The principle of TGA and its applications:

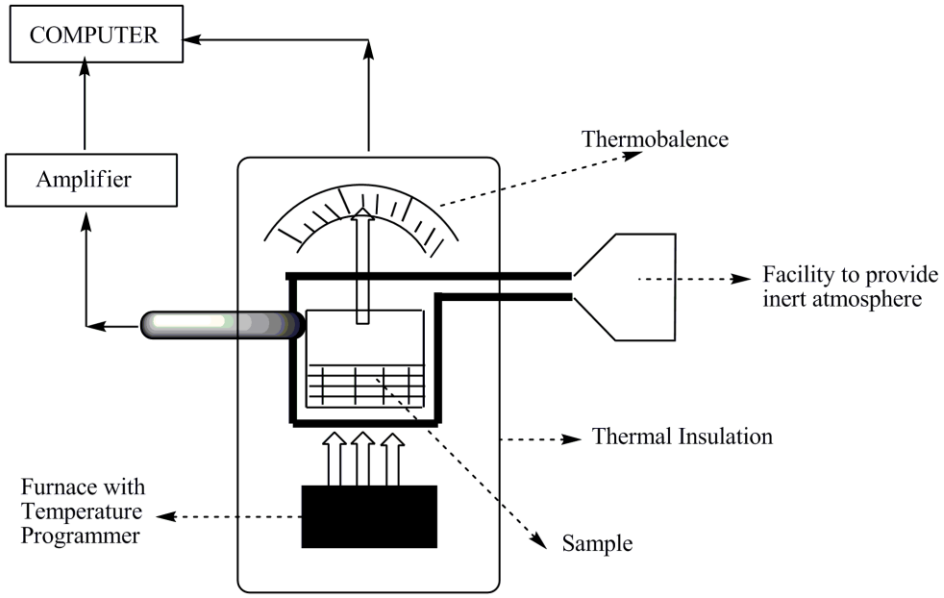
TGA is thermogravimetric analysis.

It is one of the thermal method of analysis. (Thermal methods of analysis are based on the dynamic relationship between temperature with a change in physical property like mass change or enthalpy change etc)

In TGA mass of the substance is continuously monitored as the temperature is linearly increased.

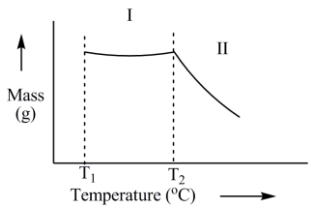
TGA apparatus is used to measure TGA. It can scan over a wide range of temperature (25 – 1200 ^{o}C)

The main components of TGA apparatus



1. **A high precision thermobalence (± 10 µg)**
2. **Furnace with temperature programming facility.**
3. **Facility for providing inert atmosphere (like N_2 gas) Or Oxidizing environment**
4. **A computer which can collect, store and process data – like plotting the graph.**

The mass vs Temperature plot is called Thermogram. (an idealised thermogram is shown below)



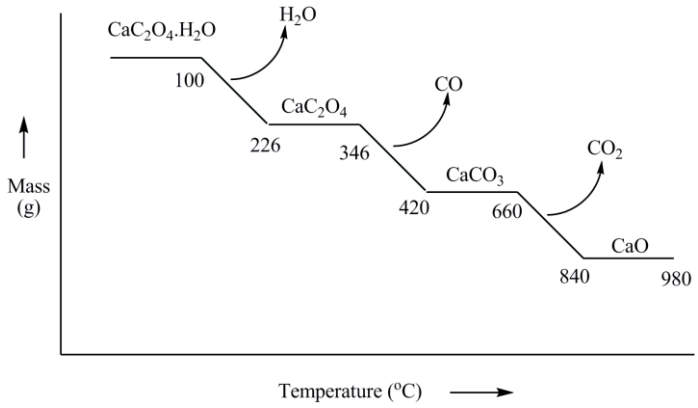
Region I: The horizontal indicates the region where there is no mass change. Ie from T_1 to T_2 the material is thermally stable.

Region II: The graph declines indicating a weight loss (weight loss can be due to dehydration, decomposition, sublimation, desorption, Evaporation etc. [Weight gain during Metal Oxidation, adsorption etc]

Applications:

1. **Thermal stability of substance**
2. **Decomposition mechanism of inorganic salts.**

Consider the TGA-thermogram of calcium oxalate monohydrate $CaC_2O_4.H_2O$.



From the graph it is seen that calcium oxalate monohydrate $CaC_2O_4.H_2O$ is stable upto 100°C.

Removal of water begins at 100°C and gets completed at 226°C.

The horizontal portion 226-346°C shows the thermal stability of CaC_2O_4.

Decomposition of CaC_2O_4 to $CaCO_3$ with the elimination of CO occurs in the temperature range 346-420°C.

The 420-660°C horizontal portion gives the thermal stability of $CaCO_3$.

Above 660°C CaCO3 decomposes to CaO and CO_2.

From the mass difference the mechanism of decomposition can be deduced.

3. **Qualitative analysis**
    a. **Identification of inorganic salts.**
    b. **Detection of purity of sample.**

Decomposition TGA-thermogram pattern is unique characteristic one. Sometimes it helps to identify many materials by comparison. Purity of sample can also be analysed from TGA-thermogram.

4. Evaporation rates of different liquid mixtures.

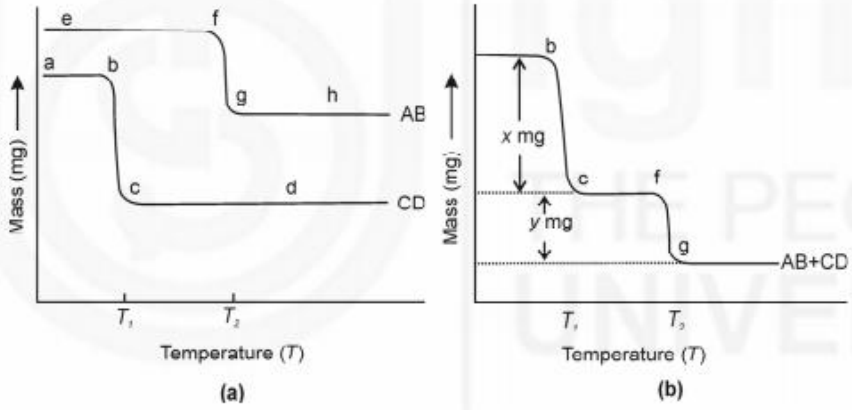
5. Quantitative analysis

a) TGA can be used to find the amount of fillers such us in $CaCO_3$ compounded in a plastic.

b) It can be used to estimate the amount of substance present in a mixture if the mechanism and temperature of decomposition is known. Example the composition of Ca and Ba in $CaCO_3$ + $BaCO_3$ mixture can be analysed.

Binary mixtures

Consider a mixture of two compounds AB and CD having characteristic TG Curves which are different from each other as shown in Fig. 10.8



Assume that CD is $MgCO_3$ and AB is $CaCO_3$. (AB+CD is Mixture of $CaCO_3$ + $MgCO_3$)

From figure b (curve bc represent decomposition of $CaCO_3$), x mg of CO_2 is evolved form $CaCO_3$

Ie, $CaCO_3 \rightarrow CaO + CO_2$

40 + 12 + (16 x 3) = 100 g of $CaCO_3$ contains 40 + 16 = 56 g CaO and 12 + (16 x 2) = 44 g of CO_2

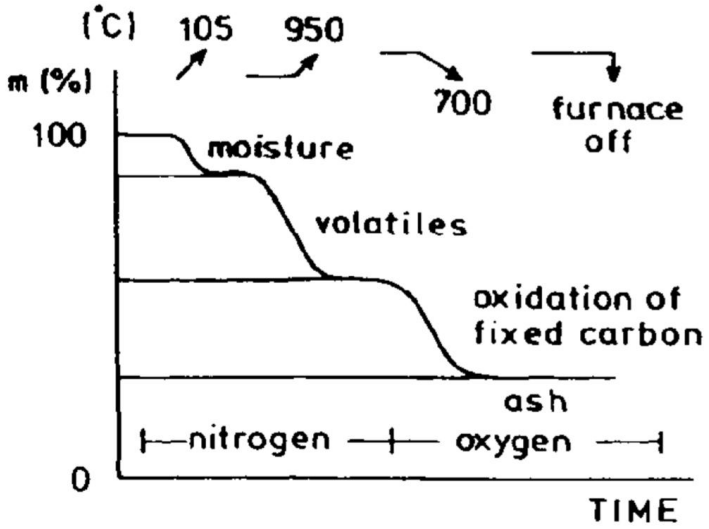
Ie, 44 g of $CO_2 \equiv$ 100 g of $CaCO_3$

