Characterization of Nanomaterials

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The future of nanotechnology rests upon approaches to making new, useful nanomaterials and testing them in complex systems. However, precise and trusting nanoparticle formation can only be promised after their thorough characterization. Here some of the basic physical and biophysical techniques are briefed which will be central to nanoparticles research.

1. X-ray Diffraction

The genesis of XRD can be traced to the suggestion of Max von Laue in 1912 that a crystal can be considered as a three-dimensional diffraction grating. It is generally used for qualitative analysis.X-ray diffraction (XRD) method is the most basic method for characterizing the crystal structures. X-rays corresponds to electromagnetic radiation in the wavelength range of 1 Å. The wavelength range is below that of ultraviolet light and above that of gamma rays.

X-rays are generally produced when electrons of several thousands of electron volts are decelerated or stopped by metals. This will produce a white radiation up to a threshold frequency corresponding to the kinetic energy of the particle. This threshold corresponds to a wavelength (in angstroms)

$$\lambda = 12399/V$$

Where,V-accelerating voltage of the electrons.

When electrons fall on matter with high energy, electrons can be ejected from various energy levels. Electron ejection from the core orbital is also accompanied by the emission of characteristic X-rays. **(Fig.1)**

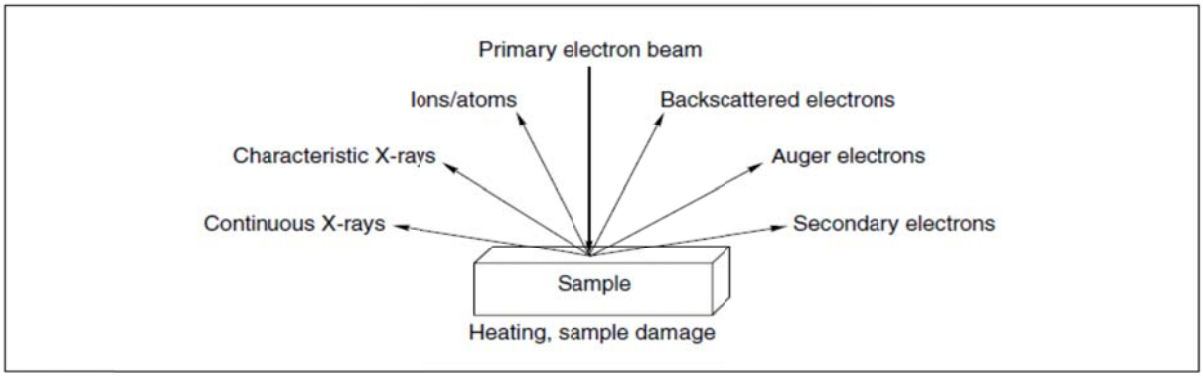


Figure 1- Electron beam induced processes in the sample

XRD method is based on the measurements of X-ray intensities scattered by the statistically distributed electrons belonging to the atoms in the material. Since the most stable structure of a pure material is crystal, where the atoms are periodically arranged, the pattern of the positions and intensities of XRD peaks can be uniquely assigned to the material. Therefore, XRD measurement is important to identify the main component of materials. The diffraction angle 2θ, the interplanar distance *d* and X-ray wavelength λare connected with each other by the Bragg's law

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

The X-ray diffraction experiment requires the following: a radiation, a sample and a detector for the reflected radiation. In each of these cases, there can be several variations.

In the Debye-Scherrer method of diffraction, we use a monochromatic X-ray and a powder sample with every possible set of lattice planes exposed to the radiation.

In the modern diffraction method called diffractometry, a convergent beam strikes the sample and the intensity as a function of diffraction angle is measured. The position of the diffraction peak and the intensity at this point are the two factors used in the determination. Both these can be measured accurately and compared with standards in the literature.

The particle size is obtained as broadening of the diffracted lines and is given by the Scherrer formula,

$$t = 0.9\,\lambda / (B\cos\theta)$$

Where t -thickness of the crystallite in (angstroms)

θ-Bragg's angle.

