Fundamental Principles of GC

Customer Support Centre
Shimadzu Asia Pacific Pte. Ltd.
Singapore

Outline

- Objective: to understand how a GC works

- Topics:
  - Gas chromatography basics
  - Basic GC data

What is GC?

The technique

- GC stands for Gas Chromatography, an analytical technique which allows separation organic compounds in a sample

What is GC?

The instrument

- The instrument used for gas chromatographic analysis is known as a gas chromatograph (also called GC)

Why we need GC

The information

- By using GC we can perform:
  - Qualitative analysis
  - Quantitative analysis

Why we need GC

Samples for GC

- Strictly speaking, samples for GC are organic compounds with
  - sufficient volatility (guideline: is in vapor form or can be turned to vapor at 400°C or less),
  - sufficient thermal stability (does not decompose on heating)

- In practice, some compounds which do not fulfill the criteria above can be made to fulfill the criteria by means of chemical reaction (‘derivatization’), thus making it possible for these compounds to be analyzed by GC

Why we need GC

Typical applications of GC:

- Pesticide residues and pollutants in water, agricultural products, foodstuff
- Organic solvents in packaging materials, ink, etc.
- Drugs of abuse in urine, blood, tablets
- Fatty acid contents in edible oils, fat, etc.
- Essential oil
- etc…

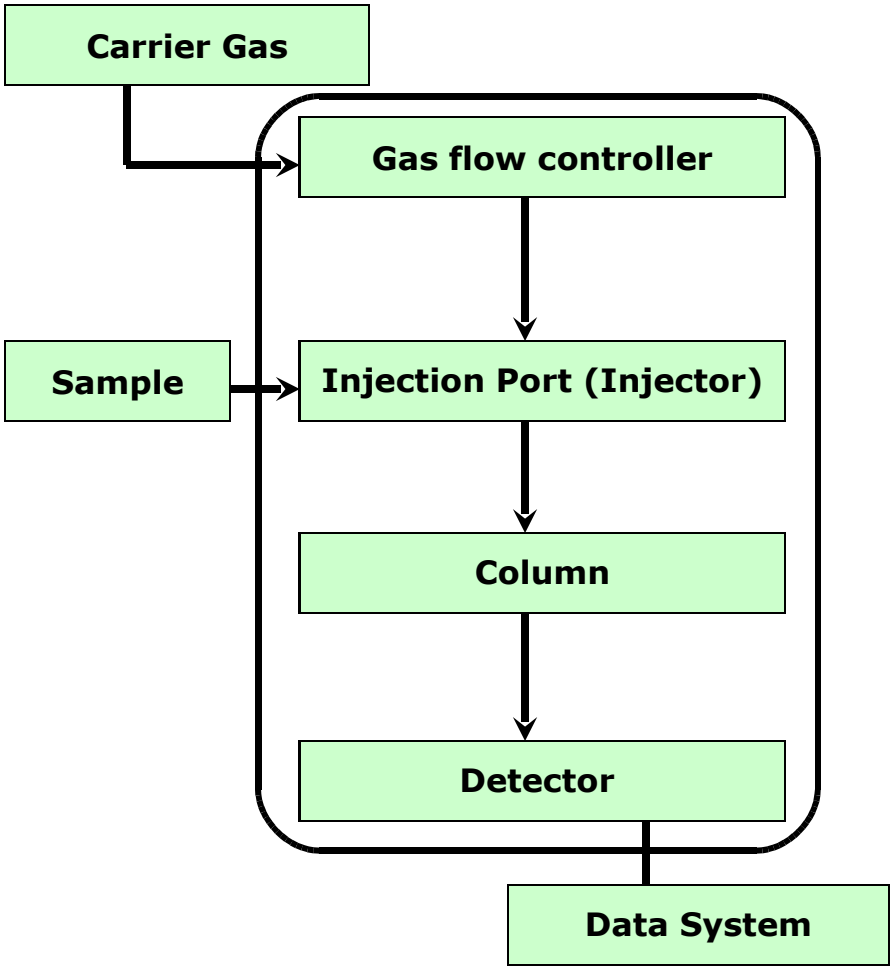
Food industry **Agriculture industry**

Environmental field **Forensic field**

Biotechnology field **Fragrance industry**

Chemical industry

Gas Chromatograph



- Controls the supply of gas(es) to the GC
- Two types: manual flow controller and electronic flow controller

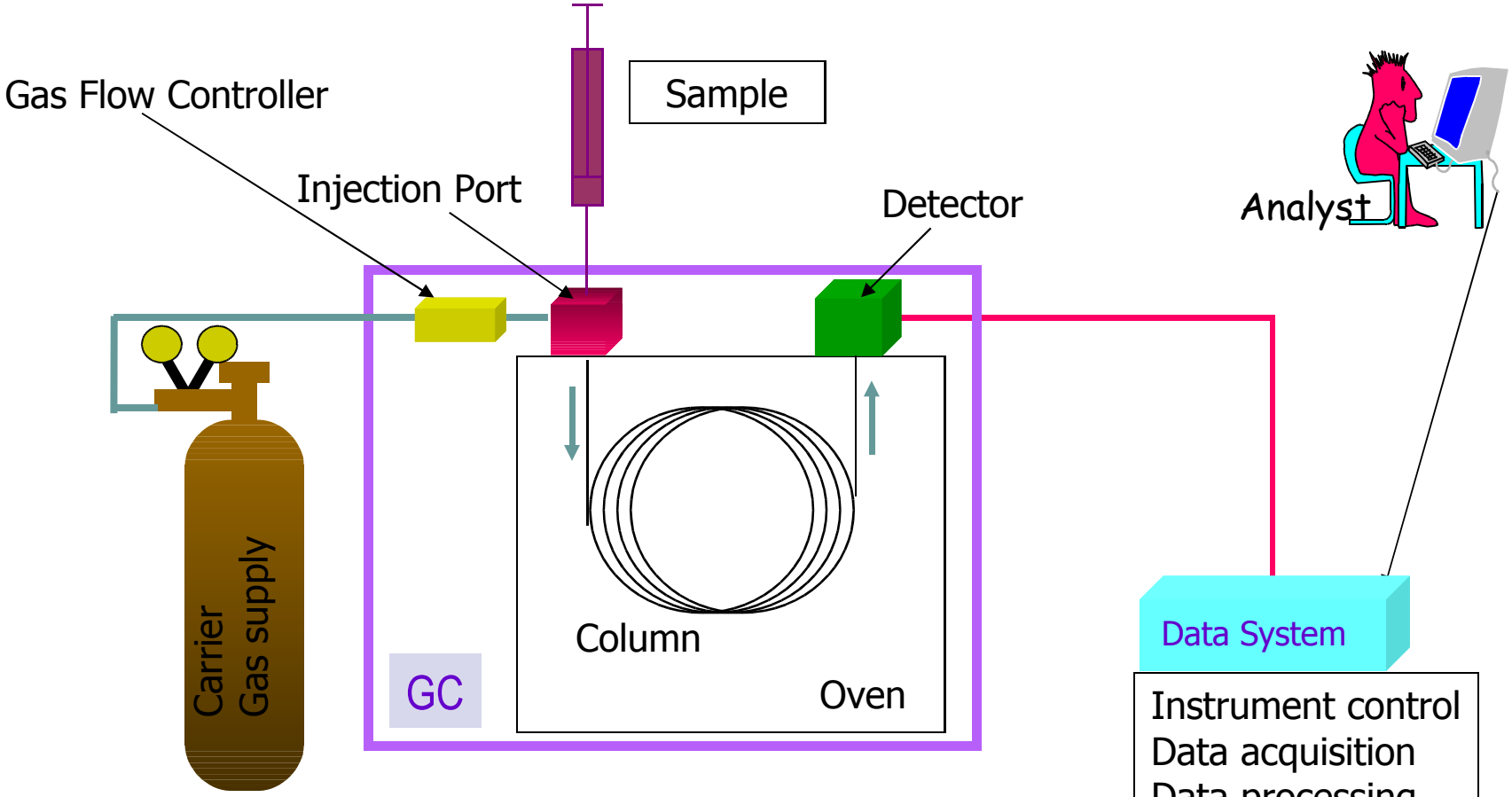
- Interface between sample introduction device (e.g. syringe) and column
- Turns liquid sample into vapor by heating
- Mixes sample vapor with carrier gas

