CHAPTER 6

GAS CHROMATOGRAPHY

Expected Outcomes

Explain the principles of gas chromatography
Able to state the function of each components of GC instrumentation
Able to state the applications of GC

6.1 Principles of Gas Chromatography (GC)

- This method depends upon the solubility and boiling points of organic liquids in order to separate them from a mixture. It is both a qualitative (identity) and quantitative (how much of each) tool.

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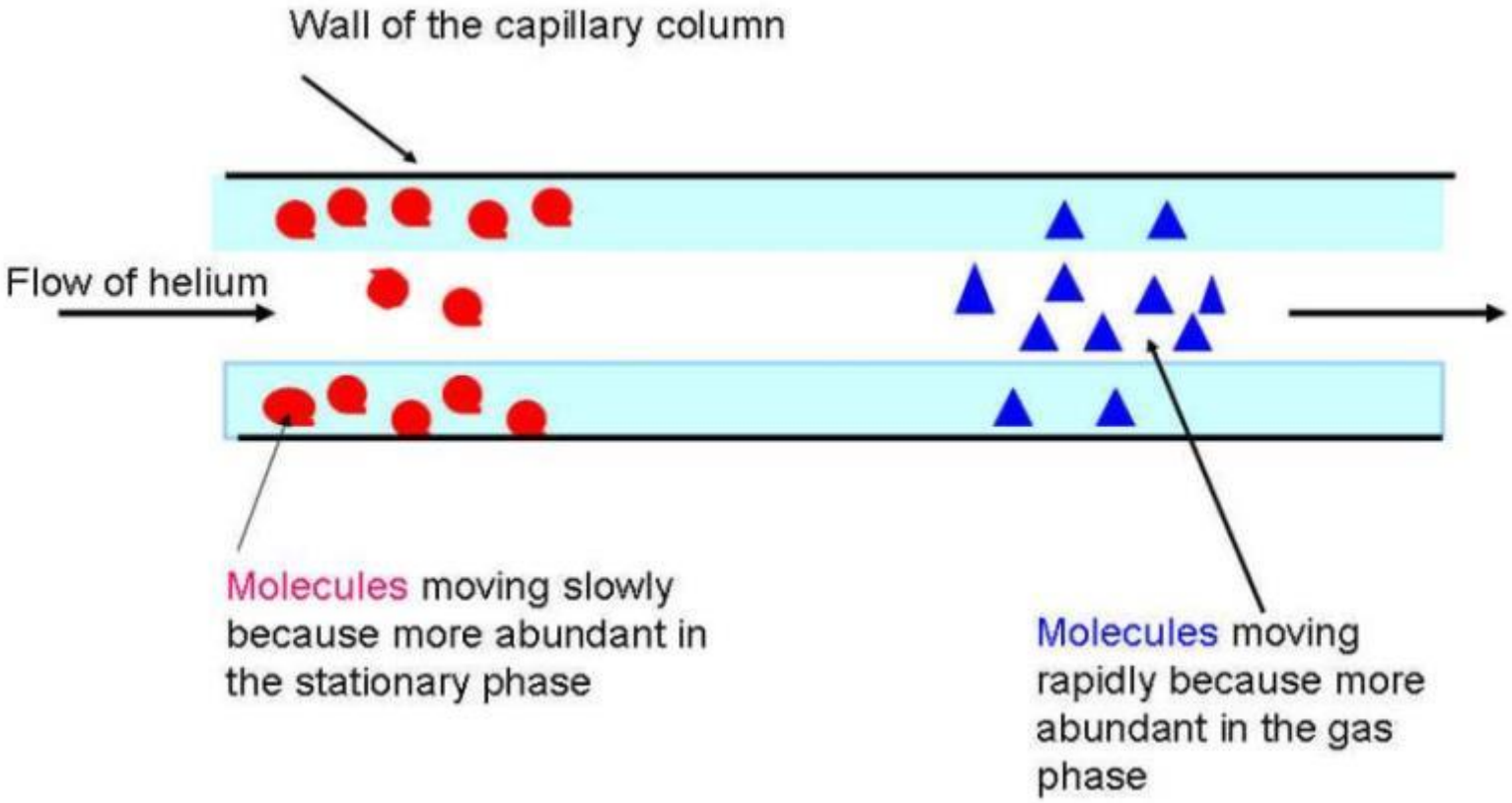
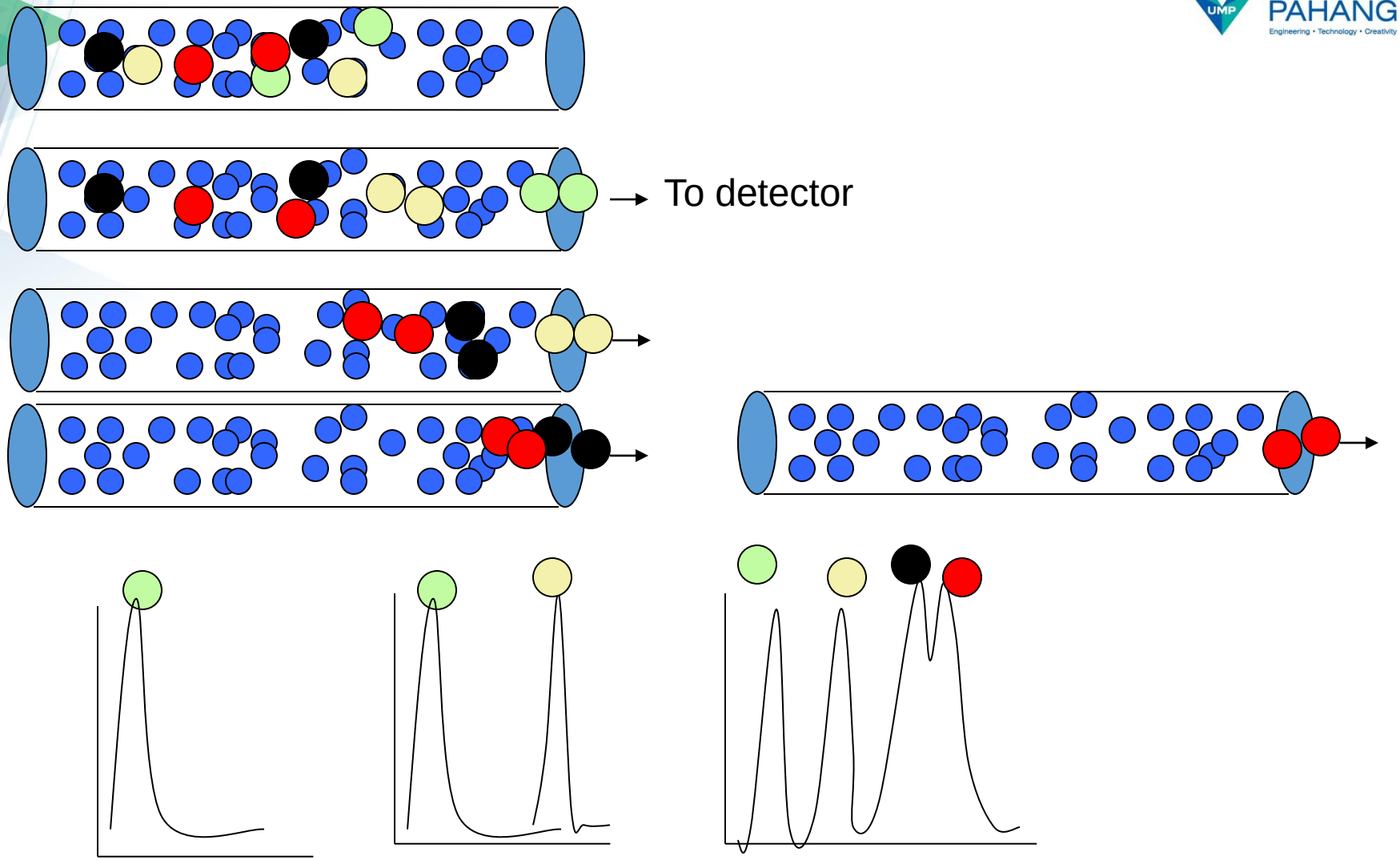
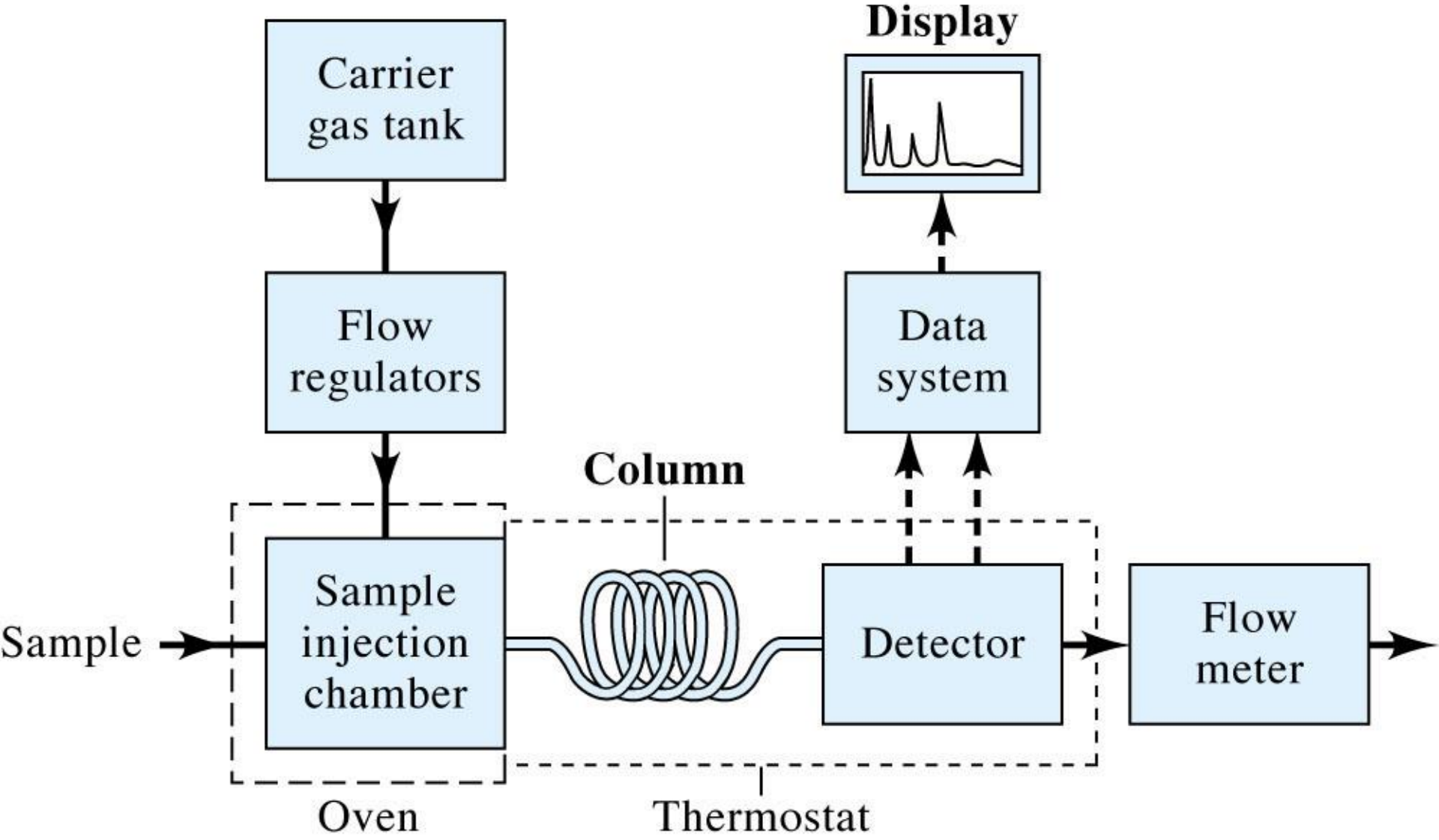


