Modelling a Gas Chromatograph

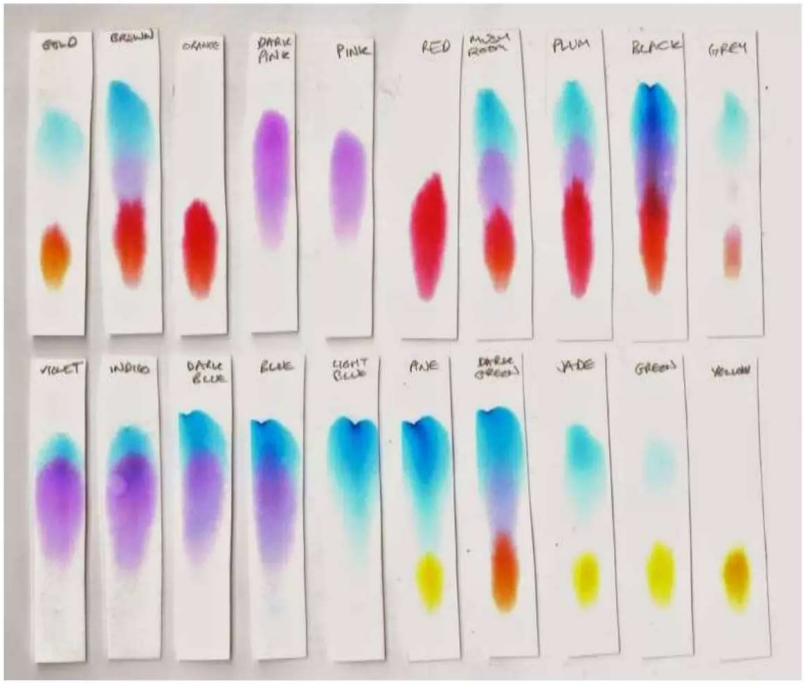
Mathematics in Study Group 2024

Alba Cabrera Codony

Chromatography

- Chromatography is a way to separate mixtures
- We become ‘lab detectives’ and look at the quality of products
- We can identify different compounds based on their chemistry
- and view chemicals which should not be present

Instruments for Gas Chromatography laboratory analysis



***Ink chromatography**: the dyes get separated pulled through the paper by water*

Applications of Chromatography

Food and Beverage Industry

- ✓ Composition of food products: Enables to identify and quantify the various chemicals
- ✓ Discovering their nutritional properties: Proteins, Fats, Sugars, …
- ✓ Nutritional Analysis: Vitamins, Preservatives, Additives, …
- ✓ Pesticide Residues and microbial analysis
- ✓ Quality control: compounds that contribute to the Aroma and Flavor.

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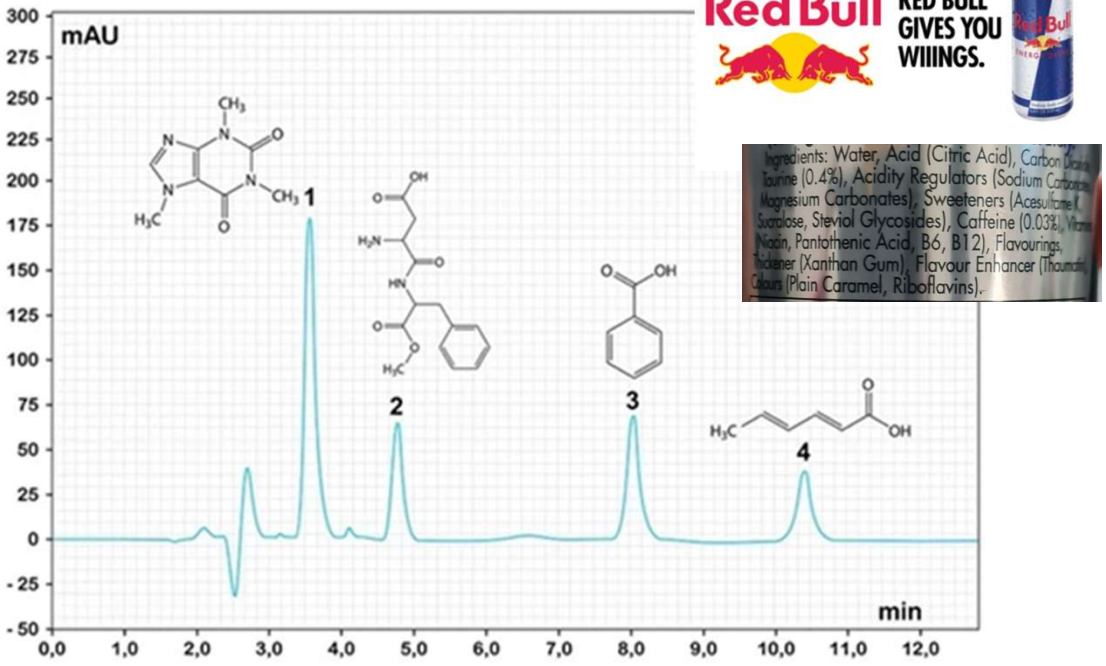
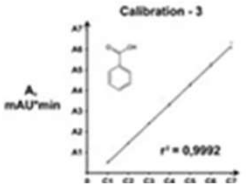
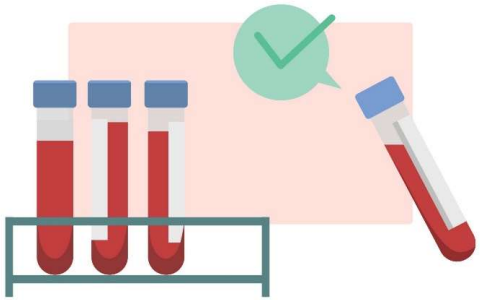


