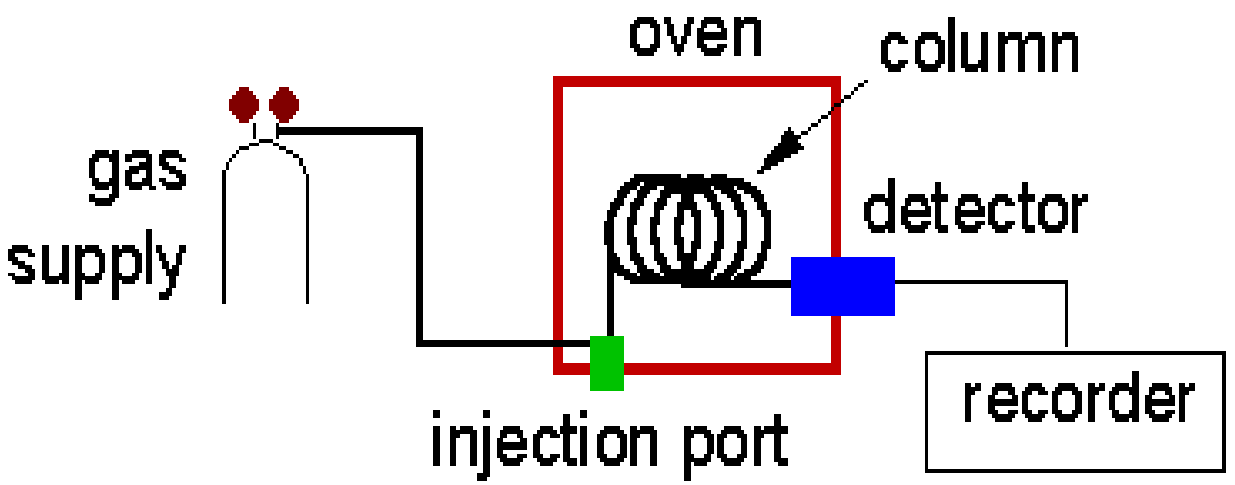
2.4. GAS CHROMATOGRAPHY

Gas Chromatography (GC)

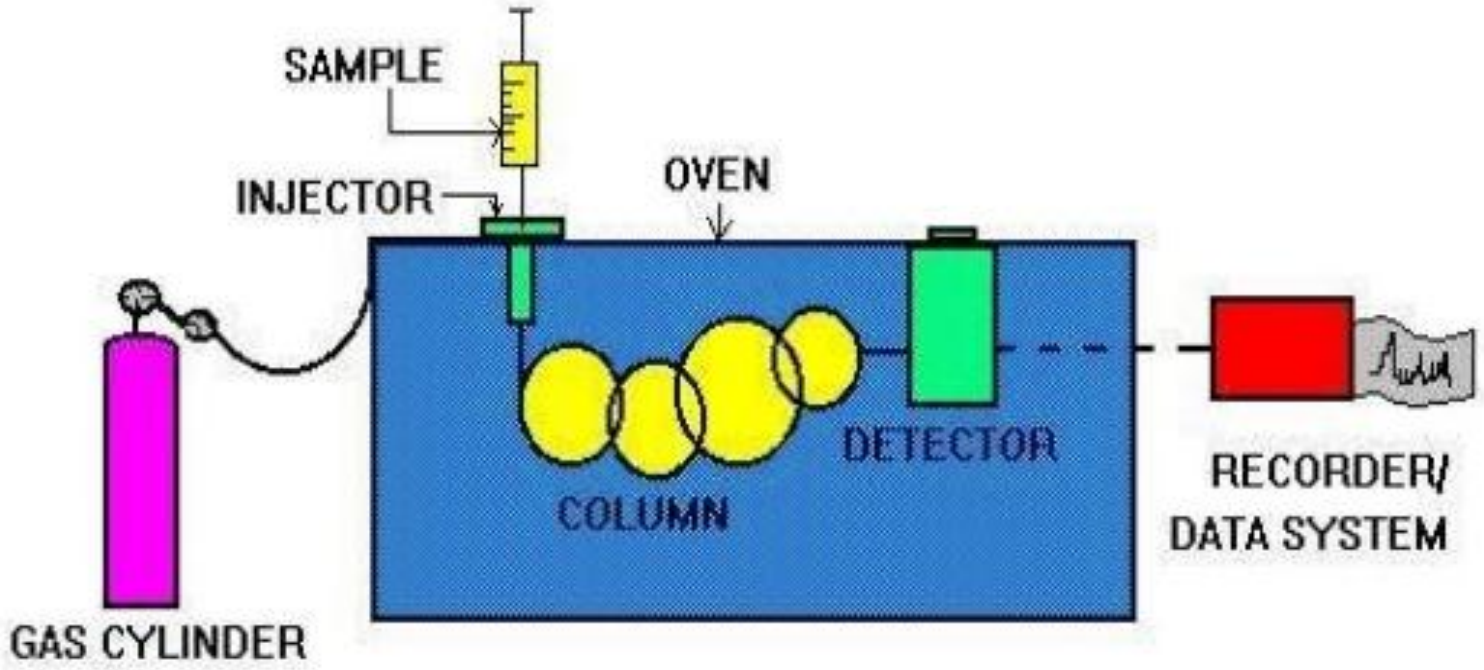
*Gas chromatography is a chromatographic technique that can be used to separate volatile organic compounds.

*It consists of

- ✓a flowing mobile phase -Gas
- ✓an injection port
- ✓a separation column (the stationary phase)-Solid/liquid/
- ✓an oven
- ✓a detector.



GAS CHROMATOGRAPHY




6000 Series


GC-2010 Plus
GAS CHROMATOGRAPH

Principle

The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column.

