Gas Chromatography

Gas chromatography is a chromatographic technique of separating volatile or gaseous substances by using gas as a mobile phase.

Presence of components (such as carbon monoxide, hydrocarbon etc.) in very small concentration can be detected by gas chromatography.

Theory and Principle of Gas Chromatography

Gas chromatography is one of the most popular method for separating and analyzing sample. In this technique sample is converted to vapor state and injected on stationary phase of chromatography, inert gas can act as mobile phase

The separation in GLC depends on the relative distribution (partition) of sample components between the stationary liquid phase and mobile gas phase.

Gas Chromatography

Theory and Principle of Gas Chromatography

1) Gas liquid Chromatography (GLC)

When stationary phase is non volatile liquid coated on inner support and the mobile phase is gas, then the technique is called as gas liquid chromatography. GLC is a partition type of chromatography

2) Gas Solid Chromatography (GSC)

When stationary phase is solid of a large surface area and the mobile phase is gas, then the technique is called as gas solid chromatography. Silica gel, alumina, charcoal, molecular sieve etc. are used as a stationary phase.

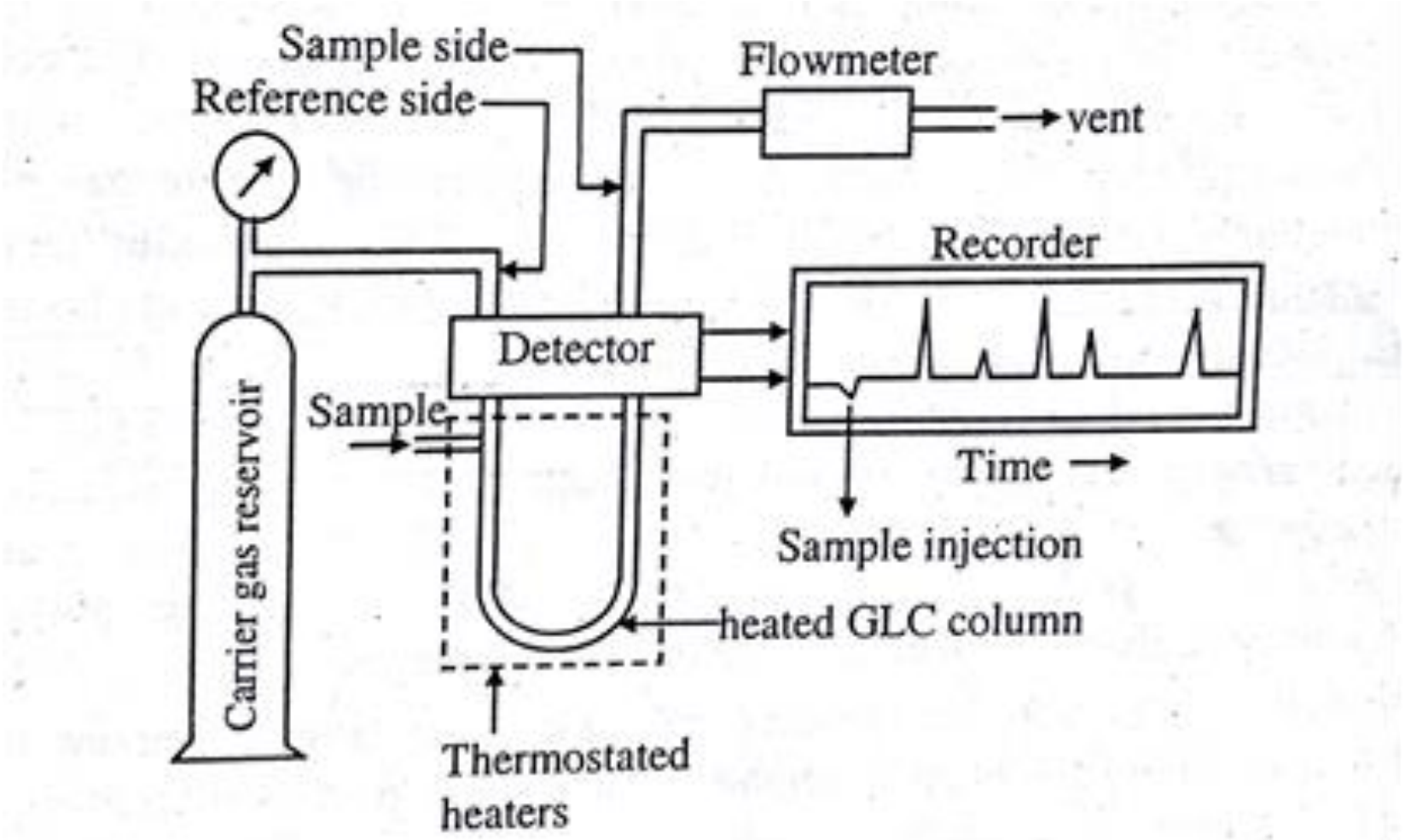
Gas Chromatography

Stationary and Mobile phases in Gas Chromatography:

Stationary phase: Non volatile liquid coated on inner support

Mobile phase: Hydrogen, nitrogen, helium, carbon dioxide and argon are some example of carrier gas (mobile phase) used in GLC

Instrumentation of GLC



Instrumentation parts

1) Carrier gas reservoir
2) Injection port
3) Chromatographic Column
4) Detector
5) Recorder

Instrumentation of GLC

1) Carrier gas reservoir

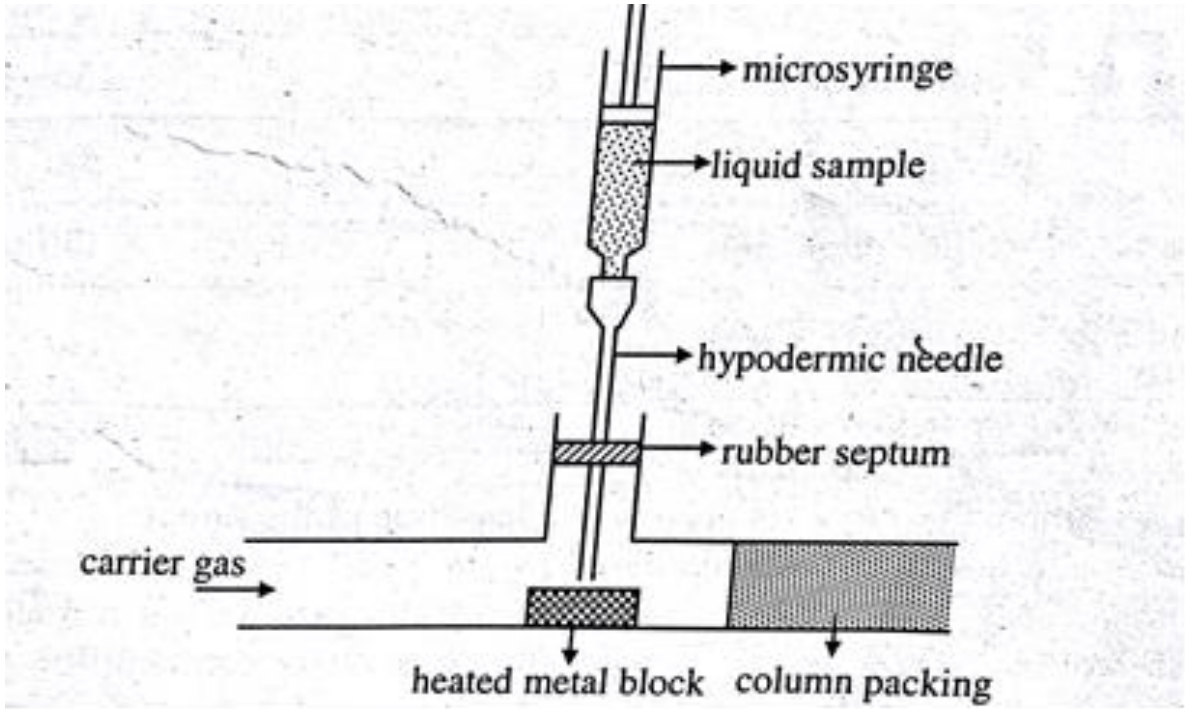
Inert gas like argon, helium, nitrogen may be used as carrier gas. Hydrogen gas is less preferred because of its explosion hazards. Selection of carrier gas depends on the nature of the mixture to be separated, purity required and detector used for the analysis.