No.	Peak name	Ret. time, min	Area, mAU*min	Height, mAU	Amount, mg/L
1	Caffeine	3,560	26,5392	181,738	22,461
2	Aspartame	4,787	10,0363	68,106	51,107
3	Benzoic acid	8,053	15,8525	70,416	5,053
4	Sorbic acid	10,511	9,9644	38,081	5,098

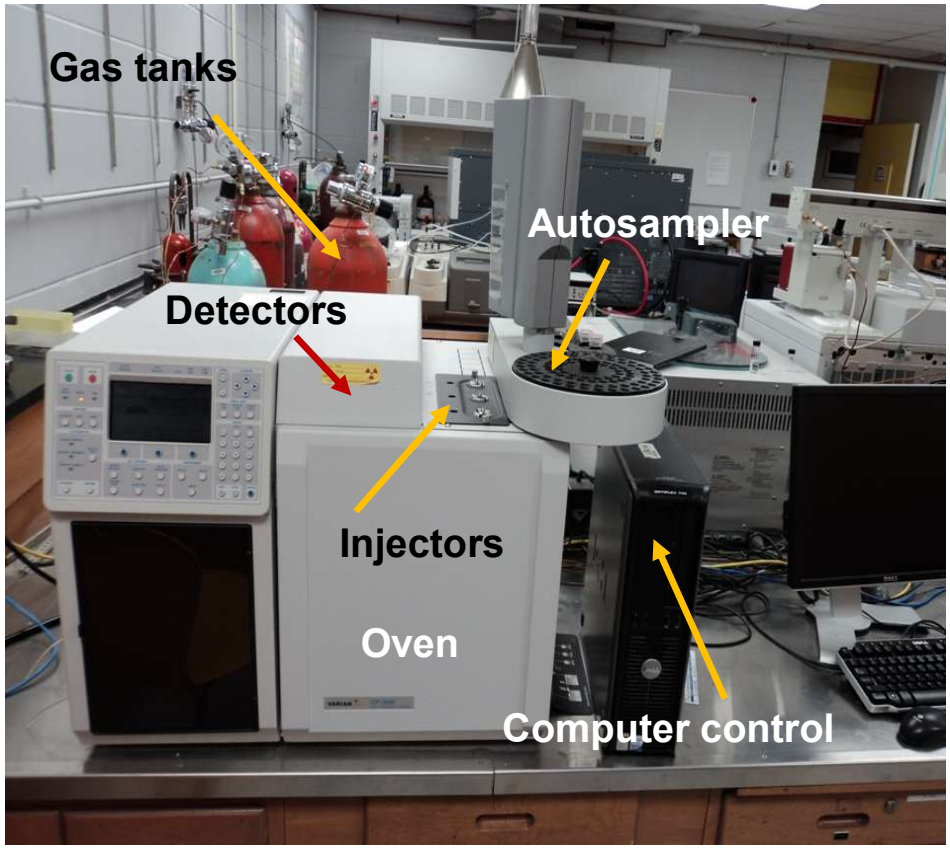


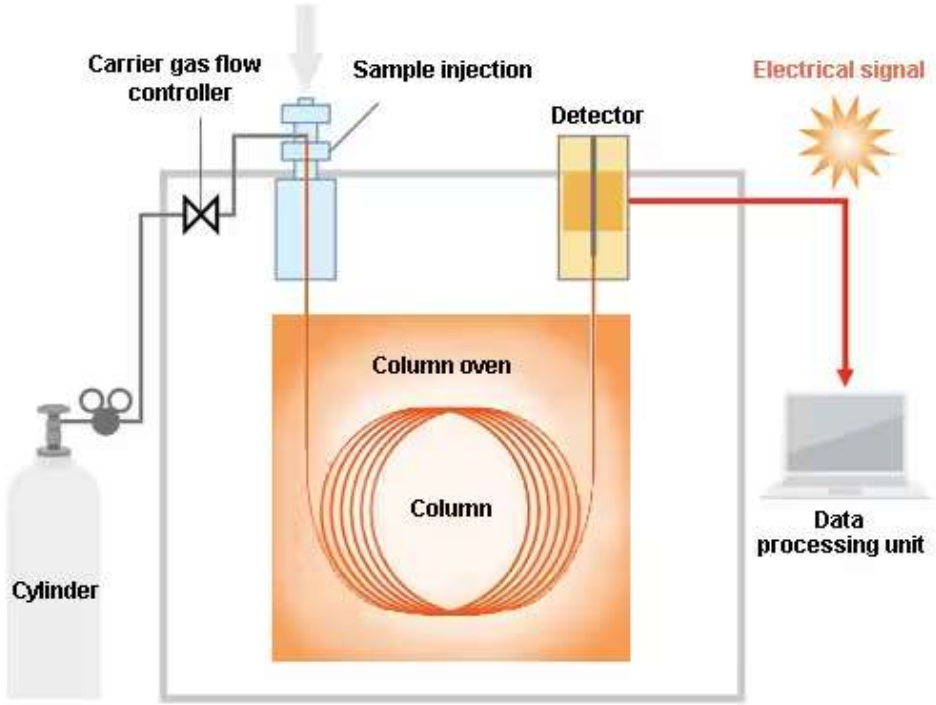
Applications of Chromatography

- Test water samples for pollution
- Test for additives in fuels and oils
