17. GAS CHROMATOGRAPHY (GC)

- ☞ Introduction
- ☞ Principle of Separation
- ☞ Criteria for analysis by GC - Volatility and Thermostability
- ☞ Practical Requirements
  - ☆ Carrier gas - H_2, He, N_2
    - Flow regulators and flow meters
      - Rotameter & Soap bubble meter
    - Injection devices
    - Columns
      - Analytical and Preparative type
      - Packed, Open tubular, SCOT columns
    - Temperature control devices
      - Isothermal and Linear programming
    - Detectors
      - Thermal Conductivity detector
      - Flame Ionisation detector
      - Argon Ionisation detector
      - Electron Capture detector
    - Recorders and integrators
- ☞ Derivatisation of sample - Precolumn & Post column
- ☞ Pretreatment of solid support
- ☞ Parameters used in GC
  - ☆ Retention time, Retention volume, Separation factor Resolution, Theoretical plate, Efficiency, Asymmetry factor
- ☞ Applications of Gas Chromatography

Scanned with CamScanner

INTRODUCTION

Gas chromatography consists of Gas Solid Chromatography (GSC) and Gas Liquid Chromatography (GLC). In both types, gas is used as mobile phase and either solid or liquid is used as stationary phase.

GSC is not widely used because of limited number of stationary phases available. In **GSC**, the principle of separation is ***adsorption***. GSC is used only in case where there is less solubility of solutes in stationary phase, which is rare. Therefore ***all*** the ***discussions in this chapter*** refers to ***GLC*** technique ***only***.

PRINCIPLE OF SEPARATION

The principle of separation in ***GLC*** is ***partition***. ***Gas*** is used as ***mobile phase***. ***Liquid*** which is ***coated on*** to a ***solid*** support is used as ***stationary phase***. The mixture of components to be separated is converted to vapour and mixed with gaseous mobile phase. The component which is more soluble in the stationary phase travels slower and eluted later. The component which is less soluble in the stationary phase, travels faster and eluted out first. No two components has the same partition co-efficient for a fixed combination of stationary phase, mobile phase and other conditions. Hence the ***components are separated according to*** their ***partition co-efficients***. (***Partition co-efficient*** is the ratio of solubility of a substance distributed between two immiscible liquids at a constant temperature)

CRITERIA FOR COMPOUNDS TO BE ANALYSED BY GAS CHROMATOGRAPHY

Two important criteria are

1. **Volatility:** Unless a compound is volatile, it cannot be mixed with mobile phase. Hence volatility is important.

2. **Thermostability:** All the compounds will not be in the form of vapour. There will be solid as well as liquid samples. Hence to convert them to a vapour form, they have to be heated to a higher temperature. At that temperature, the compounds have to be thermostable. If they are not thermostable, the compounds cannot be analysed by Gas chromatography, since they will be decomposed.

PRACTICAL REQUIREMENTS

1. Carrier gas
2. Flow regulators and flow meters
3. Injection devices
4. Columns
5. Temperature control devices
6. Detectors
7. Recorders and Integrators

Gas Chromatographic Apparatus

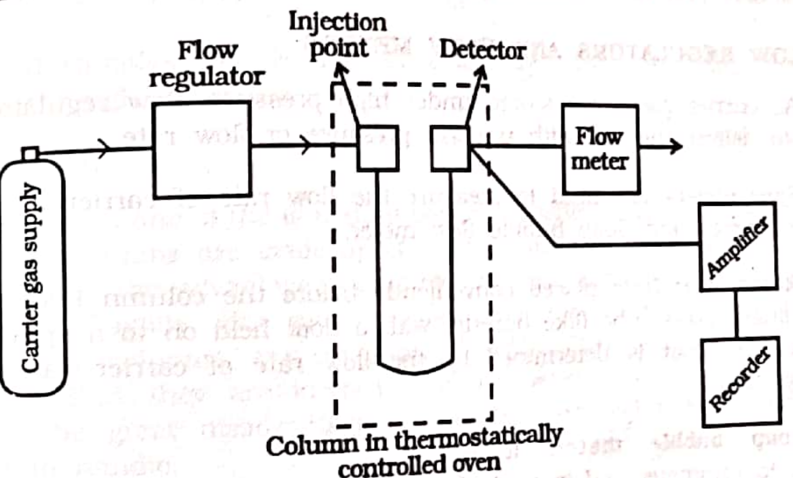


Fig 17.1. Gas chromatographic apparatus

1. CARRIER GAS

The choice of carrier gas determines the efficiency of chromatographic separation. Most widely used carrier gases are Hydrogen, Helium, Nitrogen and Argon.