The main purpose of the gas in GC is to move the solutes along the column hence; mobile phase is often referred to as carrier gas.

Carrier gas should be

1) Inert
2) Suitable for detector
3) Readily available
4) Have good flow rate
5) Free from fire and explosion hazard

Instrumentation of GLC



2) Injection port

Liquid sample is injected by means of a calibrated micro syringe.

The sample is injected through a rubber septum at the head of the column.

If the sample is gaseous then 1 to 10 ml is injected while for liquid sample 0.1 to 10 micro liter is injected.

At the temperature of the injection port liquid sample is readily converted to vapors without decomposition.

Instrumentation of GLC

3) Chromatographic Column:

This is the backbone of chromatography. Column is made up of stainless still or glass and is 2 to 3 meter long and have internal diameter 2 to 4 mm.

Types of column

a) Packed column

It is made up of Teflon having internal diameter 2 to 4 mm and length 5 meter. Column is packed with finely divided solid as absorbent in gas solid chromatography.

b) Capillary column

These columns are 15 meters to 100 meter long and have internal diameter less than 1 mm (i.e., 0.25 to 0.30 mm). This column does not contain packing but contain stationary phase coated on their inner wall.

Instrumentation of GLC

i) Wall coated open tubular column (WCOT Column)

The columns which have a liquid stationary phase coated on a wall of capillary are called wall coated open tubular column (WCOT Column).

ii) Support coated open tubular column (SCOT Column)

The column in which liquid stationary phase is deposited on solid support (i.e., inner wall of the column) is called Support coated open tubular column (SCOT Column)

Stationary phase

Solid stationary phase

Alumina, Carbon black, Silica gel, porous polymer etc.

Liquid stationary phase

Polyglycols, Paraffin oil, Silicon oil, Dodecyl phthalate, Hydroxy acid etc .

Instrumentation of GLC

4) Detectors used in gas chromatography:

Most commonly used detectors:

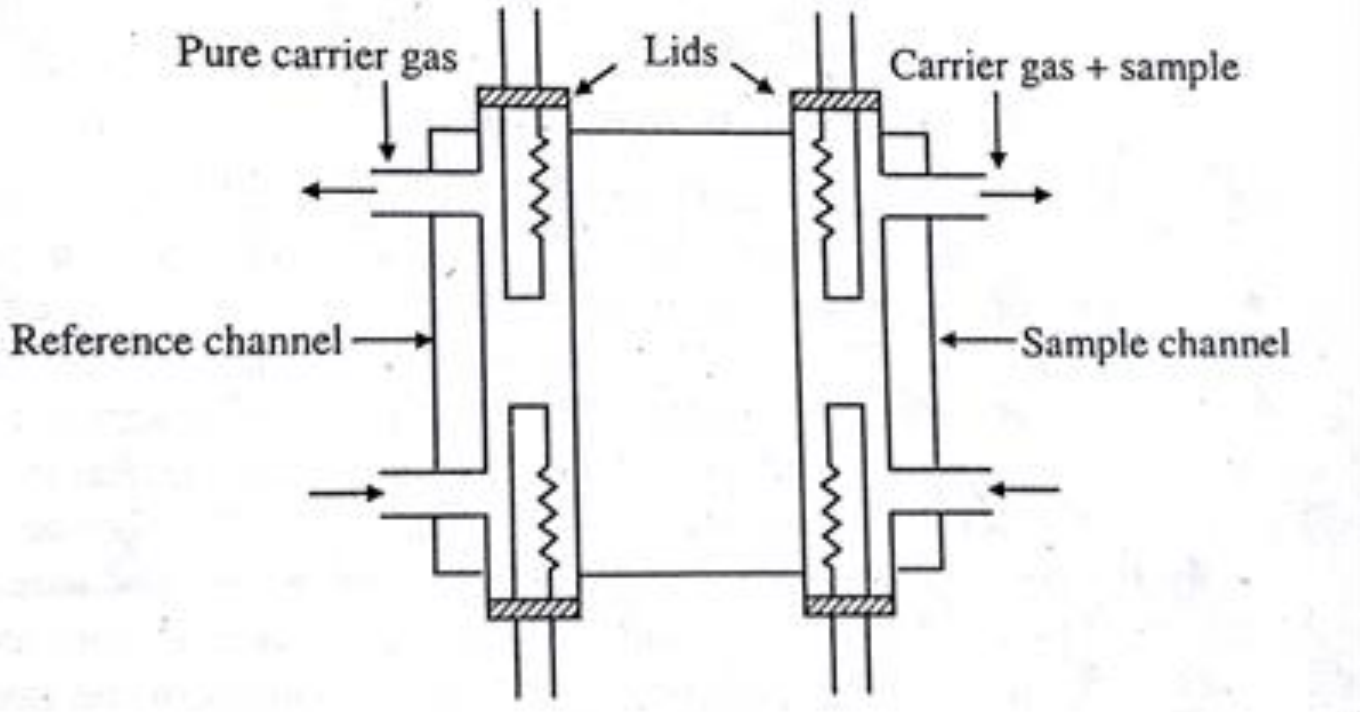
1) Thermal conductivity detector (TCD)
2) Flame ionization detector (FID)
3) Electron capture detector (ECD)

