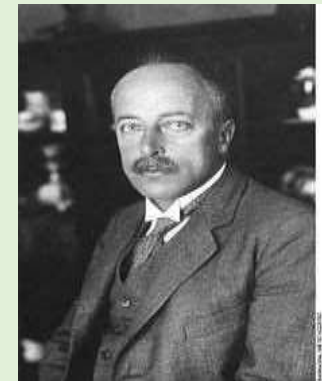# X-Ray Diffraction (XRD)

Rakesh Pani

Introduction

← X-rays were discovered by **Wilhelm Roentgen** who called them x - rays

because the nature at first was unknown so, x-rays are also called Roentgen

rays. X-ray diffraction in crystals was discovered by Max von Laue. The

wavelength range is **0.01 to about 10 nm**.

Wilhelm Röntgen

← X-rays are short wave length electromagnetic radiations produced by the deceleration

of high energy electrons or by electronic transitions of electrons in the inner orbital of

atoms

←The penetrating power of x-rays depends on energy also, there are two types of x-rays.

i) **Hard x-rays**: which have high frequency and have more energy.

ii) **soft x-rays**: which have less penetrating and have low energy.

Max von Laue

Introduction

 X-ray Diffraction (XRD) is a non-contact and non-destructive technique used to understand the crystalline phases, different polymeric forms and the structural properties of the materials

 X – ray diffraction

" Every crystalline substance gives a pattern; the same *substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others"*

 The **X-ray diffraction pattern** of a pure substance is, therefore, like a **fingerprint of the substance**. It is based on the scattering of x-rays by crystals.

 Definition

The atomic planes of a crystal cause an incident beam of X- rays to interfere with one another as they leave the crystal. The phenomenon is called X- ray diffraction.

Timeline

← 1665: Diffraction effects observed by Italian mathematician Francesco Maria Grimaldi

← 1868: X-rays Discovered by German Scientist Röntgen

← 1901: First Nobel prize in Physics to Röntgen

← 1912: Discovery of X-ray Diffraction by Crystals: von Laue

← 1912: Bragg's Discovery

Why XRD?

← Measure the average spacing's between layers or rows of atoms

← Determine the orientation of a single crystal

← Find the crystal structure of an unknown material

← Measure the size, shape and internal stress of small crystalline regions

What is Diffraction ?

A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing each other
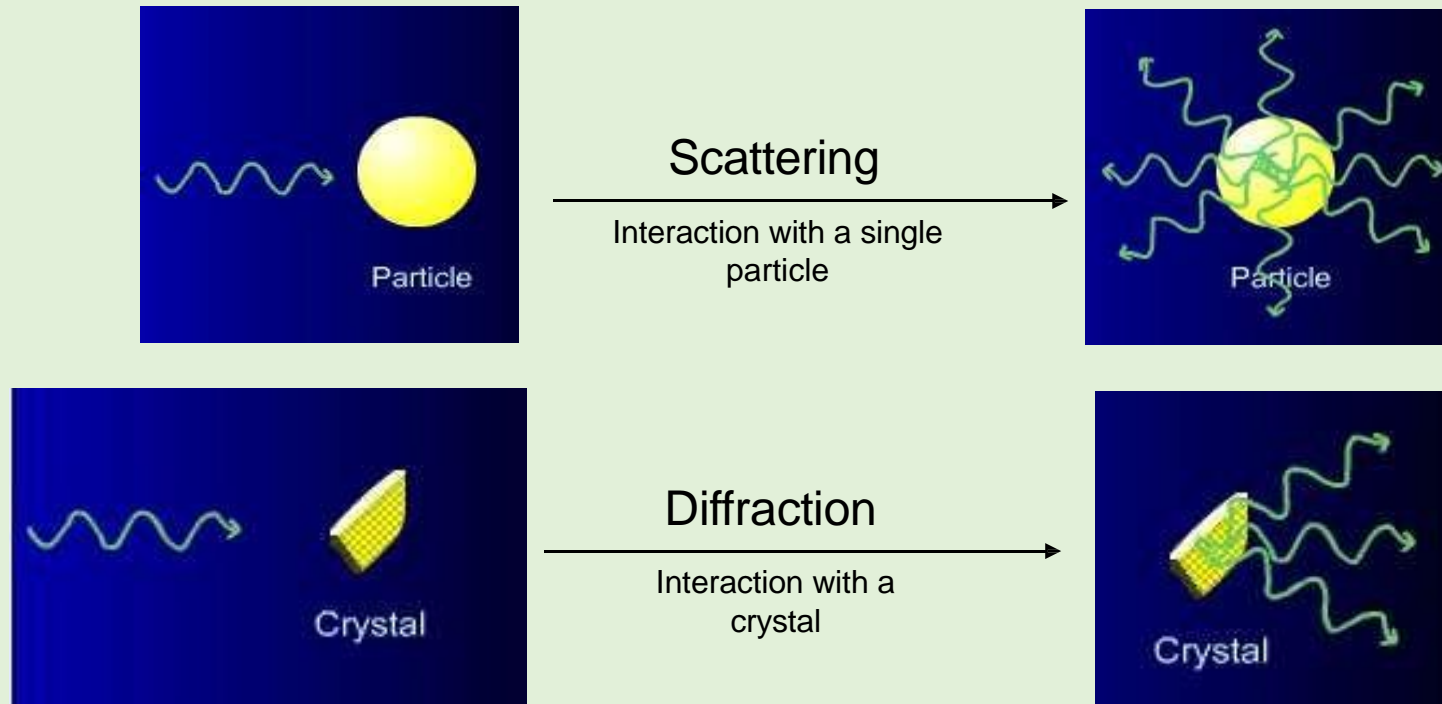
What is X-ray Diffraction ?
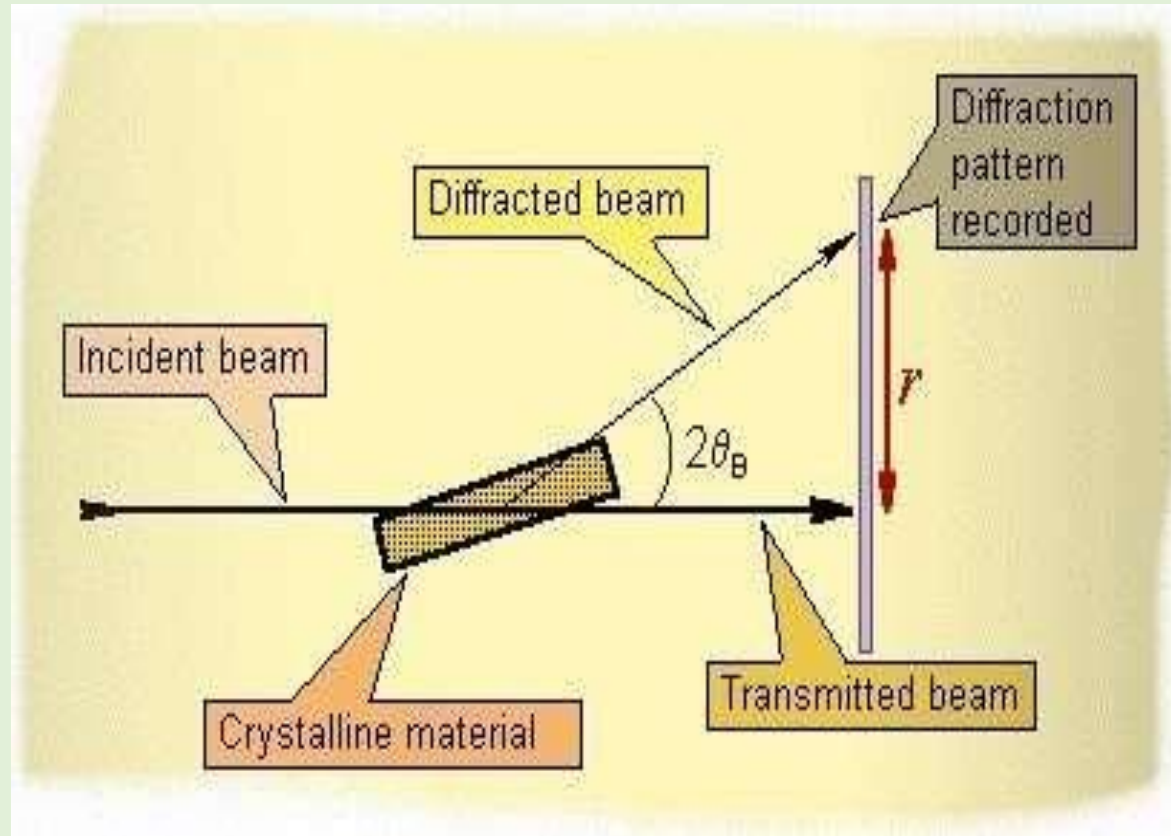
X-ray diffraction is based on **constructive interference** of monochromatic x-rays and a crystalline sample. These x-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample. The interaction of incident rays with the sample produces constructive interference when conditions satisfy **Bragg's law.**

Bragg's Law

← Constructive interference
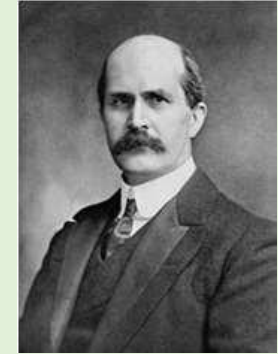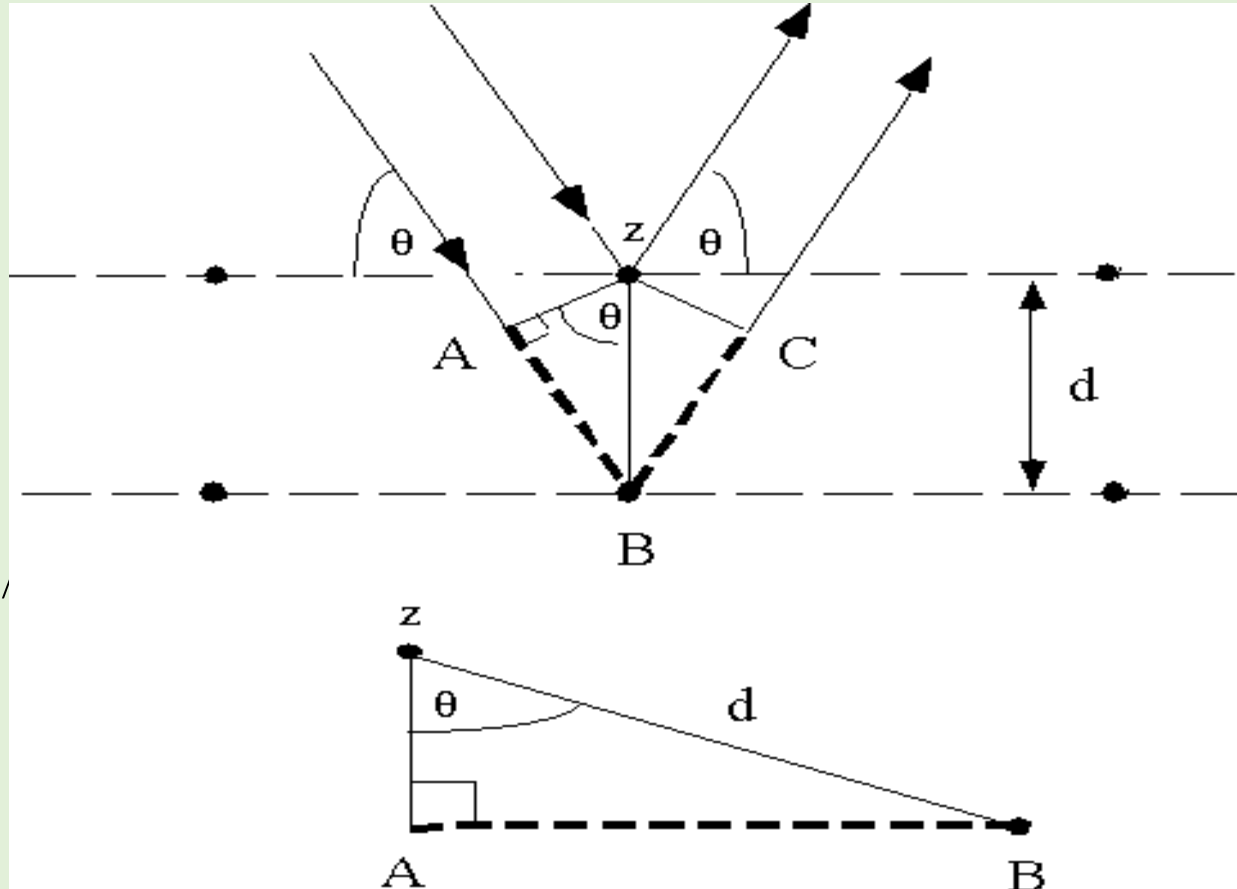
X-ray 2 occurs only when

$n\lambda = AB + BC$

$AB = BC$

$n\lambda = 2AB \sin\theta = AB$

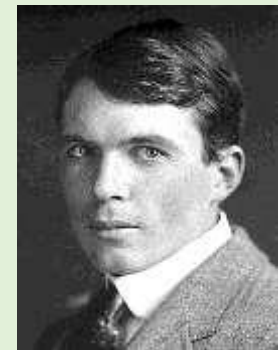$AB = d\sin\theta$

$n\lambda = 2d\sin\theta$

$\lambda = 2d_{hkl}\sin\theta_{hkl}$

Sir William Henry Bragg

Sir Lawrence Bragg
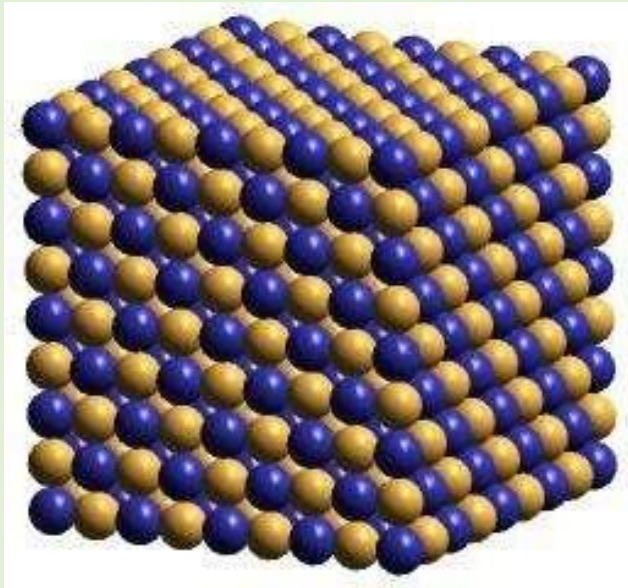
Order of Diffraction

☐ Rewrite Bragg's law $\lambda = 2 \sin\theta \, d/n$

☐ A reflection of any order as a first order Diffraction from planes, real or fictitious, spaced at a distance $1/n$ of the previous spacing.

☐ Set $d' = d/n$

☐ An nth order reflection from (hkl) planes of spacing d may be considered as a first order Diffraction from the (nh nk nl) plane of spacing $d' = d/n$

Basics of Crystallography

Lattice

← The atoms are arranged in a regular pattern, and there is as smallest volume element that by repetition in three dimensions describes the crystal. This smallest volume element is called a **unit cell**.

← Crystals consist of planes of atoms that are spaced a distance **d** apart, but can be resolved into many atomic planes, each with a different d spacing.

← The dimensions of the unit cell is described by three axes : a, b, c and the angles between them α, β , and γ are the lattice constants which can be determined by XRD.
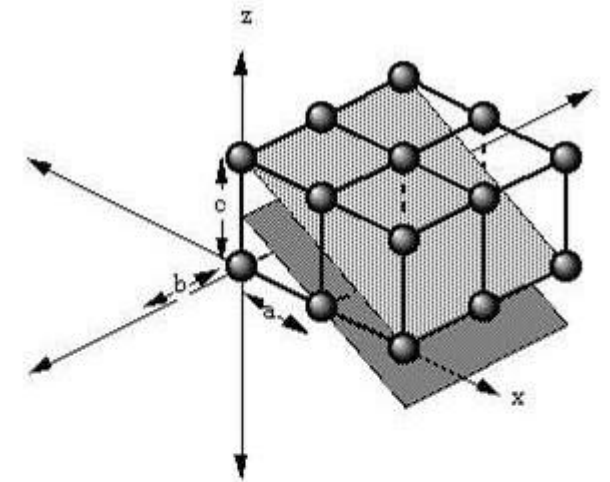
Miller Indices

William Hallowes Miller

← Crystal structures are made up of a series of planes of atoms in which each plane is spaced with a distance d with each other. But various atomic planes in a crystal can be resolved with different d- spacing. For distinguishing different planes there is a coordinate system introduced by William Hallowes Miller called Miller indices (i.e., h, k, l).

