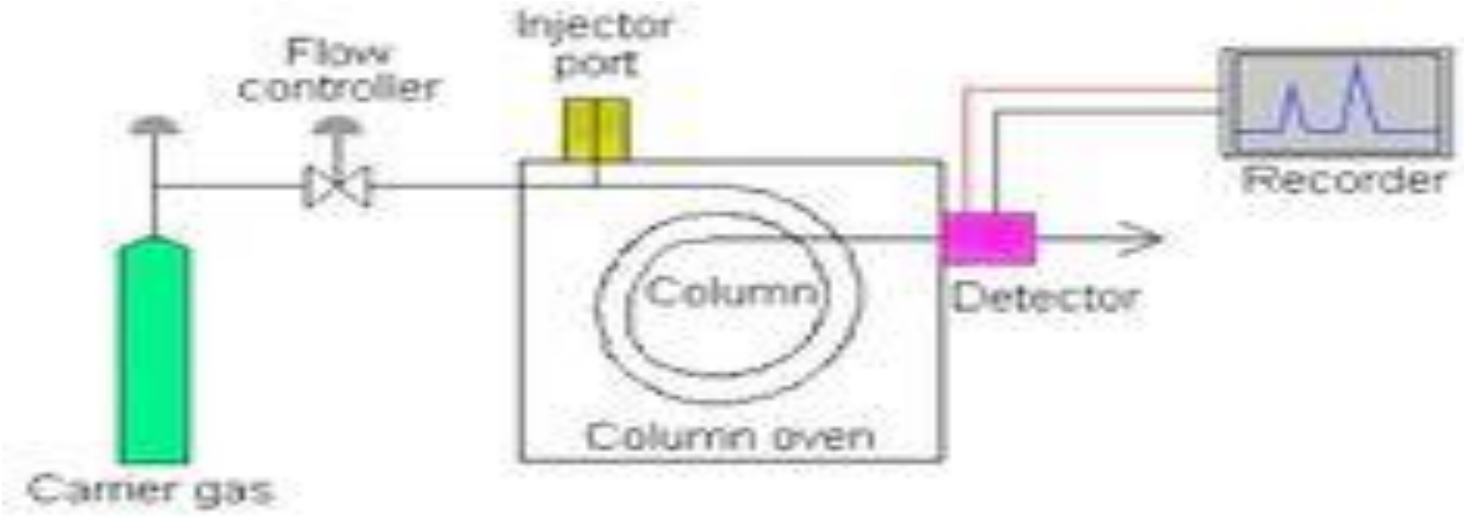
Gas Chromatography (GC)



What is chromatography?

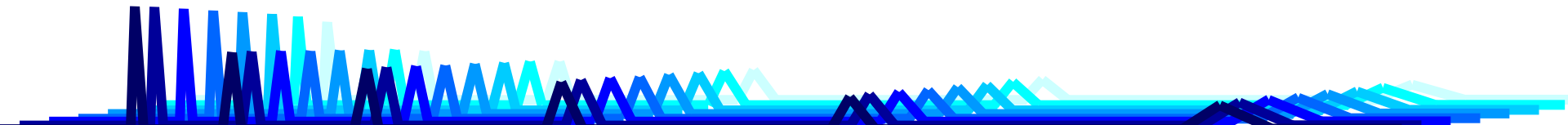
A physical method of separation

No reaction occurs during the separation process

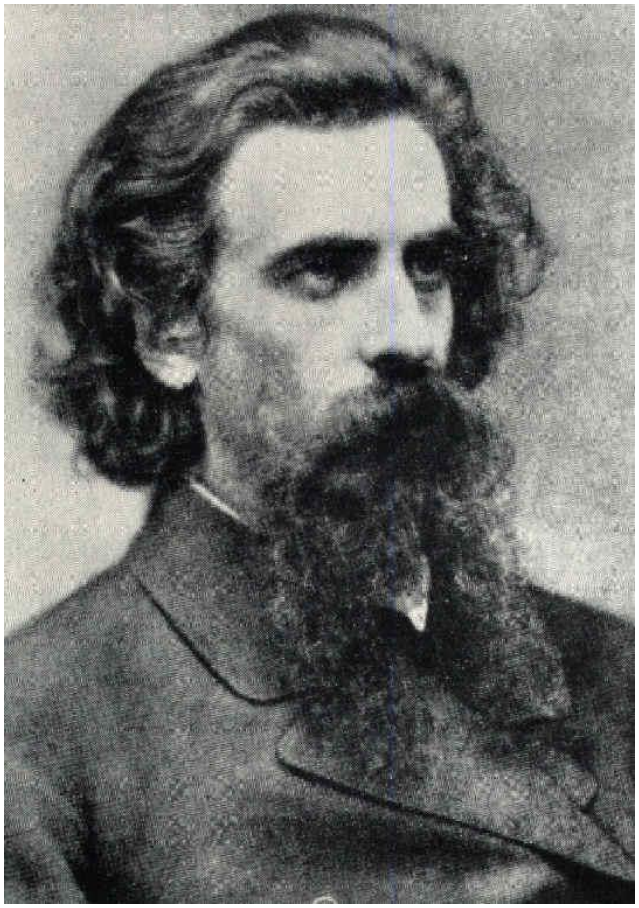
The components partition between two phases:

- the stationary phase which is fixed and does not move
- the mobile phase which moves along the column

The separation of solutes occurs owing to their volatility and the different interactions with the two phases



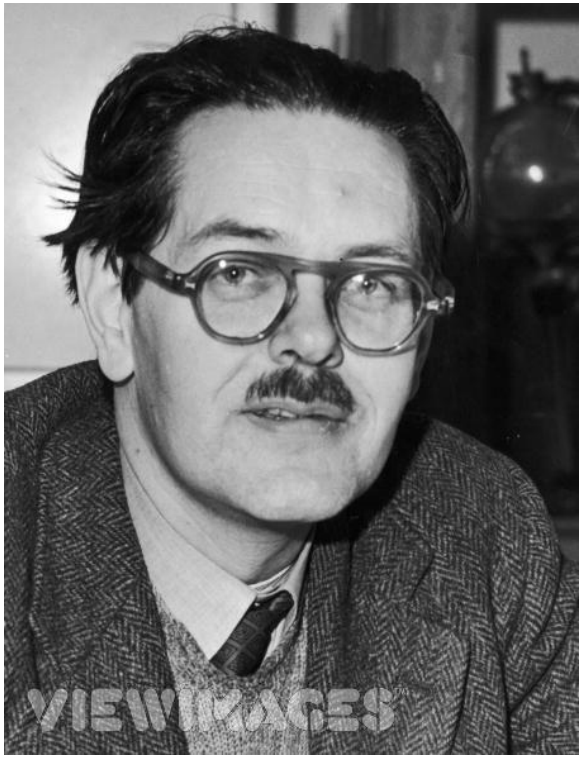
History



- Russian Scientist Mikhail Semenovich Tswett is credited for the discovery of chromatography (1903)
- German student Fritz Prior is credited for developing gas chromatography (1947)