Hydrogen: It has better thermal conductivity, low density. It is useful in case of thermal conductivity detector and flame ionisation detector. The disadvantage is that it reacts with unsaturated compounds and it is inflammable.

Helium: It also has excellent thermal conductivity, but it is expensive. It is a good carrier gas when used with thermal conductivity detector.

Nitrogen: It is inexpensive but has reduced sensitivity.

Scanned with CamScanner

Requirements of a carrier gas: 1. Inertness, 2. Suitable to the detector used, 3. High purity, 4. Easily available, 5. Cheap, 6. Less risk of explosion or fire hazards, 7. Should give best column performance consistent with the required speed of analysis.

Considering these requirements, and a compromise among inertness, efficiency and operating cost, etc make Nitrogen and Helium as the most common carrier gas.

As carrier gas is compressible, gases are stored under high pressure in cylinders and used when required.

2. FLOW REGULATORS AND FLOW METERS

As carrier gases are stored under high pressure, flow regulators are used to deliver the gas with uniform pressure or flow rate.

Flow meters are used to measure the flow rate of carrier gas. They are Rotameter and Soap bubble flow meter.

Rotameter: It is placed conveniently before the column inlet. It has an ordinary glass tube (like burette) with a float held on to a spring. The level of the float is determined by the flow rate of carrier gas and is precalibrated.

Soap bubble meter: It is similar to rotameter and instead of a float, soap bubble formed indicates the flow rate. It has a glass tube with a inlet tube at the bottom through which gas comes in. A rubber bulb is used to store soap solution. When the bulb is gently pressed, a drop of soap solution is converted into a bubble by the pressure of carrier gas and travels up. The distance travelled upwards is a measure of flow rate of carrier gas. The graduations are also precalibrated.

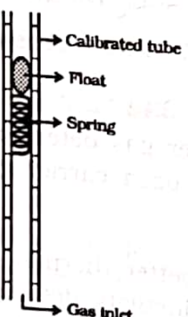


Fig 17.2. Rotameter

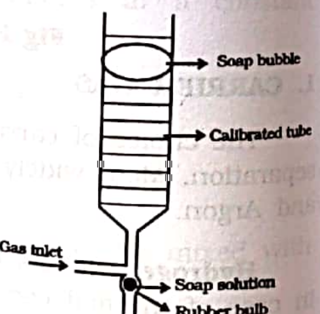


Fig 17.3. Soap bubble meter

3. INJECTION DEVICES

Samples for introducing into the column can be of any type i.e., either gas, liquid or solid in nature.

Gases can be introduced into the column by valve devices.

Liquids can be injected through loop or septum devices. Most GC instruments have a high quality rubber septum through which sample solution is injected. The rubber is made up of good quality silicone rubber, which can withstand high temperature of preheating device and withstand repeated injections over a period of time.

Solid samples are dissolved in a suitable solvent and then they are injected through a septum.

4. COLUMNS

Column is one of the important part of GC which decides the separation efficiency. Columns are made up of glass or stainless steel. Stainless steel columns have the advantage of long life and can be easily handled without the fear of fragility. But some samples react with them. Hence in such cases, glass columns are used. eg. Steroids. Glass columns have the advantage that they are inert and do not react with the any kind of sample. The great disadvantage is that they are highly fragile and are difficult to handle.

Columns can be classified according to the nature as well as its use.

A. Depending on its use

i. **Analytical column:** Analytical columns have a length of 1 - 1.5 metres and an outer diameter of 3 - 6 mm. They are packed columns and are made up of glass or stainless steel. Only small quantity of samples can be loaded on to the column.

ii. **Preparative column:** Preparative columns are larger when compared to analytical columns since large amount of sample has to be loaded. They have a length of 3 - 6 metres and outside diameter of 6 - 9mm.

Scanned with CamScanner

B. Depending on its nature

i. **Packed column:** Columns are available in packed manner commercially and hence are called as packed columns. Different columns ranging from low polar nature to high polar nature are available. Examples of such columns, operating temperature, applications of such columns are given in the following table.