← Miller indices-the reciprocals of the fractional intercepts which the plane makes with crystallographic axes.
← Reciprocals are taken to avoid ∞ in the indices.

	a	b	c
intercept length	1	∞	1/2
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2
Miller indice		(102)	

Instrumentation

← Production of x-rays (Source Of X-Rays)

← Collimator

← Monochromator
      a. Filter
      b. Crystal Monochromator

← Detectors
      a.Photographic methods
      b.Counter methods

Production   Collimation   Sample   Detection
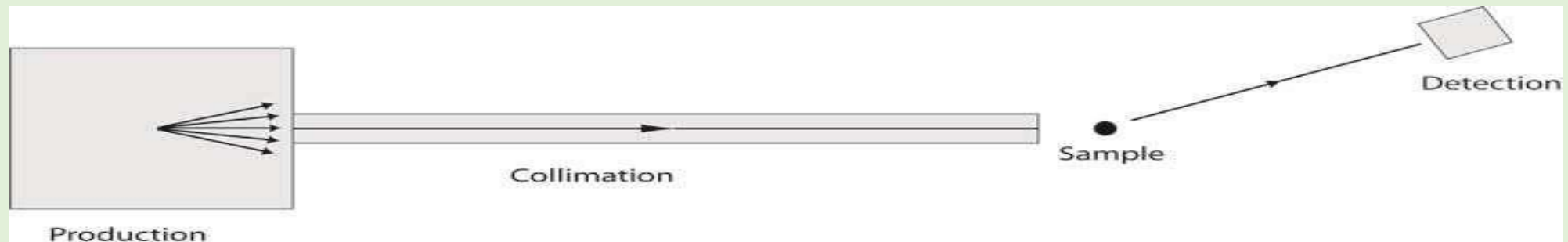
Production of x-rays
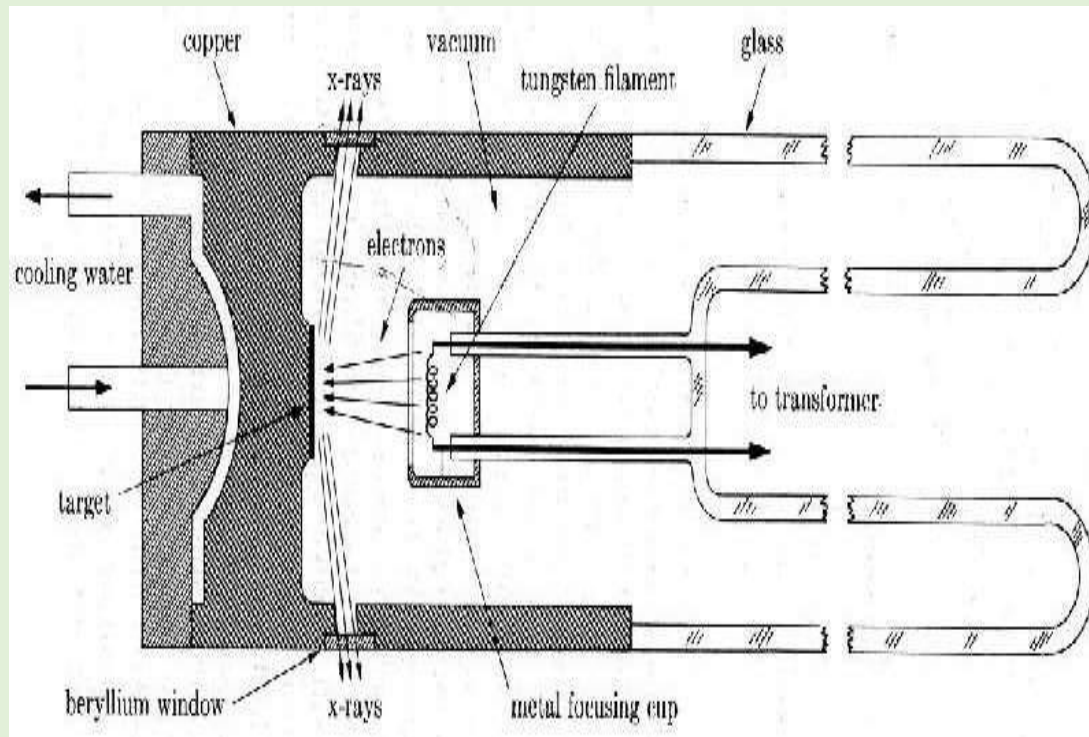
← X-rays are produced whenever a charged particles are accelerated.

← In XRD, X-rays are generated when high velocity electrons impinge on a metal target.

← A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, *Cu, Al, Mo,* Mg.

← The anode is a water-cooled block of Cu containing desired target metal.

Production of x-rays
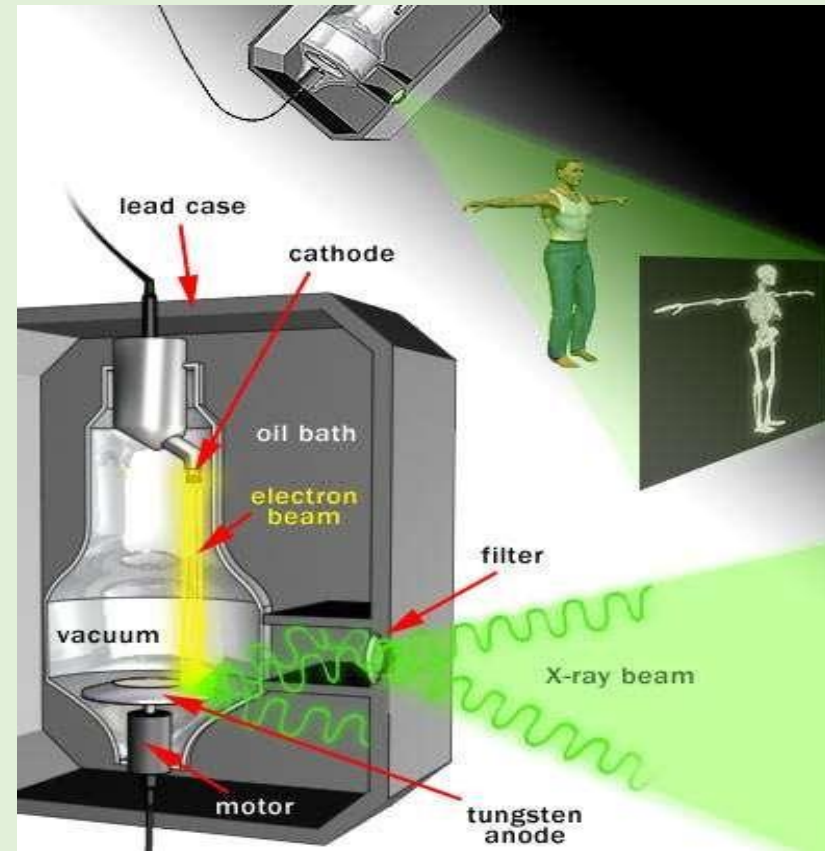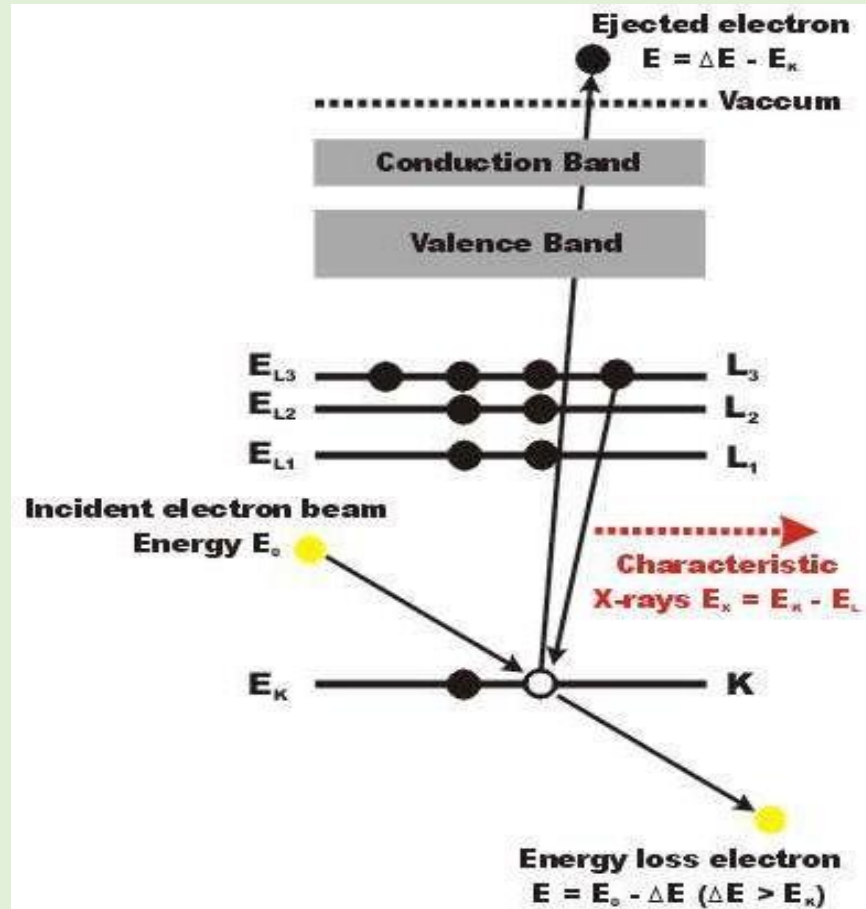
Collimator

← In order to get a narrow, focused beam of x-rays, the x- rays generated by the target material are allowed to pass through a closely packed metal plates separated by a small gap.

← The collimator absorbs all the x-rays except the narrow beam that passes between the gap.
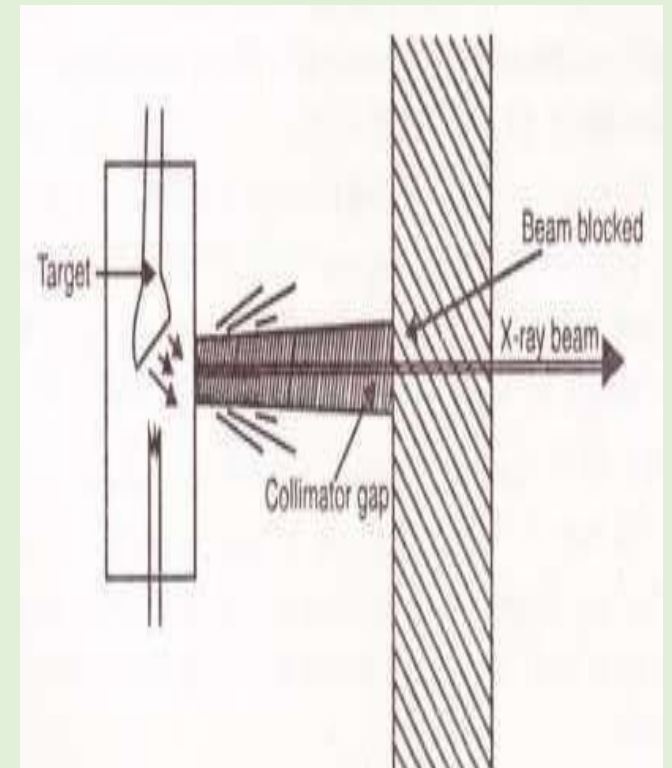
Monochromator
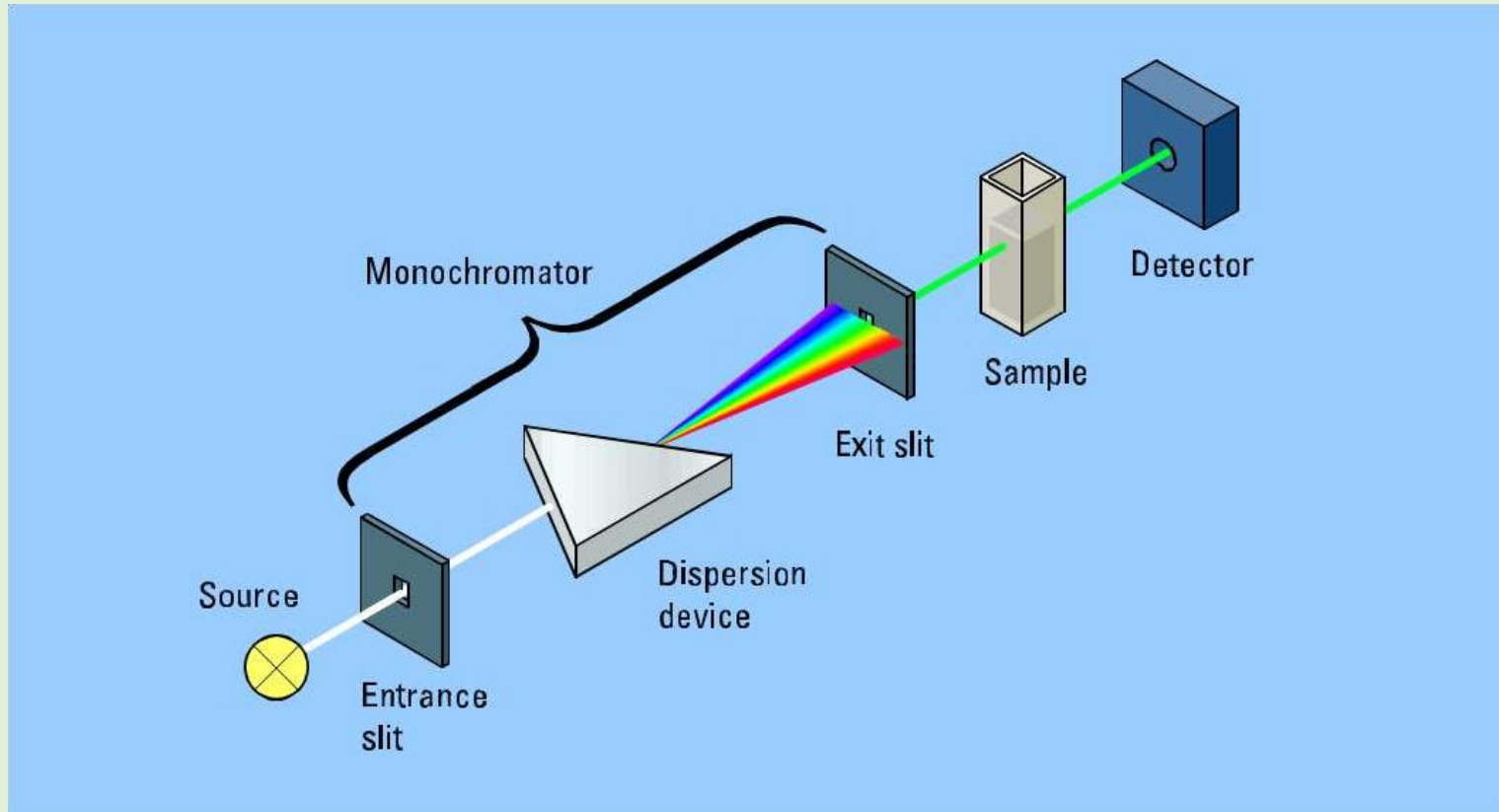
A monochromator is an optical device that transmits a mechanically selectable narrow band of wavelengths of light or other radiation chosen from a wider range of wavelengths available at the input. The name is from the Greek roots mono-, "single", and chroma, "colour", and the Latin suffix -ator, denoting an agent.

Types Of Monochromators

☐ Monochromatization can be broadly divided into two,

1.Interference Filters

2.Crystal Monochromator

☐ Crystal Monochromators can be again divided into two

i) Flat crystal Monochromator

ii)Curved crystal Monochromator

Interference Filters

← X-ray beam may be partly monochromatized by insertion of a suitable filter.

← A filter is a window of material that absorbs undesirable radiation but allows the radiation of required wavelength to pass.

← Interference filters contain several optical layers deposited on a glass substrate or transparent quartz. The specific performance characteristics of the filter are determined by the thickness of the optical layers.