- Test air samples for pollution, explosives or drugs
- Identify people using a sample from their body



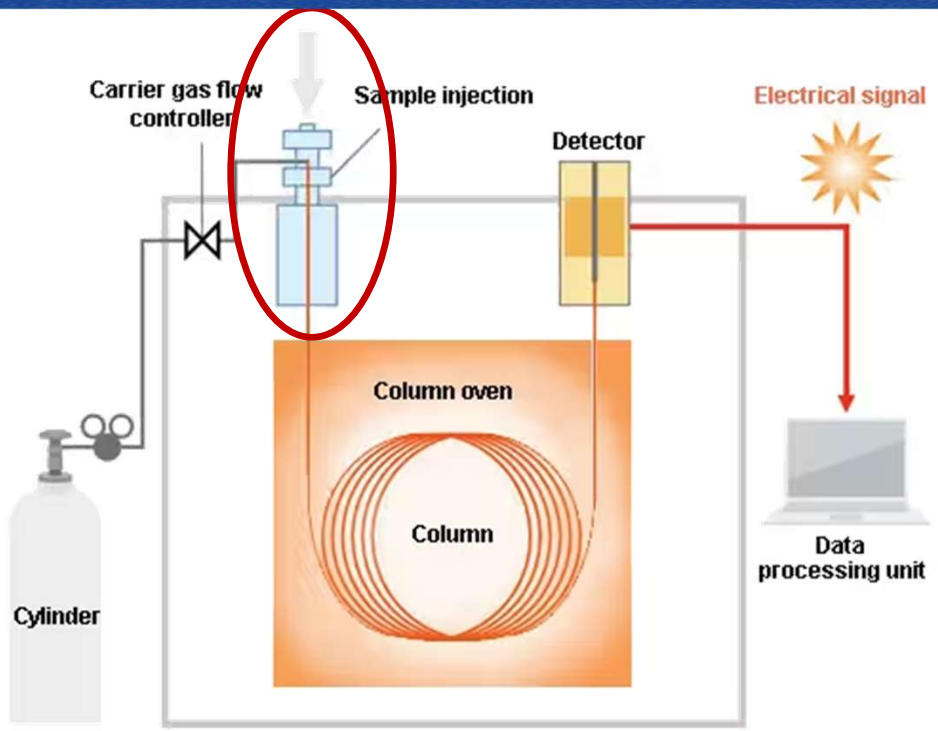
Gas Chromatograph





Gas Chromatograph: sample injection

A small amount of the sample containing different compounds is injected into the chromatograph.



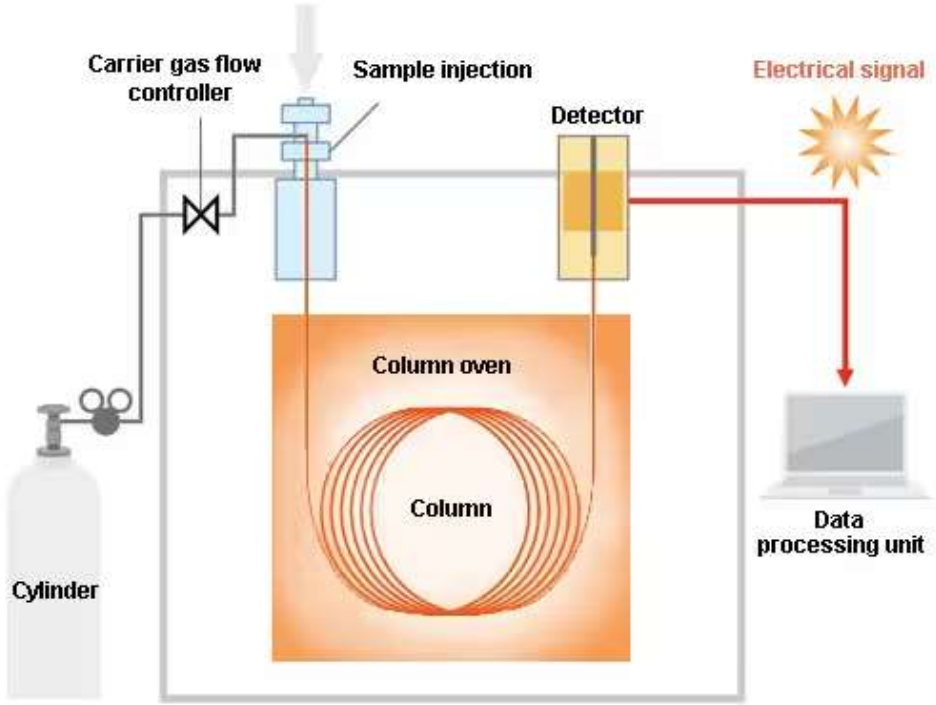
To be suitable for GC analysis a compound must have **sufficient volatility** and **thermal stability**.

