Notes in GC-MS

JP Da Silva

jpsilva@ualg.pt

Faro, 20th May 2022

Outline

GC-MS system

Gas phase chromatography

Gas, filters and injection

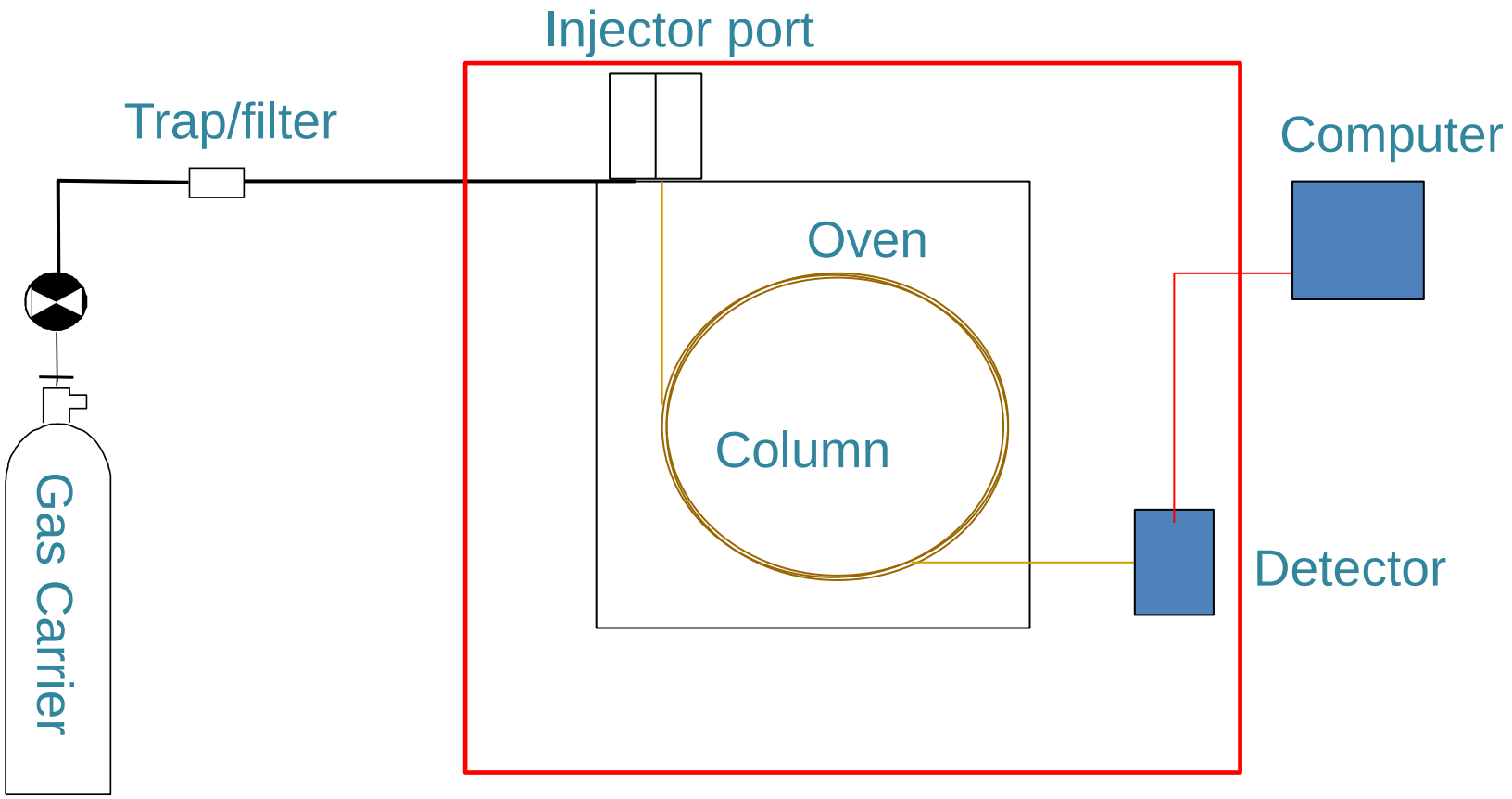
Injector. Split/splitless

The column

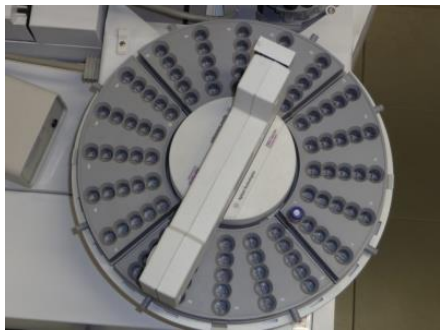
Detectors. Mass detector

Quantitation

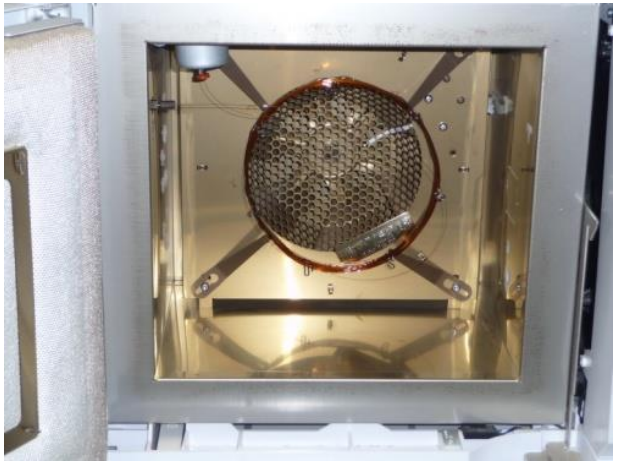
Schematic Diagram of a Gas Chromatograph

