സഹായി

SFI GEC PALAKKAD

MODULE III
INSTRUMENTAL METHODS AND NANOMATERIALS

Thermal Methods of Analysis

Thermal method of analysis is the measurement of physical property of a substance or its reaction product as a function of temperature as the substance is subjected to controlled temperature programme. Two important thermal methods are

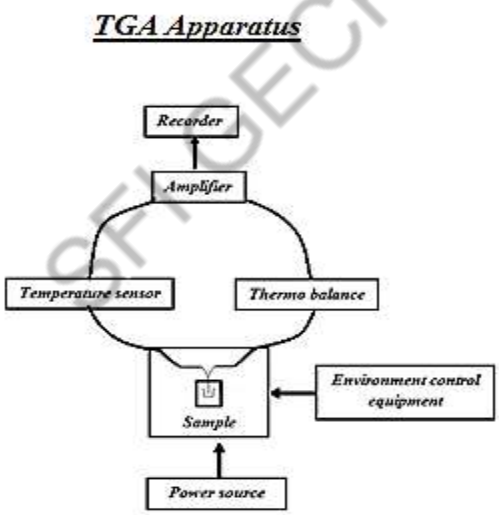
1. TGA
2. DTA

Thermo Gravimetric Analysis (TGA)

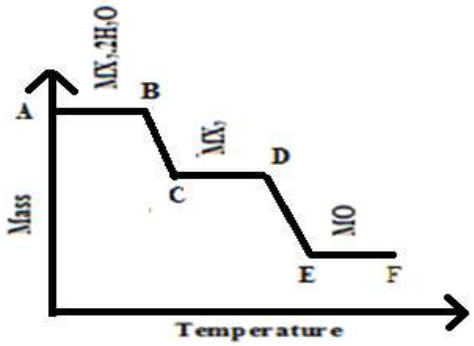
TGA is a thermal method of analysis in which the mass of the sample is measured as a function of temperature when the temperature of the sample is increased linearly from room temperature to 1200°C.

A sample on heating mass change occurs due to the physical and chemical changes undergone by the substance.

This method gives an idea about quantitative as well as qualitative picture of the sample under investigation. On heating mass of the sample changes due to physical changes like vaporisation of moisture volatile component or due to the partial or complete loss of water of crystallisation. It is also due to chemical changes like decomposition, dissociation of substance, oxidation, reduction and combination with atmospheric gases.



Principle and method:



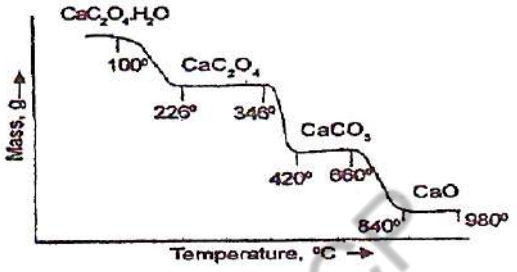
In order to explain the principle and method of TGA, let us consider the thermo gram of the compound $MX_2.2H_2O$.

From the figure it is clear that from A to B, this compound is stable and there is no weight change. At B the compound begins to loss its weight and the process is completed at C. This is due to the evolution of 2 moles of water per each mole of the compound produces anhydrous sample. From C to D, the compound is stable. So we get a horizontal weight level at this region. At D, the compound again begins to lose weight due to the decomposition of MX_2. From E to F, again we get a horizontal weight level. This shows the stability of MO.

From the various regions of the curve, the thermal stability of initial compound, intermediate compound and the final product can be obtained. It also gives an idea about the stoichiometry of the compound at any given temperature.

Applications:

1. Qualitative Analysis



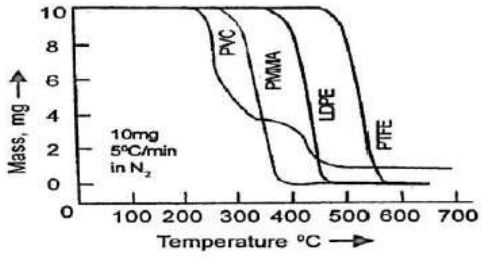
T.G. of calcium oxalate ($CaC_2O_4.H_2O$)

In order to explain the qualitative analysis, let us consider the thermogram of $CaC_2O_4.H_2O$.

$CaC_2O_4.H_2O$ is stable upto 100°C. So we get a horozontal region in this temperature region. On inceasing the temperature above 100°C it loses the two mols of water per each mole of the compound producing anhydrousCaC_2O_4.So the horizontal weight level changes.Anhydrous $CaC_2O_4$is stable from 226°C - 346°C.So again we get a horizontal weight level. Above 346°C evolution of CO takes place producing $CaCO_3$.$CaCO_3$ is stable from 420°C - 660°C. So horizontal weight level obtained in this temperature region. Above 660°C decomposition of $CaCO_3$ takes place producing CaO and the process is completed at 840°C. CaO is stable from 840°C - 980°C. So we get a horizontal weight level in this temperature region.

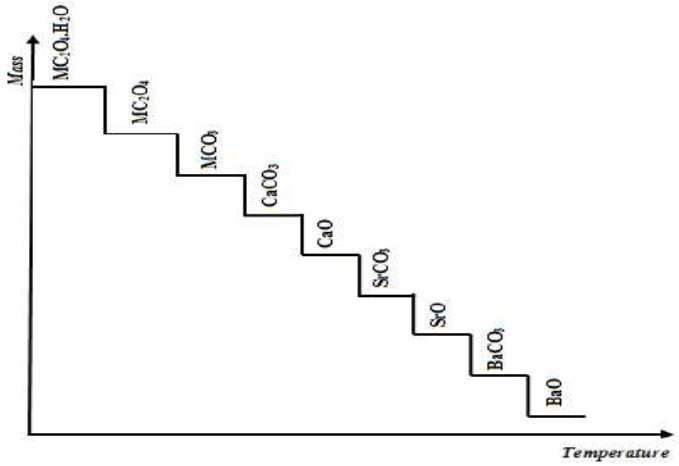
2. Study of polymers

Thermo grams provide ready information about the decomposition pattern of various polymers. Decomposition pattern is the characteristics of each type of polymer. So TGA helps for the identification of polymers.



