THINFILM INSTRUMENTATION&CHARECTERZATION TECHNIQUES

3.1 UV-VISIBLE SPECTROSCOPY

**INTRODUCTION TO UV SPECTROSCOPY**

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states (delta = hf).

Generally, the most favored transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). For most of the molecules, the lowest energy occupied molecular orbitals are s orbital, which correspond to sigma bonds. The p orbitals are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels. The unoccupied or antibonding orbitals (pie\* and sigma\*) are the highest energy occupied orbitals. In all the compounds (other than alkanes), the electrons undergo various transitions. Some of the important transitions with increasing energies are: nonbonding to pie\*, nonbonding to sigma\*, pie to pie\*, sigma to pie\* and sigma to sigma\*.

**PRINCIPLE OF UV SPECTROSCOPY**

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution**.**

The expression of Beer-Lambert law is-
A = log (I0/I) = Ecl
Where, A = absorbance
I0 = intensity of light incident upon sample cell
I = intensity of light leaving sample cell
C = molar concentration of solute
L = length of sample cell (cm.)
E = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy[52].

**INSTRUMENTATION AND WORKING OF UV SPECTROSCOPY**

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-
 Fig 3.1 working of uv-visible spectroscopy

**Light Source -** Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

**Monochromator -** Monochromators generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

**Sample and reference cells -** One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

**Detector -** Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

**Amplifier -** The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

**Recording devices -** Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

**CONCEPT OF CHROMOPHORE AND AUXOCHROME IN THE UV SPECTROSCOPY:**

**Chromophore -** Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the **ultraviolet or visible region (200-800 nm)**. Chromophores can be divided into two groups-
a) Chromophores which contain p electrons and which undergo pie to pie\* transitions. Ethylenes and acetylenes are the example of such chromophores.
b) Chromophores which contain both p and nonbonding electrons. They undergo two types of transitions; pie to pie\*and nonbonding to pie\*. Carbonyl, nitriles, azo compounds, nitro compounds etc. are the example of such chromophores.

**Auxochromes -** An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the longer wavelength of the spectrum. –OH,-OR,-NH2,-NHR, -SH etc. are the examples of auxochromic groups.

**ABSORPTION AND INTENSITY SHIFTS IN THE UV SPECTROSCOPY**

There are four types of shifts observed in the UV spectroscopy-

**(a)** **Bathochromic effect -** This type of shift is also known as red shift. Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents.
The nonbonding to pie\* transition of carbonyl compounds observes bathochromic or red shift.

**(b)** **Hypsochromic shift -** This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength. Generally it is caused due to the removal of conjugation or by changing the polarity of the solvents.
**(c) Hyperchromic effect -** Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.

**(d) Hypochromic effect** - Hyperchromic effect is defined as the effect by virtue of intensity of absorption maximum decreases. Hyperchromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.

**APPLICATIONS OF UV SPECTROSCOPY**

1. Detection of functional groups- UV spectroscopy is used to detect the presence or absence of chromophore in the compound. This is technique is not useful for the detection of chromophore in complex compounds. The absence of a band at a particular band can be seen as an evidence for the absence of a particular group. If the spectrum of a compound comes out to be transparent above 200 nm than it confirms the absence of –
a) Conjugation b) A carbonyl group c) Benzene or aromatic compound d) Bromo or iodo atoms.

2. Detection of extent of conjugation- The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy. With the increase in double bonds the absorption shifts towards the longer wavelength. If the double bond is increased by 8 in the polyenes then that polyene appears visible to the human eye as the absorption comes in the visible region.

3. Identification of an unknown compound- An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectrums coincide then it confirms the identification of the unknown substance.

4. Determination of configurations of geometrical isomers- It is observed that cis-alkenes absorb at different wavelength than the trans-alkenes. The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances. The cis-isomer suffers distortion and absorbs at lower wavelength as compared to trans-isomer.

5. Determination of the purity of a substance- Purity of a substance can also be determined with the help of UV spectroscopy. The absorption of the sample solution is compared with the absorption of the reference solution. The intensity of the absorption can be used for the relative calculation of the purity of the sample substance.

3.2 X-RAY DIFFRACTION

INTRODUCTION TO X-RAY DIFFRACTION

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

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 [42].

FUNDAMENTAL PRINCIPLES OF X-RAY POWDER DIFFRACTION (XRD)

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 toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy [**Bragg's Law**](http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html)**(*n*λ=2*d* sin θ).**

Where,

 *n-*is an integer,

*λ* - is the [wavelength](http://en.wikipedia.org/wiki/Wavelength) of incident wave,

 *d-* is the spacing between the planes in the atomic lattice, and

*θ-* is the angle between the incident ray and the scattering planes

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on [generation of X-rays](http://serc.carleton.edu/research_education/geochemsheets/xrays.html) in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

X-RAY POWDER DIFFRACTION (XRD) INSTRUMENTATION

X-ray diffractometer consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

[X-rays are generated](http://serc.carleton.edu/research_education/geochemsheets/xrays.html) in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kα1and Kα2 is sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample[43].

