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Module III

INSTRUMENTAL METHODS AND NANOMATERIALS

Module III
PART I:Instrumental Methods and Nanomaterials

Instrumental Methods include Thermal Analysis and Chromatography

Thermal Analysis: This method is based on the dynamic relationship between temperature and any of the physical properties such as mass change (Δ m) and heat change (Δ H)
The most important methods are

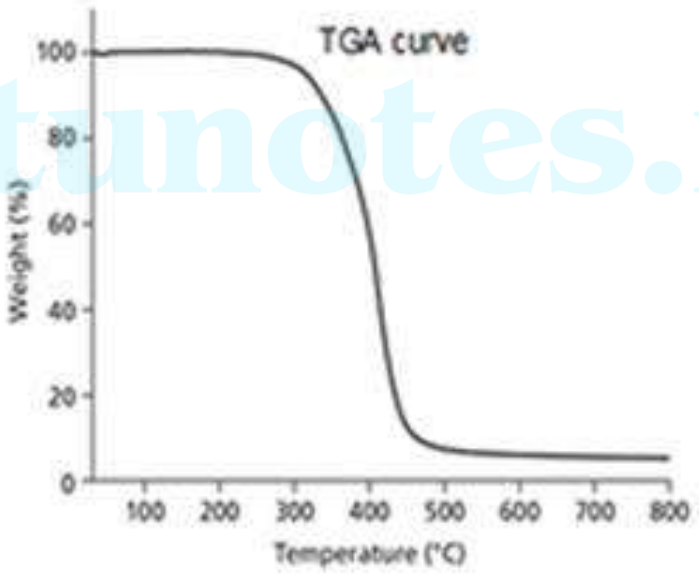
1) **TGA (Thermo gravimetric Analysis)**
2) **DTA (Differential Thermal Analysis)**

1. TGA (Thermogravimetric Analysis)

Principle

- It involves recording the mass of the sample continuously as a function of temperature.
- As the T of the sample is increased linearly from room T to a temperature of 1200°C, the sample undergoes physical or chemical change which is accompanied by mass loss.
- The measurement is normally carried out in an inert atmosphere such as **N_2, He** or **Ar** and weight is recorded as a function of increasing T

Thermogram: A plot of mass Vs T.



Region I:

- The horizontal portion indicates the region where there is no mass change.
- From this we can identify thermally stable compounds.

Region II:

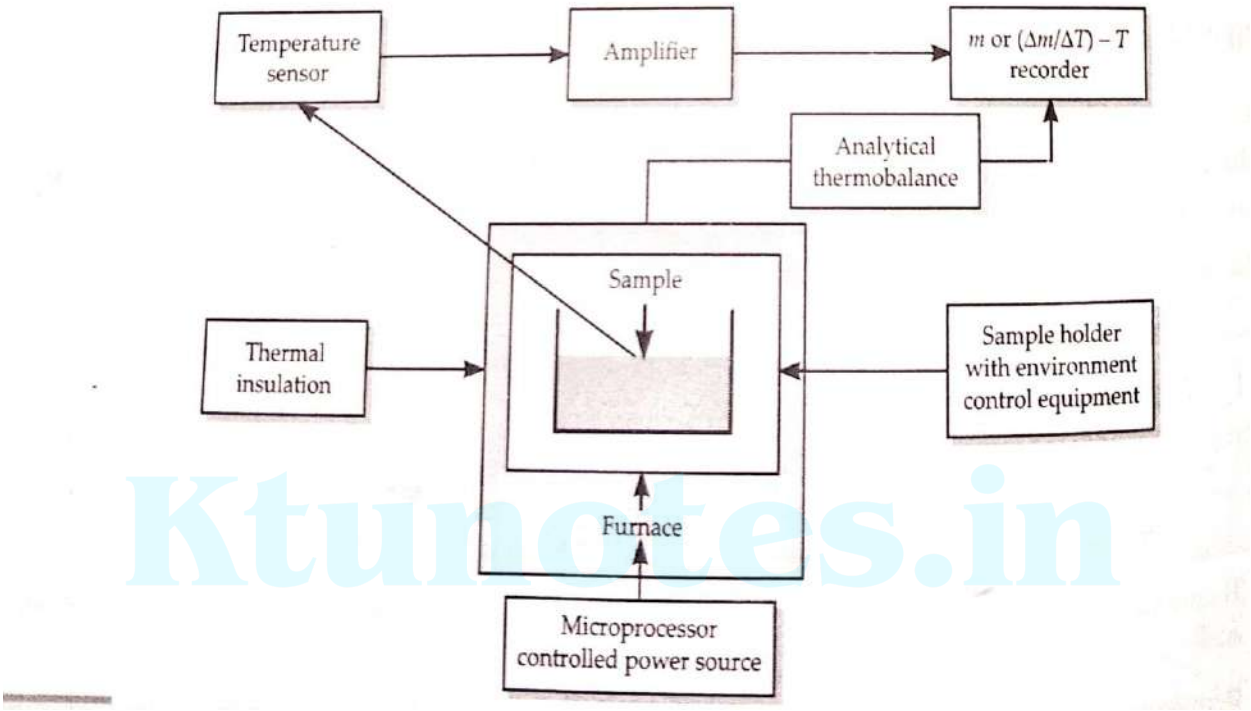
- The slanting down portion indicates the weight loss.
- This can be due to dehydration, decomposition and evaporation.
- From the % weight loss, the number of hydrated water molecules lost with T range can be determined.

Thermobalance: The instrument used for TGA.

Instrumentation

The main components of TGA apparatus are

1. Sample Holder
2. Furnace with temperature programming facility
3. Thermo balance
4. Temperature Sensor
5. Environment Control Equipment
6. Detector & Amplifier
7. Recorder



- The sample to be analyzed (≈ 3mg) is taken in the sample holder
- The Sample Holder is surrounded by furnace with temperature programming facility. ie, the heating rate can be adjusted (5°C/min or 10°C/min) according to the requirement of the apparatus.
- The environment Control Equipment provides suitable inert atmosphere for analysis such as N_2, Ar, He etc
- The Sample Holder is attached to a Thermobalance which is highly temperature sensitive. ie whenever the T changes, it automatically measures the mass of the sample.
- The temperature Sensor records the sample temperature
- The signals are amplified and recorded.
- The graph obtained is a plot of mass Vs T

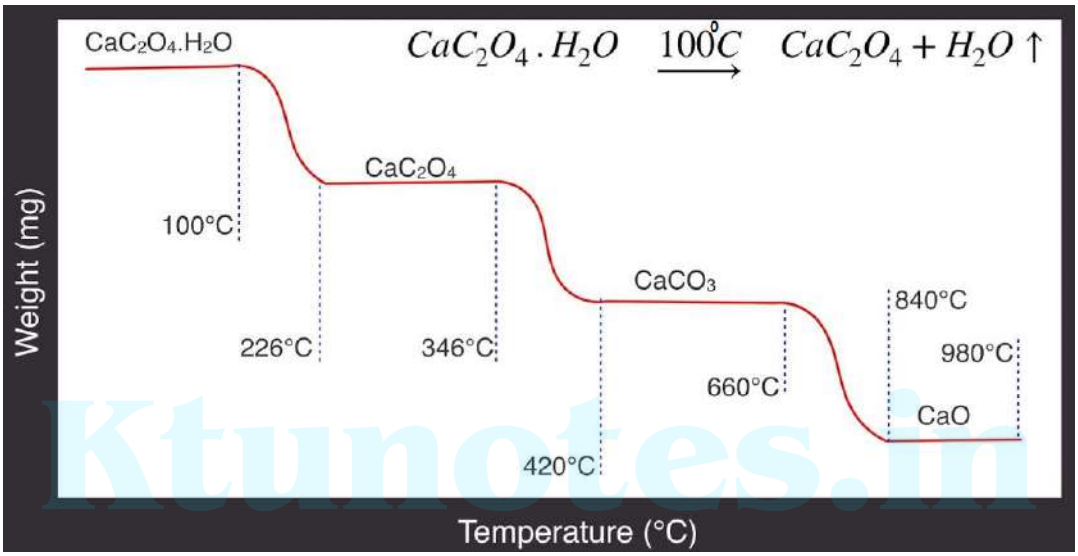
TGA of Calcium oxalate monohydrate ($CaC_2O_4.H_2O$) decomposition

The Thermogram of decomposition of pure hydrated Calcium oxalate ($CaC_2O_4.H_2O$) is obtained by increasing T at a rate of 5 °C is as shown in figure. The different reactions are

$$CaC_2O_4.H_2O \longrightarrow CaC_2O_4 + H_2O$$

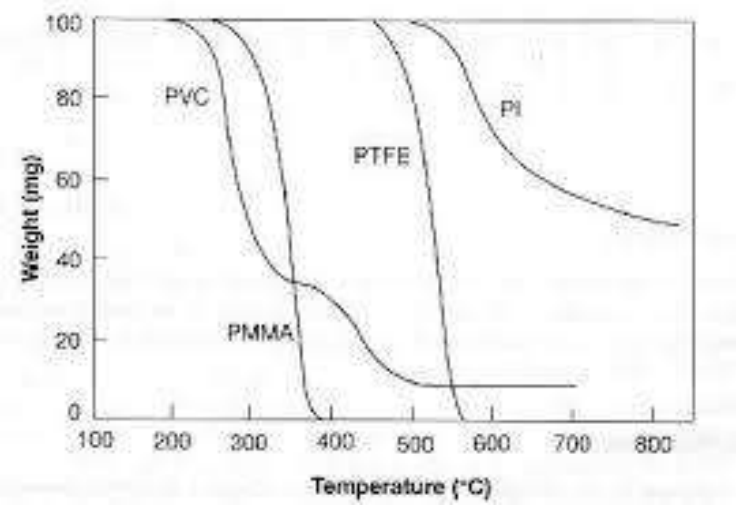
$$2CaC_2O_4 \longrightarrow 2CaCO_3 + 2CO$$
$$CaCO_3 \longrightarrow CaO + CO_2$$