Qualities of good detector

Detector must have following properties

1) Good sensitivity
2) Stability
3) Selectivity
4) Linearity
5) Easy to use

Thermal Conductivity Detector (TCD) or Katharometer

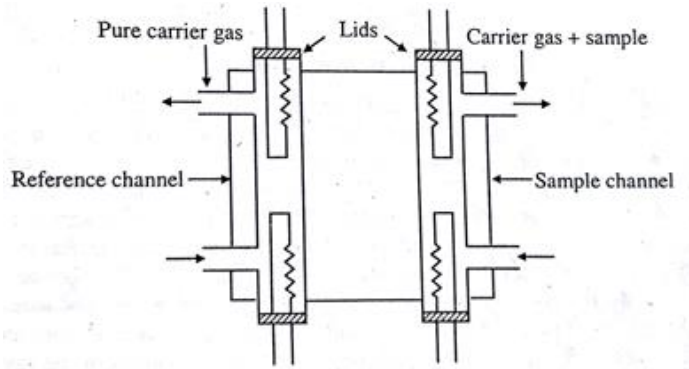


Principal: -

i) As the composition of gas changes the thermal conductivity also changes.

ii) Resistance of wire is the measure of it's temperature.

Thermal Conductivity Detector (TCD) or Katharometer



Construction and working:

Two filaments are connected to two arms of Wheatstone bridge.

Pure gas flow through the one arm of Wheatstone bridge (i.e., reference cell) and effluent (carrier gas + sample) flow through the other arm of Wheatstone bridge (i.e., sample cell)

When only pure gas flow through both arms of Wheatstone bridge then resistance of both filaments is equal and no signal is obtained.

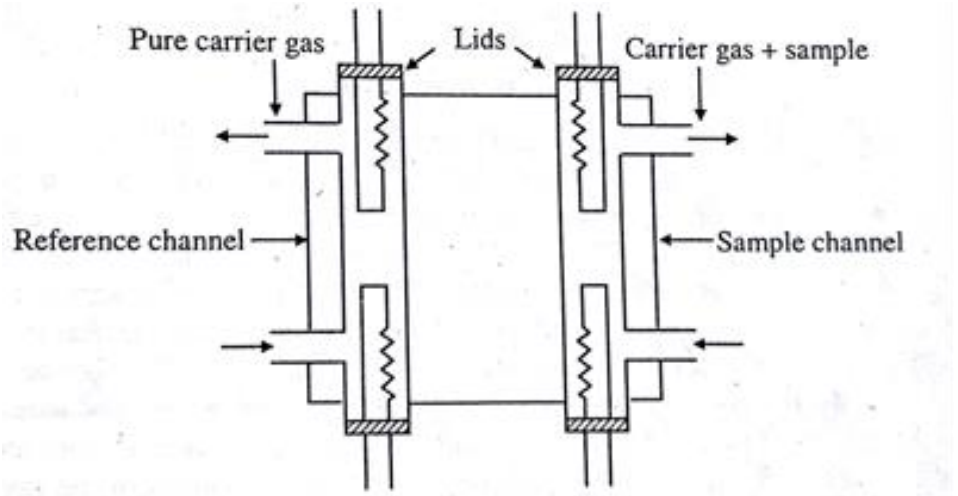
When sample + carrier gas enters in to the sample arm then rate of cooling of filament is different from the reference filament.

