

ANALYTICAL TECHNIQUES FOR CLAY STUDIES

Analytical techniques extract various information like the internal structure, elemental composition, valency state of specific ions, thermal interaction etc. of clay minerals. For multipurpose application these data can be used suitably.

6.1 DIFFERENT ANALYSES AND THEIR USES

To identify a material under study, its various properties are analyzed using different techniques. Analytical techniques utilize the interaction of incident entity (in the form of electromagnetic waves of different frequencies or particles like electrons etc.) with the sample to get the relevant information through detailed analysis of the output data.

For spectroscopic analysis (e.g. XRF, XRD, IR, Raman, Mossbauer etc.), a plot of the observed intensity versus the corresponding wavelength or frequency (or some other related parameter) is called the spectrum of that particular analytical method. The spectrum or the data obtained from such experiments contain information about nature of the interactions, atomic and molecular energy levels, chemical bonds, crystallographic information and other related processes. When only the item of interest is identified, it is called qualitative analysis and when the amount present is estimated, it is known as quantitative analysis. The effect of heat on a sample is reflected through its variation of thermodynamic properties. Such studies are done by thermal analysis.

The analytical techniques used for various types of clay studies have a long list. Due to the fine grain and opaque nature of clays, usual optical microscopic techniques are not applicable. But the high resolution electron microscopy (e.g. scanning and transmission type) is a very useful tool to

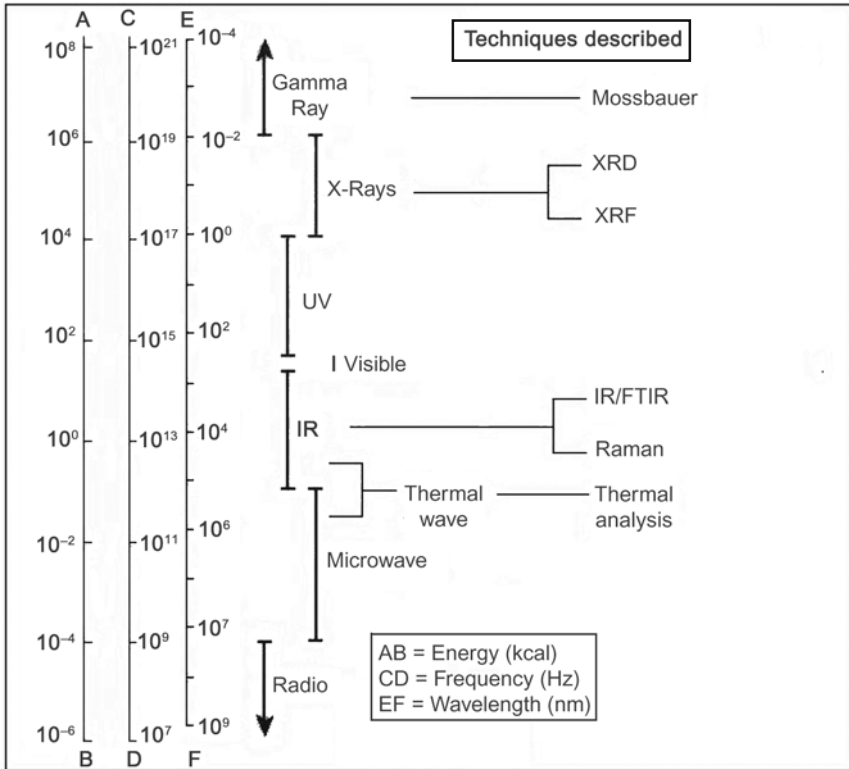


Fig. 6.1: Electromagnetic radiation and related analytical techniques.

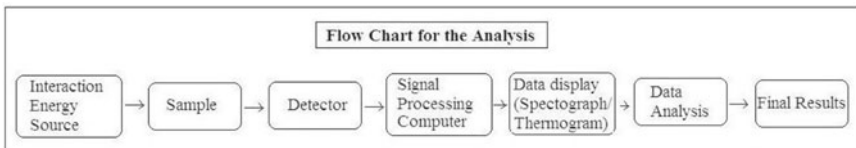


Fig. 6.2: A flow chart depicting the different analytical processes.

understand some pertinent features of clays. Clays can be uniquely identified by the finger print of their crystalline structures with X-ray powder diffraction technique. For elemental analysis (i.e. chemical composition), X-ray fluorescent is a very powerful tool. Study of infrared (IR) and Raman spectra yields information about the chemical functional groups and types of bonds present in the sample. For information regarding the valence state of iron Mossbauer spectroscopic analysis is unique and very useful for clay studies.

The accuracy and precision of data from any technique is of vital importance. The experimental results would be accurate if they show their proximity to the true values while the precision is connected with the reproducibility of the results under repeated measurements.

Table 6.1: Analytical techniques with their specialities

<i>Name of the technique</i>	<i>Principle of operation</i>	
X-ray analysis	XRD	Analyses and identifies crystalline samples clay, using standard file.
		Analyses and identifies elements from its fluorescent characteristic x-rays.
	EXD (Energy dispersive x-ray)	Output data recorded as energy of the emitted x-ray vs. corresponding line intensities.
Electron microscopy	WDX (Wavelength dispersive x-ray)	Output data presented as the emitted x-ray wavelength vs. its intensities.
		Electron beams replaces the visible light to increase its magnification and resolution. Focussing is done using magnetic lenses.
Electron probe microanalyser (EPMA)	TEM	Electron beam passes through the sample and the interactions are recorded for further analysis.
	SEM	Electron beam scans the surface of the sample and interactions are recorded for further study.
Infrared analysis		Electron beam is allowed to probe the sample resulting interactions, emits characteristics x-ray of elements present in the sample recorded in WDX-spectra and the needed information can be extracted from the data.
Raman spectroscopy		Used to identify the chemical functional groups present in the sample and also the types of bonds in it by detecting the absorption spectra of vibrational levels of atoms or molecules. In the technique, sample is exposed to a lesser beam and the scattered light is collected from the data i.e., wavelengths and intensities of the scattered light. The information about the functional groups in a molecule can be identified.

(Contd)

Table 6.1: (*Contd*)

Thermal analysis	It is the change of different properties of a material with the variation of temperature.	
Thermo gravimetry (TG)	Mass change study.	Simultaneous thermal analysis (STA)
Differential Scanning Calorimetry (DSC)	Study of heat difference	[(TG)+(DSC)]
Dilatometry (DIL)	Volume change analysis	
Evolved gas analysis (EGA)	Study of gaseous products on decomposition	
Laser flash analysis (LFA)	Thermal conductivity and thermal diffusivity study	
Thermo mechanical analysis (TMA)	Variation of dimension analysis	

6.2 X-RAY TECHNIQUES

In X-ray analytical techniques, a suitable metal target is exposed to a beam of electrons which excites the atoms of the target. De-excitation of the atom may occur in three ways, illustrated in Figs 6.3 and 6.4.

It is to be noted that the peak of the curve shifts towards low wavelength side with increase of incident electron energy.

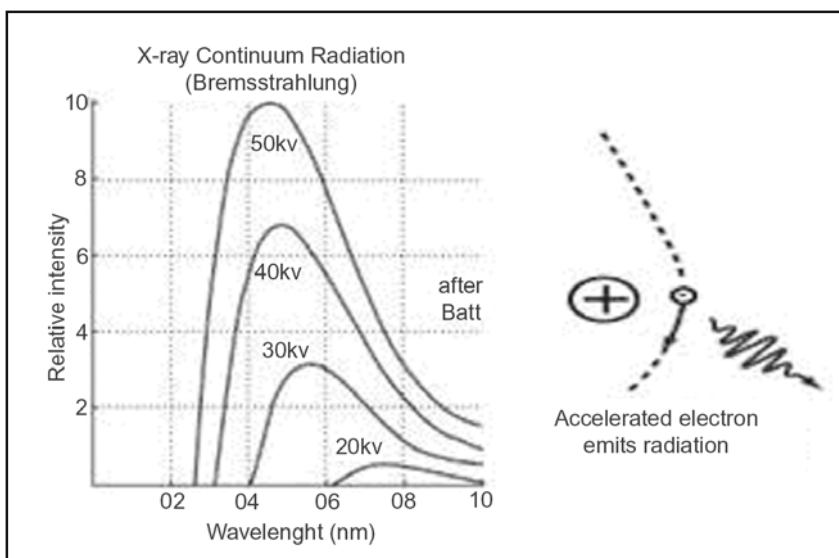


Fig. 6.3: Energy dependence of X-ray production.

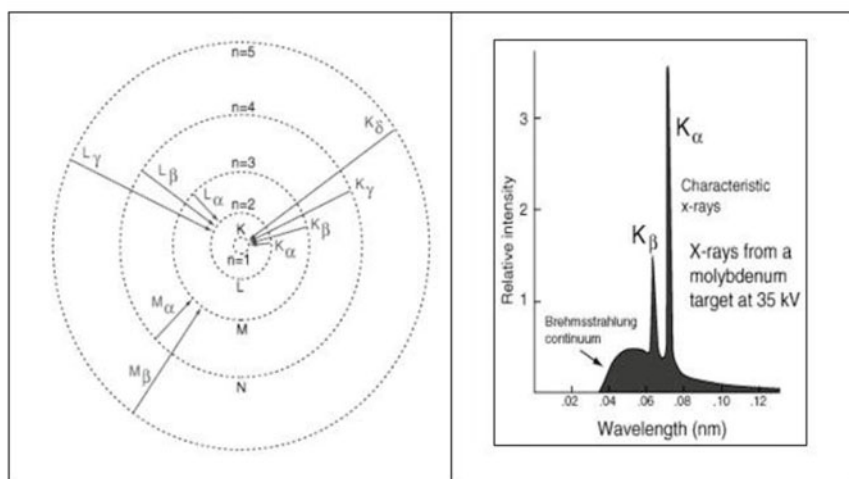


Fig. 6.4: Atomic orbital and characteristic X-ray emission.

Emission of X-rays

X-rays are generated by large energy transition of electrons within an atom from outer orbital to core orbitals. The x-ray emissions associated with these transitions are called characteristic x-rays. The labels on the illustration show the historical labelling of characteristic x-ray transitions.

Characteristic X-rays

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“Auger” Electron

The excitation energy from the inner atom is transferred to one of the outer electrons causing it to be ejected from the atom.

Sometimes, as the atom returns to its stable condition, instead of emitting a characteristic x-ray it transfers the excitation energy directly to one of the outer electrons, causing it to be ejected from the atom. The ejected electron is called an “Auger” electron. This process is a competing process to XRF. Auger electrons are more probable in the low Z elements than in the high Z elements.

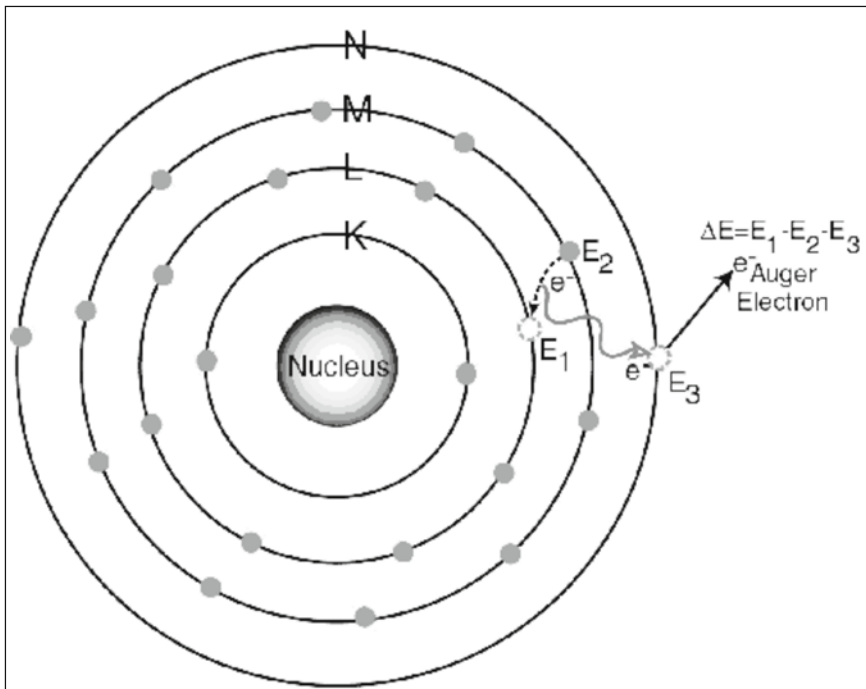


Fig. 6.5: Diagram of Auger electron.