1 g of $CO_2 \equiv$ 100/44 g of $CaCO_3$

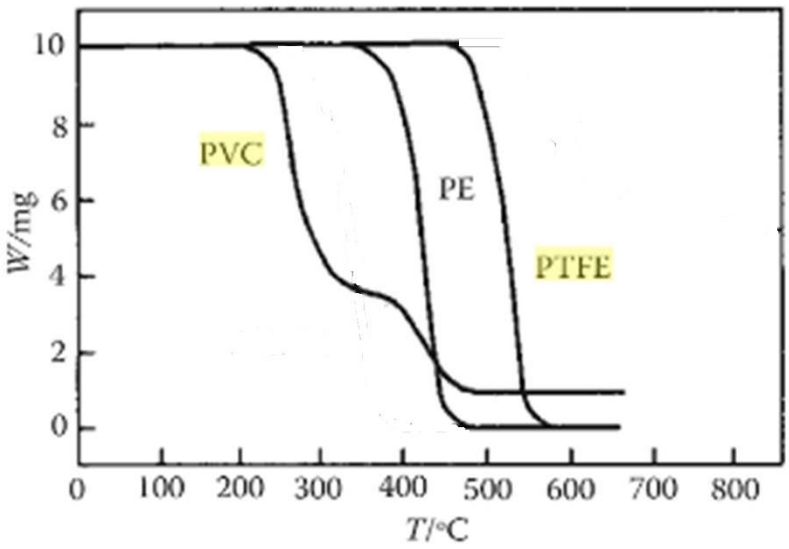
Then, x g of $CO_2 \equiv$ x (100/44) g of $CaCO_3$

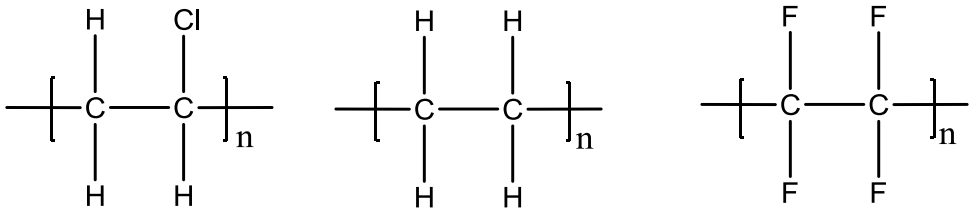
Similarly one can obtain the weight of $MgCO_3$

c) Proximate analysis of Coal (to find out moisture content, volatile matter :- Coal is heated up to 950 ^{o}C in inert atmosphere) (to find out combustible carbon and ash content ;- Coal is heated in presence of oxygen)



6. Analysis of Polymers (Thermal Stability of Polymers and Identification of polymers from the thermogram)

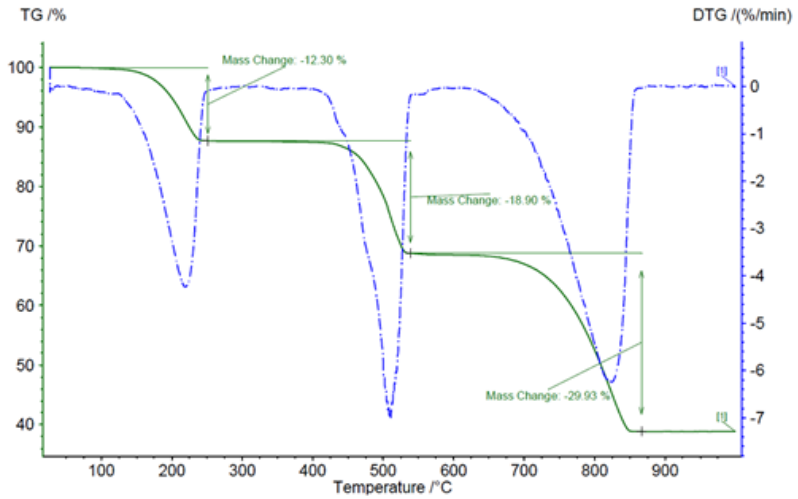




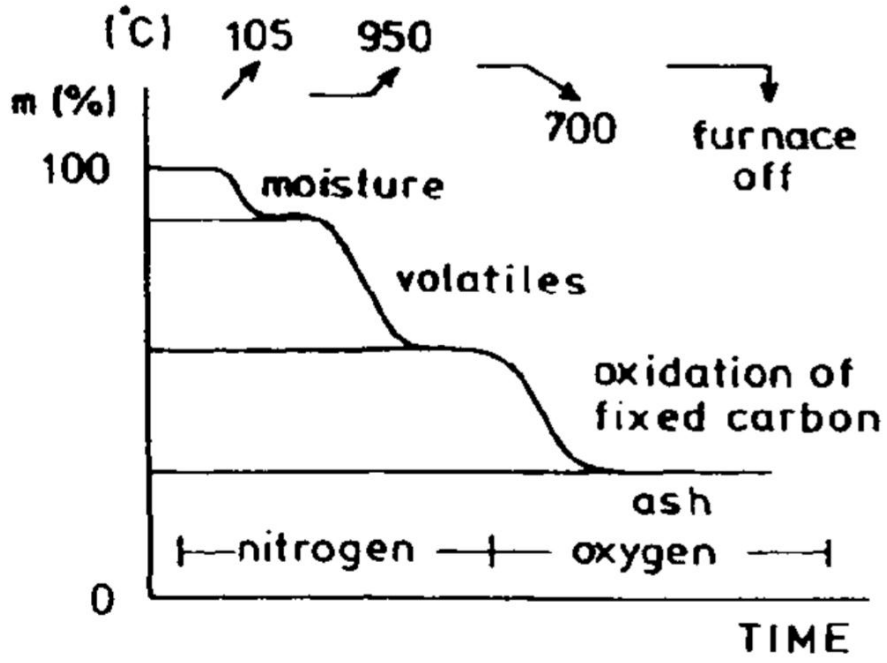
PVC PE PTFE

Thermal stability of C-Cl bond is lower than C-H bond.
Thermal Stability of C-F bond is higher than C-H bond

Differential Thermogram: (dm/dt vs T)



Application of TGA: Proximate analysis of Coal



Process that can be studied by TGA

Evaporation, Sublimation, oxidation, decomposition, desorption, adsorption etc.

Limitations of TGA

TGA can study process which accompanies a mass change. Ie it cannot study process like melting, transitions from one crystalline form to another, glass transition temperature etc.

Differential Thermal Analysis (DTA) and Its Applications

DTA is Differential thermal analysis.

It is one of the thermal method of analysis. (Thermal methods of analysis are based on the dynamic relationship between temperature with a change in physical property like mass change or enthalpy change etc)

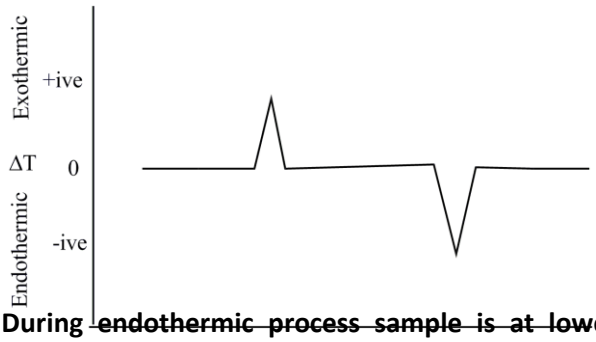
DTA basics

The material under study and an inert reference material (alumina, silicon carbide etc) are subjected to identical heating procedure – Temperature is increased linearly.

The temperature difference between the sample and reference material is recorded.

The differential temperature (ΔT) is plotted against the temperature T or time t to get DTA curve.

<u>An idealized DTA curve is shown below,</u>



There is zero temperature difference between sample and reference when the sample does not undergo a physical or chemical change.

Physical and chemical processes are either exothermic or endothermic. Therefore during such a process a temperature difference will develop. After the completion of process the temperature again becomes identical to that of reference.