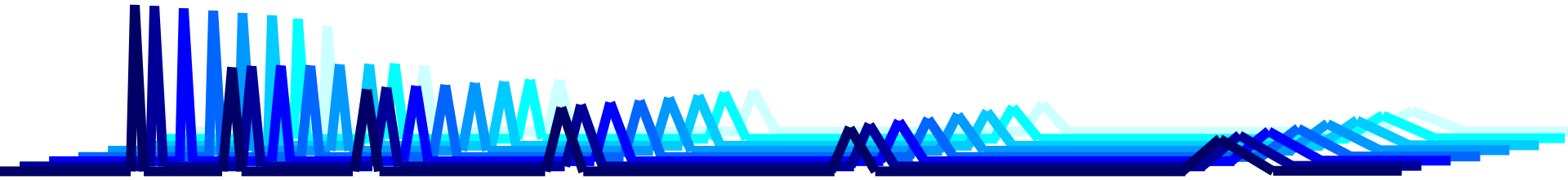
Gas Chromatography

- John Porter Martin (UK) is the father of modern gas chromatography
- He developed the first liquid-gas chromatograph instrument (1950)
- He won the Nobel Prize in Chemistry winner (1952)

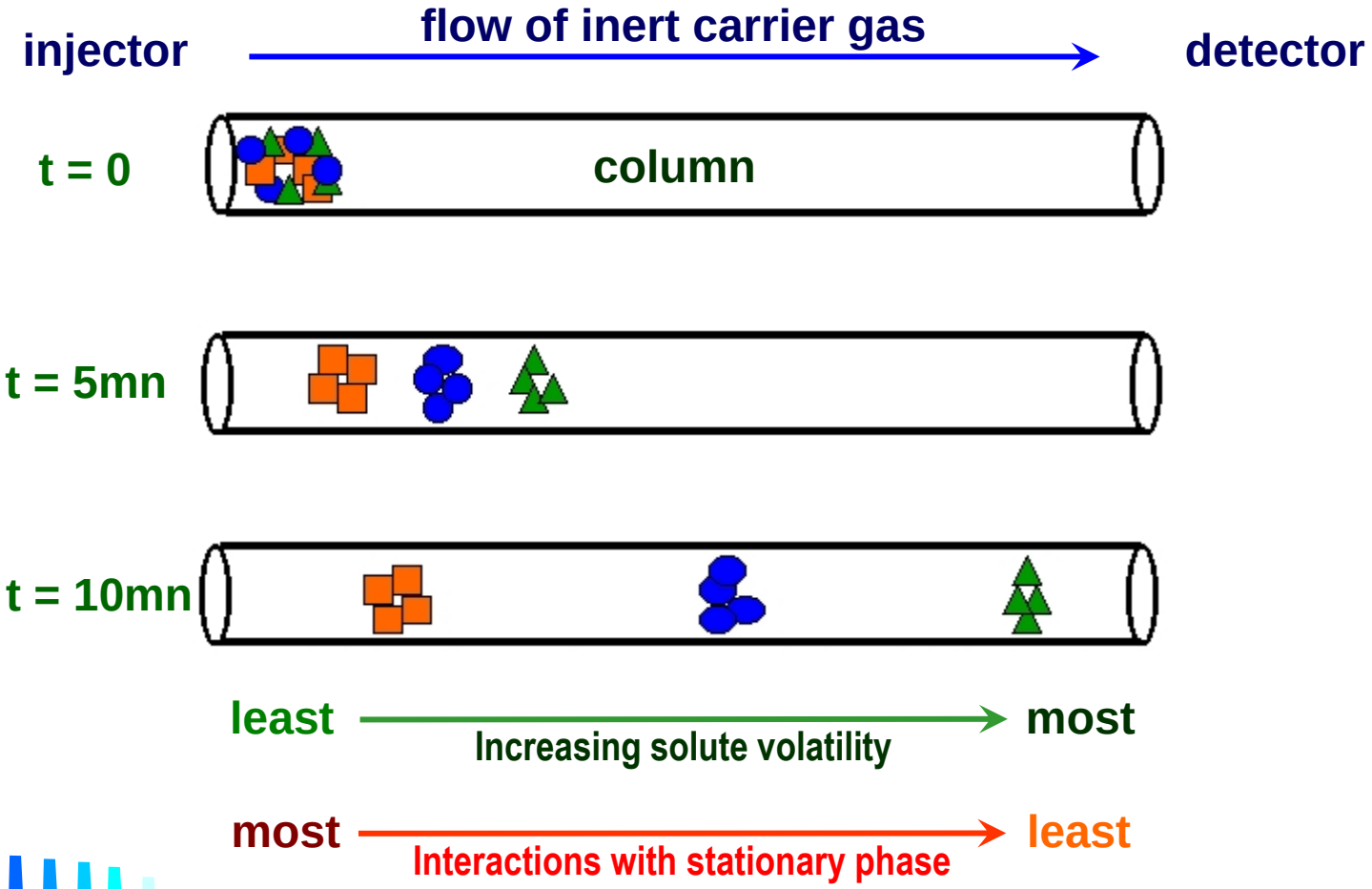


Gas chromatography principle

- Sample is injected then vaporised onto head of a chromatographic column.
- Elution is produced by the flow of an inert gaseous mobile phase.
- Separation is based upon the partition of the vaporized analyte between a gaseous mobile phase and a liquid phase immobilised on the surface of an inert solid (GLC)
- Inert carrier gas does not interact with molecules of the analyte.
- Eluted analytes are detected by a detector and recorded by the data system
- GC columns are either packed (particles coated with liquid stationary phase) or capillary (the most used now)