Red

Magenta Light Reflected

Green Light Passed

Blue

Green Interference Filter
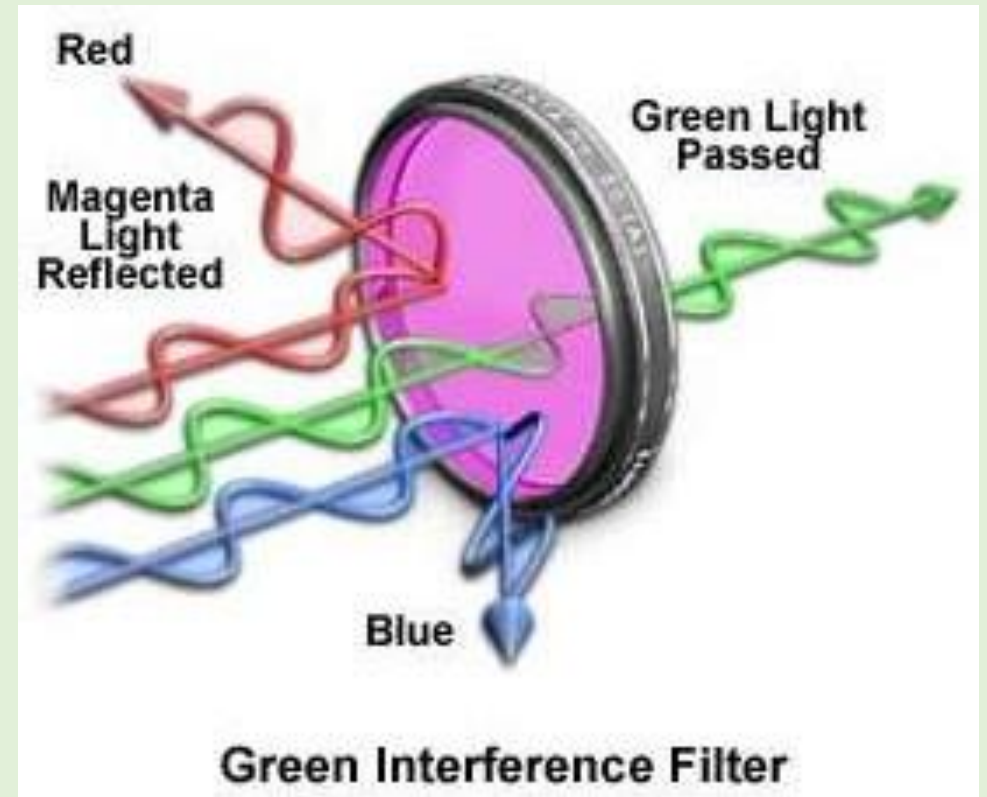
Crystal monochromators

Crystal monochromators are made up of suitable crystalline material positioned in the x-ray beam so that the angle of reflecting planes satisfied the Bragg's equation for the required wavelength the beam is split up into component wavelengths crystals used in monochromators are made up of materials like NaCl, lithium fluoride , quartz etc. Pyrolytic graphite can be used for broad band and silicon for narrow band.

(a) Flat crystal monochromator and, (b) Curved crystal monochromator.
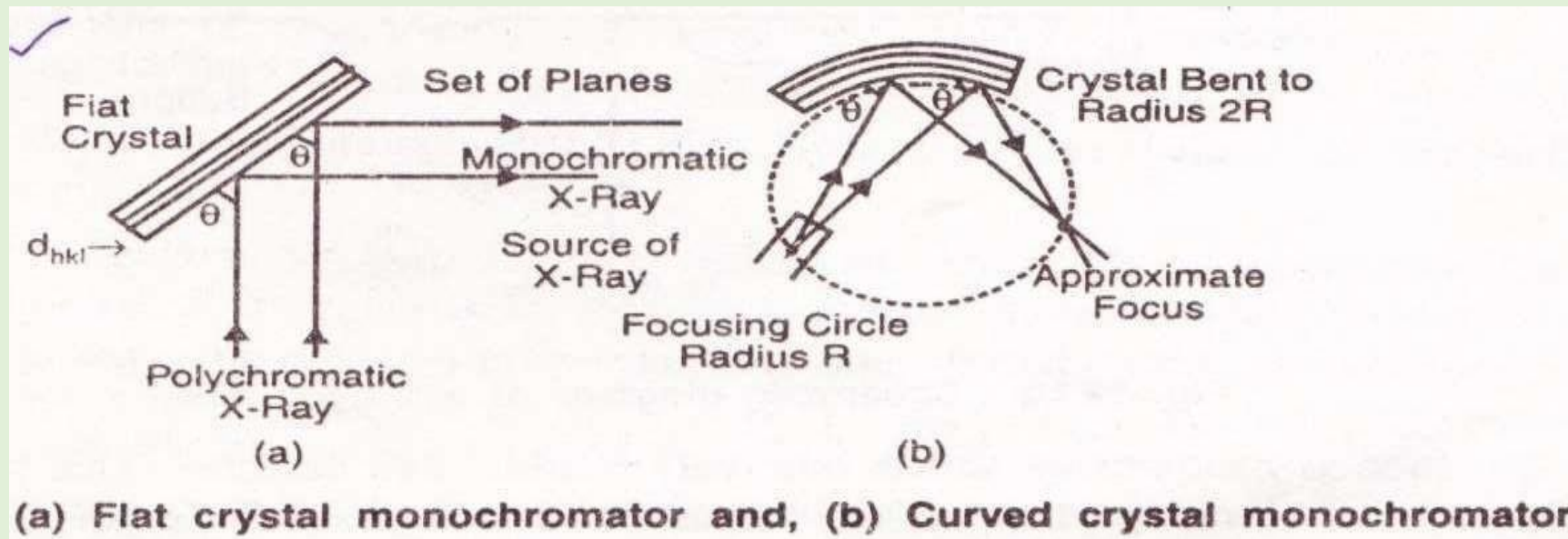
Detectors

X-ray detectors are devices used to measure the flux, spatial distribution, spectrum, and other properties of X-rays.

Detectors can be divided into two major categories: Imaging detectors, such as photographic plates and X-ray film (photographic film), now mostly replaced by various digitizing devices like image plates or flat panel detectors) and dose measurement devices called counter methods.
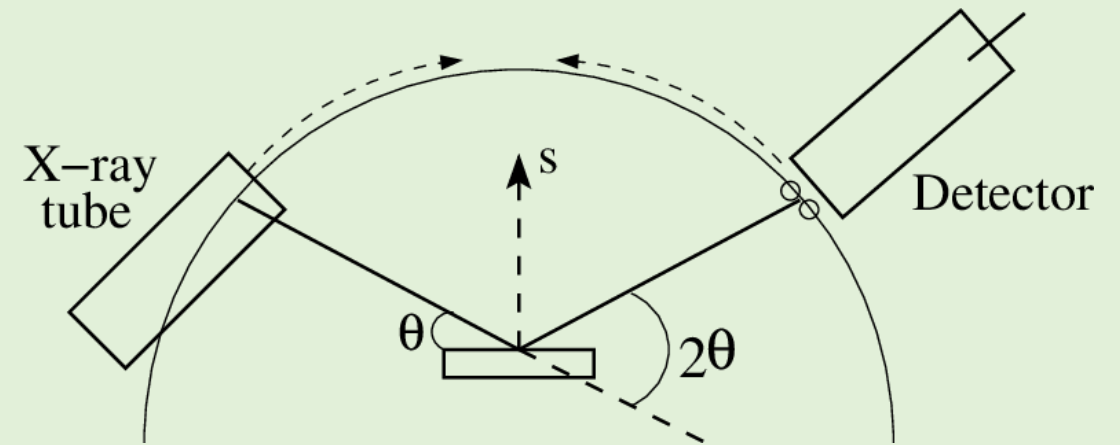
Schematic diagram of a diffractometer system

Types of detectors

The x-ray intensities can be measured and recorded either by

1)Photographic methods

2)Counter methods

    a) Geiger - Muller tube counter
    b) Proportional counter
    c) Scintillation detector
    d) Semi conductor detectors
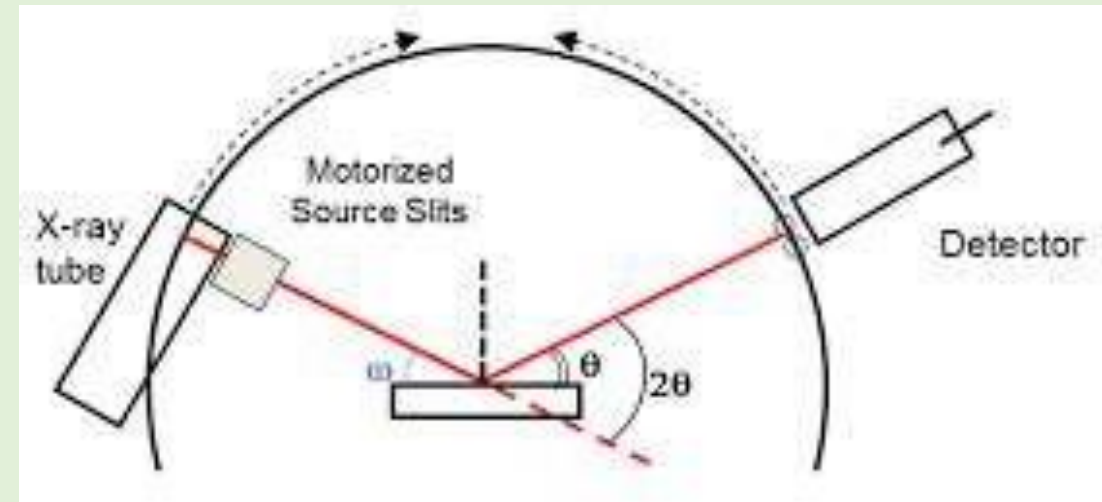
Both these types of methods depends upon ability of x-rays to ionize matter and differ only in the subsequent fate of electrons produced by the ionizing process.

Photographic method

← To record the position and intensity of x-ray beam a plane or cylindrical film is used.

← The film after exposing to x-ray is developed

← The blackening of the developed film is expressed in terms of density units D given by

$$D = \log I_0/I, \quad I_0\text{-incident intensity}$$

I - Transmitted intensity

D - Total energy that causes blackening of the film D is
measured by densitometer

    The photographic method is mainly used in diffraction

studies since it reveals the entire diffraction pattern on a single film.

← Disadvantage : time consuming and uses exposure of several hours
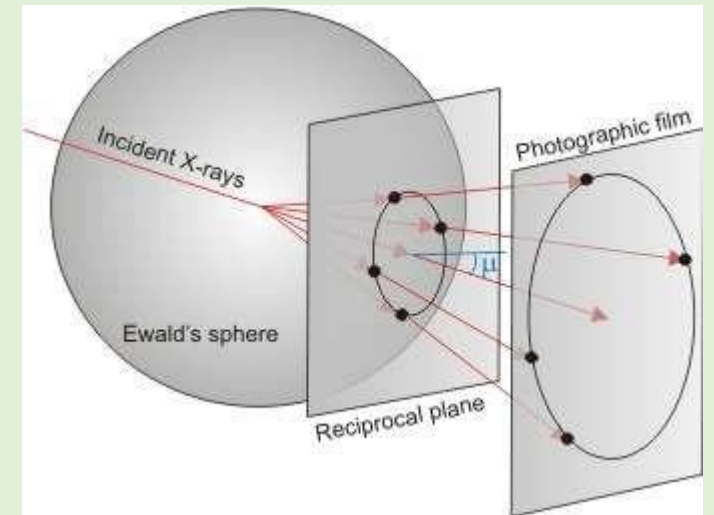
A) Geiger - Muller tube counter

Geiger tube is filled with inert gas like argon

←Central wire anode is maintained at a positive potential of 800 to 1500V .
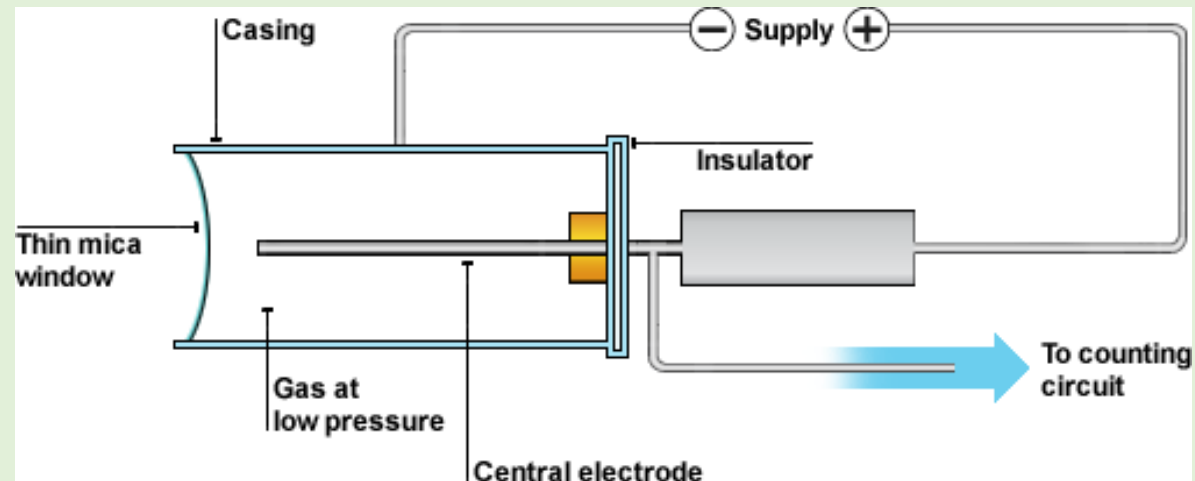
← The electron is accelerated by the potential gradient and causes the ionization of large number of argon atoms, resulting in the production of avalanche of electrons that are travelling towards central anode

B) Proportional counter

← Construction is similar to Geiger tube counter

← Proportional counter is filled with heavier gas like xenon and krypton

← Heavier gas is preferred because it is easily ionized

← Operated at a voltage below the Geiger plateau

← The dead time is very short (~ 0.2μs), it can be used to count high rates without significant error.
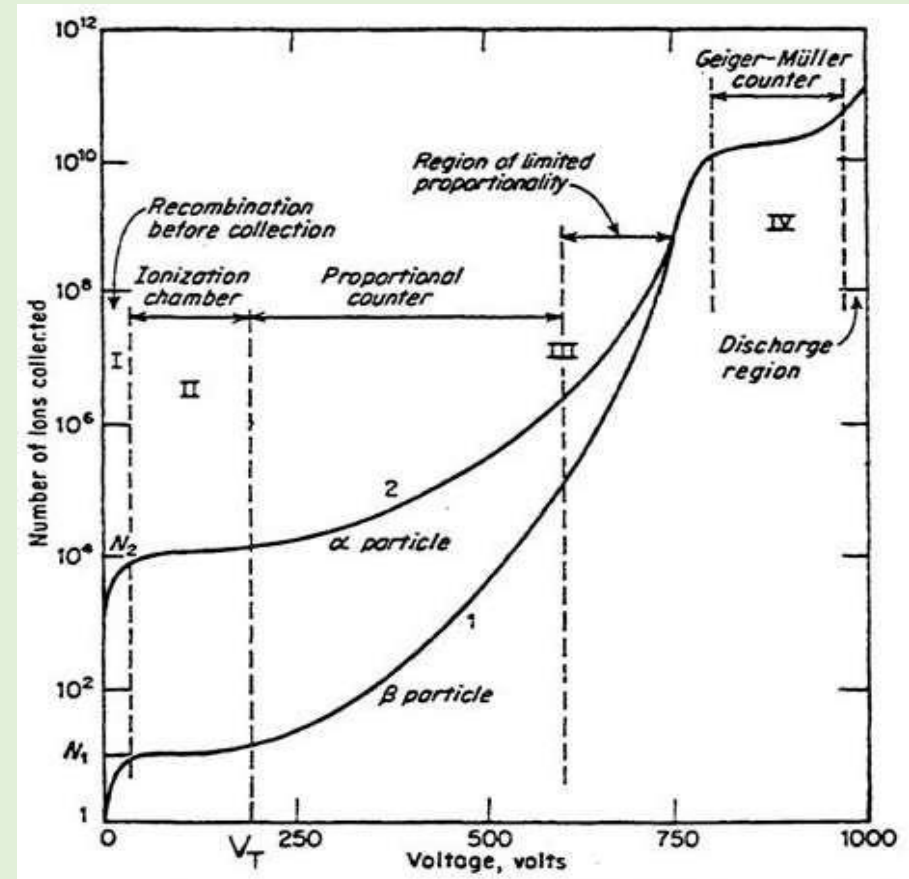
C) Scintillation detector:
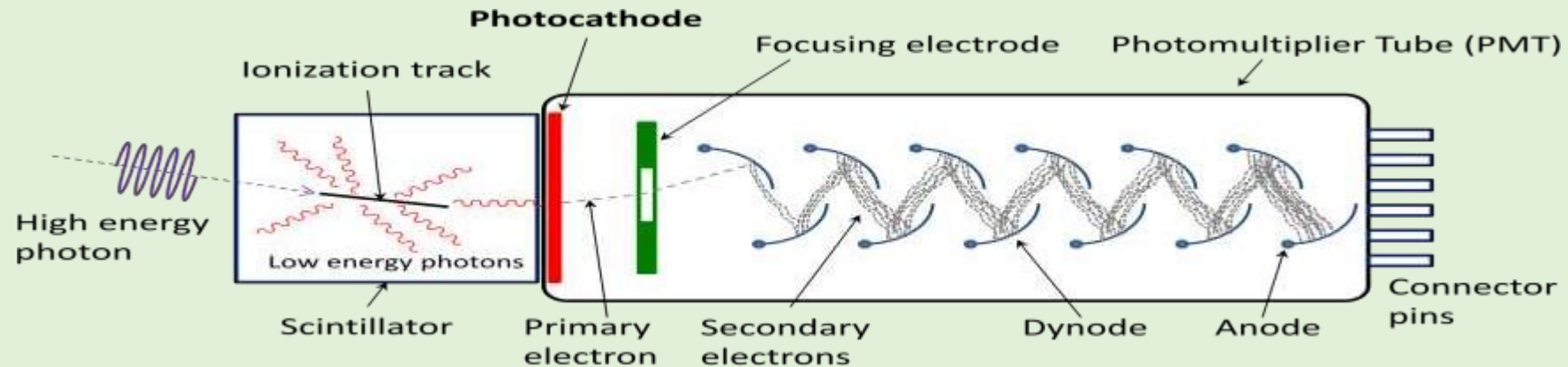
← In a scintillation detector there is large sodium iodide crystal activated with a small amount of thallium