Presence of small amount of organic material causes a large decrease in thermal conductivity. The signal is fed to recorder and signal is obtained.

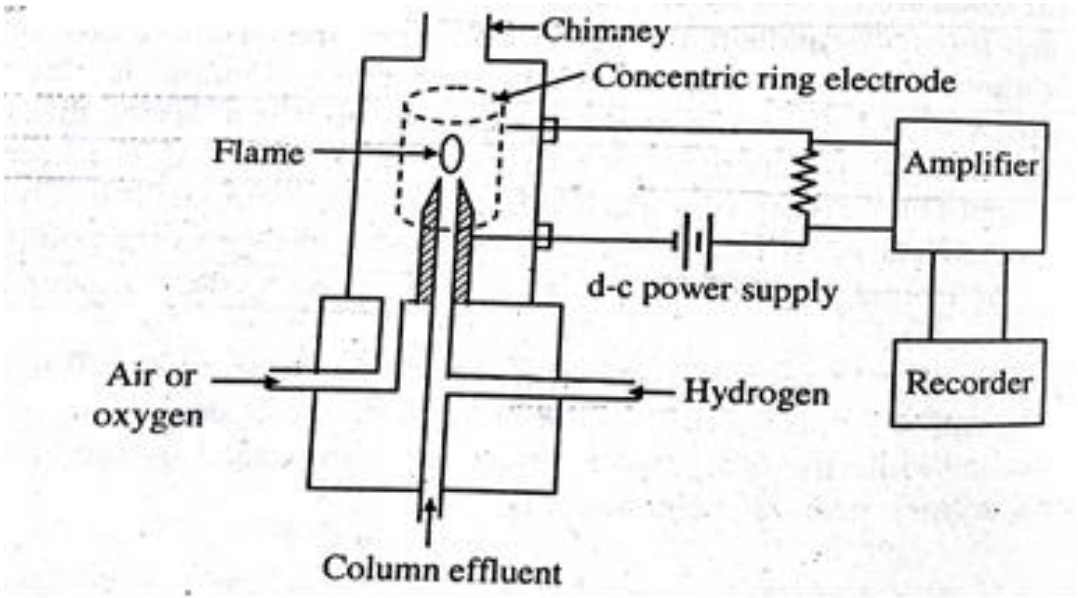
Thermal Conductivity Detector (TCD) or Katharometer

Characteristics of TCD:

1) Simple and accurate
2) Response is reproducible
3) Give response to both organic and inorganic species
4) Nondestructive (i.e., effluent can be collected and reused)



Flame ionization detector (FID)



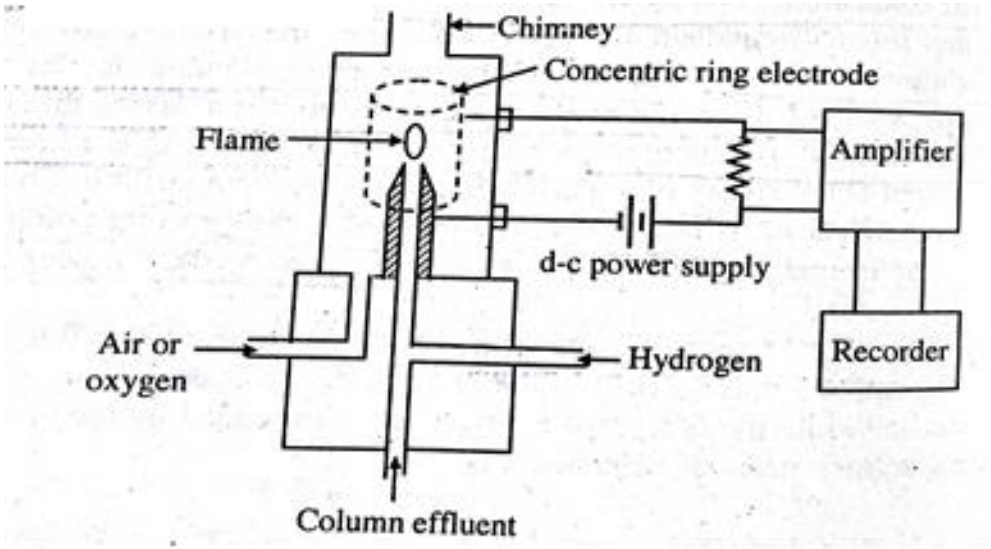
This detector has high sensitivity and selectivity for carbon containing compounds.