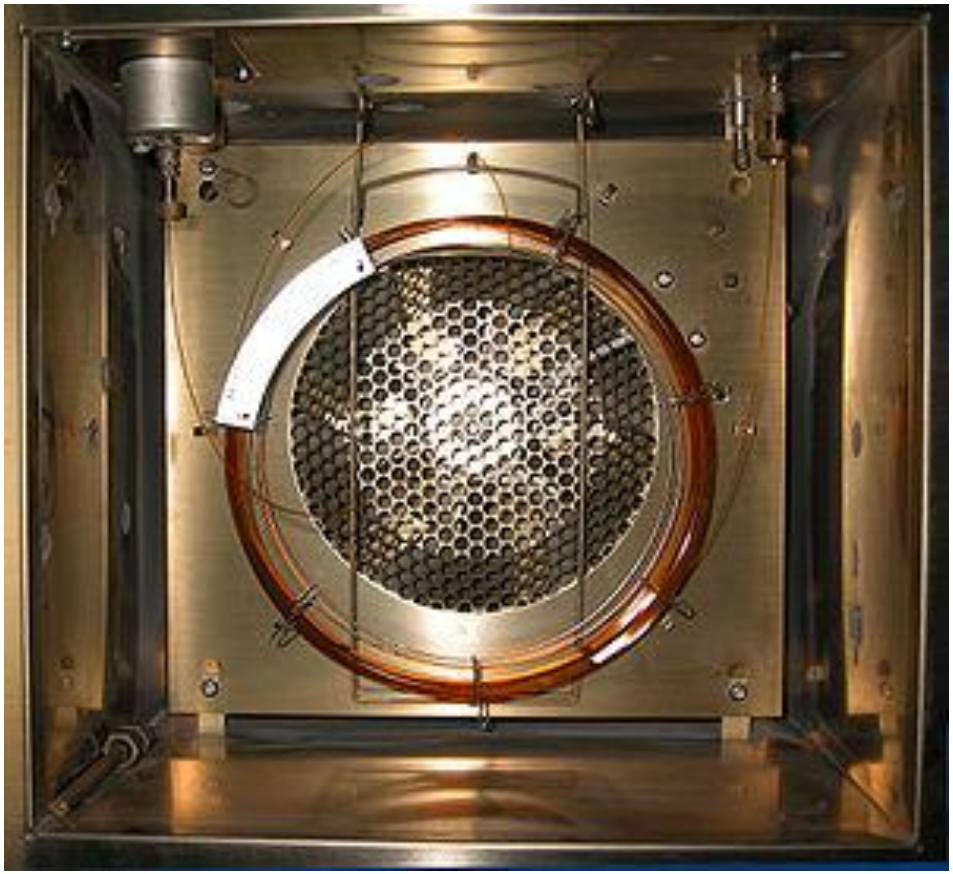
✓Mobile phases are generally inert gases such as helium, argon, or nitrogen.

✓The injection port consists of a rubber septum through which a syringe needle is inserted to inject the sample.

✓The injection port is maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture.

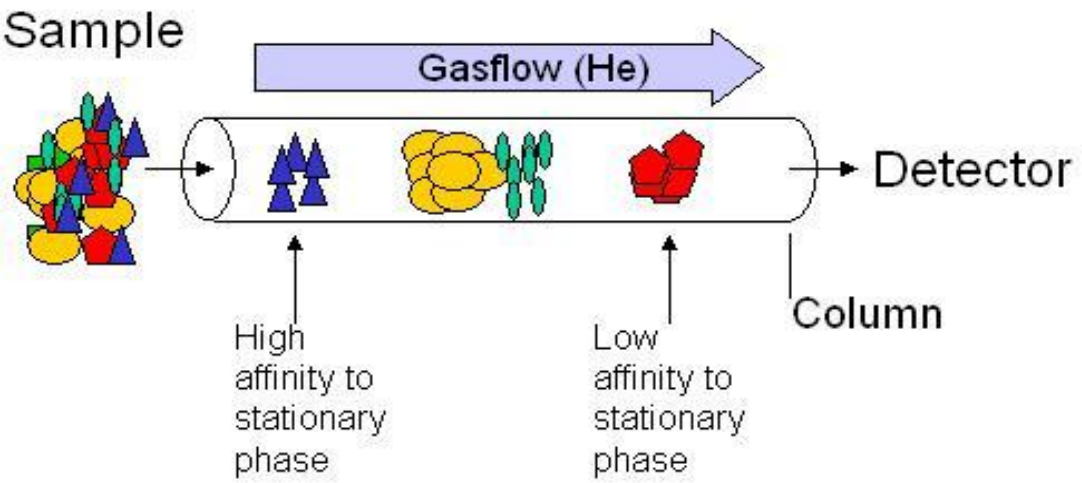
✓Since the partitioning behavior is dependent on temperature, the separation column is usually contained in a thermostat-controlled oven.

✓Separating components with a wide range of boiling points is accomplished by starting at a low oven temperature and increasing the temperature over time to elute the high-boiling point components.