Stationary phases for GLC: A wide variety of stationary phases like Polyethylene glycols, high molecular weight esters, amides, hydrocarbons, polysiloxanes, microporous cross-linked polyaromatic beads.

Stationary phase	Nature	Temperature maximum in use
Polydimethyl siloxane	Non-polar	-60° to 320°C
Poly(diphenyl)dimethyl siloxane	Non-polar bonded phase	-60° to 320°C
Polycyano propyl phenyl dimethyl siloxane	Intermediate polarity	upto 280°
Polyalkylene glycol	Polar	30° to 220°C
Polyethylene glycol	Polar	50° to 280°C
PEG modified with Nitroterephthalic acid	Polar bonded phase	60° to 200°C
Poly bis cyano propyl siloxane	Very polar Non-bonded phase	upto 250°C

ii. **Open tubular column or capillary column or Golay column:** They are made up of long capillary tubing of 30 - 90 metres in length and have uniform and narrow internal diameter of 0.025 - 0.075 cm. These are made up of stainless steel and are in the form of a coil. The inner wall of the capillary is coated with the stationary phase liquid in the form of a thin film (0.5 to 1μ). These columns offer least resistance to the flow of carrier gas and hence they are more efficient than packed columns which offer more resistance to the flow of carrier gas. But the disadvantage is that more sample cannot be loaded.

iii. **SCOT columns (Support Coated Open Tubular Column):** This is an improved version of Golay or capillary columns. As Golay or capillary columns have small sample capacity, they can be modified into SCOT columns.

These columns are made by depositing a micron size porous layer of support material on the inner wall of the capillary column and then coated with a thin film of liquid phase. These columns also have low resistance to the flow of carrier gas but offers the advantage of more sample load or capacity.

5. TEMPERATURE CONTROL DEVICES

Preheaters: Preheaters are used in Gas chromatography to convert the sample into its vapour form and mix them with the mobile phase or carrier gas. The preheaters are present along with injecting devices. As soon as liquid samples are injected, they are converted into vapour form.

Thermostatically controlled oven: The principle of separation in Gas chromatography is partition. Partition co-efficient is the ratio of concentration of a solute distributed between two immiscible liquids. Since ***partition co-efficient*** as well as solubility of a solute ***depends upon temperature, temperature maintenance*** in a column ***is highly essential*** for efficient separation. Hence the column as well as injecting devices should be maintained at a particular temperature.

As columns are long, they cannot be enclosed in oven easily. Hence the columns are in a coiled form and enclosed in thermostatically controlled oven. These ovens are highly accurate and can maintain temperature nearest to 0.1°C.

Two types of operations are available. They are

i. **Isothermal programming:** (Iso means same) in which the ***same*** temperature is ***maintained throughout*** the process of separation.

ii. **Linear programming:** in which the oven is heated ***linearly over*** a ***period of time***. eg. 150°C initially to 200°C at the end of separation with an increase in temperature at the rate of 5°C/minute. This type of linear programming is required when a sample has a mixture of low boiling and high boiling point compounds. This method is efficient for separation of such complex mixtures.

6. Detectors

Detectors are the most important part of gas chromatographic instruments. They are considered as heart of the apparatus. A detector

Scanned with CamScanner

uses some property by which it can detect the difference between a pure carrier gas and a eluted component.

The requirements of an ideal detector are:

i. Applicability to wide range of samples.

ii. High Sensitivity to even small concentrations.

iii. Rapidity of response.

iv. Linearity: i.e. less response to low concentration and proportional response to high concentration.

v. Response should be unaffected by temperature, flow rate or characteristics of carrier gases.

vi. Non destructive to the sample in case of preparative work.

vii. Simple and easy to maintain.

viii. Inexpensive.