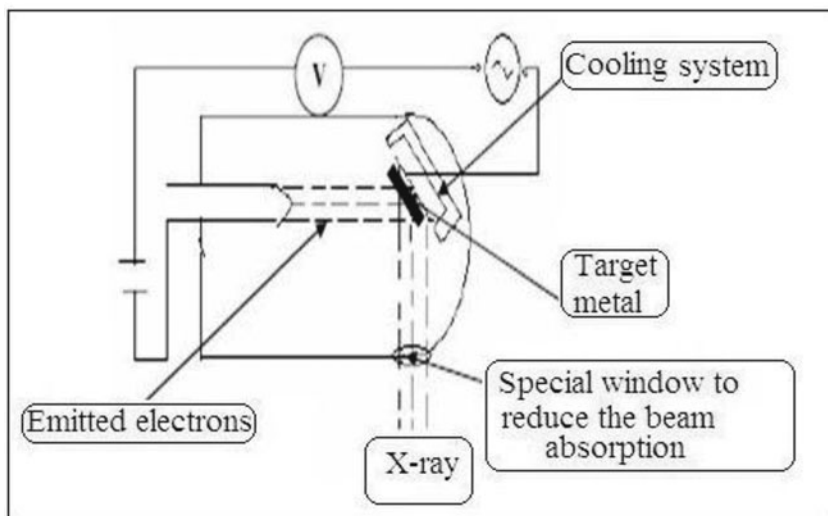


Fig. 6.6: Production of x-rays in the lab.

Table 6.2: Characteristic wavelength for common analytical x-ray tube target

Target metal	$K\alpha$ (Angstrom)	$K\beta$ (Angstrom)
Iron	1.94	1.76
Copper	1.54	1.39
Molybdenum	0.709	0.632
Chromium	2.29	2.08
Nickel	1.66	1.50
Cobalt	1.79	1.62
Silver	0.559	0.497

Properties of X-rays

1. The x-rays, like light, are *electromagnetic radiations* of extremely short wavelength (100-0.0001Å).
2. Obeys laws of reflection, refraction, interference, diffraction and also polarisation under suitable conditions.
3. They travel in straight lines like light, *unaffected by electric and magnetic fields*, indicating they are not charged particle beams, like cathode rays.
4. X-rays affect (blacken) photographic plate and the degree of blackening depends on the intensity of radiation. For this property, photography is a very suitable technique to detect/study x-rays.
5. The x-rays are having high penetrating power. The shorter the wavelength, greater the penetration power. For low density substances, the penetration is more compared to the high density ones. Usually passes through matter that are opaque to visible rays.

6. Soft (long wave length) x-rays are absorbed by materials to varying degrees; this property is used in the radiography of substances.
7. The living cells can be destroyed by x-rays of suitable intensity.
8. X-rays ionise gases through which it pass and the ionising power depends on the intensity of the radiation. This property is used to measure the intensity of x-rays—used for x-ray detection and measuring intensity.
9. X-rays cause fluorescence in many substances (e.g. ZnS, Ca-salts etc.) and are used as a distinct property for identifying such materials.
10. X-rays exhibit corpuscular nature. Compton effect is the confirmation of this property.
11. Various analytical techniques have been developed utilising the above mentioned properties e.g. x-ray absorption, emission spectroscopy, x-ray diffractometry etc.

Process of X-ray Analysis

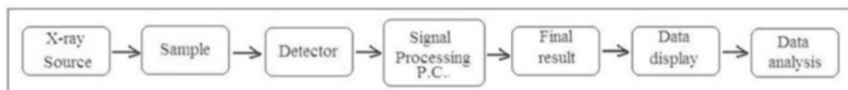


Fig. 6.7: Flow chart for the x-ray analysis.

6.3 X-RAY POWDER DIFFRACTION (XRD)

This is a non-destructive method to analyze crystalline phases of the samples. Comparing with standard data file the phases present in a sample can be exactly identified. Now a days, analytical softwares and needed data files are available with the Diffractometer Unit.

The technique can be understood following the sequence. (1) Basics of x-ray crystallography; (2) Bragg's Law; (3) Geometry of diffraction; (4) Sample preparation techniques; (4) General uses e.g. identification of unknown phases, their qualitative and quantitative estimation, grain-size analysis, crystallinity study, effect of temperature and pressure variation on crystalline phases etc. and (5) Basic errors for x-ray diffraction data.

Basics of X-ray Crystallography

Knowledge of basic crystallography starts from the conception of symmetry, symmetry planes and symmetry operations necessary to identify the parameters, like lattice, lattice planes, crystal lattices (i.e. Bravais lattice) describing different crystal symmetries. Miller indices (h, k, l) to identify crystal planes etc. are explained here.

Table 6.3: Different symmetry operation used in crystallography

<i>Symmetry operation</i>	<i>Symmetry element</i>	<i>Symbols</i>
Rotation around an imaginary axis passing through centre	<i>Rotation axis or symmetry axis</i>	1, 2, 3, 4, 6
Reflection across a plane	Plane of symmetry or mirror	<i>m</i>
Inversion through a centre	Inversion point or centre of symmetry	<i>i</i> or <i>c</i>
Combined operation of rotation around an axis followed by inversion through the centre.	Roto-inversion axis	A1, A2, A3, A4, A6

Crystal Systems etc.

A crystal has an array of points with repetitive arrangement in three dimensions. These points may be atoms, ions or molecules and the arrangement is called the Lattice. A combination of lattice and crystal system makes fourteen possible Bravais Lattices. A unit cell is the smallest volume which keeps all the properties of the crystal, e.g. chemical, physical and geometrical. A unit cell must contain enough of the various atoms to establish the chemical formula, the pattern of arrangements and the directional properties of the crystal structure.

Seven Types of Crystal Lattices (Bravais Lattices)

The crystal lattices parameters are the unit cell dimensions e.g. a , b , c . The angle between the axes are α , β and γ . The different types of crystals can be described in the framework of Bravis Lattices as shown in Fig. 6.8.

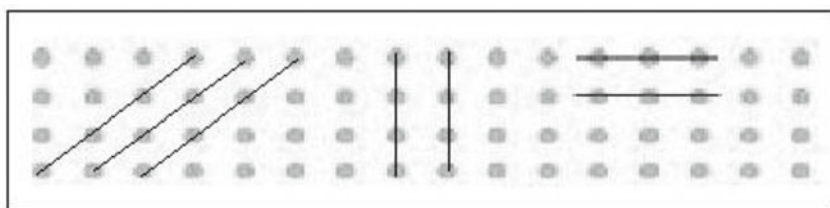


Fig. 6.8: Lattice and crystal planes in two dimensions.

Each cell must be of size and shape in relation to the atoms it contains. When many cells are stacked in three dimensions, every cell will be surrounded by exactly similar cells with no gaps whatsoever between them.

Miller Indices

The Miller indices describes the different planes in the crystal with respect to its axes, and denoted by h (for axis x or a), k (for axis y or b) and l (axis z or c). The corresponding planes are denoted by $d(h\ k\ l)$. Thus, the lattice constants are a , b , c , α , β , γ and Miller indices are h , k , l .

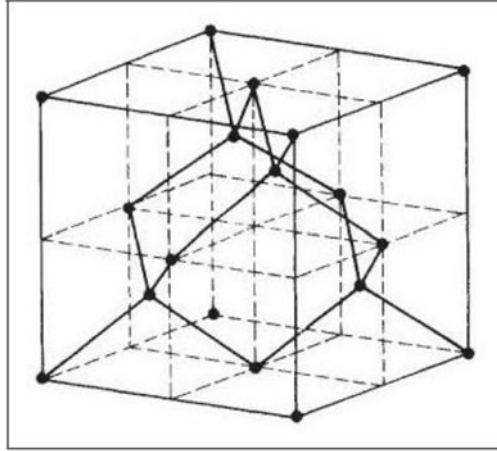


Fig. 6.9: Lattice and unit cell of diamond.

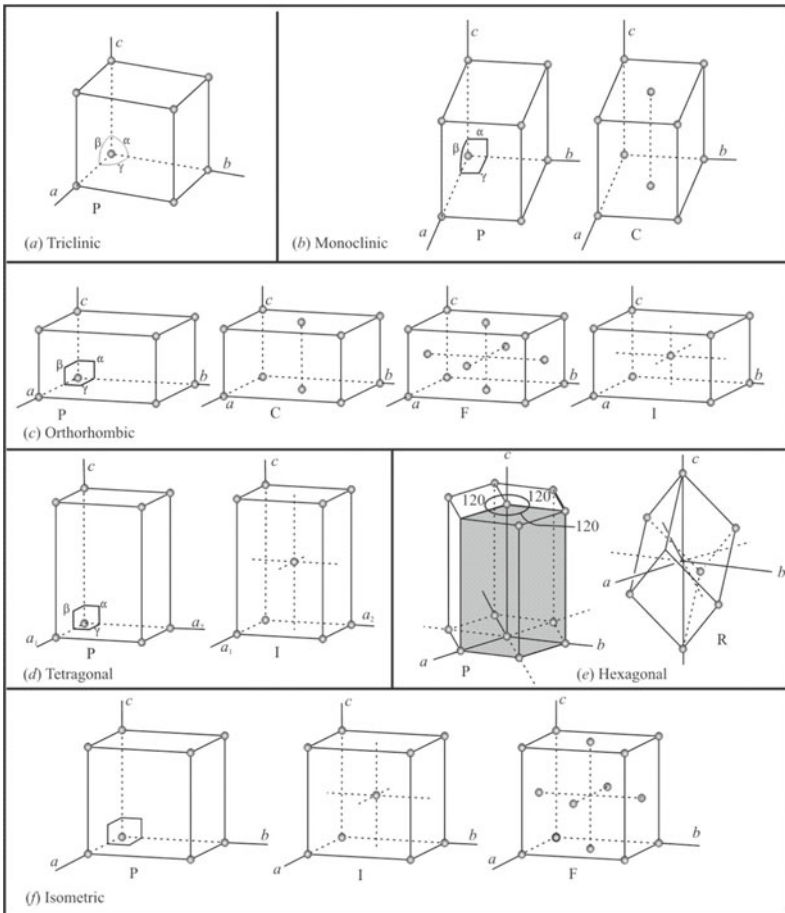


Fig. 6.10: Seven types of crystal lattices.

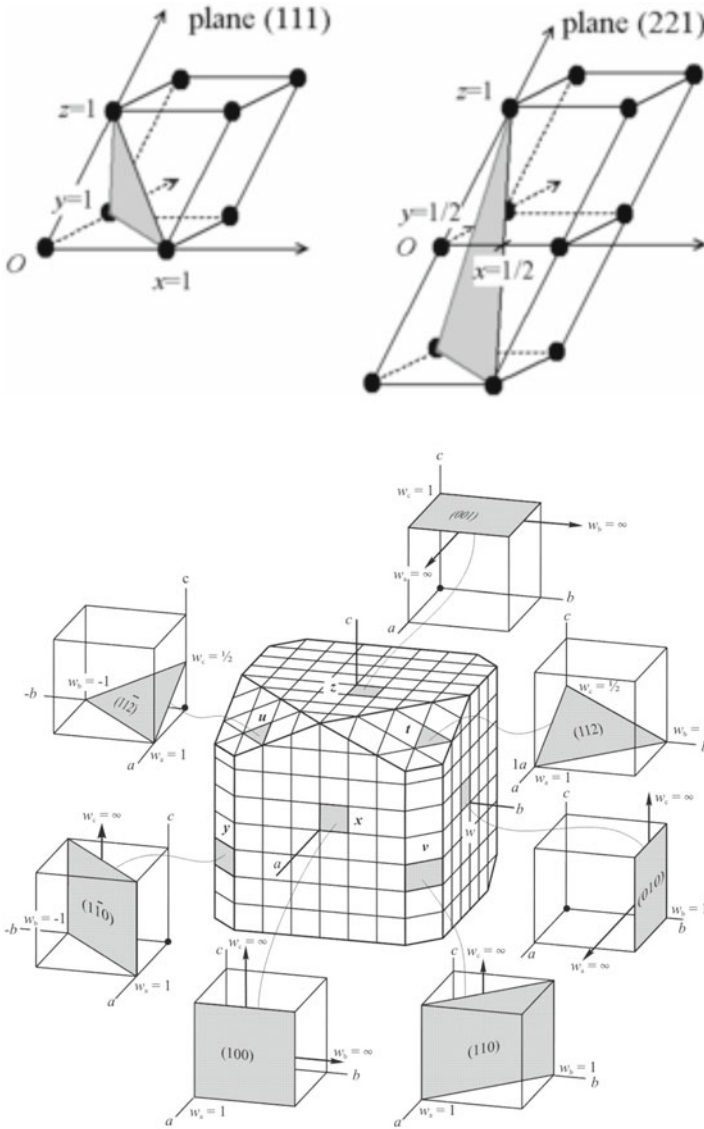


Fig. 6.11: The planes with their Miller indices.