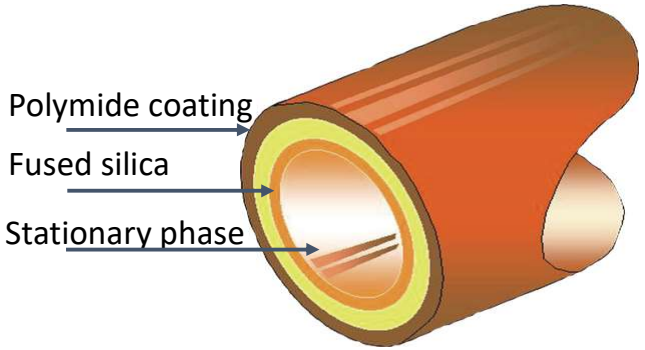
The instrument **vaporizes** a sample and **transports it via a carrier gas** into the column.

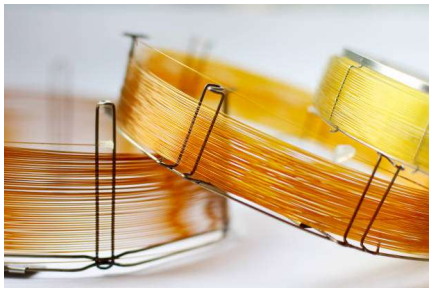
Gas Chromatograph: The Column

The separation happens here.

- A capillary GC column is composed of narrow **tubing 30 m long**, with an ID of 250-500 µm and with a thin polymer coating (0.1 – 10.0 µm) inside.
- Separations are highly temperature-dependent, so **the column is placed in a well-controlled oven**.