B –peak broadening; full width at intensity half maxima

The width of the diffraction curve (B) **(Fig.2)** increases as the thickness of the crystal decreases.

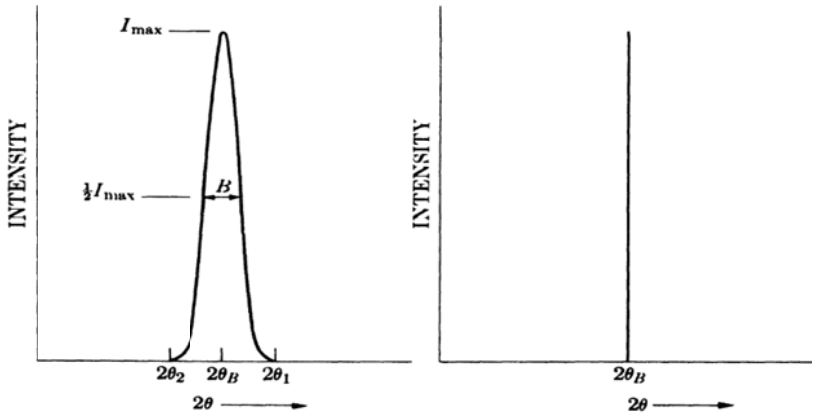


Figure 2- Effect of particle size on diffraction curves

Thus, information obtained from XRD can be used to determine the crystal structure of the sample.

2. Microscopy

2.1 ELECTRON MICROSCOPY-

Transmission electron microscopy

The properties of polycrystalline material are different from that of single crystalline material, due to the grain boundaries and their non-periodic arrangements of atoms TEM plays important roles for characterization of grain boundaries and assists the development of new polycrystalline materials. TEM is an equipment to let the incident electron beam to transmit a thin specimen at high-acceleration voltage (80–3,000 kV) which results in generating signals caused by the interaction between the specimen and

incident electrons. Structures, compositions and chemical bonds of the specimen can be determined from these signals. In general, there are three types of transmitted electrons observed by TEM **(Fig.3)-**

- Unscattered electrons- are caused by incident electrons transmitted through the thin specimen without any interaction occurring inside the specimen. Amount of unscattered electrons is inversely proportional to the specimen thickness

- Elastically scattered electrons- are caused by the incident electrons that are scattered by atoms in the specimen without losing energy. These elastically scattered electrons follow the Bragg's diffraction law. All incident electrons have the same energy and enter the specimen normal to its surface. All electrons that are scattered by the same atomic spacing will be scattered by the same angle. These "the same angle" scattered electrons are gathered by lens and form a pattern of spots; each spot corresponding to a specific atomic spacing. This diffracted pattern yields information about the orientation, atomic arrangements and phases present in the region of interest.

- Inelastically scattered electrons- are caused by the incident electrons that interact with atoms in specimen with losing their energy. These provide two types of information.
    a. The inelastic loss of energy by the incident electrons, characteristic of the elements. These energies are unique to each bonding state of each element and thus can be used to extract both compositional and chemical bonding information of the specimen.
    b. Another one is the formation of bands with alternating light and dark lines, known as Kikuchi bands. These bands are also formed by inelastic scattering interactions related to the atomic spacing in the specimen