Bragg's Law for Diffraction of X-rays from Crystal Planes

Diffraction phenomena occur when wave faces an obstacle of similar dimension to its wavelength. Since the atomic dimensions are of same order of magnitude of the X-ray wavelength, X-ray diffraction occurs with atomic crystals. This phenomenon is excellently formulated by Sir W.L. Bragg and known as Bragg's Law.

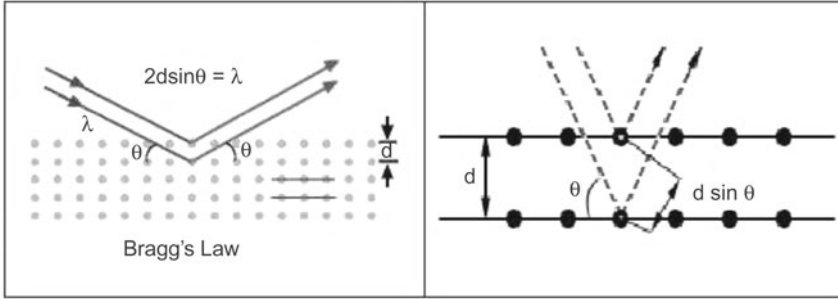


Fig. 6.12: Principles of Bragg’s law.

Any crystal plane d is identified by the Miller Indices h, k, l and accordingly, Bragg’s law can be written as

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

Geometry for X-ray Diffraction Data Collection

In the Bragg-Branton geometry of diffractometer, if the sample rotates by angle θ the diffracted beam rotate by angle 2θ . Goniometer circle correlate the positions of the sample, detector and the incident beam. By rotating the sample (kept in a holder), the scanning angle can be varied as desired and the rotation speed of the sample can also be adjusted. The sample chamber may have the temperature and pressure controlling system for suitable use.

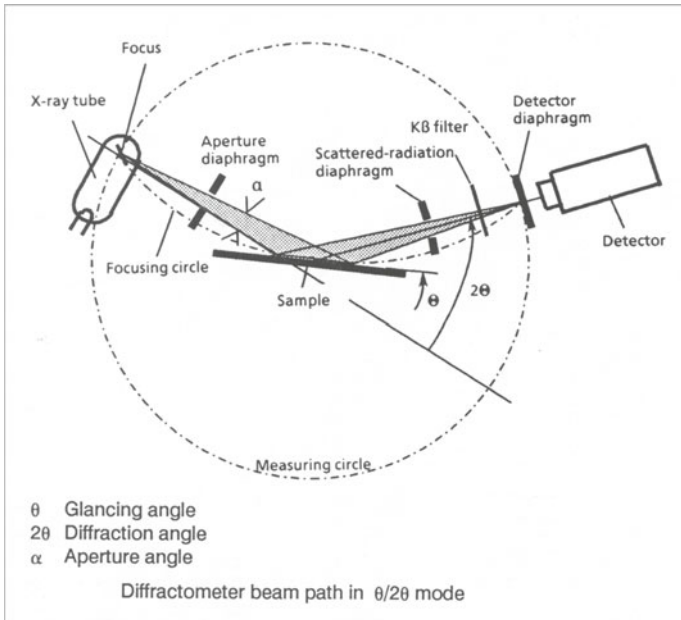


Fig. 6.13: Bragg-Brenton powder diffractometer: components and geometry.

Sample Preparation Techniques and Powder Diffraction Analysis for Identification

The sample is to be taken in powder form (about 200 meshes), the powder is to be packed in the sample holder and to be pressed slightly for right packing. No rubbing to be done while packing sample which creates preferred orientation of the grains.

Identification of any phase is done using standard data files with search match software program to identify various peaks in the diffractogram.

Applications of Powder Diffraction

1. Qualitative analysis
2. Quantitative analysis
3. Crystal structure determination
4. Crystallite size
5. Microstrain
6. Residual macrostresses
7. Thin films
8. Crystallinity

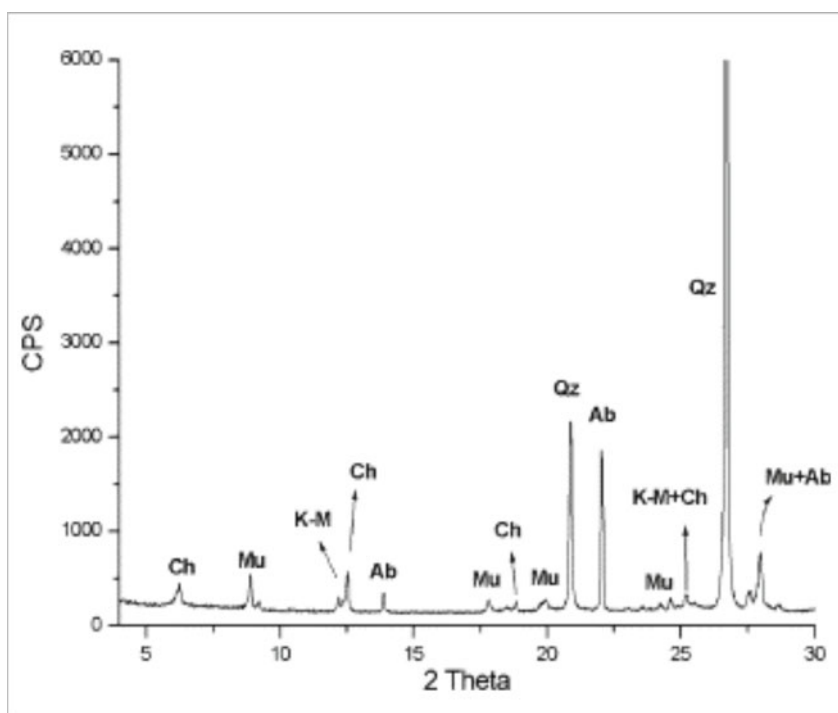


Fig. 6.14: X-ray powder diffraction pattern from the soil samples (fraction size 2 μm); the mineral phases are: chlorite (Ch), muscovite (Mu), kaolinite-montmorillonite (K-M), albite (Ab), quartz (Qz).

9. Studies of phase diagrams: (A) Phase boundaries, (B) Solid solutions and (c) Phase transitions
10. Studies of chemical reactions and identification of reaction products.
11. Determination of grain sizes
12. Preferred orientation in polycrystalline bodies.

6.4 X-RAY FLUORESCENCE (XRF)

High energy radiation (x-rays or soft gamma rays) falling on a solid target generate inner shell vacancies which are being filled up from outer shells producing secondary characteristic x rays. This is known as x-ray fluorescence (XRF). The phenomena is of intense use for element detection i.e. chemical analysis of solids like metals, ceramics, building materials and even glass. This technique is widely used in geochemical research, archaeology and in forensic science.

XRF spectroscopy is a non-destructive and fast technique used for both qualitative and quantitative elemental analysis. This method has a fairly uniform detection limit of elements heavier than fluorine with a wide range of concentration, e.g. 100% to parts per million.

The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. Depending on the application, XRF can be produced by using not only x-rays but also other primary excitation sources like alpha particles, protons or high energy electron beams.

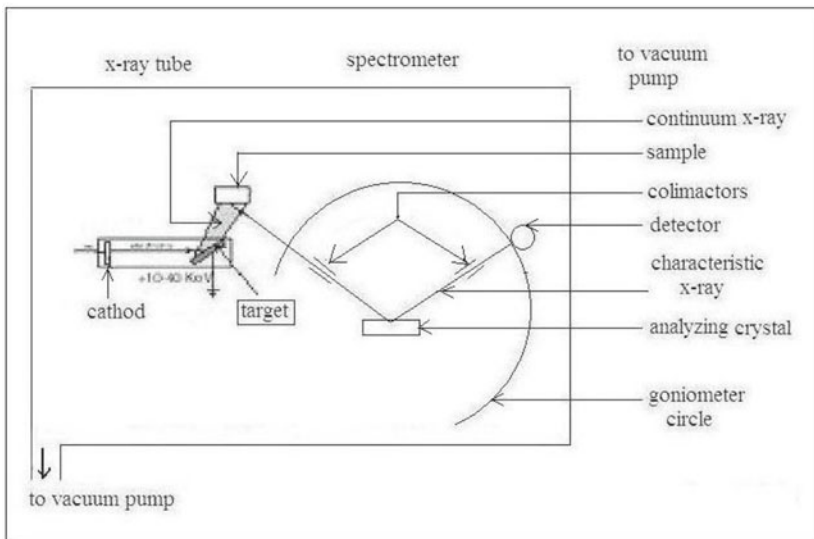


Fig. 6.15: The XRF spectrometer measures the individual component wavelengths of the fluorescent emission produced by a sample when irradiated with x-rays.

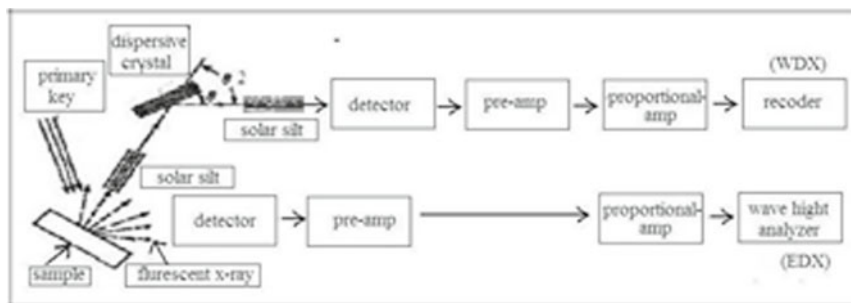


Fig. 6.16: Schematic diagram of energy dispersive and wavelength dispersive XRF spectrometers.

WDXRF

WDXRF (wavelength dispersive x-ray fluorescence) separation is achieved by diffraction, using an analyzer crystal that acts as a grid. The specific lattice of the crystal selects the correct wavelengths according to Bragg's law. A WDXRF spectrometer provides: the advantages of total application, versatility optimal measurement conditions programmable for each element, excellent light-element performance, very high sensitivity and low detection limits.

EDXRF

EDXRF (energy dispersive x-ray fluorescence) spectrometry works without a crystal. An EDXRF spectrometer includes special electronics and software modules to take care that all radiation is properly analyzed in the detector. It provides a lower cost alternative for applications where less precision is required. The high-end uses the 3D EDXRF techniques featuring a 3-dimensional, polarizing optical geometry.

XRF technique is suitable for bulk chemical analysis of major elements e.g. Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P. For trace element analysis with abundances >1 ppm can also be done for Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr and Zn with a detection limit of few ppm. For materials which are compositionally similar, suitable standards are available. Samples containing high abundances of elements corrections are to be made for absorption and fluorescence effects. XRE is commonly used to identify traces and for quantitative estimation, good resolution of the peaks are necessary. It can also analyze thin films.

As in case of x-ray fluorescence (XRF) techniques, in case of EDXRF also, other similar competing techniques are AAS (Atomic Absorption Spectroscopy), ICPS (Inductively Coupled Plasma Spectroscopy) and NAA (Neutron Activation Analysis). Modern XRF-analytical units, for its multi elemental run, is fast and cost effective.

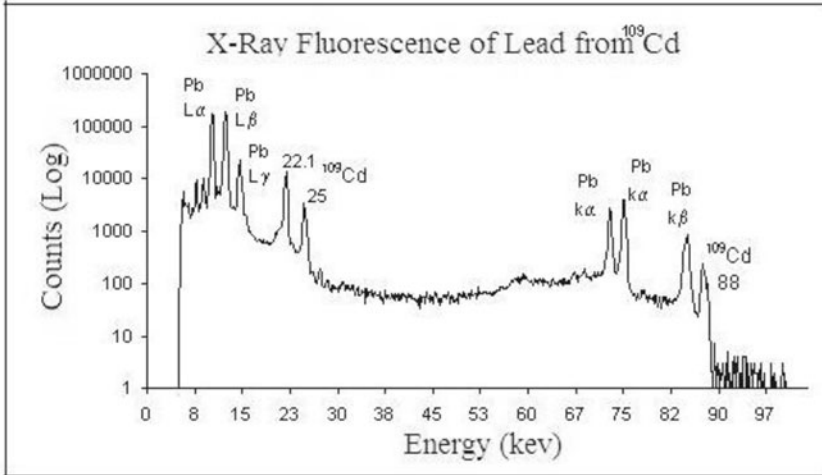


Fig. 6.17: A typical XRF spectra.