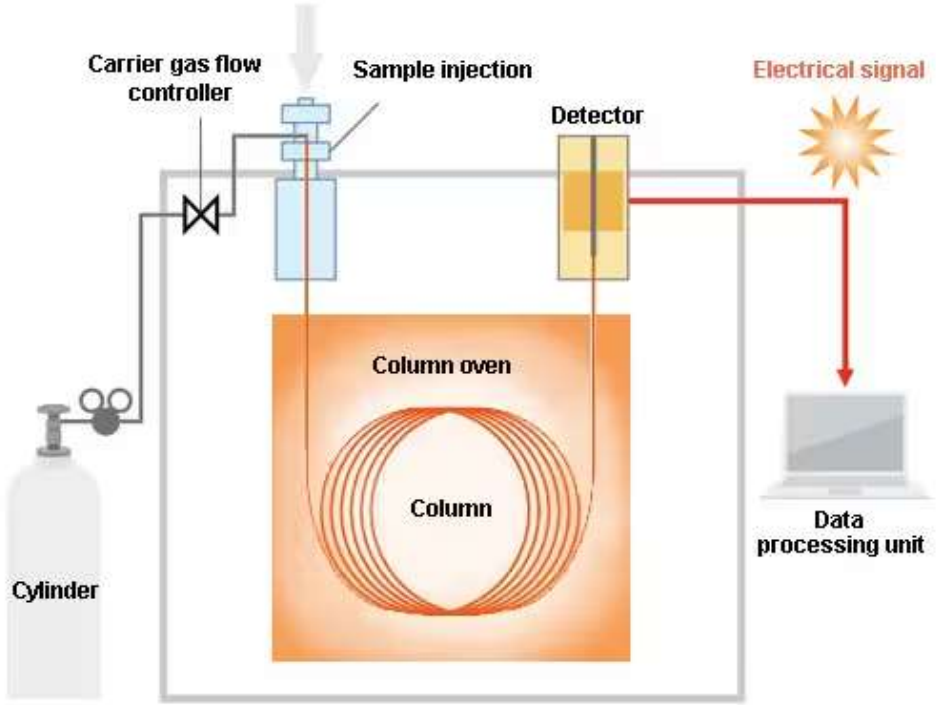


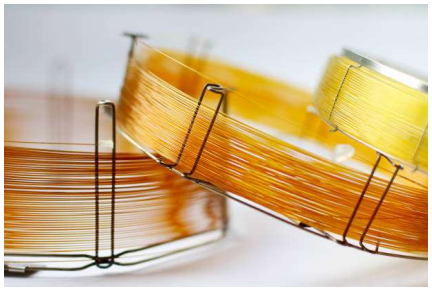


Gas Chromatograph: The Column

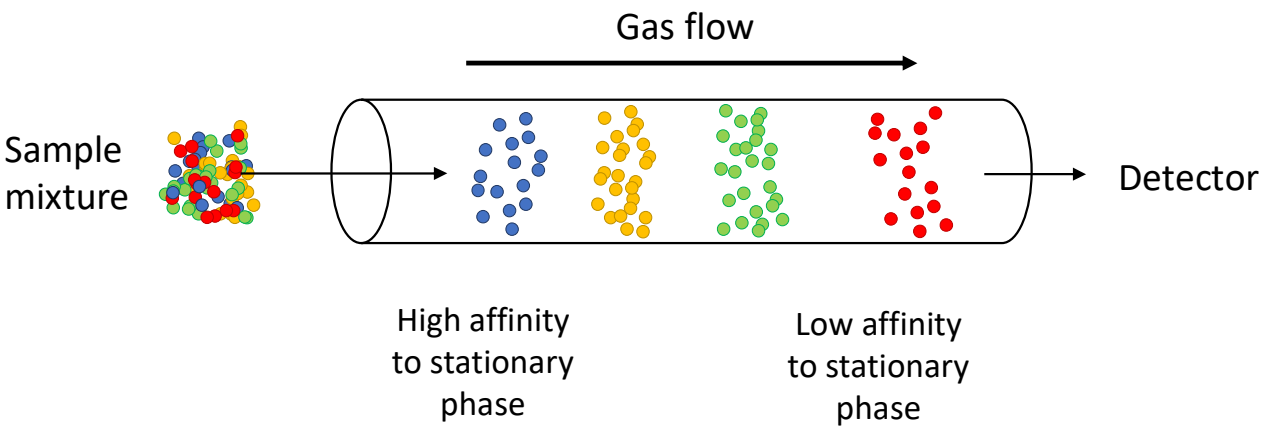
The sample vapor mixture is directed into the column by the carrier gas and is **retained by adsorption and released due to desorption**

Column **diameter and length** influences efficiency, solute retention, head pressure, and carrier gas flow rate.





Compounds Separation



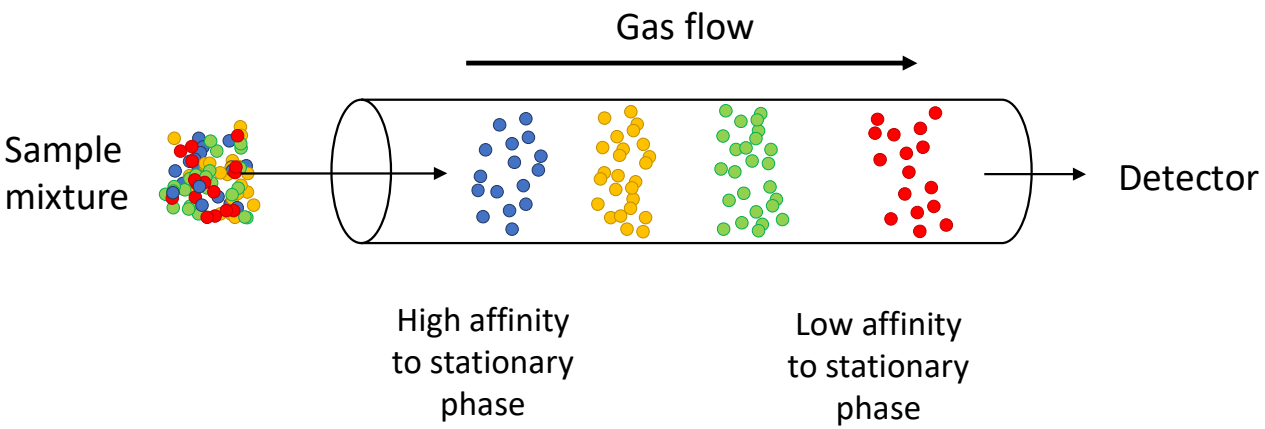
GC uses a gaseous mobile phase to transport the sample through the column.

As the GC column is heated, the compounds begin to separate.