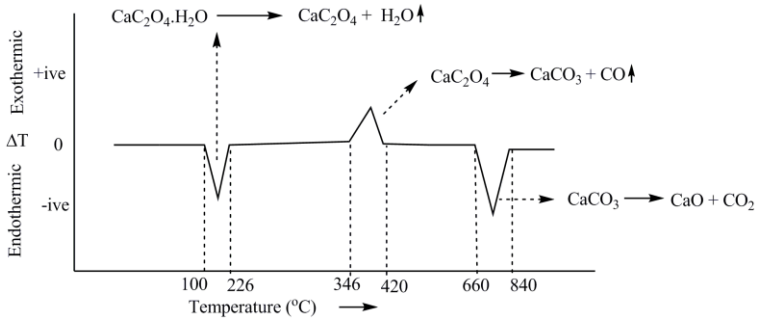
During ~~endothermic process sample is at lower~~ temperature than reference. Therefore a minimum is observed in DTA curve.

During exothermic process, sample is at a higher temperature than reference. Therefore a maximum is observed in DTA curve.

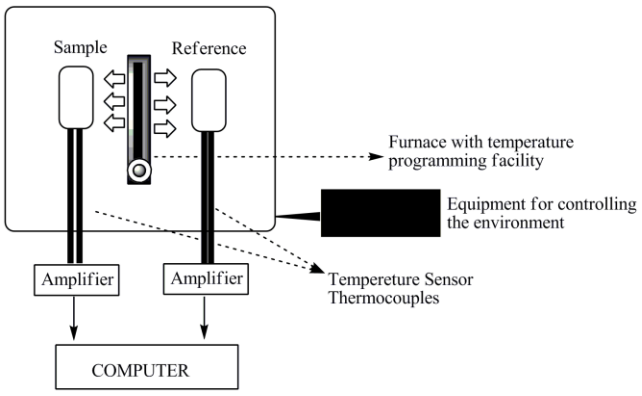
Physical changes like melting, vaporization, desorption, sublimation etc and chemical process like dehydration, reduction and decomposition are endothermic.

Physical changes like adsorption, crystallization and chemical process like oxidation, polymerization and chemisorption are exothermic.

Example: DTA of *calcium oxalate monohydrate* $CaC_2O_4.H_2O$



DTA apparatus

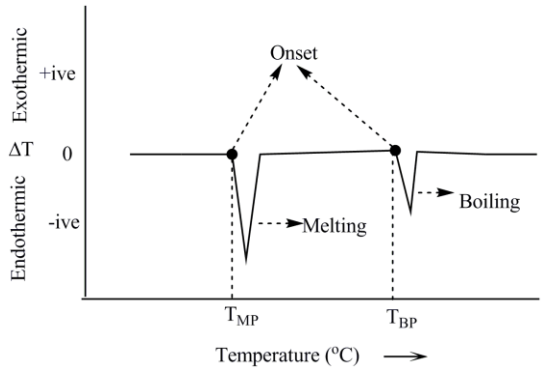


1) **A sample holder and reference hoolder with thermocouple + amplifier assembly**
2) **A furnace with temperature programming facility.**
3) **Equipment for controlling the environment**
   - **Providing inert atmosphere if needed.**
   - **Providing air circulation if oxidation is needed.**

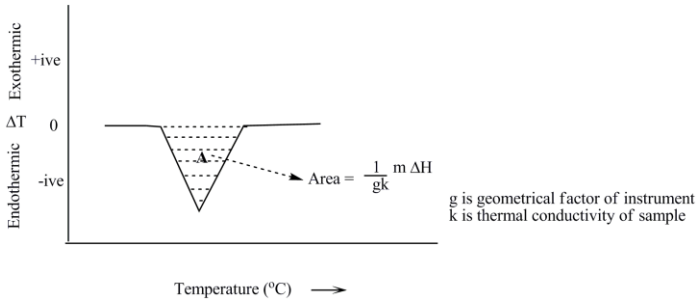
4) **A computer to collect, store, process data – like plotting the graph.**

Applications:

1) **DTA provide accurate way to determine the melting and boiling point of organic compounds.**



2) **To find the enthalpy change (ΔH) of a process.**
   The area enclosed under DTA peak is proportional to mass (m) of the sample and enthalpy change (ΔH).



3) **To distinguish exothermic and endothermic process.**
4) **Unlike TGA, DTA can give information regarding a phase change where there is no change in mass (Fusion, boiling, transition from one crystalline form to another etc).**
5) **Characterization of polymers. It is based on measurement of properties like glass transition temperature, melting point, decomposition temperature, thermal stability etc.**

1 Chapter 3

Chromatography

It is a method used for separating the components of a mixture. The purpose is separation, purification or identification. The technique was invented by Mikhail Tswett, a Russian botanist.

All chromatographic techniques consist of a mobile phase and stationary phase. Components of mixture are carried through the stationary phase (it is fixed in a place) by the flow of mobile phase. Migratory rates will be different for different components due to interaction of solute with stationary phase.

Terms --- a. **Mobile phase** b. **Stationary phase** and c. **elution**

All chromatographic separation techniques contain a mobile phase and a stationary phase.

Stationary phase is fixed in a place. Can be a solid (Finely divided solid adsorbent material packed in a column) or a liquid (Liquid held on the inner wall surface of capillary tube or liquid held on the pore structure of solid substances).

Components of the mixture are carried through the stationary phase by the flow of **mobile phase**. Mobile phase can be a liquid or gas.

Elution is the process of passing mobile phase through the column to transport solute for separation.

Types Of Chromatography – Based on interaction of solute (Adsorption Chromatography, Partition chromatography and Ion Exchange Chromatography)

Chromatographic separation is based on differences in migration rate of components in a sample. This difference in rates is due to difference in interaction of the components with the stationary phase. Based on the type of interaction chromatography is classified into,

Adsorption chromatography: The migration rate of each component differs due to the difference in extent of adsorption of components on the surface of stationary phase. Stationary phase is a solid and the mobile phase can be liquid or gas. Example: column chromatography, thin layer chromatography and gas solid chromatography.

Partition Chromatography: The migration rate of each component differs due to the difference in partition or distribution of solute in stationary phase with respect to mobile phase. Stationary phase is a liquid and the mobile phase can be liquid or gas. Example: gas liquid chromatography and liquid phase HPLC.

Ion Exchange chromatography: Here the stationary phase has ion exchange property and a particular charge. Separation is due to the difference of affinity of each ion toward the ion exchange resin

Another Classification (Based on mobile phase **-- Gas Chromatography** (Mobile is a gas and stationary phase is a solid/liquid) and **Liquid Chromatography** (Mobile phase is liquid and stationary phase can be solid/liquid)

Advantages /Main Application of chromatography

It is possible to separate very small amount of substance therefore used for purification purpose. Method is very simple.

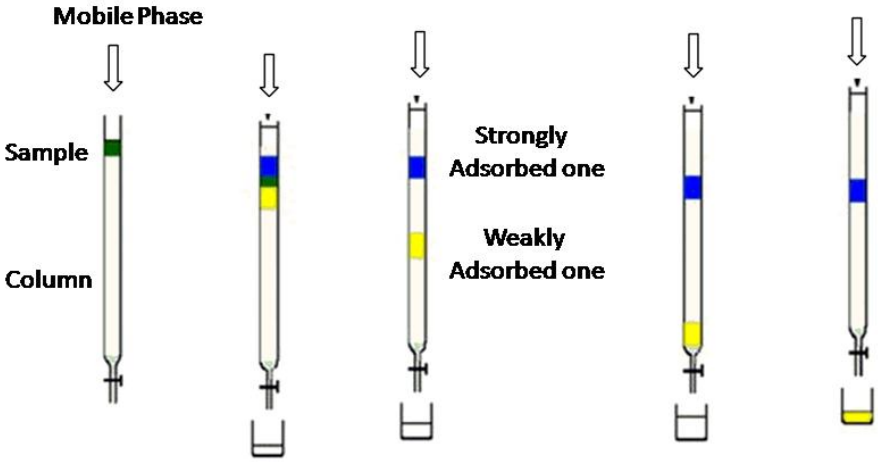
Column Chromatography

It is one of the simplest chromatographic methods of separation.

Stationary phase is finely divided solid adsorbent kept in a glass column. Commonly used adsorbent materials are silica gel and alumina gel. The mobile phase is a liquid which is continuously added to the top of column and flows down the column due to the action of gravity.

Sample (Components A+B) to be separated is dissolved in a suitable solvent and introduced to the top of the stationary phase.

Column Chromatography is Adsorption Chromatography therefore each component migrates at different rate due to the difference in extent of adsorption.



Extent of adsorption of each component in the sample will be different. When we start elution the mobile phase solvent, the weakly adsorbed one will move faster whereas the strongly adsorbed one moves very slowly.

Weakly adsorbed component will come out first and the strongly adsorbed one will come out last. The fractions obtained are collected and evaporated to remove the solvent.

