Chapter 2

Experimental techniques and data evaluation methods

2.1 Introduction

Since discovery of X-rays in 1895, various phenomena related to their interaction with atomic matter have been widely investigated both theoretically and experimentally. The experimental studies of photon-atom interactions in X-ray energy region (1-100 keV) are mainly related to photon scattering, radiative and non-radiative emission processes following photoionisation. These single, specific processes are characterised by the parameter ‘cross section’. The cross section is defined as ratio of the fraction of the incident photons which undergo specific interaction and the number of target particles per unit area of target. Alternatively, the cross section times the number of target particles per unit area of target is the probability that one incident photon will undergo the specified interaction while passing through the target. The interaction cross section determination, involves measurement of intensity of the interacting photons and emitted photons after that type of interaction, and knowledge of number of interacting atoms. It requires a source of monochromatic photons, a detection system capable of resolving mixed energies present in emitted photon beam and a target placed in an optimised source target-detector geometrical set up. Based on detection systems, two types of X-ray fluorescence (XRF) techniques are used in present work, viz., (i) Energy dispersive (ED) and (ii) Wavelength dispersive (WD). In the energy dispersive detection based XRF technique, various X-rays are distinguished on the basis of the ionization produced in the detector medium. In the wavelength dispersive XRF technique, the photons emitted from the target are diffracted from a crystal and dispersed at diffraction angles in accordance with the Bragg’s law. The diffracted X-rays are measured in sequential fashion at nearly spaced angles and an energy resolution better than energy dispersive detection system is achieved. A description of various geometrical set ups involving both of the ED and WD X-ray fluorescence techniques are given in the following sections.

2.2 Energy dispersive detection based XRF technique

In energy dispersive detection based X-ray fluorescence technique, the geometrical set up involves an arrangement of photon source, target and detector. Photon sources are to
facilitate X-ray beams of required energy for the measurement. These can be monochromatic or polychromatic in nature. Two types of photon sources are used in present photon atom interaction studies. These are radioactive isotope sources and X-ray generator. The incoming X-rays from the target interact with detector crystal to produce a distribution of voltage pulses proportional to incoming photon energy from the target. Hence, the crystal detector receives the non dispersed beam of photon from target and resolves them as separated X-ray energies. These separated X-ray energies from the target are further used by the multichannel analyser resulting in the spectrum. Two types of detection systems are utilized in present work: (i) LEGe and Si (Li) detectors (liquid nitrogen cooled) with conventional pulse processing modules, (ii) SDD (Peltier cooled) portable detector. These detectors exhibit the energy resolution in the range ~125-180 eV at 5.895 keV photon energy. Depending upon experimental considerations and availability of photon source and detector, different geometrical set ups are shown in Figs. 2.1(a-d). The point source geometries (Fig. 2.1(a-b)) can be used for measurements at forward and small angles. Whenever higher excitation efficiency is required, annular source geometries (Fig. 2.1(c-d)) having cylindrical symmetry can be used. The annular reflection mode is used for measurements at large angles. The precision and accuracy of experimental results depend upon the geometrical set up used and determination of various parameters related to the photon source, target and detector. In this section, details regarding the geometrical systems including photon sources, targets and detectors with associated electronics used for recording spectrum are given.

2.2.1 Geometrical set ups involving radioactive isotope source

The radioactive isotope sources provide unpolarised monoenergetic photons. The sensitivity of the system depends on the photon exciter system and radioactive isotope sources can facilitate selective excitation. The advantage of using the radioisotope sources is the portability and stability for provided radiations, without using any electrical power. In general, the flux from a radioisotope source consists of the characteristic X-rays of daughter element or γ-rays following de-excitation and is almost free of bremsstrahlung radiation. The sharp monochromaticity of γ-ray from the source is good for analysis. In actual practise a spread about few electrons volts due to nuclear recoil and thermal shifts appears. The most commonly used radioactive sources are $^{55}$Fe, $^{57}$Co, $^{109}$Cd, $^{133}$Ba, $^{137}$Cs and $^{241}$Am. These are available generally in two forms: (i) Point shape source, and (ii) Annular
A point source can be utilized, as shown in Fig. 2.1, in (a) transmission, (b) reflection mode geometrical setups. The annular source can be used, as shown in Fig. 2.1, in reflection based geometrical set ups in (c) direct excitation mode and (d) secondary excitation mode. A more flexible choice of the excitation energies of desired values can be obtained using secondary excitation mode, where a target excited by a highly radioactive source acts as secondary source. Characteristic X-rays from the secondary source are used as exciting X-rays.

![Diagram showing point source geometry in transmission mode and reflection mode, and annular source geometry in direct and secondary modes.](image)

In the present measurements, the incident photons from annular sources of $^{55}$Fe (50 mCi, AEA technology QSA GmbH, Germany) and $^{241}$Am (300 mCi, DUPONT, US) isotopes were utilized.
The $^{55}$Fe annular radioisotope is in the form of a circular flat ribbon of 34-mm diameter and 4 mm width and electrodeposited as iron metal on a copper ring with tungsten alloy backing sealed in a welded stainless steel capsule with beryllium window as shown in Fig. 2.2(a). To obtain monochromatic beam of 5.895 keV ($^{25}$Mn-$K\alpha$) photons the source is covered by $^{24}$Cr ($B_K = 5.9892$ keV) foil which absorbs Mn-$K\beta$ (6.492 keV) X-rays from source. Using the monochromatic Mn-$K\alpha$ beam RRS measurements were performed. The annular source was converted to point source by covering the source with thick foil of copper and a small spot was left acting as a point source. The characteristics of the radioisotopes sources used in present measurements are given in Table 2.1.

Table 2.1: Characteristics of radioisotope sources used in present measurements.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Decay mode</th>
<th>Half-life</th>
<th>Type of radiation</th>
<th>Photon energy (keV)</th>
<th>Emission probability $[1]$ per 100 decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>Alpha decay</td>
<td>432.7 y</td>
<td>Np-$L\beta$ X-ray</td>
<td>11.9</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Np-$L\alpha$ X-ray</td>
<td>13.9</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Np-$L\beta$ X-ray</td>
<td>17.6</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Np-$L\gamma$ X-ray</td>
<td>20.9</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\gamma$-ray</td>
<td>26.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\gamma$-ray</td>
<td>59.5</td>
<td>35.6</td>
</tr>
<tr>
<td>$^{55}$Fe</td>
<td>Electron capture</td>
<td>2.70 y</td>
<td>Mn-$K\alpha$ X-ray</td>
<td>5.89</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn-$K\beta$ X-ray</td>
<td>6.49</td>
<td>2.86</td>
</tr>
</tbody>
</table>