- Separates mixture of compounds into individual components

- Detects separated compounds and send signal to data system

- Controls GC system (more advanced, software-based system)
- Converts signal from detector into human-readable format
- Data analysis (process data)

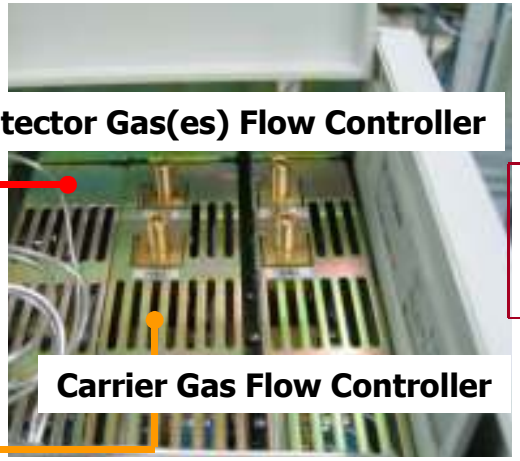
Gas Chromatograph Main Components



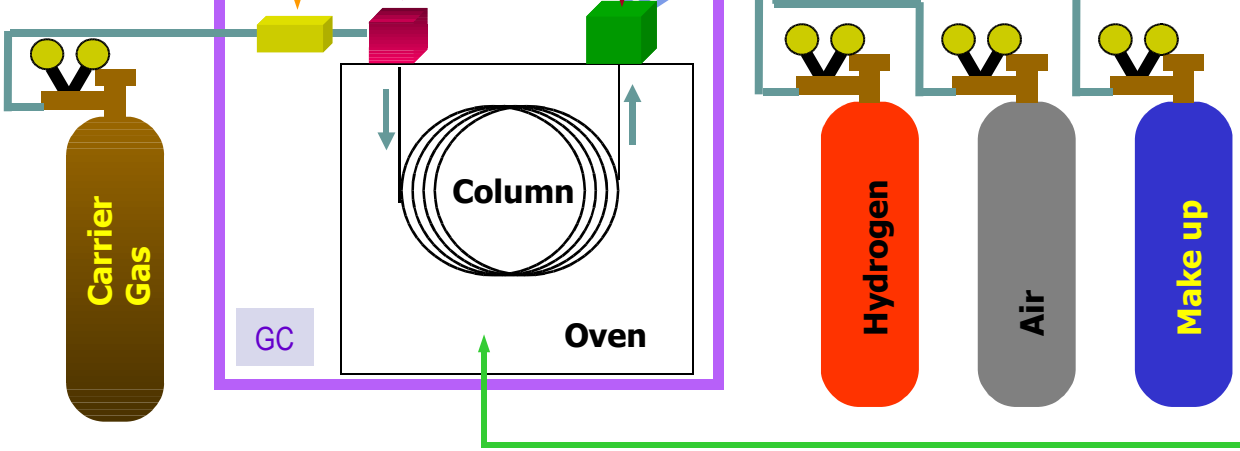
GC Components

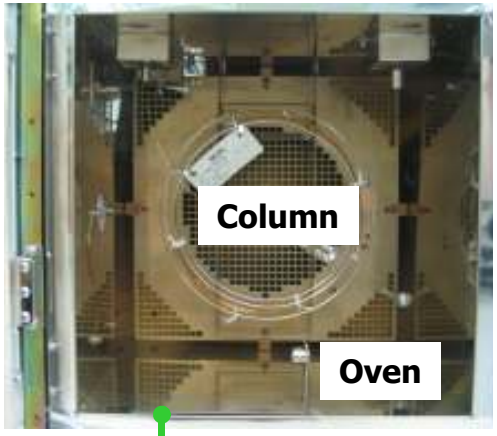
Injector

GC Detector



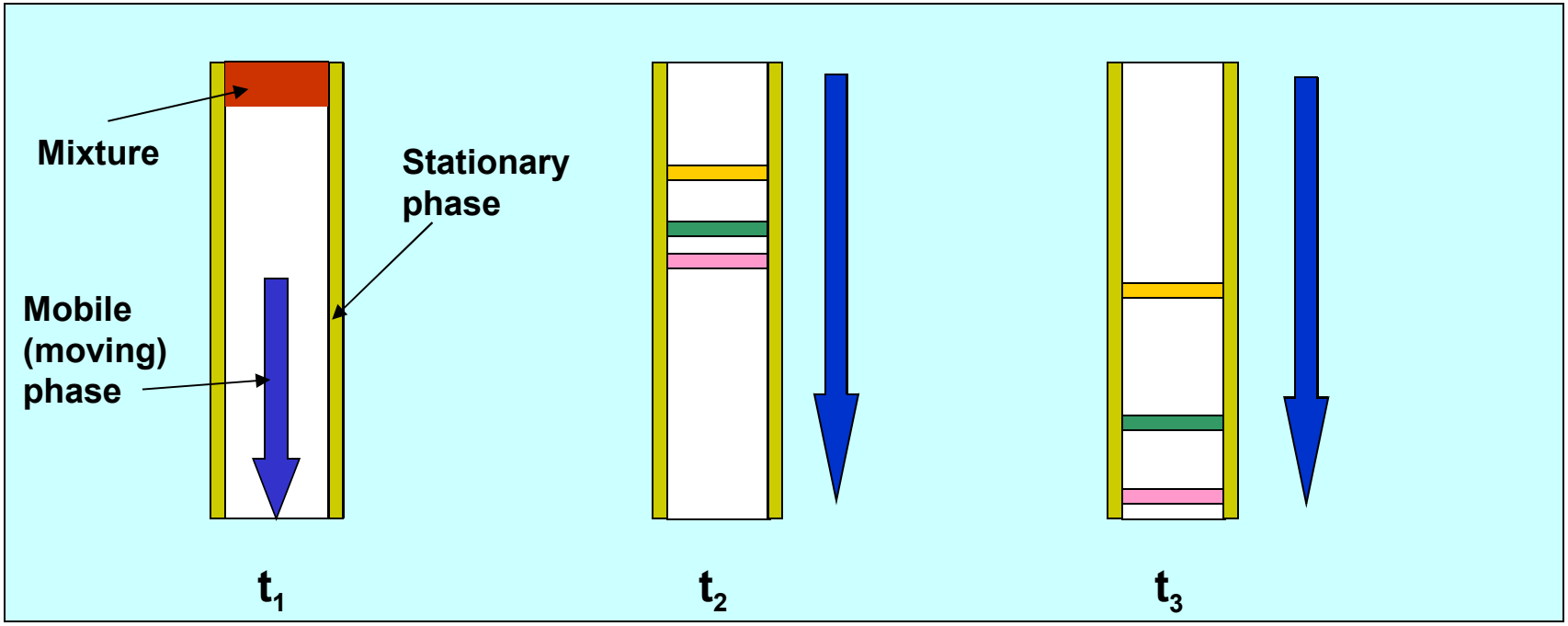
Electronic Flow Controllers



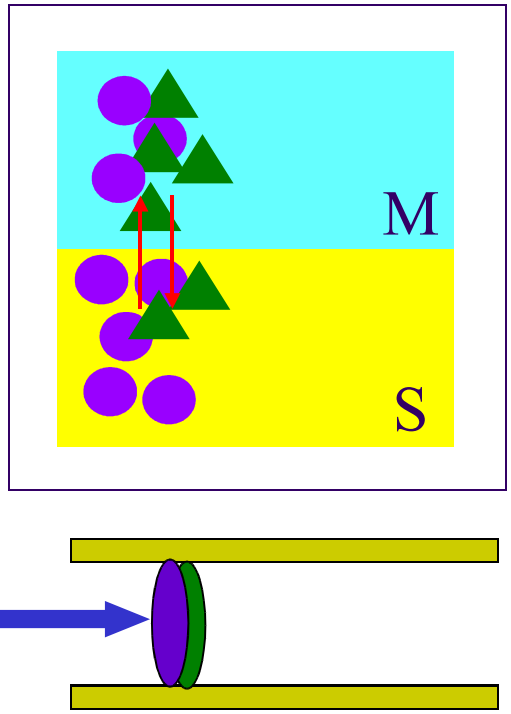


Gas Chromatography Basics

