

# Gas Chromatography

- Speed
- High separating power
- Separation of multiple classes of compounds in an analysis
- Sensitivity (ppm - ppb)
- Detector variety (specificity)

## WHAT DOES IT ANALYZE?

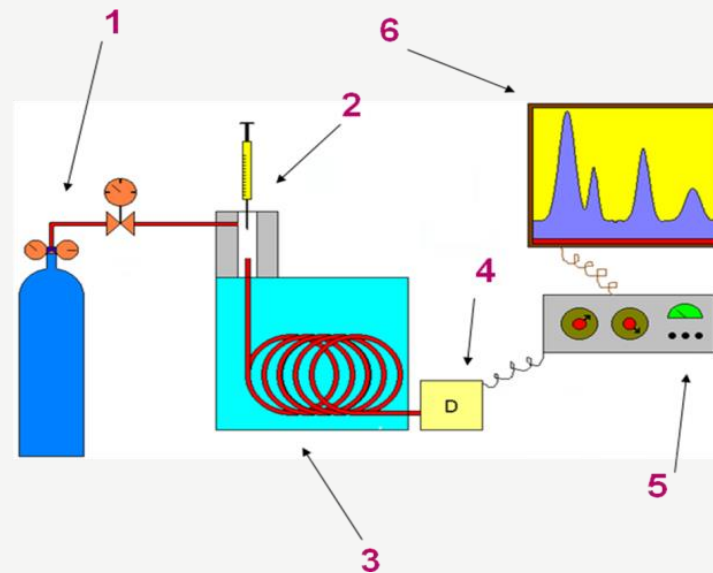
- Volatile compounds with boiling points up to 350°C and molecular masses less than 500 g/mol.
- Compounds that can produce volatile derivatives.
- Thermally stable compounds under working conditions.

## SOME APPLICATIONS

Petrochemical industry, food and beverage, medicine,  
environment...

## GAS CHROMATOGRAPH:

- 1 - Cylinder containing carrier gas (hydrogen, helium, argon or nitrogen), with controlled flow and pressure regulator
- 2 - Sample injection system
- 3 - Chromatographic Column and Oven
- 4 - Detectors
- 5 - Recorder
- 6 - Computer



**(temperature control)**

## ⦿ GASES

**Carrier Gas:** Pressurized inert gas used to transport the sample through the chromatographic system.

**Detector Gases:** Gases used in the specific operation of each detector.

## ⦿ SAMPLE INJECTION SYSTEM

Introduces the sample into the carrier gas with minimal change to the properties of the carrier gas or sample. Injection of solution ( $T$  of injection chamber  $>$   $T$  of column), followed by solute vaporization ( $T$  of injection chamber  $\approx$  boiling  $T$  of compound less volatile  $+ 50$  °C).

## ⦿ COLUMN

It is responsible for separating the sample components.

## ⦿ DETECTOR

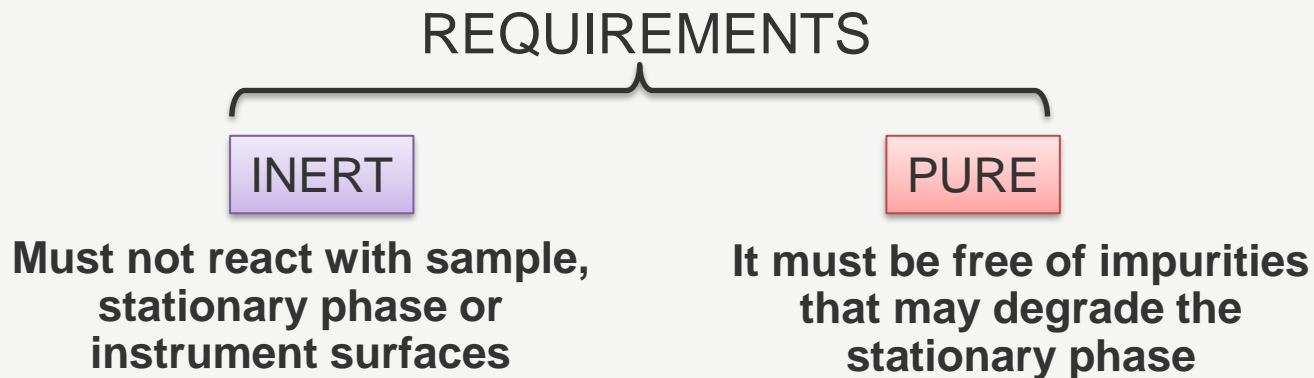
Recognizes and responds to sample components as they elute from the column.