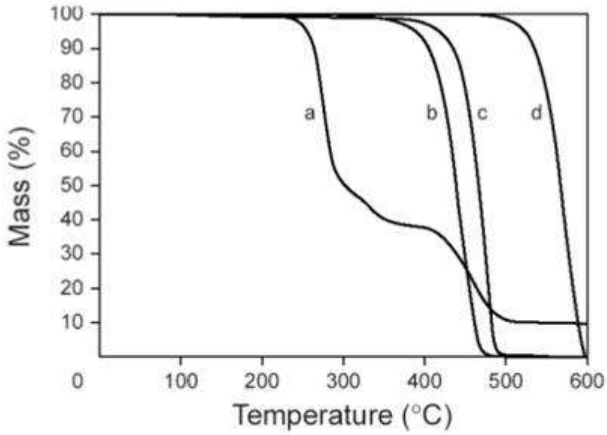
- $CaC_2O_4.H_2O$ is stable up to 100 ^oC. Removal of water starts at 100 ^oC and is completed at 226 ^oC and forms anhydrous CaC_2O_4
- The horizontal portion ranging from 226 ^oC to 346 ^oC indicates the stability of anhydrous CaC_2O_4
- Above 346 ^oC, anhydrous CaC_2O_4 decomposes to give $CaCO_3$ & CO and decomposition is completed at 420 ^oC
- The $CaCO_3$ formed is stable up to 660 ^oC and above 660 ^oC, it decomposes to CaO & CO_2. The process is completed at 840 ^oC



TGA of Polymers

- PVC starts decomposition at low T than LDPE due to the elimination of HCl takes place in PVC
- PTFE is highly stable owing to strong C-F bond.





a = PVC, b= nylon-6, c = LDPE, d= PTFE

Applications

1) It gives valuable information about **Qualitative analysis** of the sample

- Stability of substance
- Identification of substance & purity determination
- Decomposition mechanism of polymers & inorganic salts(eg. decomp.of Ca oxalate)

2) In **Quantitative analysis of**

- Mixture of $Ca^{2+,}$ Ba^{2+}& Sr^{2+}ion.
- Amount of filler in polymer sample can be calculated.

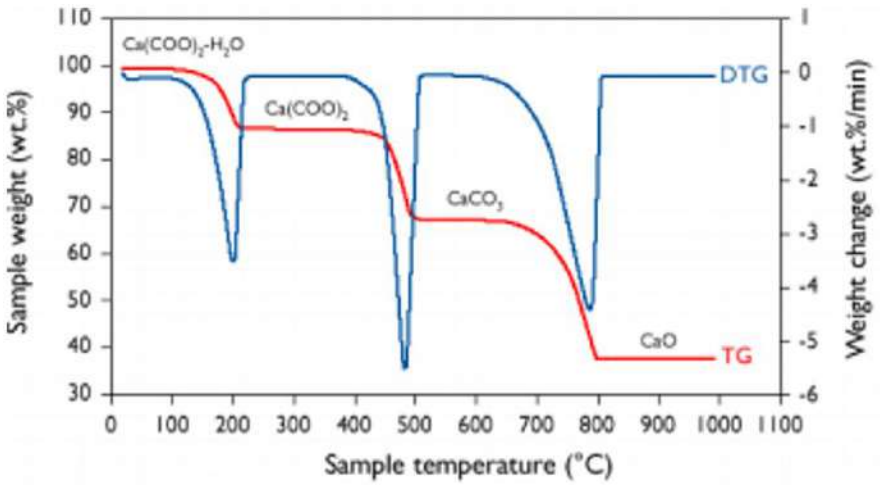
Limitations

1) TGA method is largely limited to decomposition, oxidation, physical processes like vaporization, sublimation etc

2) It cannot be used for

- Pure fusion reaction
- Crystalline transition from one crystalline form to another (Rhombic S to monoclinic)
- Glass transition &crystalline T of polymers

Differential Thermogravimetry (DTG), (Δm/ΔT)



Each peak signifies temperature at which maximum rate of decomposition takes place

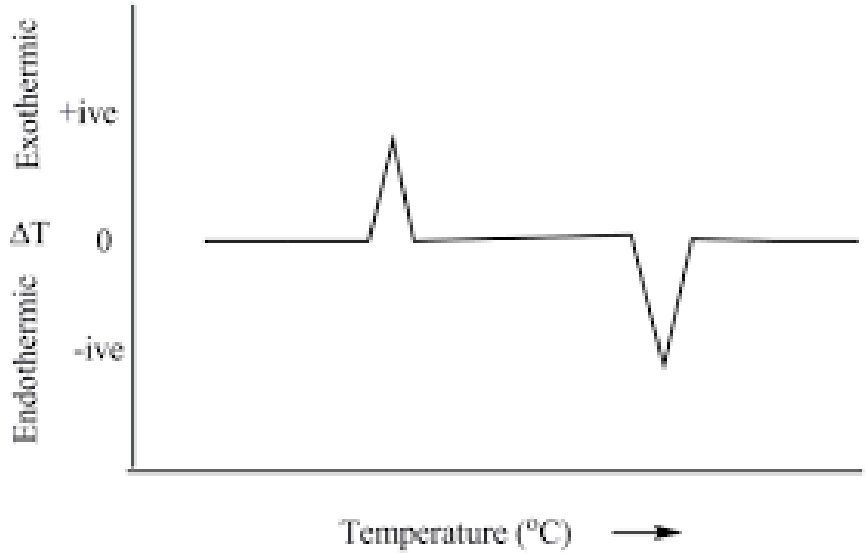
2. Differential thermal analysis (DTA)

Principle

- It is a thermo analytic technique.

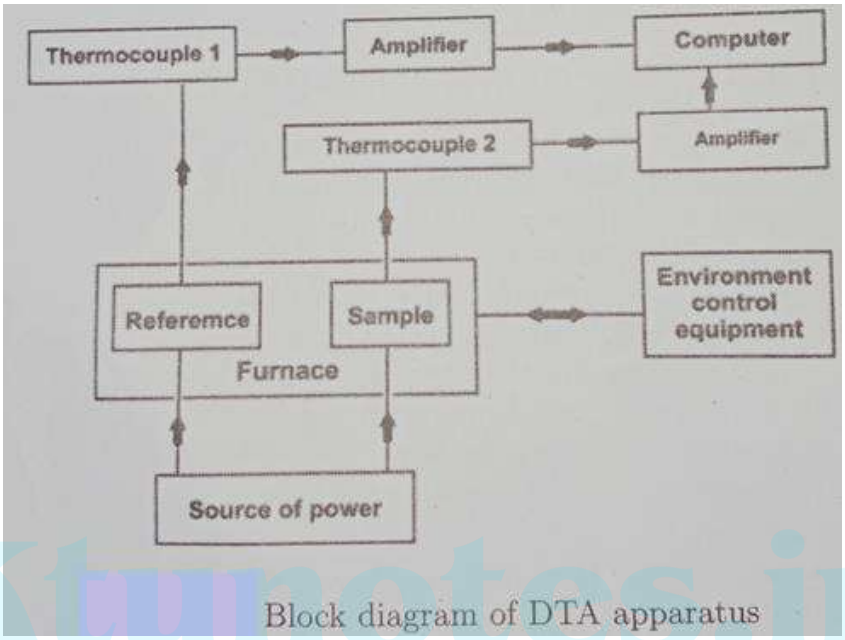
In DTA, the material under study (sample) and an **inert reference material** (usually alumina, silica, SiC or glass beads) are heated under identical conditions at a constant rate.

- The difference in temperature **ΔT** of the sample and the reference material temperature is then plotted against temperature of the sample gives DTA curve or differential thermogram.
- Heat changes in the sample can be either exothermic or endothermic
- The exothermic changes are represented by upward peak
  e.g., oxidation in air, adsorption, polymerization etc.
- The endothermic changes are represented by downward peak
  E.g. Transition, fusion, vaporization, sublimation, absorption, desorption, decomposition
- The peak area in DTA **proportional** to the mass of sample and enthalpy change, ΔH of the physical or chemical change.