Polarity of solvent (mobile phase) influence the separation. Like dissolves like, therefore highly polar solvents moves a highly polar component rapidly.

Consider a sample which is a mixture of non-polar A and polar B. If we are eluting with a non-polar solvent, A will come out first from the column. B will come out only after a long time.

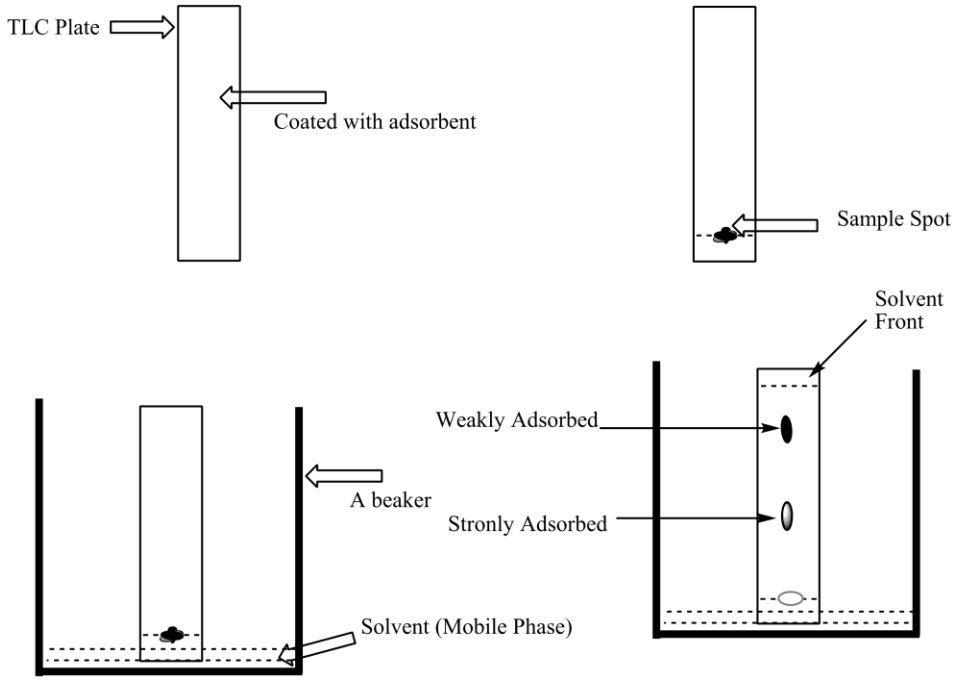
Uses of column Chromatography:

Purification of dyes, natural products, pigments etc.

It is commonly used by researchers for the separation of desired compound after synthesis.

THIN LAYER CHROMATOGRAPHY (TLC)

TLC is an adsorption chromatography. The stationary phase is a solid adsorbent, here a sheet of plastic, glass or metal is coated with a thin layer of solid adsorbent (finely divided silica or alumina)



Sampling: Small amount of mixture to be separated is dissolved in a suitable solvent and spotted near the bottom of the TLC plate using a capillary tube.

The TLC plate is placed in a solvent. The solvent level should be below the spot. This process is called **TLC development**.

The mobile phase, ie the solvent rises up the TLC plate due to capillary action. As the solvent passes the spot it carries different components at different rate. The component which is weakly adsorbed moves upward very fast and the other one which is strongly held moves very slowly.

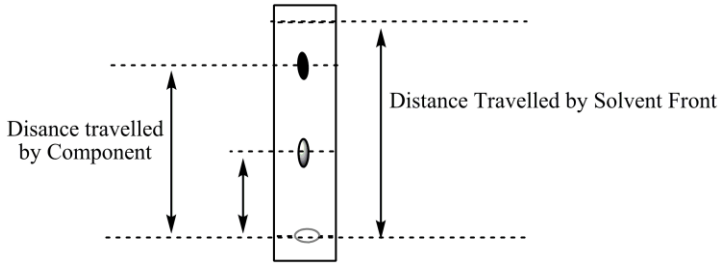
When the solvent front has reached the top of the plate, the TLC plate is removed and dried. Separated components are **visualized**. If coloured, one can differentiate it with his eyes, If not (a) put TLC plate in iodine chamber. Iodine will develop a black colour with most of the organic compounds. (b) Keep the developed TLC Plate under UV light - aromatic compounds and conjugated dienes produce blue fluorescent spots. (c) Spray stain reagents (Ninhydrin produces purple colour for amino acids, $FeCl_3$ in dil HCl produces red spot for phenols, 2,4-dinitrophenyl-hydrazine produces yellow to red spots for aldehydes and ketones, Bromocresol green produces yellow t green spots for carboxylic acids.)

Advantage and Applications:

- **Simple, quick and inexpensive procedure**
- **Used to check how many components are present in the sample.**
- **To check purity of sample**
- **To monitor progress of a chemical reaction**
- **To select ideal solvent for column chromatography based on Retention Factor.**

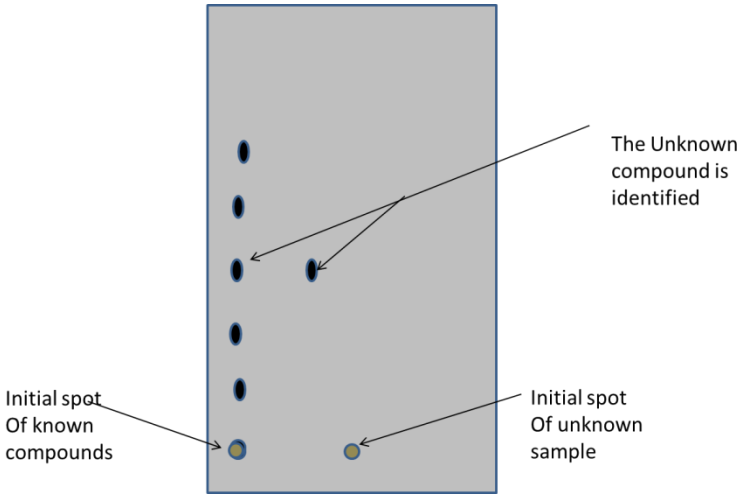
Retention Factor RF Value: It is the ratio.

$$Rf = \frac{Distance\ Travelled\ by\ component}{Distance\ Travelled\ by\ solvent\ front}$$



Uses of Retention Factor.

a) Used for identification of substance by comparing the retention factor.



b) To select ideal solvent for carrying out column chromatography is based on Retention Factor differences.

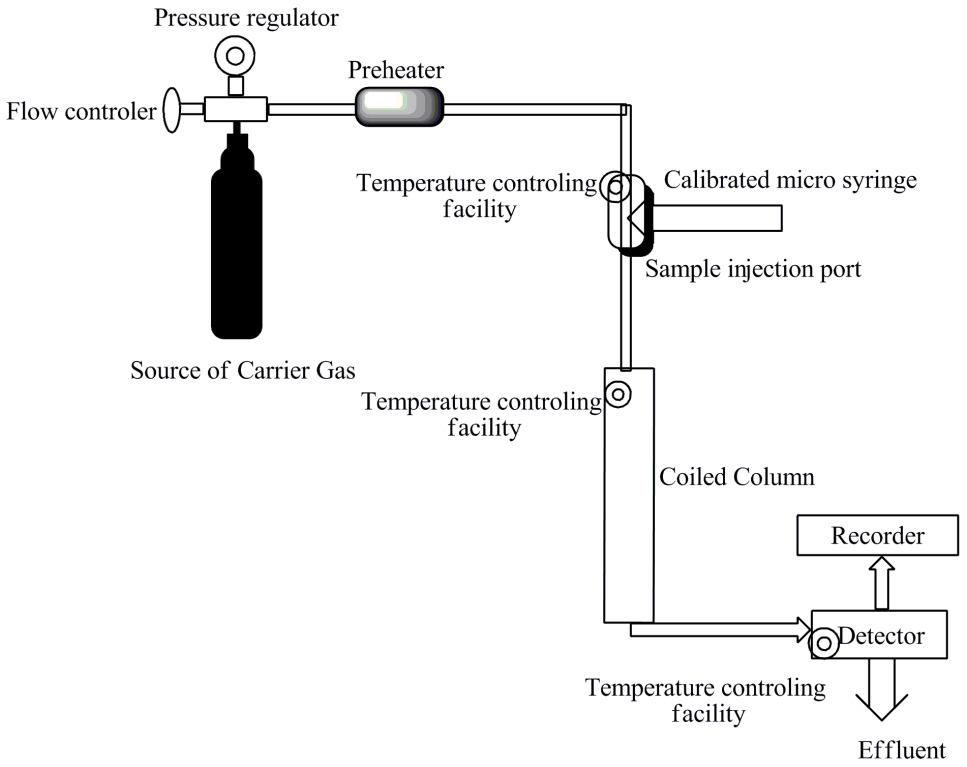
Principle, instrumentation and application of Gas Chromatography GC

GC is gas chromatography (a separation technique). Mixture is separated into its constituents by a moving gas passing over a stationary phase.