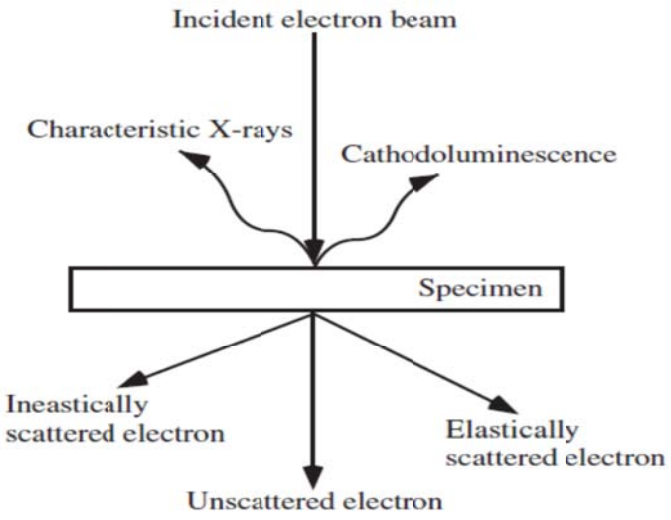
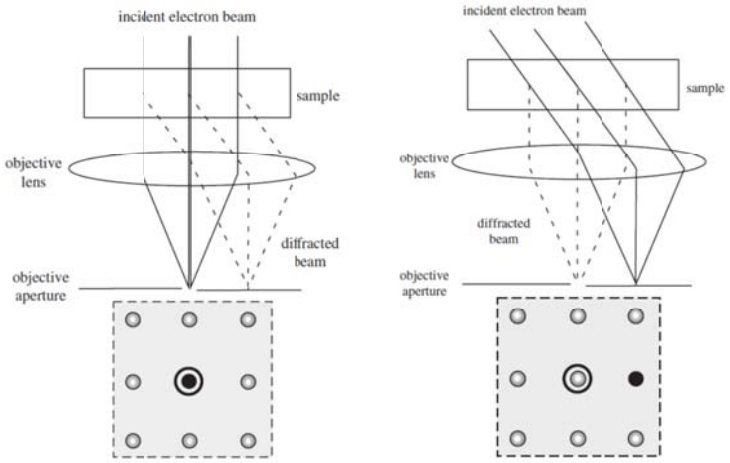


Figure 3- Interaction between incident electron beam and specimen in case of TEM

There are two main mechanisms of contrast in an image. The transmitted and scattered beams can be recombined at the image plane, thus preserving their amplitudes and phases. This results in the phase contrast image of the object. An amplitude contrast image can be obtained by eliminating the diffracted beams. This is achieved by placing suitable apertures below the back focal plane of the objective lens. This image is called the bright field image. The size of the objective aperture should be small enough to remove all diffracted electron beams caused by the specimen One can also exclude all other beams except the particular diffracted beam of interest. The image using this is called the dark field image. The advantage of the dark-field imaging method is its high-diffraction contrast. The dark-field imaging technique is usually used for observing grain size distributions and dislocations **(Fig.4)**



a) Bright field **b) Dark field**

Figure 4- Different modes of imaging in TEM

2.2 Scanning electron microscopy-

Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using Energy Dispersive analysis).

The interactions exploited for SEM analysis include-

- Secondary electrons (that produce SEM images)- most valuable for showing morphology and topography on samples
- Backscattered electrons - illustrating contrasts in composition in multiphase samples
- Diffracted backscattered electrons- are used to determine crystal structures and orientations of minerals

SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

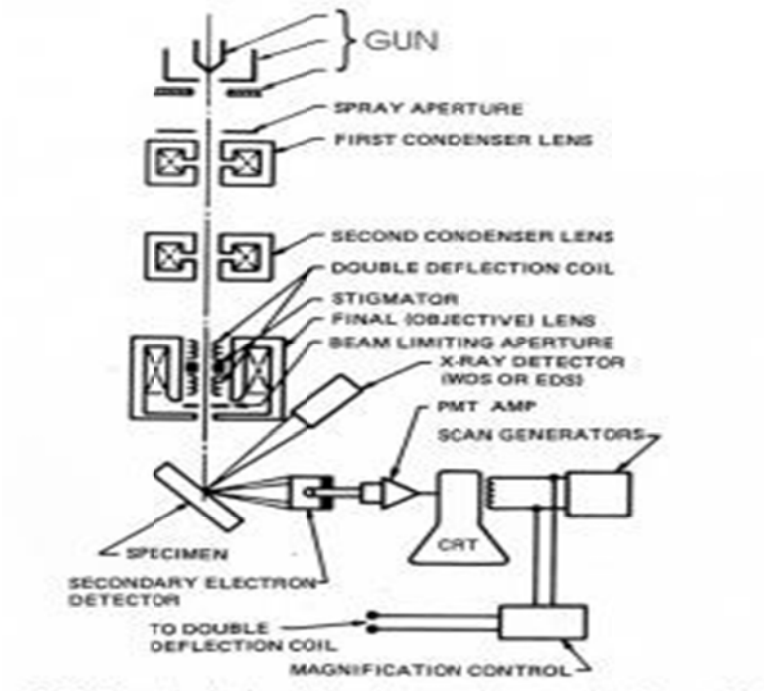


Fig 5- Schematic representation of SEM

Essential components of all SEMs include the following (Fig. 5)-

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
    - Power Supply
    - Vacuum System
    - Cooling system