Applications of X-ray Fluorescence Technique

X-ray fluorescence technique, with its bulk and trace element detection capability, has a wide application field. More specifically, it is particularly well-suited for investigations in chemicals, coatings and thin films, mining (e.g., measuring the grade of ore), ceramic and glass manufacturing, metallurgy (e.g., quality control), environmental studies (e.g., analyses of particulate matter on air filters), Petroleum industry (e.g., sulphur content of crude oils and petroleum products), field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers), cement production, forensics, pharmaceutical applications, in plastics, polymers and rubber industries, etc.

6.5 ELECTRON MICROSCOPY

The resolving power of a microscope is its ability to resolve the images of two points close to each other and expressed as $R = 1/d\theta = D/1.22\lambda$ where D is the aperture of the objective and λ is the wavelength of the light. By reducing wave length, i.e. increasing the frequency of the radiation, resolving power of the microscope can be increased. A high resolution microscope was designed replacing visible light by electron beam.

In electron microscopy (EM), a focussed beam of electrons are used (replacing visible light in optical microscope) to bombard the sample for getting information about its structure and composition. This improves the possible magnification to $\sim 2,000,000$.

Interaction with Matter

Electron bombardment in a material produces the effects as shown in Fig. 6.18.

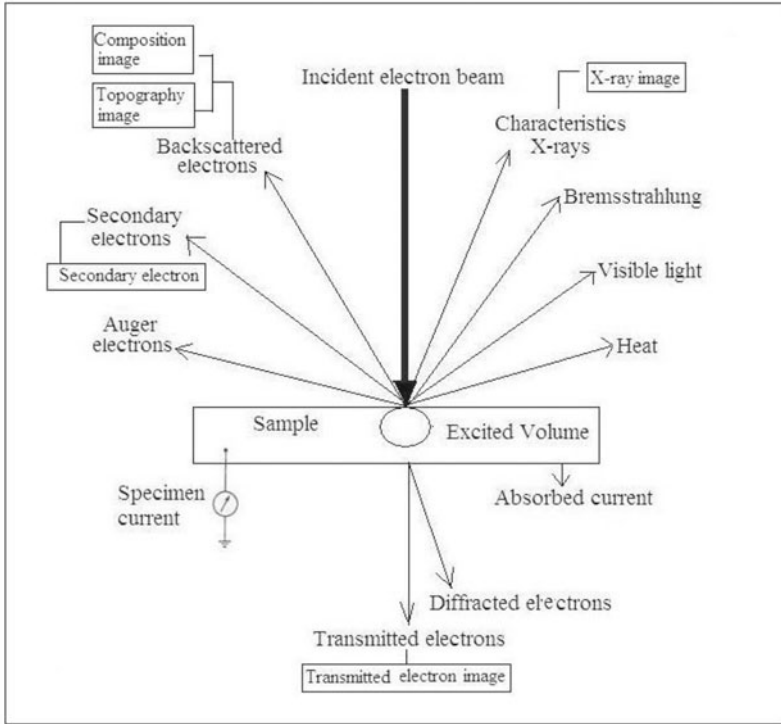


Fig. 6.18: Effects produced by electron bombardment to a material.

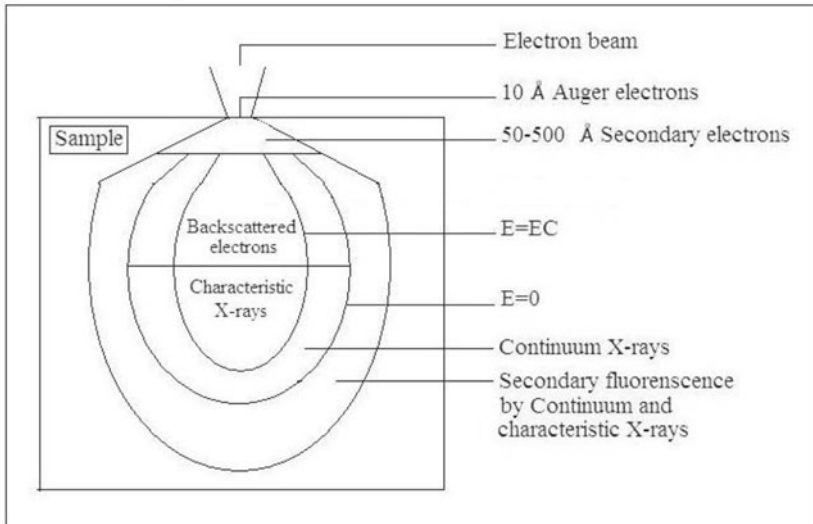


Fig. 6.19: Generalized illustration of interaction volumes for various electron-specimen interactions. Auger electrons (not shown) emerge from a very thin region of the sample surface (maximum depth about 50 Å) than do secondary electrons (50-500 Å).

The different types of electrons used for analysis:

- (a) Topography and composition: Backscattered electrons
- (b) Topography: Secondary electrons, Auger electrons
- (c) Structure and composition: Transmitted electrons
- (d) Composition: X-rays, photons

Working principle of Electron Microscope (EM)

- (i) A source producing electrons and then accelerated (by using a positive potential) towards the sample.
- (ii) The beam is focussed to a monochromatic one using apertures and magnetic lenses.
- (iii) The magnetic lenses finally focus the beam on the sample.
- (iv) The strong interact with the beam starts.
- (v) Using EDX or WDX, the acquired data get analyzed.

The types of electron microscopy:

1. Scanning electron microscopy (SEM)
2. Transmission electron microscopy (TEM)
3. Reflection electron microscope (REM)
4. Scanning transmission microscope (STEM)
5. Low voltage electron microscope (LVEM)

Main Observations Made with these Microscopes

- (a) Topographic analysis i.e. surface features, textures and the correlation between them, property of materials like reflectivity, hardness etc.
- (b) Morphological studies i.e. relation between the structures e.g. shape, size etc., properties like ductility, strength, reactivity etc. of materials.
- (c) Composition determination i.e. qualitative and quantitative analysis of elements and compounds present in the sample. These data help to understand the material properties like melting point, reactivity, hardness etc. with the composition.
- (d) Crystallographic information i.e. relating the material properties like strength, conductivity, electrical properties etc. with the crystal structure of the compounds.

Scanning Electron Microscope

A focussed (using magnetic lenses) electron beam falls on the sample surface kept in vacuum. The beam then scans over the sample surface and the scattered electrons detected and collected to have the information about the sample surface.

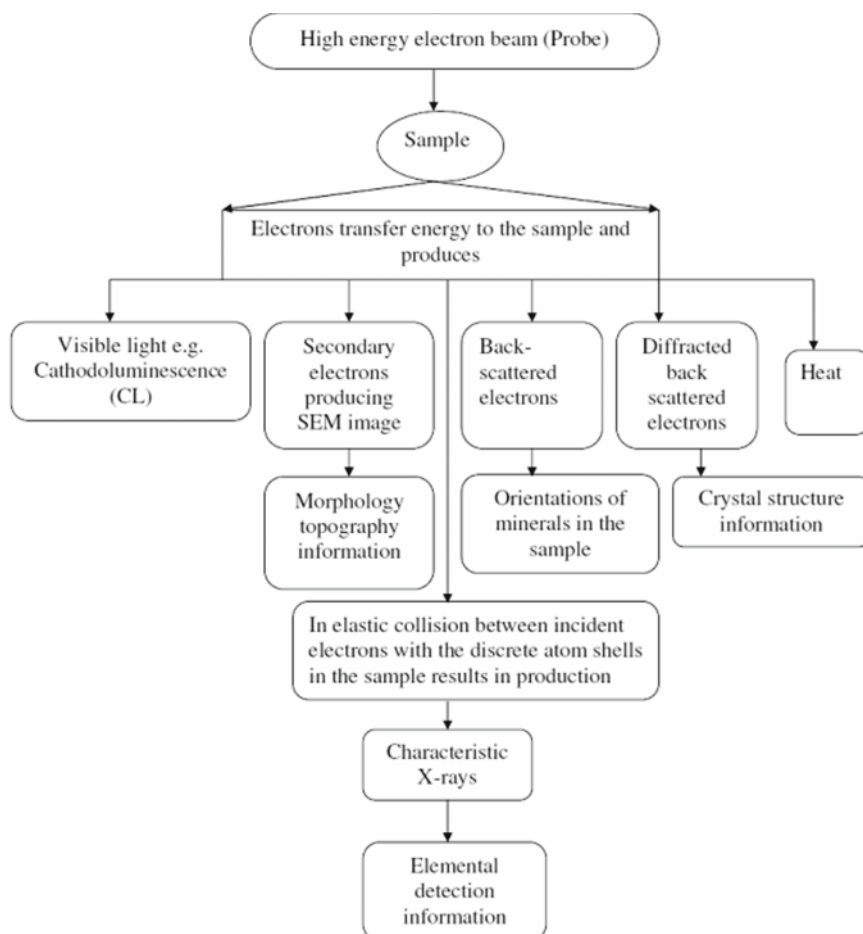


Fig. 6.20: Flowchart of function of SEM.

6.6 TRANSMISSION ELECTRON MICROSCOPY (TEM)

A high energy electron beam (~ 100 to 400 keV), collimated by magnetic lenses pass through a sample under high vacuum. The transmitted beam and part of the diffracted beam form a resultant diffraction pattern and an image is formed on the fluorescent screen kept below the specimen. This magnified images yields information about the size, shape etc. of the micro-structural constituents of the material under study. High-resolution image, that contains information about the atomic structure of the material, can be obtained by recombining the transmitted beam and diffracted beams together.

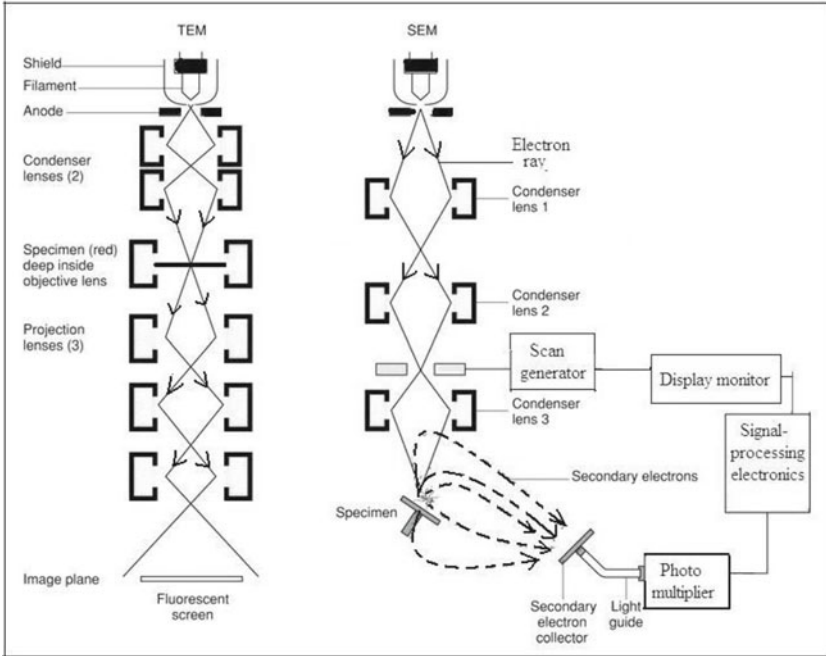


Fig. 6.21: TEM gives overall illumination and SEM gives point illumination.

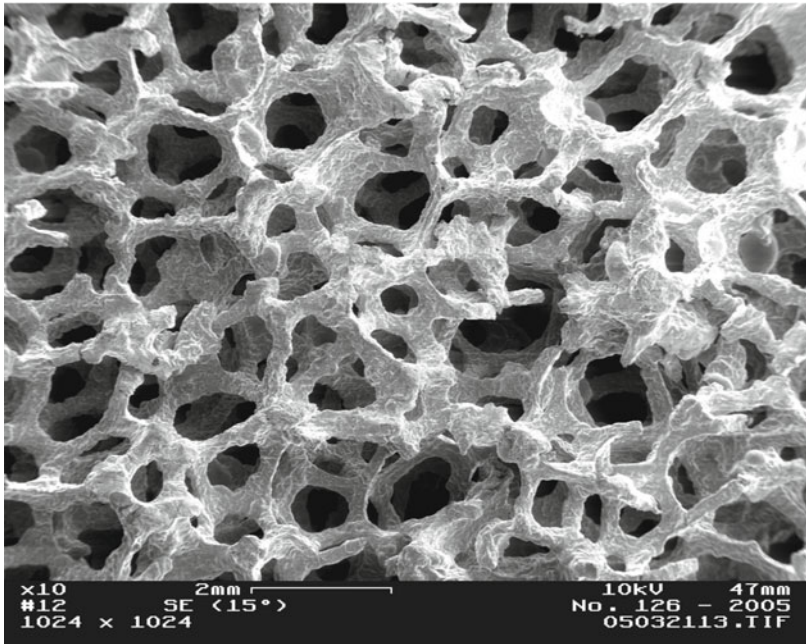


Fig. 6.22: Metal foam in scanning electron microscope.