As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.



 Fig 3.2 bragg;s law



 **Fig 3.3 working of x-ray diffraction**

APPLICATIONS

 X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

* characterization of crystalline materials
* identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
* determination of unit cell dimensions
* measurement of sample purity

With specialized techniques, XRD can be used to:

* Determine crystal structures using Rietveld refinement
* Determine of modal amounts of minerals (quantitative analysis) [45].

Characterize thin films samples by:

* determining lattice mismatch between film and substrate and to inferring stress and strain
* determining dislocation density and quality of the film by rocking curve measurements
* measuring super lattices in multilayered epitaxial structures
* determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
* make textural measurements, such as the orientation of grains, in a polycrystalline sample

 3.3. SCANNING ELECTRON MICROSCOPE (SEM)

INTRODUCTION:

The 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](http://serc.carleton.edu/research_education/geochemsheets/electroninteractions.html) 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. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). 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 [EDS](http://serc.carleton.edu/research_education/geochemsheets/eds.html)), crystalline structure, and crystal orientations (using [EBSD](http://serc.carleton.edu/research_education/geochemsheets/ebsd.html)). The design and function of the SEM is very similar to the [EPMA](http://serc.carleton.edu/research_education/geochemsheets/techniques/EPMA.html) and considerable overlap in capabilities exists between the two instruments [44].

FUNDAMENTAL PRINCIPLES OF SCANNING ELECTRON MICROSCOPY (SEM)

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by [electron-sample interactions](http://serc.carleton.edu/research_education/geochemsheets/electroninteractions.html) when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons ([BSE](http://serc.carleton.edu/research_education/geochemsheets/bse.html)), diffracted backscattered electrons ([EBSD](http://serc.carleton.edu/research_education/geochemsheets/ebsd.html) that are used to determine crystal structures and orientations of minerals), photons ([characteristic X-rays](http://serc.carleton.edu/research_education/geochemsheets/xrays.html) that are used for elemental analysis and continuum X-rays), visible light ([cathodoluminescence–CL](http://serc.carleton.edu/research_education/geochemsheets/semcl.html)), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). [X-ray generation](http://serc.carleton.edu/research_education/geochemsheets/xrays.html) is produced by inelastic collisions of the incident electrons with electrons in discrete ortitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. 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 [45].



Fig 3.3 scanning electron microscope

ESSENTIAL COMPONENTS OF ALL SEMS INCLUDE THE FOLLOWING:

* 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

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates [46].

APPLICATIONS:

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: 1) acquiring [elemental maps](http://serc.carleton.edu/research_education/geochemsheets/elementmapping.html) or spot chemical analyses using [EDS](http://serc.carleton.edu/research_education/geochemsheets/eds.html), 2)discrimination of phases based on mean atomic number (commonly related to relative density) using [BSE](http://serc.carleton.edu/research_education/geochemsheets/bse.html), and 3) compositional maps based on differences in trace element "activitors" (typically transition metal and Rare Earth elements) using [CL](http://serc.carleton.edu/research_education/geochemsheets/semcl.html). The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backescattered electron images ([BSE](http://serc.carleton.edu/research_education/geochemsheets/bse.html)) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors ([EBSD](http://serc.carleton.edu/research_education/geochemsheets/EBSD.html)) can be used to examine microfabric and crystallographic orientation in many materials.

#  3.4 PHYSICAL CHARACTERIZATION:

* + 1. **PARTICLE SIZE ANALYZER (PSA):**

Particle size analysis, particle size measurement, or simply particle sizing is the collective name of the technical procedures, or [laboratory techniques](https://en.wikipedia.org/wiki/Laboratory_technique) which determines the [size range,](https://en.wikipedia.org/w/index.php?title=Size_range&amp;action=edit&amp;redlink=1) and/or the average, or [mean size](https://en.wikipedia.org/w/index.php?title=Mean_size&amp;action=edit&amp;redlink=1) of the particles in a [powder](https://en.wikipedia.org/wiki/Powder_%28substance%29) or liquid [sample](https://en.wikipedia.org/wiki/Sample_%28material%29). Particle size Analyzer gives us information about what sizes (particle size) of particles are present in what proportions (relative particle amount as a percentage where the total amount of particles is 100 %) in the sample particle group to be measured. Volume, area, length, and quantity are used as standards (dimensions) for particle amount. However, generally, the volume standard is apparently often used. Frequency distribution indicates in percentage the amounts of particles existing in respective particle size intervals after the range of target particle sizes is divided into separate intervals.