The $^{241}$Am source is in annular form of a circular flat ribbon of 30 mm diameter, 4 mm width and 1.56 mg/cm$^2$ thickness. The source is sealed in 40 mg/cm$^2$ Al tubes with window and has a tungsten shield at bottom as shown in Fig. 2.2(b). The source is designed for
applications where Np L X-rays are also used and ~6.7 x10^7 γ-ray photons per sec steradian of 59.54 keV energy were obtained. To get the monochromatic beam of 59.54 keV γ-ray photons, the 26.345 keV γ-ray and Np L X-rays were absorbed by the annular shaped Cu-Al graded absorbers. Reflection mode arrangement (Fig. 2.1c) is used for Rayleigh scattering measurements at back angles. For Rayleigh scattering measurements the required incident photon energy is obtained by using secondary excitation mode (Fig. 2.1d). An annular foil of \(^{60}\)Nd/\(^{66}\)Dy element acting as secondary source was excited by the 59.54 keV γ-ray photons from \(^{241}\)Am source. The resulting characteristic K X-rays were used for the scattering in the targets. Figs. 2.2 (a) and (b) show the detailed specifications and the \(^{241}\)Am and \(^{55}\)Fe radioisotopes used in the present geometries.

**LEGe and Si(Li) Detectors**

An LEGe detector in horizontal configuration [100 mm\(^2\) × 10 mm, 8-μm Be window and FWHM = 150 eV at 5.895 keV, Canberra, US] and a Si(Li) detector [80 mm\(^2\) × 5 mm, 25-μm Be window and FWHM = 175 eV at 5.895 keV, Canberra, US] under reversed biased condition and low leakage current have been used for the detection purpose. The mean energy required to produce an electron-hole pair in Ge diode is 2.97 eV and in Li drifted Si diode is 3.76 eV. As smaller amount of energy is required in Ge diode, LEGe gives a better energy resolution as compared to the Si (Li) detector. The LEGe detector is used when good efficiency is required in energy region 1 to few hundred keV, whereas Si (Li) detector shows efficient performance in energy range of 1-40 keV.

The sensitive volume in these detectors is circular cylinder, centred behind Be window, mounted onto a cold Cu rod dipped in liquid nitrogen at the other end in order to reduce the thermal generation of charge carriers. The detectors are equipped with a high voltage inhibit circuit involving a platinum resistance temperature warm-up sensor which disable the high voltage power supply in case of accidental detector warm-up. The block diagram of detection system used in the present measurements is shown in Fig 2.3. A brief description of the essential parts involving the electronics in detection system is given below.

(a) Detector Bias supply

A portable Bin/power supply (CANBERRA, model 3106D) with six standard nuclear instrument module (NIM) for the high voltage power and the preamplifier power supply was used in case of LEGe and Si(Li) detector. The output voltage of Canberra power supply (model 3106D) is constantly changeable from ±30 V dc to ±6000 V dc and suitable
for all types of detectors requiring up to 6 kV bias and up to 300 μA of current. The reading of output voltage is measured by a three-digit voltmeter and displays on LED panel on power supply. The recommended operating bias voltage of 500 V with negative polarity was supplied to the LEGe and Si(Li) detector using 0-6 kV high voltage power supply (CANBERRA, model 3106D). With the help of a high voltage filter network, ripples from power supply and interference picked up by the cable between preamplifier and high voltage supply are eliminated from bias supply.

Fig. 2.3: Block diagram of the experimental setup used for the X-ray detection.
(b) Preamplifier

The absorption of a photon in the solid state detector produces weak current pulses to feed the amplifier. The preamplifier amplifies these weak pulses with possible added noise and gives suitable output pulses for further amplification for pulse height analysis. Solid state detectors are generally equipped with charge-sensitive preamplifiers. A charge sensitive loop involving a field effect transistor (FET) input operational amplifier with capacitive feedback, integrates each current pulse. Two general types of charge-sensitive preamplifiers in common use are the resistive feedback preamplifier and the pulsed-reset preamplifier or pulse optical coupled preamplifier. In resistive feedback preamplifier, the reset charge-restoration method is used to discharge the integrator, whereas in pulse optical preamplifier pulse light form an LED is used to discharge the integrator. A low-noise charge-sensitive optical pulsed coupled feedback preamplifier (Model 2008BSL, CANBERRA, US) has been used in LEGe and Si(Li) detector. The block diagram of the present used optical-coupled preamplifier is shown in Fig. 2.4. The charge from each detected X-ray photon is allowed to accumulate on the feedback capacitor to produce a step output of pulse at the preamplifier output. As before, the amplitude of each step, or pulse, is proportional to the detected photon energy. These steps produce a random step output and saturate the preamplifier, if left unchecked. The signal from preamplifier fed to spectroscopy amplifier and the amplifier output is further passed to the multichannel analyzer for processing of pulse height analysis.

![Block diagram of optical-coupled preamplifier](image)

Fig. 2.4: The block diagram of the optical-coupled preamplifier.
(c) Spectroscopy amplifier

Spectroscopy amplifier have two main purposes: (i) to amplify the preamplifier pulses (a few mV) to a suitable size for pulse-height analysis (a few volts), (ii) shaping the pulse to a convenient form for further processing by minimizing the effect of noise. Unipolar shaping is achieved using one differentiator and two active filter integrators. The spectroscopy amplifier (Model 2022, CANBERRA, US) used for Si(Li) detector provides improved pulse symmetry, minimum sensitivity of output amplitude to variations in detector rise time and maximum signal to noise ratio. The choice of the proper shaping time constant is generally a compromise between operating at a shorter time constant for accommodation of high count rates (~3000 counts/sec) and operating with a large time constant for a better signal to noise ratio. It accepts pulses with rise times < 650 ns and decay times > 40 $\mu$s. Six integrate and differentiate time (pulse shaping time) constants: 0.5, 1, 2, 4, 8 and 12 $\mu$s are switch selectable to provide optimum shaping for resolution and count rate. At low counting rates (< 100 counts/sec), the optimum value for shaping time is 10 $\mu$s for Si(Li) detector. In case of LEGe detector, a spectroscopy amplifier (Model 2026, CANBERRA, US) is employed in which the variable pole-zero cancellation network can be adjusted to match the preamplifier output decay time < 40 ns. This drastically reduces undershoot after the first differentiator and improves the overload and count rate characteristics. Base line restoration is used to compensate effect of base line shift on a unipolar signal, caused by uncancelled RC inter-stages in the amplifier. The dc level of the output, adjustable up to ±100 mV, provides unipolar and bipolar amplifier output pulses with output impedance of less than 1$\Omega$.

