signals such as X-rays, Auger electrons or light. Some of them are used in transmission electron microscopy (TEM). Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

In 1923, De Broglie showed that all particles have an associated wavelength linked to their momentum:

\[
\lambda = \frac{h}{mv}
\]  

(4)
where $m$ and $v$ are the relativist mass and velocity respectively, and $h$ the Plank’s constant. In 1927, Hans Bush showed that a magnetic coil can focus an electron beam in the same way that a glass lens for light. Five years later, a first image with a TEM was obtained by Ernst Ruska and Max Knoll. In a TEM, the electrons are accelerated at high voltage (100-1000 kV) to a velocity approaching the speed of light (0.6-0.9 $c$); they must therefore be considered as relativistic particles. The associated wavelength is five orders of magnitude smaller than the light wavelength (0.04-0.008 Å). Nevertheless, the magnetic lens aberrations limit the convergence angle of the electron beam to 0.5° (instead of 70° for the glass lens used in optics), and reduce the TEM resolution to the Å order. This resolution enables material imaging and structure determination at the atomic level.

![Diagram of TEM](image.jpg)

**Fig. 3.2** Schematic outline of a TEM
3.4 FT-IR spectrometer

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis [4]. Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. It represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. No two compounds will produce the exact infrared spectrum as each different material is a unique combination of atoms. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.
The older infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its colours (frequencies).

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was developed by employing a simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Most of the interferometers employ a beam splitter whose function is to take the incoming infrared beam and divide into two optical beams. One beam is reflected from a fixed mirror. The other beam
reflects off of a flat mirror which moves a very short distance (typically a few millimetres) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (is a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. Decoding of individual frequencies is done via a well-known mathematical technique called the *Fourier transformation*. This transformation is done with the help of a computer which provides spectral information for analysis. A schematic outline of FT-IR spectrometer is given in Fig. 3.4.

![Schematic outline of FT-IR spectrometer](image)

*Fig. 3.4* Schematic outline of an FT-IR spectrometer
3.5 *Energy dispersive X-ray spectroscopy (EDX)*

EDX measurements were taken using FEI Quanta 250. The surface of the sample is made to strike with a finely focussed electron beam that generates X-ray fluorescence from the atoms in its path. The energy of each X-ray photon corresponds to the particular element which produces it.

3.6 *Luminescence spectroscopy*

Luminescence spectroscopy is based on the absorption and reemission of light by a molecule, ion or atom. It is of great analytical utility because the emitted light is characteristic of the electronic structure of the emitting species. In other words, luminescence spectroscopy technique is the measurement of fluorescence. The instrument used to measure fluorescence is called a fluorometer or fluorimeter. A fluorometer generates the wavelength of light required to excite the analyte of interest; it selectively transmits the wavelength of light emitted, then it measures the intensity of the emitted light. The emitted light is proportional to the concentration of the analyte being measured (up to a maximum concentration). Fluorometers employ monochromators (a spectrofluorometer), optical filters (a filter fluorometer), or narrow band light sources like LED’s or lasers to select excitation and emission wavelengths. There are two primary kinds of instruments that measure fluorescence: (i) filter fluorometers and (ii) spectrofluorometers. A filter fluorometer measures the ability of a sample to absorb light at one wavelength and emit light at a longer wavelength. A spectrofluorometer uses an excitation monochromator (device which includes a wavelength-dispersing component as opposed to a filter) and an emission
monochromator. Resolution is obtained with changeable fixed slits. The advantage of spectrofluorometers is that they allow for varying wavelength selection; the operator can scan a substance over a range of wavelengths. Both types of fluorometers work as follows:

The light source sends out light in the excitation wavelength range of the compound to be measured. The light passes through an excitation filter or monochromator, the light passes through and excites the sample; a portion of the incident light is absorbed by the sample and some fluoresce. The light emitted by the sample passes through the emission filter or monochromator which is kept at a right angle to the exciting light to minimize light scatter. The emission filter or monochromator further screens the light, the emitted light is measured by the detector, and the fluorescence value is displayed on the instrument. The schematic representation of a spectrofluorimeter is shown in Fig. 3.6.

The lamp or light source provides the energy that excites the compound of interest by emitting light. Light sources include xenon lamps, high pressure mercury vapor lamps, xenon-mercury arc lamps, lasers, and LED’s. Lamps emit a broad range of light; more wavelengths than those required to excite the compound. Lasers and LED’s emit more specific wavelengths.

Xenon lamps are very versatile and powerful, providing light output from 190-1200 nm. Mercury vapour lamp are usually more intense than xenon lamps, but the intensity is concentrated in wavelengths of the Hg spectrum. Monochromators and filters may be used in fluorimeters. A monochromator transmits light of an adjustable tolerance and the monochromator could be adjusted to select which wavelengths to transmit. The excitation filter is used to screen out the wavelengths of light not absorbed by the
compound being measured. This filter allows a selected band of light energy to pass through and excite the sample; it blocks other wavelengths, especially those in the emission spectrum. Stray light such as Rayleigh and Raman scatter is also emitted from the sample. In addition, stray background light may be present that has not passed through the sample. The emission filter screens out these components, allowing primarily wavelengths of light specific to the compound to pass through. The light detector used in fluorometer is most often a photomultiplier tube, though photodiodes are increasingly being used. The light passing through the emission filter is detected by the photomultiplier or photodiode. A photomultiplier tube (PMT) contains a material which creates an anode current proportional to light intensity. Typically, a chain of 6-12 dynodes, which amplify (multiply) the current, are present. High voltage is supplied to the PMT, which determines the intensity of the signal and also affects the noise. The higher the high voltage, the more sensitive the instrument and the greater the noise. Adjusting the operating level or sensitivity of a fluorometer involves finding the right balance between sensitivity and noise.

Fig.3.6 Schematic representation of a spectrofluorimeter
3.7 Thermoluminescence spectroscopy (TL)

The as prepared samples were first annealed at different temperatures and further they were irradiated with gamma rays. The irradiated samples were then recorded to see their thermoluminescence properties. TL glow curves were recorded by using a TL recording system (model TL1404, Indotherm Instruments) with a linear heating rate of 2.2 K/s.
References