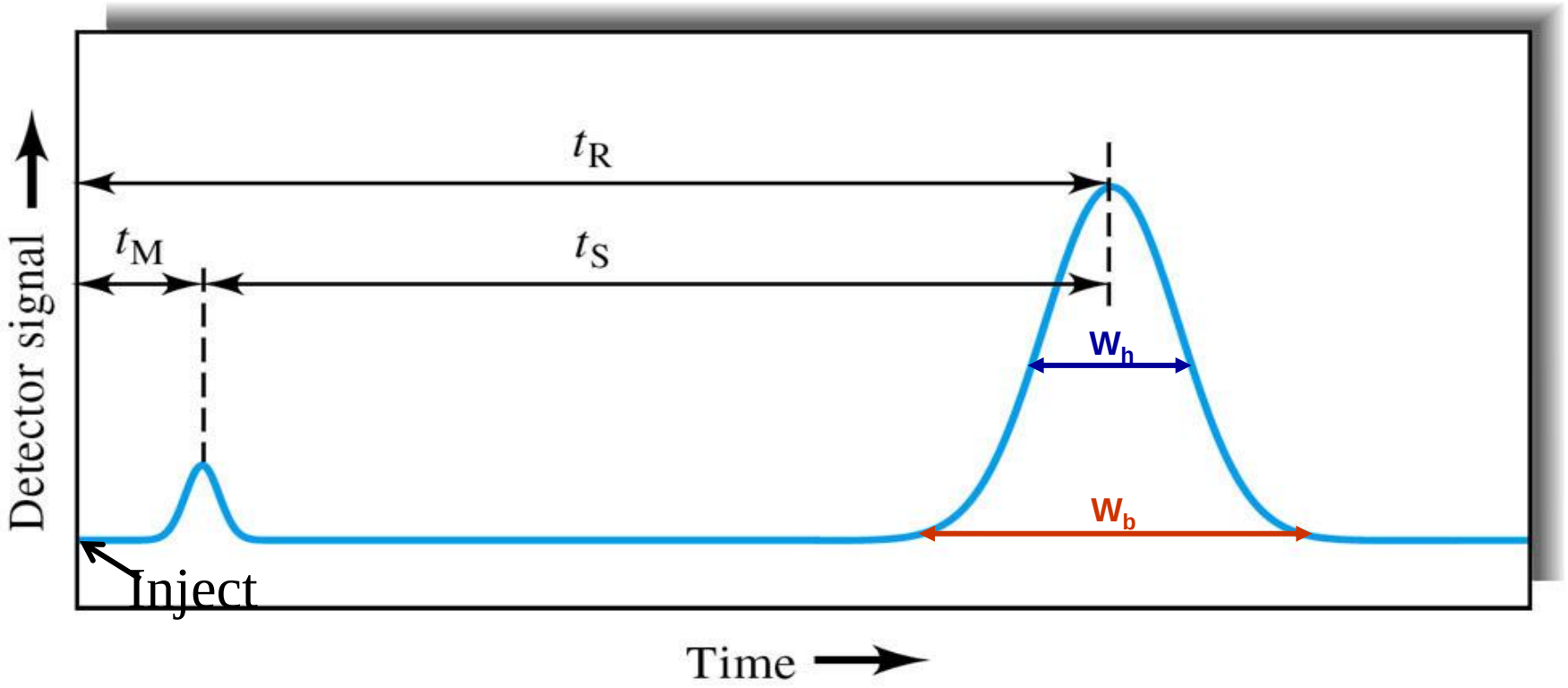


Chromatographic separation process in GC



Theory of Chromatography

Typical chromatogram: concentration versus elution time



where:

t_R = retention time

t_M = void time (dead time, non-retained solute)

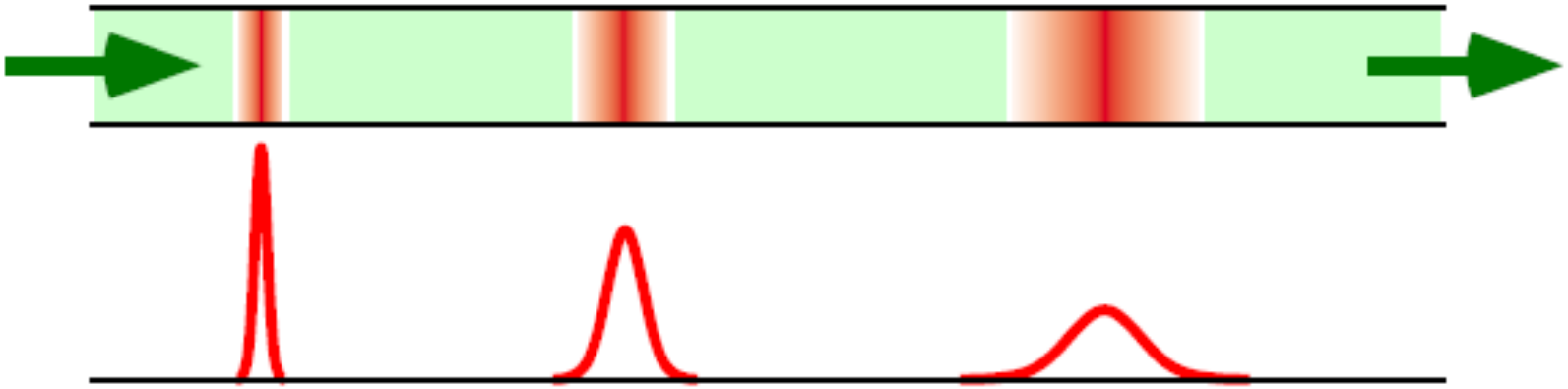
W_b = baseline width of the peak in time units

W_h = half-height width of the peak in time units (d)

What is the cause of peak width?