The different detectors used commonly are

a. Katharometer or Thermal Conductivity Detector (TCD)
b. Flame Ionisation Detector (FID)
c. Argon Ionisation Detector (AID)
d. Electron Capture Detector (ECD)

a. Katharometer or Thermal conductivity detector

The principle is based upon thermal conductivity difference between carrier gas and that of component (Fig 17.4). Katharometer has two platinum wires of uniform dimensions which form part of Wheatstone bridge. Through one of them, pure carrier gas always flows through and through the other, the effluents

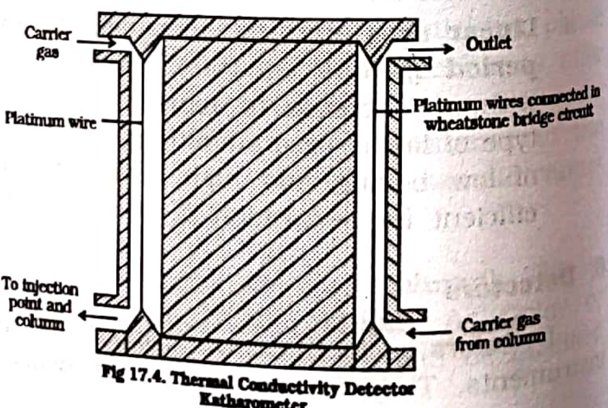


Fig 17.4. Thermal Conductivity Detector Katharometer

of the column passes. The two platinum wires are heated electrically and hence assume equilibrium conditions of temperature and electrical resistance. When pure carrier gas passes through both of them, there is no difference in temperature or resistance and hence a baseline is recorded. When a component emerges from the column, it alters the thermal conductivity and resistance of the wire. Hence this produces a difference in resistance and so conductivity between two wires, which is amplified and recorded as a signal.

The thermal conductivities of some carrier gases are given as follows:

H_2	He	N_2	Methane	Hexane
32.7	33.9	5.2	6.5	3.0

From the tabular column, it can be seen that Hydrogen and Helium have higher thermal conductivity and they are the best carrier gases for Katharometer. Hydrogen is inflammable and helium is expensive. But both of them offer good response. If any other carrier gas is used, they give rise to negative peaks because of lower thermal conductivity.

Advantages of Katharometer

i. Applicable to most compounds.

ii. Linearity is good.

iii. The sample is not destroyed & hence used in preparative scale.

iv. Simple, easy to maintain and inexpensive.

Disadvantages of Katharometer

i. Low sensitivity.

ii. Affected by fluctuations in temperature and flow rate.

iii. The response is only relative and not absolute.

iv. Biological samples cannot be analysed.

Scanned with CamScanner

b. Flame Ionisation detector (FID)

The ionisation detectors are based upon the electrical conductivity of carrier gases. At normal temperature and pressure, gases act as insulators, but become conductive if ions are present.

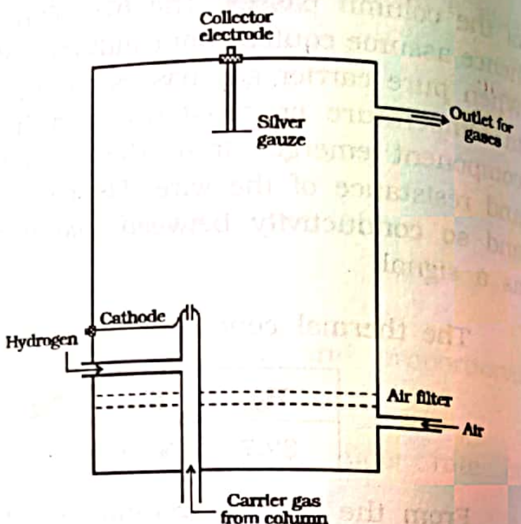


Fig 17.5. Flame Ionisation detector (FID)

The carrier gas used with this type of detector can be hydrogen. If the carrier gas is either nitrogen or argon, it can be mixed with hydrogen and reach the burner tip made up of platinum capillary, which acts as one electrode (Cathode). The anode is silver gauze placed little above the burner tip. When ***pure carrier gas*** alone passes, there is ***no ionisation*** and ***no current*** flows. When a ***component*** emerges from the column, number of ions are produced because of ionisation by the thermal energy of the flame. This causes a potential difference and causes a flow of current which is amplified and recorded as signal (Fig 17.5).

Advantages

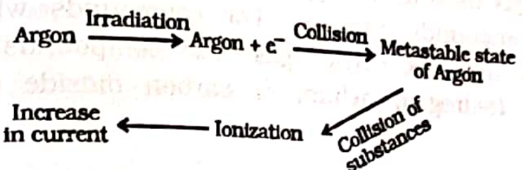
1. This detector is extremely sensitive and background noise is low. Hence µg quantities of the solute can be detected.
2. Stable and insensitive to small changes in the flow rate of carrier gas and water vapour.
3. Responds to most of the organic compounds.
4. Linearity is excellent.

c. Argon Ionisation detector (AID)

This type of detector depends on the exitation of argon atoms to a metastable state, by using radioactive energy. This is achieved by irradiating the carrier gas with either α particles or β particles. α particles can be obtained form radium-D. β particles can be obtained from ^{90}Sr or tritium.