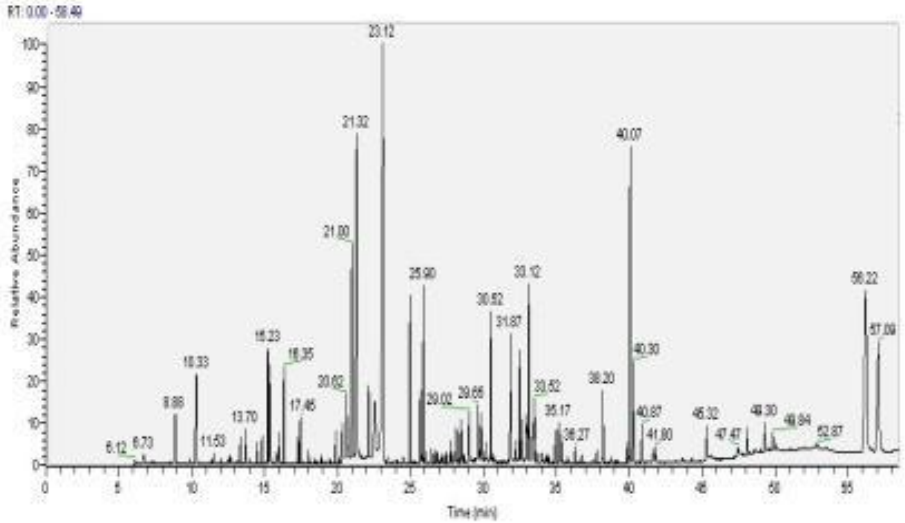


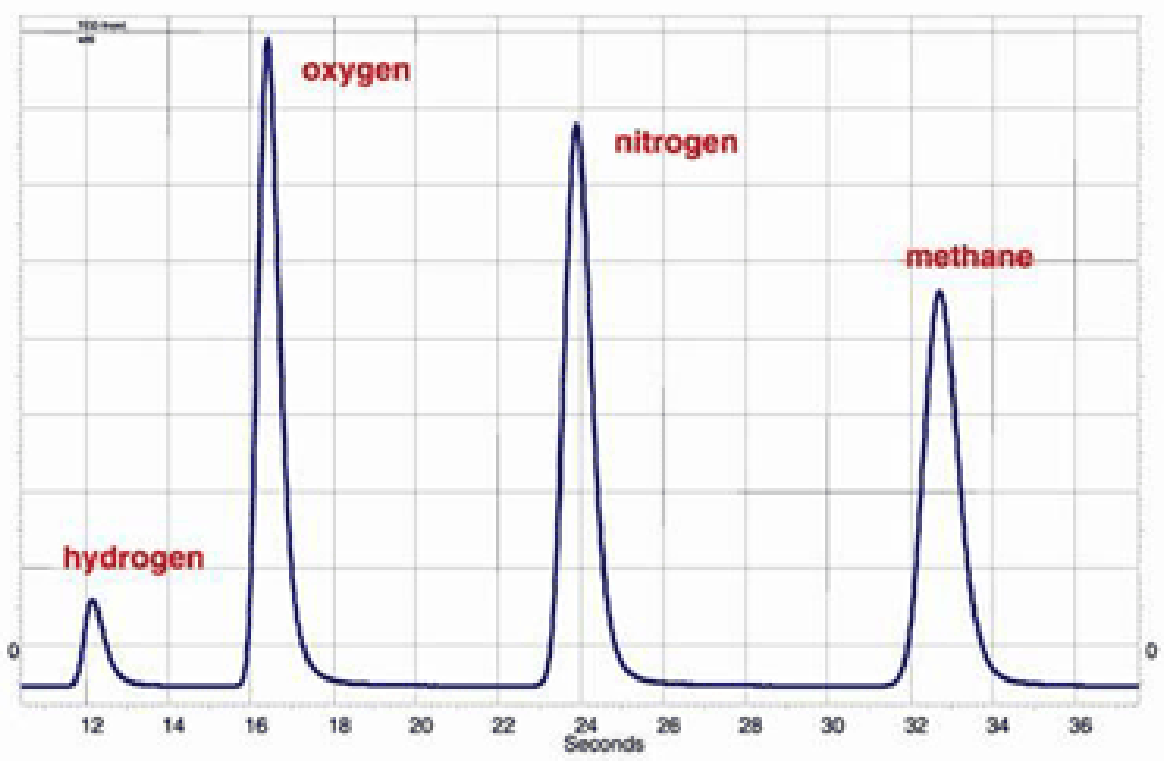
A gas chromatography oven, open to show a capillary column

A


Sample
Gasflow (He)
Detector
Column
High affinity to stationary phase
Low affinity to stationary phase

B


Relative Abundance
Time (min)


oxygen
nitrogen
methane
hydrogen
0
0
12
14
16
18
20
22
24
26
28
30
32
34
36
Seconds

GC Columns

Packed columns

•Typically a glass or stainless steel coil.
•1-5 m total length and 5 mm inner diameter.
• Filled with the stetionary phase or a packing coated with the stetionary phase.

Capillary columns

•Thin fused-silica.
•Typically 10-100 m in length and 250 μm inner diameter.
•Stetionary phase. coated on the inner surface.
•Provide much higher separation eff.
•But more easily overloaded by too much sample.

GC Detectors:

- After the components of a mixture are separated using gas chromatography, they must be detected as they exit the GC column.
- Thermal-conduc. (TCD) and flame ionization (FID) detectors are the two most common detectors on commercial GCs.

The others are:

1. Atomic-emmision detector (AED)
2. Chemiluminescence detector
3. Electron-capture detector (ECD)
4. Flame-photometric detector (FPD)
5. Mass spectrometer (MS)
6. Photoionization detector (PID)

GC Detectors Cont'd

- The requirements of a GC detector depend on the separation application.

E.g.

- An analysis may require a detector selective for chlorine containing molecules.
- Another analysis might require a detector that is non-destructive so that the analyte can be recovered for further spectroscopic analysis. You can not use FID in that case because it destroys the sample totally. TCD on the other hand is non-destructive.