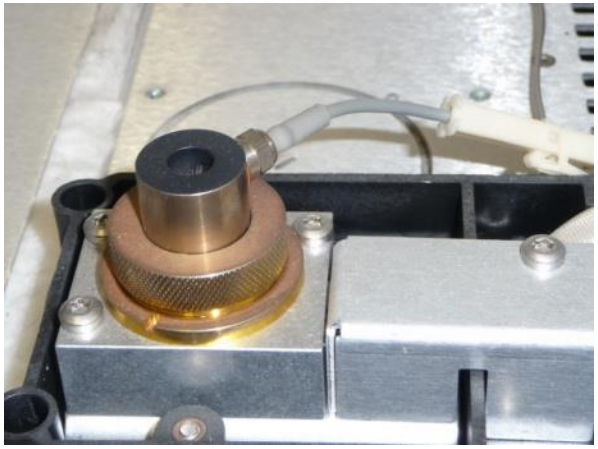


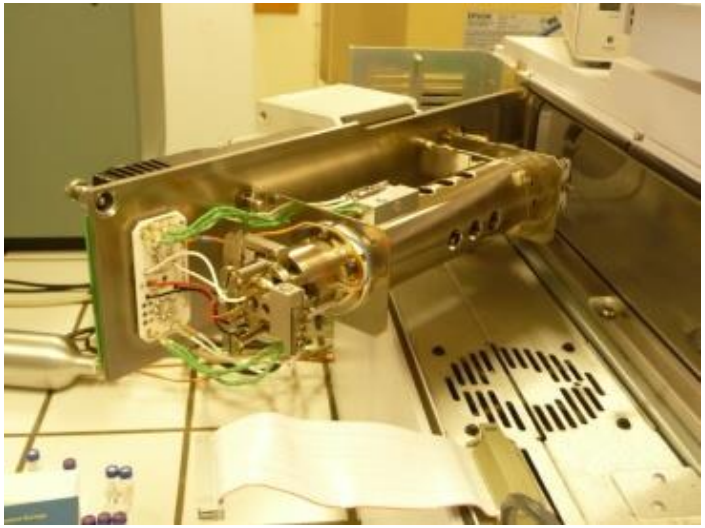
Gas carrier tanks, gas filters and injection



Oven and detector mass detector







Gas phase chroamtography

The mobile phase is a gas

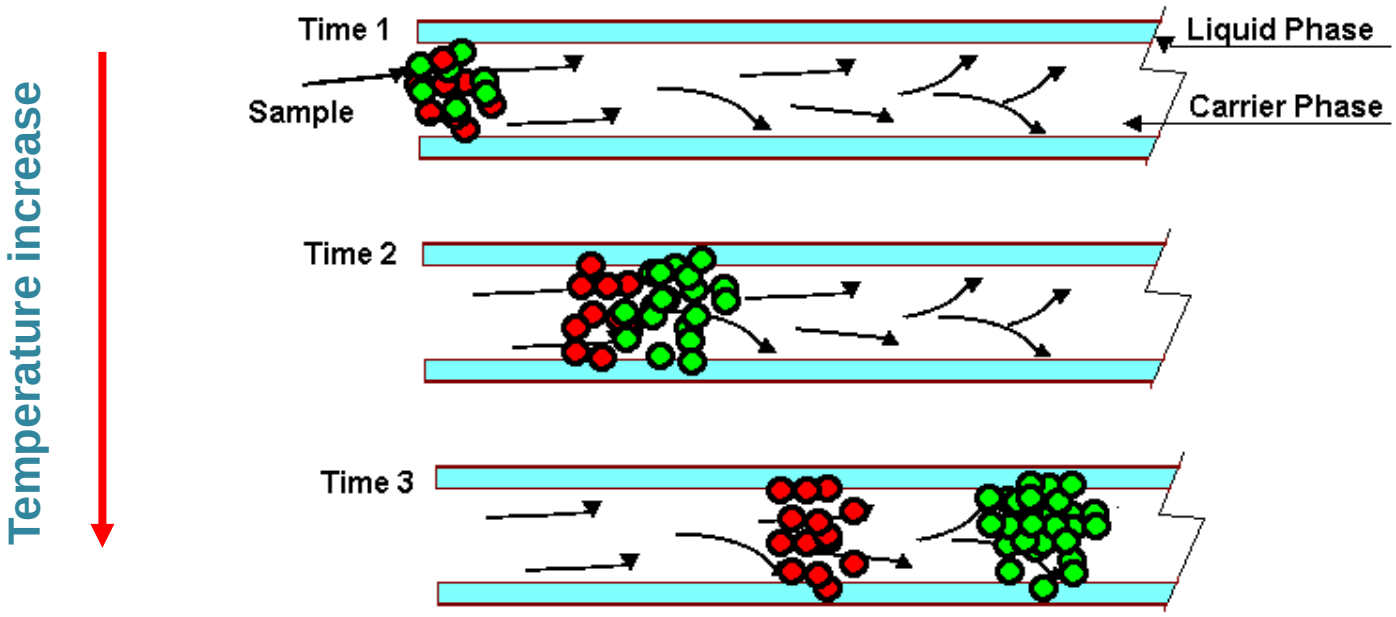
The stationary phase is a liquid or a solid. Partition/adsorption

The sample must be vaporized and injected onto the head of the chromatographic column.

The sample is transported through the column by the mobile phase flow.

The differential interaction of the vapor phase analytes with the stationary phase gives rise to the chromatographic separation

The separation process



Which compounds elute first?

Most volatile / lowest boiling point normally elutes first

Advantages and disadvantages of Gas Chromatography

a) Fast analysis

b) High Resolution

c) Sensitive detectors

(easy ppm, often ppb)

d) Highly accurate quantification

e) Automated systems

f) Non-destructive

In the sense that it allows online coupling to Mass Spec.

g) Small sample (μL)

h) Reliable and relatively simple

i) Low cost

a) Limited to volatile samples

Do not inject samples with non volatile compounds – DMSO, salts, proteins, etc

b) Not suitable for thermally labile compounds

c) Some samples may require extensive preparation

d) Requires spectroscopy (usually MS) to confirm peak identify

The gas

For high-speed analysis the ratio of viscosity to diffusion coefficient should be as small as possible. **H_2** would be the best choice, followed by **helium**.

Hydrogen is the fastest carrier gas (u_{opt}), with an optimum linear velocity of 40 cm/sec, and exhibits the flattest van Deemter profile. **Hydrogen is explosive when concentrations exceed 4% in air.**

Helium is the next best choice, with an optimum linear velocity of u_{opt} = 20 cm/sec. **Expensive**