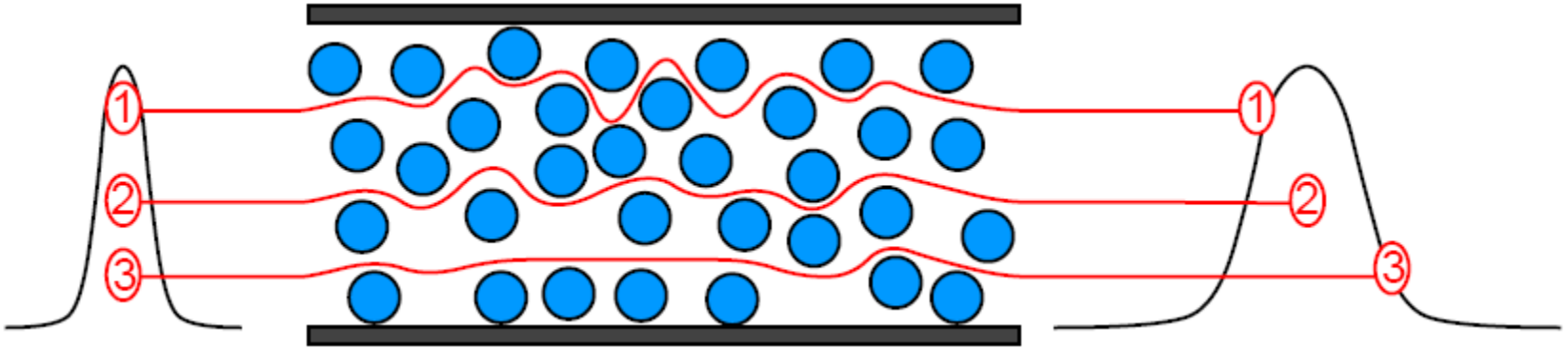
Each elution band spreads due to several phenomena:

a. Eddy diffusion
b. Mobile phase mass transfer
c. Stagnant mobile phase mass transfer
d. Stationary phase mass transfer
e. Longitudinal diffusion



Eddy diffusion

A process that leads to peak (band) broadening due to the presence of multiple flow paths through a packed column.



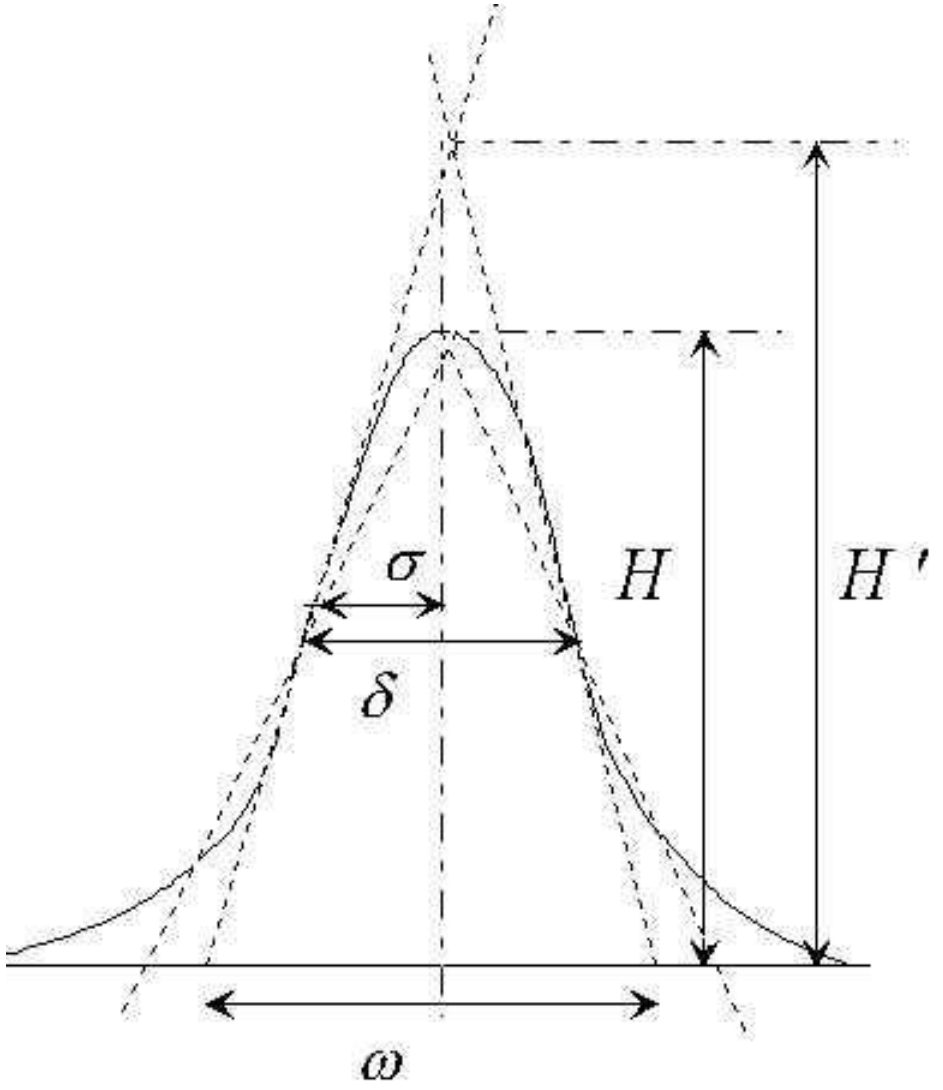
- Solute 1: longer path ➔ higher retention time
- Solute 3: shorter path ➔ lower retention time

} broad peak

- *In capillary columns there is no packing ➔ there is no Eddy diffusion, then peaks are narrower and separation is better*

Chromatographic peak:

- supposed gaussian
- σ: standard deviation
- δ: width at half-height
- ω: baseline width
- Since is often difficult to accurately evaluate the beginning and end of the peak, most equations use the width at half-height δ which can be easily measured on the chromatogram



Some fundamental equations:

- **Corrected retention time:**

$$t'_R = t_R - t_M$$

- **Capacity ratio: corresponds to a relative retention:**

$$k = t'_R / t_M = (t_R - t_M) / t_M$$

- **Column selectivity:**

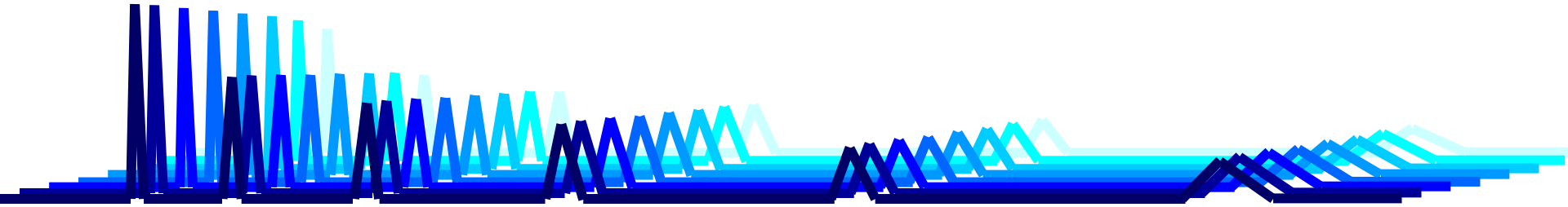
$$\alpha = t'_{R2} / t'_{R1} = k_2 / k_1 \quad (\alpha > 1 \text{ because } t'_{R2} > t'_{R1})$$

- **Resolution between two neighboring peaks:**

$$R_S = 2\,(t_{R2} - t_{R1}) / (\omega_2 + \omega_1) = 1.18\,(t_{R2} - t_{R1}) / (\delta_2 + \delta_1)$$

- *For two neighboring peaks, a resolution R_S higher than 1 means a complete separation (for $R_S = 1$, the overlapping peak surface is 2%)*

- *When R_S is less than 0.8, the separation between the two peaks is considered to be incomplete*



Column efficiency:

The chromatographic peaks being supposed gaussian, the peak broadening can be related to the separation and the column efficiency which is evaluated by the number of theoretical plates of the column N (similarly to distillation process). For a gaussian peak, N can be calculated by one of the following equations:

$$N = (t_R / \sigma)^2$$ (σ: standard deviation of the peak)

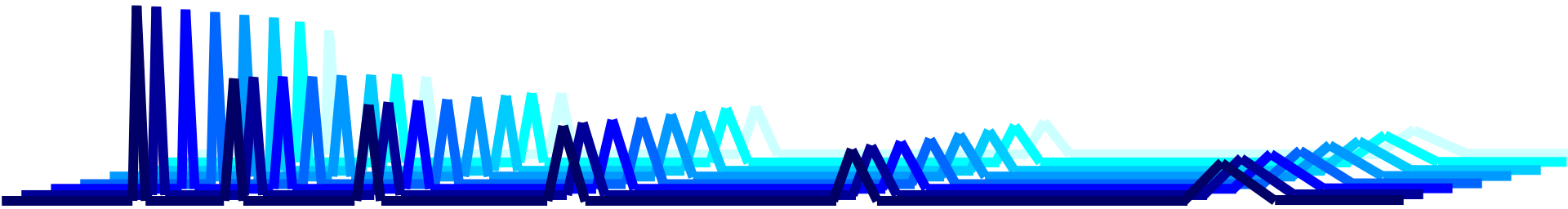
$$N = 16\,(t_R / \omega)^2$$ (ω: width at baseline)

$$N = 5.54\,(t_R / \delta)^2$$ (δ: width at half- height)

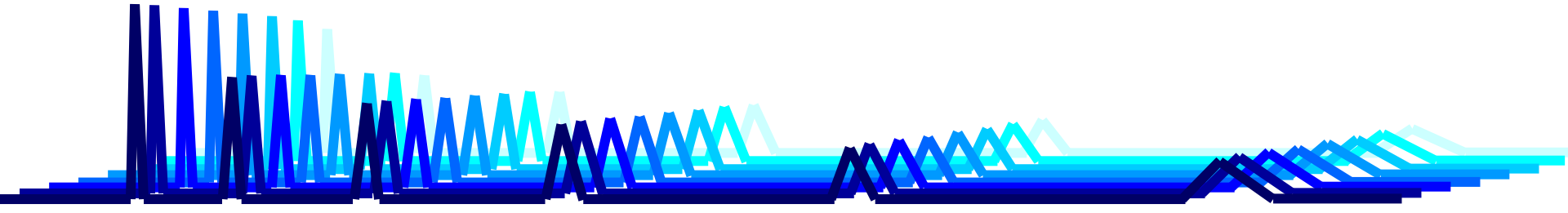
In order to compare columns having different lengths, one calculate the height equivalent to a theoretical plate HETP:

$$H = L/N$$ (L : column length)