3. Quantitative analysis – Analysis of binary mixtures

TGA is used for the quantitative analysis of a mixture of calcium, strontium and barium ions. This can be explained by considering the thermo gram of $MC_2O_4.H_2O$.



Limitations of TGA:

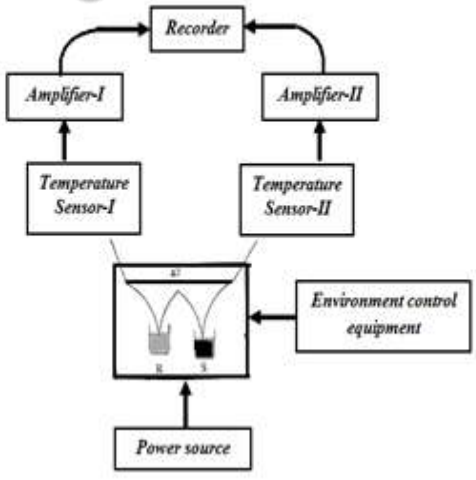
- TGA will not give any information about phase transition of crystalline substance. Since these transitions do not involve weight change.
- It will not give any information about melting point, boiling point and transition temperature of crystalline substances.

Differential Thermal Analysis (DTA)

DTA is a thermal method of analysis in which difference in temperature between the sample and inert reference compound is measured as a function of sample temperature as the sample and the reference compound are heated uniformly in a constant rate. Usually used reference compounds are alumina and silicon carbide.

In DTA, difference in temperature between the sample and the reference compound is monitored continuously and is plotted against sample temperature to obtain differential thermo gram.

DTA Apparatus

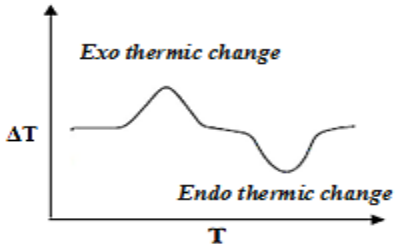


Principle and method:

In DTA, peaks are obtained due to the physical and chemical changes undergone by the substance on heating. Physical changes are endothermic or exothermic. Physical changes like

fusion, evaporation, sublimation, absorption, desorption etc. are endothermic. But adsorption and crystallisation are exothermic physical changes. Chemical changes are also endothermic or exothermic. Reduction in inert atmosphere, dehydration and decomposition are usual endothermic chemical changes. Oxidation in air, polymerisation are exothermic chemical changes.

DTA THERMOGRAM



Upward peak or maxima corresponds to exothermic change, whereas downward peak or minima correspond to endothermic change.

Peak areas in differential thermo grams depend upon the mass of the sample (m), enthalpy change (ΔH) of the physical or chemical changes and certain geometric and conductivity factors.

Peak Area (A) = -kGmΔH

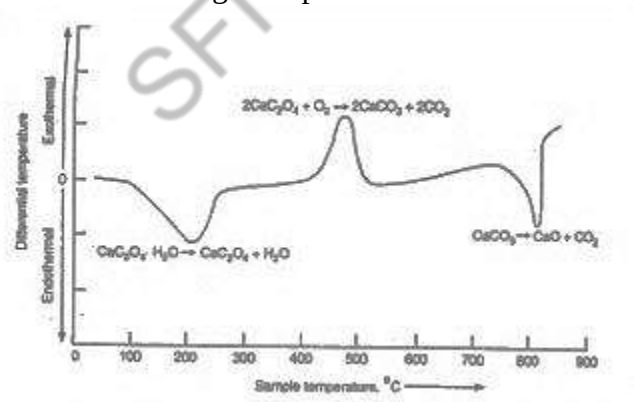
A is the peak area, G is the calibration factor which depends upon the sample geometry and k is a constant related to the thermal conductivity of the sample.

Applications:

1. Study and characterization of polymers

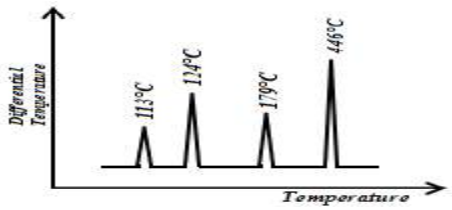
Thermal transitions of polymer occur over an extended range of temperature since polymers are mixtures of different homologues. Each peak corresponds to the melting point of the components present.

2. Study of the thermal behaviour of inorganic species



In the DTA of hydrated calcium oxalate, first peak (minima) corresponds to the dehydration of hydrated calcium oxalate. It is endothermic change. Second peak (maxima) corresponds to the oxidation of anhydrous oxalate. Oxidation is an exothermic change. Second minima correspond to the decomposition of $CaCO_3$.Decomposition is endothermic change.

3. Study of phase transition

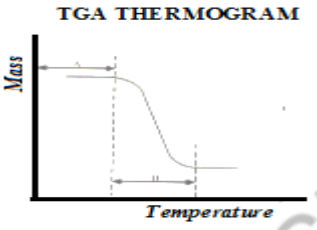
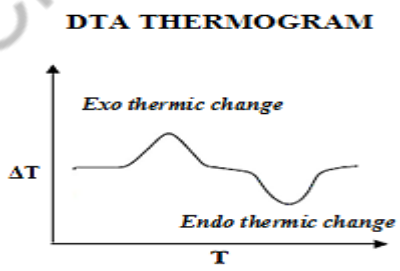
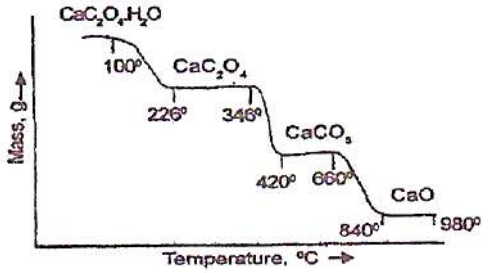
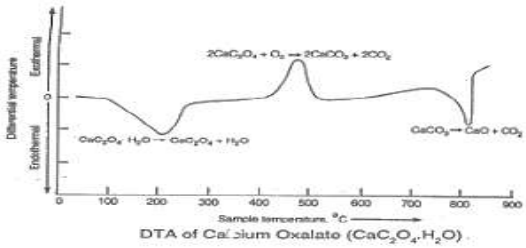


In the differential thermo gram of sulphur, a peak at 113°C represents solid phase transition from rhombic sulphur to monoclinic sulphur. Peak at 124°C represents the melting point of sulphur. Peak at 179°C represents the presence of liquid sulphur. Peak at 446°C represents the boiling point of sulphur.