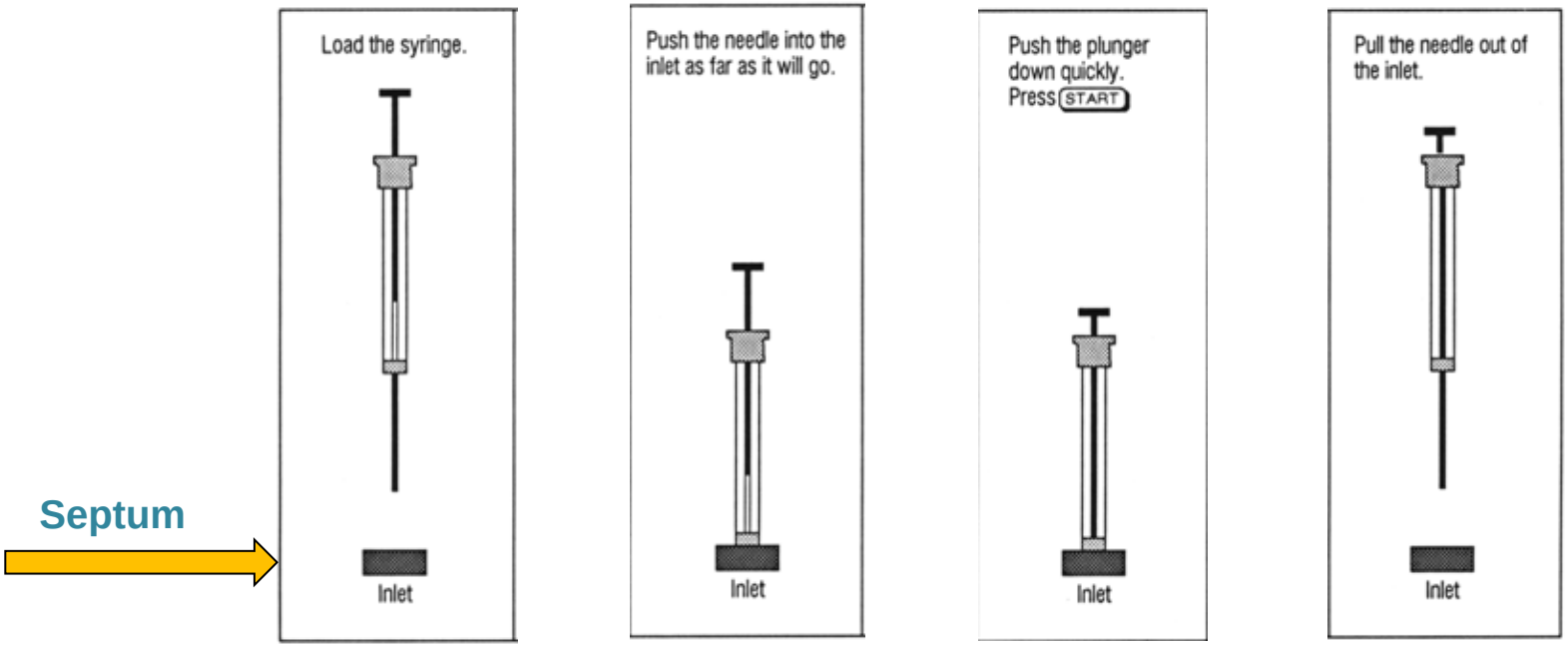
The ***purity*** of the carrier should be at least **99.995**% for best results.

The most common impurities are **air**, **water** and **hydrocarbons**.

Impurities can lead to sample decomposition, column deterioration, detector contamination and deterioration, a change the response factors, a change in the detection limits.

Manual injection

Typically 1.0 µL or less using a microsyringe. No air bubbles

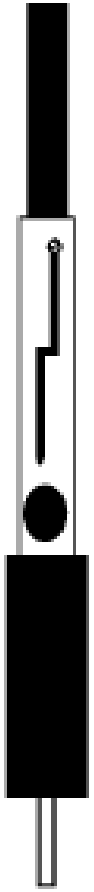


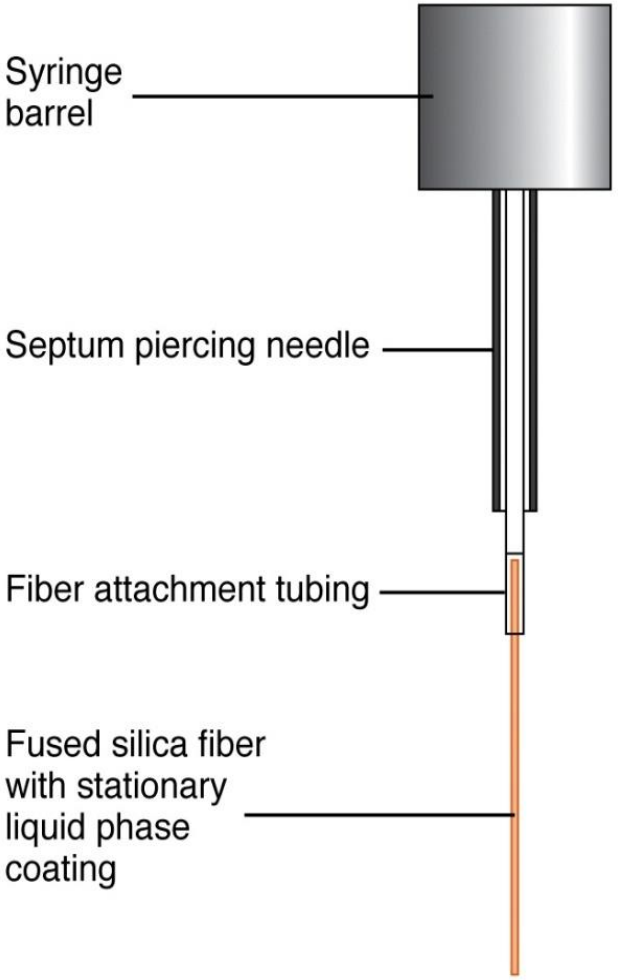
1 - The injection should be made in a single quick motion.

2 - The whole operation should only take 3 to 4 seconds.

HS-Solid phase micro-extraction (HS-SPME)

Syringe for solid phase microextraction.





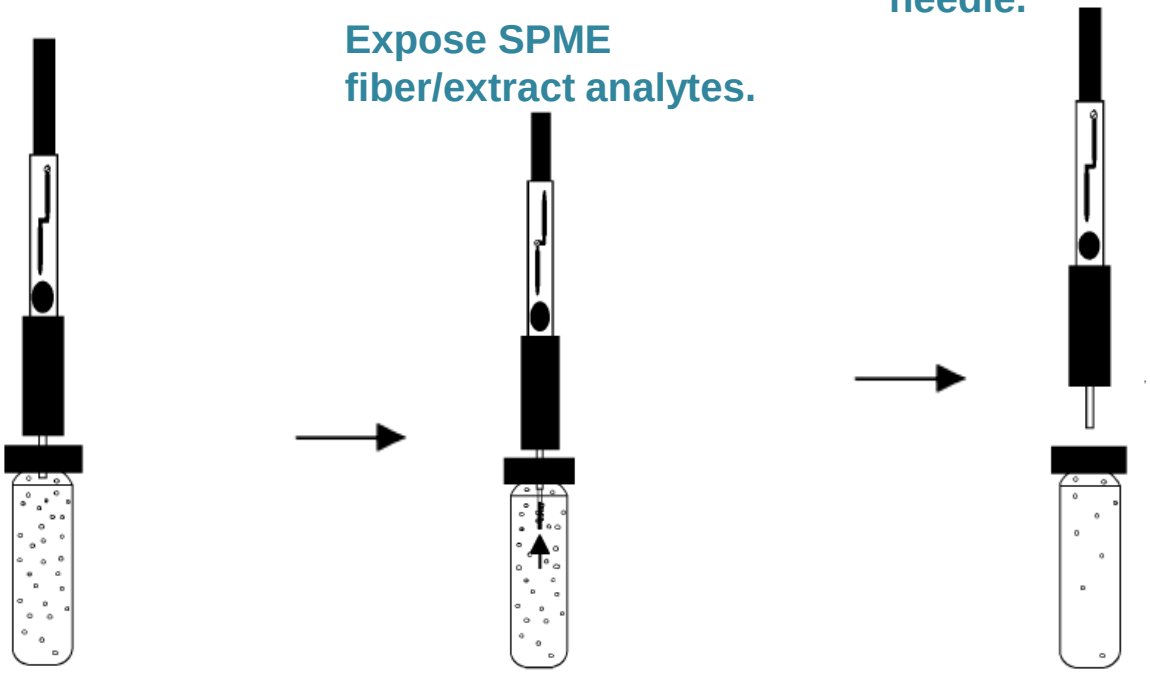
HS-Solid phase micro-extraction (HS-SPME)

Extraction Procedure

Pierce septum on sample container.