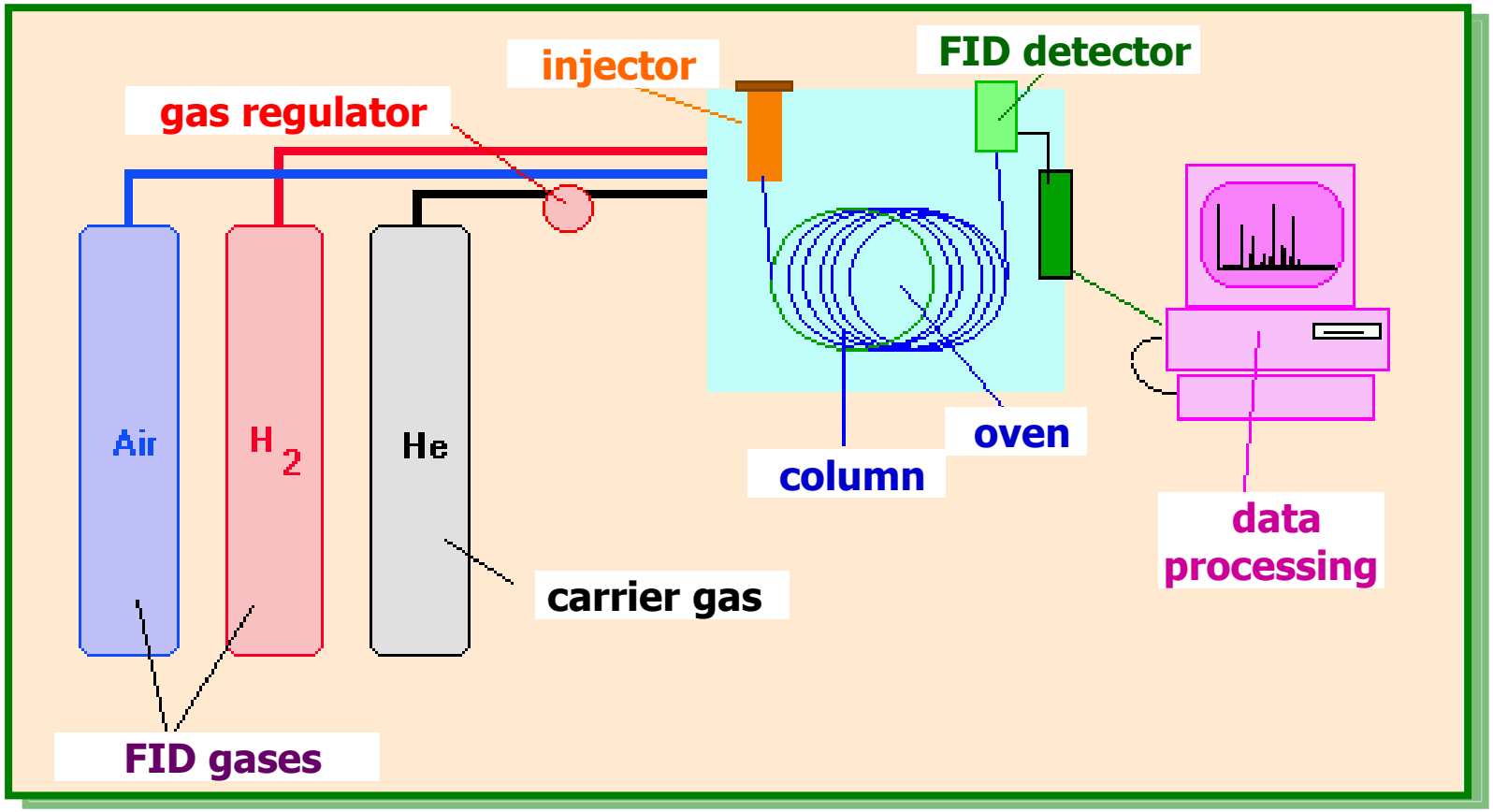
H may vary from centimeters (packed columns) to several microns (high resolution capillary columns)



Gas chromatography equipment

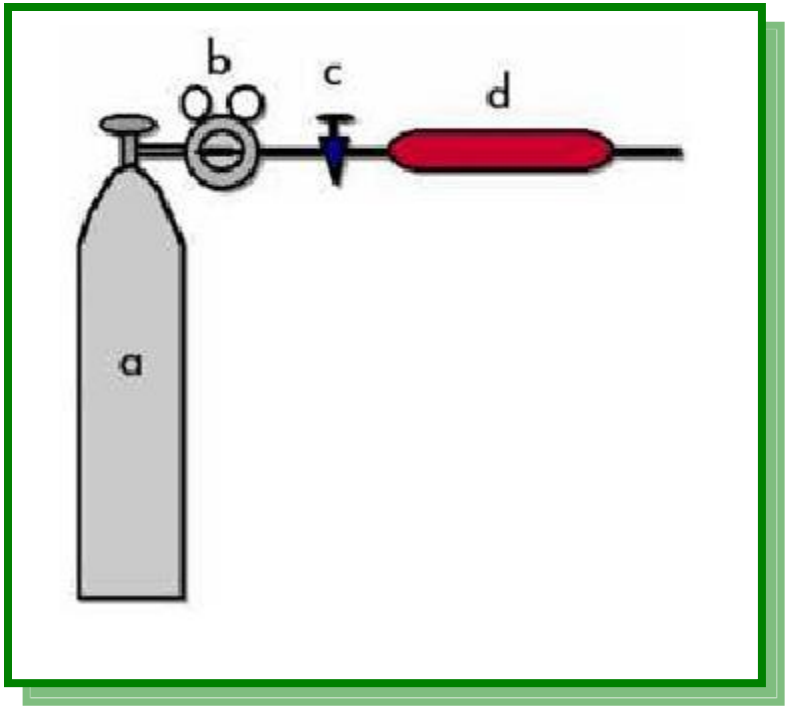


Main parts of a gas chromatograph

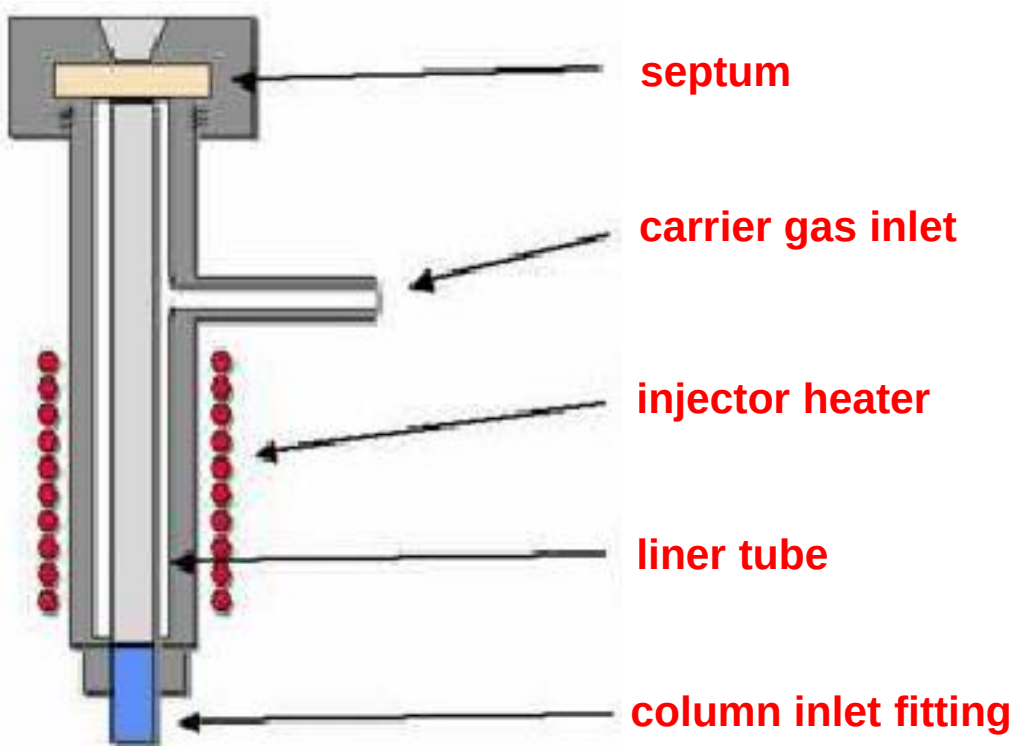


Carrier gas

- The carrier gas should be inert
- The best carrier gases are:
  - helium
  - nitrogen
  - hydrogen (highly flammable)
- *Gas supply:*
- *a* : compressed gas cylinder
- *b* : double stage pressure regulator
- *c* : valve
- *d* : gas filter (to eliminate impurities such as: water, oxygen, hydocarbons,…)