Instrumentation

- The instrument used to measure DTA is DTA apparatus.
- In DTA, the material under study and reference material are heated under identical conditions at a constant rate.
- Two thermocouples T_1 & T_2 record the temperature of the sample and the reference
- The data is amplified and recorded.(processed in a computer)

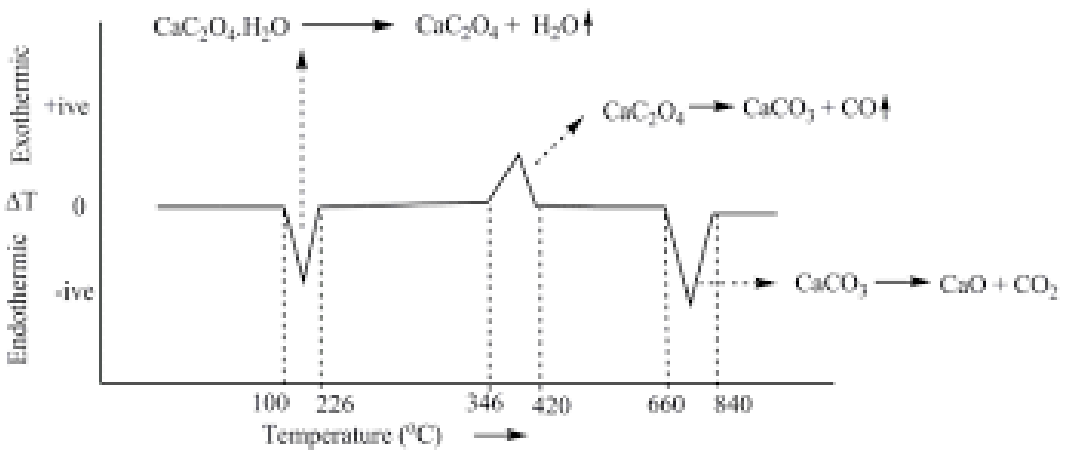


Block diagram of DTA apparatus

Applications

1) It gives information such as M. P, transition temperature etc. of a crystalline substance
2) Distinguish between endothermic &exothermic process
3) Estimation of enthalpy change (ΔH) by counting peak area
4) Study of decomposition temperature of inorganic solids
5) Characterization of polymers- based on the measurement of properties such as glass transition temperature, M. P, decomposition etc.
6) DTA is widely used in the pharmaceutical, food industries, cement chemistry, mineralogical research, environmental studies and study of archaeological materials

DTA of **Calcium oxalate monohydrate ($CaC_2O_4.H_2O$)**



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Comparison between TGA and DTA

Sl. No	Properties	TGA	DTA
1	Principle	Recording the mass of the sample as a function of temperature	Sample and a reference material are heated under identical conditions
2	Curve	Thermogram, **m** Vs **T**	DTA curve or differential thermogram, **ΔT** Vs **T**
3	Instrument	Thermo balance	DTA apparatus
4	Endo & exo	Not possible to differentiate	Possible to differentiate between endothermic & exothermic process

PART II: Chromatography

It is a modern method used for the **separation, purification and identification of mixtures**
The method was invented by **Michael Tswett** for separating plant pigments.
The term 'Chromatography' is derived from two words, Chroma = color: graphein = to write

Principle
All chromatographic techniques have two immiscible phases- **Stationary Phase and Mobile Phase**

1. **Stationary Phase (S. P.) or Fixed Phase**
S. P may be a Solid or Liquid supported on an inert solid
Solid Phase can be a column of adsorbent (Column Chromatography) or a sheet of paper (Paper Chromatography) or a thin layer of **adsorbent** supported on a glass plate (Thin-layer chromatography, **TLC**)
2. **Moving Phase (M. P) or Mobile Phase**
M. P can be a **Liquid or Gas**
The components to be analyzed are carried by the M. P. through the S. P which in turn depends on the affinity of the component towards S. P or M. P.

Classification

I. **Based on the Mechanism of Separation**
(a) Adsorption Chromatography
(b) Partition Chromatography
(c) Ion exchange Chromatography

a. Adsorption Chromatography

In this type, S. P is a solid and M. P is liquid or gas. The separation occurs due to the difference in adsorption coefficients of the components.

b. Partition Chromatography

In this type, S. P is a L supported on an inert solid and M. P is L or G. Separation is caused by partitioning the components between S. P and M. P (difference in partition coefficients)

c. Ion exchange Chromatography

S. P is an ion exchanger and the distribution of components of the mixture is based on ion exchange principle. This Chromatography is applicable to ionic species.

2. Based on the Mobile Phase

A. Liquid Chromatography (L. C)
The **M. P is a Liquid**. S. P can be a S (LSC) or L supported on inert solid (**LLC**) e.g. **HPLC**
B. Gas chromatography (G. C).
The M. P is a Gas. S. P can be a S (**GSC**) or L supported on inert solid (**GLC**)
LC----LSC & LLC
GC---GSC & GLC

Column Chromatography (C. C)

It is one of the most useful method for the separation and purification of both **solids and liquids.** It is **S-L** technique in which the S. P is a solid and M. P is a liquid

Principle

It is based on the **differential adsorption of components by the adsorbent** (S. P) followed by **selective elution using a solvent**.

Adsorbents used: **Silica, alumina, magnesia, starch, $CaCO_3$, Ca_3PO_4 etc.**

Solvents used: **Benzene, light petroleum, cyclohexane, chloroform, ethyl alcohol, acetic acid, CS_2, CCl_4 etc.**

Selection of Solvent is based on the nature of components in the mixture. The rate at which the components are separated depends upon the **activity of the adsorbent** and **polarity of the solvent.** If the activity of the adsorbent is very high and polarity of the solvent is very low, then the separation is very slow but gives a good separation. On the other hand if the activity of the adsorbent is very low and polarity of the solvent is very high, then the separation is rapid but gives a poor separation

Procedure

A proper adsorbent (S. P) is selected and is made into a slurry with a suitable liquid.
The adsorbent is packed in a long cylindrical tube (Chronographic column) and is plugged at the bottom with a glass wool or porous plug.
The mixture to be separated is dissolved in a suitable solvent and is introduced at the top of the column.
As the mixture moves down the column, the components are adsorbed at different region depending on their ability for adsorption. The component with greater adsorption will be adsorbed at the top and the one with lower adsorption will be adsorbed at the bottom.
The banded column of adsorbed components is called **Chromatogram**

Separation

In order to separate various components, the Chromatogram is pushed out of the glass tube and the various zones are cut with a knife at the boundaries.
In the second method, the different components of the Chromatogram can be collected separately by adding more solvent at the top and is known as **elution** and the solvent is called **eluent**

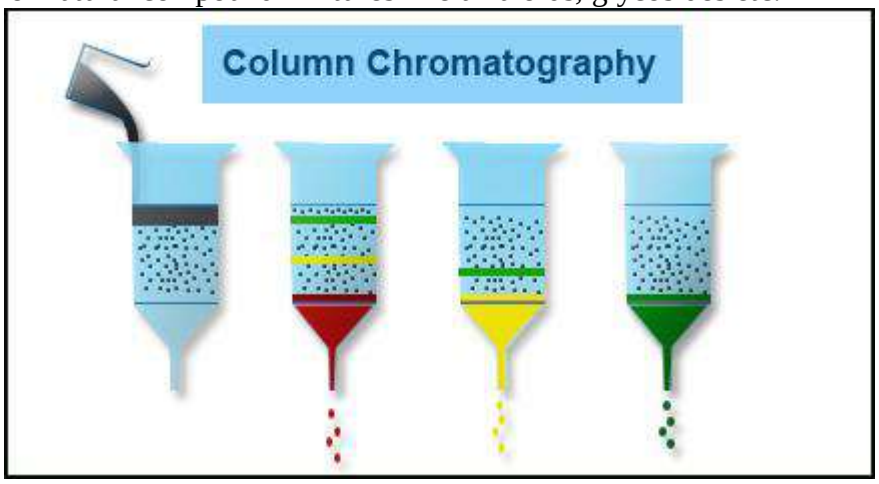
The weakly adsorbed component is eluted more rapidly than the other. The different fractions are collected separately. Distillation or evaporation of the solvent from the different fractions gives the pure components

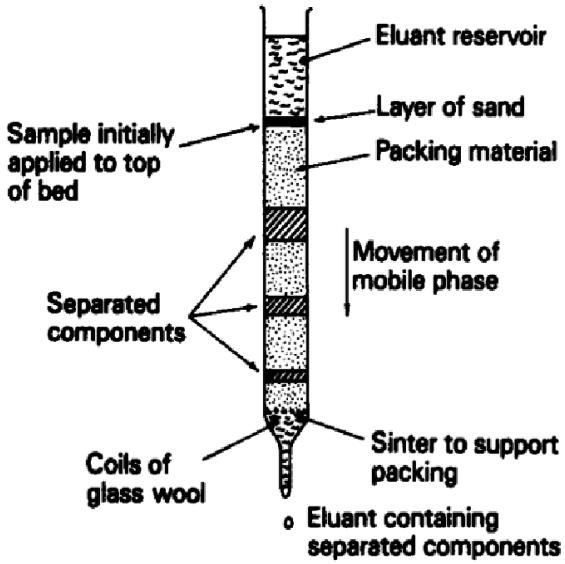
Advantages

1) Simple & versatile
2) Physical separation of compounds is possible
3) It can separate large quantities of mixtures

Applications

1) Separate organic compounds from plant materials
2) Separation of compounds after synthesis
3) Purification of natural compound mixtures like alkaloids, glycosides etc.