These high energy particles ionise the argon atoms and hence they are exited to metastable state. These molecules collide with the effluent molecules and ionises them. These ions when they reach the detector will cause an increase in current. Thus the compounds can be detected.

The series of events which take place in this detector, is given as follows:



Advantages

1. Responds to most of the organic compounds.
2. Sensitivity is very high.

Disadvantages

1. Response is not absolute and it is relative.
2. Linearity is poor.
3. Sensitivity is affected by water and is much reduced for halogenated compounds.
4. The response varies with the temperature of the detector and for high temperatures like 240°C, voltages of 1000V or less are usually necessary.

d. Electron Capture Detector (ECD)

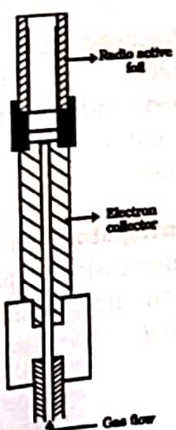


Fig 17.6. Electron capture detector

The electron capture detector (Fig 17.6) has two electrodes, with the column effluent passing between them. One of the electrode is treated with a radioactive isotope which emits electrons as it decays. These emitted electrons produce secondary electrons which are collected by the anode, when a potential of 20V is applied between them. ***When carrier gas*** alone ***flows*** through, ***all*** the secondary ***electrons are collected*** by

Scanned with CamScanner

the positively polarised electrode. Hence a steady **baseline** is recorded. ***Effluent molecules*** which have affinity for electrons, ***capture*** these **electrons** when they pass through the electrodes. Hence the amount of steady state current is reduced. This difference is amplified and recorded as output signal.

The carrier gas used in this type of detector depends upon the electron affinity of the compounds analysed. For compounds with high electron affinity, argon is used as carrier gas. For compounds of low electron affinity, nitrogen, hydrogen, helium or carbon dioxide can be used as carrier gas.

The advantage of this type of detector is that it is highly sensitive. Even nanogram quantities can be detected. But the disadvantage is that it can be used only for compounds with electron affinity. Halogenated compounds, several pesticides, etc can be detected using this type of detector.

Comparison of the Sensitivity of Detectors

Detector	Katharometer	Flame ionisation	Argon ionisation	Electron capture
Minimum detectable concentration % v/v	10^{-6}	10^{-11}	10^{-11}	10^{-12} (For CCl_4)

7. Recorders and Integrators

Recorders are used to record the responses obtained from detectors after amplification, if necessary. They record the baseline and all the peaks obtained, with respect to time. Retention time for all the peaks can be found out from such recordings, but the area of individual peaks cannot be known.

Integrators: Integrators are improved version of recorders with some data processing capabilities. They can record the individual peaks with retention time, height and width of peaks, peak area, percentage of area, etc. Integrators provide more information on peaks than recorders.

DERIVATISATION OF SAMPLE

Derivatisation is a technique of treatment of the sample to improve the process of separation by column or detection by detector. There are two types based upon its need. They are

Precolumn derivatisation: This is done to improve some properties of the sample for separation by column. By this derivatisation technique, the components are converted to more volatile and thermostable derivatives. Moreover improved separation and less tailing will be seen after such treatment.

In the following conditions, pre column derivatisation is done.

1. The component is less volatile.
2. The compounds are thermolabile, i.e. heat sensitive.
3. To reduce tailing.
4. To improve separation factor.

Example: Carboxylic acids, sugars, phenols, alcohols, etc can be converted to less polar compounds by using reagents like BSA reagent (Bis trimethyl Silyl Acetamide reagent).

They can also be converted to acetyl derivative or triflouro acetyl derivative.

Post column derivatisation: Post column derivatisation is done to improve the response shown by detector. The components may not be detected by detector unless derivatisation is done. The components may be converted in such away that their ionisation or affinity towards electrons is increased. Normally this is 'On-Line' detection technique where the flowrate is neither stopped nor altered.