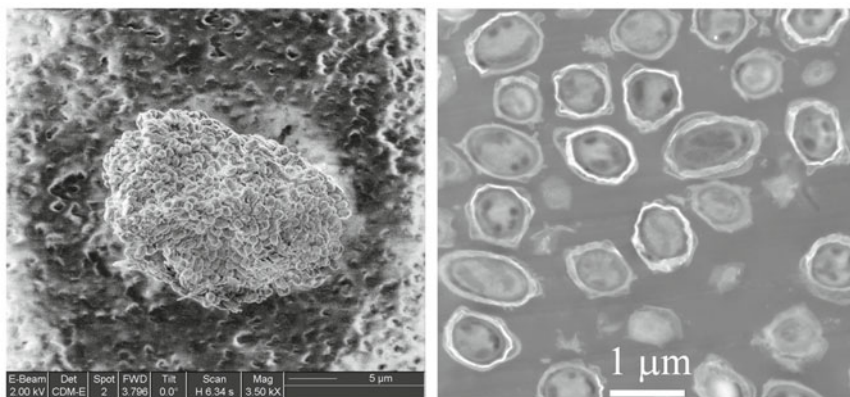


Fig. 6.23: Bacillus anthracis as viewed in scanning electron microscopy (left) and transmission electron microscopy (right).

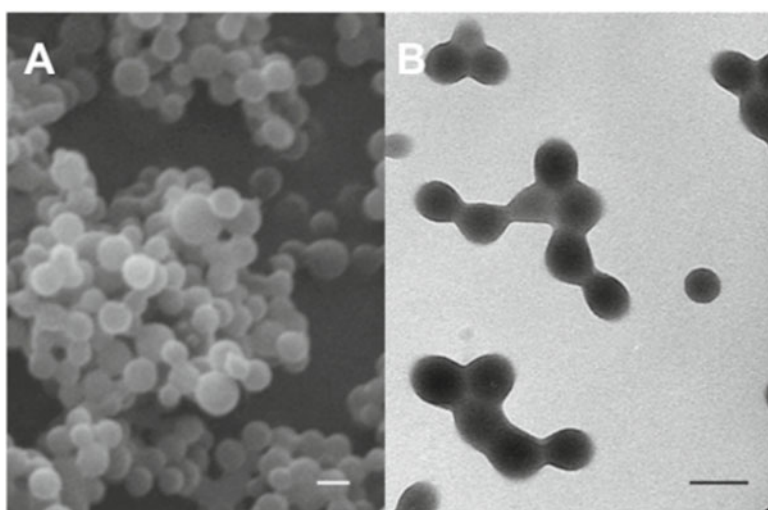


Fig. 6.24: Scanning electron microscope (A) and high resolution transmission electron microscope (B) images of PCL NPs.

Note: All scale bars shown in the figure are 150 nm. Abbreviations: NPs, nanoparticles; PCL, poly(ϵ -caprolactone).

6.7 APPLICATIONS OF ELECTRON MICROSCOPY

- (i) Differentiating phases based on mean atomic number (related to relative density) using BSE.
- (ii) Compositional map shows the variation of different trace elements.
- (iii) High resolution image of the shape of the object is produced.
- (iv) Very small feature of the object can be observed by using SEM.
- (v) Crystallographic orientation and microfabric can be studied in detail by using the backscattered electron image.
- (vi) The different phases can easily be distinguished by BSE image.

6.8 ELECTRON PROBE MICRO ANALYSER

This technique utilizes a highly focussed electron beam (5-30 keV) to probe the elemental composition of the sample. The electrons in the beam interact with the sample over a very minute area and excite the elements present there to produce their characteristic x-rays. These characteristic x-rays are recorded and the elements present in the sample can be identified using a Wavelength Dispersive XRF spectrometer (WDF). Both qualitative and quantitative analysis is possible with this non-destructive method, with ppm detection level and 1% reproducibility.

A schematic diagram of the experimental arrangement is shown in Fig. 6.25. Electron gun produces electrons from the low energy tungsten filament and then accelerated by a positively biased plate to 10-30 keV. The beam passes through central hole of the anode plate, then collimated (using suitable apertures) and focussed. The beam is focussed using a number of magnetic lenses (condensing coils) and allowed to fall in the sample. This sharply focussed high energy beam excites a volume of the sample as small as three micrometres. The x-rays thus produced are analyzed using a WDX spectrometer. This detecting system identifies the elements by detecting corresponding characteristic x-rays. Chemical composition is determined by comparing the intensity of each peak with the standards. Higher beam currents produce more x-rays from the sample and improve both the detection limits and accuracy of the resulting analysis. A transmitted light optical microscope is attached to the system for locating the study area with an accuracy of one micrometre.

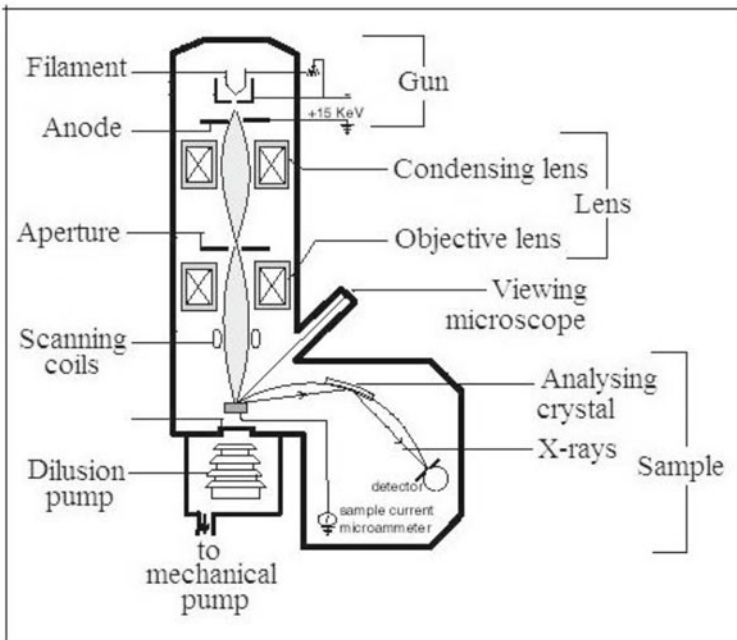


Fig. 6.25: A sketch of EPMA.

Using suitable detector, the following image analysis can be done:

1. Analysis of the images occurred from the secondary electrons (SEI), backscattered electrons (BSE) and cathode luminescence (CL).
2. Possible to take 2D elemental maps.
3. Using EDS and WDS, compositional information data collection is possible.
4. Analysis of crystal lattice preferred orientation (EBSD) is possible.

The electron microprobe can do quantitative analysis of samples for elements from fluorine ($Z=9$) to uranium ($Z=92$). This can determine elemental compositions in stratified layers of material from nm to mm thickness.

Major applications are in geochemistry, mineralogy, material science e.g. glass, ceramics, cement, microelectronics, physical metallurgy, nuclear metallurgy and biochemistry.

Advantages

- (a) It is very useful for analyzing solid samples in a very small spot e.g. 1-2 micron diameter, and can identify a very minute single phase present.
- (b) In situ analysis of very small compositional variations in a sample spot or chemically zoned material is possible.
- (c) With the array of imaging detectors (SEI, BSE and CL) attached to microprobe, the surface and internal compositional study is possible.

Limitations

- (a) Waters in the hydrous minerals cannot be analyzed and also unable to detect very light elements like Li, He etc.
- (b) Microprobe analysis results as oxide of elements not as cations. Thus following stoichiometric rules, formula of the sample composition/mineral composition to be derived.
- (c) Precaution must be taken for composite/overlapping peak analysis.
- (d) Since probe is unable to distinguish valence states e.g. ferric/ferrous ratio, some complimentary technique (e.g. Mossbauer) to be used when needed.

6.9 IR SPECTROSCOPY

Infrared spectroscopy is used to study the chemical functional groups present in the sample and also the types of bond present. It allows exposing the sample with infrared radiation and studying its absorption spectra.

Natural vibrational frequencies of atoms in molecules and crystals fall in the infrared range and are quantized. Exposing the sample to infrared radiation, the absorbed energy causes enhanced vibrations of the molecules. Depending on the functional group present (i.e. the chemical bonds), the characteristic frequency is absorbed and the absorption spectra are obtained. Four different vibration modes are bending, rocking, twisting and scissoring as shown in Fig. 6.27.

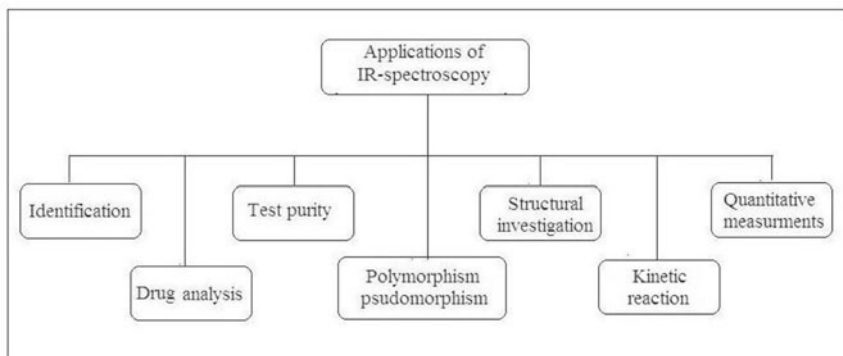


Fig. 6.26: Various applications of IR spectroscopy.

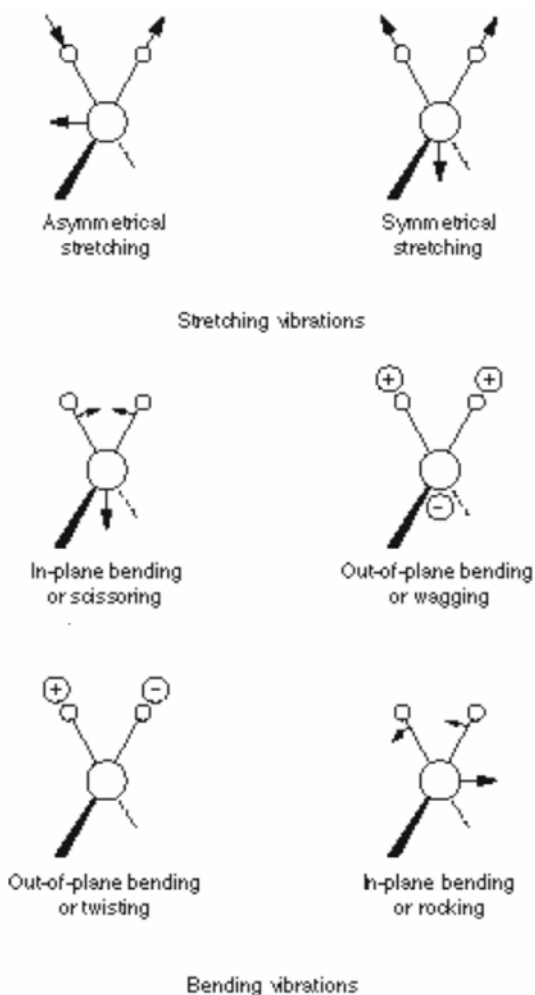


Fig. 6.27: Different vibration modes of molecules.