Mobile Phase is gas.

Stationary phase can be solid or liquid. If stationary phase is solid then the basis of separation is difference in adsorption and the chromatography is called **gas solid chromatography GSC**. if the stationary phase is liquid the basis of separation is partition (distribution of solute in mobile and stationary phase) and the chromatography is called **gas liquid chromatography GLC**.

Instrumentation for GC. (For GLC and GSC the difference is only in the column)



Carrier gas system:

A source for carrier gas – the mobile phase. Carrier gas is used to transport vaporized sample through the column. Carrier gas should be inert to stationary phase and components in sample Most commonly used one is N_2 gas. H_2 He and Ar can also be used.

Pressure regulator and flow controller are used to adjust flow rate.

Pre-heater heats the carrier gas before elution.

Sample injection system:

Sample is injected using a calibrated micro syringe. Injection is almost instantaneous.

The sample must be converted into vapour state. Resistance heating is used to vaporize sample.

Column and stationary phase:

Column is the heart of chromatographic instrument.

GLC Column : Long capillary column made from capillary tube. Length of column is 3 to 300 meter. Inner diameter is 0.1 to 1mm. Stationary phase is thin film of liquid coated on the inner surface of capillary tube.

Or

Short tube like packed column can also be used. The column is packed with finely divided glass beads. Length of column is 3 to 6 meter. Inner diameter is 1 to 6mm. Stationary phase is liquid held on the pores of this material.

In general choice of the liquid phase is based on polarity of substances to be separated. The liquid should be inert, should be non-volatile and thermally stable under operation conditions. Example polar liquid --- Carbowax-400 . Non-polar liquid ---- n-cetane and silicone oil.

GSC Column : A short tube like packed column is used. Column is packed with finely divided activated solid adsorbents like silica, alumina, activated charcoal etc. Length of column is 0.7 to 6 meter. Inner diameter is 1 to 6mm. Stationary phase is solid adsorbents. It should be thermally stable, chemically inert and should have large surface area.

Efficiency of column is directly proportional to the length of column.

The performance of column increases with decrease of column diameter.

Detectors:

Any physical property which varies from one gas to another and which can be easily monitored forms the basis of detector.

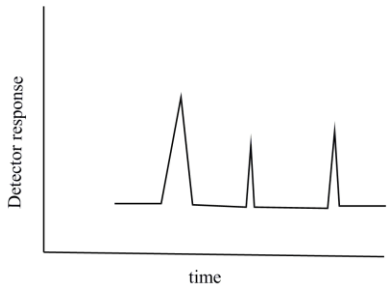
Thermal conductivity detector (kathrometer) TCD or KCD: Most commonly used detector. Property monitored is thermal conductivity. Thermal conductivity of pure carrier gas will be different from the one containing the sample and carrier gas. Sensing element is a thermistor. Temperature across the thermistor varies depending on the variations in thermal conductivity which in turn changes the resistance. Resistance changes can be sensed by a wheat-stone bridge circuit. TCD is a non-destructible detector system, therefore can be used for preparative works.

Flame ionization detector FID: Ions are formed during combustion of organic compounds in Hydrogen flame. FID is based on detection of these ions. The ions generated are collected by an electrode. A potential difference develops between this electrode and a base electrode which causes a current to flow. The current is proportional to concentration of ions which depends on the concentration of organic compound and the nature of organic species. High sensitivity (can even detect very low concentrations to high concentrations). Low cost and low maintenance. It is destructible analytical technique.

.

Recording device:

Recording device give the chromatogram. A plot of detector response vs time is chromatogram. With only carrier gas flowing through the detector, the recorder is calibrated to zero ie base line. Each separated components evokes a detector response which registers a peak in chromatogram.



Procedure: The sample is injected to the injection port using a calibrated micro syringe. It is vaporized using resistance heating. Pre-heated carrier gas carries the vaporized sample through the column where it gets separated out depending on the interaction of components with stationary phase. Detector will give a differentiating response for each component separation.

Application:

1. GC is widely used to test purity of organic compounds (impurity is revealed by additional peaks).
2. GC is used to monitor air pollution.
3. By using GC ethyl alcohol content in the blood can be determined with high accuracy.
4. Banned drugs used by athletes can be detected by taking GC of blood and urine sample.
5. GC coupled with mass spectrometry (GC-MS) is used for analysis of hydrocarbon fuels. Perfumes, flavours etc.
6. Separation of close boiling liquids (Benzene 80.1 ^{o}C and cyclohexane 80.9 ^{o}C)

Factors Affecting retention time (chromatographic separation)

a. ***The polarity of components versus the polarity of stationary phase on column***
   If the polarity of the stationary phase and compound are similar, the retention time increases because the compound interacts stronger with the stationary phase. As a result, polar compounds have long retention times on polar stationary phases and shorter retention times on non-polar columns using the same temperature.
b. ***Column temperature***
   A excessively high column temperature results in very short retention time but also in a very poor separation because all components mainly stay in the gas phase.
c. ***Carrier gas flow rate***
   A high flow rate reduces retention times, but a poor separation
d. ***Column length***
   A longer column generally improves the separation
e. **Order of elution is mainly determined by *volatility of sample***
   Least volatile is most retained in the column. Polar compounds (ex: alcohols) are the least volatile and will be the most retained on the GC system

Principle, instrumentation and application of HPLC

High performance liquid chromatography (a separation technique).

Mobile Phase is liquid

Stationary phase can be solid or liquid (most commonly used is liquid). If stationary phase is solid then the basis of separation is difference in adsorption, and if it is liquid the basis of separation is partition (distribution of solute in mobile and stationary phase).

Unlike gas chromatography vaporization of sample is not required for HPLC.

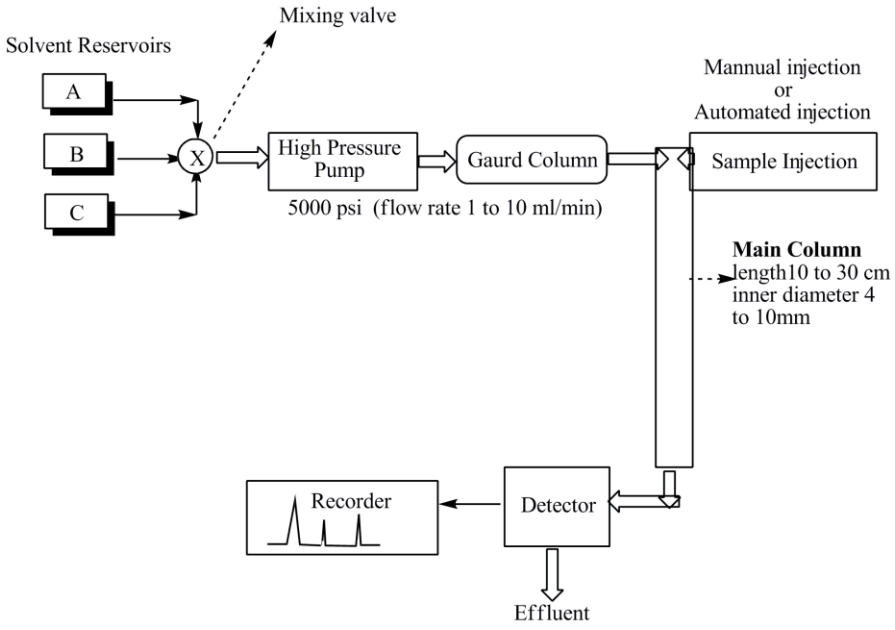
Elution can be done in two ways.

Isocratic elution: mobile phase composition remains constant throughout the chromatographic separation procedure.

Gradient elution: mobile phase composition is varied during separation process. Required polarity for separation is achieved by mixing. Gradient elution helps to shorten the retention time. Therefore overall time required for separation can be considerably reduced.

The common organic solvents used as mobile phase are benzene, cyclohexane, acetone, ethanol etc.

Instrumentation for HPLC.



The main column:

Quite narrow column. Column is packed with particles of small size (3-10 µm). Efficiency of HPLC column increases when the particle size is reduced.