Merits of DTA:

- It can be used for studying phase transition which cannot be studied using TGA.
- It gives information about melting point, transition temperature etc. of crystalline substance, whereas TGA cannot give these data.

- **Differentiate between TGA thermo gram and DTA thermo gram graphically**

TGA Thermo gram	DTA Thermo gram
1. TGA thermo gram is the plot of mass (m) against temperature (T)	1. DTA thermo gram is the plot of difference in temperature between the sample and the reference compound (ΔT) against temperature (T).
2. 	2. 
3.  T.G. of calcium oxalate ($CaC_2O_4.H_2O$)	3.  DTA of Calcium Oxalate ($CaC_2O_4.H_2O$)
4. TGA cannot be used for phase transition study.	4. DTA can be used for phase transition study.

Distinguish between TGA & DTA.

TGA	DTA
1) TGA is a thermal method of analysis in which mass of the sample is measured as a function of temperature as the temperature of the sample is increased linearly from room temperature to 1200°C. 2) In TGA, mass of the substance is recorded continuously as a function of temperature. 3) TGA is used to study physical and chemical changes that is followed by mass changes	1) DTA is a thermal method of analysis in which difference in temperature between the sample and inert reference compound is measured as a function of sample temperature as the sample and reference are heated uniformly in a constant manner. 2) In DTA, temperature of the sample and the inert reference compound is measured as a function of temperature 3) DTA is used to study physical and chemical changes that occurs with or without mass change

Chromatography

The term chromatography means clour writing. This was introduced by the scientist Mikhail Tswette. He employed itfor the separation of plant pigments such as chlorophyll and xanthophyll by passing the solution of these substances through a glass column packed with finely divided $CaCO_3$. The seperated components appeared as coloured bands in the column. So he choose th name chromatography.This method is generally used for the seperation of complex mixtures which cannot be seperated by other methods. It is also useful for the seperation and purification of organic compounds when they are available in very smaller quantity.

General principle of chromatography

It is based on the principle of selective distribution of mixture of compounds between two phases, viz stationary phase and mobile phase.

Stationary phase is the fixed phase. For exmple, a column of adsorbent, paper, a thin film of liquid supported on an inert solid, a thin layer of adsorbent coated over a glass plate can be used as stationary phase.

Stationary phase is a solid or a liquid. If the stationary phase is a solid, then the principle adsorption and such type of chromatography is called adsorption chromatography. Example column chromatoraphy.

If the stationary phase is a liquid, then the principle artition and such type of chromatography is called partition chromatography. Example Gas liquid chromatoraphy.

Mobile phase is the moving phase. It can be a liqid or gas. The components to be seperatedis carried by the mobile phase through the stationary phase.

Classification of chromatography based on mechanism of separation,

a) Adsorption chromatography:

In this chromatography stationary phase is solid and mobile phase is a liquid or gas. Here separation occurs due to the difference in the adsorption coefficients of the components.

b) Partition chromatography:

In this chromatography stationary phase is a liquid supported on inert solid and mobile phase is a liquid or gas. Here separation occurs due to the difference in the partition coefficients of the components.

c) Ion exchange chromatography:

In this chromatography stationary phase is an ion exchanger and the separation of the mixture is based on ion exchange principle and applicable for ionic species.

Classification of chromatography based on the mobile phase,

a) Liquid chromatography:

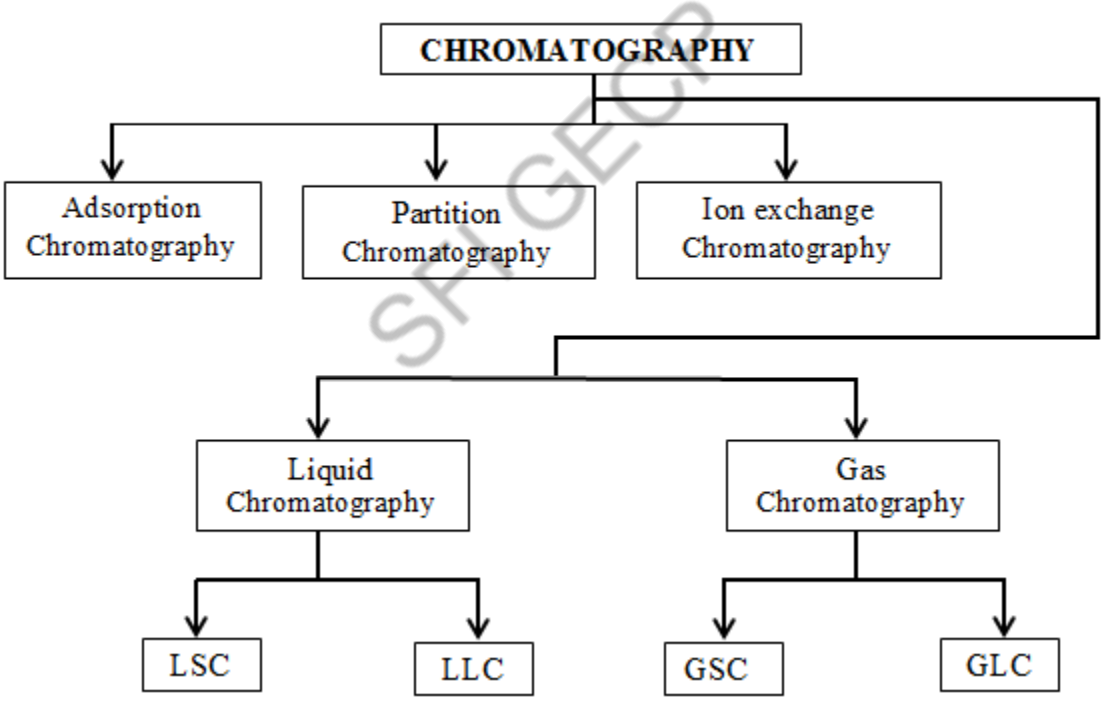
If the mobile phase is liquid and the stationary phase is solid, then the chromatography is called LSC (Liquid Solid Chromatography)