Thin Layer Chromatography (TLC)

It is an extremely valuable technique in organic Lab. It is used to **separate mixtures, to check the purity of mixtures or to monitor the progress of the reaction**

1) Preparation of Chromatoplate

In this method a **glass plate or aluminum foil or plastic plate** is **coated with a thin uniform slurry of the adsorbent by adding water**—by spraying, spreading etc. The adsorbents usually used are silica gel, aluminium oxide (alumina), cellulose powder etc. which act as stationary phase. The glass plate with a thin layer of S. P. is called **Chromatoplate**

2) Activation of Adsorbent

The plate is dried in air for 30 minutes and then heated in an electric oven at 120^0 C, for another half an hour

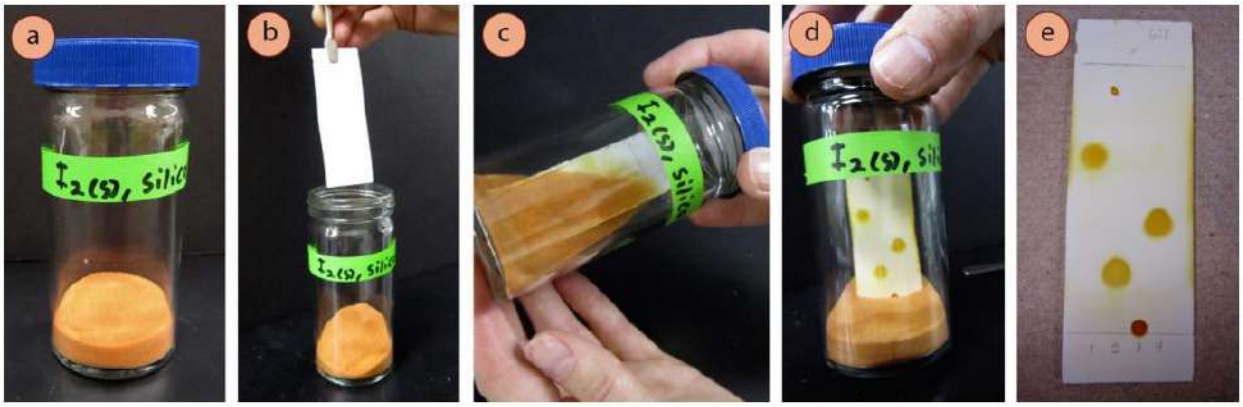
3) Developing action (Procedure)

A small amount of mixture to be separated is applied at one end of the glass plate using a capillary tube or a micro syringe.
It is placed on the solvent
The solvent rises up the plate due to capillary action
As the solvent passes the spot, it carries the components at different rates and separation of mixtures occurs
When the solvent reaches near the top, the plate is removed from the developing chamber, dried and separated components are visualized.
If the components are not colored, the **following visualization techniques** are used.

1) U. V lamp (254nm) is used to visualize the plate

A fluorescent dye is incorporated into the S. P. All the parts fluoresces except non fluorescent sample components. Thus the components appear as dark spot in bright background.

2) Iodine vapors are used to identify the compounds (dark spot)



3) Specific color reagents are sprayed onto the plate.
E.g.: $KMnO_4$ solution, 1% H_2SO_4 spray, 10% NaOH spray etc.

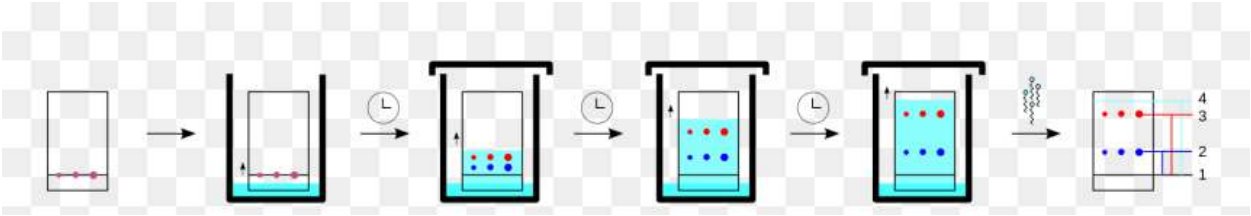
Retention factor (R_f)

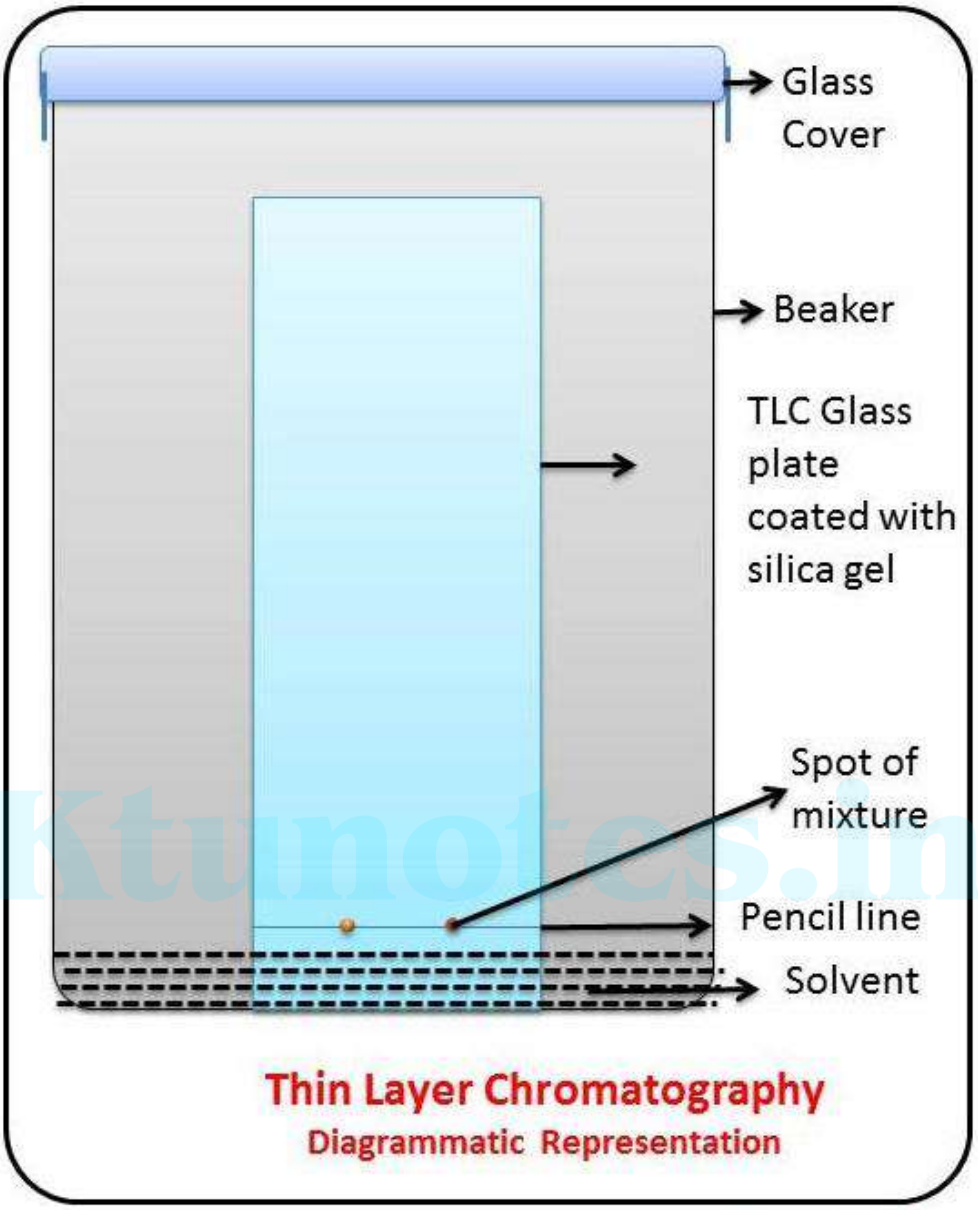
In T. L. C, after the separation is completed, the individual components appear as spots separated vertically. Each spot has a R_f value, which is the ratio of distance travelled by the component (**Component front)** to the distance travelled by the solvent **(Solvent front)**

$$\mathbf{R_f} = \frac{\textbf{Component front}}{\textbf{Solvent front}}$$

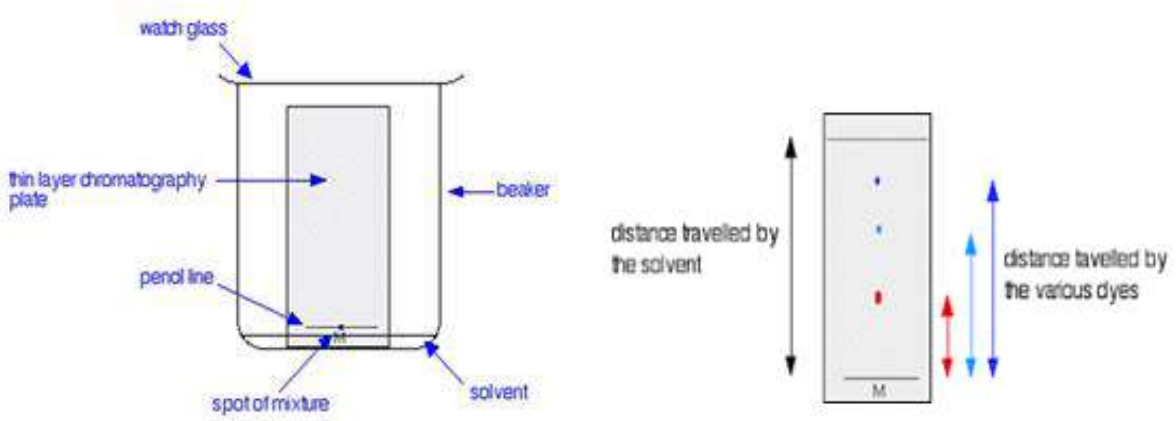
(The distances are measured from the point of application of sample to the solvent front and to the centre of each spot on the strip)

An R_f value is a constant for a given compound. Hence it is possible to identify the various components by determining R_f values.