PRETREATMENT OF SOLID SUPPORT

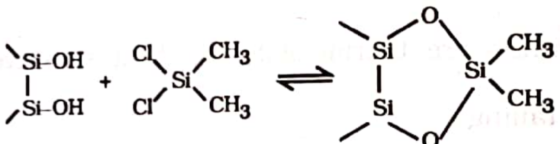
Solid support is used to hold the stationary phase liquid as a thin film. But sometimes due to some defects, uniformity and stability of the film of liquid stationary phase may not exist. In such cases, tailing of peaks and low separation efficiency can be observed. Therefore to overcome such demerits, it is best to do pretreatment of the stationary phase.

Scanned with CamScanner

Generally while doing separation of non-polar components like esters, ethers, etc ***tailing of peaks*** are observed. These problems can be ***overcome*** by the following techniques:

1. By using more polar liquid stationary phase.
2. Increasing the amount of liquid phase on the support.
3. By selecting a less active support.
4. Pretreatment of the solid support to remove active sites.

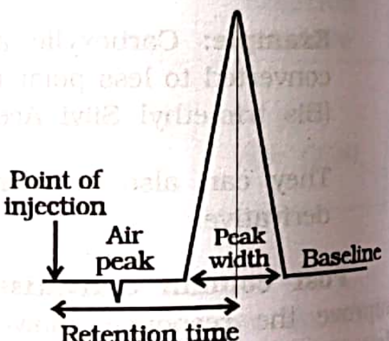
Example: By using hexamethyl disilazone or dimethyl silyl dichloride. This converts the hydroxy groups (polar) to dimethyl group (non-polar) and hence the active adsorption sites are deactivated.



PARAMETERS USED IN GAS CHROMATOGRAPHY

Retention time (R_t)

Retention time is the difference in time between the ***point of injection*** and appearance of ***peak maxima***. Retention time is the time required for 50% of a component to be eluted from a column. Retention time is measured in minutes or seconds. Retention time is also proportional to the distance moved on a chart paper, which can be measured in cm or mm.



Retention volume (V_r)

Retention volume is the volume of carrier gas required to elute 50% of the component from the column. It is the product of retention time and flow rate.

Retention volume = Retention time × flow rate

Separation factor (S)

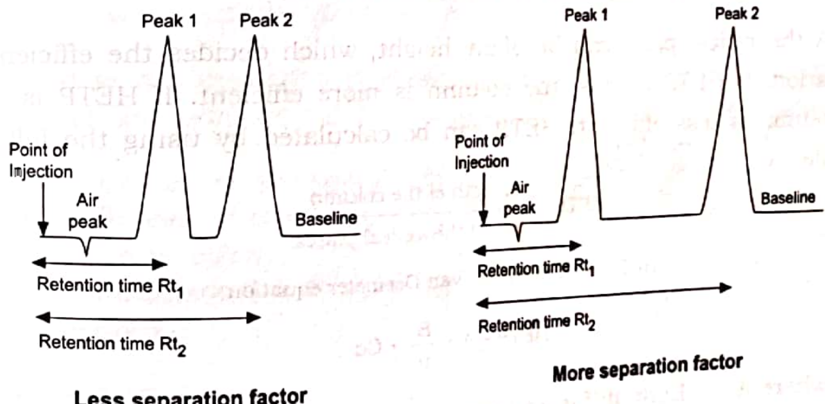
Separation factor is the ratio of partition co-efficient of the two components to be separated. It can be expressed and determined by using the following equation:

$$S = \frac{K_b}{K_a} = \frac{K'_a}{K'_b} = \frac{(t_b - t_0)}{(t_a - t_0)}$$

where

t_0 = Retention time of unretained substance
K_b, K_a = Partition coefficients of b and a
t_b, t_a = Retention time of substance b and a
S = depends on liquid phase & column temperature

If there is more difference in partition coefficient between two compounds, the peaks are far apart and the separation factor is more. If the partition coefficients of two compounds are similar, then the peaks are closer and the separation factor is less.