If the mobile phase is liquid and the stationary phase is liquid supported on solid, then the chromatography is called LLC (Liquid Liquid Chromatography)

b) Gas chromatography:

If the mobile phase is gas and the stationary phase is solid, then the chromatography is called GSC (Gas Solid Chromatography)

If the mobile phase is gas and the stationary phase is liquid, then the chromatography is called GLC (Gas Liquid Chromatography)



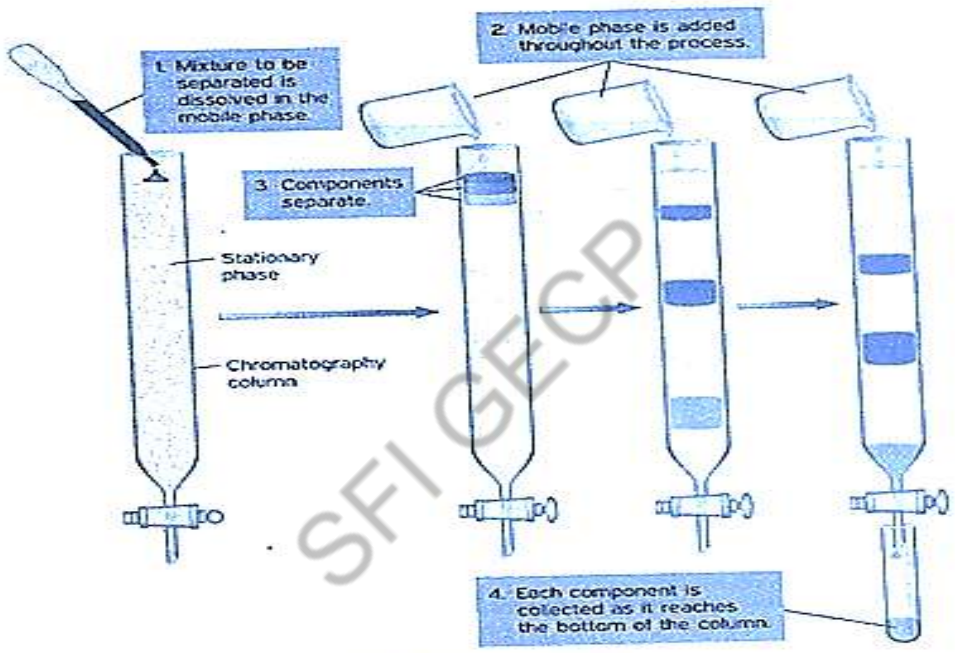
Column chromatography.

In column chromatography stationary phase is held in a narrow tube and is packed with solid adsorbents like Al_2O_3, silica gel, MgO etc. This can function as the stationary phase. The mixture to be separated is dissolved in a suitable solvent will constitute the mobile phase. Mobile phase is forcefully passed through the stationary phase under pressure or by gravity. Then the most readily adsorbed components get retained at the top, whereas the less readily adsorbed components penetrate various distances down the column depending on the degree to which they

get adsorbed. As a result components in the mixture are separated as a series of rings or bands in the column. If the components are coloured then the bands obtained are also coloured. Such coloured banded column of adsorbent is called ***chromatogram***. If the components are colourless, then a colour developing reagent is sprayed on the chromatogram to make the separated components coloured and visible. This process is called development of chromatogram

. The process of recovery of components from the chromatogram is called elution. Different methods are employed for this purpose.

- Column of adsorbent is pushed out of the tube and is then cut at the boundaries using a knife. Every zone can then be extracted with suitable solvent.
- Column of adsorbent is washed with more and more solvent which separate out the components one by one.



Column Chromatography

Applications:

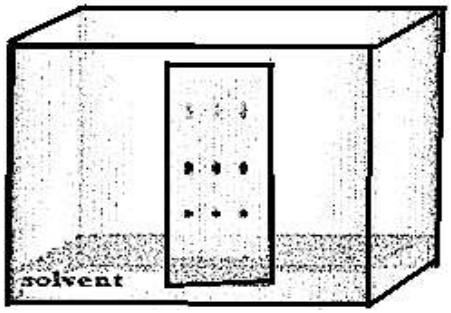
- This method is used for the separation of organic compounds from plant pigments.
- It is also used for the separation and purification of natural compounds like alkaloids, glycosides etc.
- It is also used for large scale separation and purification of pharmaceuticals.

Thin Layer Chromatography (TLC)

Thin layer chromatography was developed by Izmailov and shraiber. It is better than column chromatography. This method is used for determining the number of components in a mixture. This method will give an idea about the identity of components in the mixture. This will give an idea about the purity of compounds.

In TLC, a glass plate coated with adsorbent (Silica gel, alumina) is used as the stationary phase. The adsorbent is made as a slurry or paste with water and is spread over the glass plate. These coated glass plates are dried and activated by heating in an oven at 120ºC. The mixture to be separated is applied at one end of the glass plate. The glass plate is then placed in the

development tank at an angle of 45º and the bottom of the tank is filled with solvent (nearly 1mm). When the solvent moves upwards, it carries the components in the mixture to different heights. Thus components in the mixture get separated. This process takes about 20- 40 minutes.