- Separation of compounds occurs inside the GC column



Separation of compounds

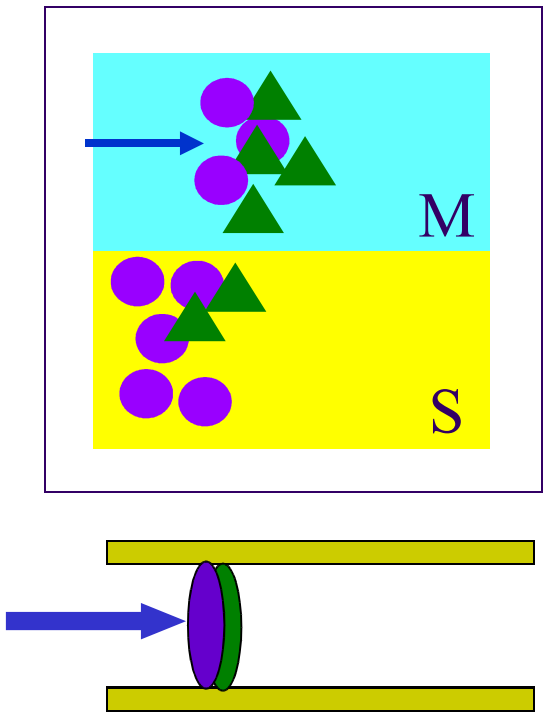


- When analytes are introduced into the column, the molecules ***distribute*** between the stationary and mobile phases
- The molecules in the mobile phase are carried down the column
- Those in the stationary phase are temporarily immobile and do not move down the column

M = mobile phase (carrier gas)

S = stationary phase

Separation of compounds



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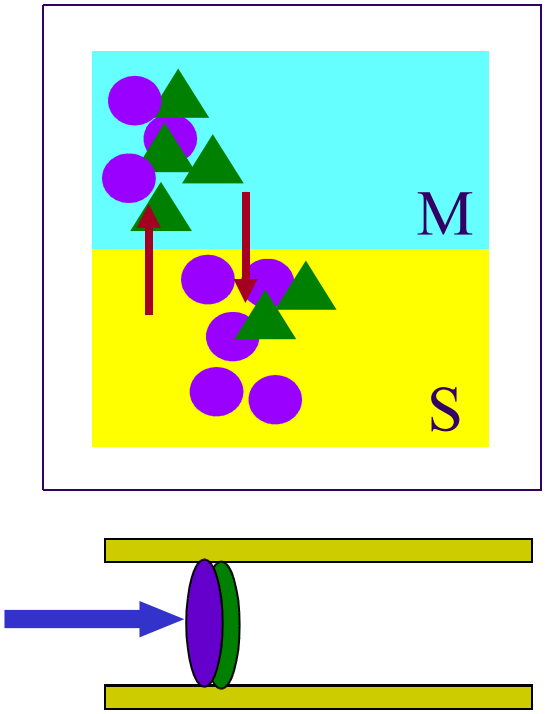
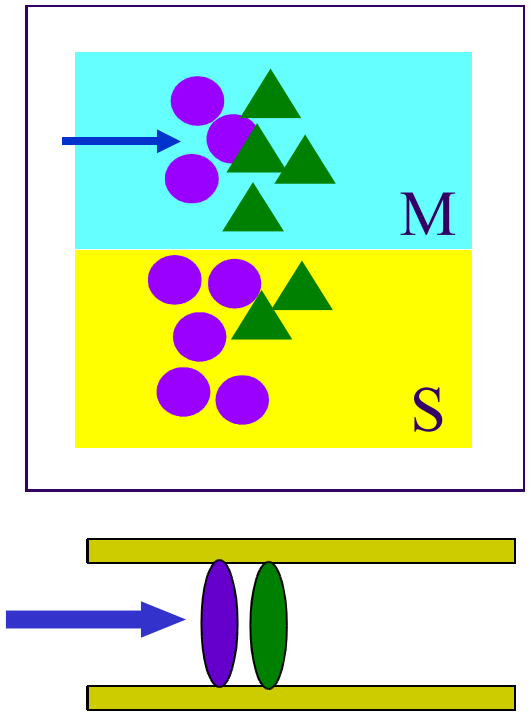
Separation of compounds