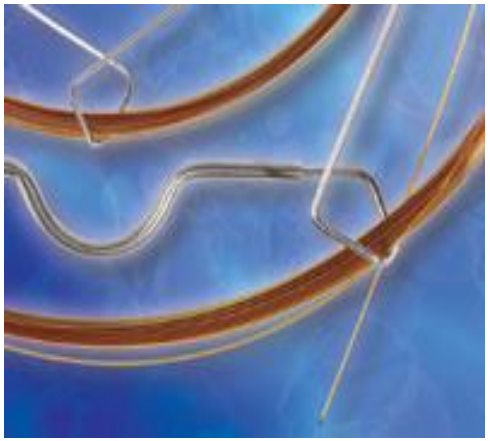
Injection port



Columns in gas chromatography

Packed columns

- 2 to 4 mm I.D. and 1 to 4 meters long.
- Packed with a suitable adsorbent.
- Mostly used for gas analysis.
- Peak broadening due to zone (eddy) diffusion resulting from multitude of pathways a molecule can pass through column.



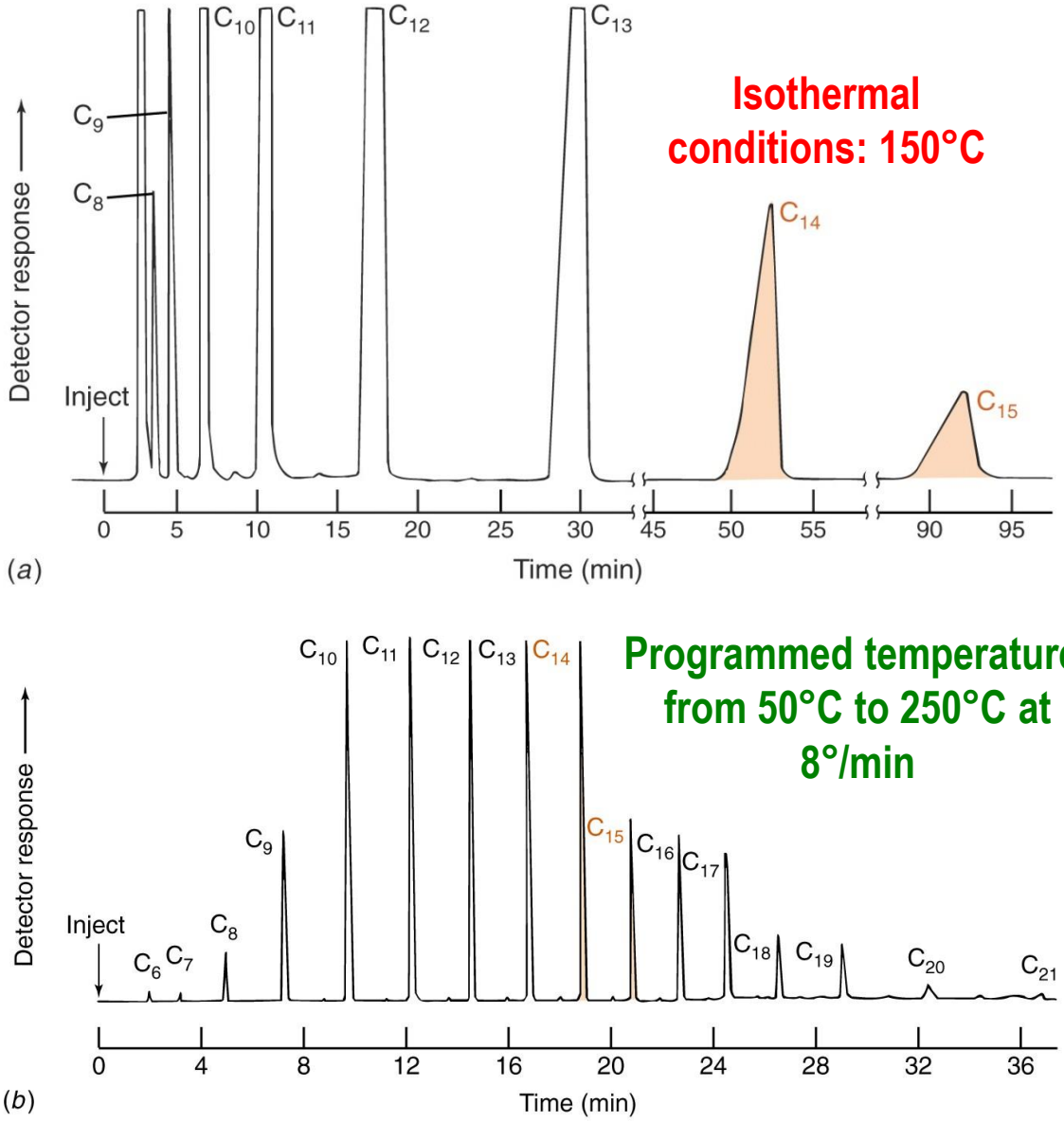
Capillary columns

- 100 mm to 500 mm I.D. and 10 m to 100 m long
- Stationary phase is coated on the internal wall of the column as a film 0.2 mm to 1 mm thick
- Sharper peaks – no Eddy diffusion.
- Up to 500,000 theoretical plates – excellent separations.
- Most popular type of column in use.