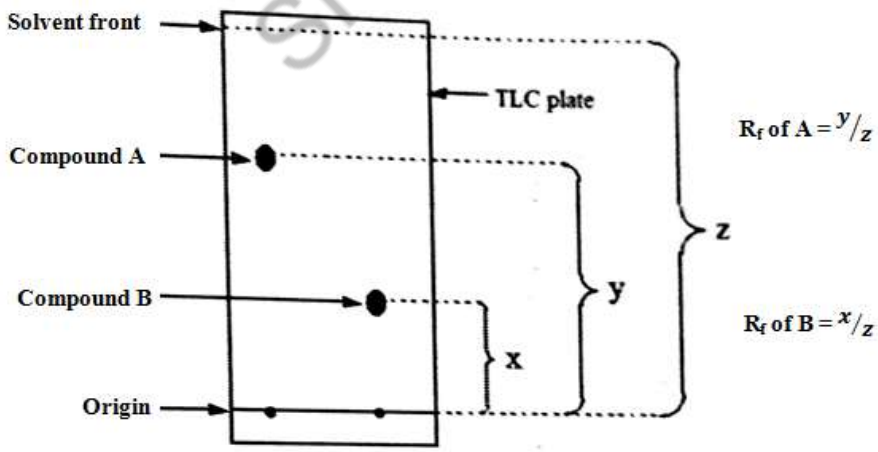


Then the glass plate is taken out of the development tank and the solvent front is marked. It is then allowed to dry. If the components in the mixture are coloured then they can be visually detected as coloured spots in the glass plate. If the separated components are colourless, then they can be visualized in the following manner.

- Using UV-lamp
- Using colour developing reagents such as $KMnO_4$
- Using 2,4-dinitro phenyl hydrazine reagent to detect carbonyl compounds
- Iodine vapours are also used

In this way position of all the components in the mixture are located and they can be identified by knowing their R_F values. R_F value (Retention factor or ratio of fronts) is the ratio of distance travelled by the sample component to that of the solvent front. It is the characteristics of each component and is specific for each component.

$$R_F \text{ value} = \frac{distance\ travelled\ by\ the\ component}{distance\ travelled\ by\ the\ solvent\ front}$$



Hence we can identify the components in a mixture.

Applications:

- It is used for finding the purity of compounds.
- To determine appropriate solvent for column chromatographic separation.
- It is used for the identification of a compound.
- It is used for monitoring column chromatographic separation.

Advantages:

- It requires simple equipment.
- Speed of separation is high.
- Very sharp and sensitive separation.

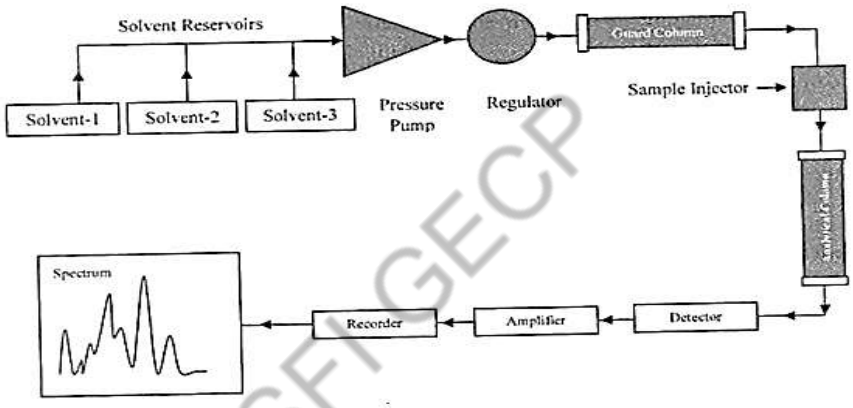
High Pressure Liquid Chromatography (HPLC)

HPLC is widely used for analytical separation because of its high sensitivity, accurate quantitative determination and its ability to separate non – volatile species.

HPLC Apparatus

i) Solvent delivery system
ii) Sample injection system
iii) Chromatographic column
iv) Detector
v) Recorder

Instrumentation:



Working

In HPLC solvents are introduced from two or more reservoirs into the mixing chamber at rates that vary continuously with time. The solvents used here are filtered through a Millipore filter under vacuum to remove the dissolved gases and suspended matter. Solvent is then pumped through the column at the same time a dilute solution of the sample under analysis is also introduced into the column by a sample injection system. As the solution flows through the column, some more solvent is introduced into it. Generally narrow column of 10–30 cm length are used. Usually columns are made up of heavy glass or stainless steel to withstand high pressure. The efficiency of HPLC columns improves significantly as the particle size is reduced. Hence HPLC columns are packed with particles having narrow particle size. Pumping pressures of several thousand pounds per square inch (psi) is required. HPLC systems usually make use of pump working at a pressure of 6000 psi so that flow ranging from 0.1 -10 ml/minute can be obtained. Three types of pumps are used. They are pneumatic (constant pressure) pump, displacement pump and reciprocating pump.

Column packing material:

Packing in HPLC column consists of small rigid particles having narrow particle size. A solid glass bead of 30-50µm in diameter can be coated with a thin layer of porous material. These coated glass beads are called pellicellar beads. The porous layer serves as the solid

stationary phase. The porous layer is chemically bonded to the solid glass bead. So that it is not washed away by the mobile phase under high pressure.

Solvents:

Successful separation can be achieved by matching the polarities of sample and the packing material. But the solvent has a very different polarity. Lower the viscosity of the solvent, greater the chromatographic affinity.

Guard column:

It helps to remove the particulate and contaminants from the solvent.

Detector:

Bulk property detector and solute property detector are used as detectors. Bulk property detectors respond to the bulk properties like refractive index, dielectric constant, density etc., of the mobile phase. When a particular molecular species is separated out, these properties will change and the detector gives the signal. Solute property detectors respond to the solute properties like UV absorbance, fluorescence of the solute molecules. For example paracetamol can be detected using UV detector since it gives absorption at 255 nm due to the presence of benzene ring in the molecule. Every separated component at the detector produces electrical signals.