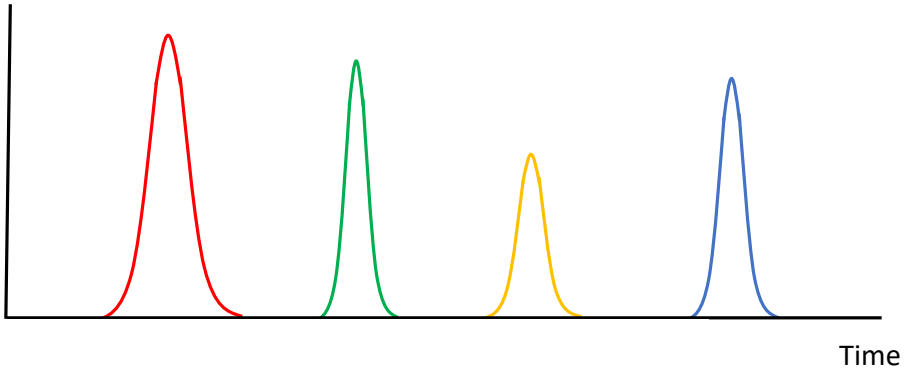
Compounds are separated by their different affinities to the column.

Compounds with less affinity will elute from the column sooner; compounds with greater affinity will elute later.

Compound Separation



The visual output of the chromatographic system is the **chromatogram**



The Detector

Thermal conductivity detector	• Detects compounds with thermal conductivity that differs from carrier gas
Flame ionization detector	• Detects compounds that burn or ionize in a flame
Electron capture detector	• Detects electron-capturing compounds (for example, halogenated compounds)
Nitrogen-phosphorus detector	• Detects compounds that contain nitrogen and phosphorus
Flame photometric detector	• Detects compounds that contain sulfur and phosphorus
Atomic emission detector	• Tunable to many elements
Mass selective detector	• Identifies components from mass spectra (when combined with GC, the most powerful identification tool available)

The Detector: Flame Ionization Detector

Mobile phase leaving the column is mixed with H_2 and air and burned in a flame

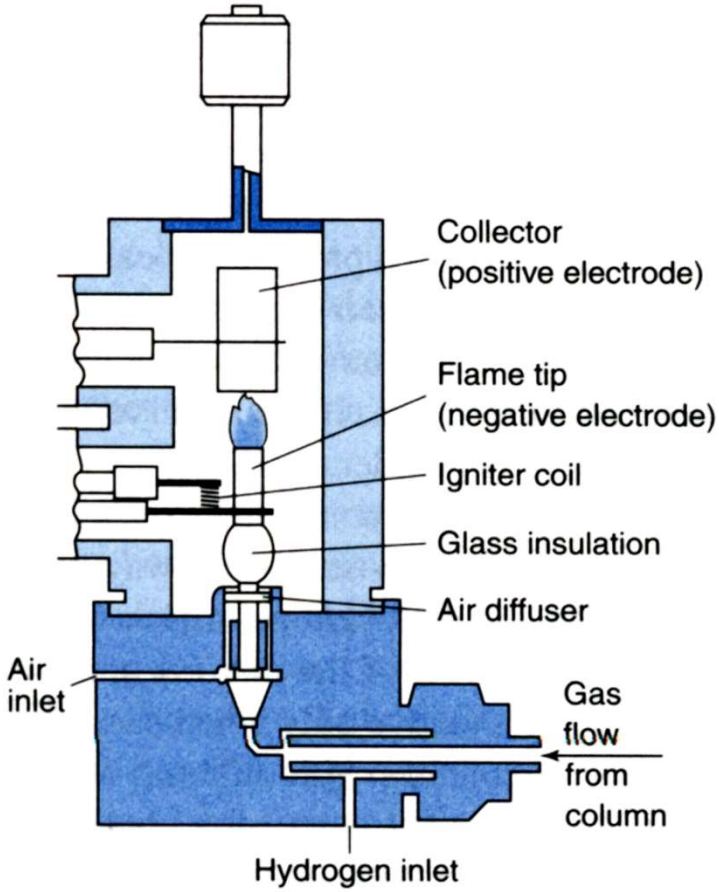
- Carbon present in eluting solutes produces CH radicals which produce CHO^+ ions
- Electrons produced are collected at an electrode and measured