Source:http://www.specmetcrime.com/introduction_%C3%A0_la_gcms.htm

Separations



6.2 Components of GC Instrumentation



GC Instrumentation

- An inert gas such as helium is passed through the column as a carrier gas and is the moving phase.
- A sample is injected into a port which is much hotter than the column and is vaporized.
- The gaseous sample mixes with the helium gas and begins to travel with the carrier gas through the column.
- As the different compounds in the sample have varying solubility in the column liquid and as these compounds cool a bit, they are deposited on the column support.
- However, the column is still hot enough to vaporize the compounds and they will do so but at different rates since they have different boiling points.

INSTRUMENTS FOR GC

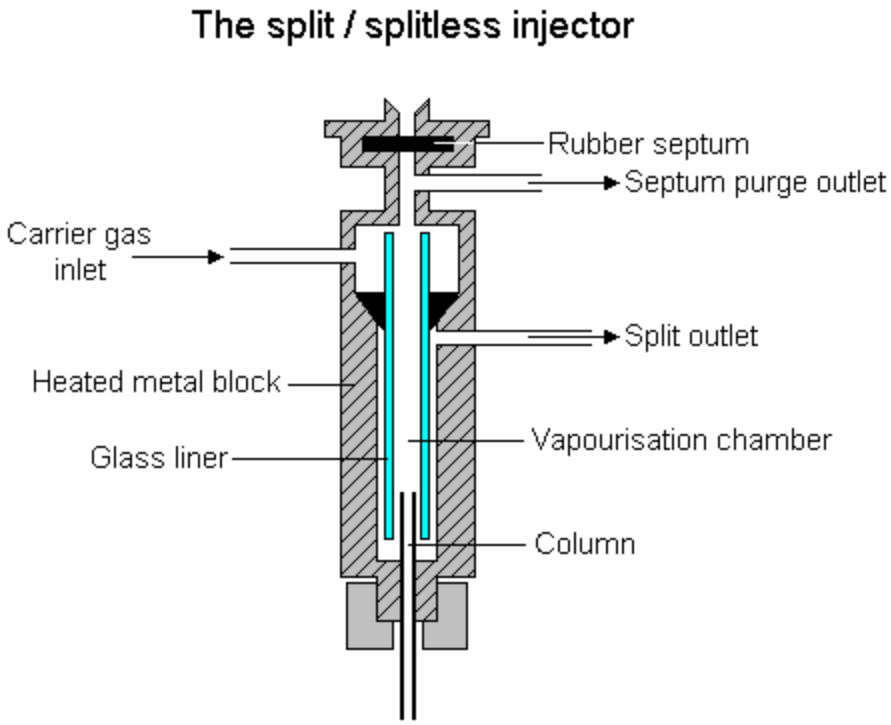
Carrier Gas-Supply

Carrier gases, which must be chemically inert, include helium, nitrogen, and hydrogen.