Recorder:

The signals from the detector can be recorded as different peaks. The area under each peak represents the amount of components present in the sample.

Applications:

- Used in pharmaceutical biological study.
- Used in the analysis of water soluble and fat soluble vitamins.
- Used in the analysis and separation of amino acids & proteins.
- Used in the separation of lipids & steroids.

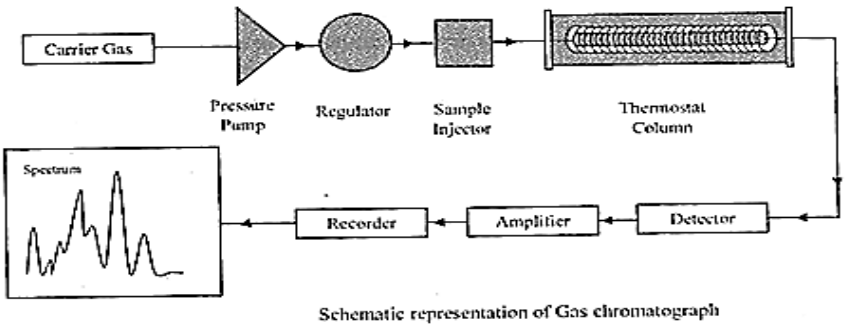
Gas chromatography (GC)

Gas chromatography is based on the principle of selective distribution components of mixture between two phases, viz stationary phase and mobile phase. In gas chromatography separation occurs between gas mixture and the stationary phase. ***Mobile phase is a mixture of vaporized sample and inert carrier gas***. Usually used carrier gas is nitrogen. Sometimes Ar, He, H_2 can also be used as the carrier gas depending on the nature of mixture. Stationary phase may be a solid or liquid. So there are two types of gas chromatography

1) Gas Solid Chromatography (GSC)
2) Gas liquid Chromatography (GLC)

In GSC, stationary phase consists of silica, alumina etc. and the principle is adsorption. In GLC, a thin film of high boiling liquid paraffin or poly ethylene glycol coated on an inert solid material like celite or kieselghur is used as the stationary phase. Here the principle is partition.

Instrumentation Gas Chromatography Apparatus



Schematic representation of Gas chromatograph

Working:

In gas chromatography ***a mixture of vaporized sample and inert carrier gas*** (mobile phase) is passed through the stationary phase. Stationary phase is held in a narrow column. As the mixture of gases pass through the column, separation of components occurs via adsorption or partition on the basis of the physical state of the stationary phase. In GSC separation of components occurs on the basis of the degree to which they get adsorbed. In GLC, separation of components occurs on the basis of the difference in the partition coefficients. Since the partition coefficients of individual components in the mixture are different. So they are carried along the column at different rates. The components which leave the column passes leave column passes through the detector and recorder. The detector produces electrical signals and the recorder converts it as a trace on a paper. The resultant trace is a plot of signal intensity against time and is called chromatogram. By GC even 10^{-12}g quantity of mixtures can be separated and identified. Hence it is an important analytical technique.

Detectors used in GC:

i) Flame Ionization detector (FID)

FID is one of the most widely used detector for GC.

Advantages:

High sensitivity, low noise, easy to use.

Disadvantage:

It causes the destruction of the sample.

ii) Thermal Conductivity Detector (TCD)

It works on the principle that presence of analyte molecule in the gas stream will produce a change in thermal conductivity.

Advantages:

Simple to use, non – destructive in nature and it gives respond to both organic and inorganic matter.

Disadvantage:

Low sensitivity

Some other detectors like ***thermionic detector (TID), atomic emission detector (AED) and electron capture detector (ECD)*** are also used.

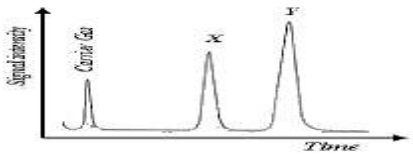


Figure shows the chromatogram of mixture of two gases X & Y. First peak always represents the carrier gas and other two peaks represent the pure components X & Y. Each component can be identified by actual isolation time or retention time. It is the time required for the components to

emerge from the column. This can be compared with the retention time of known samples under identical conditions.

Applications:

- Used for qualitative analysis
- Used to test the purity of compounds. The presence of impurities will be revealed by the appearance of extra peaks.
- Widely used for study of air pollution.
- By GC ethyl alcohol content in the blood can be determined with high degree of accuracy.
- Banned drugs used by athletes can be detected by taking the GC of blood or urine sample.

Comparison of GSC & GLC.

Point of differences	GSC	GLC
Stationary phase	Solid	Liquid
Mobile phase	Gas	Gas
Principle	Adsorption	Partition
Packing of the column	Granular powder of adsorbent is packed in the column	Both packed and capillary column can be used
Length of the column	0.7 – 2m	3 – 300m
Thermal stability of stationary phase	Good stability	Less stable above 300°C
Reactions in the column	Packing may catalyze chemical change	Packing does not catalyze
Application	Useful for the separation of permanent gases and low boiling substances	Useful for the separation of volatile high boiling substances

Nanomaterials

Materials having the dimension of the order of billionth of a meter or nano meter are called **nanomaterials.**

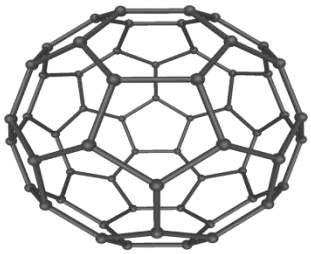
Classification:

1. **Nano crystalline materials**
2. **Fullerenes**
3. **Dendrimer**
4. **Polyhedral silsesqui oxane**
5. **Nano intermediates**
6. **Nano composites**
7. **Biological nanomaterials**

Nano crystalline materials:

These are aggregates containing a few hundred to several thousands of atoms which are joined to form crystalline form of matter. Resultant crystalline form of matter is called clusture. So these nanomaterials are called nano crystals. They can be used for getting semiconductor crystals. Their diameter is nearly 1nm. They are used for making very strong and long lasting metallic parts. On mixing nano crystals with plastic we get nano composites.