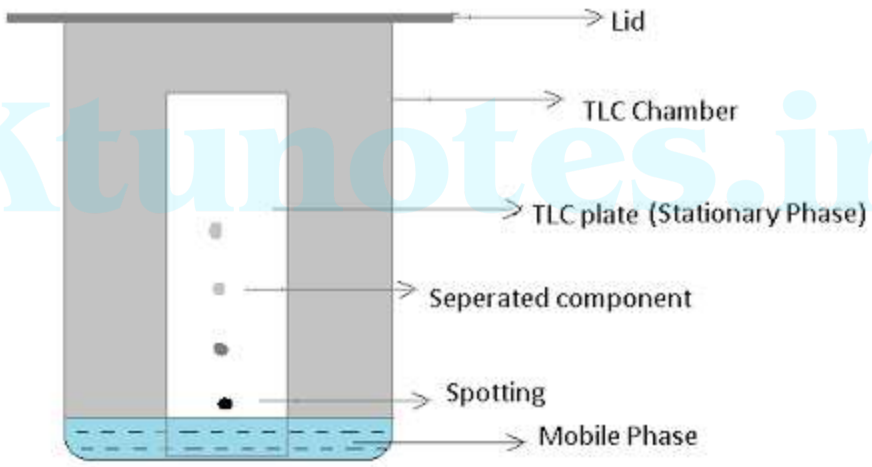




TECHNIQUE OF THIN LAYER CHROMATOGRAPHY



Thin Layer Chromatograhy



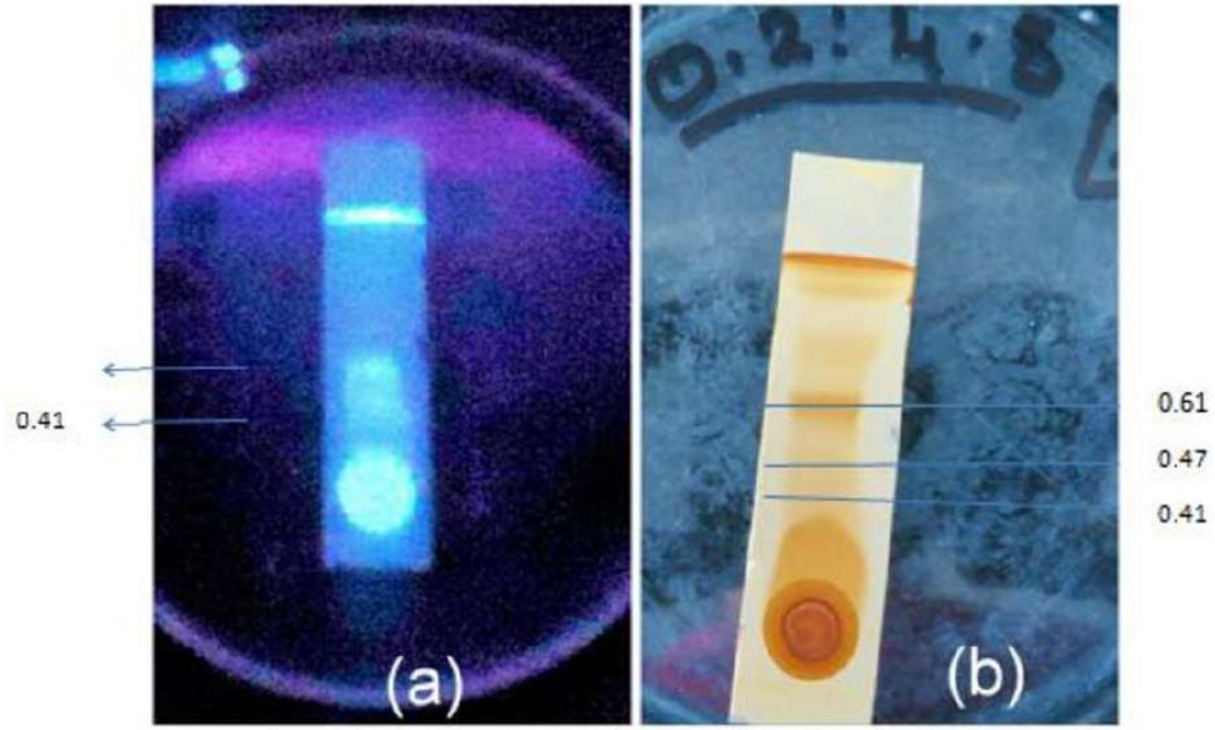
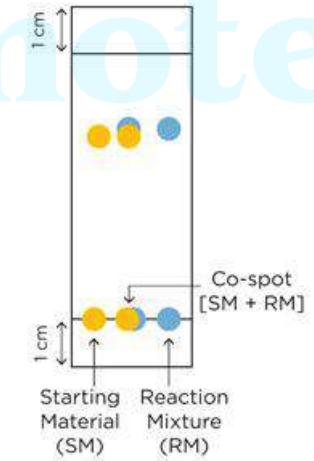


Figure 4.5: TLC under (a) Short UV (b) Iodine chamber



Compound with larger R_f value—less polar---it does not stick to S. P
LowerR_f value—more polar-stick to S.P
For silica coated T.L.C Plate, the solvent polarity increases in the following order
Hexane < CCl_4<benzene<dichloromethane<chloroform<ethyl acetate <acetone<ethanol<methanol<water<acetic acid<formic acid (strongest)
For alumina coated T. L.C Plate, the order is reverse.

Advantages

- It can be used for the determination of minute quantity (small mg of sample)
- Sensitive and sharp separation is possible

- High speed of separation
- It provides a wide choice of S.P.

Applications

- To check the Purity of sample
- To Identify compounds
- To compare the polarity of solvents
- To determine appropriate solvent for C.C
- To monitor the column chromatographic separation
- To monitor the progress of a chemical reaction by observing the appearance of a product or the disappearance of a reactant

Gas Chromatography (G. C)

This technique is applied for the identification of **V**olatile **O**rganic **C**ompounds

Principle

G.C is the differential distribution of components between two phases- Stationary Phase and Mobile Phase

The M. P is a gas (Carrier gas) usually nitrogen. Depending on the nature of mixture, Ar, He and H_2 are used.

The S. P may be S or L

If the S. P is solid like silica or alumina or C, the Chromatography is termed as **G. S. C**

If the S. P is a nonvolatile liquid on a thin layer of inert solid, the Chromatography is termed as **G. L. C**

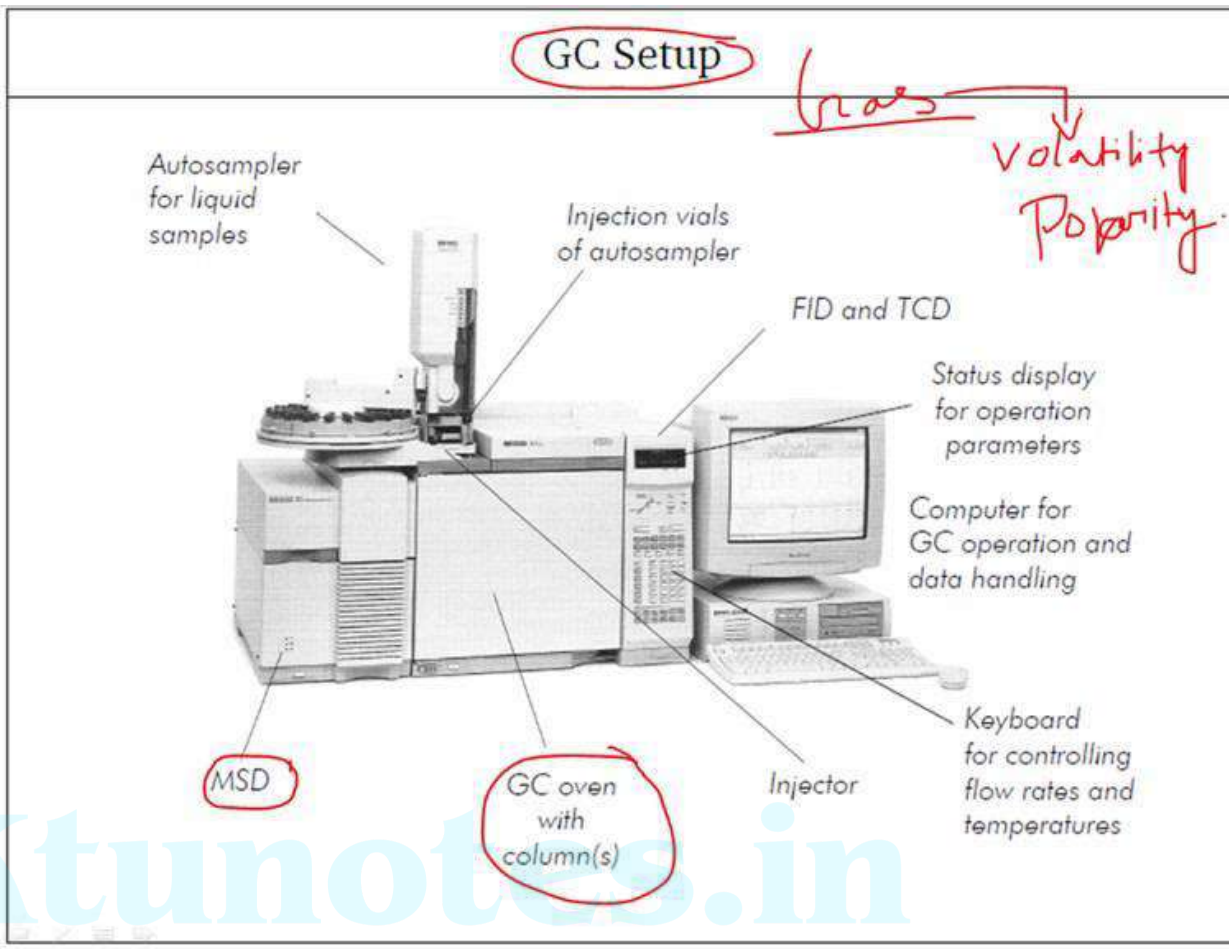
The most common inert support used in G.S.C is diatomaceous earth or kieselguhr.