Working: -

Column effluent and hydrogen gas are mixed and burned at the tip of the metal jet in presence of oxygen. The flame is surrounded by anode (Collecting electrode) and cathode. A steady potential is maintained across the two electrodes. Due to burning of effluent, ions are produced and collected at the electrodes and resulting ion current is measured.

Selectivity of detector for inorganic compounds containing Nitrogen, Phosphorus and Halogen can be increased by placing KCl or CsBr above the flame. This alkali flame detector is called as Nitrogen-Phosphorus Detector (NPD).

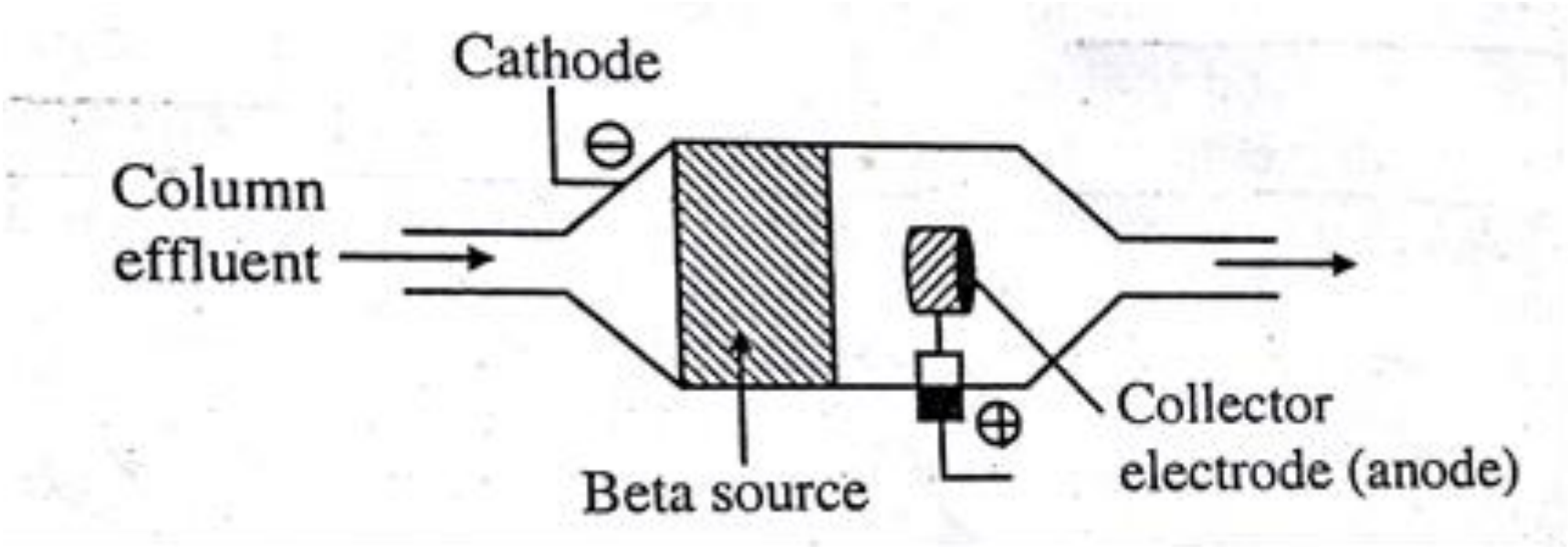
Flame ionization detector (FID)