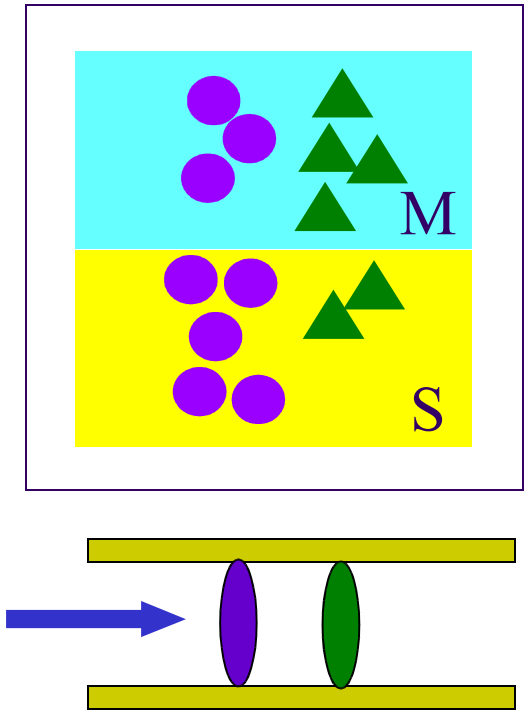
- Molecules in the mobile phase re-enter the stationary phase when they collide with the stationary phase
- At the same time span, molecules leave the stationary phase and enter the mobile phase

Separation of compounds



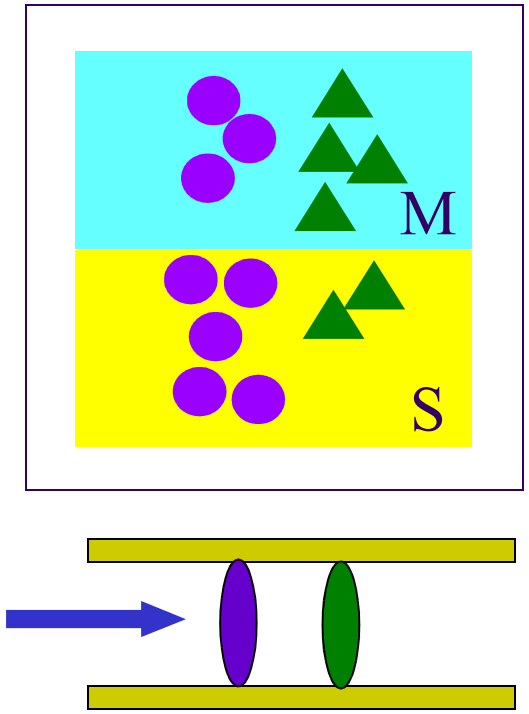
- The molecules in the mobile phase are carried down the column
- The process is repeated many many times inside the column
- While the process is repeated, separation takes place

Separation of compounds



- All molecules of the same compound travel through the column at nearly the same rate and appear as a band of molecules (called *sample band*)

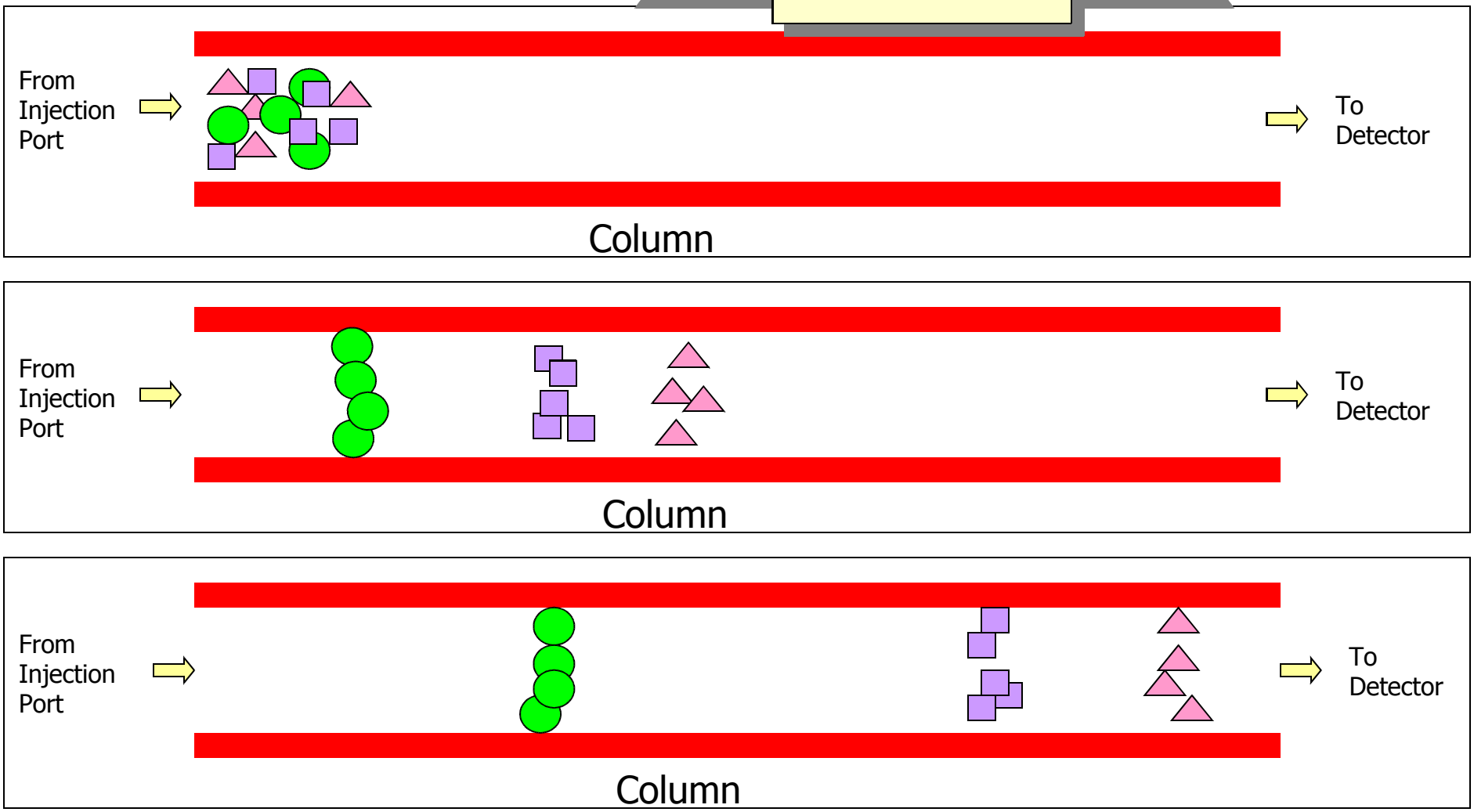
Separation of compounds



- Sample band of compound which is less ‘soluble’ in the stationary phase moves faster, because more of the molecules spend more time in the mobile phase (carrier gas)