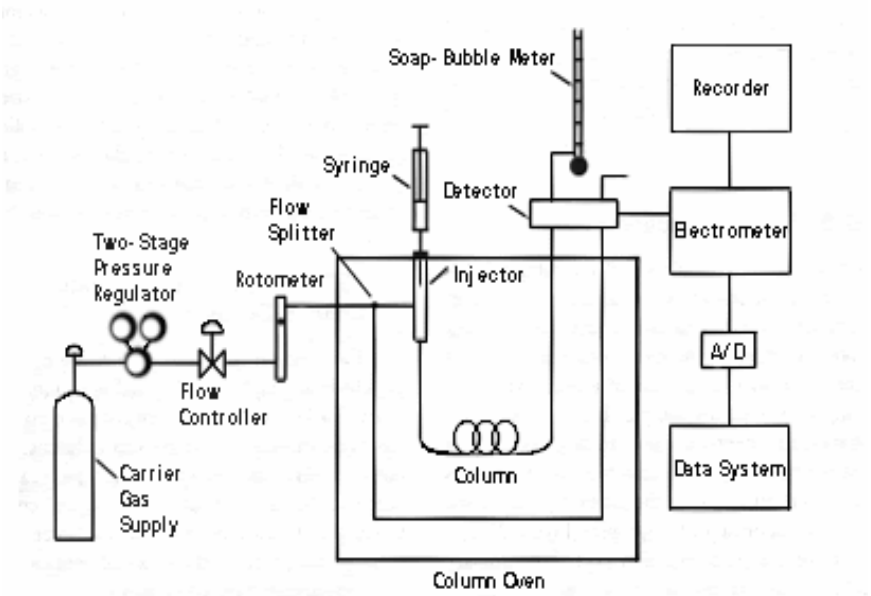
When the S. P is solid, the basis of separation is **adsorption** and if it is a liquid, the principle of separation is **partition**

Instrumentation

The basic requirement of a Gas Chromatographic instrument are

1. Carrier gas
2. Sample injection System
3. Separation Column
4. Stationary Phase
5. Detector
6. Recorder





Schematic of a Gas Chromatograph

1.Carrier gas

The sample mixture in the vapor state along with carrier gas from a high pressure cylinder (having a Pressure regulator and flow meter) is allowed to flow through the column.
The carrier gas should be
a) Chemically inert
b) Suitable for the detector employed and type of sample analyzed
c) Best column performance (consistent with required speed of analysis)

2. Sample Injection Systems

The carrier gas from the gas reservoir is connected to the sample port injector. The sample must be converted into vapor state. Usually the sample (L or G) is introduced by means of a micro syringe to a flash vaporizer port located at the head of the column.

3. Separation Column

Two types of columns are in use.
a) Packed column or wide bore column
b) Open tubular or capillary column

The columns are usually made of Cu, Al, Ni, glass, Teflon tube etc.

The Packed column is packed with either solid support material (GSC) or a liquid coated on a solid support (GLC)

The capillary column is coated with a thin liquid phase eg: dimethyl polysiloxane

4. Stationary Phase

The characteristics of an ideal S. P. should be low volatility, thermal stability and chemical inertness

5. Detectors

Any physical property which varies from one gas to another can be easily monitored from the detector.The physical property of carrier gas changes when a component is present
They are of three types
A) **Thermal C**onductivity **D**etector (TCD) or KCD (Katharometer)
B) **Flame I**onization **D**etector (FID)
C) **Electron-C**apture **D**etector (ECD)

TCD and FID are universally accepted detectors

A) TCD

It is one of the early detector used and respond to all types of organic and inorganic compounds.

The principle is based on the rate of heat loss from a heated wire (Pt or Tungsten wire) placed in a gas stream which depends on the thermal conductivity of gas. So the temp. of the wire changes.(consequently the resistance)

B) FID

It is the most widely used detector and is based on the electrical conductivity of gases. Here the effluent from the column is mixed with hydrogen air flame and ignited electrically with a burner. Most of the organic compounds produce ions and electrons when pyrolyzed at the temperature of air-hydrogen flame. Thus conduct electricity through the flame. The resulting current is then measured with high-impedance amplifier.

6. Recorder gives the peak for each component

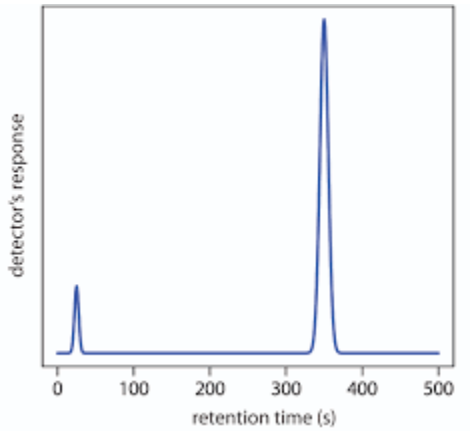
Procedure

The sample mixture is injected into the injection port where it gets vaporized and carried by the Carrier gas into the heated chromatographic column. During the process the components of the mixture gets distributed between two phases depending on the extent of adsorption or partition.

Thus different components are carried through the column at different time. The time taken by each component to pass through the column is a characteristic property for its identification--- **Retention Time.** They are detected by the detector and the recorder gives a peak for each component. The size and location of peak gives an indication of nature of component

The apparatus employed in G.C is called **Chromatograph**

The series of peaks obtained in G.C is called **Chromatogram**



Retention Time(R_t)

In G. C, the time taken by the solute or component to pass between the Sample Injection port and the detector (or to pass through the column)

Identification of component is carried out by the comparison of G.C Retention Time against those of reference or standard

Advantages

- Used in case of minute quantity
- Complex mixtures can be identified
- Large number of compounds can be identified
- Rapid separation
- High efficient technique
-

Applications

- To check the purity of organic compounds. The presence of impurities are recorded by the presence of additional peaks.
- G.C coupled with spectroscopic techniques like IR, NMR, Mass spectroscopy(GC-MS) is widely used for the analysis of hydrocarbon fuels, perfumes, fragrance chemicals etc
- It is used to study the extent of air pollution
- Ethyl alcohol content in blood can be determined with great accuracy(glycol column)
- Banned drugs used by athletes can be detected by taking G.C of blood or urine sample.
- Detection of carcinogenic compounds

Limitations

- It cannot be used for physical separation

- It cannot be used for the separation of **N**on**v**olatile **O**rganic **C**ompounds
- It is expensive

Comparison between GSC&GLC

Sl.No	Property	GSC	GLC
1	S.P	Solid	Liquid
2	M.P	Gas	Gas
3	Separation of mechanism	Adsorption	Partition
4	Column packing	Granular solid adsorbent is packed in the column	Capillary columns can be used
5	Column length	0.72 m	3 to 300 m
6	Thermal stability of S.P	Good	Less stable above 300^{o}C
7	Application	Limited	Wide
8	Resolution of peaks	Reasonable range of resolution	Better resolution

High Performance (Pressure) Liquid Chromatography (HPLC)

It is a modern method and powerful tool for the, separation, purification and identification of various **nonvolatile organic compounds**, natural products like cholesterol($C_{27}H_{46}O$) terpenoids containing 30 C atoms, polypeptides etc. It is used for the identification of **N**on **V**olatile **O**rganic **C**ompounds

Principle-- It is the based on the distribution of components between two phases- S. P&M. P. The M. P is a liquid.

When the S. P is solid, the basis of separation is adsorption.---LSC and

When the S. P is liquid supported on a solid, the basis of separation is partition.---LLC

Now a days, liquid S.P is more common

Instrumentation

The instrument consists of the following parts

1. Reservoirs
2. Pressure Pump
3. Guard column (Pre column)
4. Sample Injector
5. Analytical column
6. Detector
7. Recorder

1) Reservoirs or solvent Reservoirs are used to collect different solvents (M. P)

2) Pressure Pumps are used to apply a pressure of 5000 psi. The flow rate of 1 to 10ml can be achieved under high P

3) Guard column -A short Guard column is kept before the analytical column. This helps to remove the particulate matter and contaminants from the solvent. This increases the life of analytical column.