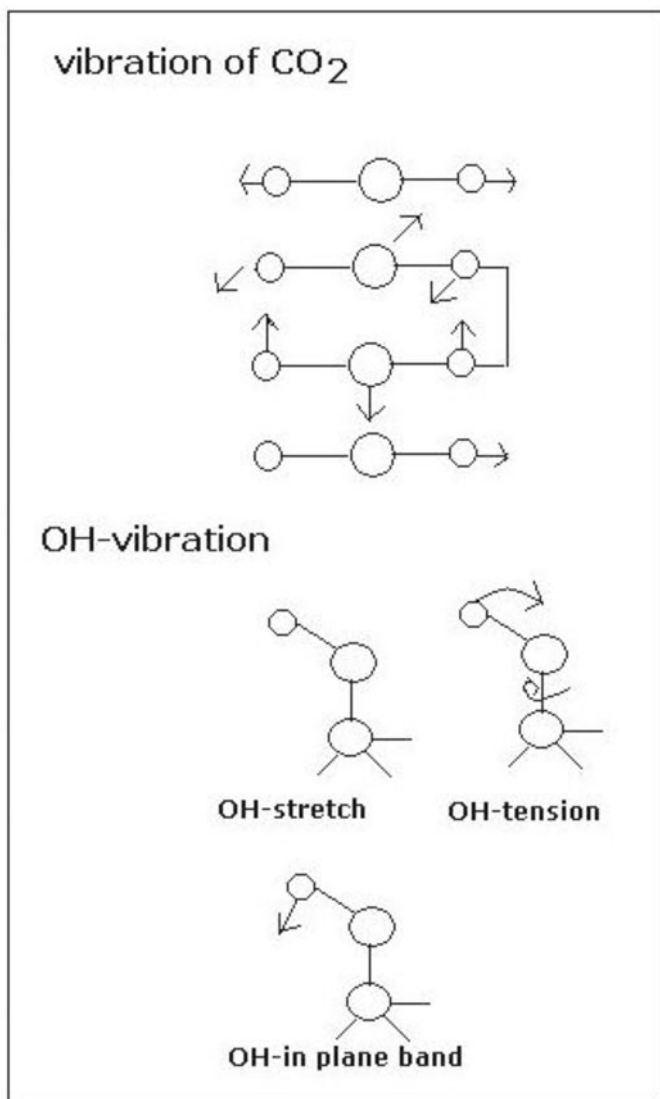


Fig. 6.28: Vibration modes of specific chemical groups.

Infrared frequencies fall between visible and radio waves and is divided in three ranges of wave number [ν (in cm^{-1}) = $1/\lambda$ (in μm)]

Near-Infrared

$13000\text{-}4000\text{ cm}^{-1}$, $\lambda = 0.782.5\ \mu\text{m}$. Region with its higher energy level and higher frequencies can excite overtones or harmonic vibrations.

Medium Infrared

$4000\text{-}200\text{ cm}^{-1}$, $\lambda = 2.5\text{-}50\ \mu\text{m}$ may be used to study the fundamental vibrations and associated rotational vibrational structure.

Far Infrared

$200\text{-}10\text{ cm}^{-1}$, $\lambda = 50\text{-}1000\ \mu\text{m}$. The longer wavelength far-IR has lower energy and may be used for rotational spectroscopy.

Infrared absorption frequency depends on strength of bonds, mass of atoms and stretching or bending modes and vibrations.

IR analysis use absorbance and transmittance properties of the sample and defined as follows:

$$\text{The transmittance } T = \frac{\text{Power transmitted by the sample } (I)}{\text{Powder incident on the sample } (I_0)}$$

And the absorbance A is related as

$$A = \log_{10}(1/T) = -\log_{10} T = -\log_{10} I/I_0$$

The transmittance range is 0-100% whereas absorbance is from infinity to zero.

Collection of Output Information

A block diagram of the simplest analysis process is shown in Fig. 6.29 where output information is sequentially collected in time using a single detector by scanning each spectral element at a time. This simple instrument was modified using multiple detectors.

On further improvement, multiple devices are used with a single detector. The signals are then decoded for identifying in the spectral elements. A double beam IR-spectrometer is shown in Fig. 6.30. The incident beam is split into two and one is falling on the sample and another on the reference and compared. Commercially available reference materials are used.

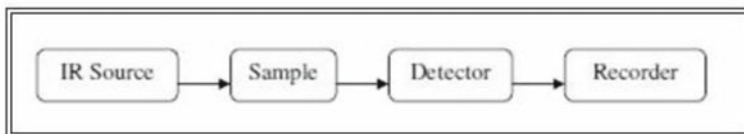


Fig. 6.29: Flow chart of IR data collection.

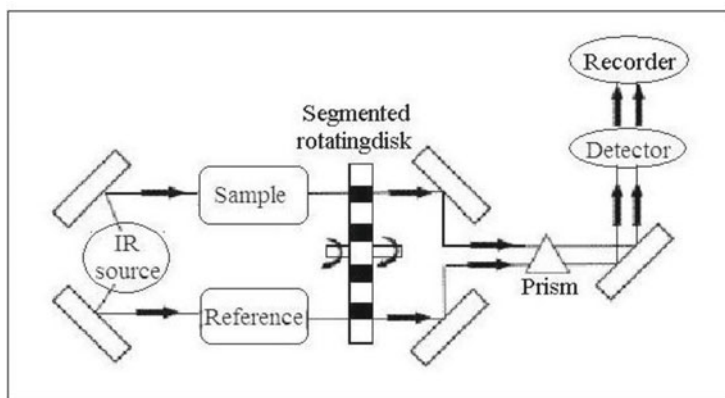


Fig. 6.30: Double beam IR-spectrometer.

There are many varieties of IR-spectrometers developed according to the need of experimental analysis. These are summarized in a sketch (Fig. 6.31).

Further improved version of the IR-spectrometers is the FTIR (Fourier Transformed IR) unit. FTIR method collects all wavelengths simultaneously and thus making the data collecting process very fast. The output data from the sample is collected using an interferometer and digitized in an interferogram. Fourier transform is then performed on the data to obtain the spectrum.

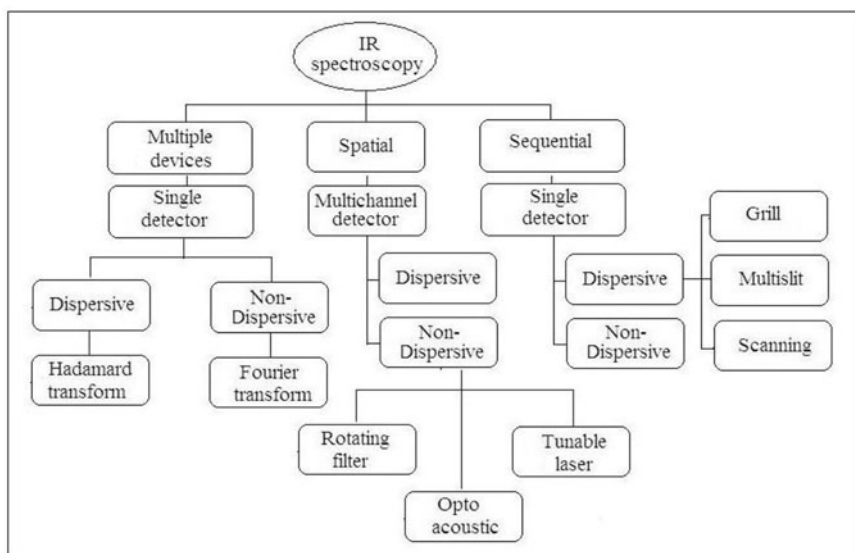


Fig. 6.31: Variations in IR spectrometry.

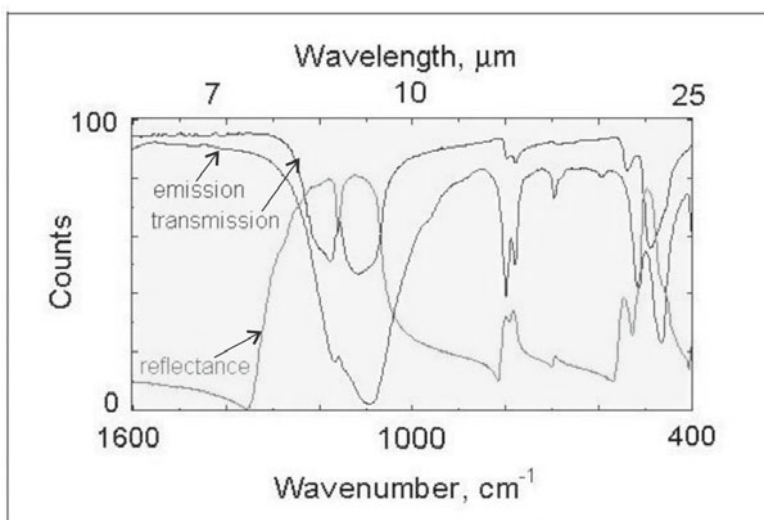


Fig. 6.32: Typical IR-spectra of quartz.

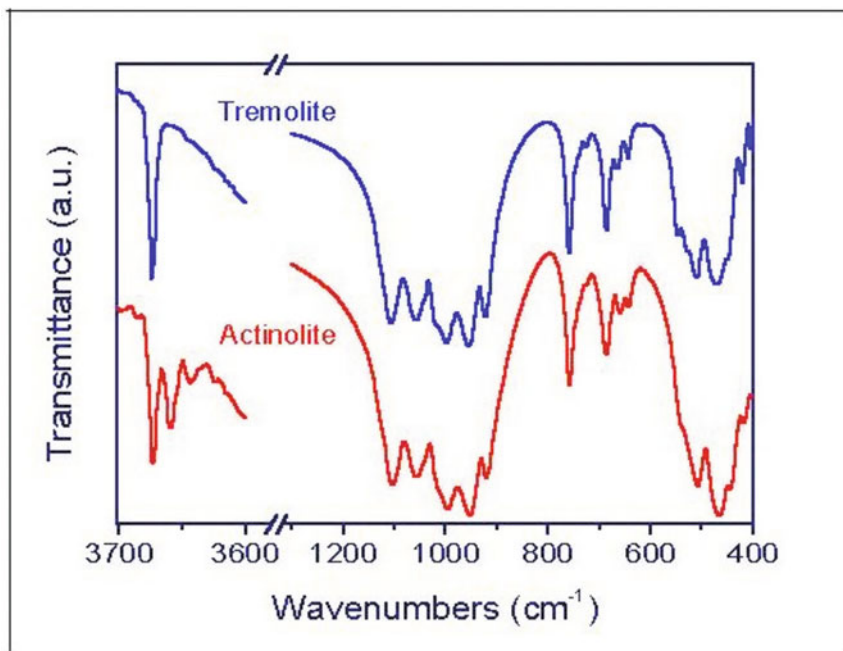


Fig. 6.33: Typical IR-spectra of tremolite-actinolite.

Analytical Technique

For inorganic compounds and minerals IR-wave length range generally from 0.2 to 50 μm . This technique can analyse solid, liquid and gaseous phases. Sample preparation methods are accordingly different. For solid samples, usual preparation process is to mix homogeneously grinded solid sample with KBr and make a pellet by pressing. For reflectance spectra, special attachments are necessary. For transmission spectra, the grain size of the sample must be around 20 μm and good absorption spectra needs finer particle size, around 5 μm . When the refractive index of the sample is nearing 1, transmission band wave length is more prominent. The peak positions shift with average particle size variation and should be considered during sample preparation. For molecules containing more than one chemically active group in their unit cell (e.g. CO_3 in calcite), vibrations in individual molecules couple with each other and frequency shift occurs resulting in band splitting. For such complicated interactions interpretations of IR-bands on solid samples are more difficult compared to the liquid or gaseous samples.

The sample is put to the sample position for analysis. In analysis of mixtures accuracy is 1% under optimum condition, and 5% for routine analysis. The points to be considered for good data are: (i) Molecules must be active in the IR-region. (ii) Minimum elemental information is given for most samples. (iii) In the required spectral region, transparent background matrix for solvent or solid is essential.

Comparing the spectra of unknown samples with the band of standard samples, identification is done. As the coordinated atomic bonds increase, possible rotational or vibrational modes will increase and also the wavelength range, e.g. for silicate minerals, wavelength range is 9-12 μm . Increased ratio of Si:O (isolated silica tetrahedral, like SiO_4 Olivine), the strong absorption range is 0.25 and in quartz (SiO_2) is 0.50. Hydroxyl group containing minerals (goethite, serpentine, lepidocrocite etc.) have their characteristic absorption band wavelengths greater than 2800 cm^{-1} and are due to the stretching vibrations within the hydroxyl group. This technique is thus able to characterise the types of bond present and can get the finger print of the sample under study.

6.10 RAMAN SPECTROSCOPIC ANALYSIS

Raman spectroscopy is an inelastic light scattering technique used to study the vibrational, rotational, and other low frequency modes in molecular system. In this method of chemical analysis, the sample is exposed to a beam of monochromatic light or a laser beam in the frequency range of visible, infrared or near-ultraviolet region. It is having wide applications in geochemistry, mineralogy and also organic and biological studies.

Raman effect is a scattering phenomenon where the photons incident on the sample are scattered with or without changing its energy. Major part of these photons are scattered without energy change and exhibit Rayleigh scattering phenomena. A small fraction of the photons, interacting with the molecular centres of the sample, have their energy altered to both high energy and low energy side. This is called Raman scattering and the scattered energy levels are known as stokes (on higher energy side) and anti-stokes (lower energy side) lines.