(d) Multichannel analyzer (MCA)

Multichannel analyzer (Model S100, Multiport II, CANBERRA, US) receives output positive unipolar pulse from spectroscopy amplifier for pulse height analysis. An MCA basically consists of an analogue to digital converter (ADC), memory and display units. The ADC digitizes the amplitude of the unipolar output pulses from the spectroscopy amplifier to obtain processed energy spectrum of the X-ray photons incident on the detector. The ADC used in the present work has input impedance of 1 k$\Omega$ and accepts positive unipolar or bipolar pulses. The ADC has full scale conversion gain of 256, 512, 1K, 2K, 4K, 8K and 16K channels and conversion rate of 100 MHz on all gains. The number of events in each channel of the MCA is counted which gives energy spectrum of
the photons as viewed by the detection system. The output signal from ADC is fed to USB port of a PC equipped with a software program (Gennie 2000, CANBERRA, US) installed. A number of functions such as data acquisition, display of spectra and linear energy calibration are performed by Gennie 2000. The efficacy of shielding encapsulating the detector was studied by recording background counts for very large duration to take care of statistics.

2.2.2 Geometrical set up involving portable X-ray tube

The X-ray tubes are available with variety of anode materials such as $^{24}$Cr, $^{29}$Cu, $^{42}$Mo, $^{45}$Rh, $^{46}$Pd, $^{47}$Ag, and $^{74}$W, coupled with the facilities of energy and intensity variation. The tube voltage is chosen up to the two times the absorption thresholds of the highest energy lines to be excited. The generated photon flux contains the characteristic X-rays of the anode material along with bremsstrahlung continuum due to retardation of electrons inside anode material. Such photon flux is useful in exciting a broad range of elements with good efficiency. The trace elemental analysis becomes difficult with the bremsstrahlung continuum overlapping the region for fluorescence peaks for corresponding elements, as the background becomes very high. The monoenergetic photon beam can be obtained by using secondary target in conjunction with X-ray tube and suitable critical absorber. An X-ray tube known as Mini-X (Amptek, US) is used as source of excitation. Mini-X is designed by using a grounded Ag anode, providing variable current and voltage via USB, and ease of operation. It features a 50 kV/80 µA power supply, a 0.75 µm Ag transmission target and 127 µm Be end window. An adapter providing the 12 VDC power is provided. A flux of $\sim10^6$ counts/s/mm$^2$ on the axis at a distance of 30 cm (50 keV/1 µA) is obtained. In present measurements for phytoremediation of soil by plants, different elements present in the plant sample targets were excited using Mini X-ray tube giving K X-rays of Ag and bremsstrahlung radiation at 30 kV. The present geometry uses direct excitation in back reflection mode having angle of incidence equals to 45° and 0° emission angle. The characteristic X-rays from excited elements in target were detected by a peltier cooled Silicon drift detector. The X-ray tube-target-detector arrangement is shown in Fig. 2.5. In this portable set up a small silicon drift (SDD) detector [80 mm$^2 \times 5$ mm, 25-µm Be window and full width at half maximum (FWHM) = 125 eV at 5.895 keV, Amptek, US] has been used for measurements. Portability lies in the fact that in SDD the detecting active crystal is cooled using peltier effect. Both the Mini X-ray tube and SDD are mounted on a thick plate using screws and
Fig. 2.5: The reflection mode geometry involving X-ray tube and SDD.

Fig. 2.6: SDD detector inner view.
are operated from a laptop using software mini-X controller and ADMCA, respectively, connected through USB cables.

**Silicon drift detectors (SDD)** consists of a fully depleted thin silicon cylinder in which an electric field parallel to the surface is applied, and under the effect of this field electrons moves towards the anode located at the centre [2,3]. The field is produced by many concentric ring electrodes and the anode is directly connected to an integrated FET working as a current preamplifier. The inner view and process is shown in the Fig. 2.6. An SDD detector gives its best performance at a temperature around \(-20^\circ C\). The PC5 power supply for Peltier cooled SDD detector and preamplifier was manufacturally inbuilt in the SDD detector.

**Detector Bias supply**

The detector is given recommended 160 V reverse bias voltage. PC5 power supply can provide high voltage bias to the detector up to 1500V and power for the thermoelectric cooler (with closed loop temperature control). It also provides the low voltages for the preamplifier (±5V or ±8.5V). The signal from the preamplifier is processed by digital pulse processing unit. Digital pulse processor (DP5, Amptek, US) used with Peltier cooled SDD is a compact device replacing both the shaping amplifier and multichannel analyser and digitizes the output signals of preamplifier used traditionally in analog spectroscopy system.

**Digital Pulse processor**

The block diagram of DP5 system is shown in Fig. 2.7. The DPP (i) digitizes the preamplifier output, (ii) applies real-time digital processing to the signal, (iii) detects the peak amplitude (digitally), and (iv) bins this value in its histogram memory generating an energy spectrum. The spectrum is transmitted over the DPP’s interface to the user’s computer. The DP5 provides various distinct advantages over analog systems, including better performance as better resolution and higher count rates, flexibility due to available options for configuration, improved stability and reproducibility. The various components shown in block diagram are given below.

a) **Analog Prefilter**

The DP5 is designed to process signals coming directly from a charge sensitive preamplifier used with solid-state radiation detectors. These signals typically have (i) a
small amplitude ~ a few mV, (ii) a fast rise times (tens of ns and slow decay time ~ hundreds of $\mu$s), and (iii) the small pulses ride up on one another as the signal pulses accumulate. The analog prefilter prepares the signal so it can be accurately digitized. The prefilter applies: (i) a high pass filter with a 3.2 $\mu$s time constant, so that the pulses no longer ride up on one another, (ii) a coarse gain so that the largest pulses are ~1 V (to maximize the ADC resolution), and (iii) a DC offset so that the signal always falls within the range of the unipolar ADC. The 12-bit ADC digitizes the output of the analog prefilter at a 20 or 80 MHz rate. This stream of digitized values is sent, in real time, into the digital pulse shaper.
**b) Digital Pulse Shaper**

The ADC output is processed continuously using pipeline architecture to generate a real time shaped pulse. There are two parallel signal processing paths inside the DPP, the fast and slow channels. The slow channel of the DPP is optimized for accurate pulse height measurements. It utilizes trapezoidal pulse shaping, with a typical output pulse shape shown in Figure 2.8. This shape provides a near optimum signal to noise ratio for many detectors. Relative to conventional analog shapers, the trapezoid provides lower electronic noise and, simultaneously, reduced pulse pile-up.