← When x-ray is incident upon crystal , the pulses of visible light are emitted which can be detected by a photo multiplier tube

← Useful for measuring x-ray of short wavelength

← Crystals used in scintillation detectors include sodium iodide ,anthracene, napthalene and p-terphenol

D) Semi-conductor detectors

← When x-ray falls on silicon lithium drifted detector an electron (-e) and

   a hole (+e)

← Pure silicon made up with thin film of lithium metal plated onto one end

← Under the influence of voltage electrons moves towards +ve charge and

   holes towards –ve

← Voltage generated is measure of the x-ray intensity falling on crystal

← Upon arriving at lithium pulse is generated

← Voltage of pulse=q/c; q-tot charge collected on electrode, c-detector

   capacity.
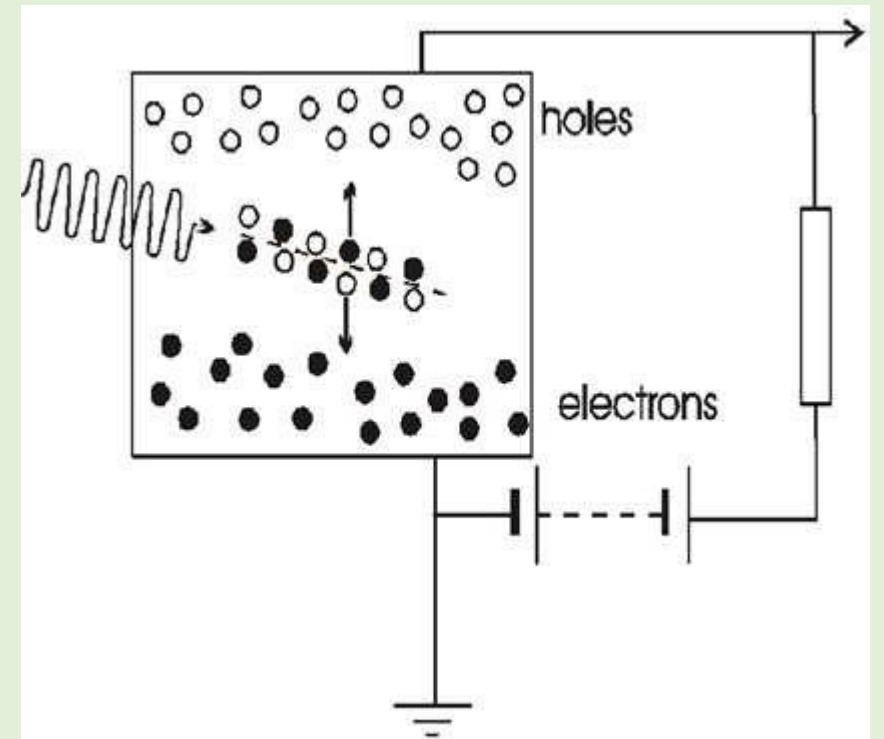
X-ray diffraction methods

← There are several XRD methods which are generally used for investigating the internal structures and crystal structures of various solid compounds.

X-Ray Diffraction Method

Laue	Rotating Crystal	Powder
•Different Orientation • Single Crystal • Polychromatic Beam • Fixed Angle	Lattice constant Single Crystal Monochromatic Beam VariableAngle	Lattice Parameters Polycrystal (powdered) Monochromatic Beam VariableAngle

1. Laue's photographic method
   a)Transmission method
   b)Back reflection method

2.Rotating crystal method

3.Powder method

The Laue method

Laue in his very first experiments used white radiation of all possible wavelengths and allowed this radiation to fall on a stationary crystal. The crystal diffracted the X-ray beam and produced a very beautiful pattern of spots which conformed exactly with the internal symmetry of the crystal. Let us analyze the experiment with the aid of the Bragg equation. The crystal was fixed in position relative to the X-ray beam, thus not only was the value for d fixed, but the value of was also fixed.
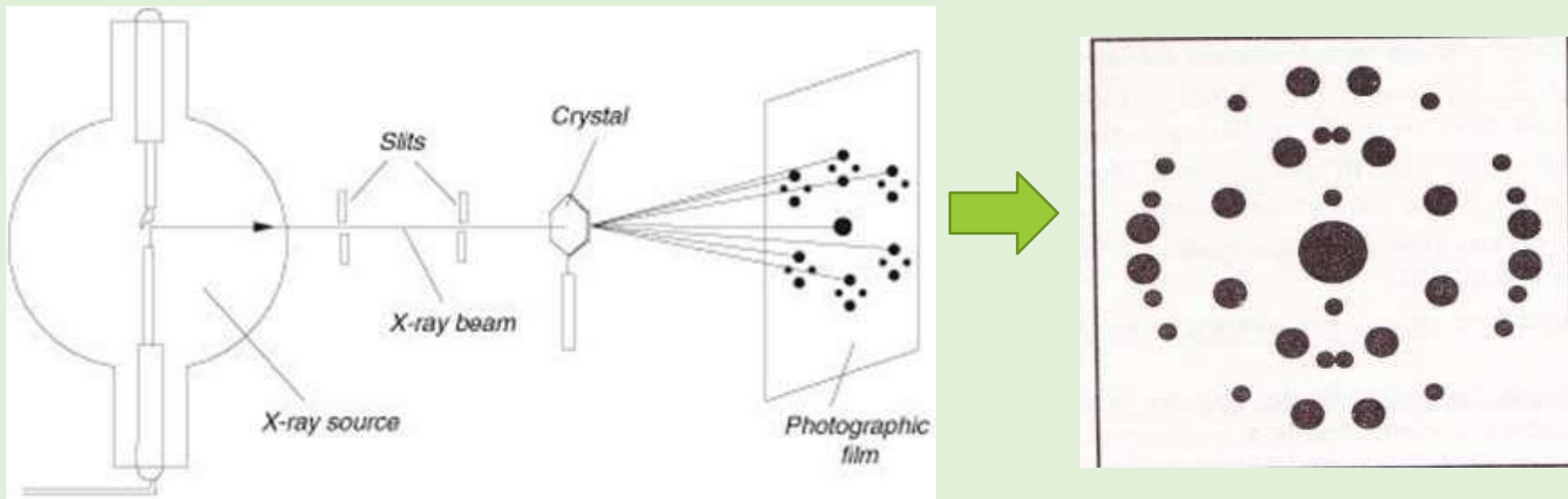
X-Ray Laue Method

A) Transmission Laue method

In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.

← Can be used to orient crystals for solid state experiments.

← Most suitable for the investigation of preferred orientation sheet particularly confined to lower diffraction angles.

← Also used in determination of symmetry of single crystals.
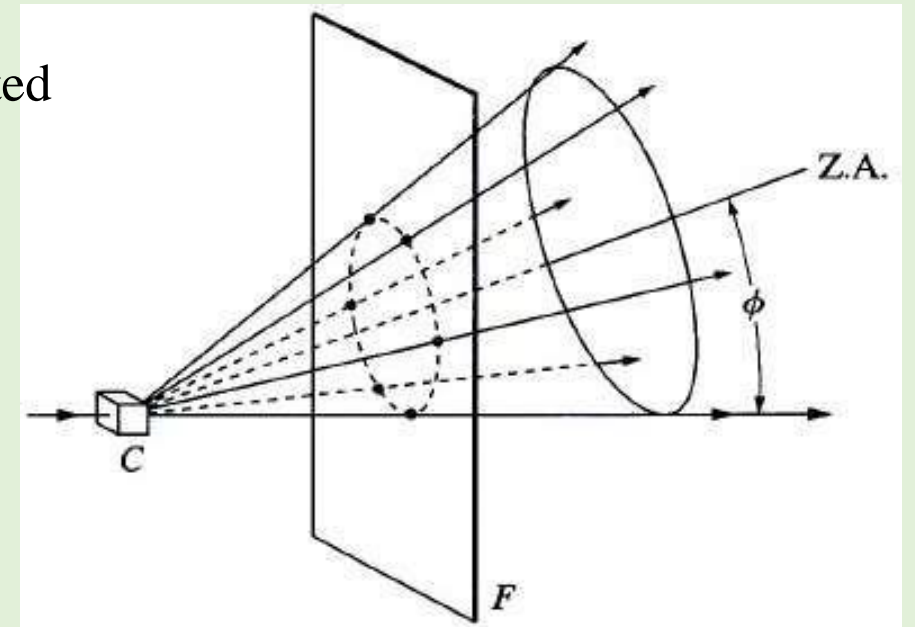
Transmission Laue method

B) Back-reflection Laue method

← In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

← One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects with the cone in which the diffraction spots generally lie on a hyperbola.

← This method is similar to Transmission method however, back-reflection is the only method for the study of large and thick specimens.
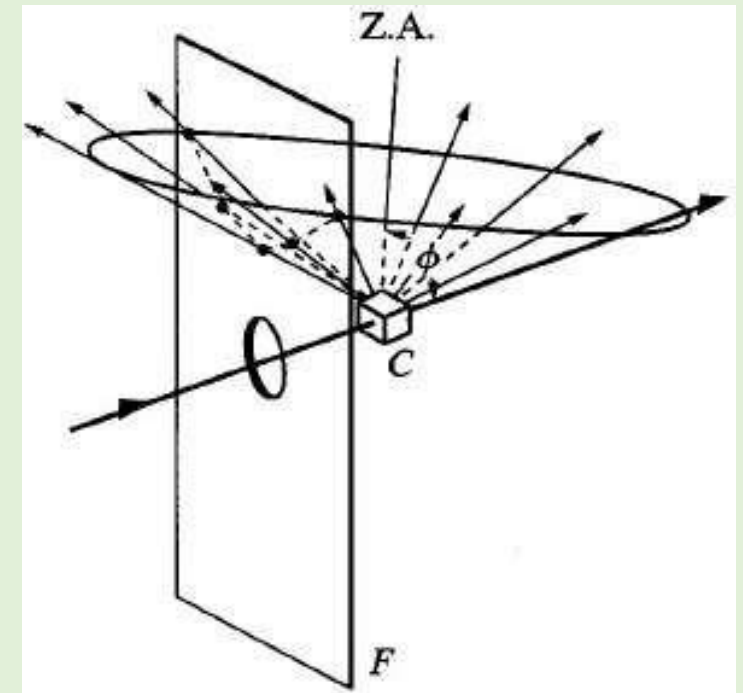
Back-reflection Laue method

Disadvantages of Laue method

← Big crystals are required

← Crystal orientation is determined from the position
of the spots. Each spot can be indexed,
i.e. attributed to a particular plane, using
special charts.

← The Greninger chart is used for back-reflection

patterns and the Leonhardt chart for transmission

patterns.

← The Laue technique can also be used to assess

crystal perfection from the size and shape
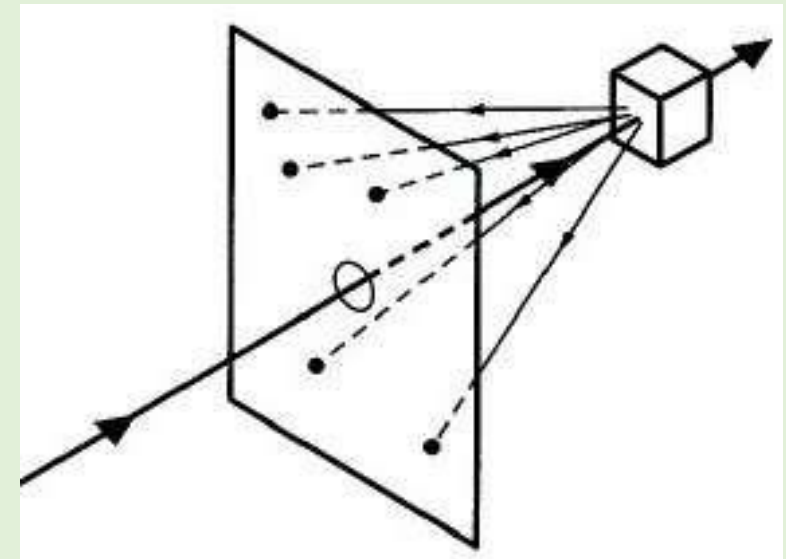
Back-reflection Laue method

The Bragg's x-ray spectrometer
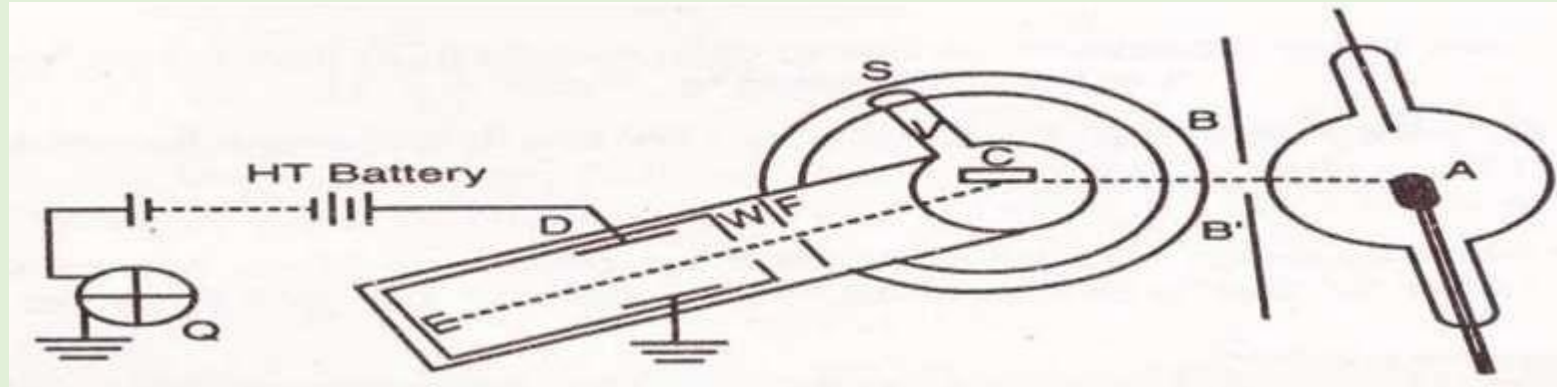
Bragg's x-ray spectrometer

← A - Cathode

← B-B' – Adjustable slits

← C - crystal

← E - ionization chamber

← One plate of ionization chamber is connected to the positive terminal of a H.T Battery , while negative terminal is connected to quadrant electrometer(measures the strength of ionization current)

Working of Bragg's x-ray spectrometer

← Crystal is mounted such that $\theta = 0°$ and ionization chamber is adjusted to receive x-rays

← Crystal and ionization chamber are allowed to move in small steps

← The angle through which the chamber is moved is twice the angle through which the crystal is rotated

← X-ray spectrum is obtained by plotting a graph between ionization current and the glancing angle θ

← Peaks are obtained, corresponding to Bragg's diffraction.