Raman spectroscopy measures the wavelength and intensity of the inelastically scattered light from molecules. Depending on the molecular vibration energy, the Raman scattered light is being shifted from the incident light. This is called *Raman shift* and measured in wave numbers (in cm^{-1}). For relation between wave length and wave numbers of shift in the Raman spectrum, the following formula can be used:

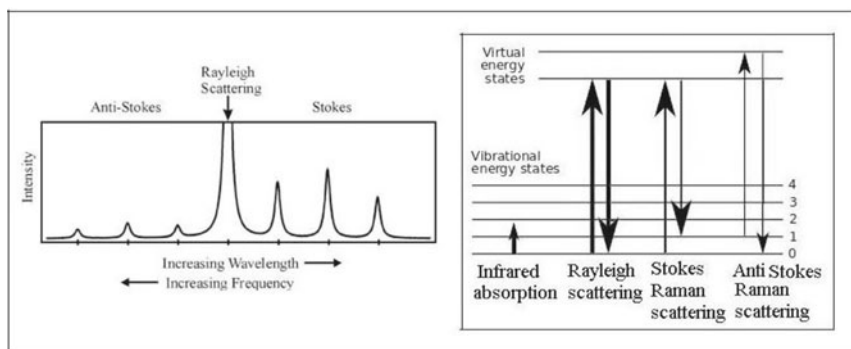


Fig. 6.34: Rayleigh and Raman scattering spectra.

$$\Delta\omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right)$$

where $\Delta\omega$ is the Raman shift expressed in wave number, λ_0 = the excitation wavelength and λ_1 is the Raman spectrum wave length.

Most commonly, the units chosen for expressing wave number in Raman spectra is inverse centimetres (cm^{-1}). Since wave length is often expressed in units of nanometres (nm), the formula above can scale for this units conversion explicitly, giving

$$\Delta\omega (\text{cm}^{-1}) = \left(\frac{1}{\lambda_0(\text{nm})} - \frac{1}{\lambda_1(\text{nm})} \right) \times 10^7,$$

effectively multiplying by $\frac{(\text{nm})}{(\text{cm})}$

The basic parts of Raman spectrometer are (i) excitation source, a laser beam, (ii) sample illumination system (usually an intense, polarized and coherent laser beam in the UV, visible, or near-infrared range) and light collection optics (collected with a lens and is sent through interference filter or spectrophotometer), (iii) wave length selector i.e. filter spectrophotometer and (iv) detector system.

In the experimental arrangement, the sample is exposed to laser beam of suitable energy and the scattered light is collected. The wave lengths of these scattered light yield information about the status of the chemical functional group and hence the bond features of the sample under study. This non-destructive technique can analyse solid, liquid and gaseous samples. Needed sample amount is about 10 mg and in some specific cases the amount is as low as 10 to 50 ng. Liquid samples can run in aqueous solutions.

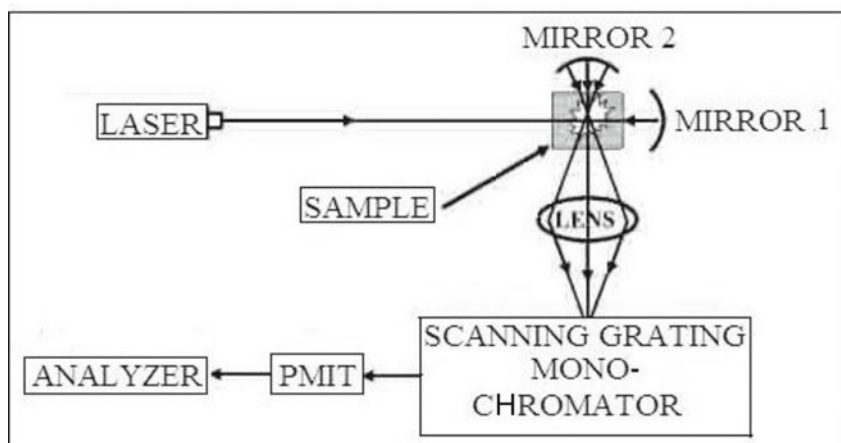


Fig. 6.35: A sketch of Raman spectrometer principle.

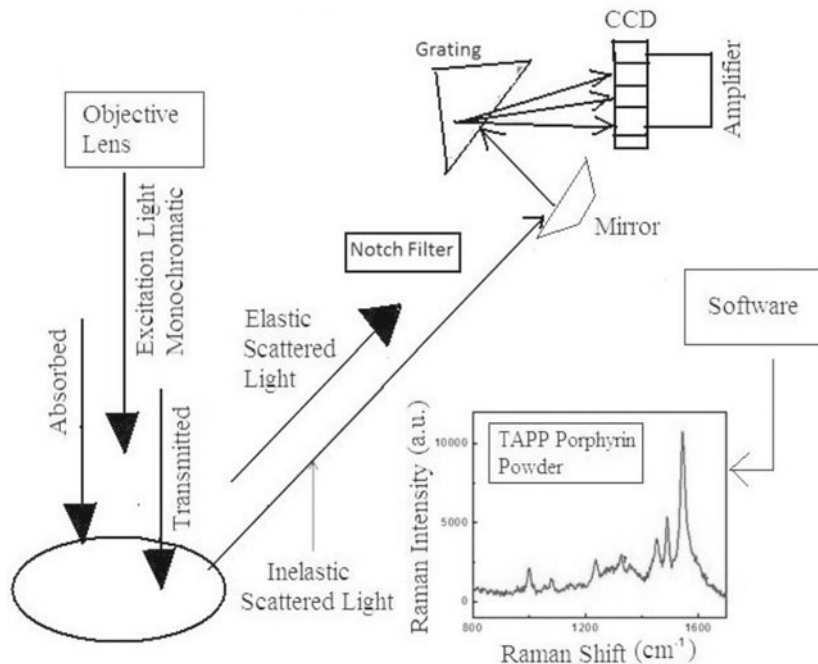


Fig. 6.36: Arrangement details (Notch filter to remove stray light) of a Raman Spectroscopy.

Rayleigh scattering line is very strong compared to the Raman scattering lines. The stray lights of Rayleigh line are also of comparable (or a little stronger) intensity and also in the frequency range, close to the Raman lines. These stray lines are generated in the spectrometer during the light dispersion on gratings. This dispersion is reduced using a holographic gratings. The separation of these lines is a problem. Commercially available interference filters (notch) is used to cut off the spectral range close to the region where the effect of these stray lines are prominent.

6.11 TYPES OF RAMAN SPECTROSCOPE

For specific types of data, needed developments are incorporated in the Raman spectroscopic analysis. These are:

1. Surface Enhanced Raman Spectroscopy (SERS)

Enhances the Raman scattering by adsorbing molecules on rough metal surfaces (colloidal metals, e.g. gold/silver) and the enhancement factor may be of the order of 10^{11} .

2. Resonance Raman Spectroscopy (RRS)

To enhance the vibrational modes of the excited electronic states of a molecule or crystal, the excitation wavelength is matched accordingly. This is useful for studying large molecules.

3. *Tip Enhanced Raman Spectroscopy (TERS)*

In this method, Raman signals are enhanced using a metallic tip (usually silver or gold coated) in the vicinity of the molecules of interest. The spatial resolution is of the size of the tip (20-30 nm). This is a very useful method for bio analysis.

4. *Polarized Raman Spectroscopy (PRS)*

It studies the polarization of Raman scattered light using a polarized laser excitation and a polarization analyzer. The molecular orientation and vibrational symmetry information (relating to the molecular shape e.g. polymorph analysis, liquid crystal study etc.) can be obtained by this technique.

5. *Spontaneous Raman Spectroscopy (SRS)*

Variation of molecular behaviour with temperature variation is studied using this technique.

6. *Transmission Raman Spectroscopy (TRS)*

This is a very useful method for studying powder, capsules, living tissues etc. types of turbid materials in bulk. In medical diagnostic applications, this special method is of immense use.

7. *Hyper Raman Spectroscopy (HRS)*

When the second harmonics of the excited beam interact to the vibrational modes, the non-linear effects can be revealed which are normally not observed. This method depends on SERS type enhancement for analysis.

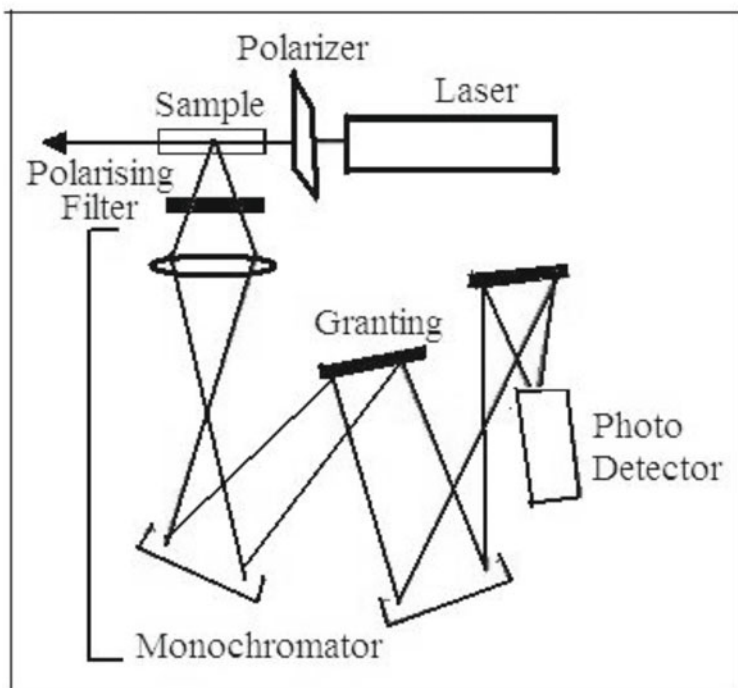


Fig. 6.37: A sketch of Raman spectrometer fitted with polarization facilities.

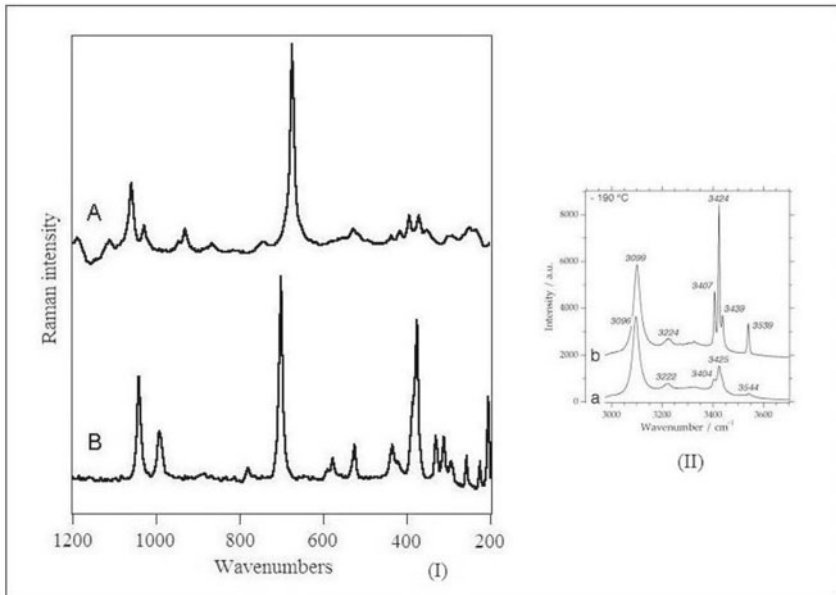


Fig. 6.38: (I): Raman spectra of (A) nephrite and (B) jadeite minerals. (II): Raman spectra of fluid and crystal mixtures in the systems H_2O , $\text{H}_2\text{O}-\text{NaCl}$.

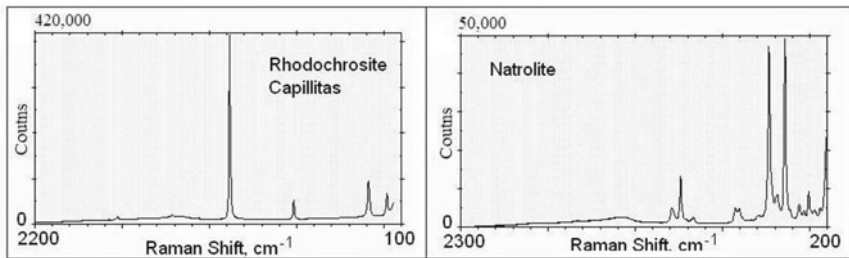


Fig. 6.39: Raman spectra of rhodochrosite and natrolite.

6.12 APPLICATIONS OF RAMAN SPECTROSCOPY

The major applications are:

1. Identification of functional groups in unknown substances in solids and aqueous solutions.
 2. Identification of reaction components—Reaction kinetics study.
 3. Detection of molecular impurities or additives.
 4. Quantitative estimations of compounds in mixtures.
 5. Non-destructive analysis of biochemical systems.
 6. Surface studies using Surface enhanced Raman spectroscopy (SERS).
 7. Studies of electronically excited molecular states.
 8. Routine quality control analysis.
- And many more.