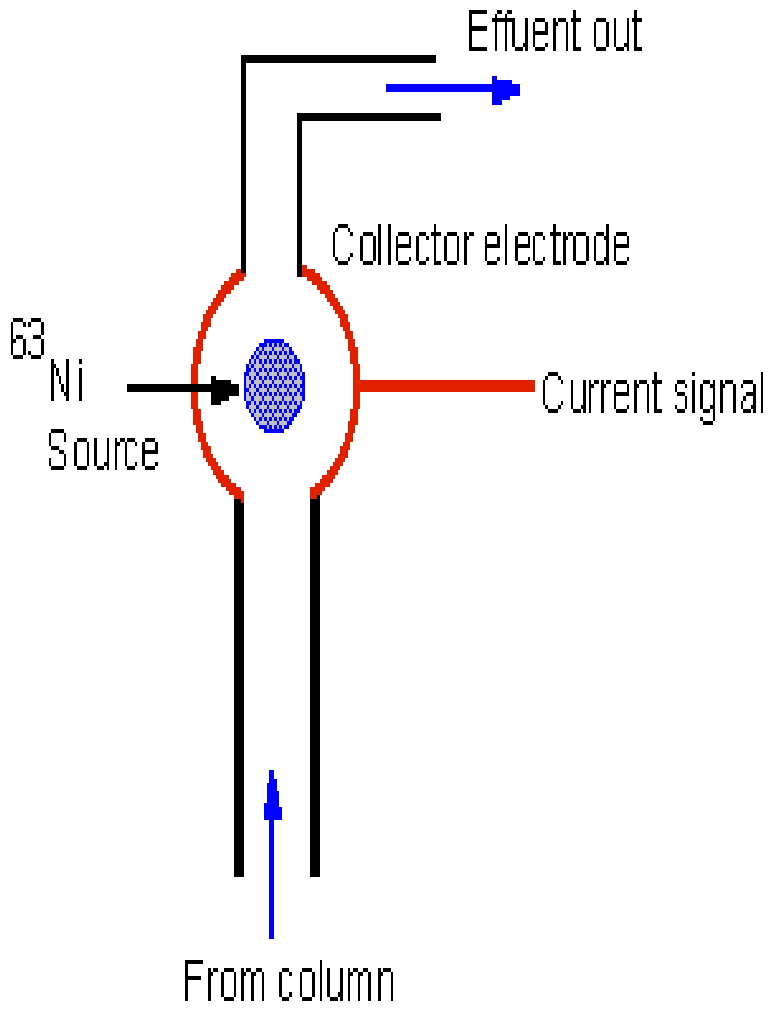
TCD Detector

A TCD detector consists of an electrically-heated wire.The temperature of the sensing element depends on the thermal conductivity of the gas flowing around it. Changes in thermal conductivity, such as when organic molecules displace some of the carrier gas, cause a temperature rise in the element which is sensed as a change in resistance. The TCD is not as sensitive as other detectors but it is non-specific and non-destructive.

ECD Detector

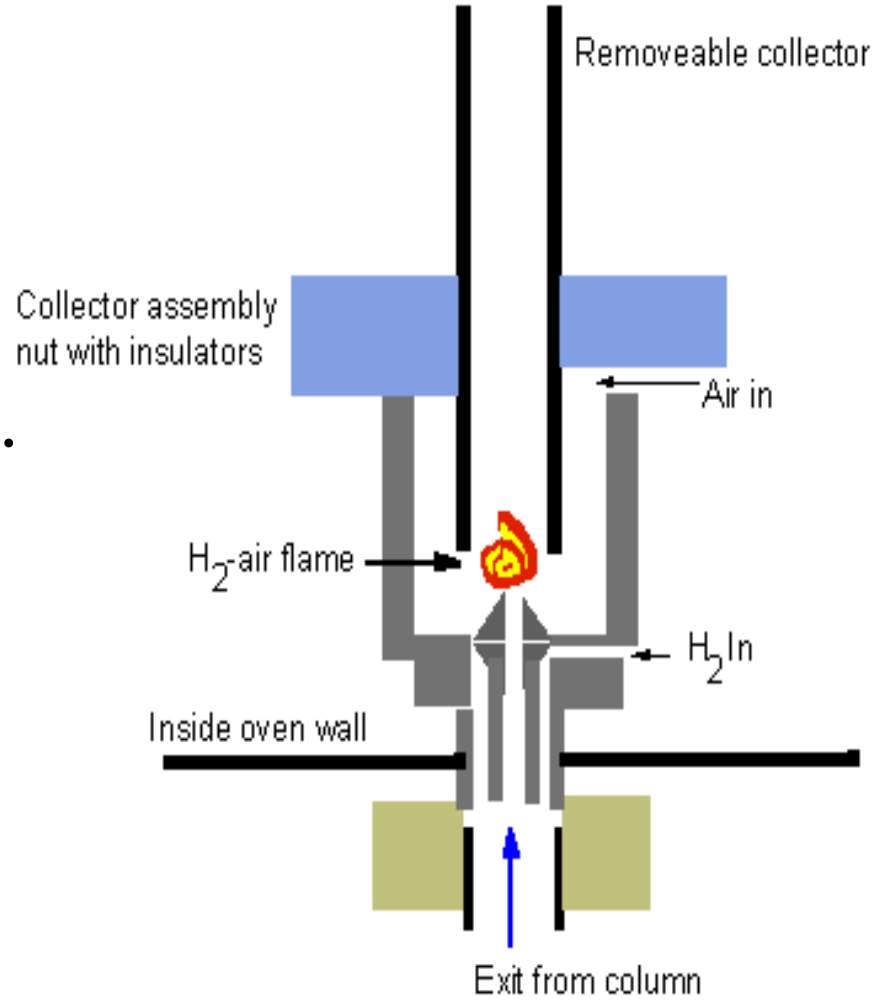
Uses a radiactive Beta emitter (electrons) to ionize some of the carrier gas and produces a current between a biased pair of electrodes.

When an org. mol. that contains electornegative functional gr., such as halojens, phosphorous and nitro groups, pass by the detector, they capture some of the electrons and reduce the current.



FID Detector

- Consists of a hydrogen/air flame and a collector plate.
- The eff. from the GC column passes through the flame, shich breaks down org. mol. and produces ions.
- The ions are collected on a biased electrode and produce an elec. sig.
- Extremely sensitive, large dynamic range.



MS Detector

Uses the difference in mass-to-charge ratio (m/e) of ionized atoms or molecules to separate them from each other.

Molecules have distinctive fragmentation patterns that provide structural information to identify structural components.

The general operation of a mass spectrometer is:

1. create gas-phase ions
2. separate the ions in space or time based on their mass to charge ratio
3. Measure the quantity of ions of each mass-to-charge ratio.

MS Detector Cont'd

The ion separation power of an MS is described by the resolution:

$$R = m/\Delta m$$

Where m is the ion mass and Δm is the difference in mass between two resolvable peaks in a mass spectrum.

E.g., an MS with a resolution of 1000 can resolve an ion with a m/e of 100.0 from an ion with an m/e of 100.1.

❑How a gas chromatography machine works:

- First, a vaporized sample is injected onto the chromatographic column.
- Second, the sample moves through the column through the flow of inert gas.
- **Third**, the components are recorded as a sequence of peaks as they leave the column.

❑Chromatographic separation:

- Deals with both the stationary phase and the mobile phase.
- ✓ **Mobile:** inert gas used as carrier
- ✓ **Stationary:** liquid coated on a solid or a solid within a column.

❑Chromatographic separation:

- In the mobile phase, components of the sample are uniquely drawn to the stationary phase and thus, enter this phase at different time.
- The parts of the sample are separated within the column.
- Compounds used at the stationary phase reach the detector at unique times and produce a series of peaks along a time sequence.
- The peaks can then be read and analyzed by a forensic scientist to determine the exact components of the mixture.
- Retention time is determined by each component reaching the detector at a characteristic time.

❑Chromatographic analysis:

- The number of components in a sample is determined by the number of peaks.
- The amount of a given component in a sample is determined by the area under the peaks.
- The identity of components can be determined by the given retention times.