4) The Sample Injector is used to inject the sample mixture into the analytical column

5) Analytical column ia long narrow smooth stainless steel of length 10 to 30 cm &diameter

1-3mm.The column is packed with adsorbent material in the range 3-10g
Two types of column packings are generally used.

- **NPSP**---Normal Phase Silica Powder—Silica bonded with-OH gp
- **RPSP**---Reverse Phase Silica Powder—Silica bonded with-OCH_3 gp

In NPSP, polar compounds are adsorbed to a great extent and retention time will be more.
In RPSP, it is reverse.

6) Detectors—Two types are used

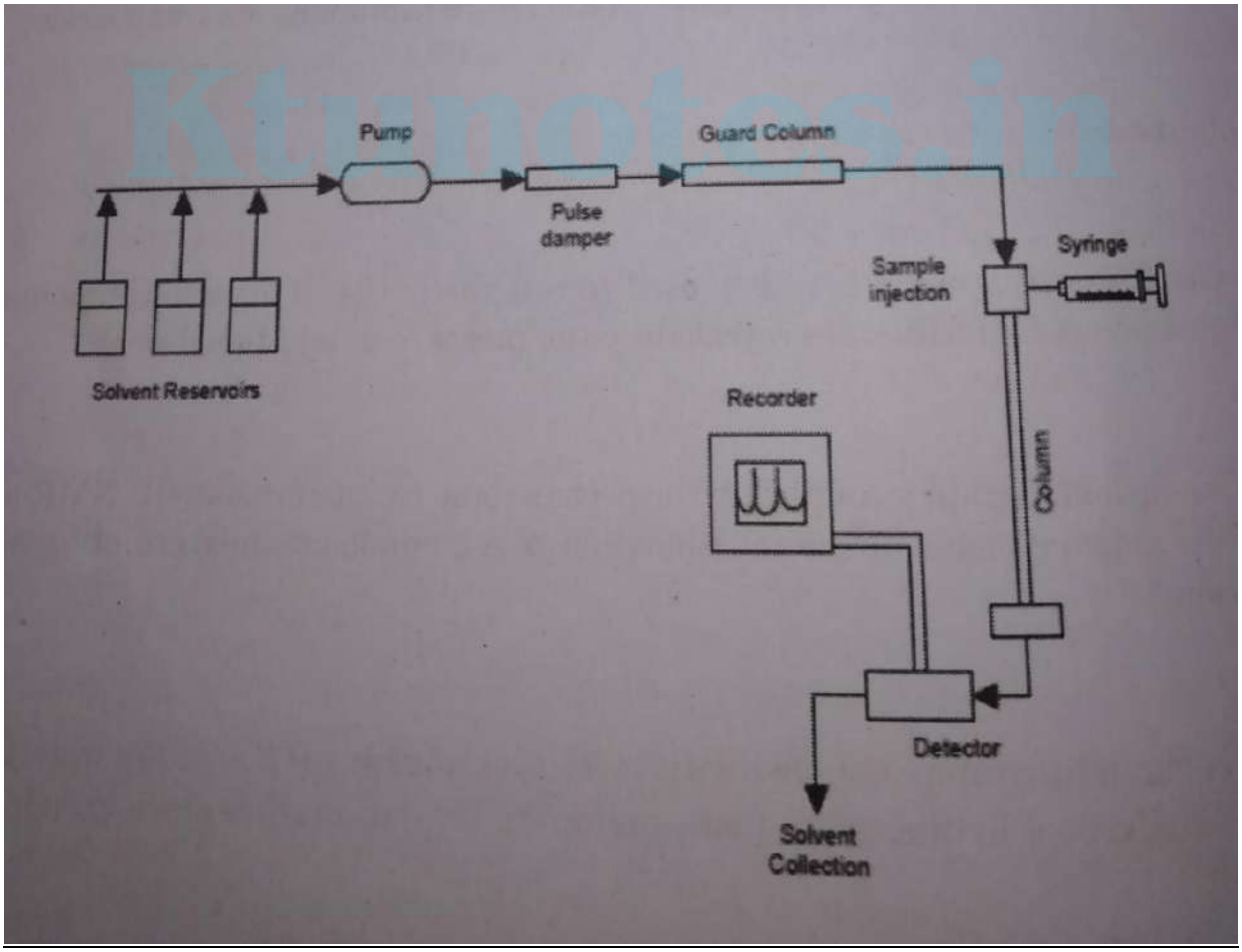
- Bulk property detectors
- Solute property detectors

Bulk property detectors respond to bulk properties like density, refractive index, dielectric constant etc. of the M. P (solvent)

Solute property detectors respond to solute properties like, u.v absorbance, fluorescence properties of the solute molecules which are not possessed by M. P. These detectors give the spectra of the mixtures

When a particular species is eluted out, the properties will change and detector gives the signal and component is collected along in the sampling tube along with the solvent. The solvent is distilled out and the pure component can be recovered.

7) Recorder



Procedure

- The liquid M.P is pumped at required P and flow rate through the analytical column which contains S.P
- The nonvolatile samples are injected into the analytical column with the help of a micro syringe (sample Injector)
- The components are carried along the column at different rates and distributed between S.P&M.P

The **elution** can be done in two ways.

- Isocratic elution---A single solvent of constant composition is used
- Gradient elution(Multiple solvent system)-----Two or more solvents which differ in their polarity can be used.

  Gradient elution is more effective. During elution, the ratio of solvent is varied in a programmable manner. It gives better separation in less time.

Advantages

- High speed of separation
- Excellent column separation
- Solvent consumption is minimum
- Sensitive and accurate
- Determination of compounds in trace amount(PPT)
- Separation can be done at an ambient T(T of envt)
- Used for physical seperation of **N**on **V**olatile **O**rganic **C**ompounds-Preparative HPLC

Applications

- Used for the separation of non volatile organic compounds & Polypeptides
- More amount of compounds can be separated when compared with GSC &GLC
- Forensic analysis
- Environmental monitoring(determin. of phenolic compds in drinking water)
- Biomedical research work
- Pharmaceutical Quality control
- Measurement of Quality of soft drinks , water &sugar analysis in fruit juices
- Process control
- Identification of steroids &determination of cocaine and other drugs in urine,blood etc
- Detection of Cholesterol in food

Disadvantages

- It is not as versatile as G.C

  Retention Volume (R_v)—Volume of M.P required to elute the component from the column **$R_v = R_t$ x flow rate (**rate with which M.P is flowing)

PART III: Nanomaterials

Nanomaterials are any type of material of nanosized thickness, i.e. less than 100 nm in thickness or the materials whose characteristic length scale lies within the nanometric range (1-100nm) in one dimension One nanometer is one billionth of a meter, or the length of 10 hydrogen atoms lined

up. Nanosized structures include the smallest of human-made device and the largest molecules of living systems.The word 'nano' is derived from the Greek word 'Dwarf' .It is one billionth of a metre ($1/10^9$)

Nanoparticles have much greater surface area per unit mass compared with larger particles.One common factor of nanomaterials is that this thickness range is also known as the quantum regime, where quantum effects play a major role in defining the properties.

Classification

I) <u>Based on Dimension</u>

1**. Zero dimension(0-D)** :- Here all the three dimensions are in the nanometric range. (no dimensions are larger than 100 nm). Most commonly, 0-D nanomaterials are nanoparticles.

Eg:-Atomic structures,filaments,cluster assemblies etc

2. **One dimension(1-D)**:-Here one dimension is outside the nanometric range

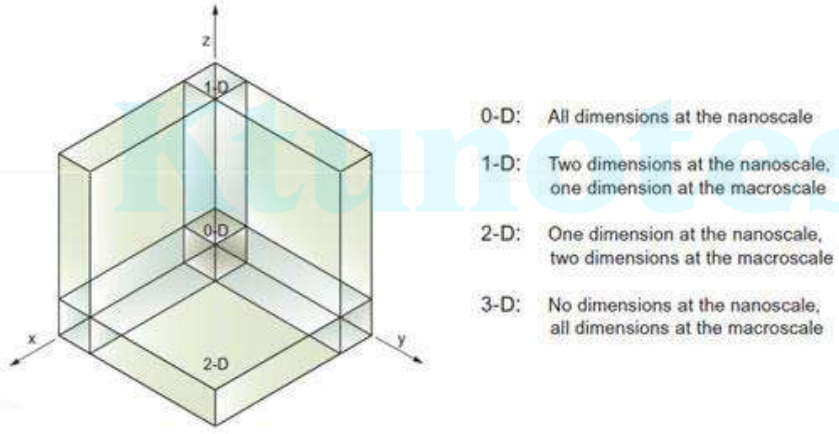
Eg:nanotubes, nanorods, and nanowires.

3. **Two dimension(2-D)**:-Here two of the dimensions are outside the nanometric range.

Eg:- graphene, nanofilms, nanolayers, and nanocoatings.

4.**Three dimension(3-D)**:-Here all the dimensions are outside the nanometric range.

Eg:- bundles of nanowires, and nanotubes as well as multi-nanolayers.