Associated with the gas supply are pressure regulators, gauges, and flow meters.

Sample Injection System

- The most common method of sample injection involves the use of microsyringe to inject a liquid or gaseous sample



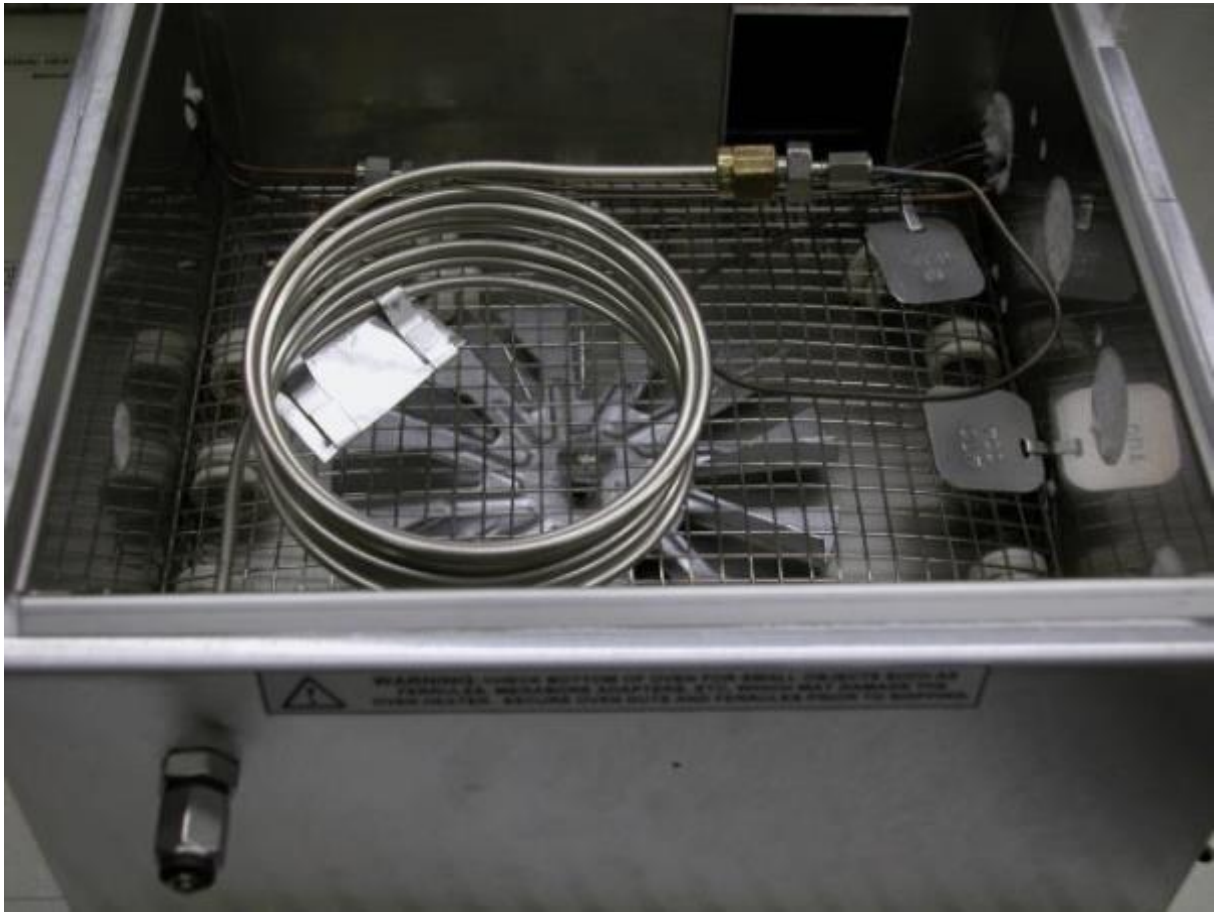
Source: http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

Column

- Two general types of columns are encountered in gas chromatography, packed and open tubular, or capillary.

- Chromatographic columns vary in length from less than 2 m to 50 m or more. They are constructed of stainless steel, glass, fused silica, or Teflon. In order to fit into an oven for thermostate, they are usually formed as coils having diameters of 10 to 30 cm.