← Different order glancing angles are obtained with known values of λ and n and from the observed value of θ and d can be measured.

Determination of crystal structure by bragg's law

← X-Rays fall on crystal surface

← The crystal is rotated and x-rays are made to reflect from various lattice planes

← The intense reflections are measured by bragg's spectrometer and the glancing angles for each reflection is recorded

← Then on applying bragg's equation ratio of lattice spacing for various groups of planes can be obtained.

← Ratio's will be different for different crystals

← Experimentally observed ratio's are compared with the calculated ratio's ,particular structure may be identified.

Rotating Crystal Method

← Single crystal mounted with one axis normal to a

monochromatic x-ray beam

← Cylindrical film placed around the sample

← As sample rotates, some sets of planes momentarily satisfy

Bragg condition

← When film is laid flat, a series of horizontal lines appears

← Because crystal rotates about a single axis, possible Bragg

angles are limited - not every plane is able to produce a

diffracted spot

← Sometimes used to determine unknown crystal structures
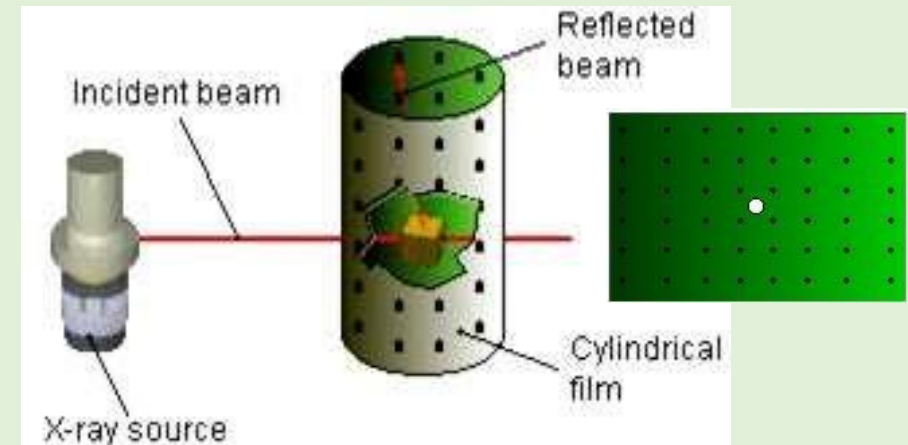
Powder crystal method:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.
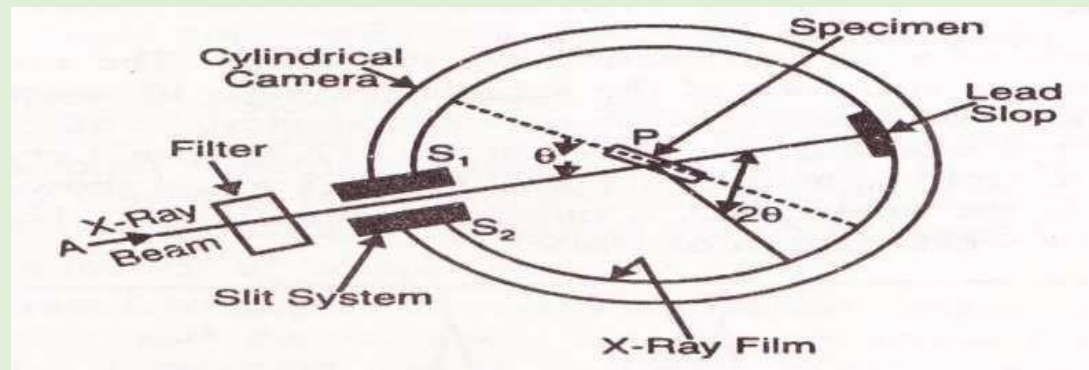
Fine powder is struck on a hair with a gum ,it is suspended vertically in the axis of a cylindrical camera

← When monochromatic beam is allowed to pass different possibilities may happen
1. There will be some particles out of random orientation of small crystals in the fine powder
2. Another fraction of grains will have another set of planes in the correct positions for the reflections to occur
3. Reflections are possible in different orders for each set

Powder crystal method:

← If the angle of incidence is θ then the angle of reflection will be 2θ.

← If the radius is r the circumference 2πr corresponds to a scattering angle of 360°.

$$\theta = 360 * 1/\pi r$$

← From the above equation the value of θ can be calculated and substituted in Bragg's equation to get the value of d.
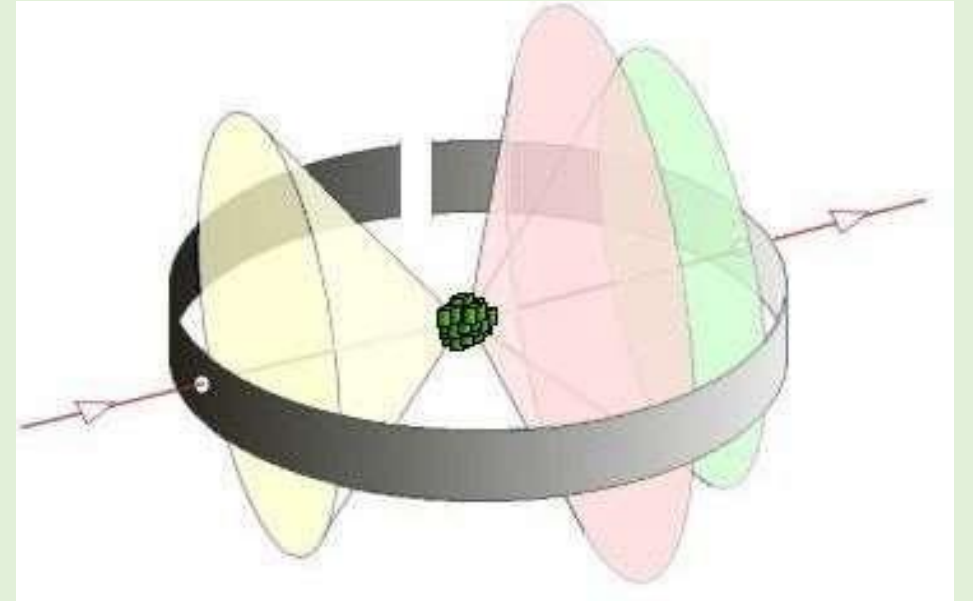
POWDER CRYSTAL DIFFRACTION

Applications

- The electron density and accordingly, the position of the atoms in complex structures, such as penicillin may be determined from a comprehensive mathematical study of the x-ray diffraction pattern.

- The elucidation of structure of penicillin by xrd paved the way for the later synthesis of penicillin.

- The powder xrd pattern may be thought of as finger print of the single crystal structure, and it may be used conduct qualitative and quantitative analysis.

- XRD can also be used to determine whether the compound is solvated or not.

- Particle size determination by applying the relation.

$$v= V. \delta\theta. \cos \theta / 2n$$

Where   v = the volume or size of an individual crystalline

V = the total volume of the specimen irradiated

n = the number of spots in a deffraction ring at a Bragg angle θ

It is used to assess the weathering and degradation of natural and synthetic , minerals.

Limitations

☐ Homogeneous and single phase material is best for identification of an unknown

☐ Must have access to a standard reference file of inorganic compounds (d-spacings, *hkl*s)

☐ Requires tenths of a gram of material which must be ground into a powder

☐ For mixed materials, detection limit is ~ 2% of sample

☐ For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated

☐ Peak overlay may occur and worsens for high angle 'reflections'

Conclusions

☐ For materials including metals, minerals, plastics, pharmaceuticals and semiconductors XRD apparatus provide highly accurate tools for non-destructive analysis.

☐ The diffraction systems are also supported by an extensive range of application software.

☐ X-ray Diffraction is a very useful to characterize materials for following information.

- Phase analysis
- Lattice parameter determination
- Strain determination
- Texture and orientation analysis
- Order-disorder transformation and many more things.

X-RAY FLUORESECENCE

Rakesh Pani

X-ray fluorescence

- An X-ray fluorescence (XRF) spectroscopy is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids.

- It is typically used for bulk analyses of larger fractions of geological materials.

- One of the most widely used methods due to its relative ease, low cost of sample preparation and the stability and use of X- ray spectrometers.

- One of the best analytical techniques to perform elemental analysis in all kinds of samples, no matter if liquids, solids or loose powders.

2D & 3D MODELS OF XRF
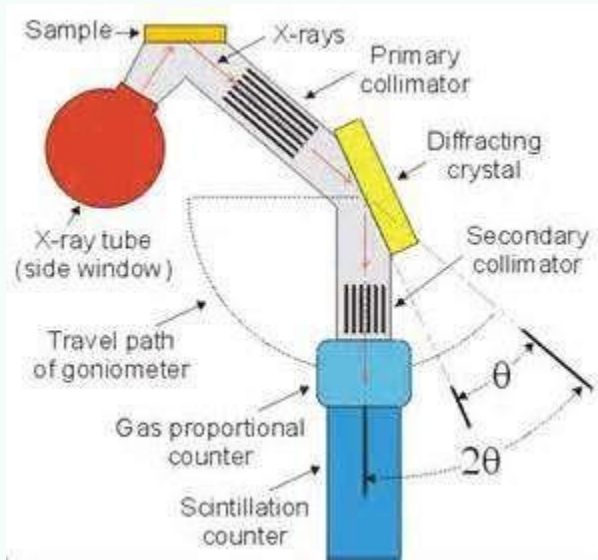
What can be analysed by X-Ray Fluorescence?

Oils

Polymers

Ores and Raw Materials

Chemicals

Metals, Slags

Ceramic

Glass

Food Products

Typical Samples for X-Ray Fluorescence

Fundamental Principles of XRF

- XRF works on methods involving interactions between electron beams and x-rays with samples.

- Made possible by the behavior of atoms when they interact with radiation.

- When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized.

- If the energy of the radiation is sufficient to dislodge a tightly- held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron.

- When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one.

- The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation.

- Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample.

Excitation of the sample

Sample

Secondary X-Rays or X-Ray Fluorescence which is characteristic for the elemental composition of the sample

X-Ray Tube

Spectrometer
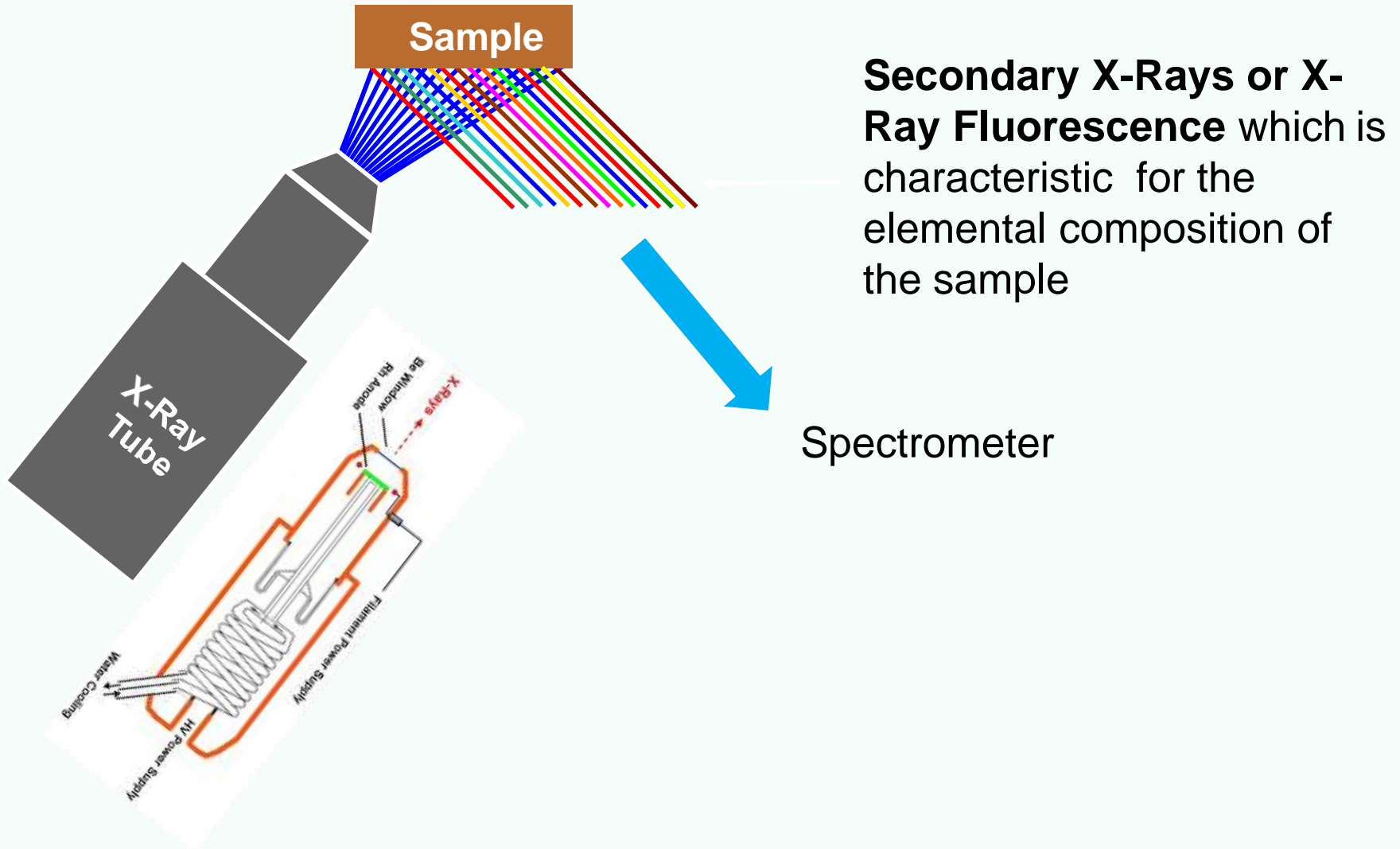
Principle of the excitation by X-Rays
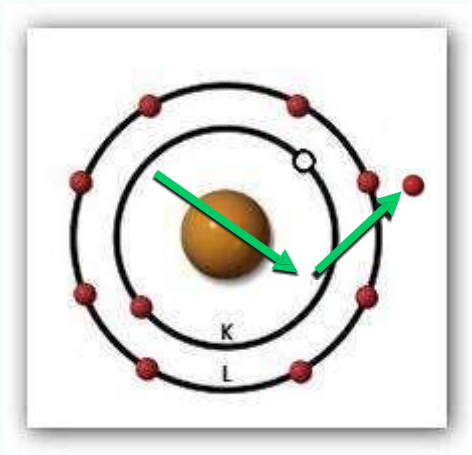
- An Incoming X-Ray photon strikes an electron, the electron breaks free and leaves the atom.

Principle of the excitation by X-Rays
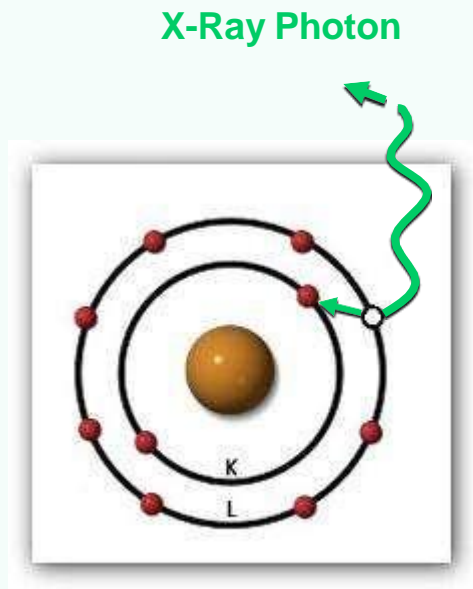
X-Ray Photon

- This leaves a void that must be filled by an electron from an outer shell.

- The excess energy from the new electron is released (fluorescence) in the form of an x-ray photon.