Expose SPME fiber/extract analytes.

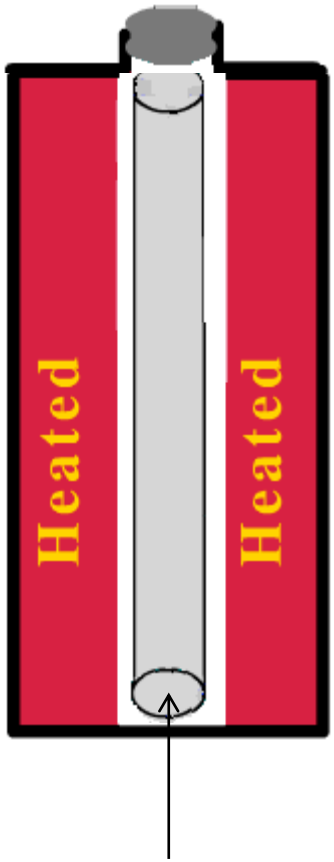
Retract fiber/withdraw needle.



Expose the fiber to a solution or headspace for fixed time under stirring.

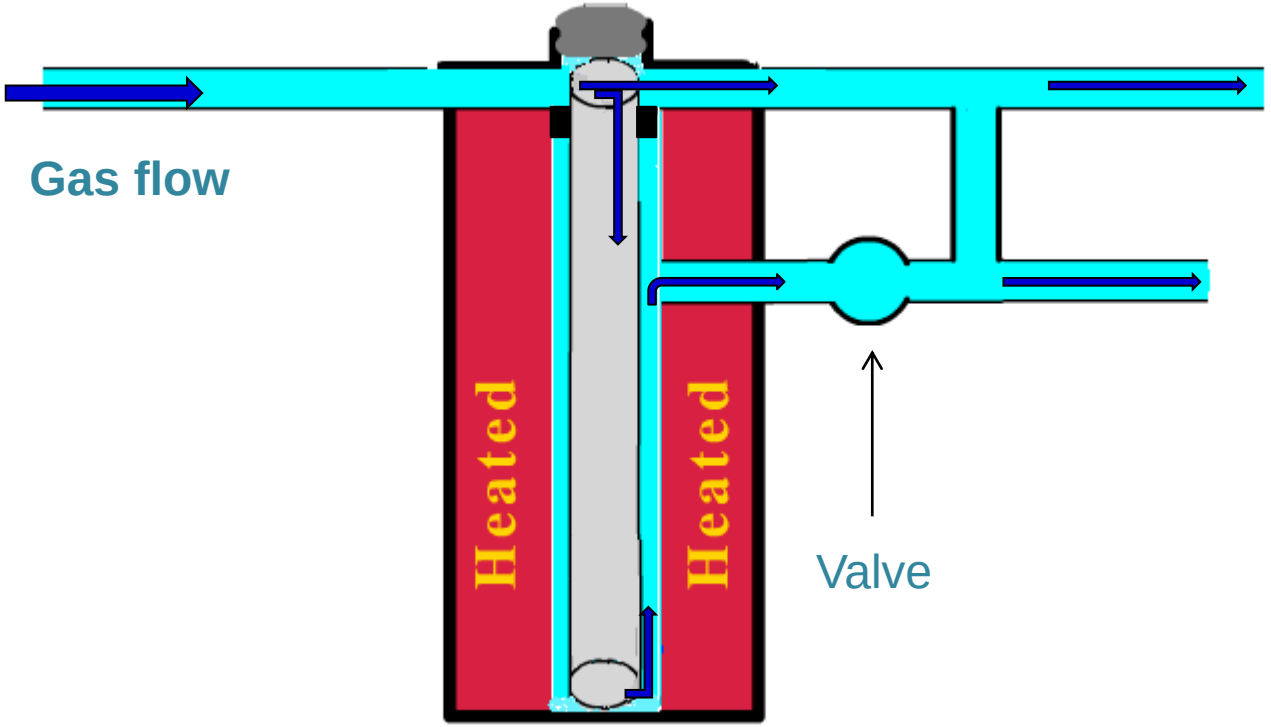