GC Column and Oven



Source: http://slideplayer.com/slide/1676116/

Capillary column

Source:http://departments.agri.huji.ac.il/zabam/GC.html

TABLE 27-3 Some Common Liquid Stationary Phases for GLC

Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase, hydrocarbons, polynuclear aromatics, steroids, PCBs
5% Phenyl-polydimethyl siloxane	OV-3, SE-52	350	Fatty acid methyl esters, alkaloids, drugs, halogenated compounds
50% Phenyl-polydimethyl siloxane	OV-17	250	Drugs, steroids, pesticides, glycols
50% Trifluoropropyl-polydimethyl siloxane	OV-210	200	Chlorinated aromatics, nitroaromatics, alkyl substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids, alcohols, ethers, essential oils, glycols
50% Cyanopropyl-polydimethyl siloxane	OV-275	240	Polyunsaturated fatty acids, rosin acids, free acids, alcohols

Picture taken from Fundamentals of Analytical Chemistry by Douglas A. Skoog, Donald M. West and F. James Holler Page 804]

Column Ovens

- Column temperature is an important variable that must be controlled to a few tenths of a degree for precise work.

- The optimum column temperature depends upon the boiling point of the sample and the degree of separation required.

- A temperature equal to or slightly above the average boiling point of a sample results in a reasonable elution time (2 to 30 min).

Detector

Characteristics of the Ideal Detector: The ideal detector for gas chromatography has the following characteristics:

1. Adequate sensitivity

2. Good stability and reproducibility.

3. A linear response to solutes that extends over several orders of magnitude.

4. A temperature range from room temperature to at least 400^{o}C.

Detectors

- FID (flame ionization detector) is the most widely used detector. Based on the production of ions when compounds are burned then detecting the current produced from the ionization.

- TCD (thermal conductivity detector). Operates on the changes in the thermal conductivity of the gas stream brought about by the presence of analyte molecules.

Different GC detectors

TABLE 27-1 Typical Gas Chromatographic Detectors

Type	Applicable Samples	Typical Detection Limit
Flame ionization	Hydrocarbons	1 pg/s
Thermal conductivity	Universal detector	500 pg/mL
Electron capture	Halogenated compounds	5 fg/s
Mass spectrometer (MS)	Tunable for any species	0.25 to 100 pg
Thermionic	Nitrogen and phosphorous compounds	0.1 pg/s (P), 1 pg/s (N)
Electrolytic conductivity (Hall)	Compounds containing halogens, sulfur, or nitrogen	0.5 pg Cl/s, 2 pg S/s, 4 pg N/s
Photoionization	Compounds ionized by UV radiation	2 pg C/s
Fourier transform IR (FTIR)	Organic compounds	0.2 to 40 ng

Picture taken from Fundamentals of Analytical Chemistry by Douglas A. Skoog, Donald M. West and F. James Holler Page 793]

6.3 Applications of GC

- There are still numerous GC applications involving both quantitative and qualitative identification of the active components and possible contaminants, adulterants or characteristic features which may indicate the source of the particular sample.

- Analysis of foods is concerned with the assay of lipids, proteins, carbohydrates, preservatives, flavours, colorants and texture modifiers, and also vitamins, steroids, drugs and pesticide residues and trace elements.

- Non-volatile materials, such as plastics, natural and synthetic polymers, drugs and some microbiological materials

Qualitative Analysis of GC

- The chromatogram shows the order of elution (order of components coming off the column), the time of elution (retention time), and the relative amounts of the components in the mixture.

- The order of elution is related to the boiling points and polarities of the substances in the mixture.

- In general, they elute in order of increasing boiling point but occasionally the relative polarity of a compound will cause it to elute "out of order". This is analyzing your sample.