## ⦿ DATA ACQUISITION

It converts the detector signal into a chromatogram that allows the determination, identification and quantification of sample components.

## ◎ CARRIER GAS

**MOBILE PHASE IN GC: DOES NOT** interact with the sample; it just loads it through the column. It is commonly referred to as carrier gas.



## © CARRIER GAS - COMPATIBLE DETECTORS

**Each detector requires a specific carrier gas for best operation.**

<b>Thermal Conductivity Detector</b>	He, H <sub>2</sub>
<b>Flame Ionization Detector</b>	N <sub>2</sub> , H <sub>2</sub>
<b>Electron Capture Detector</b>	N <sub>2</sub> , Ar + 5% CH <sub>4</sub>



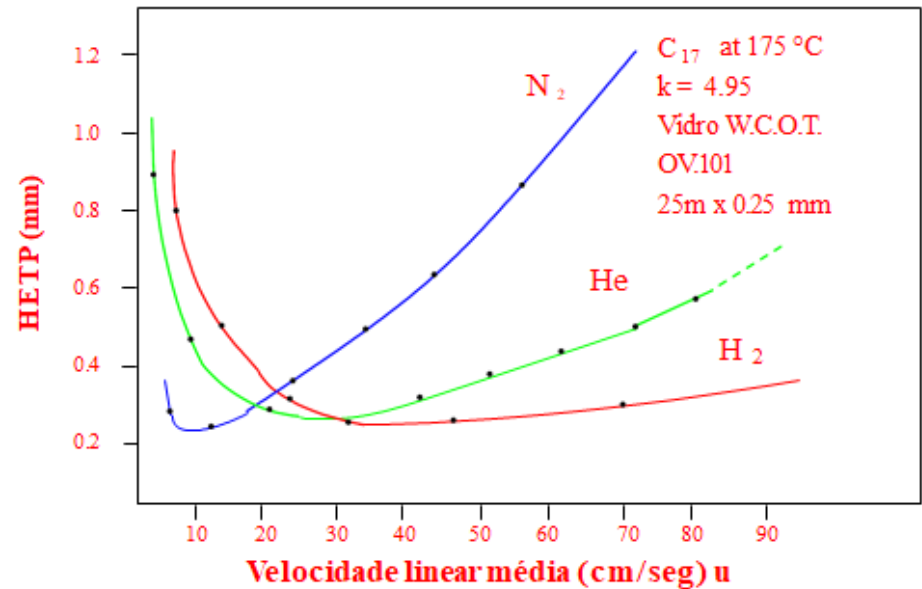
## ◎ CARRIER GAS

In GC the mobile phase, i.e., the eluent (inert gas) does not interact with the solute. However, it has an influence on the height equivalent to a theoretical plate (H).

### Choice of mobile phase:

Although N<sub>2</sub> has a higher efficiency, this optimal situation only applies to a very narrow range of gas velocities. Using He can greatly increase the optimal range of u without losing much resolution.

H<sub>2</sub> should be avoided as it is a combustible gas.



**Working conditions of the mobile phase:**

$$\Delta p = P_{\text{gas entry}} - P_{\text{gas out}} < 2 \text{ atm}$$

(for higher pressures there are leakage problems)

## ⊙ SAMPLE INJECTION SYSTEM

- Also called injectors.
- Introduction of the sample to the chromatographic column.