Responds to almost all organic compounds and has good limits of detection

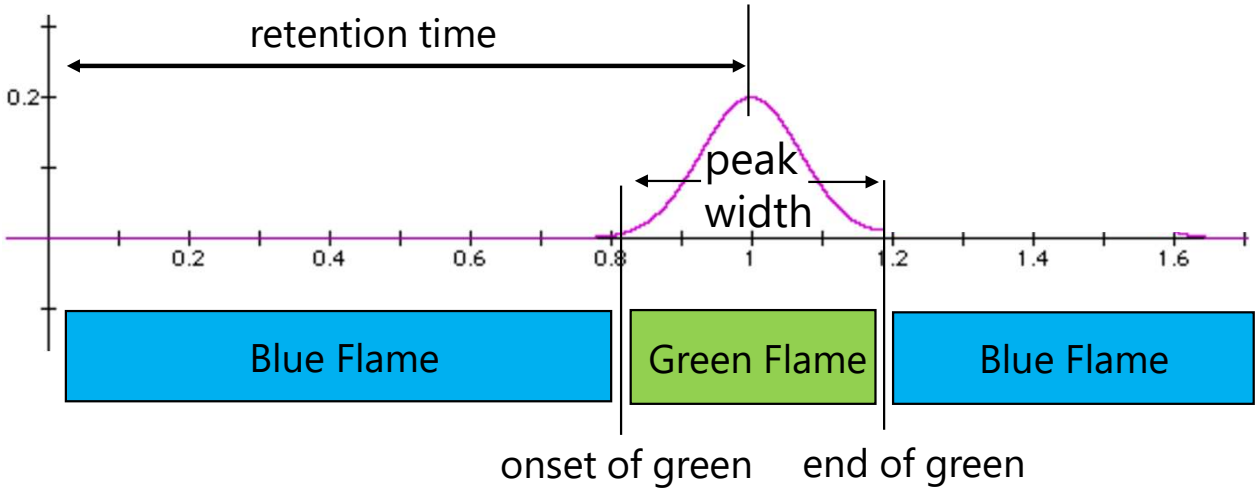
- 100 times better than thermal conductivity detector
- Stable to changes in flow rate and mobile phase impurities

$$CH + O \longrightarrow CHO^+ + e^-$$

Burn sample and measure amount of produced electrons



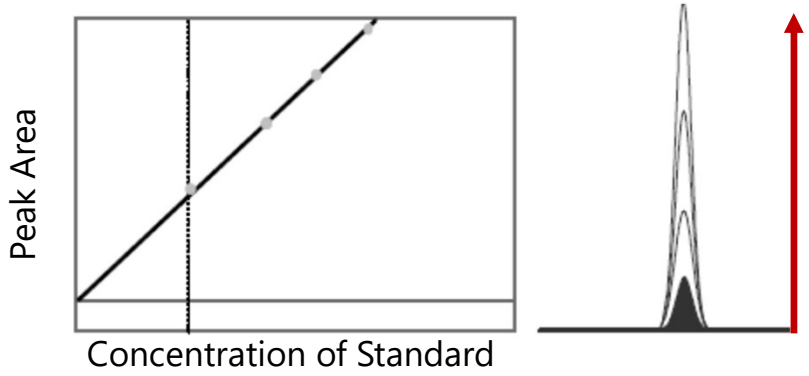
The Detector



Peak area increases proportional to concentration

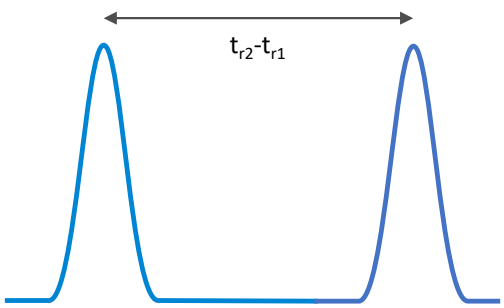
The peak height is proportional to the amount of material eluting from the column at any given time

The area under the peak is a measure of the total amount of material that has eluted from the column.