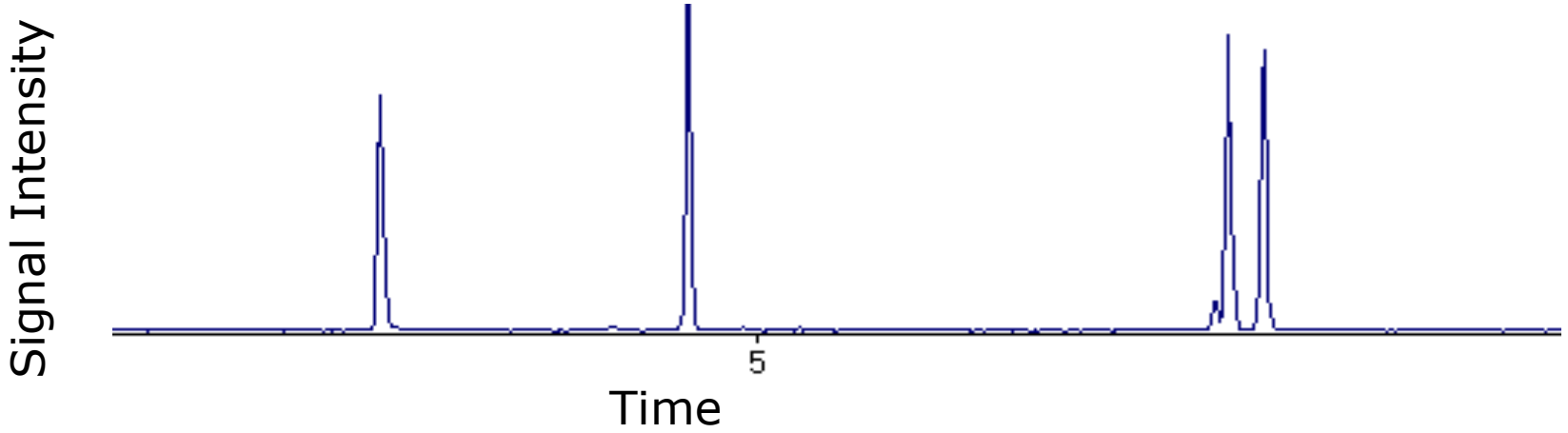
Separation in column

Retention Time = time spent by a compound inside the column

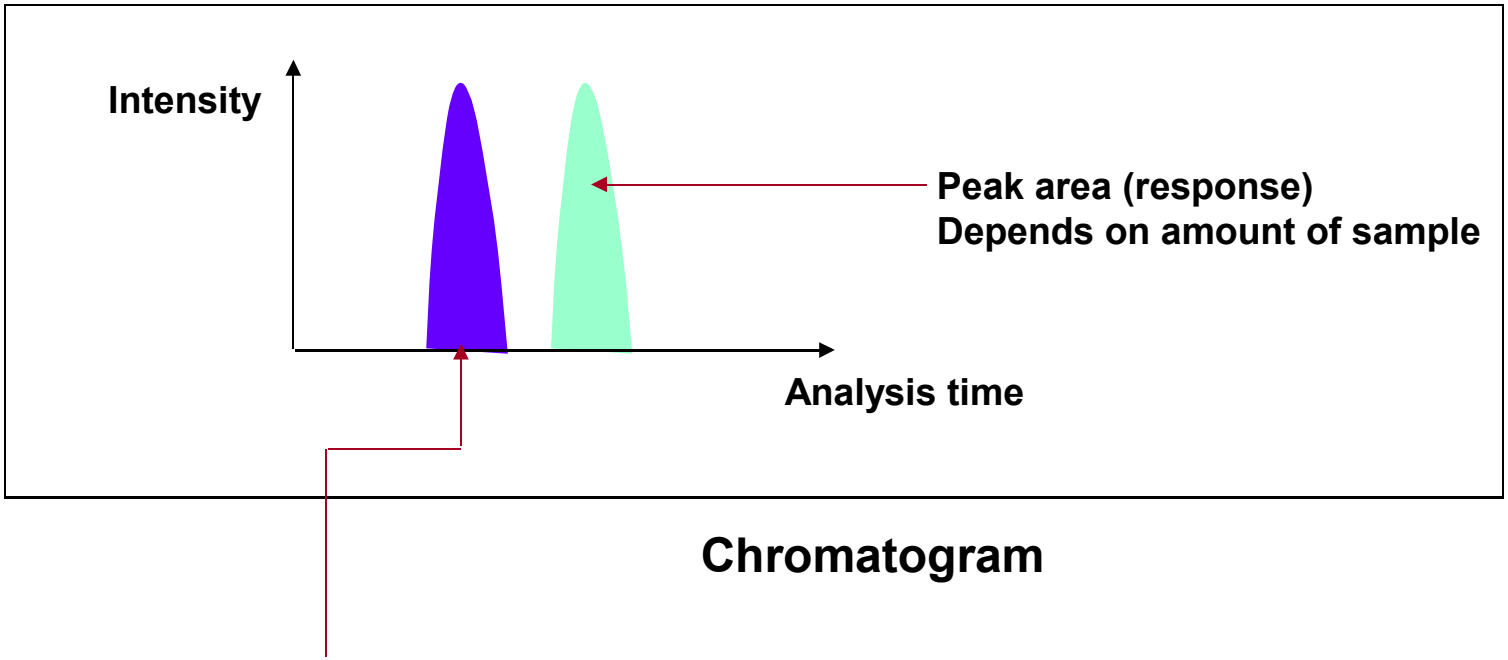


Chromatogram

- Data obtained from chromatographic analysis
- Retention time of a peak is determined by the time corresponds to the maximum of the peak.