The injector

Septum

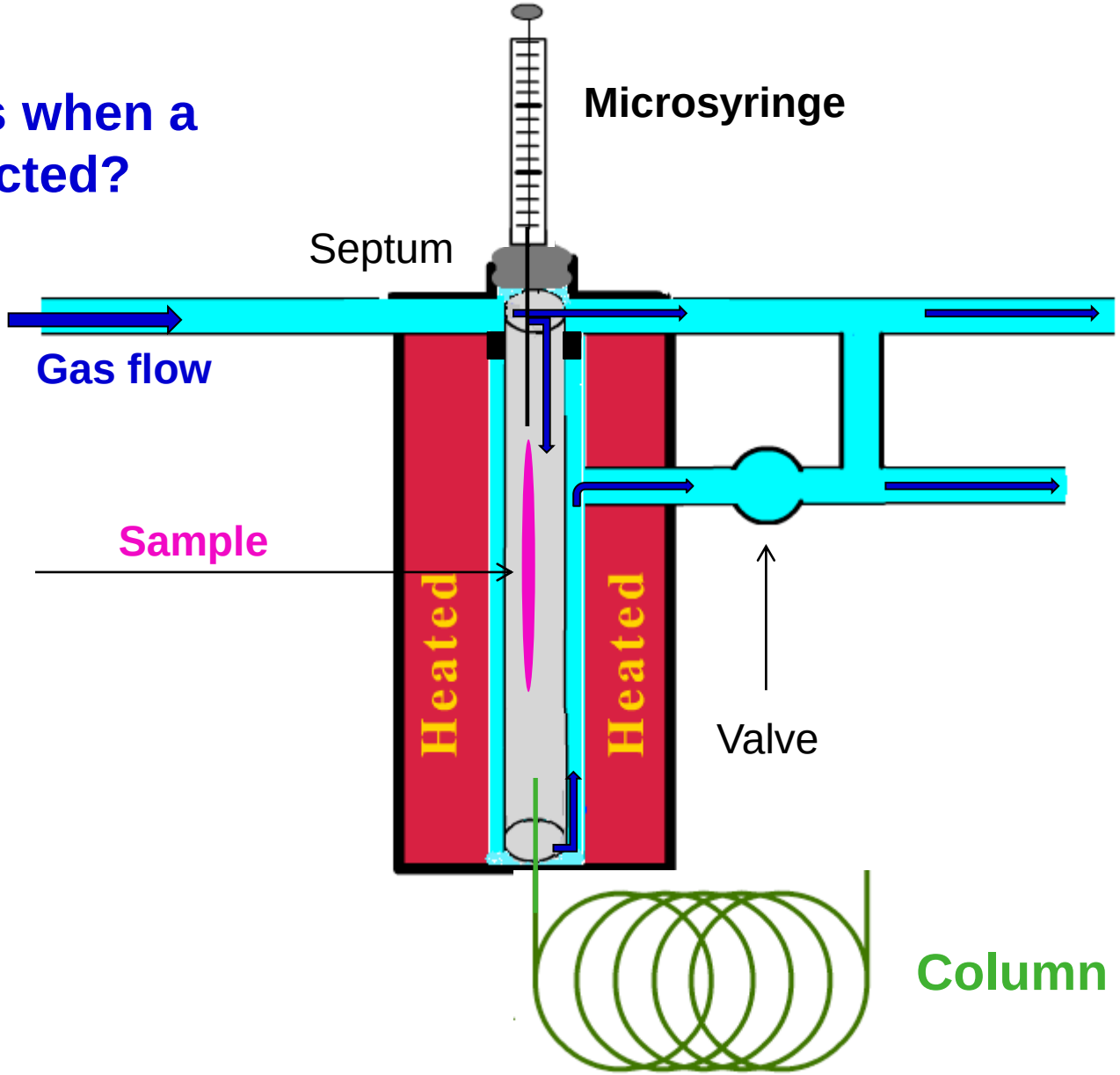


Liner

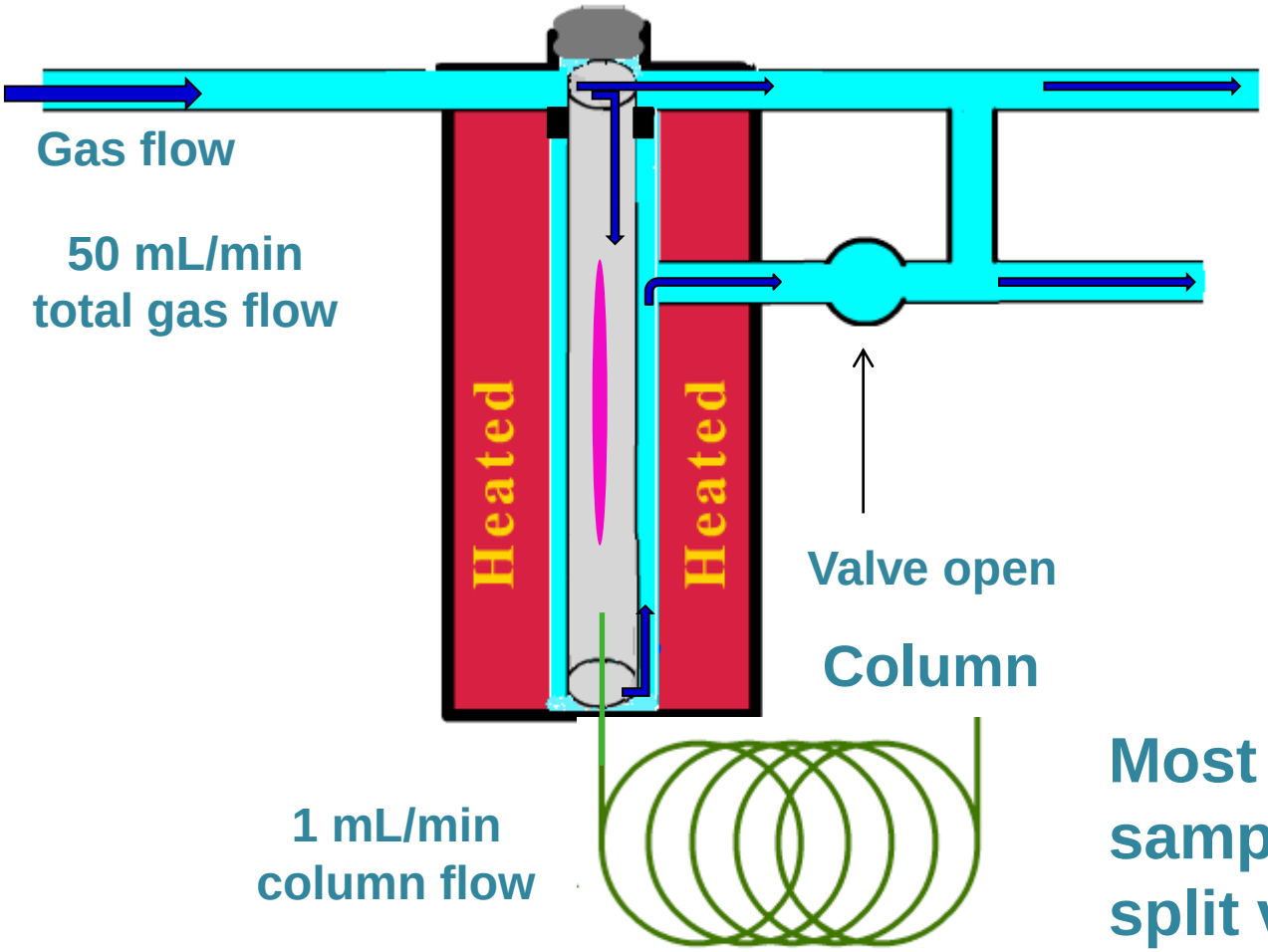
The injector and the flow system



What happens when a sample is injected?