## ⊙ SAMPLE INJECTION PARAMETERS

**INJECTOR TEMPERATURE:** It should be high enough for the sample to vaporize immediately, but without decomposition.

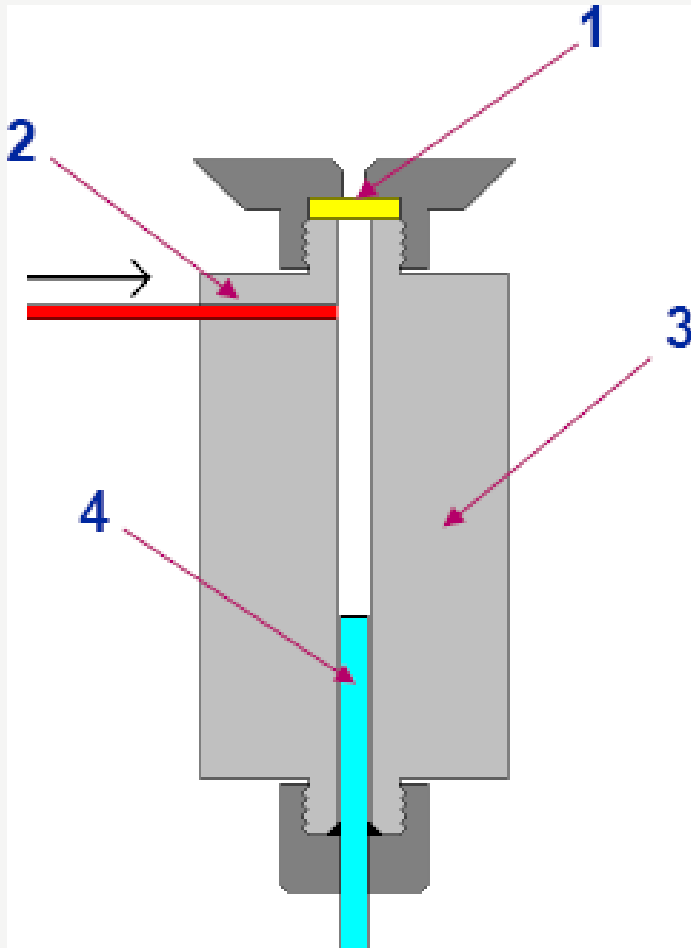
General rule:

$T_{inj} = 50^{\circ}\text{C}$  above the boiling temperature of the less volatile compound.

**INJECTED VOLUME:** It depends on the type of column and the physical state of the sample.

***Solids are conventionally dissolved in a suitable solvent and the solution injected.***

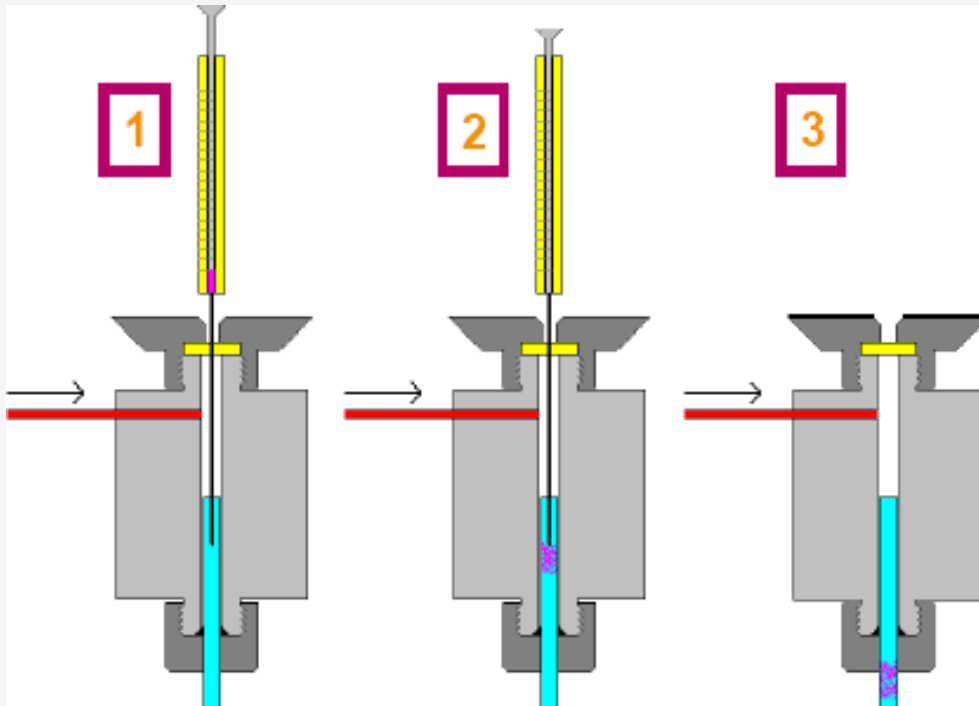
## ◎ SAMPLE INJECTION SYSTEM - "ON COLUMN" INJECTOR