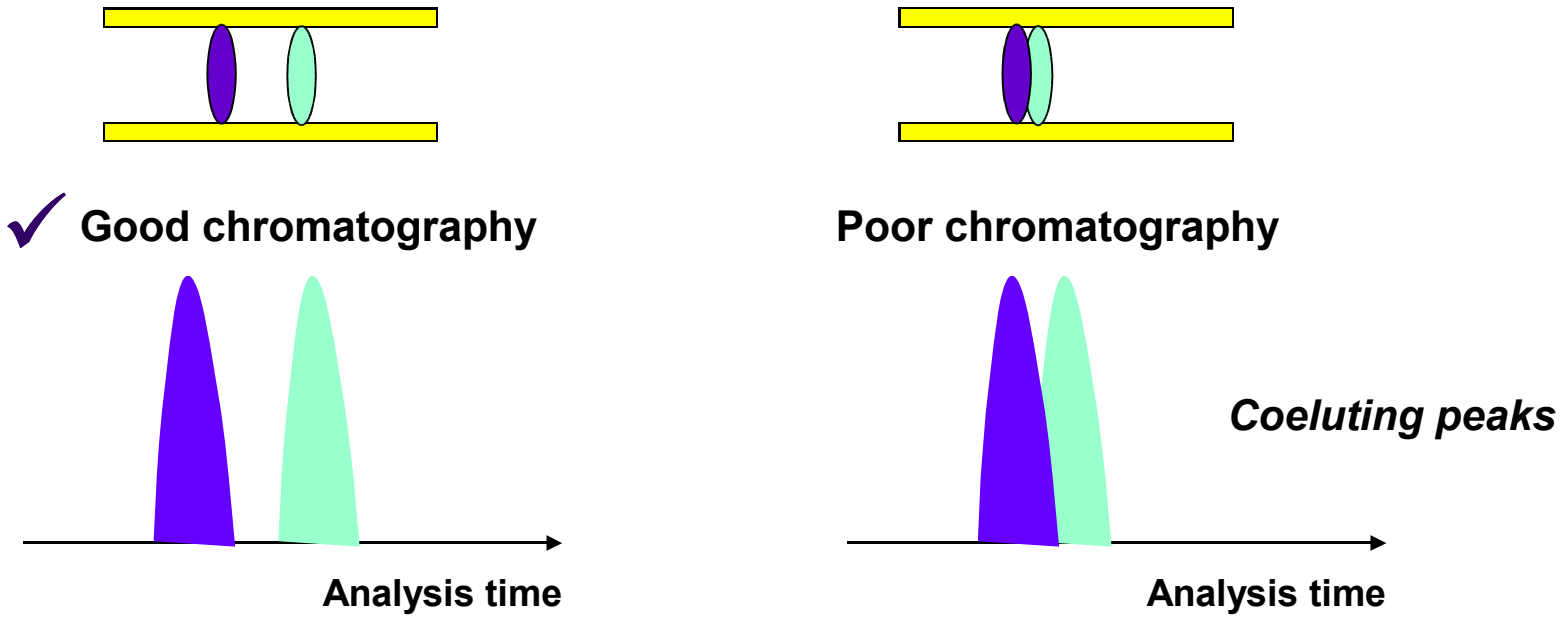


Chromatographic Data



Goal of Gas Chromatography

- *No overlap between adjacent sample bands as they exit the column*

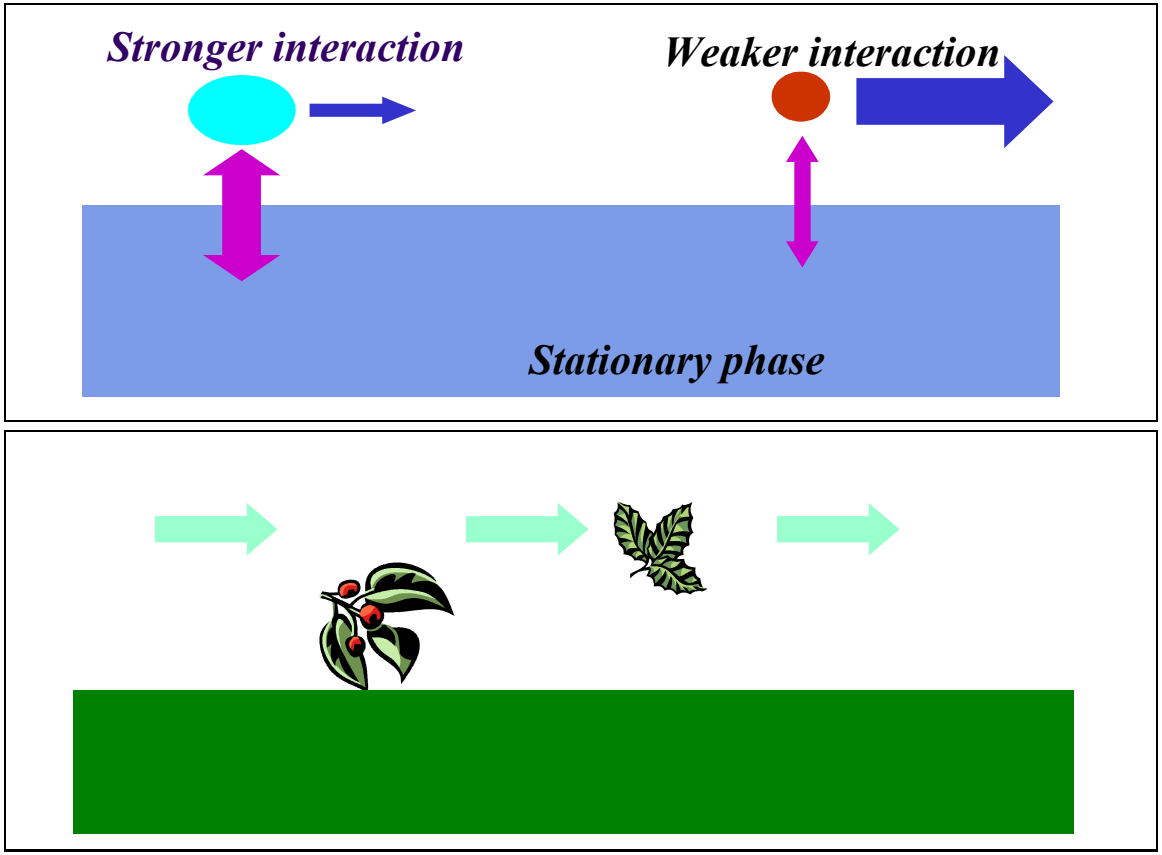


➔ Make each sample band travel at a different rate

➔ Minimize the width of the sample band

Migration rates of compounds in column (1)