![DPP Trapezoidal Response](image)

**Fig. 2.8: Pulse shape produced by slow channel pulse shaper**

The rise/fall time (the rise and fall must be equal) and the duration of the flat top over many steps can be adjusted. A DPP with 2.4 \( \mu s \) peaking time will be roughly equivalent to a semi-Gaussian shaper with a 1 \( \mu s \) time constant. A semi-Gaussian amplifier with shaping time \( \tau \) has a peaking time of \( 2.2\tau \) and is comparable in performance with the trapezoidal shape of the same peaking time. The shortest peaking times minimize dead time, yielding high throughput and accommodating high count rates, but the electronic noise usually increases at short peaking times. The optimum setting will strongly depend on the detector and preamplifier. The electronic noise of a detector will generally have a minimum at some peaking time known as the ‘noise corner’. At peaking times shorter or longer than this, there is more noise and hence degraded resolution. If this peaking time is long relative to the rate of incoming counts, then pulse pile-up will occur. In general, a detector should be operated at a peaking time at the noise corner, or below the noise corner as necessary to accommodate higher count rates.
The fast channel is optimized to obtain timing information: detecting pulses which overlap in the slow channel, measuring the incoming count rate, measuring pulse rise times. The fast channel is used for pile-up reject logic (rejecting pulses which are so closely spaced that they cannot be distinguished in the slow channel) and for determining the true incoming count rate (correcting for events lost in the dead time of the slow channel). The fast channel also utilizes trapezoidal shaping, but the peaking time is commendable to either 100 ns or 400 ns.

c) Pulse Selection Logic

The function of pulse selection logic in DPP uses thresholds to identify the pulses. Both of the fast and slow channels have their independent thresholds. The DPP uses the slow channel threshold and events having lower amplitude than the slow channel threshold are ignored. The slow channel threshold is the equivalent of a low-level discriminator (LLD). Fast channel threshold also functions as an LLD. In fast channel the noise is higher, so the threshold is set just above the noise. It is used for several functions as (i) the rate of events over the fast threshold is the DPP’s measurement of the incoming count rate (ICR), (ii) Pile-Up Rejection (PUR) logic identifies events which overlap in the slow channel but are separated in the fast channel, (iii) Rise Time Discrimination (RTD) uses the amplitude of the fast channel signal to measure the current at the beginning of a pulse. It also contains logic for an external gating signal. The ADMCA software includes an Auto Tune function to set these.

The histogram memory operates as in a traditional MCA. When a pulse occurs with a particular peak value, a counter in a corresponding memory location is incremented. The result is a histogram, an array containing, in each cell, the number of events with the corresponding peak value. This is the energy spectrum and is the primary output of the DPP. The DP5 includes hardware and software to interface between these functions and the user’s computer. The communications interfaces are the primary means to control the DP5 and to acquire the data. The DP5 supports USB, RS232, and Ethernet interfaces. The unit sends three classes of data packets back to the computer: status packets (which include the counter outputs), spectral data packets (which contain the MCA output array), and oscilloscope packets. The DP5 also includes a power interface. It takes a loosely regulated 5V DC input and generates the various levels required by the circuitry (± 5.5V, 3.3V, 2.5V). Amptek’s ADMCA software provides the quickest way to control and readout the DP5. It lets one start and stop data acquisition, reads and displays the data, performs very simple analyses, and saves the data in an ASCII format.
2.3 Wavelength dispersive detection based XRF technique

The wavelength dispersive detection based XRF technique differs from energy dispersive system by the presence of an analysing crystal used in between the target and detector. The beam of photons having multiple energies emitted from target after excitation is allowed to fall on an analysing crystal known as mono-chromator. The lattice planes of the crystal reflect the photons and each wavelength is diffracted according to Bragg’s law, \( n\lambda = 2ds\sin\theta \), where \( n \) is integer determined by the order of diffraction, \( \theta \) is the scattering angle, \( d \) is the interplanar length of crystal’s lattice and \( \lambda \) is the wavelength of incident radiation. The intensity of Bragg diffracted X-rays were scanned by the detector as function of scattering or granzing angle \( \theta \). Since in the process wavelength plays the role due to the wave phenomenon, it is known as wavelength dispersive system. The schematic for the available wavelength dispersive spectrometer S8 TIGER (Bruker, Germany) [4] installed at SAIF, Panjab University, Chandigarh is given in Fig. 2.9.

This set up involves the most compact beam path to attain the optimum detection limits, resolution, reliability and best sensitivity. It is equipped with the high intensity Rh anode X-ray tube, combination of four collimators to obtain a parallel beam, up to six different analyser crystals to separate the respective wavelength, and a specific detector to allow the recording of the fluorescent signal. Fig. 2.10 shows the main components of WDXRF set up. The combination of X-ray source and primary beam filter assured the finest excitation of each element in the sample. The low background mask changer (of size 23, 28, 34 mm) prevented the unwanted signals from the sample cup to move towards the detector. The vacuum seal separates the sample chamber from the goniometer chamber. The goniometer chamber is always in vacuum, so during measurement sample chamber is evacuated.

A robotic arm is installed in set up to change the samples placed in the sample holder. Collimator masks eliminate the X-rays coming from the sample holder surface being excited with the sample. The X-rays from the sample incident to the crystal are collimated as parallel rays using the solar slits consisting of a no of parallel rows of slats. A 4-position collimator changer is equipped in set up. A set of collimators improve the resolution for incoming rays. Various monochromators are fitted on crystal changer dispersing the multiple wavelength spectrum into particular wavelength for corresponding element. A high-precision goniometer with two independent stepper motors for separate \( \theta/2\theta \) drive is equipped with modern electronics. In this state-of-art equipment, precise alignment attained for all drives and the swift adjustment of the crystal (\( \theta \)) and the detector (\( 2\theta \)) in the...
Fig. 2.9: Schematic diagram of WDXRF setup.

goniometer is the most crucial step. The standard collimators with aperture angles of 0.23° and 0.46° are pre-fitted depending upon the application for the sample under study; two additional collimators can also be installed to optimize the measurement parameters. When
the light elements are analyzed using the low resolution collimators, the intensity increases significantly without a loss in angle resolution, e.g., the collimator of 1.0° and 2.0° are advantageous for light elements like Be, B and C. For high-resolution measurements using the S8 TIGER, two collimators of 0.17° and a 0.12° with LiF(420) crystal are available.

### 2.3.1 End-window X-ray tube

The S8 TIGER spectrometer consisted of an end-window Rh-anode X-ray tube, as shown in Fig. 2.11, which is supplied maximum tube current of 150 mA and high voltage of 60 kV at a output power of 4 kW. In the end window X-ray tube anode has a positive high voltage and the beryllium window is located on the front end of the tube. The cathode is set around the anode in a ring (angular cathode) and is set at zero voltage. The electrons originating from the heated cathode are accelerated towards the electrical field lines on the anode. Due to the developed potential difference between the positive anode and surrounding, electrons get backscattered to the anode. This deceleration of electrons produce X-rays and a major part of electrical energy is converted to heat, which is cooled by using a chiller maintaining the flow of deionized water. Both the characteristic and bremsstrahlung radiations from the Rh anode are used to excite the sample elements.