Excitation and Interactions between shells
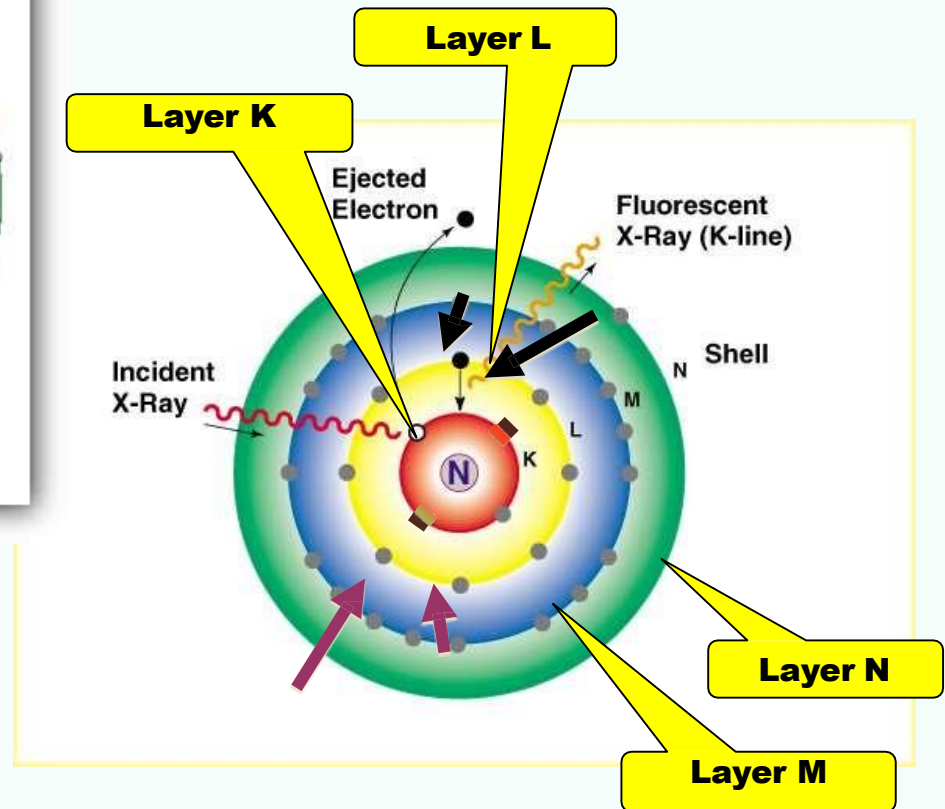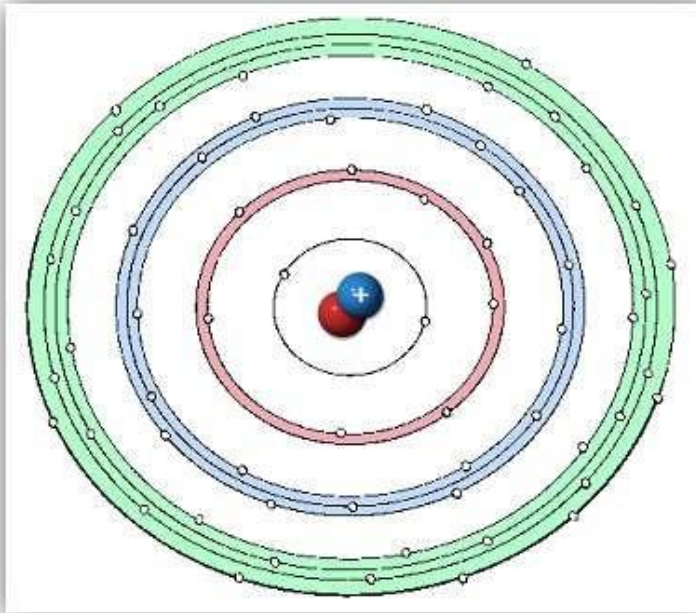
XRF - HOW IT WORKS

- An XRF spectrometer works because if a sample is illuminated by an intense X-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed within the sample in a manner that depends on its chemistry.
- The incident X-ray beam is typically produced from a Rh target, although W, Mo, Cr and others can also be used, depending on the application.
- When x-ray hits sample, the sample emits x-rays along a spectrum of wavelengths characteristic of the type of atoms present.
- If a sample has many elements present, the use of a Wavelength Dispersive Spectrometer allows the separation of a complex emitted X-ray spectrum into characteristic wavelengths for each element present.
- Various types of detectors used to measure intensity of emitted radiation.
- Examples of detector used the flow counter and the scintillation detector.
- Flow counters measure long wavelength(>0.15nm) x-rays typical of elements lighter than zinc.
- The scintillation detector is commonly used to analyze shorter wavelengths in the X-ray spectrum(K spectra of element from Nb to I; L spectra of Th and U).
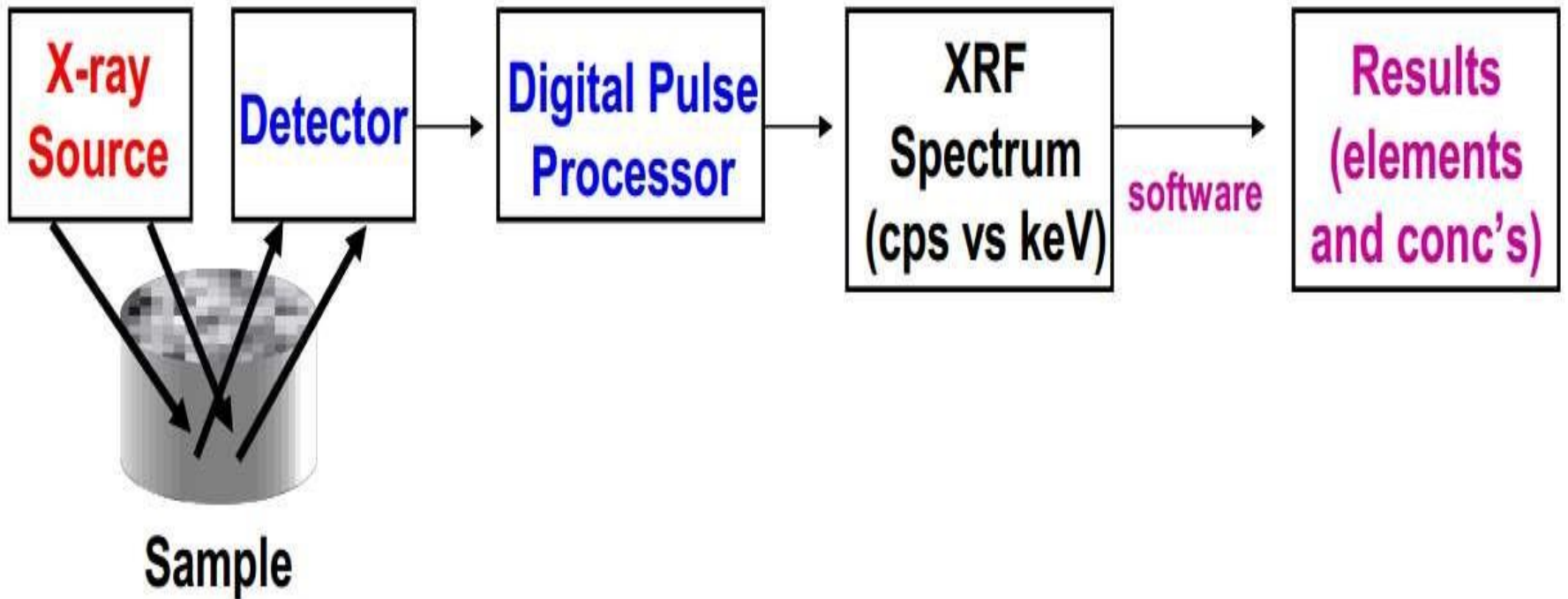
Benefits of XRF analysis

- Minimal or no sample preparation

- Non-destructive analysis

- Na11 to U92 analysis, ppm to high % concentration range

- No wet chemistry – no acids, no reagents

- Analysis of solids, liquids, powders, films, granules etc.

- Rapid analysis – results in minutes

- Qualitative, semi-quantitative, to full quantitative analysis

- For routine quality control analysis instrument can be 'used by anyone'

Applications

X-Ray fluorescence is used in a wide range of applications, including

- research in igneous, sedimentary, and metamorphic petrology

- soil surveys

- mining (e.g., measuring the grade of ore)

- cement production

- ceramic and glass manufacturing

- metallurgy (e.g., quality control)

- environmental studies (e.g., analyses of particulate matter on air filters)

Applications

- petroleum industry (e.g., sulfur content of crude oils and petroleum products)

- field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers)

X-ray fluorescence is limited to analysis of :

- relatively large samples, typically > 1 gram

- materials that can be prepared in powder form and effectively homogenized

- materials for which compositionally similar, well-characterized standards are available

- materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood

Strengths & limitations of XRF

Strengths

X-Ray fluorescence is particularly well-suited for investigations that involve:

- bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment

- bulk chemical analyses of trace elements (>1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment

Limitations

In theory the XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength and intensity of incident x-rays. However...

- In practice, most commercially available instruments are very limited in their ability to precisely and accurately measure the abundances of elements with Z<11 in most natural earth materials.

- XRF analyses cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments.

- XRF analyses cannot distinguish ions of the same element in different valence states, so these analyses of rocks and minerals are done with techniques such as wet chemical analysis or Mossbauer spectroscopy.

XRF detection system

No mater how the secondary X-ray radiation (X-Ray fluorescence) is produced in XRF machines there are TWO WAYS to detect this radiation:

- **Wavelength Dispersive System (WDS) and**
- **Energy Dispersive System (EDS).**

EDS spectrometer
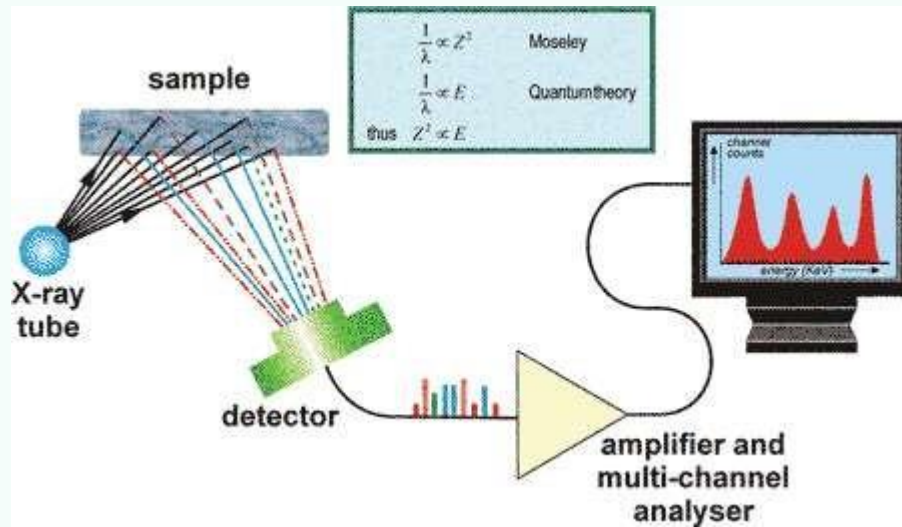
ED-XRF
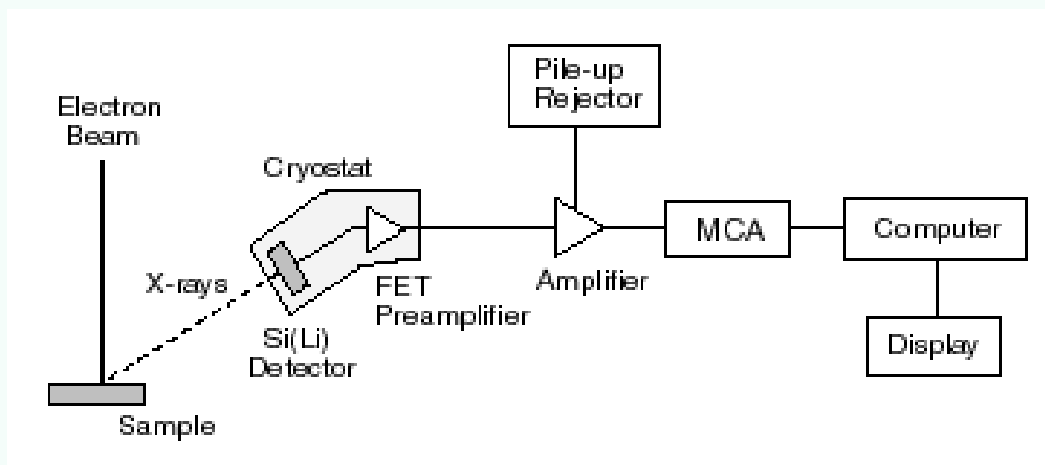
SEM-EDX

Handheld XRF
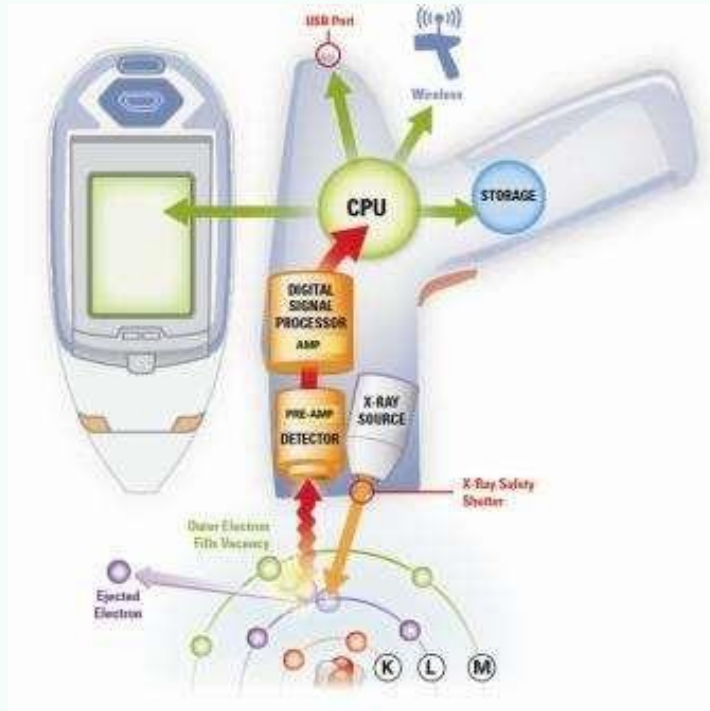
Specifically designed for the rigorous demands of nondestructive elemental analysis in the field.

Spectroscopic techniques

3.1 INTRODUCTION

Infrared, Raman and UV spectroscopic techniques are the most inspiring research tools for the physicists and chemists since these techniques provide structural information of chemical compounds. In recent years, Fourier transform (FT) spectroscopy techniques enjoy the advantages over the conventional IR and Raman spectroscopy by offering some unique features. The ultimate performance of any IR spectrometer depends on the signal to noise ratio (SNR) value. The improved SNR value is attained by incorporating FT-techniques in infrared and Raman spectrometers. Frequency precision, good spectral subtractions and high resolution are difficult to achieve with conventional Raman spectroscopy. Hence a new technique, in which the Raman module is an accessory to FT-IR spectrometer, called FT-Raman spectroscopy. FT-IR, FT-Raman and UV techniques have been found to be useful in increasing the spectral sensitivity and thus yielding new information about the atomic or molecular species or the functional group molecular bonds that exist in the sample.

Modern spectrometers are generally attached with sophisticated computers and high energy sources like lasers which allow spectrum storage and retrieval, scale expansion, repetitive scanning, spectral comparison, spectral simulation, automatic control of slit, etc. Often these are under the control of a microprocessor and microcomputers. Accessories such as beam condensers, reflectance units, polarizers and microcells can usually be added to extend versatility or accuracy. In this chapter the instrumentation and sample handling techniques of FT-IR, FT-Raman and UV spectrometers are presented.

The IR and Raman spectroscopic techniques are based on different principles. Change in electric dipole moment is necessary for IR activity, whereas the Raman criterion depends on the change in polarizability during vibration. The intensity of the

IR and Raman spectra mainly depends on the magnitude of the change in dipole moment and the polarizability respectively. The IR and Raman methods are used to study the materials existing in various states. The molecular vibrational frequencies obtained by these methods have been used in molecular mechanics and they yield considerable information about the interatomic forces in various molecules [1]. An ultraviolet spectrum of the molecule is based on the transitions of electrons between the electronic energy levels by absorbing UV radiation. UV spectroscopic techniques used to examine bonding and charge transfer interactions in the sample.