# PRINCIPLE OF PSA:

Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

# WORKING OF PSA:

A representative sample, dispersed at an adequate concentration in a suitable liquid or gas, is passed through the beam of a monochromatic light source, usually a laser. The light scattered by the particles at various angles is measured by a multi-element detector and numerical values relating to the scattering pattern are then recorded for subsequent analysis. These numerical scattering values are then transformed, using an appropriate optical model and mathematical procedure, to yield the proportion of total volume to a discrete number of size classes forming a volumetric particle size distribution.

Figure 3.4 Schematic Diagram of PSA

3.5 **ENERGY-DISPERSIVE X-RASPECTROSCOPY** (**EDS**)

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the [elemental](http://en.wikipedia.org/wiki/Chemical_element) analysis or [chemical characterization](http://en.wikipedia.org/wiki/Characterization_%28materials_science%29) of a sample. It relies on an interaction of some source of [X-ray](http://en.wikipedia.org/wiki/X-ray) excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of haracteristic X-rays from a specimen, a high-energy beam of charged particles such as [electrons](http://en.wikipedia.org/wiki/Electron) or [protons](http://en.wikipedia.org/wiki/Proton) (see [PIXE](http://en.wikipedia.org/wiki/Particle-Induced_X-ray_Emission)), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains [ground state](http://en.wikipedia.org/wiki/Ground_state) (or unexcited) electrons in discrete energy levels or [electron shells](http://en.wikipedia.org/wiki/Electron_shell) bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured [47].

EQUIPMENT

 Four primary compounds of the EDS setup are

1. the excitation source (electron beam or x-ray beam)
2. the X-ray detector
3. the pulse processor
4. the analyzer.[[*citation needed*](http://en.wikipedia.org/wiki/Wikipedia%3ACitation_needed)]

Electron beam excitation is used in [electron microscopes](http://en.wikipedia.org/wiki/Electron_microscope), [scanning electron microscopes](http://en.wikipedia.org/wiki/Scanning_electron_microscope) (SEM) and [scanning transmission electron microscopes](http://en.wikipedia.org/wiki/Scanning_transmission_electron_microscope) (STEM). X-ray beam excitation is used in [X-ray fluorescence](http://en.wikipedia.org/wiki/X-ray_fluorescence) (XRF) spectrometers. A detector is used to convert X-ray energy into [voltage](http://en.wikipedia.org/wiki/Voltage) signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.[[*citation needed*](http://en.wikipedia.org/wiki/Wikipedia%3ACitation_needed)] The most common detector now is [Si(Li) detector](http://en.wikipedia.org/wiki/X-ray_fluorescence#Si.28Li.29_detectors)cooled to cryogenic temperatures with liquid nitrogen; however newer systems are often equipped with [silicon drift detectors](http://en.wikipedia.org/wiki/Silicon_drift_detector)(SDD) with Peltier cooling systems.

PRINCIPLE OF EDS

The excess energy of the electron that migrates to an inner shell to fill the newly created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an [Auger electron](http://en.wikipedia.org/wiki/Auger_electron), and the method for its analysis is known as [Auger electron spectroscopy](http://en.wikipedia.org/wiki/Auger_electron_spectroscopy) (AES).

[X-ray photoelectron spectroscopy](http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy) (XPS) is another close relative of EDS, utilizing ejected electrons in a manner similar to that of AES. Information on the quantity and[kinetic energy](http://en.wikipedia.org/wiki/Kinetic_energy) of ejected electrons is used to determine the [binding energy](http://en.wikipedia.org/wiki/Binding_energy) of these now-liberated electrons, which is element-specific and allows chemical characterization of a sample [52].

EDS is often contrasted with its spectroscopic counterpart, WDS ([wavelength dispersive X-ray spectroscopy](http://en.wikipedia.org/wiki/Wavelength_dispersive_X-ray_spectroscopy)). WDS differs from EDS in that it uses the X-rays [diffraction](http://en.wikipedia.org/wiki/Diffraction) on special crystals as its raw data. WDS has a much finer spectral resolution than EDS. WDS also avoids the problems associated with artifacts in EDS (false peaks, noise from the amplifiers, and[microphonics](http://en.wikipedia.org/wiki/Microphonic)). In WDS, only one element can be analyzed at a time, while EDS gathers a [spectrum](http://en.wikipedia.org/wiki/Spectrum) of all elements, within limits, of a sample.



 Fig 3.8 principles of eds