- 1 – Septum (silicone)
- 2 – Carrier gas
- 3 – Heated metal block
- 4 – Tip of the chromatographic column



## ◎ SAMPLE INJECTION SYSTEM - "ON COLUMN" INJECTOR

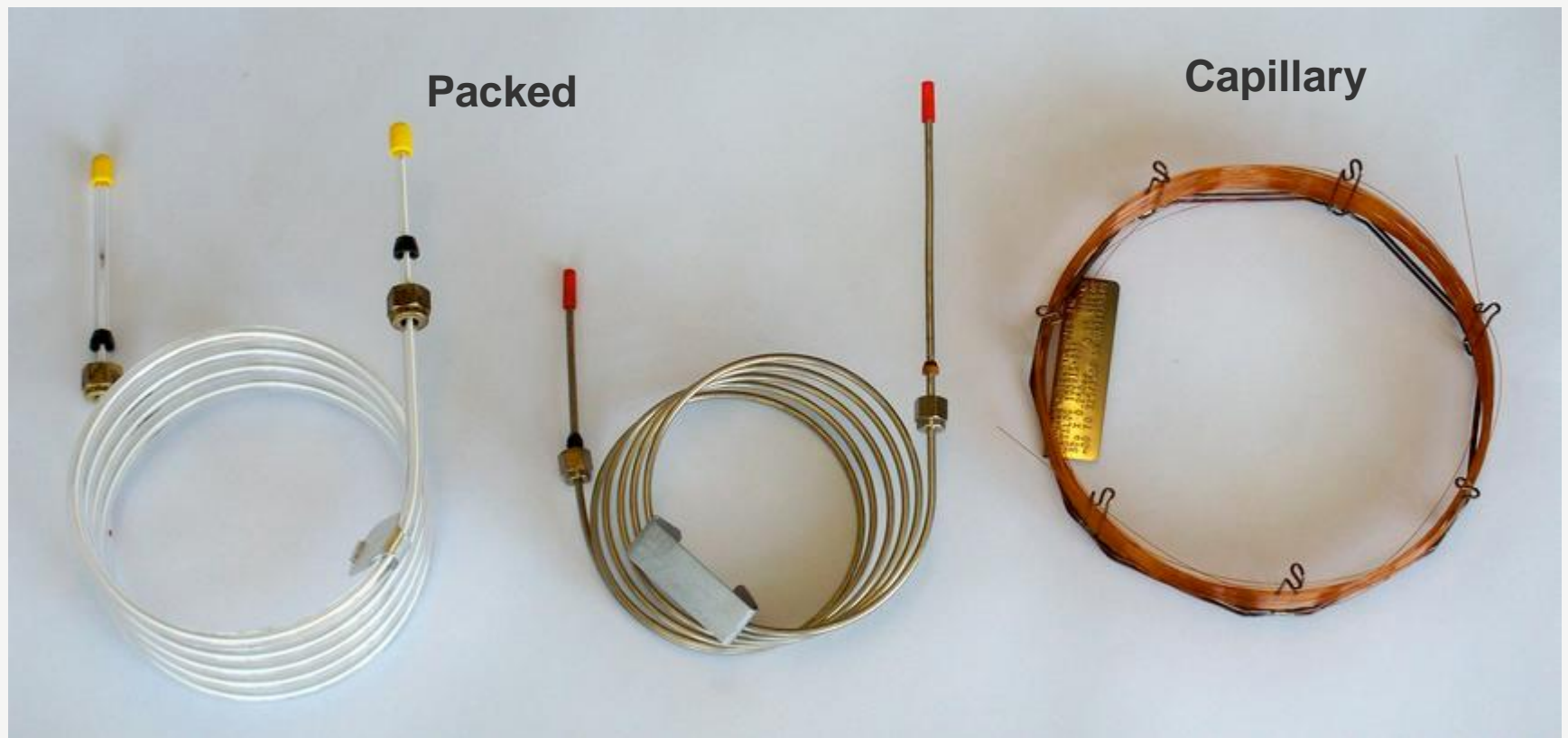


1 – Needle is introduced into the beginning of the column.

2 – Sample is injected in the beginning of the column and vaporized immediately.

3 – The vapour of the sample is forced by the carrier gas into the column.

## © CHROMATOGRAPHIC COLUMNS



## © COLUMNS - PACKED

### BENEFITS

**Simple to prepare and use, classic technology, large number of liquid phases, high capacity and long service life, used for gas analysis with TCD**

### DISADVANTAGES

**Limited number of