3.2 INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

3.3 INSTRUMENTATION

3.3.1 Introduction

The basic components of an infrared spectrophotometer are shown in Fig.3.1. A source provides radiation over the entire range of the infrared spectrum. The monochromator disperses the light and then selects a narrow wave number range. The

detector measures the energy and transforms it into an electric signal. This signal is further amplified and registered by the recorder. With recent improvements in instrumentation, the infrared region of the electromagnetic spectrum is now considered to cover the range from approximately 12500-10 cm^{-1} (0.8-1000 m). It is generally subdivided into three sections: near infrared (12500-4000 cm^{-1}), mid infrared region (4000 - 400 cm^{-1}) and the far infrared (400-10 cm^{-1}). The mid infrared region is one of the most commonly used standard laboratory investigations as it covers almost all the vibrational and rotational transitions. The FT-IR spectra of most of the samples were recorded in mid and far IR regions and are used for the present investigation [2-7].

SOURCE	—	SAMPLE	—	MONO-CHROMATOR	—	DETECTOR

RECORDER	—	AMPLIFIER
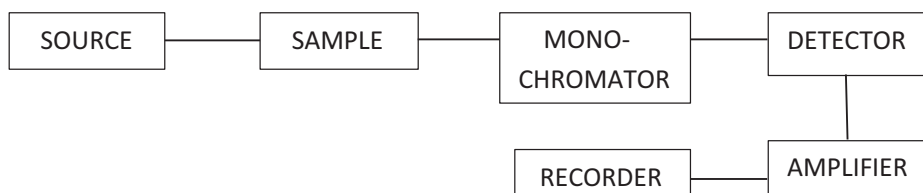
**Fig.3.1 Block diagram of the major components of
an infrared spectrophotometer.**

3.3.2 Source

The source of radiation for FT-IR spectrometer is a black body radiator. The ideal infrared source gives a continuous and high radiant energy output over the entire infrared region. The total amount of energy radiated and the spectral distribution of this energy are dependent upon the temperature of the source. The usual sources of infrared radiation are Nernst glower and Globar. The Nernst glower is composed of oxides of thorium, zirconium and yttrium. It is operated at a temperature of 1000 to 1800ºC. The Globar is a small rod of silicon carbide usually 5 cm in length and 0.5 cm in diameter. It is operated at temperatures between 1300 and 1700ºC. The maximum radiation for the Globar occurs in the 5500-5000 cm^{-1} region. Nichrome

wire, carbon arc, rhodium wire and tungsten filament lamp are also used as light source. In a commercial infrared spectrometer either a nichrome wire or a platinum filament contained in a ceramic tube is commonly used as infrared source for the range 4000-400 cm^{-1} [8].

3.3.3 Monochromator

A monochromator is a means of separating wavelengths of the source radiation. The monochromator is used to separate polychromatic radiation into a suitable monochromatic form. This is achieved by means of prisms or diffraction gratings. A grating or a prism disperses the radiation from the source into its spectral elements according to the equation nλ=2dsinθ. The most common prism material is NaCl and it has a lower frequency cut-off at about 650 cm^{-1}. It has a good resolution in the range 1000 to 650 cm^{-1} and moderate resolution throughout 4000 to 1000 cm^{-1}.

A monochromator thus carries out three functions: (i) it disperses the radiation according to its wave number components (ii) it restricts the radiation falling on the detector into a narrow wave number range, and (iii) it maintains the energy incident on the detector to an approximately constant level when no sample is present throughout the wave number range of the instrument [9]. Some instruments use a double monochromator. That is, the exit slit of the first monochromator serves as the entrance slit for the second monochromator. As a result, the spectra obtained with spectrophotometers having double monochromator have higher resolution [2].

3.3.4 Detector

Detectors used in infrared spectrophotometers usually convert the thermal radiant energy into electrical energy. The infrared detectors may be selective or non-selective. The selective detectors are those whose response is markedly dependent upon the wavelength of the incident radiation. Examples of this type are photocells,

photographic plates, photoconductive cells and infrared phosphors. Photoconductive cell has a rapid response and high sensitivity. These cells are made of materials such as PbS, lead selenide or selenium. When illuminated by infrared light these cells show an increase in conductivity. These cells are useful in the range 0.5 and 3.5 microns.

The non-selective detectors are those whose response is directly proportional to incident energy but relatively independent of wavelength. Common examples include thermocouples, bolometers and pneumatic cell. Recent detectors, fabricated from crystals are known as pyroelectrics and take less time than other thermal detector. Hence with these crystals, radiation can be chopped at a higher rate. However, these are more expensive and not widely employed.

3.3.5 Amplifiers and recorders

The radiant energy received by the detector is converted into measurable electrical signal and is amplified by the amplifiers. The amplified signal is registered by a recorder or a plotter. The recorder is driven with a speed which is synchronized with that of a monochromator, so that, the pen moving across the chart, records the transmittance of the sample as a function of the wavenumber.

3.4 SAMPLE HANDLING TECHNIQUES

Sample handling is considered as an important technique in infrared spectroscopy. There are various methods of sample preparation to enable almost any type of sample to be examined. Some significant problems arise when trying to construct sample containers for vibrational spectrometry, because every material has some vibrational absorption. The material that has a minimum interference in the regions of interest is used as sample. The material of choice for IR spectroscopy is a solid potassium bromide plate. Such plates are used in a number of ways. Polyethylene pellets are used for recording the far IR spectra.

(a) Solids

Solids are sampled in a wide variety of ways. If the sample is soluble, it may be dissolved and handled as for a liquid. Solid samples for which no solvent is suitable can be prepared for analysis by incorporating them into a pressed pellet of alkali halide, usually potassium bromide. The sample is mixed with a weighed amount of powdered potassium bromide and the mixture is admitted to a pressure of several tones in a die, to produce a highly transparent plate or disc which can be inserted into the spectrophotometer. The use of KBr eliminates the problems of additional bands due to mulling agent. KBr does not absorb infrared light in the region 2.5–15 m and a complete spectrum of the sample is obtained. Solid samples have also been examined in the form of a thin layer deposited by sublimation or solvent evaporation on the surface of a salt plate. Another method, called mulling has also been developed, in which the powdered sample is mixed to form a paste with little heavy paraffin oil. The mull is sandwiched between salt plates for measurement. Mulls are formed by grinding 2 to 5 mg of finely powered sample in the presence of one or two drops of a heavy hydrocarbon oil called Nujol [2, 10-12].

(b) Liquids

The spectra of a pure liquid can be measured as very thin films squeezed between two alkali halide windows of a demountable cell. This technique can produce a film of thickness 0.01 mm or less. The cells are then taken apart and cleaned. This method is most useful for qualitative work only because the sample thickness cannot be controlled. For quantitative work sealed liquid cells of fixed path length in the range 0.01 to 0.1mm are used. Liquid cells consist of two alkali halide windows usually NaCl or KBr, separated by a spacer of suitable thickness made of teflon or lead which limits the volume of the cell [2].

(c) Gases

The vapour is introduced into a special cell, usually about 10cm long that can be placed directly in the path of one of the infrared beams. The end walls of the cell are usually made of sodium chloride, which is transparent to infrared. Most organic compounds have too low a vapour pressure for this phase to be useful. The low frequency vibrational changes in the gaseous phase often split the high frequency vibrational bands [13].

(d) Solvents

Solvents of good infrared transparency over a convenient frequency range are available and the spectra of the sample dissolved in carbon tetrachloride and carbon disulphide provide the complete range. Chloroform is considered to be an important solvent and is frequently used because it shows absorptions though it has less symmetric molecule than carbon tetrachloride and carbon disulphide.

3.5 FOURIER TRANSFORM INFRARED SPECTROMETER

Fourier transformation technique is now of great importance in nuclear resonance, microwave, infrared and Raman spectroscopy. The absorption spectrum in a Fourier transform infrared spectrometer is obtained through interference technique [14]. Interferometry is therefore known as Fourier transform spectroscopy. The structural information from the observed diffraction patterns is obtained through a mathematical manipulation known as Fourier transformation. Fourier transformation is accomplished using a digital computer.

FT infrared spectrometer consists of two parts: (a) an optical system which uses an interferometer and (b) a dedicated computer which stores data performs computations on data and plots the spectra. A schematic diagram of the essential components of an FT spectrometer based on Michelson interferometer is shown in

Fig.3.2. It consists of two perpendicular mirrors; one of which is a stationary mirror and the other a movable mirror which can be displaced perpendicularly to the fixed mirror at a constant velocity. Between these two mirrors the beam splitter is set at 45^0 from the initial position of the movable mirror. A parallel beam of radiation from an infrared source is passed to the mirrors through the beam splitter. The beam splitter reflects about half of the beam to the fixed mirror which reflects it back to the beam splitter and transmits the other half to the movable mirror which reflects it back to the beam splitter. The returning beams are again split and mixed about half going back to source and half passing through the sample compartment. The composition of the beam splitter depends on the spectral region of interest. For example, in the mid-infrared region (4000-400 cm^{-1}), a beam splitter of germanium coated on KBr plate (substrate) is often used. Germanium reflects the radiation while KBr transmits most of the desirable radiation. In the far infrared region, germanium coated on CsI (800–200 cm^{-1}) or germanium coated on Mylar (polyethylene terephthalete) (650–10 cm^{-1}) is used as beam splitter. A thin film of the beam splitter material is coated on an optically flat substrate.

The return beams from both the mirrors along the same path length as their incident path are recombined into a single beam at the beam splitter. The path length of one of the return beams is changed in order to create phase difference to cause an interference pattern. The recombined radiation is then directed through the sample and focused on to the detector. The detector measures the amount of energy at discrete intervals of mirror movement.

The movable mirror can be moved in a range of say ±5 cm. The mirror velocities from 0.05 to 5 cm s^{-1} are used. Interferometer instruments need detectors with response times short enough to detect and transmit rapid changes to the recorder.

The detector used in conjunction with rapid scanning interferometers in the mid-infrared region at room temperature is triglycine sulfate with KBr windows as pyroelectric bolometer. It has a high response time. Other most common detectors used such as thermocouples, bolometers and Golay detectors have short response time. The design of the Michelson interferometer is such as to make measurement in any infrared region possible by simply changing the beam splitter and the detector [2].

3.6 ADVANTAGES OF FOURIER TRANSFORM TECHNIQUE

The main advantages of FT spectroscopy are the greater ease and speed of measurement. The entire spectrum can be recorded within few seconds using sophisticated computers. Recent developments in FT infrared spectrometers have thus led to higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. It can also be used in the characterization of all kinds of samples. In FT method, all the source energy passes through the instrument and the resolving power is constant over the entire spectrum. The signal to noise ratio is also improved [15]. The smoothening of peaks and the vertical and horizontal expansion of selective region is also possible.

3.7 RAMAN SPECTROSCOPY

The Raman spectroscopy is made sophisticated with the advent of gas lasers and computers. The advantages of lasers are their high intensity, high monochromaticity, narrow band width, high resolution and coherence. From the time of invention of Raman Effect, both infrared and Raman spectra of chemical compounds have been effectively used for the determination of molecular structure and also for the quick identification of the presence of the characteristic group frequencies in the compound as discussed in the literature [16].
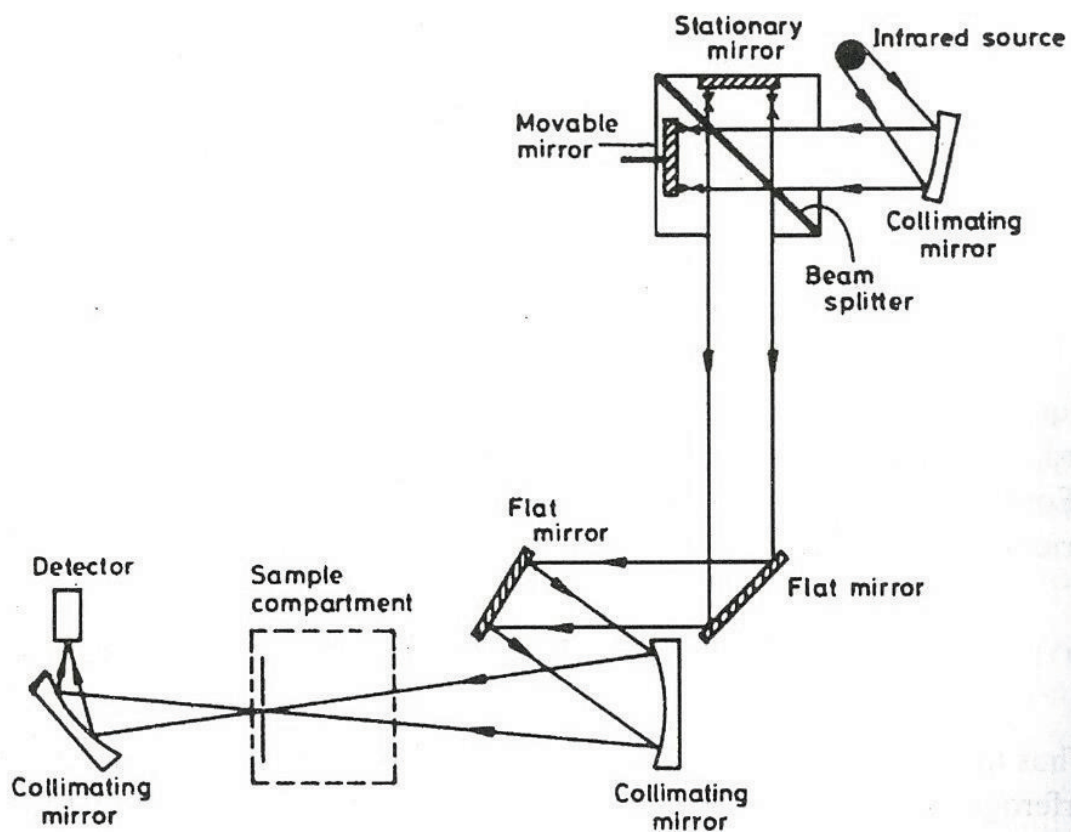
Fig.3.2 Simplified diagram of Fourier transform infrared spectrometer.

In order that for a molecular vibration to be Raman active there must be a change in the polarizability of the molecule. An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials. Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. A major advantage of FT-Raman over conventional dispersive Raman spectroscopy is its ability to render spectra that are generally free of fluorescence interference. FT-Raman enjoys the wavelength precision of FT-IR so that spectra may be co-added, resulting in a rapid improvement in signal-no-noise ratio (SNR) performance.

3.8 INSTRUMENTATION

3.8.1 Introduction

In Raman spectrometer the sample is irradiated with monochromatic light and the scattered light is observed at right angles to the incident radiation. Raman spectrometer consists of source, interferometer and detector. Fig.3.3 represents the basic diagram of an FT-Raman spectrometer.

3.8.2 Source

The sources used in modern Raman spectroscopy are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal to-noise ratio. Five of the most common lasers along with their wavelength (nm) used for Raman spectroscopy are Argon ion (488 or 514.5 nm), Krypton ion (530.9 or 647.1 nm), Helium / Neon (632.8 nm), Diode laser (782 or 830 nm) and Nd: YAG (1064 nm). Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion

sources that emit in the blue and green region of the spectrum have an advantage over the other sources. Diode and Nd:YAG laser which emit near-infrared radiation are used as powerful excitation sources. Near-infrared sources have two major advantages over shorter wavelength lasers. The first is that they can be operated at much higher power (upto 50W) without causing photodecomposition of the sample. The second is that they are not energetic enough to populate a significant number of fluorescence producing excited electronic energy states in most molecules. Consequently, fluorescence is generally much less intense or non-existent with these lasers. The Nd/YAG line at 1064 nm is particularly effective in eliminating fluorescence. The two lines of the diode array laser at 782 and 830 nm also markedly reduce fluorescence in most cases.

The laser radiation is directed to the sample by means of a lens and a parabolic mirror and the scattered light from the sample is collected and passed to a beam splitter and to the moving mirrors. It is then passed through a series of dielectric filters and focused onto a liquid nitrogen cooled detector.

3.8.3 Detectors

Raman spectrum can be photographed with an ordinary spectrograph. Basically there are two different ways to detect and record Raman lines. The easiest way is to gather the scattered light emerging through a glass window at the end of the Raman sample tube. It is passed through a prism or grating and then focused on a photographic plate. The plate is then developed and both the line frequencies and intensities can be measured using external equipment. Modern spectrometers which have photo multiplier tubes are direct measurements and facilitate automatic scanning of a spectrum. The spectrum produced by the monochromatic is passed through a slit which allows a narrow wavelength region to pass through which is focused on to a

photo multiplier type detector. This detector employs an amplifier and a recorder. It directly provides the Raman Spectrum.