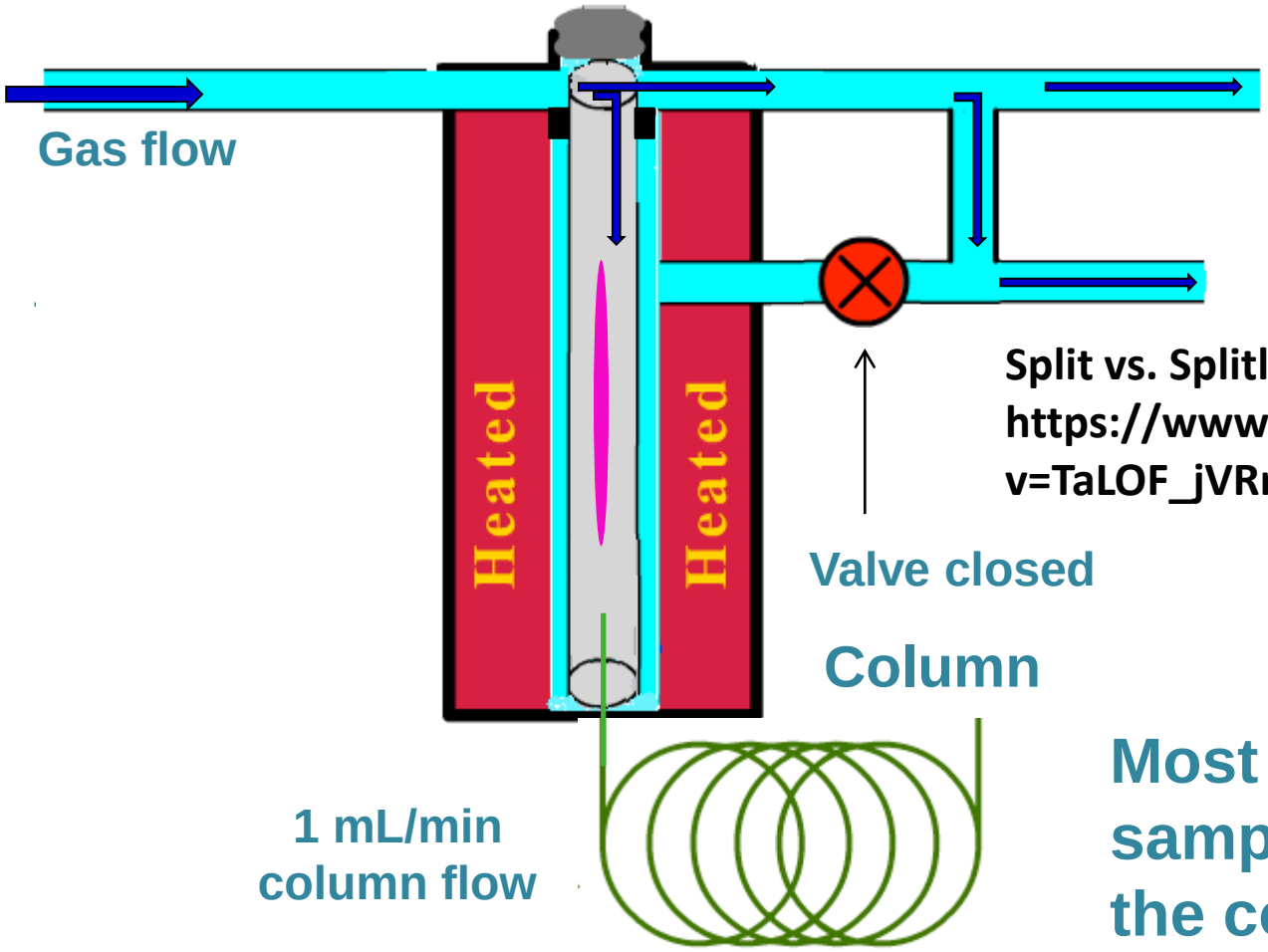


The split mode



Most of vaporized samples goes to split vent

The splitless mode



Split vs. Splitless Injection video at https://www.youtube.com/watch?v=TaLOF_jVRno

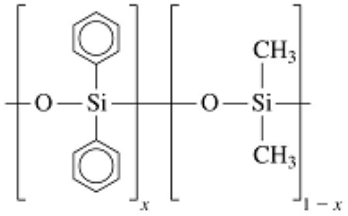
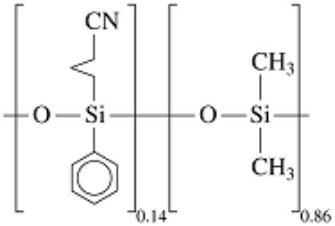
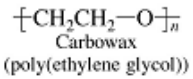
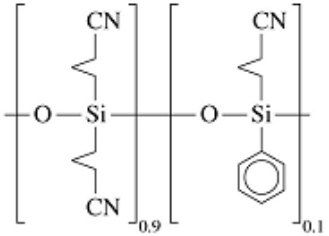
Most of vaporized samples goes onto the column

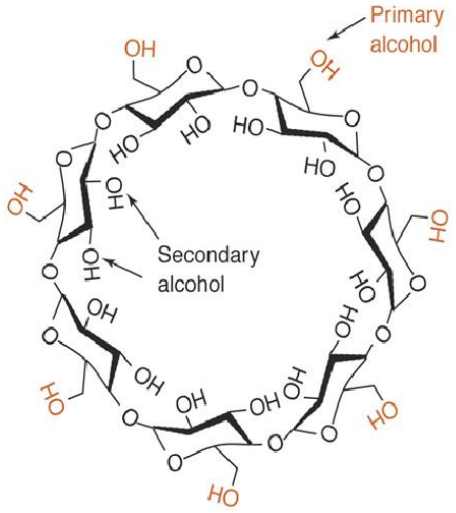
Open tubular columns

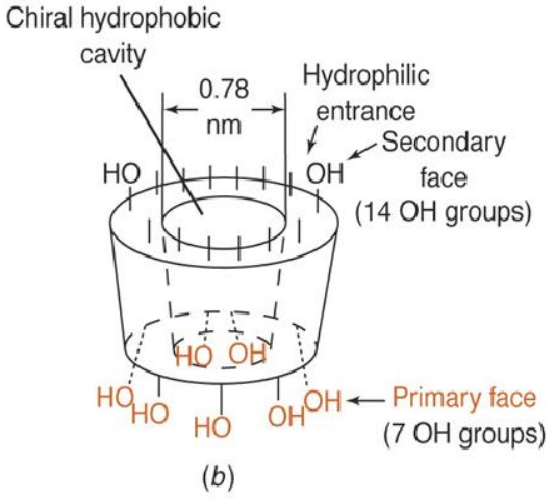
Check the column properties before use

Description	Thin-film narrow-bore	Thick-film narrow-bore	Thick-film wide-bore
Inner diameter	0.10–0.32 mm	0.25–0.32 mm	0.53 mm
Film thickness	~0.2 μm	~1–2 μm	~2–5 μm
Advantages	High resolution Trace analysis Fast separations Low temperatures Elute high b.p. compounds	Good capacity Good resolution (4 000 plates/m) Easy to use Retains volatile compounds Good for mass spectrometry	High capacity (100 ng/ solute) Good for thermal conductivity and infrared detectors Simple injection techniques
Disadvantages	Low capacity (≤1 ng per solute) Requires high sensitivity detector (not mass spectrometry) Surface activity of exposed silica	Moderate resolution Long retention time for high b.p. compounds	Low resolution (500–2 000 plates/m) Long retention time for high b.p. compounds