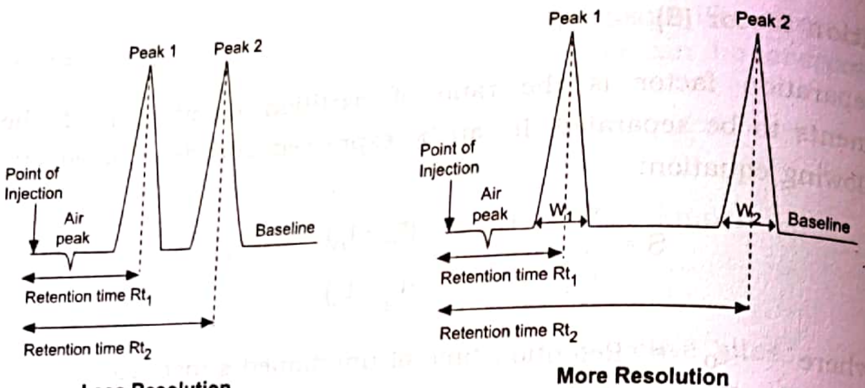


Resolution

Resolution is a measure of the extent of separation of two components and the baseline separation achieved. It can be determined by using the following formula:

$$R_s = \frac{2(Rt_2 - Rt_1)}{W_1 + W_2}$$

Scanned with CamScanner



Theoretical Plate (Plate theory)

A theoretical plate is an imaginary or hypothetical unit of a column where distribution of solute between stationary phase and mobile phase has attained equilibrium. A theoretical plate can also be called as a functional unit of the column.

HETP - Height Equivalent to a Theoretical Plate

A theoretical plate can be ofany height, which decides the efficiency of separation. If HETP is less, the column is more efficient. If HETP is more, the column is less efficient. HETP can be calculated by using the following formula:

$$\text{HETP} = \frac{\text{length of the column}}{\text{no. of theoretical plates}}$$

HETP is given by the Van Deemeter equation

$$\text{HETP} = A + \frac{B}{u} + Cu$$

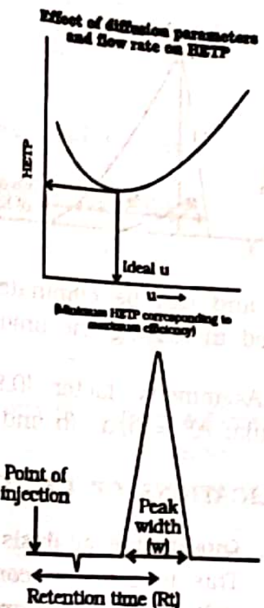
where A = Eddy diffusion term or multiple path diffusion which arises due to packing of the column. This is unaffected by carrier gas velocity or flow rate. This can be minimised by uniformity in packing.

B = Longitudinal diffusion term or molecular diffusion which depends on flow rate.

C = Effect of mass transfer which depends on flow rate

u = Flow rate or velocity of the mobile phase.

The following figure is the effect of flow rate on HETP. A ***column is efficient*** only ***when HETP is minimum***. Hence an ***ideal flow rate*** corresponding to the ***minimum value of HETP is used***.



Efficiency (No. of theoretical plates)

Efficiency of a column is expressed by the number of theoretical plates. It can be determined by using the formula:

$$n = 16\frac{Rt^2}{w^2}$$

where n = no. of theoretical plates

R_t = retention time

w = peak width at base

R_t and w are measured in common units (mm or cm or minutes or seconds) and are proportional to the distances marked on chart paper.

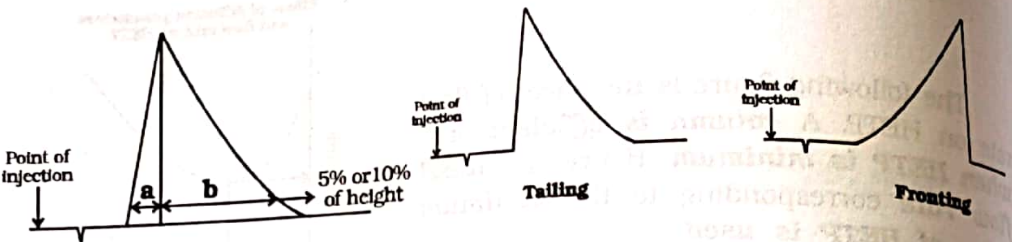
If the number of theoretical plates is ***high***, the ***column is*** said to be ***highly efficient***. If the number of theoretical plates is low, the column is said to be less efficient. For gas chromatographic columns, a value of 600/metre is sufficient. But in HPLC, high values like 40,000 to 70,000/metre are recommended.