- Vibration-free floor
- Room free of ambient magnetic and electric fields

Sample preparation for SEM is a crucial task in particular for insulating samples. Most electrically insulating samples are coated with a thin layer of conducting material, commonly carbon, gold, or some other metal or alloy. The choice of material for conductive coatings depends on the data to be acquired for eg.-carbon is most desirable if elemental analysis is a priority, while metal coatings are most effective for high resolution electron imaging applications.

SEM finds use for varied applications some of them are-

1. Routinely used to generate high-resolution images of shapes of objects
2. To show spatial variations in chemical compositions
3. To identify phases based on qualitative chemical analysis and/or crystalline structure.
4. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM.

SEM offers advantage of wide applicability and rapid data acquisition but suffers from drawbacks of high vacuum requirement of the order 10^{-5} - 10^{-6} torr.

2.3Atomic force microscopy-

AFM provides a 3D profile of the surface on a nanoscale, by measuring forces between a sharp probe (<10 nm) and surface at very short distance (0.2-10 nm, probe-sample separation). The probe is supported on a flexible cantilever. The AFM tip "gently" touches the surface and records the small force between the probe and the surface.

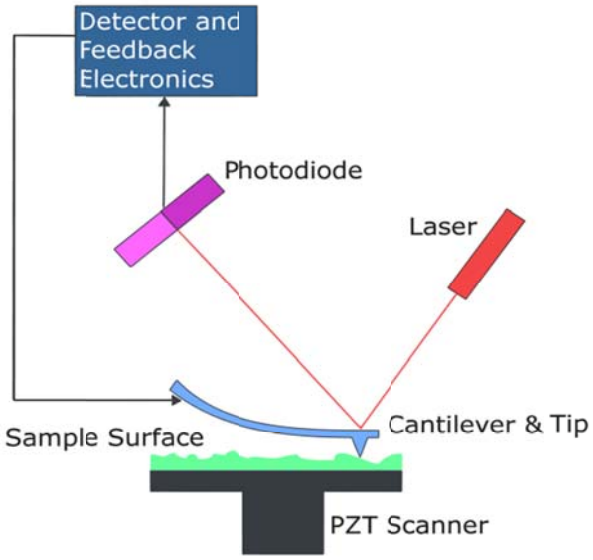


Fig 6. Block diagram of AFM

The probe is placed on the end of a cantilever (which one can think of as a spring). The

amount of force between the probe and is dependent on the spring constant (stiffness of the cantilever and the distance between the probe and the sample surface. This force can be described using Hooke's Law: ample)

$$F=-k\cdot x$$

F = Force

k = spring constant

x = cantilever deflection

If the spring constant of cantilever (typically ~ 0.1-1 N/m) is less than surface, the cantilever bends and deflection is monitored. Probes are typically made from Si3N4, or Si. Different cantilever lengths, materials, and shapes allow for varied spring constants and resonant frequencies. The motion of the probe across the surface is controlled using feedback loop and piezoelectronic scanners.There are 3 primary imaging modes in AFM-

(1) Contact AFM (< 0.5 nm probe-surface separation)

When cantilever bends are due to sample interaction the force on the tip is repulsive. By maintaining a constant cantilever deflection (using the feedback loops) the force between the probe and the sample remains constant and an image of the surface is obtained.

Advantages: fast scanning, good for rough samples, used in friction analysis

Disadvantages: at time forces can damage/deform soft samples (however imaging in liquids often resolves this issue)

(2) Intermittent contact (0.5-2 nm probe-surface separation)

However, in this mode the cantilever is oscillated at its resonant frequency, Figure 4. The probe lightly "taps" on the sample surface during scanning, contacting the surface at the bottom of its swing. By maintaining constant oscillation amplitude a constant tip-sample interaction is maintained and an image of the surface is obtained.