plates, relatively time-consuming analyses, low resolution for complex samples**

## ◎ COLUMNS - CAPILLARY

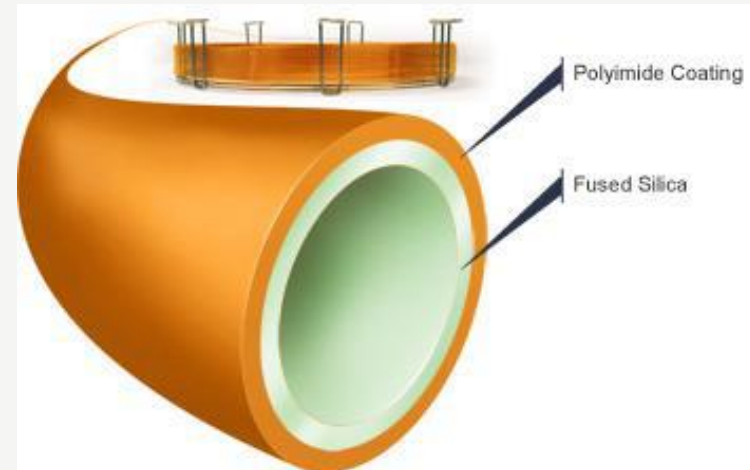
Very flexible and can be bent into a colloidal shape (int. diameter = 0.1-0.3 mm)

### ADVANTAGES:

- longer length -> greater efficiency
- separation of complex mixtures
- faster analysis
- greater separation

### DISADVANTAGES

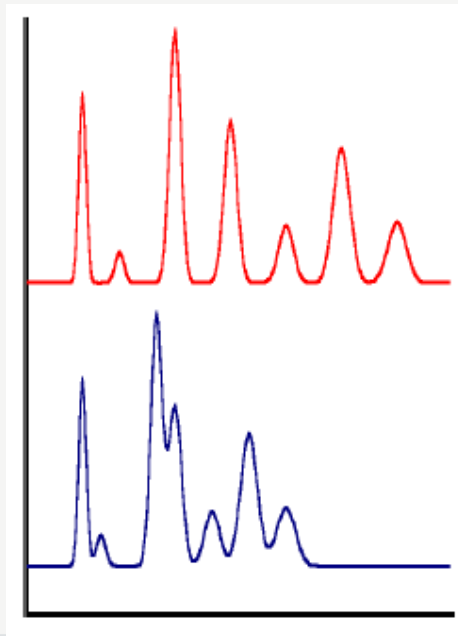
- smaller amount of sample
- saturates quickly



## ◎ COLUMNS - IDEAL STATIONARY PHASE

Must interact differentially with sample components.

It should have characteristics as close as possible to those of the solutes to be separated (polar, non-polar, aromatic...).