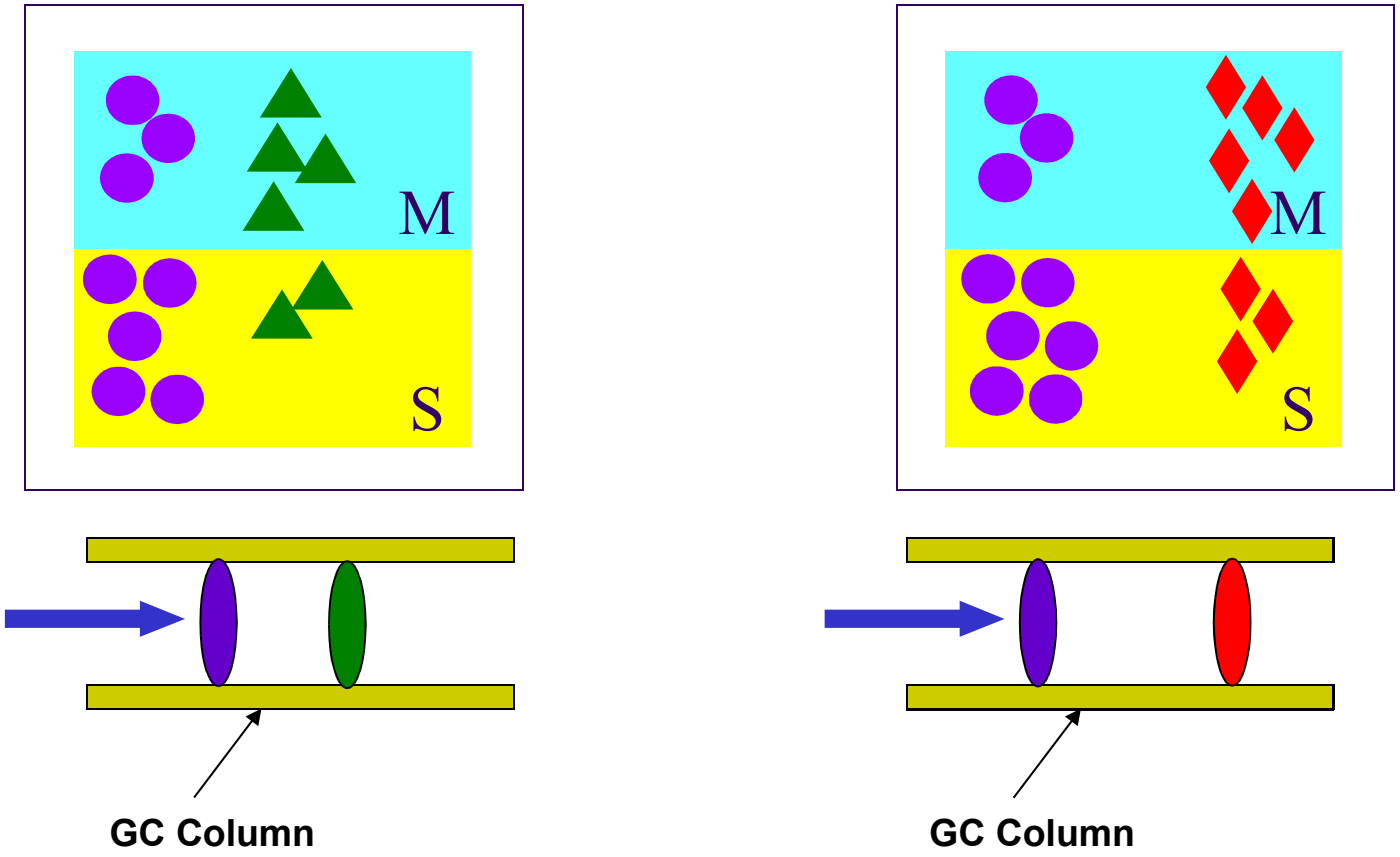
- Different migration rates of compounds can be achieved if these compounds have different interaction strengths with the stationary phase



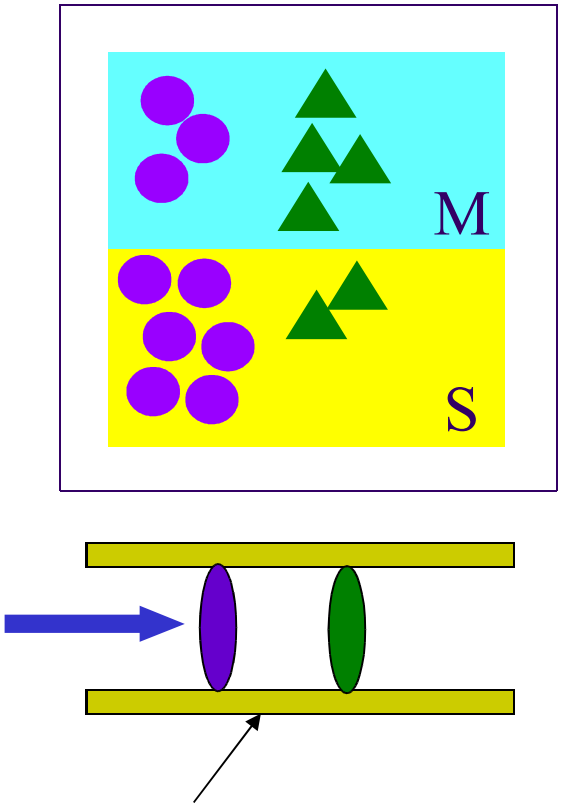
Migration rates of compounds in column (2)

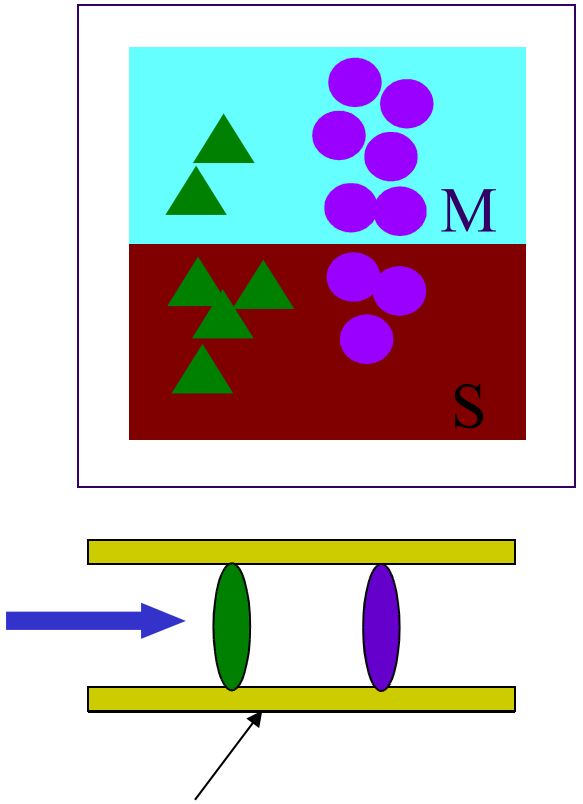
- Migration rate of compounds in column depend on:
  - Compound chemical structure
  - Stationary phase chemical structure
  - Column temperature

Effect of compound chemical structure on migration rate

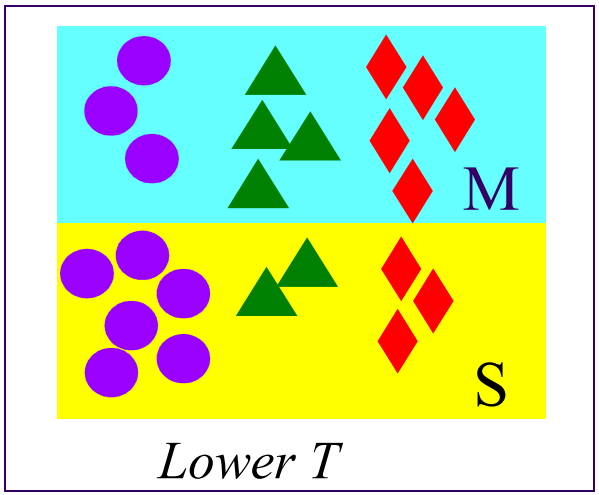


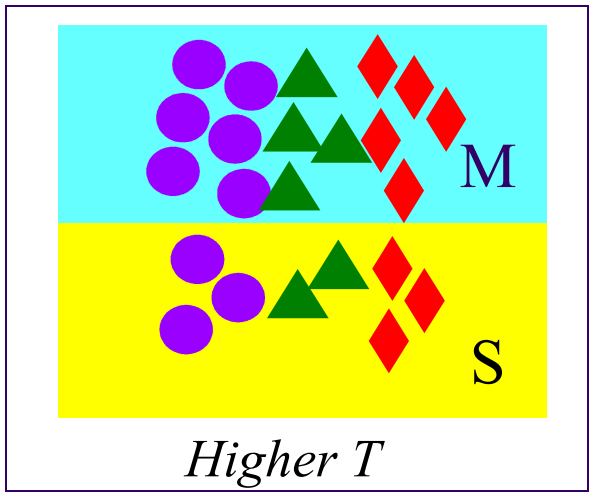
Effect of stationary phase on migration rate