Advantages: allows high resolution of samples that are easily damaged and/or loosely held to a surface; good for biological samples

Disadvantages: more challenging to image in liquids, slower scan speeds needed

(3) Non-contact AFM (0.1-10 nm probe-surface separation)

The probe does not contact the sample surface, but oscillates above the adsorbed fluid layer on the surface during scanning. (Note: all samples unless in a controlled UHV or environmental chamber have some liquid adsorbed on the surface). Using a feedback loop to monitor changes in the amplitude due to attractive VdW forces the surface topography can be measured.

Advantages: very low force exerted on the sample (10-12N), extended probe lifetime

Disadvantages: generally lower resolution; contaminant layer on surface can interfere with oscillation; usually need ultra-high vacuum (UHV) to have best imaging.

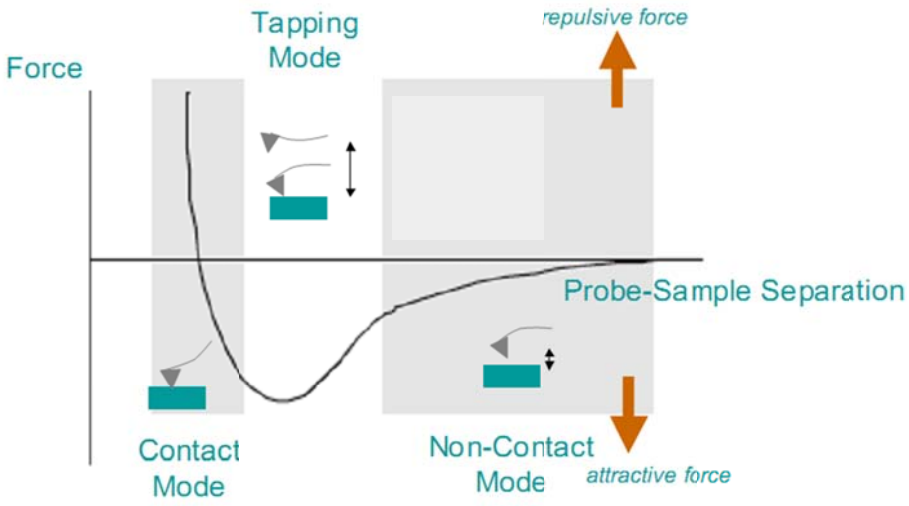


Fig. 7-Plot of force as a function of probe-sample separation

3. Spectroscopy

3.1 UV-Visible spectroscopy

The word ‘spectroscopy’ is used as a collective term for all the analytical techniques based on the interaction of light and matter. Spectrophotometry is one of the branches of spectroscopy where we measure the absorption of light by molecules that are in a gas or vapour state or dissolved molecules/ions. Spectrophotometry investigates the absorption of the different substances between the wavelength limits 190 nm and 780 nm (visible spectroscopy is restricted to the wavelength range of electromagnetic radiation detectable by the human eye, that is above ~360 nm; ultraviolet spectroscopy is used for shorter wavelengths). In this wavelength range the absorption of the electromagnetic radiation is caused by the excitation (i.e. transition to a higher energy level) of the bonding and non-bonding electrons of the ions or molecules. A graph of absorbance against wavelength gives the sample’s absorption spectrum.

Spectrophotometry is used for both qualitative and quantitative investigations of samples. The wavelength at the maximum of the absorption band gives information about the structure of the molecule or ion and the extent of the absorption is proportional with the amount of the species absorbing the light.

Quantitative measurements are based on Beer’s Law which is described as follows:

$$\mathbf{A = \varepsilon\, c\, l}$$

Where; *A*-absorbance [$A = \log_{10} (I_0/I)$, I_0 is the incident light’s intensity and I is the light intensity after it passes through the sample];

e- Molar absorbance or absorption coefficient [in $dm^3\ mol^{-1}\ cm^{-1}$ units];

c- Concentration (molarity) of the compound in the solution [in $moldm^{-3}$ units];

l - Path length of light in the sample [in cm units].