SP selective:  
Proper separation of  
sample constituents

SP not selective:  
Bad resolution even with  
good efficiency column

## ◎ COLUMNS - STATIONARY PHASE

### IDEALLY

- **WIDE TEMPERATURE RANGE FOR USE:** Greater flexibility in optimizing separation.
- **GOOD CHEMICAL AND THERMAL STABILITY:** Greater durability of the column, does not react with sample components.
- **LOW VISCOSITY:** More efficient columns (lower resistance to analyte transfer between phases).
- **AVAILABLE IN HIGH PURITY:** Reproducible columns; absence of “ghost” peaks in the chromatograms.

## ◎ COLUMNS - STATIONARY PHASE

The stationary phase liquid must have the following characteristics:

- (i) Volatility (SP boiling  $>$   $T_{\text{column}} + 100^{\circ}\text{C}$ )
- (ii) Thermally inert
- (iii) Chemically inert
- (iv) good resolution

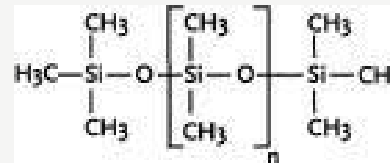
Stationary Phase	Common Trade Name	Maximum T ( $^{\circ}\text{C}$ )	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs
Poly(phenylmethyl dimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters; alkaloids; drugs; halogenated compounds
Poly(phenylmethyl) siloxane (50% phenyl)	OV-17	250	Drugs; steroids; pesticides; glycols
Poly(trifluoropropyl dimethyl) siloxane	OV-210	200	Chlorinated aromatics; nitroaromatics; alkyl-substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acid; alcohol; ethers; essential oils; glycols
Poly(dicyanoallyl dimethyl) siloxane	OV-275	240	Polyunsaturated fatty acids; rosin acids; free acids; alcohols

## ◎ COLUMNS - STATIONARY PHASE

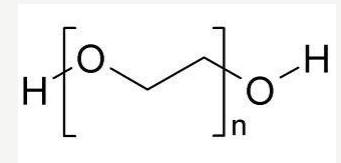
### The stationary phase liquid:

- **Apolar:** non-aromatic hydrocarbons, silicones (e.g., SE-30)
- **Polar:** contains large amounts of polar groups (e.g., Carbowax) - hydrogen bond-like interactions.
- **Intermediate:** polar or potentially polar groups in nonpolar skeleton (Ex. SE-52).

Stationary Phase	Common Trade Name	Maximum T (°C)	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs
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Silicones - Polydimethyl siloxane  
(apolar phase)



Polyethylene glycol  
(polar phase)