6.13 THERMAL ANALYSIS

Study of properties of materials with change in temperature is Thermal Analysis. Branches of thermal analysis are developed and named according to the study of various properties of the material. When on thermal treatment of a sample, heat is evolved, it is called *Exothermic* process and when heat is absorbed, known as *Endothermic* reaction. Possible processes of enthalpy changes and types of thermal reaction, i.e. exothermic or endothermic are listed in Table 6.4.

Table 6.4: Thermal effects corresponding to different reaction processes

Reaction process	Adsorption	Desorption	Solid-solid transition
	Catalytic reactions	Melting	Solid-liquid reaction
	Crystallisation	Vapourisation	Solid-gas reaction
	Polymerisation	Sublimation	Solid-solid reaction
	Curing	Desolvation (drying)	Decomposition
Observed effects	Exothermic	Endothermic	Exothermic and endothermic

Main applications of thermal analysis are: (1) Soil and clay analysis; (2) Determination of Glass transition; (3) Compositional effects on glass transition; (4) Heat capacity determination; (5) Characterization of polymer blends; (6) Study the effects of additives added to polymer; (7) Polymer degradation analysis; (8) Crystallinity and crystallization rate study; and (9) Reaction kinetic studies.

Different types of thermal analysis developed are on the basis of: (1) weight change, (2) energy change, (3) dimensional change and (4) evolved gas. They are grouped in Table 6.5.

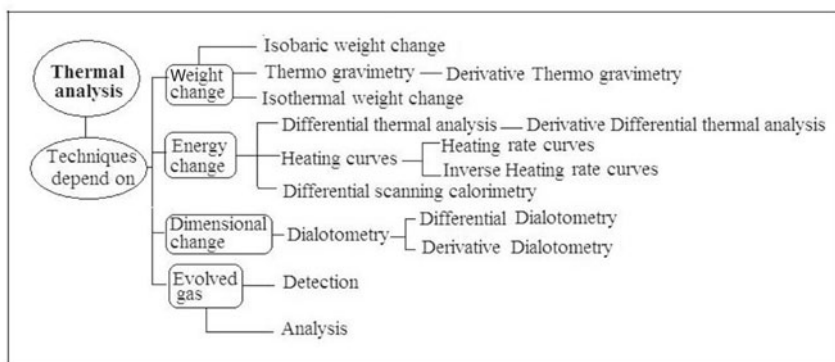


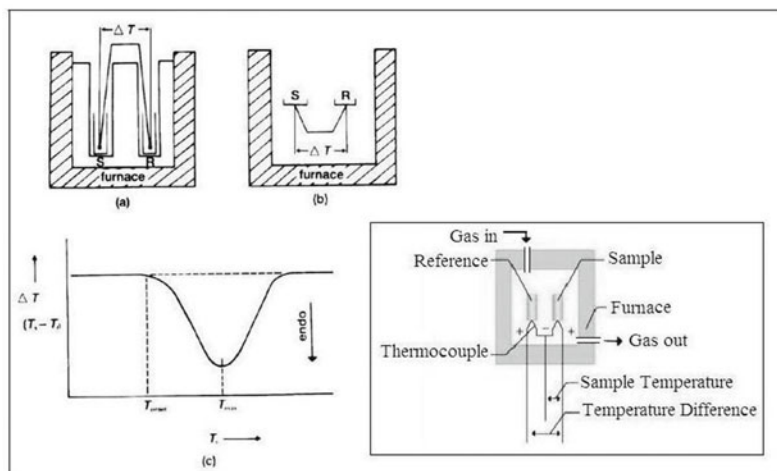
Fig. 6.40: Flow chart showing different types of thermal analysis.

Table 6.5: Different types of thermal analysis

<i>Name of analysis</i>	<i>Description</i>
Thermo gravimetric analysis (TGA)	Measures the change of weight of the sample with temperature variation.
Differential thermal analysis (DTA)	Measures the temperature differences in thermal reaction.
Differential scanning calorimetry (DSC)	Takes the data of heat difference in the thermal reaction under study.
Evolved gas analysis (EGA)	Studies the gaseous products under thermal decomposition.
Thermo mechanical analysis (TMA)	Is the study of dimension under thermal treatment.
Dynamic mechanical analysis (DMA)	Studies the mechanical stiffness and damping under thermal treatment.
Dilatometry (DIL)	Records the volume change in thermal reactions.
Thermo-optical analysis (TOA)	Is the study of thermal effects on change of optical properties.
Dielectric thermal analysis (DEA)	This is the study of dielectric permittivity and loss factor of the material under thermal reactions.

During thermal analysis, the main controlling parameters are sample heating rate, choices of gas for the needed environment and its flow rate, collection of evolved gas (for EGA) for further analysis. For each specific types of thermal analysis mentioned above, suitable accessories are needed for appropriate data collection.

A sketch for the basic instrument is shown in Fig. 6.41. It consists of two crucibles, one for the sample and other for the reference material (must be having steady thermal behaviour over the operating temperature range).

**Fig. 6.41:** Basic parts of a thermanalyser.

Both the crucibles are attached to an electrically controlled heating arrangement. By changing the heater current, the heating rate can be controlled (mostly linear heating/cooling rate or stepwise isothermal measurements used). The temperatures of the sample and reference are measured by thermocouples attached to each crucible. In response to the change in the system properties (sample controlled thermal analysis), more advanced temperature controlling systems (oscillating in sine wave or square wave mode) is being developed and is known as Modulated Thermal Analysis.

Change in the weight of the sample during thermal treatment is recorded using electronic balance, attached to the crucibles. The whole set up is enclosed in a chamber with gas inlet and outlet for controlling the desired environment around the sample. According to the needed environment (atmosphere) of the experiment, measurements can be made using air (oxidizing atmosphere) or inert atmosphere using gases like nitrogen or helium and also may be used in suitable reducing atmosphere.

A separate arrangement may be provided for collecting evolved gas during thermal analysis, which may be used for further studies using some other suitable technique (may be using other relevant techniques like FTIR or mass spectrometry MS).

During thermal treatment, emission of light (electrical discharge from a dielectric material) or the mechanical relaxation (may be with the sound emission) in a stressed specimen can also be studied with the recorded time-temperature variation.

Thermal energy may be absorbed by causing structural changes in the sample. This heat transfer through structures is reflected in the sample's thermal conductivity or heat capacity and has many applications in engineering aspects of material science.

Thermogravimetric analyses measure the weight gain/loss with increasing temperature under inert or reactive environment. Each weight change corresponds to physical (i.e. crystallization, phase transformation etc.) or chemical (oxidation/reduction reactions) processes occurring with temperature change. For quantitative clay analysis in a mixture of clay minerals, TGA is a very effective method. Each clay phase is having its own decomposition temperature and from the corresponding weight loss data, each phase can be quantified. Differential scanning calorimetry (DSC) usually accompanies TGA and is used for calculating enthalpy energy changes or heat capacity changes associated with phase transitions.

An ideal DSC curve showing the change of heat flow process is in Fig. 6.42. Exothermic and endothermic peaks are marked as EX and EN. Due to the imbalance in the thermal capacities of the sample crucible, its contents etc., offset O is observed. The base line of the curve (B) is decided by the heat capacity of the sample. For a precise measurement, the baseline corrections can be made by comparing the empty and with the sample loaded pan data.

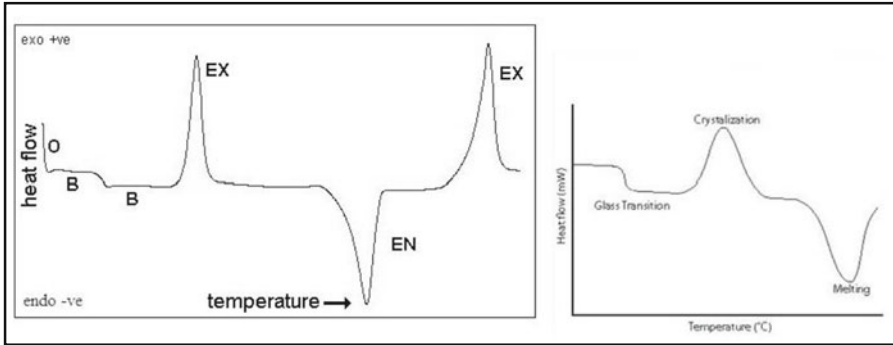


Fig. 6.42: Features of a DSC curve with a base line variation.

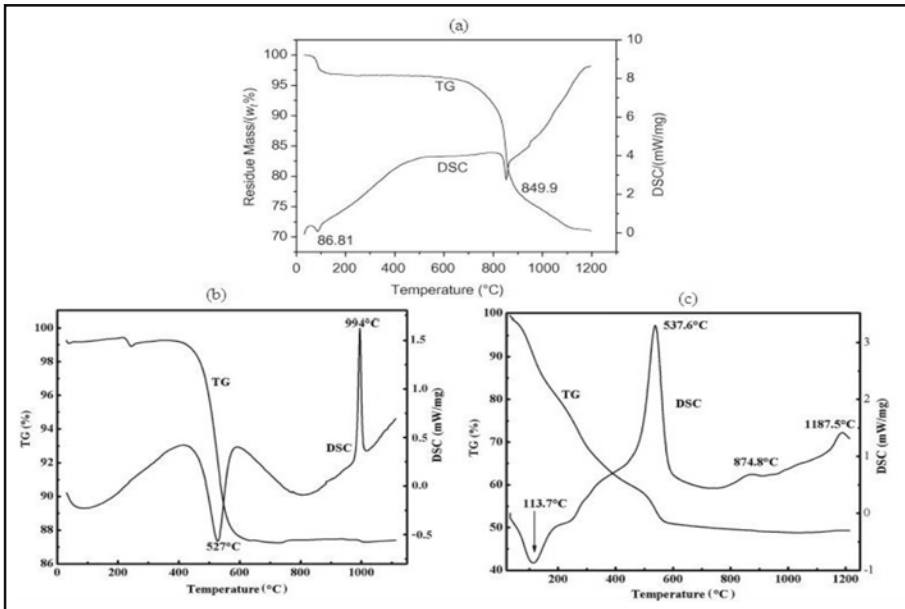


Fig. 6.43: (a) TG-DSC curves for K-feldspar; (b) TG-DSC curves for kaolinite; and (c) TG-DSC curves for Al (hydrus) oxide.

6.14 APPLICATIONS OF THERMAL ANALYSIS

1. Soil and clay analysis.
2. Determination of glass transition.
3. Compositional effects on glass transition.
4. Heat capacity determination.
5. Characterisation of polymer blends.
6. Study the effects of additives mixed with polymer.

7. Polymer degradation analysis.
8. Crystallinity and crystallization rate study.
9. Reaction kinetic studies.

Typical TG-DSC thermograms (simultaneous) are shown in Fig. 6.43. Peaks are yielding information by its position (e.g. temperature, start, end and extrapolated onset), size (depends on the amount on material and energy of reaction) and its shape related to the kinetics of the processes.

Concluding Remarks

For getting specific type of data to unfold the needed information the details of techniques described in this chapter helps to understand and choose a particular technique. For instance x-ray diffraction for internal structure analysis, XRF for elemental composition and XRD for crystal structure analysis, Mossbauer techniques for identification of iron valency state, thermal interaction analysis for decomposition/internal structure change.

QUESTIONS

1. Which technique is essential for clay mineral identification? Why? Can it identify more than one clay phase in a sample? What is the limitation of this technique?
2. For fast and non-destructive chemical composition (elements) analysis, name a suitable technique and explain the process with block diagram. What are the limitations?
3. Compare the difference of wavelength dispersive (WDX) and energy dispersive (EDX) XRF spectrum. In which other techniques these special dispersive spectrums are used?
4. In which technique, oxidation state can be identified? Explain the principle and its applications. What are the limitations?
5. Compare the difference of TEM and SEM and explain the principle and its applications.
6. Explain the process of identification of chemical groups (e.g., CO_3^- , $(\text{OH})^-$ etc.) using infrared spectra.
7. How the elemental mapping is done with EPMA analyzer?
8. In the spectroscopic analysis, identify different techniques appropriate to energy range.
9. What are the different aspects of thermal analysis? Explain them with example.
10. In clay samples, more than one clay phases are detected using XRD. Is it possible to quantify them using some other technique?

11. Why the decomposition temperatures are different even when the chemical compositions are same, e.g. calcite and aragonite? How the heat energy is used when there is no gas emission (like CO₂ from CO₃ group or H₂O from OH⁻ group etc.)?

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