Peaks and Data

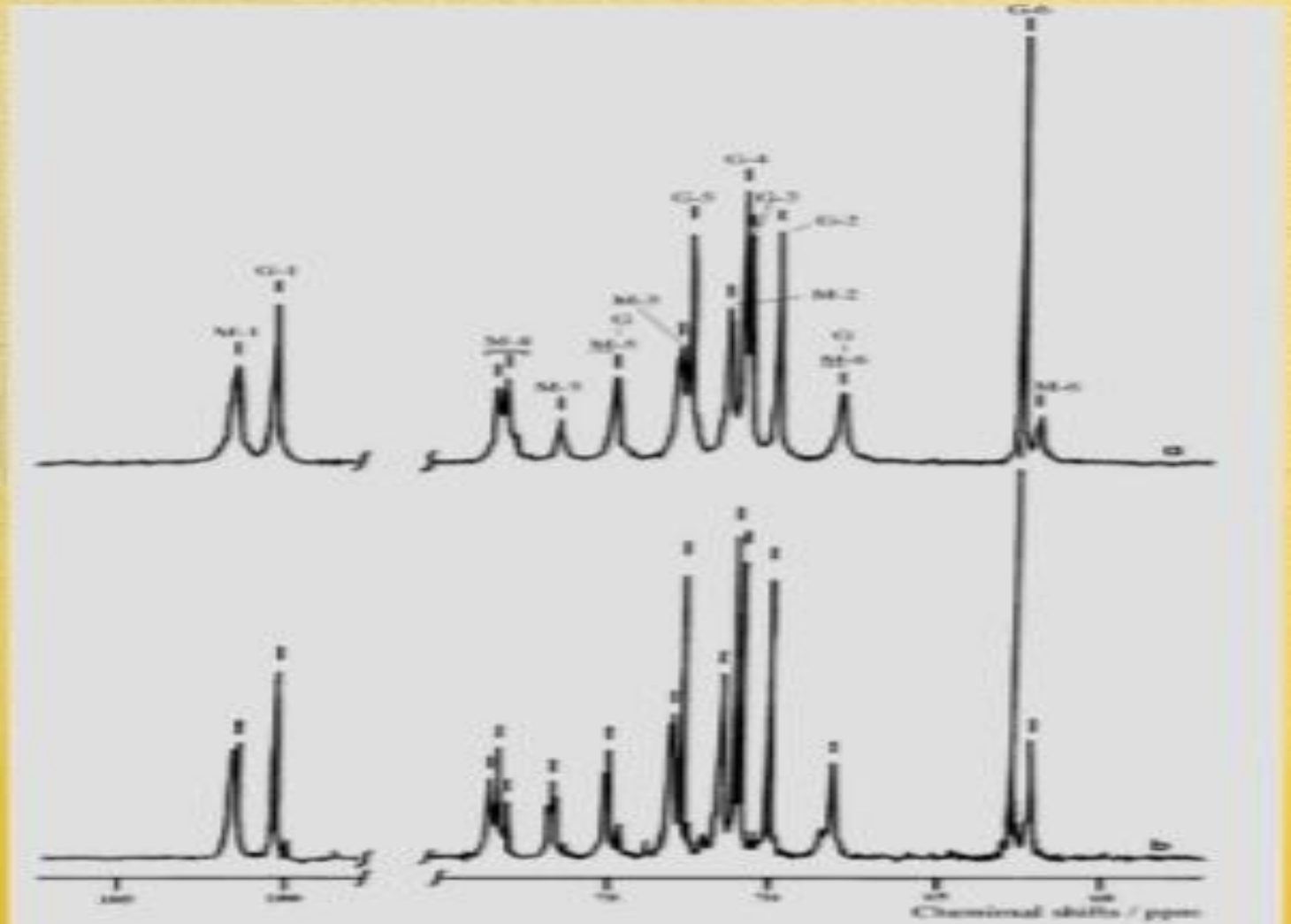


Figure 1. ^{13}C NMR spectra of partially degraded PJ (trace a) and GG (trace b) galactomannans; M – mannose, G – galactose residues.

❑Practical requirements:

- Carrier gas
- Flow regulators and flow meters
- Injection devices
- Columns
- Temperature control devices
- Detectors
- Recorders and integrators
-

❑Carrier gas are:

- Hydrogen: better thermal conductivity
- Disadvantage: it reacts with unsaturated compounds & inflammable
- Helium: excellent thermal conductivity
- It is expensive
- Nitrogen:

✓Reduced sensitivity

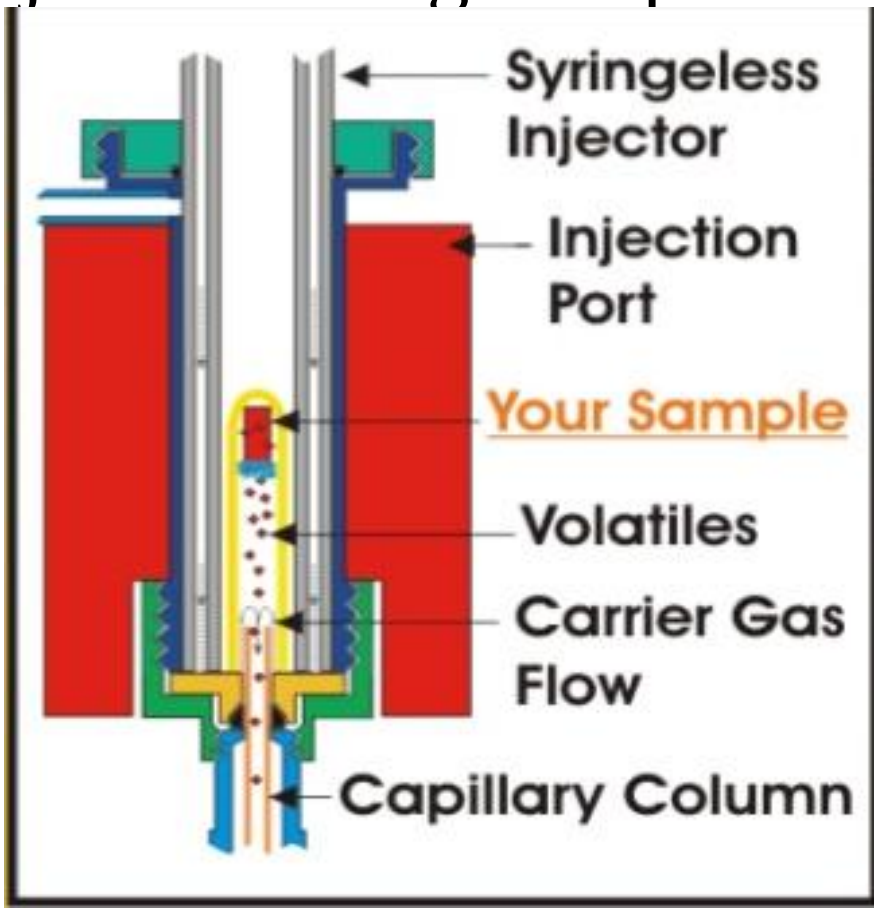
✓It is inexpensive

❑Requirements of a carrier gas:

- Inertness
- Suitable for the detector
- High purity
- Easily available
- Cheap
- Should not cause the risk of fire
- Should give best column performance

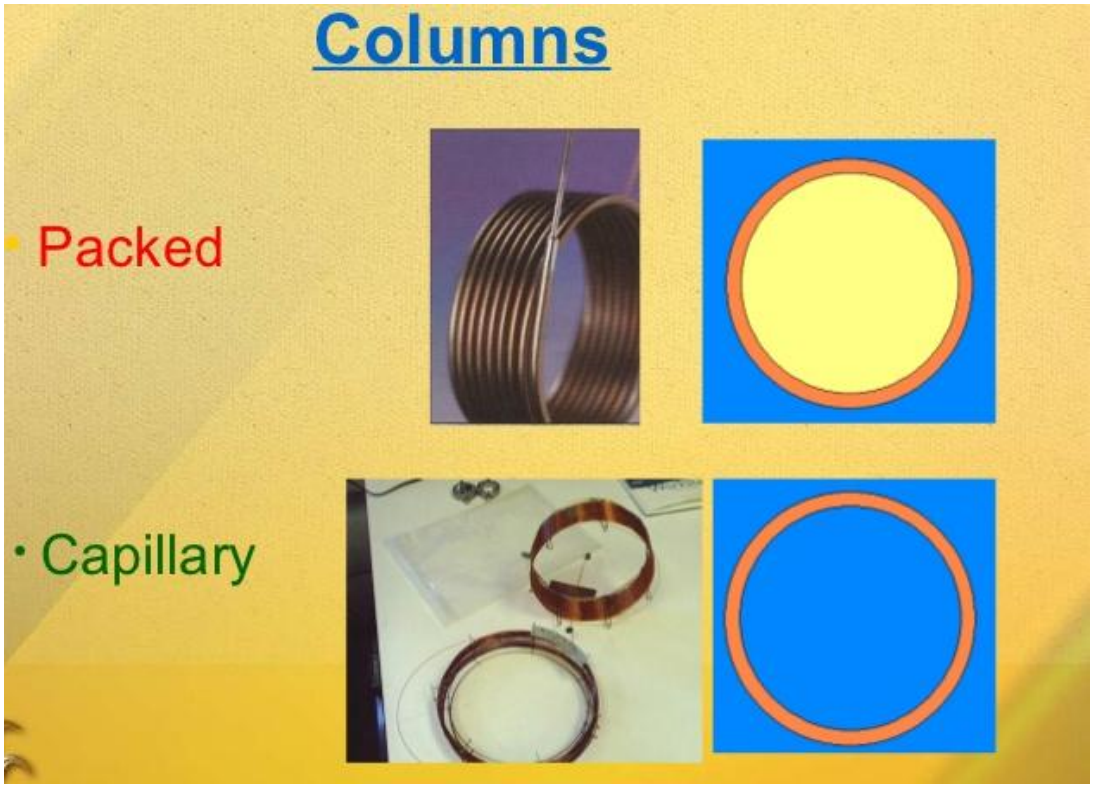
Injection Devices:

- Gases can be introduced into the column by valve devices:
- Liquids can be injected through loop or septum devices



Columns :

- Important part of GC
- Made up of glass or stainless steel
- Glass column-inert, highly fragile



❑Detectors :

- Heart of the apparatus

❖The requirements an ideal detector are:

- Applicability to wide range of samples
- Rapidity
- High sensitivity
- Linearity
- Response should be unaffected by temperature, flow rate
- Non destructive
- Simple & inexpensive

Parameters used in GC:

1. Retention time (Rt):

- ✓ It is the difference in time between the point of injection & appearance of peak maxima.
- ✓ Rt is measured in minutes or seconds

2. Retention volume(Vr):

- ✓ It is the volume of carrier gas which is required to elute 50% of the component from the column.
- ✓ Retention volume = retention time* Flow rate

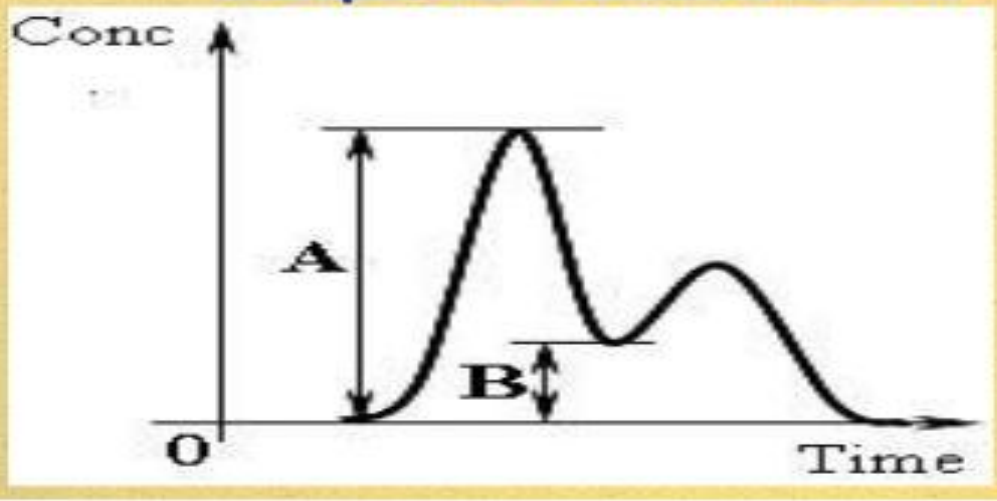
3.Separation factor(S)