Common stationary phases in capillary gas chromatography

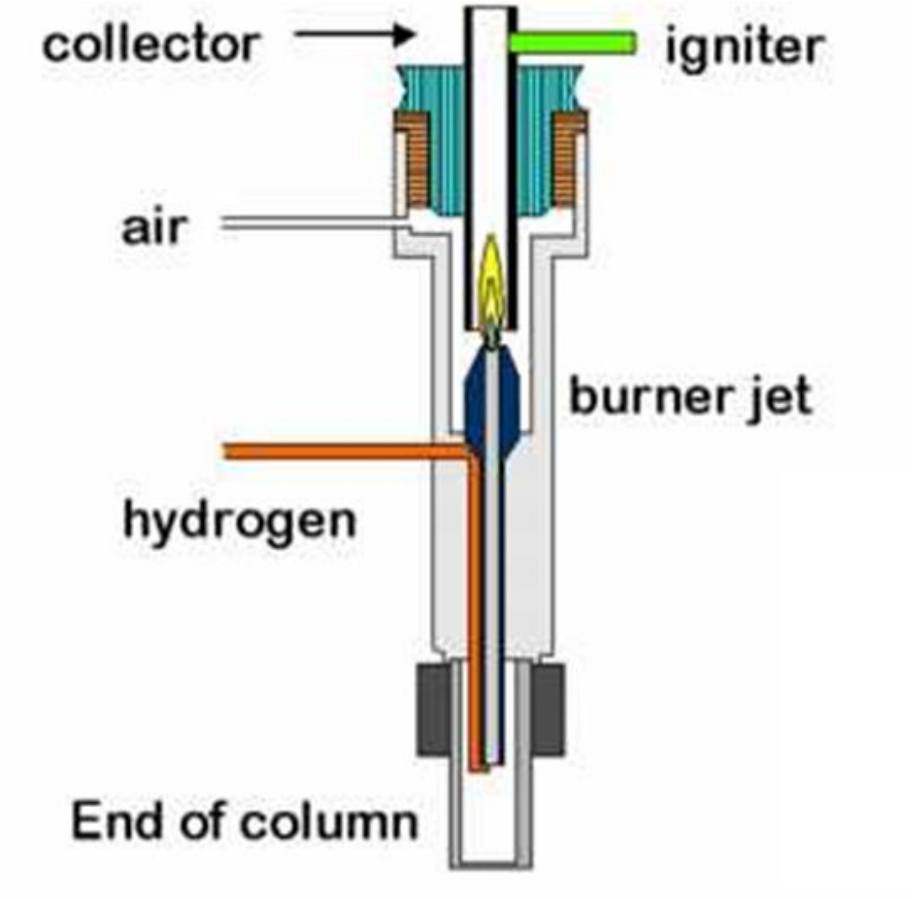
Structure	Polarity	Temperature range (°C)
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$ Nonpolar $x = 0.05$ Nonpolar $x = 0.35$ Intermediate polarity $x = 0.65$ Intermediate polarity	−60°−320° −60°−320° 0°−300° 50°−370°
 (Cyanopropylphenyl)$_{0.14}$ (dimethyl)$_{0.86}$ polysiloxane	Intermediate polarity	−20°−280°
 Carbowax (poly(ethylene glycol))	Strongly polar	40°−250°
 (Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar	0°–275°





(b)

Flame Ionization Detector



1 - sample burned in H2/air

2 - flame

3 - sample must be combustible

4 - must use electrometer ppm sensitivity

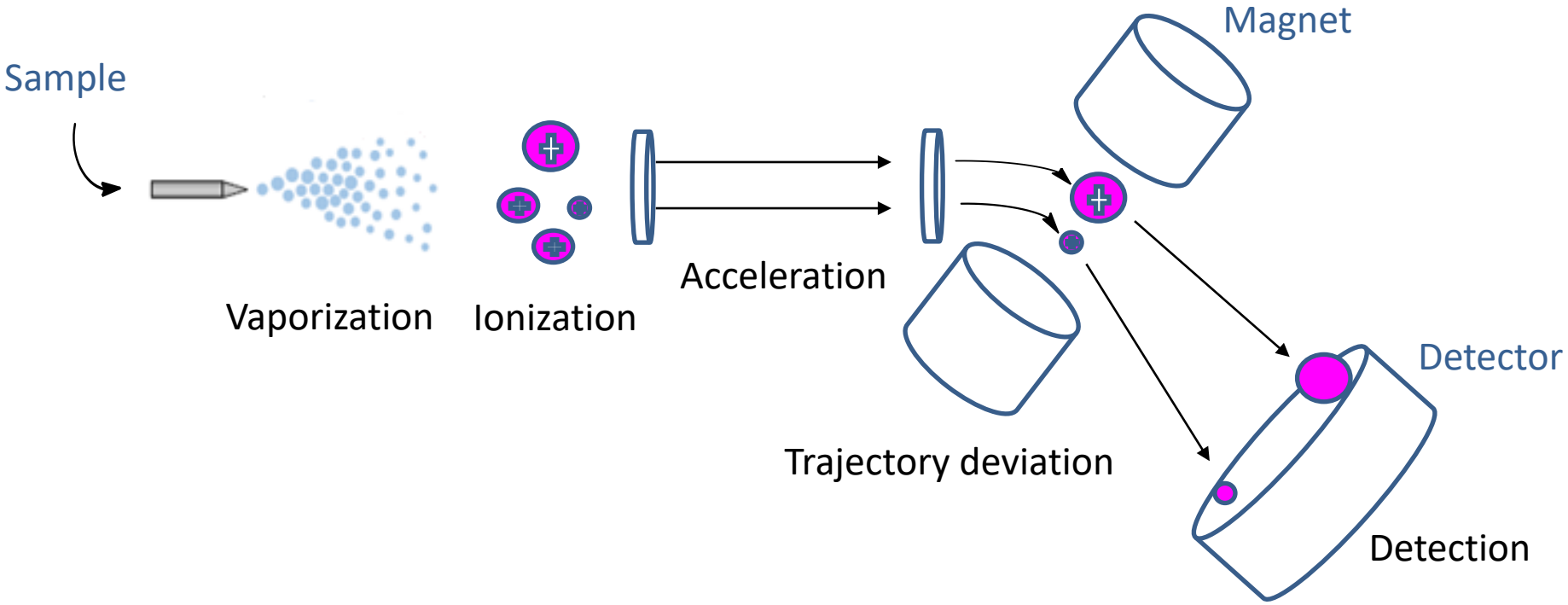
5 - destructive

What is mass spectrometry?

Mass spectrometry is the "weighing" of individual molecules by transforming them into ions in vacuo and then measuring the response of their trajectories to electric and magnetic fields or both.