![End-window X-ray tube](image)

**Fig. 2.11: End-window X-ray tube.**

### 2.3.2 Diffraction crystals

The WDXRF technique is capable of detecting elements having \( Z > 4 \). The theoretically possible values of angle \( \theta \) existed between 0° and 90° but in actual practice it value exists in between 2° to 75° in the given setup, therefore, admitted values of \( \sin \theta \) is between 0 and +1. Applying the Bragg's equation, we get
Thus only few elements can be detected for a crystal with a lattice plane spacing $d$. Therefore, it is necessary to have a variety of crystal types with different $2d$ values to detect the entire range of elements across the periodic table. The specifications of diffraction crystals used in the WDXRF setup are given in Table 2.2.

### 2.3.3 Detection systems

Two types of detectors are used in S8 TIGER WDXRF set up, a gas proportional counter and a scintillation counter. Proportional counter is used for the detection of light element and

Table 2.2: Various types of crystals used in S8 TIGER WDXRF spectrometer.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Name</th>
<th>Element range</th>
<th>2d-value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF(220)</td>
<td>Lithium fluoride</td>
<td>$\geq 23$ V</td>
<td>0.2848</td>
</tr>
<tr>
<td>LiF(200)</td>
<td>Lithium fluoride</td>
<td>$\geq 19$ K</td>
<td>0.4028</td>
</tr>
<tr>
<td>PET</td>
<td>Pentaerythite</td>
<td>$^{13}$Al - $^{22}$Ti</td>
<td>0.874</td>
</tr>
<tr>
<td>XS-55</td>
<td>Multilayer [W/Si]</td>
<td>$^{8}$O - $^{14}$Si (C)</td>
<td>5.5</td>
</tr>
<tr>
<td>XS-N</td>
<td>Multilayer [Ni/BN]</td>
<td>$^{14}$N</td>
<td>11</td>
</tr>
<tr>
<td>XS-C</td>
<td>Multilayer [TiO2/C]</td>
<td>$^{12}$C</td>
<td>12</td>
</tr>
</tbody>
</table>

scintillation counter is used for heavy ones. The scintillation counter is located behind the flow counter with a separation of 0.1 mm Al foil with an angle scope of $17^\circ$-$152^\circ$ outside the chamber. Gas proportional counter consists of a thin anode wire mounted along the axis of metallic cylinder at its centre. A suitable mixture of gas i.e. P10 (90 % Ar + 10 % CH₄) is flowed inside the tube at constant rate to eliminate the fluctuations in peak positions in the pulse height spectrum. The primary electrons produced due to incidence move along the increasing electric field to further cascade the secondary electrons and produce measurable pulse towards pre-amplifier. There was a continuous supply of P10 gas to the flow counter. Inside the spectrometer chamber, the flow counter has an angle scope of 0° to 115°. The flow counter is located inside the vacuum chamber and has an entrance window made of a thin, Al-coated foil that be selected with a thickness of 0.6 $\mu$m or 0.3 $\mu$m. This allows optimum measurement of the light elements from Be to Na.

Scintillation counter made up of a thallium (TI) doped sodium iodide crystal (NaI) followed by photomultiplier tube producing a signal and feeding to preamplifier. The density of
crystal was so high that it absorbed all the high energy X-ray photons. Incoming X-rays pass through the flow counter, 0.1 mm thick vacuum seal and a 0.2 mm Be window when approach scintillation counter. Energies above ~ 4.5 keV (Cr Kα1) are detected by this counter. It can be moved from 17° to 152°. Electronic pulse processing unit counts the pulses produced in the detector by X-rays. The preamplifier amplifies and shape the flow counter’s signals before further processing as voltage pulses in a main sine amplifier and discriminator. A discriminator window set lower and an upper level pulse-height thresholds, pulse heights lying within these limits are only the recorded ones. Hence, the higher order peaks or interference radiation with pulse heights beyond the window are suppressed and are not counted. In this way, the undesirable pulses are discriminated and the background is reduced. Amplifier shapes the pulses. All the instrumental operations of S8 TIGER spectrometer are controlled by Spectra\textsuperscript{plus} software [5]. Spectra\textsuperscript{plus} [5] software interface optimize the peak acquisition time and calculate the time required to achieve an average selected detection limit. Spectra\textsuperscript{plus} software automatically determines the elemental concentration in target samples using Lachance-Traill formula [6].

### 2.4 Target preparation methods

Targets used in present measurements can be prepared in the form of thin films deposited on Mylar film, thick and thin foils, or self-supporting pellets depending upon the materials. Spectroscopically pure, self-supporting targets of various types in foil and pellet form were used in the present measurements. The term ‘Spectroscopically pure’ means the impurity level of the order of 1ppm. Further the intensity of emitted X-rays depends upon the surface roughness, homogeneity, particle size and shape of the sample. The thickness of samples plays very important role as the absorption coefficient depends upon effective thickness, incident and emergent angles. The irregularities at the surface of sample act as heterogeneities in the path of incident photon and largely affecting secondary fluorescent X-rays. To get significant information from the experiments, the target should have enough number of photon interaction centres so that sufficient numbers of interaction events must be recorded within the reasonable interval of time. Target thickness is expressed in unit of mass thickness (μg/cm\textsuperscript{2}) for thin targets which is closely associated with the density of interaction centres and is a more fundamental quantity, thus, having the effect of normalizing materials of different mass densities as this particular unit is independent of the form of element. For preparing self-supporting uniform targets/secondary exciters of
desired thickness without loss of the material, the rolling machine (Durston rolling mill, DRM 100 mm with Toshiba inverter, Tosvert VF-NC1, U.K) has been used (Fig. 2.12).

Fig. 2.12: Rolling mill used for making thin self-supporting targets foils.