In order to achieve constant flow rate pressure pumps are used to drive solvent (5000 psi pressure to achieve flow rate of 1 to 10 ml/min).

Glass tubes cannot withstand such a high pressure therefore smoothly bored stainless tube like columns are used. Column length 10 – 30 cm , inner diameter 4-10mm.

Two types of modes of operation are there for HPLC:

Normal phase operation: Highly polar stationary phase and non-polar mobile phase. Polar compounds are retained for longer time. For normal phase silica powder bonded with OH group is used as stationary phase.

Reverse phase operation: Non-polar stationary phase and polar mobile phase. Non-polar compounds are retained for longer time. Here silica powder bonded with O-CH3 group is used as stationary phase.

Detectors:

Bulk property detector: These monitor a difference in physical property of the pure solvent (mobile phase) with respect to the one containing sample + solvent. Properties usually monitored are refractive index, dielectric constant, density etc.

Solute property detector: These detector respond to physical property of the solute such as UV-visible absorption, fluorescence etc. Mobile phase may or may not have such a response.

Recorder gives the chromatogram (plot of detector response vs time).

Applications:

Can be used for separating volatile and non-volatile organic compounds like natural products (such as cholesterol, tri-terpinoids etc)

Separation of polypeptides

More amount of compound can be separated when compared with GC.

Can be used to find concentration of trace components

Monitor pesticides level.

To ensure purity of raw materials

Can be used to check food adulteration

HPLC is useful for pharmaceutical, forensic and environmental application.

Why oxygen is unsuitable as carrier gas in GLC?

Oxygen is not chemically inert. It may oxidise some components in the sample. Therefore it is not suitable as a carrier gas.

Differentiate between GLC and GSC?

		GSC	GLC
1.	Mobile phase	Gas	Gas
2.	Stationary phase	solid	Liquid
3.	Column	Packed column	Packed or capillary column
4.	Basis of separation	Difference in Adsorption	Difference in Partition
5.	Length of column	Relatively short	long column
6.	Thermal stability of stationary phase	Good stability	Less stable above 300^{o}C
7.	Reaction in column	Adsorbent may catalyse some reaction.	relatively inert
8.	Applicability	useful for separation of permanent gas and low Boiling substances.	all volatile materials except more permanent gases.

What are the information obtained from a chromatogram?

a. The number of peaks will tell us the number of species present.
b. Retention time: time between injection of a sample and the appearance of solute peak at the detector. Compound can be identified from retention time.
c. Quantitative estimation. Area enclosed by the peak is related to the quantity.

Differentiate between GC and HPLC?

Mobile phase in GC is gas while mobile phase of HPLC is liquid.

Volatile compounds can only be separated using GC. Even non-volatile compounds like natural products such as cholesterol, tri-terpenoids can be seperated using HPLC.

Using HPLC more amount of compound can be separated than GC.

Q. What are the various visualization Technique used in TLC?

Ans: If coloured once can visualize with naked eye

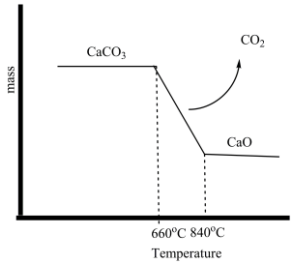
One can visualize spots by irradiating with UV light – blue spot for aromatics and dienes.

Put TLC plate in iodine chamber, iodine develops a black colour with organic compounds.

Use a stain agent, example Ninhydrin develops a purple colour for amines and aminoacids.

Q. Explain the basic principles of TGA with example.

TGA is a technique that monitors mass of substance as the temperature is linearly increased. Process like dehydration, desorption and decomposition results in a weight change. The TGA thermogram of $CaCO_3$ is given below,

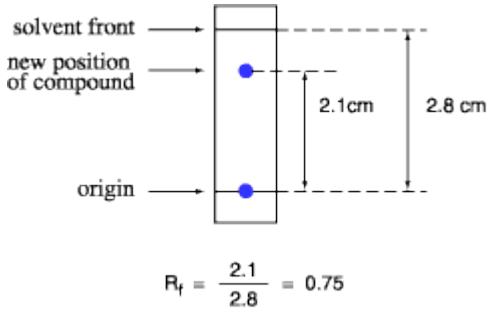


From the graph it is clear that the $CaCO_3$ is thermally stable up to 660°C. In the region 660-840°C the decomposition of $CaCO_3$ to CaO and CO_2 takes place.

Q. What is RF value in chromatography?

R_f value = $\frac{Distance\ Travlled\ by\ compound}{Distance\ travelled\ by\ solvent}$

For example, if a compound travels 2.1 cm and the solvent front travels 2.8 cm, the R_f is 0.75.



Q. How do we measure cell constant?

$Conductivity\ k = GK_{cell}$ $(Conductance\ .\ Cell\ Constant)$. Cell constant is a factor that is used to convert measured conductance to conductivity. Cell constant of conductivity cell is geometric factor L / A. It is the ratio of distance between electrodes to area of electrodes. It is very difficult to precisely obtain the geometric factors. Therefore cell constant is experimentally determined by measuring conductance of solutions having known conductivity (aqueous KCl solutions). $K_{cell} = \frac{k}{G}$

Q. Give the principles of HPLC. How does it differ from gas chromatography?

Ans: HPLC – High performance liquid chromatography is a separation technique. The mobile phase is liquid and stationary phase can be a liquid or solid. Liquid stationary phase is most common one. Here the basis of separation is difference in partition (relative solubility) of solute in stationary phase and mobile phase.

A small amount of sample to be separated is dropped into the injection port. A high pressure pump is used to drive the solvent for elution. It carries the components to be separated through the stationary phase. The relative migration rate of each component is different due to the deference in relative solubility of each component in stationary phase and mobile phase. The separated components are detected by bulk property or solute property detector.

Differences

Mobile phase of GC is a gas, whereas mobile phase of HPLC is liquid.

Only Volatile compounds (or gaseous) can be separated using GC. Even non-volatile compounds can be separated using HPLC.

Gradient elution and Isocratic elution is possible for HPLC.

Using HPLC more amounts of compounds can be separated than GC.

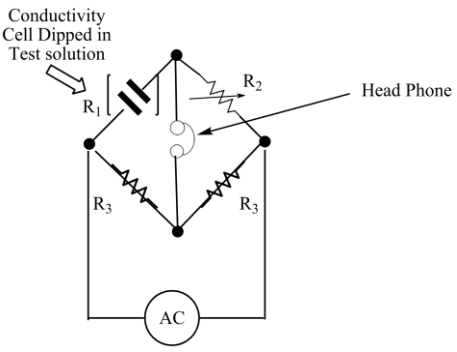
For HPLC a high pressure pump is required to drive solvent for elution whereas for GC tit is not required.

Q. Explain the experimental procedure involved in measurement of conductivity of a solution.

Construct a wheat stone bridge circuit. One arm of the bridge is connected to the conductivity cell dipped in test solution (R_1). The other arms two connected to fixed resistanceR_3 and R_4 and the fourth arm is connected to a variable resistance (R_2). AC current is given. A suitable detector is also connected (Head phone?). The bridge is balanced when no current pass through the detector. The head phone will not produce any sound when the bridge is balanced. $\frac{R_1}{R_2} = \frac{R_3}{R_4}$

If we make R_3 and R_4 identical, then $R_1 = R_2$ ie the resistance of the test solution is the resistance of variable resistor when the bridge is at balance. From the resistance conductance can be measured.

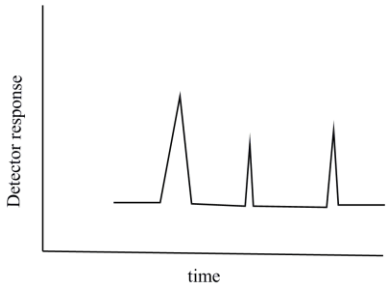
Then conductivity = conductance x cell constant.



Q. What are the applications of Conductivity Measurement:

Ionic concentrations, Salinity, Sodium Concentrations in Urine, Total dissolved salts etc....

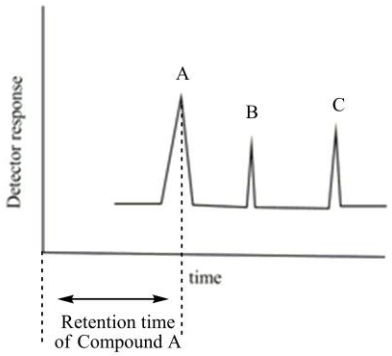
Q. What are the information obtained from a chromatogram?



d. The number of peaks will tell us the number of species present.
e. Retention time: time between injection of a sample and the appearance of solute peak at the detector. Compound can be identified from retention time.
f. Quantitative estimation. Area enclosed by the peak is related to the quantity.