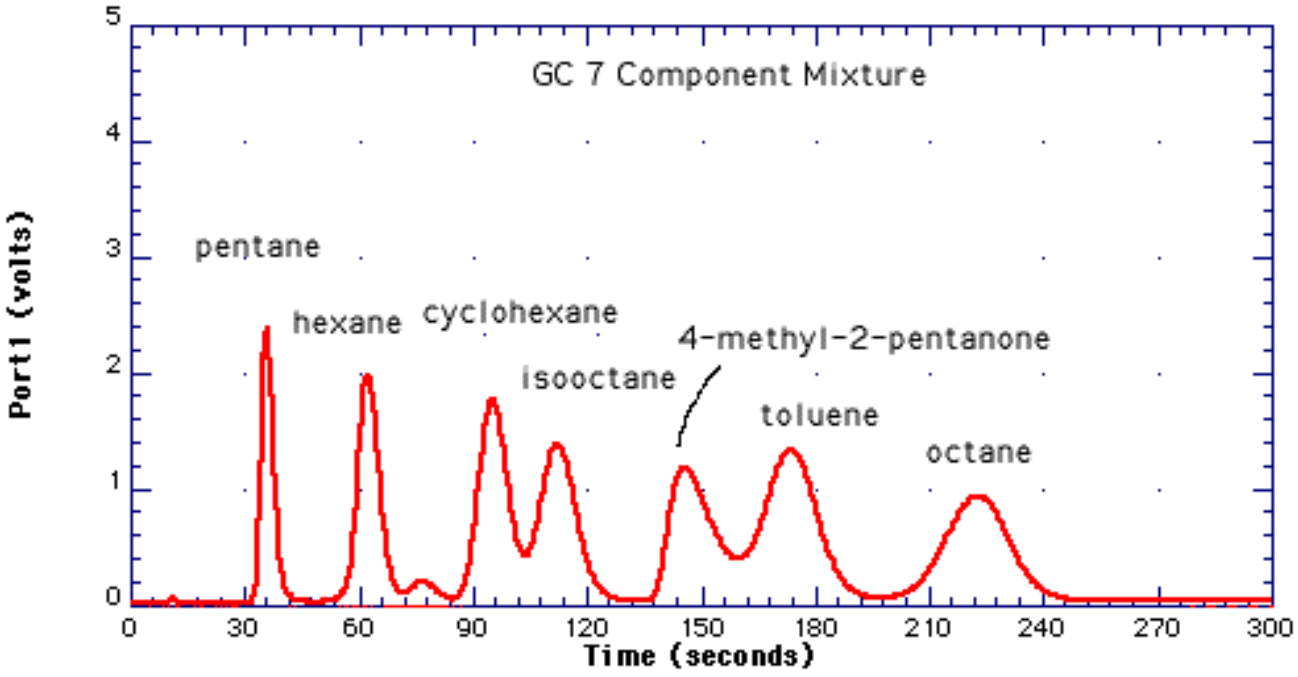
Elution Order

Compound	Boiling Point (^{0}C)
pentane	36
hexane	69
cyclohexane	80
isooctane	99
toluene	110
4-methyl-2-pentanone	117
octane	126

Example Chromatogram

- The observed elution pattern appears below. Notice the reversed elution of toluene and 4-methyl-2-pentanone.

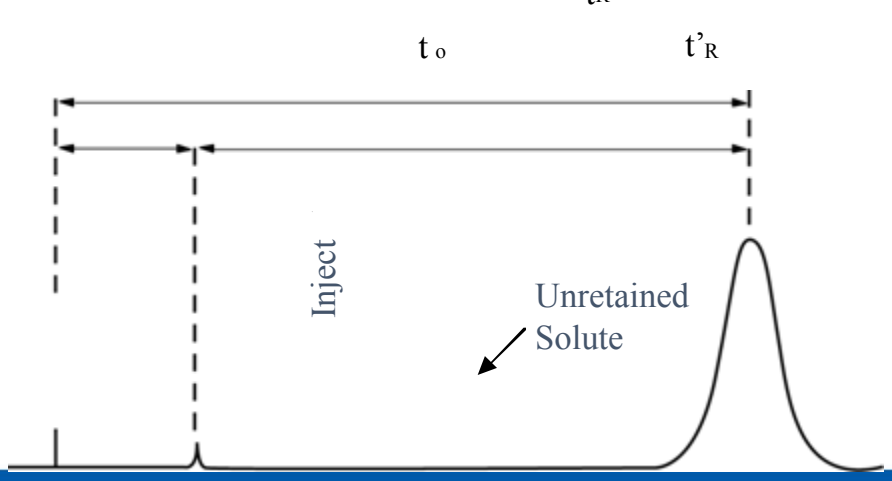
GC Chromatogram



Quantitative Analysis
Capacity Factor (k')

•• While inside the column, a retained component spends part of its time on the stationary phase and part time in the mobile phase

- • When in the mobile phase, solutes move at the same speed as the mobile phase
- • this means that all solutes spend the same amount of time in the mobile phase (t_o)
- • the amount of time the solute spends on the stationary phase is equal to t_R- t_o(adjusted retention time, t'_R)
- •the ratio t'_R / t_o is the capacity of the column to retain the solute (k')



$$k' = (t_r - t_0) / t_0$$

$$k' = (t'_r) / t_0$$

When k' is ✂ 1.0, separation is poor
When k' is > 30, separation is slow
When k' is = 2-10, separation is optim

Measures of Solute Separation:

separation factor (α) – parameter used to describe how well two solutes are separated by a chromatographic system:

$\alpha = k'2/k'1$ $\quad$ $k' = (tR - tM)/tM$

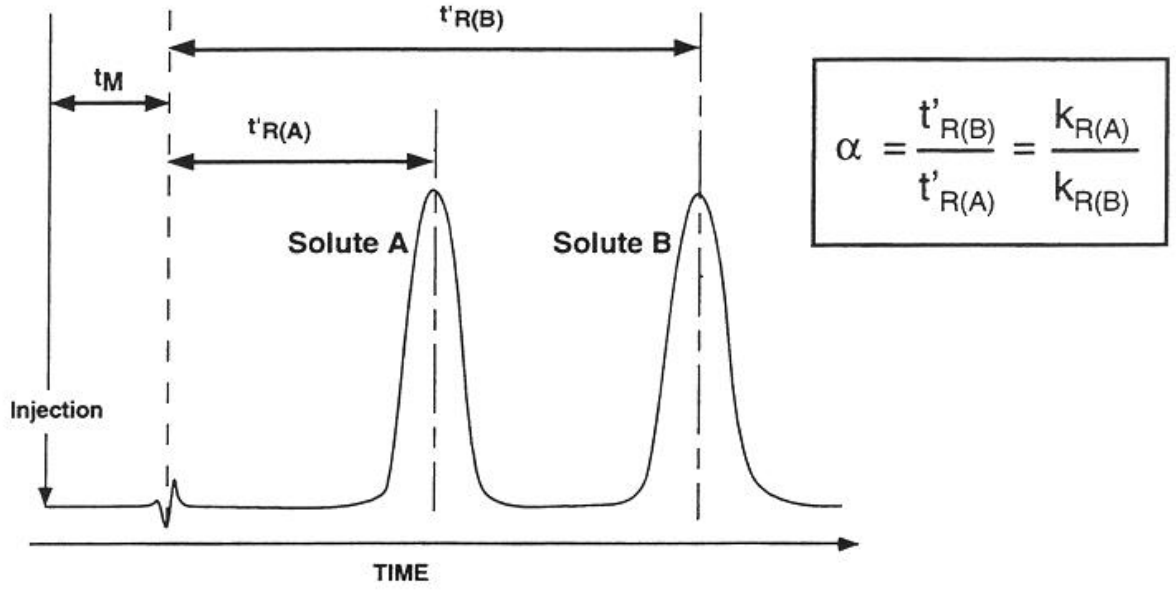
where:

k'1 = the capacity factor of the first solute

k'2 = the capacity factor of the second solute,

with $k'2 \geq k'1$

A value of $\alpha \approx 1.1$ is usually indicative of a good separation



Does not consider the effect of column efficiency or peak widths, only retention.

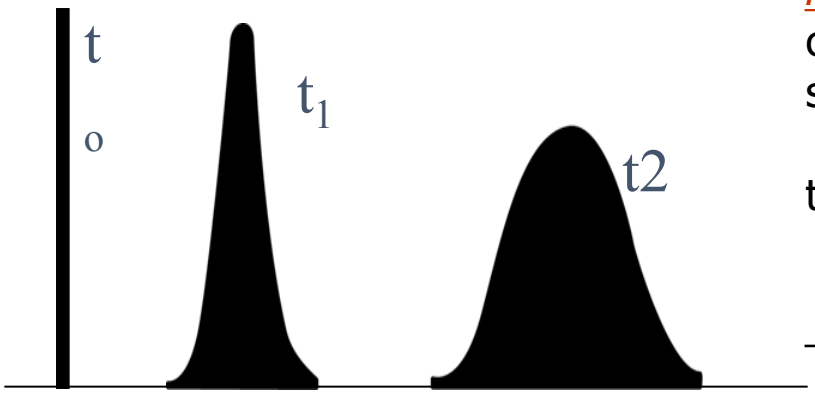
Column Efficiency (N)

➔**Solutes are placed on an GC column in a narrow band**

➔ • **Each solute band spreads as it moves through the column due to diffusion and mass transfer affects**

➔ • **The later eluting bands will spread more**

➔ • **Peak shape follow a Gaussian distribution**



Number of theoretical plates (N): compare efficiencies of a system for solutes that have different retention times

for a Gaussian shaped peak

$$N = 16\,(tR/Wb)^2$$

Band spreading eventually causes peaks to merge into the baseline. We want to minimize band spreading as much as possible.

The larger the value of N is for a column, the better the column will be able to separate two compounds.

Plate height or height equivalent of a theoretical plate (H or HETP): compare efficiencies of columns with different lengths:

$$H = L/N$$

where: L = column length

N = number of theoretical plates for the column

Note: H simply gives the length of the column that corresponds to one theoretical plate