Characteristics of FID: -

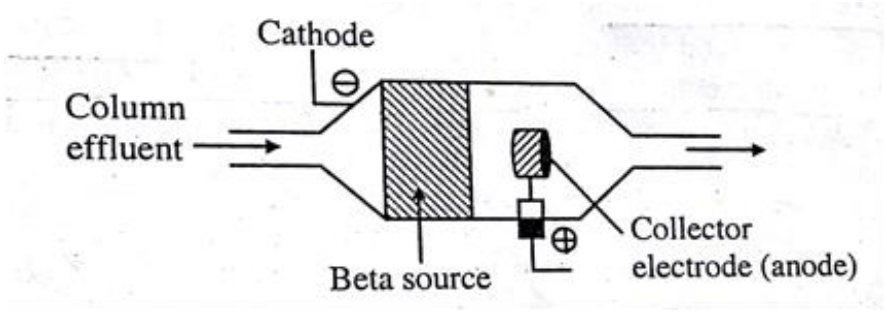
1) This detector is 1000 times more sensitive than Thermal conductivity detector (TCD)
2) It can detect component at ppb (parts per billion) level
3) Fast sensitive and give response to almost all organic compound
4) Not sensitive to inorganic compound
5) It is widely used detector of Gas chromatography.

Electron capture detector



Construction: Detector consists of metal box acting as cathode (negative electrode). Inside this box there is beta (β) emitting source (i.e., ^{3}H or ^{63}Ni). Collector electrode act as anode (Positive electrode).

Electron capture detector



Working: - β- rays ionizes carrier gas as below

N_2 ----------→ $N_2^+ + e^-$

These electrons are captured by anode and definite current is produced. When compound AM (Sample + carrier gas) enter in chamber and combine with electron and produce AM^-, which combine with N_2^+ and produce neutral species and energy.

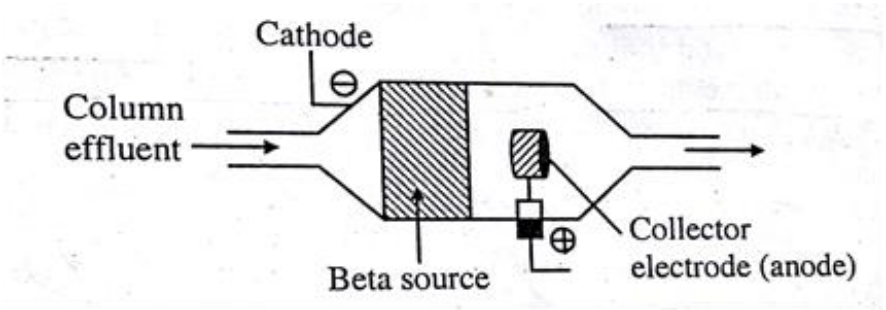
$AM + e^- \text{ ----------→ } AM^- + \text{Energy}$

$AM^- + N_2^+ \text{ ----------→ } AM + N_2$

(Neutral species)

Due to decrease in number of ions, there is decrease in current which is proportional to concentration of component present in effluent.