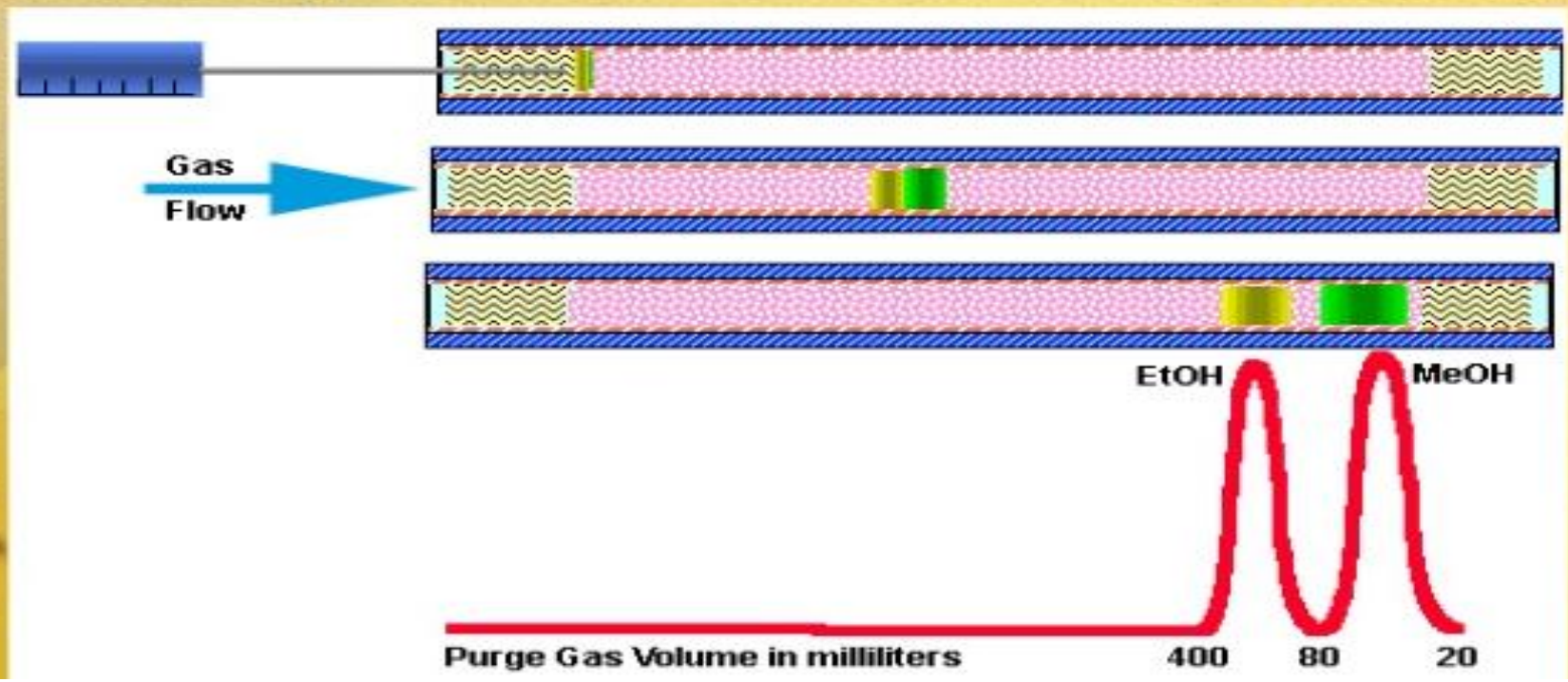
- ✓ Ratio of partition co –efficient of the two components to be separated.
- ✓ If more difference in partition co-efficient b/w two compounds the peaks are far apart &separation factor(S) is more.
- ✓ If partition co-efficient of two compounds are similar, then peaks are closer

- 4. Resolution(R) :

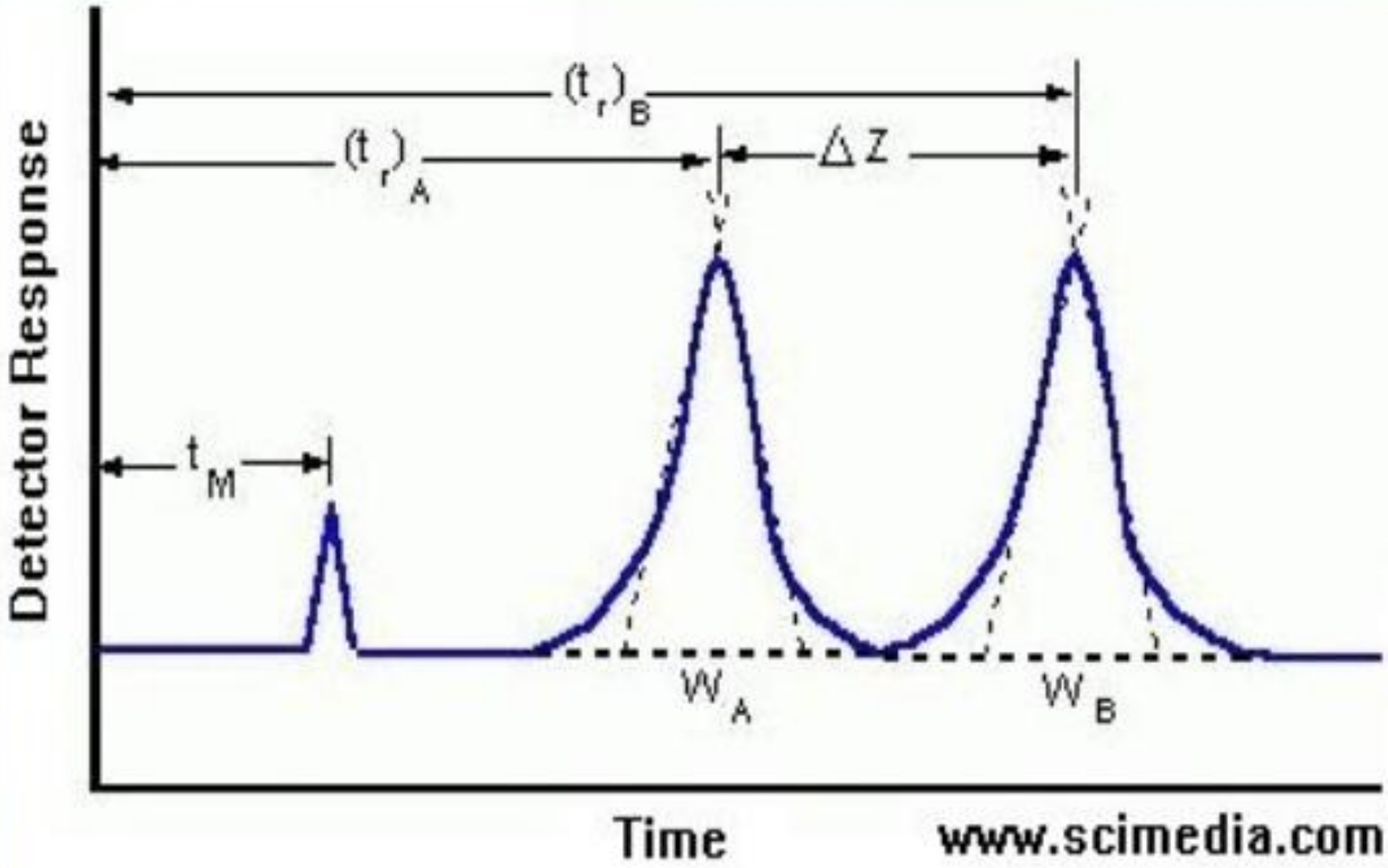
- ✓ The true separation of 2 consecutive peaks on a chromatogram is measured by resolution .
- ✓ It is the measure of both column & solvent efficiencies.