Fig. 2.13: (a) The manual (Paul-Otto-Weber Co., Germany) pellet making machine and (b) automatic spex pelletizer (Insmart, Hyderabad).
Thin targets of different pure elements and compounds (thickness 50-300 µg/cm², Micromatter, USA) evaporated on 3.5 and 6.3 µm Mylar backing were used for detector efficiency measurements [7]. The uncertainty in the thickness of these standard foils is ±5% as quoted by manufacturer. Few layers of the thick targets were capable of absorbing the incident radiations through them, only a thin surface layer contributes to the measured elemental X-rays. So, as to reduce the surface effects (roughness, irregularities) and to prepare self-supporting pellets, only the desired amount of finely pulverized sample was used. The self-supporting pellets of one inch diameter of powder sample were made using a die of stainless steel (Paul-Otto-Weber Co., Germany). A constant force of 50-120 kN was applied to the die head by using hydraulic pressure so as to get pellet of uniform thickness and to reduce the surface effects, which otherwise lead to a variation in the count rate at low X-ray energies. Fig. 2.13 shows the manual (Paul-Otto-Weber Co., Germany) and automatic (Insmart, Hyderabad) pellet making machines used to make pellets which have been used in the present investigations. To get rid of moisture, the deliquescent pellets were dried under heat of incandescent lamp and then their counts were monitored under vacuum before taking the final run. In the compound pellet targets, matrix absorption is the factor which needs to be considered as it arises from the absorption of both incident and emitted radiations from other elements present in the compound target except target of interest in the sample. Enhancement is significant only if the characteristic X-rays of an interfering abundant element lies above the absorption edge of the element of interest. If the target is composed of elements of low atomic number then this effect can be safely ignored. In such cases, only matrix absorption contributes notably. The direct relationship between the characteristic X-ray intensity and the elemental concentration is annulled by the matrix effects. Therefore, special effort must be made to overcome the matrix effects in a compound target for which accurate quantification is desired. Hence those compound targets were selected in which inter elemental excitation was minimal. Both thick (~mg/cm²) and thin (~µg/cm²) targets were used in present experimental investigations. In order to minimize multiple scattering in the target, and bremsstrahlung from photoelectrons and Compton electrons produced in the target, thin scattering target are used such that \( \mu t \ll 1 \), where \( \mu \) is the attenuation coefficient and \( t \) is the target thickness. Depending upon the target dimension, the source to target and target to detector distances is optimized in order to get good quality of photon interaction data. The targets for Ga and Hg are prepared by sandwiching the element between two layers of 10µm thick Mylar.
2.5  Relationship between fluorescent/scattered photon intensity and cross section

The evaluation procedure for various processes is related to the observed intensity of the detected fluorescence/scattered X-ray peaks, which is count rate recorded by the detector. In classical physics, the intensity refers to amount of energy crossing the surface of unit area per unit time. The mass of an element, cross section for a process at incident energy, and other geometrical factors affect the observed intensity intensity. 

A simple work out for the intensity of fluorescent/scattered photons is presented.

Supposing \( I_0 \) the intensity of X-ray photons emitted from X-ray source within the solid angle \( d\Omega \) and \( \theta_i \) is the incident angle at which X-ray photons strike the surface of target specimen containing single element with thickness \( t \), as shown in Fig. 2.14. \( dx \) is supposed as an infinitesimally small thickness element, through which X-ray covers a path \( dx/\cos\theta_i \). The intensity of photons that reach a point P at the depth, \( x \), in the target is given by

\[
I_1 = I_0 G_1 \exp\left(-\frac{\mu_1}{\cos\theta_i} \rho x \right) d\Omega_1
\]  

(2.2)

Fig.2.14: Schematic diagram for derivation of incident and emitted X-ray intensities.
where, \( G_1 \) term includes all geometrical factors for the incident photon, \( \mu_i \) is the mass attenuation coefficient for the incident photons and \( \rho \) is the density of the target element. The photons will be emitted isotropically in all directions \( i.e., \) into solid angle of \( 4\pi \) steradian. The rate of photons emitted into differential solid angle \( d\Omega_2 \) towards the detector is written as

\[
I_2 = I_1 \frac{d\Omega_2}{4\pi} \sigma \rho \, dx
\]  

Where, \( \sigma \) denotes the X-ray florescence cross-section. The rate of X-rays emitted towards the detector after absorption in the path length \( x/\cos \theta_2 \) is

\[
I_3 = I_2 \exp \left( -\frac{\mu_2}{\cos \theta_2} \rho \, x \right)
\]

where, \( \mu_2 \) is the mass attenuation coefficient at emitted photon energy. \( \varepsilon \) is the detector efficiency and \( \theta_2 \) is the angle of emission. The X-rays from the target element will reach the detector at the rate given as

\[
I = G_2 \, I_3 \, \varepsilon
\]

The factor \( G_2 \) takes into account the geometric factor for emitted photons reaching the detector. The detected count rate for solid angle \( d\Omega_1 \) and \( d\Omega_2 \) is

\[
I \, d\Omega_1 \, d\Omega_2 = I_0 \, G' \frac{d\Omega_1 \, d\Omega_2}{4\pi} \sigma \rho \varepsilon \left[ \exp \left( -a \, \rho \, x \right) \right] \, dx
\]

where, the product of \( G_1 \) and \( G_2 \) is replaced by \( G' \) and \( a = (\mu_i/\cos \theta_1 + \mu_2/\cos \theta_2) \). As the terms in the above equation are nearly constant over the entire range defined by finite geometry, so, \( d\Omega_1 \) and \( d\Omega_2 \) can be replaced by \( \Omega_1 \) and \( \Omega_2 \), respectively. A more explicit relation can be obtained by deleting \( \Omega_1 \) and defining total incident photon rate \( (I_0) \) instead of the total incident photon rate per steradian. By integrating over the thickness ‘\( dx \)’ and multiplying the denominator by ‘\( t \)’, the equation for the total rate of characteristic X-ray photons simplifies as

\[
N = I_0 \, G \, \sigma \, \rho \, t \varepsilon \left[ \frac{1-\exp (-a \, \rho \, t)}{a \, \rho \, t} \right]
\]
where, \( G = G' \int d\Omega_2 \) and is called the geometric factor, \( \Omega_2 \) is the detector solid angle and \( \rho t \) is thickness of the target in g/cm\(^2\), which is normally denoted as ‘m’. The factor in square bracket is the target self-absorption correction factor and takes into account absorption of the incident and emitted photons in the target and is denoted by \( \beta \).

\[
\beta = \frac{1 - \exp(-\lambda \rho t)}{\lambda \rho t} = \frac{1 - \exp\left(-\left(\frac{\mu_1}{\cos \theta_1} + \frac{\mu_2}{\cos \theta_2}\right)m\right)}{\left(\frac{\mu_1}{\cos \theta_1} + \frac{\mu_2}{\cos \theta_2}\right)m} \quad (2.8)
\]