Electron capture detector



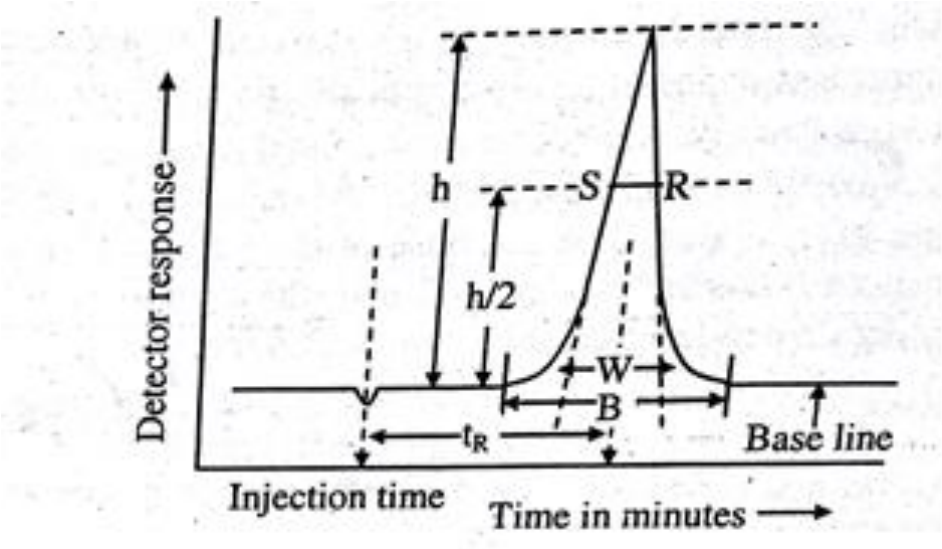
Characteristics

1) Very good detector for electronegative elements.
2) N_2 gas can be used as carrier gas.
3) Give very little response to electropositive elements.
4) Can be used up to 350^0C
5) Less electronegative compounds can be detected by preparing their derivatives.

Working of Gas Chromatography

1) When sample is solid it is converted to liquid form by dissolving in suitable solvent.
2) Sample is injected on hot metal block placed at injection system.
3) The sample, injection port, column and detector are heated to suitable temperature to prevent condensation of sample.
4) The separated components coming out along with mobile gas phase are directly passed in to the detector system for their analysis.
5) Detector response is recorded in the form of chromatogram.

Working of Gas Chromatography



Area under the peak is proportional to the concentration of component.

Area under the peak is given by following equation

Area under the peak = Height of the peak x Width of the peak at half height.

Chromatogram

Plot of the detector response against time is called chromatogram. Number of peaks represents the number of components presents in the sample (mixture).

Separation of component is based on their partition coefficient. The separated component exit along with the mobile phase at the end of the column. These components are then passed through the detector and detector give response to read out device. Magnitude of the response depends upon the concentration of the component.

Working of Gas Chromatography

Example: -

Mixture of four components is analyzed by gas chromatography. Peak area corresponding to component A, B, C, D is 30 cm^2, 15 cm^2, 20 cm^2, 25 cm^2 respectively. Calculate % of each component.

Total peak area = 30 +15 +20 +25 = 90 cm^2

% of component A = (Peak area / Total area) X 100

(30/90) X100

= 33.33%

% of component B = (15 / 90) X 100

= 16.66%

% of component C = (20/ 90) X 100

= 22.22%

% of component D = (25 / 90) X 100

= 27.77%

Retention time (t_R)

The time taken by the sample to come out from the column after it's injection is called retention time.

$t_R = t_2 - t_1$

t_2 = time of elution

t_1 = time of injection

Features of t_R

1) t_R is characteristic of each compound similar to Rf value in TLC.
2) t_R depend on nature of mobile phase, flow rate and temperature of the column.
3) t_R is used for only qualitative analysis of mixture.
4) It depends upon the nature of stationary phase used for preparation of column.
5) Retention time (t_R) = d /chart speed

If flow rate, mobile phase and temperature remain constant and same column is used for analysis then retention time (t_R) for given compound is always same. Hence from t_R value we can identify the components present in mixture.

1) Which of the following is not a feature of carrier gas used in gas chromatography?

a) It must be chemically inert
b) It should be suitable for the detector employed
c) It should not be completely pure
d) It should be cheap

2) Which of the following is the disadvantage of hydrogen, which can be used as carrier gas in gas chromatography?

a) Dangerous to use
b) Expensive
c) Reduced sensitivity
d) High density

3) What must be done to the solid samples for it to be introduced into the column without using solid injection syringes in gas chromatography?

a) Introduced in hot-zone of the column
b) Dissolved in volatile liquids
c) Introduced using rotary sample valve
d) Introduced using sampling loops

4) Capillary columns are open tubular columns constructed from which of the following materials?

a) Glass
b) Metal
c) Stainless steel
d) Fused silica

5) Sample injection port must be maintained at a temperature at which rapid vapourisation occurs but thermal degradation does not occur.

a) True

b) False

6) Which of the following gas is **not suitable** as carrier gas in GC?

a) Nitrogen

b) Helium

c) Oxygen