John B. Fenn et al., Science, 246, 64, 1989

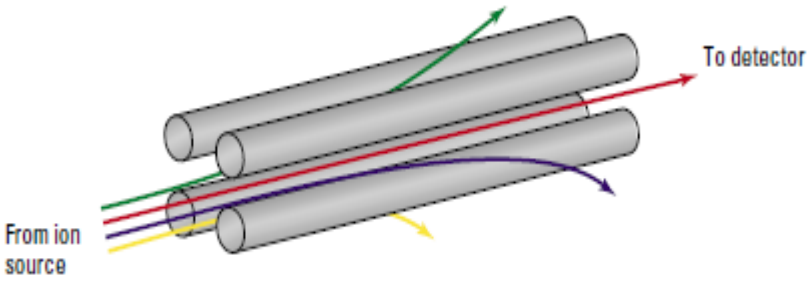
Mass spectrometer, how does it work?



Mass analysis

Quadrupole

a) A quadrupole mass analyzer consists of four parallel rods arranged in a square.



b) Voltages applied to the rods generate electromagnetic fields.

d) Quadrupoles tend to be the simplest and least expensive mass analyzers.

e) Quadrupole mass analyzers can operate in two modes:

- Scanning (scan) mode
- Selected ion monitoring (SIM) mode – quantitative, target compounds

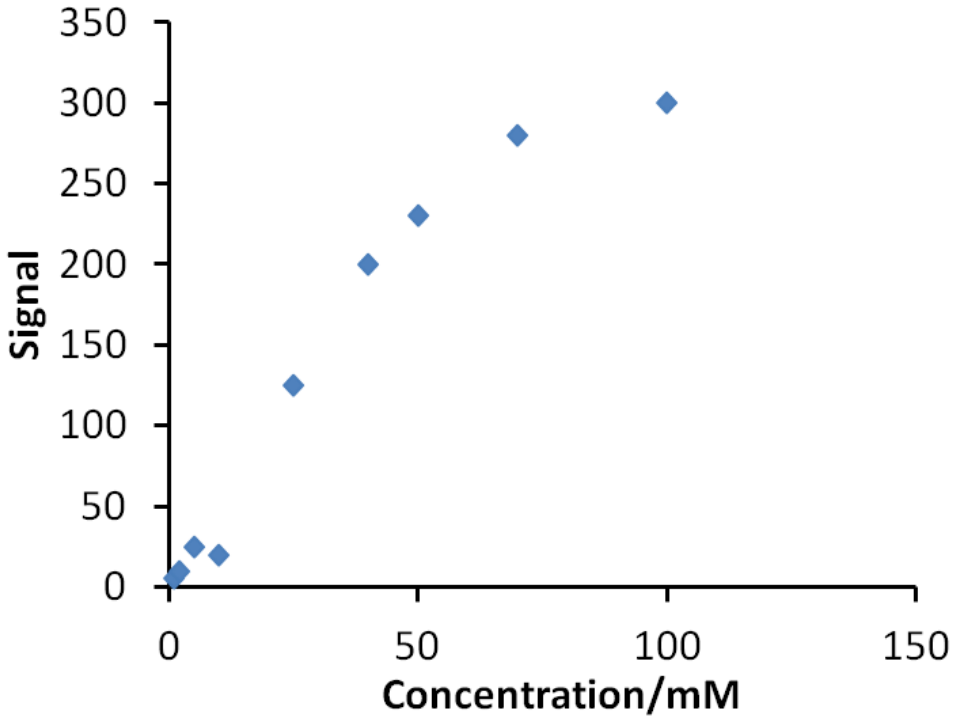
Quantitative analysis

1 - It usually involves the use of the peak areas (sometimes the peak height)

2 – Needs the comparison of the area (or height) of analyte peak with that of one or more standards.

3 – Calibration curve

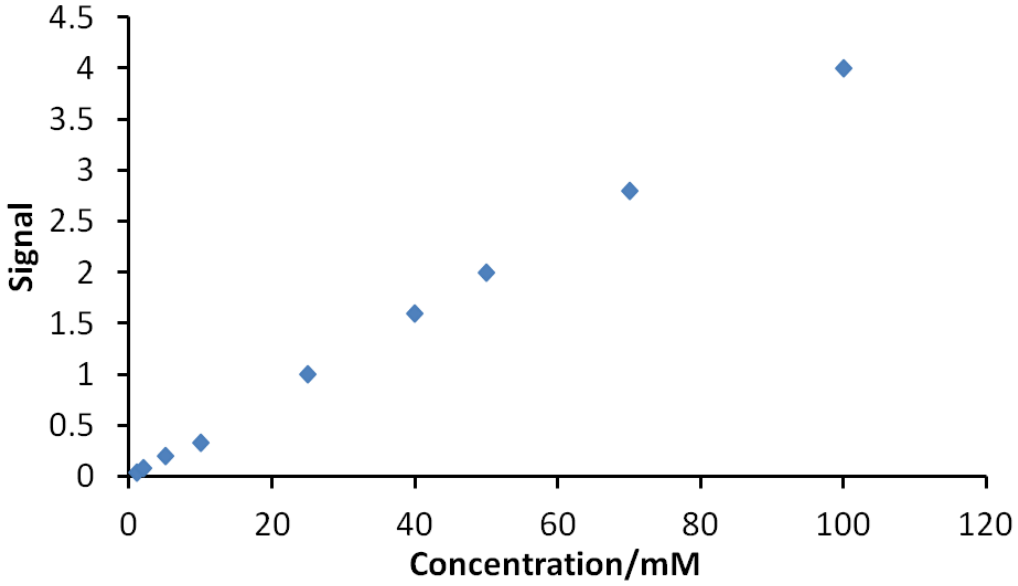
Conc	Signal
1	5
2	10
5	25
10	20
25	125
40	200
50	230
70	280
100	300



Quantitative analysis

The quantification using an internal standard

Conc	Signal	Signal	IS
1	0.04	5	125
2	0.08	10	125
5	0.2	25	125
10	0.333	20	60
25	1	125	125
40	1.6	200	125
50	2	230	115
70	2.8	280	100
100	4	300	75



Its use corrected the uncertainties introduced by the sample injection

Remarks

1 – Do not inject solution with particles

2– Volatile and semi-volatile compounds only

No salts, such and NaCl, borates, phosphates or other

3 – Only compounds stable in the gas phase

4 – The injection of samples containing non-volatile compounds such as salts and high molecular weight compounds will contaminate the liner and might block the column

5 – Do not inject water

6 – For GC-MS use a solvent delay (for example 2 min) to preserve the filament

Selected videos

Replacing Your Liner, Septum and O-Ring

https://www.youtube.com/watch?v=mExb2mj0eEk

Replacing the Gold Seal

https://www.youtube.com/watch?v=uMTKMbmSvRI

GC Column Installation - Part 1

https://www.youtube.com/watch?v=Nx1FzgwlCiE

GC Column Installation - Part 2

https://www.youtube.com/watch?v=YmkKikaakSI