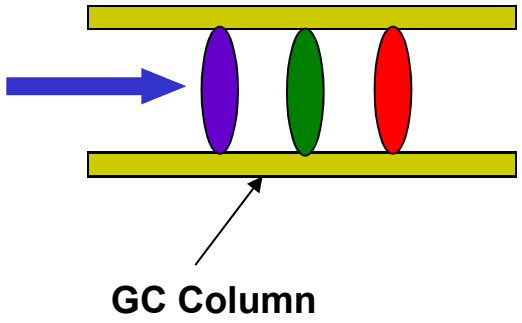


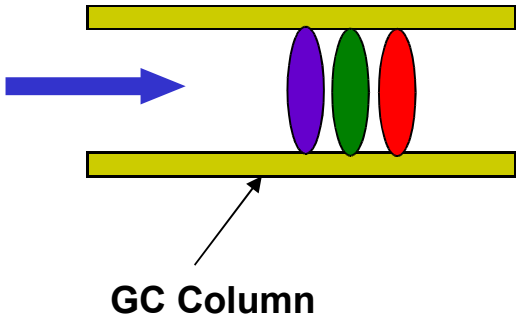


Effect of column temperature on migration rate









Sample Band Width

- Sample band width depends on:
  - Operating conditions
  - Dimensions of the column

GC Parameters

- Retention time (t_R)
- Retention time of unretained compound (t_M)
- Retention factor (k)
- Distribution constant (K)
- Phase ratio (β)
- Separation factor (α)
- Resolution (R)
- Number of theoretical plates (N)
- Height equivalent to a theoretical plate (HETP)
- Carrier gas linear velocity (v)

Retention Time (t_R)

- The time an analyte takes to travel through the column
- A measure of the amount of time an analyte spends in the column
- Sum of the time spent in the stationary phase and the mobile phase

Retention time of an unretained compound (t_M)

- The time an unretained compound takes to travel through the column
- Unretained compound travels down the column at the same rate as the mobile phase (carrier gas)
- Equivalent to the time a compound spends in the mobile phase

Retention factor (k)

- Another measure of retention
- Ratio of the amount of time a compound spends in the stationary and mobile phases
- A measure of retention by the stationary phase
- Previously called capacity factor, or partition factor

$$k = \frac{t_R - t_M}{t_M}$$

Distribution constant (K)

- Ratio of analyte concentration in the stationary phase and mobile phase
- K is constant for a given compound, stationary phase, and column temperature

$$K = \frac{c_S}{c_M}$$

c_S = concentration in stationary phase

c_M = concentration in mobile phase

Phase Ratio (β)

- The change in the phase ratio can be used to calculate the change in a compound's retention, provided that the same stationary phase and column temperature (program or isothermal) are maintained

- An increase in phase ratio results in a decrease in retention (k), since K is constant; and vice versa

$$\beta = \frac{r}{2d_f}$$

$$K = k\beta$$

r = column radius (μm)

d_f = film thickness (μm)

Separation Factor (α)

- A measure of the time or distance between the maxima of two peaks

- α = 1 means the two peaks have the same retention and co-elute

$$\alpha = \frac{k_2}{k_1}$$

Resolution (R)

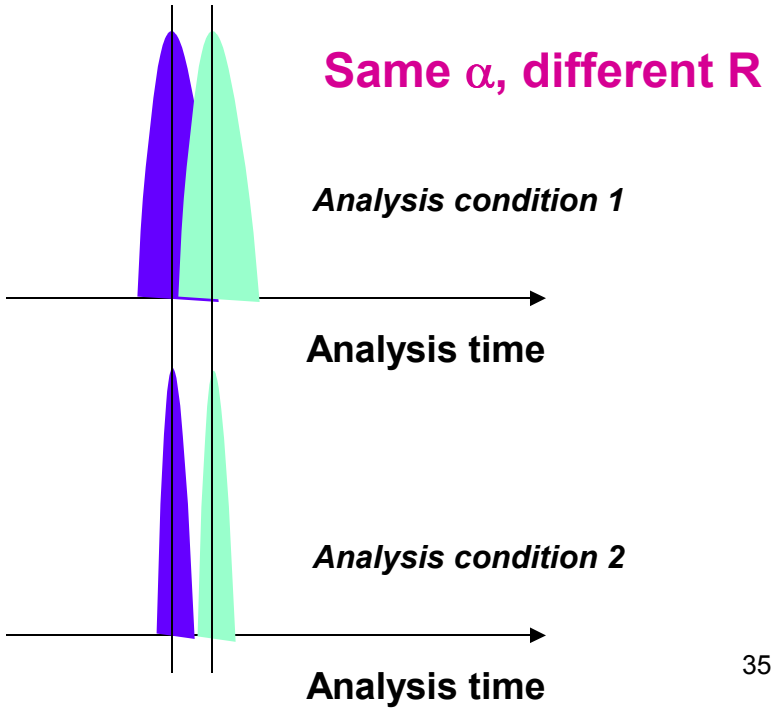
- A measure of overlap between two peaks; the higher the resolution, the less the overlap
- Separation (α) is only the distance between two peak maxima; resolution takes both α and the width of the peaks into account
- Baseline resolution usually occurs at R = 1.50

$$R = 1.18 \left(\frac{t_{R2} - t_{R1}}{w_{h1} + w_{h2}} \right)$$

$$R = 2 \left(\frac{t_{R2} - t_{R1}}{w_{b1} + w_{b2}} \right)$$

w_h = peak width at half peak height

w_b = peak width at base



Number of theoretical plates (N) or Column Efficiency

- Theoretical plates is a concept
- Theoretical plates numbers are an indirect measure of peak width for a peak at a specific retention time
- Columns with high N are considered to be more efficient than those with lower N
- A column with a high N will have a narrower peak at a given retention time
- Column efficiency is a function of:
  - Column dimensions
  - Type of carrier gas and its average linear velocity
  - Compound and its retention

$$N = 5.545 \left(\frac{t_R}{w_h} \right) \qquad N = 16 \left(\frac{t_R}{w_b} \right)$$

Height equivalent to a theoretical plate (HETP or H)

- Another measure of column efficiency

- Small plate heights indicate higher efficiency

$$H = \frac{L}{N}$$

L = column length (mm)
N = theoretical plates number

Carrier Gas Linear Velocity (v)

- Affects the chromatographic resolution (i.e. separation)

- For each gas there is a linear velocity where optimum separation can be achieved (minimum HETP)

Van Deemter Curve