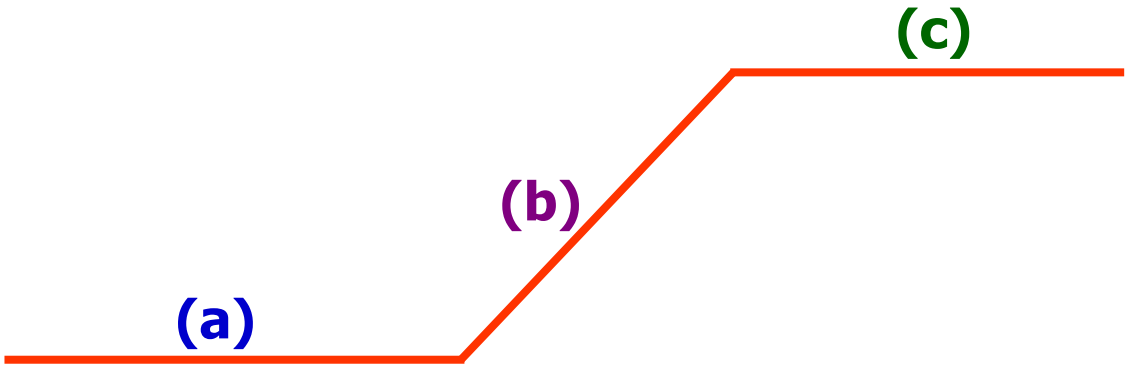
Isothermal and programmed temperature in GC

Example: GC separation of n-alkanes

Temperature gradient improves resolution while also decreasing retention time



A typical **temperature program in GC**

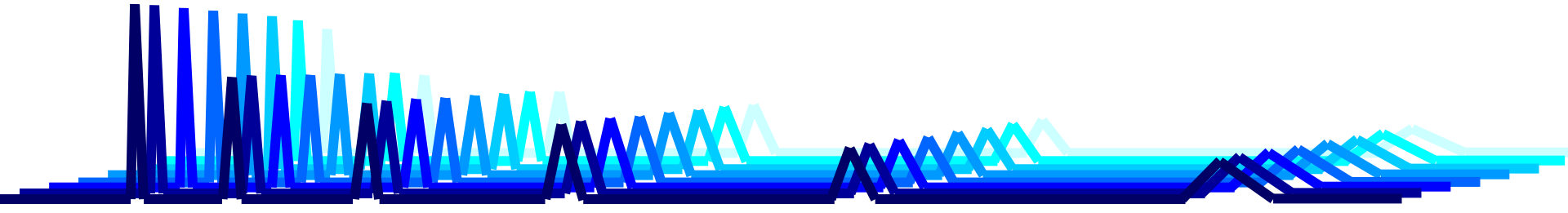


- **(a)** : initial temperature and time
- **(b) : temperature ramp (°/min)**
- **(c) : final temperature and time**

The temperature program can be more complex

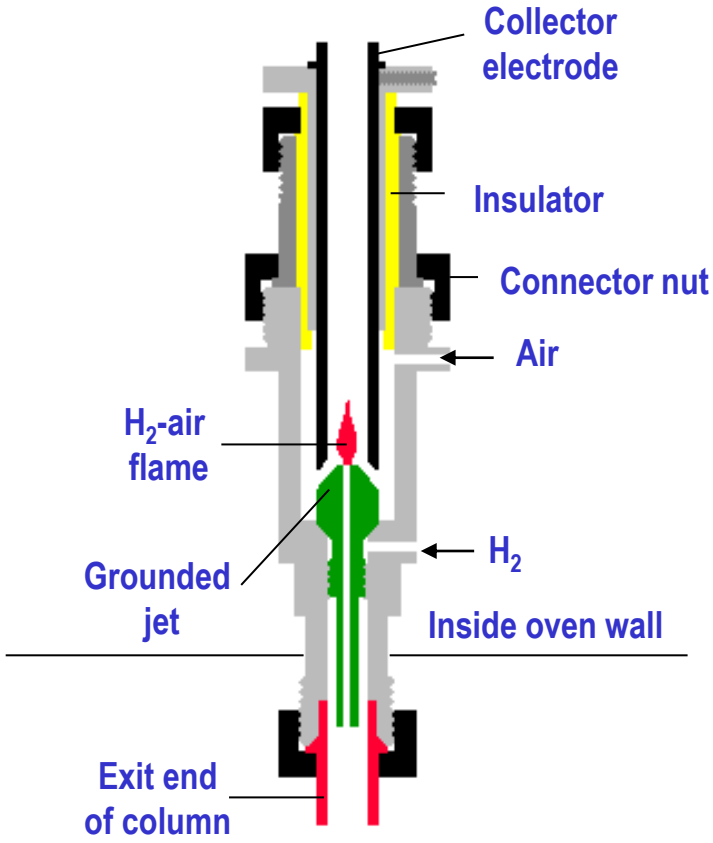
Characteristics of a GC detector

- *Stability and reproducibility.*
- *General or specific detector*
- *Destructive or non-destructive.*
- *Linear response to analytes that extends over several orders of magnitude.*
- *Temperature range (better: from room temperature to 400ºC).*
- *Response time: short and independent of flow rate.*
- *High reliability and ease of use.*



Flame ionisation detector (FID)

- FID is the most used detector in GC
- Most organic compound pyrolyse in H_2 -air flame and produce ions and electrons.
- A potential of a few hundred volts is applied across the burner jet and a collector electrode located above the flame.
- The resulting current is amplified and proportional to the number of carbon atoms in the flame.
- General detector for GC. However, heteroatom containing groups yield few electrons. Also insensitive to H_20 CO_2 SO_2 NO_X.
- Large linear response range (~ 10^7) and low noise
- Exhibits very high sensitivity ~ 10^{-13} g/s of analyte/second



Advantages and disadvantages of GC

- Fast analysis
  * typically minutes (even sec.)
- High resolution
  * Plate number N can be higher than 10^6
- Sensitive detectors (easy ppm, often ppb or less)
- Highly accurate quantification (1-5 % RSD)
- Automated systems
- Non-destructive detectors
  * allows online coupling to mass spectometry
- Small sample (µL)
- Reliable and relatively simple
- Low cost (~ €20,000)

- Limited to volatile samples
- - Temperature limited to ~ 380°C
- Needs P_{vap} ~ 60 Torr at that temperature
- Not suitable for thermally labile samples
- Some samples may require extensive preparation (derivatization)
- Requires spectroscopy (usually MS or MSMS) to confirm peak identify