Therefore relation between the observed count rate and other parameter can be written as

\[
N = I_0 G \varepsilon \sigma m \beta \quad (2.9)
\]

where \( I_0 \) is the intensity of the incident photons falling on target visible to the detector, \( G \) is the geometrical factor related to the source-target and target-detector solid angles, \( \varepsilon \) denotes the detector efficiency corresponding to energy of the observed photons, \( \beta \) is self absorption correction factor accounts for the absorption of the incident and emitted photons in the target and \( m \) is the mass in g/cm\(^2\) of the target element. In case of compound target containing more than one element, the expression for the absorption correction factor is given by

\[
\beta = \frac{1 - \exp\left[-\sum_i \left(\frac{\mu_{i1}}{\cos \theta_{i1}} + \frac{\mu_{i2}}{\cos \theta_{i2}}\right)m_i\right]}{\sum_i \left(\frac{\mu_{i1}}{\cos \theta_{i1}} + \frac{\mu_{i2}}{\cos \theta_{i2}}\right)m_i} \quad (2.10)
\]

where \( i \) stands for different elements present in the target. \( \mu_{i1} \) and \( \mu_{i2} \) are the mass attenuation coefficients for the incident and the emitted X-rays of \( i \)th element of interest present in the target, respectively. The values of \( \mu \) are used from the tables of Storm and Israel [8] and XCOM [9]. The values of \( \mu \) at desired energy \( (E) \) are interpolated by assuming a relation showing energy dependence of \( \mu = aE^\eta \) and using relations

\[
\mu(E) = \mu(E_1) \left(\frac{E}{E_1}\right)^\eta \quad \text{or} \quad \mu(E) = \mu(E_2) \left(\frac{E}{E_2}\right)^\eta \quad (2.11)
\]
where $E_1 < E < E_2$ and $\eta$ is given by

$$\eta = \frac{\ln[\mu_i(E_1)] - \ln[\mu_i(E_2)]}{\ln(E_1) - \ln(E_2)}$$  \hspace{1cm} (2.12)$$

while using above relation, the energy interval $(E_1 - E_2)$ was carefully selected so that its magnitude should be smallest possible and no absorption edge was existing between $E_1$ and $E_2$. The values of $\beta$ are $\sim 0.95$ for thin targets and $< 0.21$ for thick targets. The targets in the pellet form are taken as infinitely thick targets, i.e., having thickness more than a value that can provide $99\%$ of the maximum count rate for the emitted fluorescent X-rays. A value of $\beta$ equal to $0.21$ corresponds to $99\%$ attenuation and below this value of $\beta$, the product $m\beta$ can be safely taken as constant, equal to $[\mu_1 \sec \theta_1 + \mu_2 \sec \theta_2]^{-1}$. The effective thickness of the multielement target from which a characteristic X-ray of the $i$th element contributes can safely be taken as constant equal to the limiting value of the $m\beta$ factor when $m \rightarrow \infty$, i.e.,

$$m\beta = \sum_i w_i \left( \frac{\mu_i}{\cos \theta_1} + \frac{\mu_i}{\cos \theta_2} \right)^{-1}$$  \hspace{1cm} (2.13)$$

where $w_i$ represents fractional intensity of the $i$th element in the multielemental target. The effective thickness, $m\beta$, especially in case of thick targets depends upon the incident ($\theta_1$) and emission ($\theta_2$) angles of photons.

### 2.6 Data evaluation procedures for EDXRF measurements

#### 2.6.1 Determination of area under the scatter/fluorescent X-ray peak

An X-ray spectrum consists of characteristic X-rays from excited elements; Compton scatter and Rayleigh scatter peaks with background. The spectrum evaluation is a decisive step in quantification and qualitative analysis in the EDXRF spectroscopy. The minimum amount of an element that must be present in a sample in order to give a count rate that is greater than the uncertainty in the background spectrum is known as detection limit. The minimum peak counts must be larger than or equal to two times the square root of the background counts under the photo peak, then the probability that our assumption is correct, is $95\%$ [10], if more certainty is required say $99.7\%$ then minimum peak counts must be larger than or equal to three times the square root of the background counts under
the photo peaks, the conventional criterion of statistical detectability, *i.e.*, \( N_p \geq 3\sqrt{N_B} \)

where \( N_p \) is the number of counts under the photo peak, \( N_B \) is the number of counts in the background. Detection limit (minimum analyzable limit) depends on various factors such as energy and intensity of the incident photons, measuring time, solid angle of detector and characteristic of X-ray spectrometer. Detection limit can be enhanced by increasing the peak to background ratio. To improve the detection limit, the emitted particles are detected in coincidence which eliminates the background. The background is estimated using extrapolation by the selecting two regions in the vicinity of peak generally using polynomial approximations.

The Voigtian function shape of the X-ray peaks arises from convolution of Lorentzian profile due to natural spread in energy of the atomic levels involved in X-ray transition, with Gaussian profile taking into account the instrumental broadening, *i.e.*, response due to detector and associated electronics. Various profiles are given by

\[
G(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(E - E_0)^2}{2\sigma^2} \right) \quad (2.14)
\]

\[
L(E) = \frac{\Gamma/2\pi}{(E - E_0)^2 + (\Gamma/2)^2} \quad (2.15)
\]

\[
V(E) = \int_{-\infty}^{\infty} L(E') G(E - E') \, dE' \quad (2.16)
\]

In low energy detectors, there becomes a small tail on the lower energy side of the photo peak accounts for many factors. Interaction of photons near detector surface leads to collection of incomplete charge pairs increasing tailing amplitude. In Ge detector, tailing can be compared with the variation of linear absorption coefficient of Ge for the same energy range. As the linear absorption coefficient increases, the photons path inside the Ge becomes shorter. At 3 keV interaction depth corresponding to 90% photons absorption is \(~5 \mu m\), at 5 keV photons, it is \(~20 \mu m\), at 11 keV, it is \(~150 \mu m\) and at 11.2 keV, just above the \( K \)-shell binding energy of Ge it reduces to \(~25 \mu m\). The relative amplitude of tail is \(~\text{few percent at low energy and monotonically decreases as the energy increases}.\) Similarly, the traversing electrons loose energy continuously all along its path. If an electron escapes from the detector active volume, it will take only part of its initial energy. The escape of the photoelectrons and Auger electrons results in tailing. The range of electrons in Ge is short, *e.g.*, for 10 keV electrons it is \(~1 \mu m\) and 20 keV electrons it is \(~3 \mu m\). To calculate
the peak area two methods are used. Firstly a computer code PEAKFIT [11] involving a non-linear least-squares-fitting routine [12], involving fitting of multi-Gaussian function plus polynomial background, is used. Area can be evaluated by fitting taking desired peak centroid, FWHM and nature of the background. Secondly, the photo peak areas were calculated by adding the counts under the peak and subtracting the background interpolated linearly from above and below the peak.

2.6.2 Efficiency of detector and geometrical system

The product of detector efficiency ($\varepsilon$), geometrical factor ($G$) and intensity ($I_0$) of incident photons can be calculated using the Eq. 2.9 as given by

$$I_0 \, G \, \varepsilon = \frac{4\pi N}{\sigma \, m \, \beta} \quad (2.17)$$

Where $\sigma$ is the X-ray fluorescence cross section of the target element at incident energy, $N$ is count rate for corresponding peak, $\beta$ is the self-absorption correction factor for the incident and emitted X-rays in the element. In the present work, each experiment was performed using different geometrical set up. Therefore, every time the set up was calibrated

![Graph showing relative efficiency vs. energy](image)

Fig. 2.15: Relative efficiency of low energy Ge Detector calculated using $^{133}$Ba radioisotope source.