Asymmetry factor

A chromatographic peak should be symmetrical about its centre and said to follow Gaussian distribution. In such cases, the peak will be like an isosceles triangle. But in practice, due to some factors, the peak is not symmetrical and shows tailing or fronting as shown in the following figures.

Fronting is due to saturation of stationary phase and can be avoided by using less quantity of sample. ***Tailing*** is due to more active adsorption

Scanned with CamScanner



sites and can be eliminated by support pretreatment, more polar mobile phased increasing the amount of liquid phase.

Asymmetry factor (0.95 to 1.05) can be calculated by using the formula: AF = b/a (b and a calculated at 5% or 10% of the peak height)

APPLICATIONS OF GAS CHROMATOGRAPHY

1. **Qualitative analysis:** It is nothing but identification of a compound. This is done by ***comparing*** the ***retention time*** of the ***sample*** as well as the ***standard***. Under identical conditions, the retention time of the standard and the sample are same. If there is a deviation, then they are not the same compound.

2. **Checking the purity of a compound:** By comparing the chromatogram of the standard and that of the sample, the purity of the compound can be reported. If additional peaks are obtained, impurities are present and hence the compound is not pure. From the percentage area of the peaks obtained, the percentage purity can also be reported.

3. **Presence of impurities:** This can be seen by the presence of additional peaks when compared with a standard or reference material. The percentage of impurities may also be calculated from peak areas.

4. **Quantitative analysis:** The quantity of a component can be determined by several methods like

a. Direct comparison method

By injecting a sample and standard separately and comparing their peak areas, the quantity of the sample can be determined.

Area of the peak = peak height x width of peak at the half height

$$\frac{A_1}{A_2} = \alpha \frac{W_1}{W_2}$$

where A_1 and A_2 are peak area of sample and standard

W_1 and W_2 are weight or concentration of sample and standard

α is the response factor

b. Calibration curve method

In calibration curve method, standards of varying concentrations are used to determine their peak areas. A graph of peak area Vs concentration of the drug is plotted. From the peak area of the unknown sample, by intrapolation, the concentration of the sample can be determined. This method has the advantage that errors, if any are minimised.

c. Internal standard method

In this method, a compound with similar retention characteristics is used. A known concentration of the internal standard is added separately to the standard solution and sample solution whose concentration is not known. The chromatogram is recorded and the peak area ratio of standard and internal standard is determined. By using the peak area ratio of sample and internal standard, the concentration of the unknown solution is determined. This method is useful when more extraction steps are involved in sample preparation and the sample matrix is complex.

5. Multicomponent analysis or Determination of mixture of drugs:

   Similar to the quantification of a single drug, multicomponent analysis can also be done easily. The quantity of each component is determined by using any one of the above methods. Marketed formulations are available which contain several drugs and each component can be determined quantitatively.

6. Isolation and identification of drugs or metabolites in urine, plasma, serum etc can be carried out.

7. Isolation and identification of mixture of components like amino acids, plant extracts, volatile oils, etc.

Scanned with CamScanner

Some of the pharmaceutical applications are described below:

1. Purity of compounds

Drug	Column	Temperature	Internal Standard
Atropine sulphate tablets	Phenylmethyl silicone	230°	Homatropine hydrobromide
Fenfluramine tablets	Carbowax 20 (10%) KOH (2%)	200°	n-tetradecane
Scopolamine hydrobromide	Phenylmethyl silicone	230°	Atropine sulphate

2. Presence of foreign or related substances

Drug	Purpose	Column	Temp	Internal Standard
Ethyloestrenol tablets	17α-ethylestran-17β-ol	Phenylmethyl silicone	200°	Arachidic alcohol
Cimetidine	Residual solvent	Porapak Q	135°	n-Butyl alcohol
Tranylcypromine sulphate tablets	Cis isomer	OS 124 (10%)	220°	4-bromo aniline HCl
Novobiocin sodium	Residual solvent	Polyethylene glycol (10%)	100°	Propanol

3. Assay of drugs

Drug	Column	Temperature
Diphenhydramine HCl	Carbowax	230°
Antazoline HCl	Carbowax	230°
Triprolidine HCl	Carbowax	230°
Trifluoro acetyl methyl esters of amino acids Alanine Valine Glycine	Neopentyl glycol succinate	137°

Scanned with CamScanner