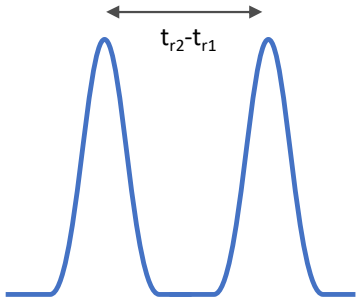
Resolution

Resolution describes the ability of a column to separate the peaks of interest

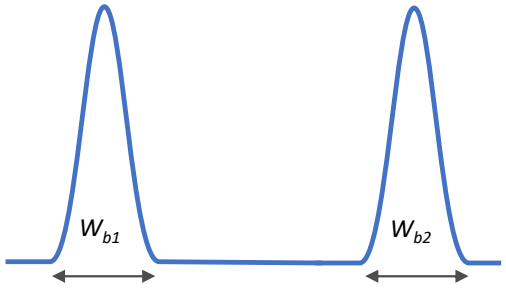


Superior separation

vs



Inferior separation



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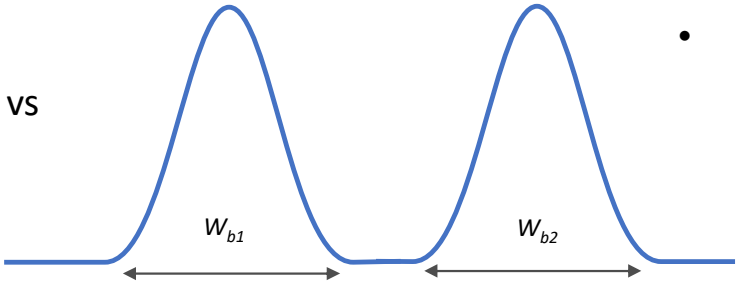
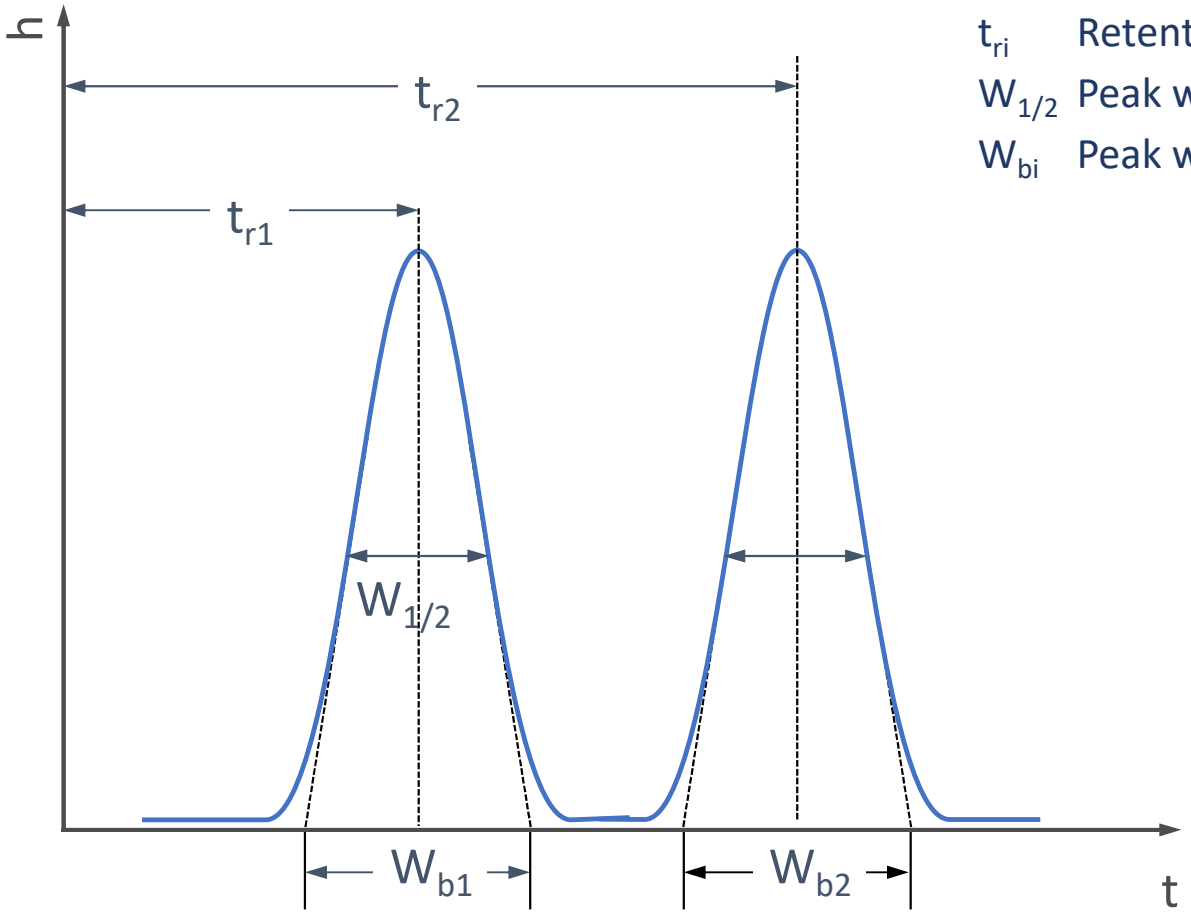


Inferior separation

One can improve resolution by improving any of these parameters:

- **Selectivity** has the highest influence on the resolution. Small changes in selectivity lead to big changes in resolution.
- **Retention** has a significant influence at small partition coefficients.
- **Efficiency** describes the separation power of the column.

Resolution



t_{ri} Retention time compound i

$W_{1/2}$ Peak width at half height

W_{bi} Peak width at baseline

$$R_s = \frac{t_{r2} - t_{r1}}{1/2 \cdot (W_{b2} + W_{b1})}$$

A value of 1 is the minimum for measurable separation and adequate quantitation.

A value of 0.6 is required to discern a valley between two equal-height peaks.

Values of 1.7 or greater generally are desirable for rugged methods.

Efficiency or Number of Theoretical Plates N

- Theoretical plates describe the **Column efficiency**, which may be usefull for GC modelling
- Represent a hypothetical segment of the column where separation occurs, dividing the column in to small section behaving as idealized septation units
- Columns with high theoretical plate numbers (N) are more efficient.

$$N = 16 \cdot \left(\frac{t_r}{W_b} \right)^2$$

- A column with high N provides:
  - Sharp and Narrow peaks
  - Better detection
  - Peak capacity to resolve complex samples
- But resolution increases only with the square root of the plate number.

$$R_s \sim \frac{1}{4}\sqrt{N}$$

- Plate number increase is limited by experimental conditions

What do we want to understand?

What happens inside the column?

Can we mathematically model the compounds separation and the peak's shape?

Can we explain/relate the model to theoretical plates result?