3.9 SAMPLE HANDLING TECHNIQUES

Sample handling techniques for Raman spectroscopic measurements are simpler than for infrared spectroscopy because glass can be used for windows, lenses and other optical components instead of the more fragile and atmospherically less stable crystalline halides. In addition, the laser source is easily focused on a small sample area and the emitted radiation efficiently focused on slit. Consequently, very small samples can be investigated. In fact, a common sample holder for non-absorbing liquid sample is a glass melting-point capillary.

(a) Liquid samples

The spectrum of a liquid can be recorded as neat or in solution. Ordinarily about 0.3 ml of a liquid may be required. The sample could be taken in glass or silica containers or capillaries. The spectra can be measured directly from the reaction vessel. Water is a good solvent for recording the Raman spectra. Water absorbs strongly in the infrared but it gives a poor Raman scattering. Raman spectroscopy is thus a valuable tool for studying water soluble biological materials.

(b) Solid samples

The Raman spectra of solids as polycrystalline material or as a single crystal can be recorded. No medium such as null, KBr or solvent is needed. A few milligrams of the solid samples are required. Solid can be packed into a capillary tube as a powder. The crystal can be mounted in a goniometer on a glass or silica fibre. The spectra can be measured for different orientation of the crystal. For a single crystal, the Raman spectrum varies depending on the direction of the crystal axis, when

polarized light is used as incident radiation. Raman spectra of adsorbed species can be recorded at different temperatures and pressures [2].

(c) Gas samples

The Raman spectra of gases are generally weaker than those of liquids or solids and hence may require cells of larger path length. The gas may be filled in a glass or silica tube of 1 to 2 cm diameter. If the resolving power of the instrument is good and if the molecule has sufficiently low moment of inertia, the rotational fine structure may be observed on either side of the Rayleigh line. Generally a broad band contour may be observed. The main advantage of Raman spectroscopy is that it may be used for a wide variety of sizes and forms of the sample. Samples in gas, liquid and solid states can be examined easily. In this study, the spectral data are recorded on BRUCKER IFS 66V, FT-IR with FRA 1064 nm FT-Raman spectrophotometer.

3.10 FT-RAMAN SPECTROMETER

The FT-Raman method consists of measurement of spectra using a near infrared laser, the collection of the scattered light and its analysis using appropriately designed Michelson interferometers and Fourier transform processors. Fourier transform Raman spectra are almost exclusively obtained with neodymium yttrium aluminum garnet (Nd: YAG) lasers. The laser radiation is filtered to perfect its monochromaticity and is then focused on to the sample. Light reflected and scattered off the sample in a direction the reverse of illumination the so-called back scattering arrangement is then filtered to remove the Rayleigh scattered light and allow only the Raman scattering to pass. The noise associated with the intense Rayleigh scattering is distributed over the entire spectrum in the Fourier transformation step and it seriously degrades the desired Raman spectrum. Therefore, strong suppression of Rayleigh scattering by means of a laser line rejection filter must be achieved before good

quality FT-Raman spectra can be obtained. Then the scattered light passes through a Michelson interferometer. The incorporated beam splitter may be a wide range component capable of operating from 1nm and through the mid infrared or it may be a limited range device. The interferogram is then collected and detected on a near infrared detector. The germanium photo resistor operating at the liquid nitrogen temperature or indium doped gallium arsenide photo detector which operates at room temperature is employed. The detector signal is digitized and then Fourier transformed to generate a spectrogram. The spectrum is recorded as intensity of scattering versus frequency shift using software [2].

3.11 APPLICATIONS OF RAMAN SPECTROSCOPY

Raman spectroscopy is an important tool for solving the intricate research problems concerning the constitution of compounds. The technique can be applied to investigate bond angles, structure, ionic-equilibria, nature of bonding, degree of dissociation of strong electrolytes and the corresponding activity coefficients. Raman spectra can be interpreted in terms of unit cells which may contain a few elements of different polymer chains. Since peak overlap is low in Raman spectroscopy, mixtures can easily be analyzed [9].

3.12 INTERPRETATION OF SPECTRA

The assignments of fundamental modes of vibrations and interpretations of the spectra have been carried out by following empirical correlation of group frequencies, infrared and Raman selection rules, the magnitude and relative intensities of the spectra [17, 18]. In the case of polyatomic molecules, the interpretation of spectra is highly complex due to the appearance of combination and overtone bands.
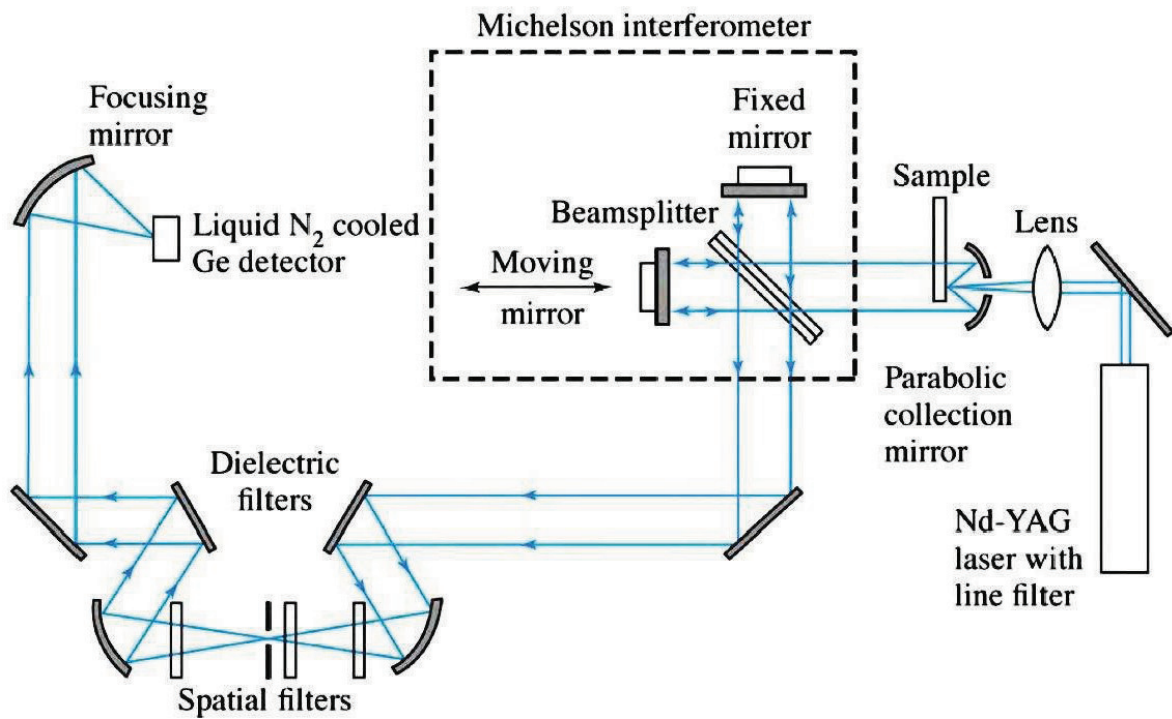
Fig.3.3 Basic diagram of an FT-Raman spectrometer.

3.13 ULTRAVIOLET SPECTROSCOPY

Ultraviolet spectroscopy employs ultraviolet and visible radiations for making the transitions between the electronic energy levels. It helps to identify the functional groups and nature of the bond in the organic compounds. It also provides the information about molecular structure and oxidation state.

3.13.1 Instrumentation

An UV-vis spectrophotometer consists of source, dispersive system (combined in a monochromator), and detection system. In a double beam spectrometer, the radiation coming from the monochromator is split into beams with the help of a beam splitter. These are passed simultaneously through the reference and the sample cell. The transmitted radiations are detected by the detectors and the difference in the signal at all the wavelengths is suitably amplified and sent for the output. UV-visible double beam spectrophotometer is shown in Fig.3.4.

3.13.2 Radiation Source

In ultraviolet spectrometers, the most commonly used radiation sources are hydrogen or deuterium lamps, the xenon discharge lamps and mercury arcs. The sources should provide stable output over the entire UV- visible range (190 nm to 780 nm). For measurements in the UV region, electric discharge sources like hydrogen or a deuterium lamp are used. In these, the excitation of the gaseous molecules is brought about by the passage of electrons through the gas at low pressures. A hydrogen lamp is commonly used in spectrophotometers and it gives light in the wavelength region of 160-375 nm. The radiant power of the hydrogen lamp is low and it is replaced by deuterium lamps. The modern instruments use a tungsten filament lamp as the radiation source. This consists of a thin, coiled tungsten wire that is sealed in an evacuated glass bulb. This gives radiations in the range of

350-2200 nm. As the output depends on the voltage, the tungsten lamp is energized by the output of a constant voltage transformer [19].

3.13.3 Monochromators

The monochromator is used to disperse the radiation according to the wavelength. The essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit. The entrance slit sharply defines the incoming beam of heterochromatic radiation. The dispersing element disperses the heterochromatic radiation into its component wavelengths, whereas exit slit allows the nominal wavelength together with a band of wavelengths on either side of it. The position of the dispersing element is always adjusted by rotating it to vary the nominal wavelength passing through the exit slit. The dispersing element may be a prism or grating. Quartz and fused silica prisms which are transparent throughout the entire UV range are widely used in UV spectrophotometers

3.13.4 Detectors

The detectors are used to convert a light signal into an electric signal which can be suitably measured and transformed into an output. The detectors used in most of the instruments generate a signal, which is linear in transmittance i.e. they respond linearly to the radiant power falling on them. The transmittance values can be changed logarithmically into absorbance units by an electrical or mechanical arrangement in the signal read out device. Phototube, photomultiplier tube and diode array detectors are three types of detectors which are widely used in UV spectrophotometers.

3.14 SAMPLE HANDLING TECHNIQUES

The UV-vis absorption spectra are usually determined either in vapour phase or in solution. In order to take the UV spectrum of the sample, it is taken in a cell called a cuvette which is transparent to the wavelength of light passing through it.
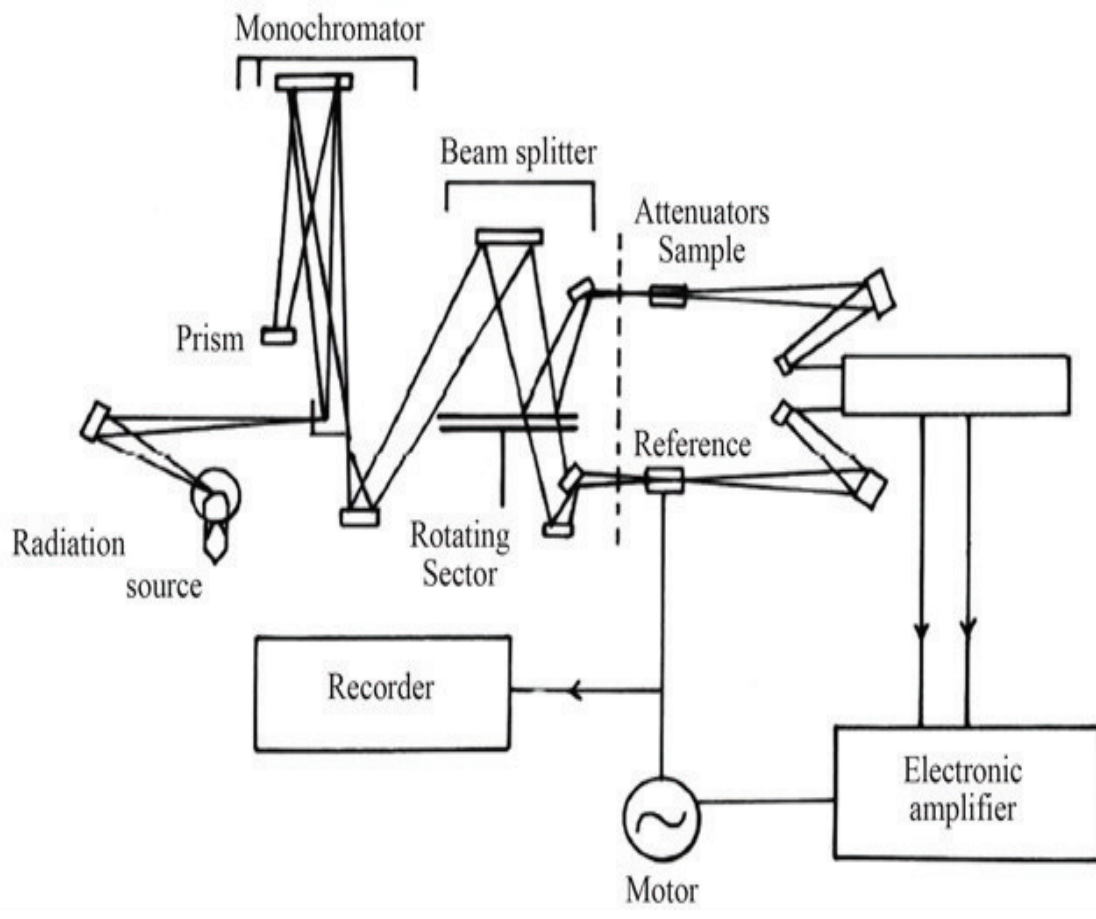
Fig.3.4 UV-visible double beam spectrophotometer.

Most of the spectrophotometers employ quartz cuvettes for both visible and UV region. The sample whose spectrum is to be measured is dissolved in a solvent that is transparent in the UV region. Hexane, ethanol and methanol are commonly employed as solvents. In a typical measurement of a UV spectrum, the solution of the sample is taken in a suitable cuvette and the spectrum is run in the desired range of the wavelengths. The absorption by the solvent, if any, is compensated by running the spectrum for the solvent alone in the same or identical cuvette and subtracting it from the spectrum of the solution. This gives the spectrum only due to the absorption species under investigation. In double beam spectrometers, the sample and the solvents are scanned simultaneously.

REFERENCES

1. P.S. Sindhu, Molecular Spectroscopy, Mc Graw Hill, New Delhi, 1985.

2. D.N. Sathyanarayana, Vibrational Spectroscopy Theory and Applications, New Age International publishers, New Delhi, 2004.

3. B.K. Sharma, Spectroscopy, GOEL Publishing House, Meerut, Eleventh Edition, 1995.

4. H.H. Willard, L.L. Merritt, J.A. Dean, F.A. Settle, Instrumental Methods of Analysis, Sixth Edition, CBS Publishers and Distributers, Delhi, 1986.

5. R.S. Khandpur, Handbook of Analytical Instruments, Tata McGraw-Hill Publishing Company Limited, New Delhi, 2002.

6. K.A. Rubinson, J.F. Rubinson, Contemporary Instrumental Analysis, Prentice Hall International, New Jersey, 2000.

7. D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, Fifth Edition Harcourt Asia PTE Ltd., Singapore, 1998.

8. N.B. Colthup, L.H. Daly, S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.

9. H. Kaur, Instrumental Methods of Chemical Analysis, Second Edition, Pragathi Prakashan, India, 2003.

10. R.A. Nyquist, C.L. Pulzig, M.A. Leugers, The Hand Book of Infrared and Raman Spectra Of Inorganic Compounds and Organic Salts, Academic Press, San Diege, 1997.

11. William Kemp, Organic Spectroscopy, ELBS, Macmillan, UK, 1987.

12. R. John, Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall, 1971.

13. G. Rahut, P. Pulay, J. Phys. Chem., 99 (1995) 3093.

14. P.R. Griffiths, J.A. de Haseth, Fourier Transform Infrared Spectroscopy, Wiley, New York, 1986.

15. C. N. Banwell, Fundamentals of Molecular Spectroscopy, Tata McGraw-Hill Publishing Company Limited Company Limited, New Delhi, 1972.

16. T. Sundius, Vib. Spectroscopy, 29 (2002) 89.

17. S. Mohan, N. Sundaraganesan, Mink, Spectrochim. Acta A, 47 (1991) 1111.

18. R.M. Silverstein, G. Clayton Bassler, C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 1981.

19. Gurdeep R. Chatwal, Sham K. Anand, Instrumental Methods of Chemical Analysis, Himalaya Publishing House Pvt. Ltd., Mumbai.