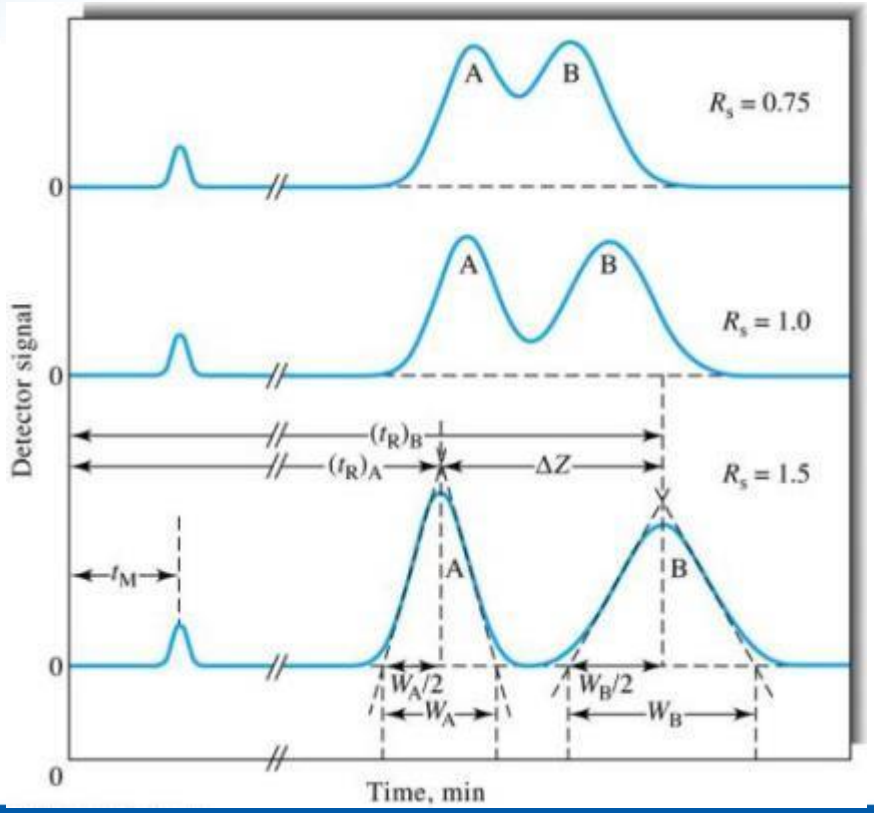
resolution (RS) – resolution between two peaks is a second measure of how well two peaks are separated:

where:

$$R_S = \frac{t_{r2} - t_{r1}}{(W_{b2} + W_{b1})/2}$$

tr1, Wb1 = retention time and baseline width for the first eluting peak

tr2, Wb2 = retention time and baseline width for the second eluting peak

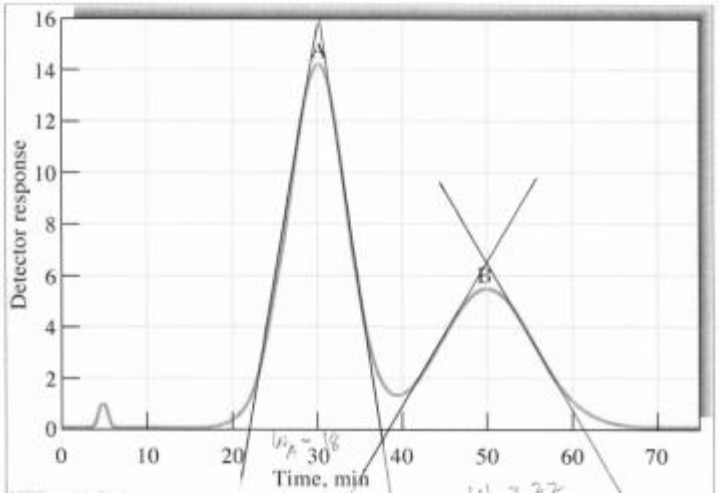


Rs is preferred over α since both retention (tr) and column efficiency (Wb) are considered in defining peak separation.

Rs ≈ 1.5 represents *baseline resolution*, or complete separation of two neighboring solutes → ideal case.

Rs ≈ 1.0 considered adequate for most separations.

Exercise



A chromatograph of a two component mixture is shown next page. The LC column is 25-cm long. The flow rate was 0.40 ml/min. Using the chromatograph determine/calculate the following:

A. The time components A and B spends on the stationary phase.
B. The retention factor for components A and B
C. The resolution between the two peaks
D. What is the column efficiency

A chromatograph of a two component mixture is shown next page. The LC column is 25-
rate was 0.40 mL/min. Using the chromatograph determine/calculate the following:

A. The time components A and B spends on the stationary phase. (4 pts)

$t_{RA} = 30$ min

$t_{RB} = 50$ min

B. The retention factor for components A and B. (4 pts)

$$k'_A = \frac{t_{RA} - t_M}{t_M} = \frac{30-5}{5} = 5$$

$$k'_B = \frac{t_{RB} - t_M}{t_M} = \frac{50-5}{5} = 9$$

C. The resolution between the two peaks (4 pts)

$$R_S = \frac{2(t_{RB} - t_{RA})}{w_A + w_B} = \frac{2(50-30)}{18+22}$$

D. What column

$$N_A = 16\left(\frac{t_{RA}}{w_A}\right)^2 \qquad N = 16\left(\frac{t_{RB}}{w_B}\right)^2$$

$$= 16\left(\frac{30}{18}\right)^2 \qquad N = 16\left(\frac{50}{22}\right)^2$$

$$= 44 \qquad N = 82$$

$$N_{AVE} = 63$$