Fullerenes:



These are the molecular form of very pure carbon. They are discovered in 1995. They possess cage like structure of carbon atoms. Most abundant fullerene is buck minister fullerene (buckymann, C_{60}). They possess spherical structure of 60 carbon atoms. Fullerenes contain twelve five membered rings and twenty six membered rings and possess a perfect icosahedral geometry. This geometry is similar to that of a soccer football. In fullerene, each carbon atom is bonded to three other carbon atoms and is SP^2 hybridized.

Uses:

- They are used in drug delivery system.
- They are used in electronic circuits.
- They are used as lubricant in ball bearings.

Dendrimer:

These are organic nano particles. These are highly branched tree like organic polymers. These are obtained from monomers which are added in discrete steps to get tree like appearance. Highly controlled step wise reactions and purifications are required at each step to control the size, structure and functionality of dendrimer.

Eg. PAMAM Dendrimer (Poly Amido Amine)

Polyhedral silsequioxane:

These are inorganic organic hybrid nano particles. They possess unique set of physical and chemical properties such as high solubility, thermal stability, dielectric constant, permeability and optical transparency. The stoichiometry of the compound is $RSiO_{1.5}$. That means every silicon atom is bound to an average of one and half oxygen (Silsequiox) and to a hydrocarbon group (ane). Hence the name polyhedral silsequioxane.

Nano intermediates:

They include nano structured films, dispersions, high surface area materials, supra molecular compounds etc. They are used in solar cells, sensors, battery etc.

Nano composites:

On mixing solid nano particles with plastc resin we get nano composites. They possess more strength. They are lighter and stiffer than thermoplastics. They are less brittle. They possess excellent corrosion resistance. Hence they are used as an anticorrosive material.

Biological nano materials:

These are nano materials of biological origin.

Properties of biological nano materials:

- Self assembly property
- Specific molecular recognition

Eg. DNA nano particles, nano structured peptides

Self assembled nano particles can be used to release compounds under specific conditions and are used in drug delivery systems.

(*Self assembly is a phenomenon where the components of the system assemble themselves spontaneously via an interaction to form larger functional unit.**)**

(* Molecular Recognition is the specific interaction between two or more molecules through non covalent bond.***)**

Classification based on dimension

This is the classification based on the number of dimensions which are not confined to the nanoscale range(<100 nm).

1. Zero dimension (0-D)

Here all the three dimensions are in the nanometric range. Eg. Nano particles

2. One dimension (1-D)

Here one of the dimensions is outside the nanometric range and the other two are within the range. Eg. Nano wires, fibres and tubes.

3. Two dimension (2-D)

Here two of the dimensions is outside the nanometric range and one is within the range. Eg. Nano films, layers and coatings

4. Three dimension (3-D)

Here all the dimensions are outside the nano metric range and one is within the range. Eg. Bundles of nano wires and tubes, multinanolayers.

Nanotubes

CNT is a tiny hollow cylinder with outside diameter of a nanometer. These are formed spontaneously from carbon atoms. CNT's are sheets of graphene rolled to make a tube. Graphene is one atom thick planar sheets of SP^2 hybridized carbon atoms as in graphite. On aligning in specific manner, their atoms can conduct electricity as effectively as copper. On aligning in a slightly different manner they become electrical semiconductor. They are stronger than steel.

Classification of nano tubes:

On the basis of alignment of carbon atoms, nanotubes are three types.

1. Arm chair nanotube
2. Zig–zag nanotube
3. Chiral nanotube

- **Arm chair nanotube:**

If the line of hexagons is parallel to the axis of the nanotube, then the resultant nanotube is called arm chair nanotube.

- **Zig–zag nanotube:**

If the line hexagon is arranged in a zig–zag manner, then the resultant nanotube is called zig – zag nanotube.

- **Chiral nanotube:**

Line of hexagon exhibit a twist or spiral around the axis of the nanotube which is called chirality. Hence the name chiral nanotube.

On the basis of number of cylindrical structures, nanotubes are of two types.

1. SWCN (Single Walled Carbon Nanotubes)
2. MWCN (Multi Walled Carbon Nanotubes)

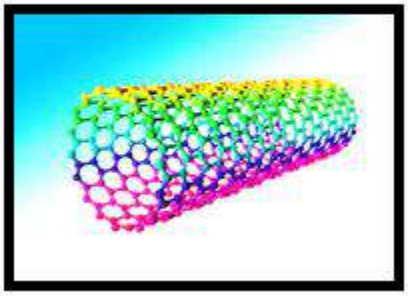
- **SWCN:**

They contain only one nanotube cylinder.

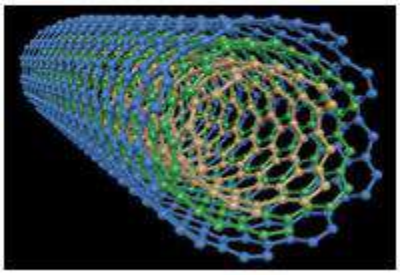
- **MWCN:**

They contain more than one nanotube cylinders.

SWCN



MWCN



Properties:

- Young's modulus is 10 times more than that of steel.
- They possess excellent magneto resistance.
- They are very stiff, hard to bend. Once they are bent, they are very resilient.
- Their thermal conductivity is more than diamond and is very high.
- They are very good conductors of electricity.

Uses of nanotubes:

- They can be used as mechanical reinforcement material.
- It can be used a catalyst in many reactions.
- Lithium which is a charge carrier in some of the batteries can be stored inside the nanotube.
- They can be used in field effect transistors.
- They can be used as paper batteries.
- They can be used in solar cells.

Synthesis of nano materials:

1. Reduction :

a) Chemical Reduction:

Molybdenum nano particles can be obtained by reducing molybdenum chloride in toluene using tri ethyl boro hydride.