Q. What is meant by retention time?

Retention time: It is the time interval between injection of a sample and the appearance of solute peak at the detector. It gives as an idea of How much time a compound stayed on the stationary phase. If the conditions maintained are same, compound can be identified from retention time.



Q. Explain the applications of TLC and Column Chromatography.

Uses of column Chromatography:

Purification of dyes, natural products, pigments etc.
It is commonly used by researchers for the separation of desired compound after synthesis.

Uses of TLC

... Simple, quick and inexpensive procedure

... Used to check how many components are present in the sample.

... To check purity of sample

... To monitor progress of a chemical reaction

... To select ideal solvent for column chromatography based on Retention Factor.

Q. Explain the significance of R_f value. ?

Every compound (dye, pigment, organic substance etc) have a specific R_f value for every specific solvent and solvent concentration. Also the relative differences in Rf value helps in the selection of solvent for preparative chromatographic separation.

Q. Based on mechanism of separation classify chromatographic techniques.

Ans: a. If separation occurs due to relative differences in adsorption -- Adsorption chromatography.

b. If separation occurs due to relative differences in partition (ie solubility) -- Partition chromatography.

c. If molecules are separated according to their differences in size ---- size exclusion chromatography.
d. Based on the differences in affinity towards ion exchanger - ion exchange chromatography.

Q.What are the different types of detectors used in gas chromatography?

Ans:

Thermal conductivity detector (kathrometer) TCD or KCD: Most commonly used detector. Property monitored is thermal conductivity. Thermal conductivity of pure carrier gas will be different from the one containing the sample and carrier gas. Sensing element is a thermistor. Temperature across the thermistor varies depending on the variations in thermal conductivity. Resistance changes can be sensed by a wheat-stone bridge circuit. TCD is a non-destructible detector system, therefore can be used for preparative works.

Flame ionization detector FID: Ions are formed during combustion of organic compounds in Hydrogen flame. FID is based on detection of these ions. The ions generated are collected by an electrode. A potential difference develops between this electrode and a base electrode which causes a current to flow. The current is proportional to concentration of ions which depends on the concentration of organic compound and the nature of organic species. High sensitivity (can even detect very low concentrations to high concentrations). Low cost and low maintenance. It is destructible analytical technique.

Q. Define elution. Mention types of elution in HPLC?

Elution is the process of passing mobile phase through the stationary phase to transport solute for separation.

In HPLC elution can be done in two ways,

Isocratic elution: mobile phase composition remains constant throughout the chromatographic separation procedure.

Gradient elution: mobile phase composition is varied during separation process. Required polarity for separation is achieved by mixing. Gradient elution helps to shorten the retention time. Therefore overall time required for separation can be considerably reduced.

.....

Q. What is the necessity of guard column in HPLC?

The main column used in HPLC instrument is very costly and sensitive. So in order to protect it from contaminants in the mobile phase a guard column is used.

Q. What are the main components of a TGA instrument?

Q. What is the importance of HPLC in chemical analysis?

Q. In what way DTA study of polymer helpful to a chemist?

Q. Discuss the information obtainable by applying thermal analysis techniques in the study of solid polymers.

Q. Describe and interpret the thermogram obtained from a TGA experiment by taking a suitable example.

Q. What is the significance of peaks in a differential thermogram?

Q. Given a perfume sample, how will you analyse it using GC?

Q. Distinguish between TGA and DTA?

Q. Draw and illustrate the thermogram showing the decomposition of hydrated calcium oxalate.

Q. Suggest the best chromatographic technique for the separation of natural dyes?

Q. Athletes takes performance enhancer drugs. How can you as a chemist analyse if such a malpractice has taken place?

Q. What is the use of pre-heater in GC?

Q. Compare reverse phase operation and normal phase operation in HPLC.

Q. Outline the GC procedure.

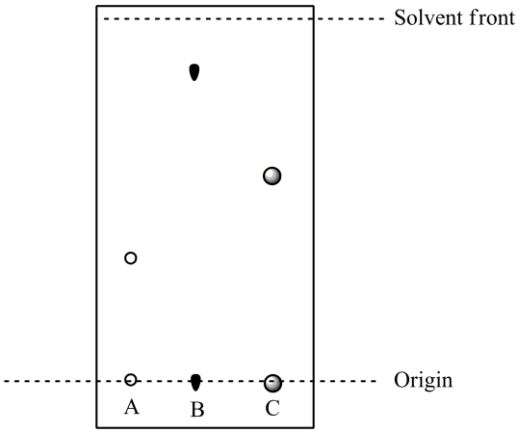
Q. How is Rf value for a spot on TLC plate is calculated? What can Rf value be used for?

Q. What are the advantages of TLC as compared to column chromatography?

Q. Compare column chromatography with TLC.

Q. What are the two most common stationary phase used in column and thin layer chromatography?

Q. Consider the following silica gel TLC plate of compounds A, B, C developed in hexane,



a. Which compound A, B or C is most polar?

Ans: Compound A is most polar. It does not travel as far as the other two compounds.

Q. What are the two basic components of any chromatography system?
Q. What is the difference between analytical and preparative chromatography?

Q. List some ways you could reduce the retention time.

Ans: One way to reduce retention time is by gradient elution in HPLC, changing the composition of solvent for polarity changing.

The other way increasing the flow rate of mobile phase

Increasing the operating temperature in gas chromatography reduces retention time.

Decreasing the length of column containing stationary phase.

Q. What is meant by a bulk property detector? Give an example of an HPLC detector that is based on bulk properties and one that is not.

Q. What is gradient elution and how does this differ from an isocratic one? What advantage does gradient elution have over isocratic separations?

Q. What is the significance of maxima and minima in a differential thermogram?

Q. What are the main components of DTA instrument?

Q. What kind of reference materials are used in DTA? Give two examples.

Q. How can you identify a polymer from TGA analysis?

Q. List three reasons for weight loss in TGA analysis?

Q. Explain why all chemical and physical process can be studies with DTA while some physical process cannot be studied using TGA.

Q. What is the limitations of TGA experimens and explain how the DTA overcomes it?

Q. Suggest an instrumental method to measure the evaporfation rates of liquid mixtures and to determine the purity of a chemical compound. Mention its principle.

Q. Suggest an instrumental method to measure the boiling point and melting point of a chemical compound. Mention its principle.

Q. Give two examples each of endothermic Physical and chemical process.

Q. Give two examples each of exothermic Physical and chemical process.

Conductivity

Conductors: Materials that can pass electric current through it. It can be electronic (current is carried by the movement of electrons as in metals and semiconductor metals) or electrolytic (Current is carried by the movement of cations and anions)

Insulators: Materials that cannot pass electric current through it.

Electrical Resistance R (unit is ohm): It is a measure of obstructions to the current flow.

R is proportional to the Length L of Conducting medium and inversely proportional to the cross sectional Area A of the conducting medium

Ie, $R = \rho \frac{L}{A}$ Where ρ is the proportionality constant Resistivity or Specific Resistance (unit is ohm cm)

When L = 1unit (1 cm) and A = 1 unit^2 (1cm^2) then ρ = R is **specific resistance** or resistivity is the resistance of a conducting medium of unit length and unit cross section.

Electrical Conductance G (unit is ohm-1, mho or Siemens): It is a measure of ease with which current is flowing. It is the reciprocal of electrical resistance.

G = 1/R

$G = \frac{1}{R} = \frac{1}{\frac{\rho L}{A}} = \frac{1}{\rho}\frac{A}{L} = k\frac{A}{L}$ Where k is specific conductance or Conductivity (S cm^{-1})

Conductivity is the conductance of 1 cm^3 of conducting medium. It is the ability of solution to pass electric current. $k = G\frac{L}{A} = GK_{cell}$ L/A is cell constant K_{cell} of conductivity cell. Cell constant is a factor that is used to convert measured conductance to conductivity. It is the ratio of distance between the electrodes to area of electrodes.

Conductivity Cell and cell constant measurement: Consist of two platinum coated electrodes having 1cm^2 area and they are kept 1cm apart.