II) <u>Based on Materials</u>

1. Carbon Based Materials
2. Metal Based Materials
3. Nano Polymers or Dendrimers
4. Nanocomposites
5. Biological nanomaterials

1.**Carbon Based Materials**

These nanomaterials are composed mostly of carbon.-- most common are in the form of a hollow spheres, ellipsoids, or tubes

Eg:-1) CNT ----- Cylindrical nanomaterials

2) Fullerene ----- Spherical and ellipsoidal nanomaterials

2. Metal Based Materials

These nanomaterials are made of metallic nanoparticles include like gold, silver and metal oxides such as TiO2. Eg:-Nano gold, Nano silver etc

3. Nano composites

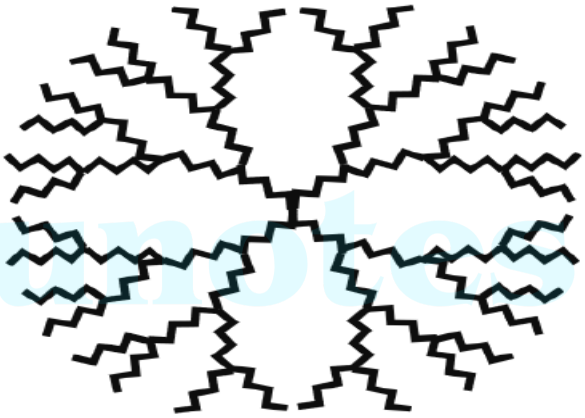
They contain a mixture of simple nanoparticles or compounds such as nanosized clay with larger or bulk type material. The nanoparticles give physical, mechanical and chemical properties to bulk material.

E.g.:-Colloids, gels, copolymers etc.

4. Nano Polymers or Dendrimers

These nanomaterials are nanosized polymers built from branched units. These are tree like molecules with defined cavities. The three-dimensional dendrimers contain interior cavities into which other molecules could be placed.

Application:-They may be useful for drug delivery



5. Biological nanomaterials

They are of biological origin and are used for nano technological applications.The important feature of these particle are

1) Self-assembly property and
2) Specific molecular recognition.

Eg:-DNA nano particles,nano structural peptides etc

Chemical Synthesis of Nanoparticles

1. Hydrolysis: Nanoparticles of metal oxides are prepared by the hydrolysis of their alkoxide solutions under controlled conditions.

Eg: Silica(SiO2)Alumina(Al2O3),Titania(TiO2) etc

$Ti(OR)4 + 2H2O \rightarrow TiO2 + 4ROH$

This method can be divided into two.

A) Hydrothermal Synthesis

The .process involves the use of solvent under moderate to high pressure(between 1 atmos to 10000 atmos)and temp (between 100oCand 1000oC) that facilities the interaction of percursors (a substance from which another substance is formed)during synthesis.

If water is used as the solvent,the method is called Hydrothermal Synthesis. It is performed below super critical temp. of water.(374oC)
Eg. Thin films, bulk powders, Nano crystals etc

B) Sol-gel method

The Sol-gel method is based on the. Phase transformation of Sol into a gel.
A sol is a colloidal system of nano solid particles dispersed in a liquid.
A gel is a colloidal system in which liquid particles are dispersed in a network of solid nano particles.
Hydrolysis of metallic alkoxides or metal sols can give a sol at a suitable temp.and PH
The sol contains many other impurities.
In order to remove impurities the sol is transformed into a gel by changing the PH or other factors.
The gel can be .purified by filtration and washing with suitable solvent
The .purified gel on drying give solid nano particle.
Eg:Al_2O_3 nano particle is obtained by hydrolysis of Aluminium alkoxide
$Al(OR)_3 + 3H_2O \; Al(OH)_3 + 3ROH$

2. Reduction Method

Nanoparticles of gold,silver etc are prepared by the reduction of their respective solutions
Reducing agents used: $NaBH_4$ (sodium boro hydride), Ascorbic acid, Glucose etc.
Protective agents: Thyol, Gucose etc.
This method can be divided into two.

A) Reduction using reducing agents

.Preparation of Ag nano particle
50 ml of 1mM AgNO3solution is taken in a beaker.,covered with a watch glass and heated in hot plate.
The solution is stirred using a magnetic stirrer.
On boiling the solution, 6ml of 10mMtrisodium citrate is added in drowise, about one drop/second.
The beaker is then closed and ke.pt for sometime.till the colour of the solution is changed to a light golden colour.
Then it is allowed to cool.The solvent can be removed by freeze -drying.

B) Electro reduction

Preparation of Cu nano particle

Prepared by using Cu plating bath containing homogeneously acidified CuSO4 solution. The nano particles formed as spongy layers of ball structures at the cathode. The spongy layers of Cu can be easily separated to give fine particles.

In conclusion, Nanoscience is the study of extremely small things which are in the nano range and Nanotechnology is the application of these materials in various fields such as in medicine, industries, electronics, textiles etc.

Applications

Magnetic nano-composites are used as ferrofluids (It is a liquid that becomes strongly magnetized in the presence of a magnetic field), high density information storage and magnetic refrigeration.

1) Nanostructured metal-oxide thin films are used as gas sensors (for CO, CO_2 etc)
2) Nano semiconductors are used as window layers in solar cells.
3) Carbon nanotubes based transistors used for miniaturizing elctronic devices.
4) Carbon nanotubes are used for making paper batteries.
5) A mixture of carbon nanotubes and fullerenes is used for making solar cells.
6) Nano medicine is the medical application of nanotechnology where nanoparticles based treatment are used for tumors.
7) Nano-cadmium-telluride exhibit different colour depending upon its size. It can be used for dyeing fabrics such as nano colorants never fades.

SEM (Scanning Electron Microscope)

It is a powerful tool for the surface characterization of materials. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This examination can provide information about the surface topography (surface features), morphology(shape &size of the particles) composition and crystallography

Principle

The electrons interact with atoms in the sample, producing various signals that can be used to provide information about the surface topography and composition of the sample. The electrons which are produced at the top of the column are accelerated down and passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample. As a result of electron- sample interaction, a no. of signals are produced. These signals are the detected by appropriate detectors.SEM produces a black and white 3D images

Instrumentation

SEM consists of the following components

1) **Electron Source ("Electron Gun**"):-It is the source of electron (eg:Tungsten wire). It generates a beam of energetic electrons down the column and onto a series of electromagnetic lenses. These lenses are tubes wrapped in coil and referred to as solenoids
2) **Condenser Lens**:-compresses the electrons to a narrow beam
3) **Aperture:**- It controls the diameter of the electron beam
4) **Objective lens**:- It focuses the electron beam to the sample
5) **Sample chamber & Stage**:-This chamber keeps the sample.Most samples require some preparation before being placed in the vacuum chamber. Two most commonly ued preparations are
    (i) Sputter coating for nonconductive samples
    (ii) Dehydration of biological specimens
6) **Detectors**:-To detect the signals
7) **Amplifier**:-To amplify the signals

8) **Display / Data output devices**:-To show the SEM image obtained

Procedure

- When the incident electrons interact with the sample, energetic electrons are released from the surface.
- The scatter pattern made interaction gives information about size, shape and composition of the sample.
-A variety of detectors are used to attract different types of scattered electrons including secondary (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.
- X-rays emitted from beneath the sample surface can provide element and mineral information.
- SEM produces a black and white 3D images.

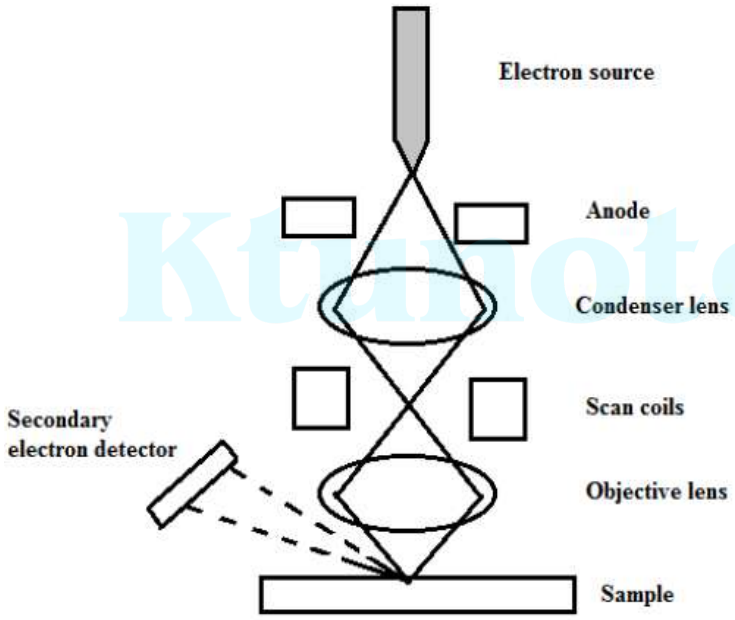


Figure 3.13: Block diagram of SEM

Advantages

- It gives 3D topographical images.
- Instrument is very fast & easy to operate
- Data is available in digital form

Disadvantages

- Instrument is expensive & large
- Special training is required to operate the machine
- Risk of radiation associated with electrons

Applications

SEM is used

1) As very essential research tool in fields such as life science, nano science, gemology, medical &forensic science &metallurgy
2) SEMs have practical industrial &technological applications such as semiconductor inspection, production line of miniscale products &assembly of microchips for computers
3) To characterize nanowires & their gas sensing behavior
4) In material science for research, quality control etc.
5) It helps in the characterization of solid materials
6) It can detect &analyze surface fractures surface contamination &provide information of micro structure