Separation factor



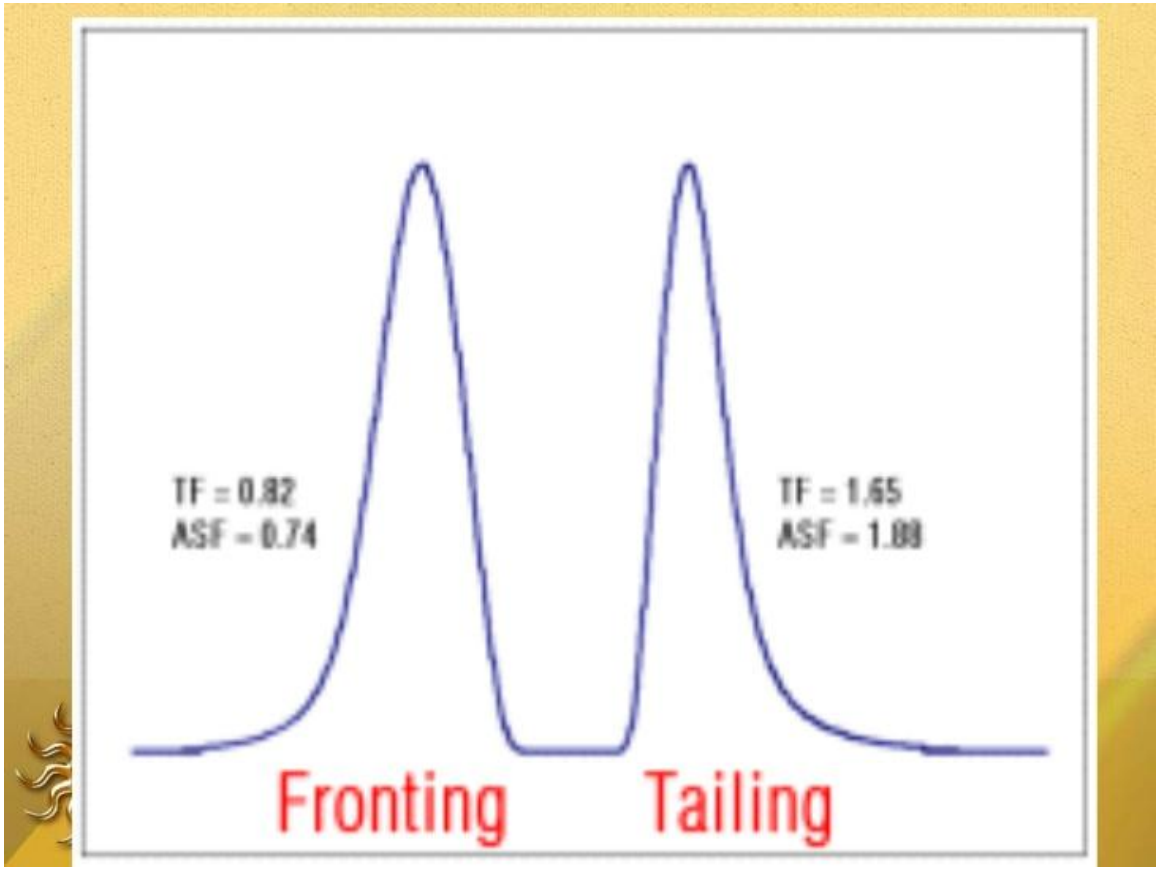


Resolution


Detector Response
$(t_r)_B$
$(t_r)_A$
ΔZ
t_M
W_A
W_B
Time
www.scimedia.com

Asymmetry Factor:

- Chromatographic peak should be symmetrical about its center
- If peak is not symmetrical –shows Fronting or Tailing.
- FRONTING:
- Due to saturation of stationary phase &can be avoided by using less quality of sample.
- Tailing: Due to more active adsorption sites &can be eliminated by support pretreatment.


TF = 0.82
ASF = 0.74
TF = 1.65
ASF = 1.88
Fronting
Tailing

Chromatographic analysis:

- The number of components in a sample is determined by the number of peaks.
- The amount of a given component in a sample is determined by the area under the peaks.
- The identity of components can be determined by the given retention times.

❑ Advantages of gas chromatography:

- Very good separation
- Time(analysis is short)
- Small sample is needed -µl
- Good detection system
- Quantitatively analyzed

- THANK YOU!!!