The instruments used for spectrophotometry are called photometers and Spectrophotometers. The difference between them is that we can only make measurements at a particular wavelength with a photometer, but spectrophotometers can be used for the whole wavelength range. Both types of instruments have suitable light sources, monochromator (that selects the light with the necessary wavelength) and a detector. The solution is put into a sample tube (called a “cuvette”). The light intensity

measured by the detector is converted into an electric signal and is displayed as a certain absorbance on the readout **(Fig.8)**

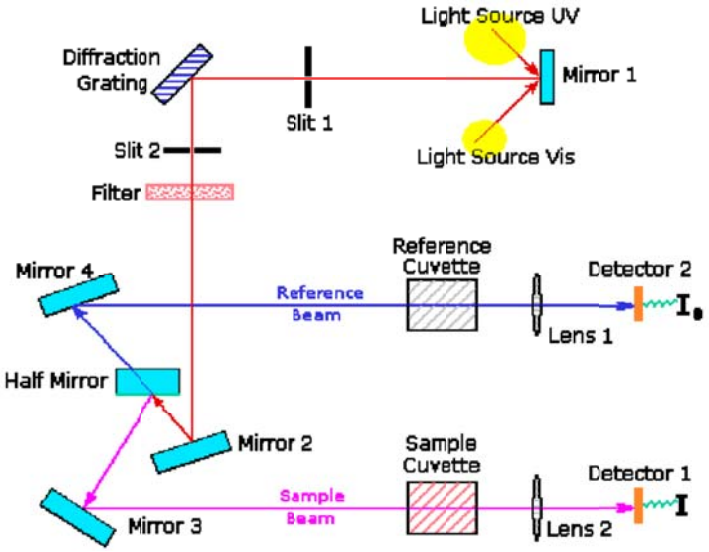


Figure 8- UV/Vis spectrophotometer

3.2 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties.

Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state **(Fig.9)**. The quantity of the emitted light is related to the relative contribution of the radiative process. Photoluminescence is used for band gap determination particularly in case of semiconductors.

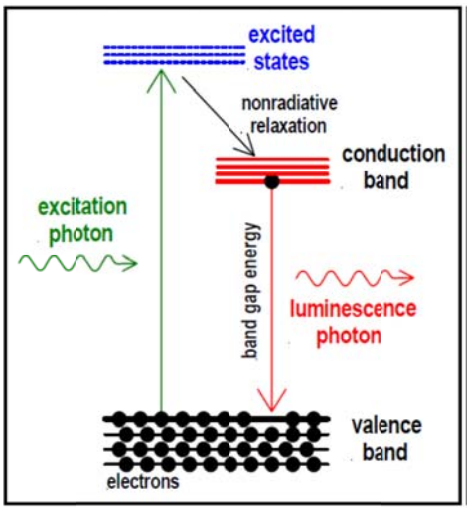


Figure 9- Photoluminescence

The light from an excitation source passes through a filter or monochromator, and strikes the sample. A proportion of the incident light is absorbed by the sample, and some of the molecules in the sample fluoresce. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second filter or monochromator and reaches a detector (photosensor), which is usually placed at 90° to the incident light beam to minimize the risk of transmitted or reflected incident light reaching the detector.Various light sources may be used as excitation sources; including lasers, photodiodes, and lamps; xenon arcs and mercury-vapor lamps in particular.Filters and/or monochromators may be used in fluorimeters. A monochromator transmits light of an adjustable wavelength with an adjustable tolerance. The most common type of monochromator utilizes a diffraction grating, that is, collimated light illuminates a grating and exits with a different angle depending on the wavelength. The monochromator can then be adjusted to select which wavelengths to transmit. As mentioned before, the fluorescence is most often measured at a 90° angle relative to the excitation light. This geometry is used instead of placing the sensor at the line of the excitation light at a 180° angle in order to avoid interference of the transmitted excitation light. The detector can either be single-channeled or multichanneled.

Source:
http://nptel.ac.in/courses/118107015/12