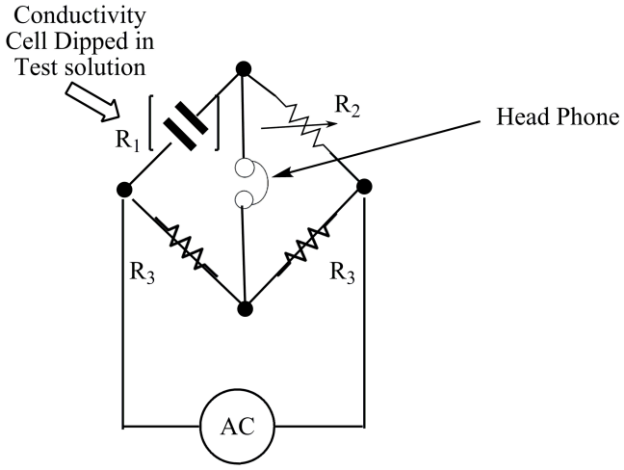
Cell constant can be theoretically determined from the geometry of cell. K_{cell} = L/A. But it is very difficult to precisely obtain the geometric factors. Therefore cell constant is experimentally determined by measuring conductance of solutions having known conductivity (aqueous KCl solutions). $K_{cell} = \frac{k}{G}$

Experimental set up to determine conductance and conductivity

Construct a wheat stone bridge circuit. One arm of the bridge is connected to the conductivity cell dipped in test solution (R_1). The other arms two connected to fixed resistanceR_3 and R_4 and the fourth arm is connected to a variable resistance (R_2). AC current is given. A suitable detector is also connected (Head phone?). The bridge is balanced when no current pass through the detector. The head phone will not produce any sound when the bridge is balanced. $\frac{R_1}{R_2} = \frac{R_3}{R_4}$

If we make R_3 and R_4 identical, then $R_1 = R_2$ ie the resistance of the test solution is the resistance of variable resistor when the bridge is at balance. From the resistance conductance can be measured.

Then conductivity = conductance x cell constant.



Applications of Conductivity Measurement:

Total dissolved solids, Ionic concentrations, Salinity, Sodium Concentrations in Urine etc.....

Advantages

Non-destructive measurements

Fast and reliable

Inexpensive

Drawback

Not ion selective (give a reading of Combined effect of all the dissolved ions)

Pblm1: Calculate the conductivity of given sodium chloride solution at 298 K which shows a conductance of 500 micro-mho in a cell. A standard solution of 0.01 M KCl shows a conductance of 128 micro-mho in that cell. Given that conductivity of 0.01 M KCl solution is 0.00128/(ohm cm) at 298 K.

Soln: $Conductivity\ k = GK_{cell}$ $(Conductance\ .\ Cell\ Constant)$

$K_{cell} = \frac{k}{G} = \frac{0.00128}{128\ X\ 10^{-6}} = 10\ cm^{-1}$.

$Conductivity\ of\ given\ NaCl\ soln\ k = GK_{cell} = 500\ X\ 10^{-6}\ X\ 10 = 0.005$ $ohm^{-1}cm^{-1}$.

Pblm2: The specific conductance of N/50 KCl solution at 25°C is 0.0002765 $Ohm^{-1}cm^{-1}$. If the resistance of the cell containing this solution is 500 ohm, what is the cell constant?

Soln: $Conductivity\ k\ =\ GK_{cell}$ $(Conductance\ .\ Cell\ Constant)$

$$K_{cell} = \frac{Conductivity\ k}{Conductance\ G}$$

Conductance G = 1/R = 1/500 = 0.002 Simens

Conductivity = Specific conductance = 0.0002765 $Ohm^{-1}cm^{-1}$ = 0.0002765 Siemens cm^{-1}

$K_{cell} = \frac{Conductivity\ k}{Conductance\ G} = \frac{0.0002765}{0.002} = 0.138$ cm^{-1}

Pblm3: The resistance of 0.01 N NaCl solution at 25 °C is 200 Ohm. Cell constant of conductivity cell is unity. Calculate the solution specific conductance (conductivity).

Soln: $Conductivity\ k\ =\ GK_{cell}$ $(Conductance\ .\ Cell\ Constant)$

$K_{cell} = 1$ cm^{-1}

Conductance G = 1/R = 1/200 = 0.005 Simens

$Conductivity\ of\ given\ NaCl\ soln\ k = GK_{cell} = 0.005\ X\ 1 = 0.005$ Siemens cm^{-1}.

Pblm4: The resistance of a conductivity cell when filled with 0.02 M KCl solution is 164 ohm at 25 °C. however when filled with 0.05 M $AgNO_3$ solution its resistance is dropped to 82 ohm. Calculate the conductivity of $AgNO_3$ solution. Give that specific conductivity of 0.02 M KCl is 2.788 $mOhms^{-1}$ cm^{-1}.

Soln: $Conductivity\ k\ =\ GK_{cell}$ $(Conductance\ .\ Cell\ Constant)$

$$K_{cell} = \frac{Conductivity\ of\ KCl\ k}{Conductance\ of\ KCl\ G}$$

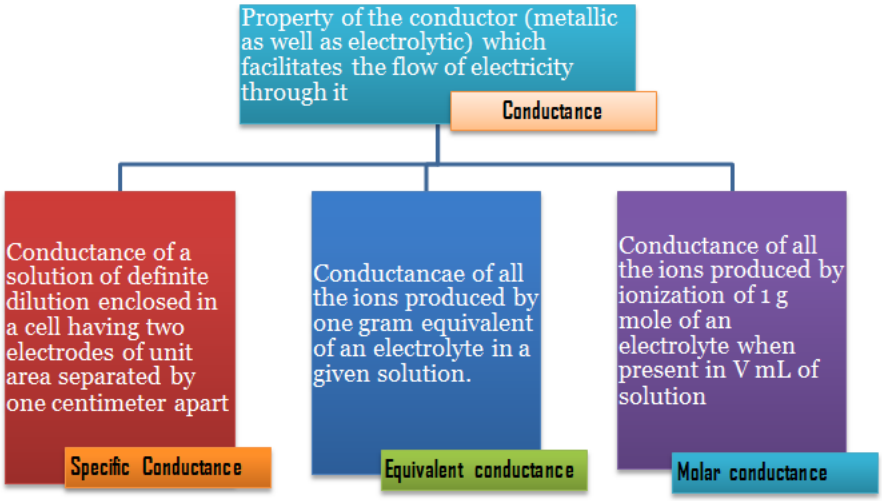
Conductivity k of KCl = 2.788 x 10^{-3} Simens Cm^{-1}

Conductance of KCl G = 1/R = 1/164 = 0.006 Simens

Conductance of $AgNO_3$ G = 1/R = 1/82 = 0.012 Simens

$\frac{Conductivity\ of\ KCl\ k}{Conductance\ of\ KCl\ G} = \frac{0.002788}{0.006} = 0.46$ cm^{-1}

$Conductivity\ of\ given\ \mathrm{AgNO3}\ soln\ k = GK_{cell} = 0.012\ X\ 0.46 = 0.0055$ $ohm^{-1}cm^{-1}$.



PBLM: Imagine that you have 1 ml of solution that contains 1 gram equivalent (Equivalent weight in grams) of an electrolyte and the conductance is 0.100 μS. If the solution is diluted to 9ml, what will be the conductance, specific conductance and equivalent conductance of the diluted solution?

Soln: hint

If the solution is diluted to say (9 cm3) (9 mL), the conductance of the solution will be the same but specific conductance becomes 1/9th as it contains nine cubes.

PBLM: **A column of diameter 1 cm and length 50 cm filled with 0.05 M NaOH. The resistance of the solution is found to be 5.55 x 10^3 ohm. Calculate its resistivity, conductance and conductivity. Hint Area = πr^2**

$A = \pi r^2 = 3.14 \times (0.5)^2\ cm^2 = 0.785\ cm^2$

$l = 50\ cm$

$$R = \frac{\rho l}{A} \ OR\ \rho = \frac{RA}{l}$$

$$= \frac{5.55 \times 10^3\ \Omega \times 0.785\ cm^2}{50\ cm}$$

$$= 87.135\ \Omega\ cm$$

$$Conductivity = k = \frac{1}{\rho} = \left(\frac{1}{87.135}\right) Scm^{-1}$$

$$= 0.01148S\ cm^{-1}$$

$$Molar\ conductivity;\ \Lambda_m = \frac{k \times 1000}{c}\ cm^3 L^{-1}$$

$$= \frac{0.01148\ S\ cm^{-1} \times 1000\ cm^3 L^{-1}}{0.05\ mol\ L^{-1}}$$

$$= 229.6\ Scm^2\ mol^{-1}$$