$MoCl_3 + 3NaB(C_2H_5)_3H \rightarrow Mo + 3NaCl + B(C_2H_5)_3 + {}^3/_2H_2$

Tri ethyl lithium boro hydride, sodium boro hydride can also be used as reducing agents.

b) Electro reduction:

Copper nanoparticles can be prepared by this method. The electro reduction process chamber consists of a copper plating bath containing homogeneous acidified $CuSO_4$ solution. The nano particles formed as spongy layers of ball structures at the cathode. These spongy layers of Cu can be easily separated to give fine nano particles.

2. Hydrolysis: Sol- Gel Method or Chemical Solution Deposition

This method is used for the synthesis of nano crystalline titanium powder.

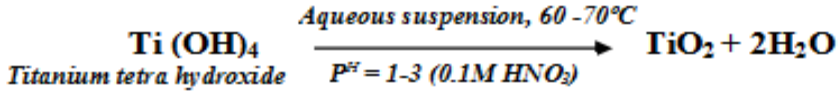
STEP I:

Nano crystalline TiO_2 powder is prepared by the hydrolysis of titanium isopropoxide to get a sol(Solid in liquid).

$$\underset{\text{Titanium isoprpoxide}}{Ti(OC_3H_7)_4} \xrightarrow[P^H = 1\text{-}3\ (0.1M\ HNO_3)]{\text{Aqueous suspension, } 50^\circ C} \underset{\text{Titanium tetra hydroxide}}{Ti(OH)_4} + C_3H_7OH$$

STEP II:

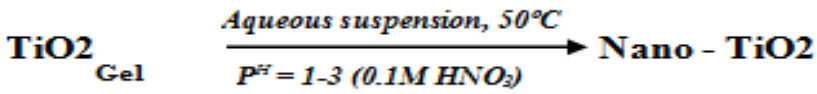
Titanium tetra hydroxide sol will undergo poly condensation by peptisation at a temperature of 60 - 70°C for a period of 18 – 20 hours to produce a precipitate.



Resultant TiO_2 precipitate possesses three dimensional network structure. The precipitate is then washed with ethanol and dried under vacuum conditions for three hours at a temperature of 100°C to get TiO_2 gel(Liquid in solid).

STEP III:

In this step TiO_2 gel is annealed to get Nano crystalline TiO_2.



Scanning Electron Microscopy (SEM)

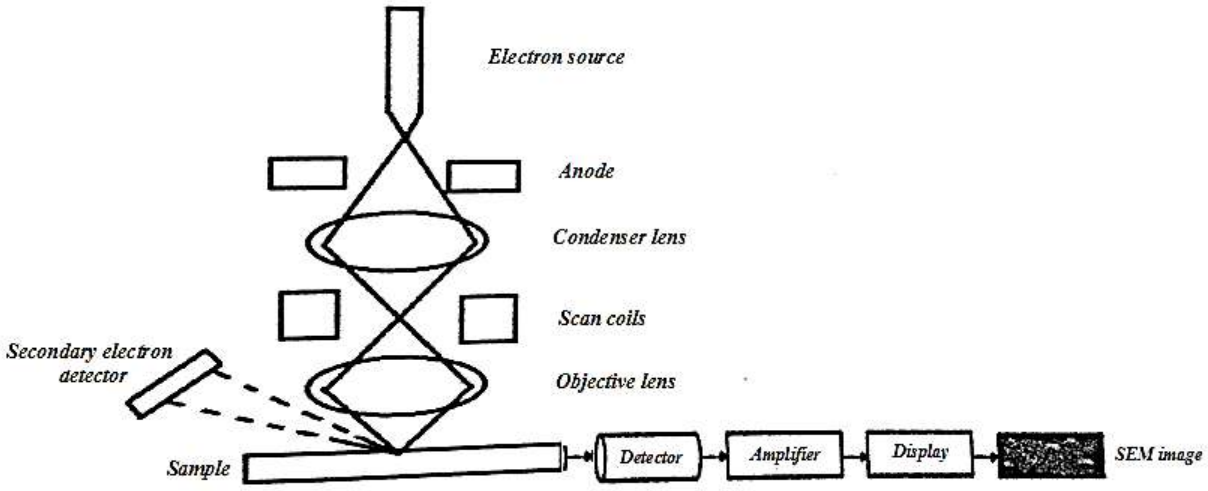
SEM is an important surface characterisation technique used in nanotechnology. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This can provide information about topography (surface features), morphology (shape and size of the particles), composition and crystallographic information.

Principle

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can give information about the surface topography and composition. Electrons from the top of the column is accelerated down and passed through a combination of lenses to produce a focused beam of electrons which hits the surface of the sample. As a result of the electron sample interaction, signals are produced. These signals are then detected by appropriate detectors. Thus high resolution three dimensional images are produced.

Instrumentation

SEM provides detailed surface information by tracing a sample with an electron beam. This process begins with an electron gun (electron source) generating a beam of energetic electrons down the column and are then passed through a series of electromagnetic lenses. Usually used electron gun is a tungsten wire. Condenser lens compresses the electrons to a narrow beam and the objective lens focuses the electron beam to the sample chamber. This chamber holds the sample under vacuum to eliminate interference of unwanted particles. When the electrons come in contact with the sample, energetic electrons are released from the surface of the sample. Finally detectors will detect signals from the sample. The signals usually include secondary electrons (SE), back scattered electrons (BSE) and X-rays. BSE are incidental electrons reflected backwards. This comes from the deeper regions of the sample. SE originates from the surface of the sample. Therefore BSE and SE provide different types of information. X-rays emitted from beneath the sample surface can provide element and mineral information. SEM produces black and white three dimensional images. A display monitor can be used for the display of images.



Applications

- In morphological and topographical analysis of materials.
- Forensic investigations utilize SEM to uncover the evidence.
- SEM is used study bacteria and viruses.
- In microchip design and production.

Disadvantages

- SEM is very expensive.
- Special training is required to operate SEM.
- Small risk of radiation exposure.

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