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for the measurement using the above relationship between the fluorescent X-ray yield \((N)\) and mass \((m)\) of the target. The curve between \(I_0 G\) and energy was produced by measuring the K X-ray yields from the targets of various elements excited by photons obtained from the \(^{55}\)Fe and \(^{241}\)Am radioactive sources and from the knowledge of X-ray production (XRP) cross sections. The characteristic X-rays obtained from different thin elemental standard foils were used to provide efficiency points. In addition, more efficiency points are obtained using a number of radioactive sources. Every time when the setup is modified or the source is replaced, the whole process of the system of calibration is repeated in its full or partial form, only then the measurements are taken up. The detail of efficiency calculation and calibration optimism for each measurement is given in the respective measurement. The relative efficiency of LEGe detector is shown in Fig.2.15. The efficiency is calculated using the direct energy spectrum emitted from \(^{133}\)Ba radioisotope source. Efficiency is calculated by dividing the count rate of a peak by the corresponding peak intensity as given in table of radioisotopes [1].

### 2.6.3 Target thickness measurements

The measurements performed in present work involve use of both thick \((\sim \text{mg/cm}^2)\) and thin \((\sim \mu\text{g/cm}^2)\) targets. The value of \(m\) used in the evaluation procedure is used as g/cm\(^2\). The thicknesses \((m)\) of thin standard targets \((\sim 50-300 \ \mu\text{g/cm}^2)\) evaporated on 3.5 \(\mu\text{m}\) and 6.3 \(\mu\text{m}\) mylar backing procured from Micromatter, USA, is certified with quoted accuracy of \(\pm 5\%\) by the manufacturer [13]. D.W. Mingay [14] confirmed the thickness of these standard foils using Rutherford scattering measurements. Weighing technique is used for calculation of thick foils and pellets by dividing the mass of the foil/pellet by the cross sectional area. In compound targets, mass fraction is further used to deduce the weight of element present in the total weight of the compound. When the value of absorption factor \((\beta)\) become equal or lower than 0.21, it can be treated as infinitely thick and count rate is supposed to be maximum \(\sim 99\%\). For infinite target, the effective thickness \((m\beta)\) of the target can safely be taken as constant and given by Eq. (2.16). The mass of thin targets were deduced using \(K\) or \(L\) X-ray fluorescence intensities of present elements. These intensities are compared to those of known standard foils available using unitary method. During measurements the uncertainty in mass \((m)\) values arises from the non-uniformity which is reduced by exciting the target over different portions.
2.7 Data evaluation procedures for WDXRF measurements

The elements are identified using the qualitative scanning mode in the equipment, which involves peak identification corresponding to an element using Spectraplus software [5]. The programs in Spectraplus include various correction such as matrix effects, peak overlap, varying atmospheres, impurities for a number of sample sizes. The obtained multispectra were split into the different individual spectra and were converted to energies by inversion of the channels to be treated to perform spectral deconvolution and fitting and to evaluate element net peak areas from the spectra. Peak fitting was performed by iteration to adjust the peak and background to minimize the chi-square on each spectrum. The software automatically determined the elemental concentration in samples using Lachance-Traill formula [6]

\[ m_i = A_0 + A_1 I \times (1 + \sum_{k \neq i} \alpha_{ik} \cdot m_k) \]  

(2.18)

where \( m_i \) is the element concentration and \( I \) the measured intensity of the corresponding line and \( m_k \) are the concentrations of the other element \( k \). \( A_0 \) and \( A_1 \) are the coefficients of the calibration regression line which are available either in the line library or in the calibration file depending on whether default or specific calibration to be used. The coefficients \( \alpha_{ij} \) takes into account the matrix influence i.e., absorption of the radiation by the other elements and secondary fluorescence. The concentrations \( m_k \) are common factors for these corrections. The program itself can calculate \( \alpha \) from the tube power, geometry and sample composition using the Sherman equation [6]. The software Spectraplus provides greater flexibility in analysing the produced data by varying parameters to best detection mode.

2.8 X-ray diffraction

XRF techniques are based on the interaction of photons with matter at atomic level. When the target is a periodic array of atoms or a crystalline solid, then wave nature of X-ray photons play a significant role. The photons coherently scattered from the atoms present at various positions in crystal, interference of the photons takes place and constructive interference for the photon waves in phase with each other leads to sharp intensities in a pattern. This phenomenon is called X-ray diffraction. The technique uses an X-ray source and a detector attached to some arrangement, called goniometer, able to move these at different angles. It is a versatile and non-destructive technique used to determine the quantity of various crystalline phases of compounds in a sample. Identification is
performed by comparing the X-ray diffraction pattern obtained from an unknown sample with internationally recognized databases containing reference patterns for more than 200,000 phases. Modern computer controlled diffractometer systems uses automatic routine to measure, record and interpret the unique XRD pattern produced by individual constituents in even highly complex mixture. The result of XRD measurements is a pattern showing present crystalline phases (peak positions), phase concentration (peak height), amorphous content (background hump) and crystalline size/strains (peak width). By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice are attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral by comparison of d-spacings with standard reference patterns, discussed in following section.

**Miniflex 600 benchtop X-ray diffractometer**

Present work utilized, Miniflex 600 benchtop X-ray diffractometer [15] using Cu-Kα radiation, operated at 40 kV, 15 mA. The 2θ operating range is 2°-145° and scanning speed is 0.01 to 100°/min. The photograph of X-ray diffractometers and its inside view is shown in Fig. 2.16 and Fig. 2.17, respectively.

![X-ray diffractometer](image)

**Fig. 2.16: Photograph of Miniflex 600 benchtop X-ray diffractometer.**
Three basic elements constituting XRD set up: an X-ray tube, a sample holder, and an X-ray detector. Scintillation detector (NaI (Tl)) with beryllium window (Size: 13 mm (W) x 20 mm (H), Diameter: 23 mm, Length: 80 mm) has been used in the system. In X-ray diffractometer the sample rotates in the path of the incoming collimated X-ray beam at an angle $\theta$ while the X-ray detector is mounted on a rotating arm to collect the diffracted X-rays at angle up to $2\theta$. The segment controlling the angle and rotate the sample is termed as goniometer. Different accessories are used with X-ray diffractometer for better resolution and to serve specific function. A software miniflex controller (Rigaku corporation, Japan) is installed in PC records the pattern. The peaks in obtained patterns are analysed using a software PDXL2 supplied by Rigaku, Japan, which contains standard data for different phases for compounds of all the elements in periodic table. The software automatically finds the phase once the pattern is fed to the analysing software.
References