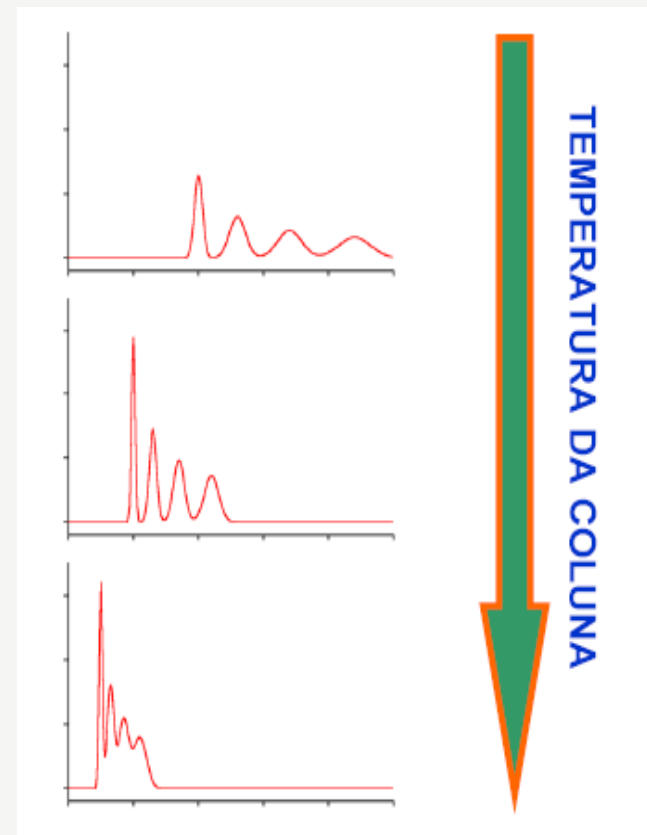
## ◎ OVEN - COLUMN TEMPERATURE CONTROL



## ◎ OVEN - COLUMN TEMPERATURE CONTROL

***Essential for obtaining good separation (resolution) in GC.***

In addition to the SP interaction, the time it takes for an analyte to travel through the column depends on its vapor pressure ( $p^0$ ).

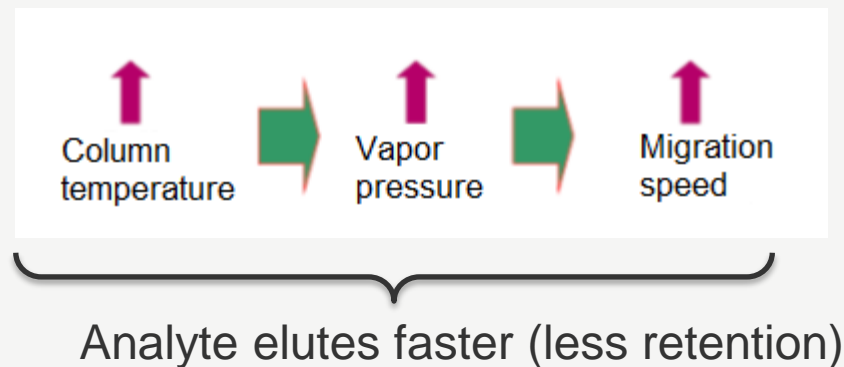


## ◎ OVEN - COLUMN TEMPERATURE CONTROL

***Essential for obtaining good separation (resolution) in GC.***

In addition to the FE interaction, the time it takes for an analyte to travel through the column depends on its vapor pressure ( $p^0$ )

$$p^0 = f \left\{ \begin{array}{l} \text{Chemical structure} \\ \text{of the analyte} \\ \text{Column temperature} \end{array} \right.$$



## ◎ COLUMN OVEN

### IDEALLY

- Easy column access: Column changeover operation can be frequent.
- Wide temperature range for use: from T room to 400°C.
- Temperature independent of other modules: It should not be affected by the temperature of the injector and detector.
- Uniform temperature inside: Very efficient internal ventilation systems to maintain an even temperature throughout the oven.
- Stable and reproducible temperature: The temperature must be maintained with precision and accuracy of  $\pm 0.1$  ° C

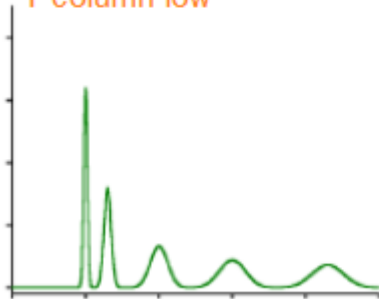
## ⊙ CONTROL OF COLUMN TEMPERATURE - ISOTHERM

### Isothermal Analysis

- ❑ Samples with high boiling T do not elute.
- ❑ First peaks: unresolved
- ❑ Last peaks: low, wide, very resolved

Example: complex mixtures (constituents with very different volatilities)  
ISOTHERMICALLY separated.

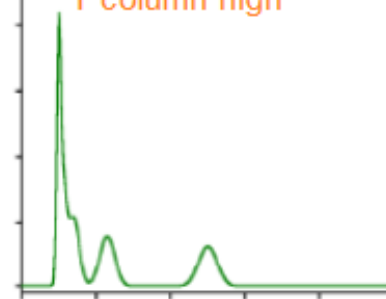
T column low



The most volatile components are separated.

Less volatile components take longer to elute and come out as broad peaks.

T column high



More volatile components are not separated.

Less volatile components elute quicker.

## ◎ COLUMN TEMPERATURE CONTROL - PROGRAM

The temperature ranges as a function of time are programmed according to the composition of the analyte.

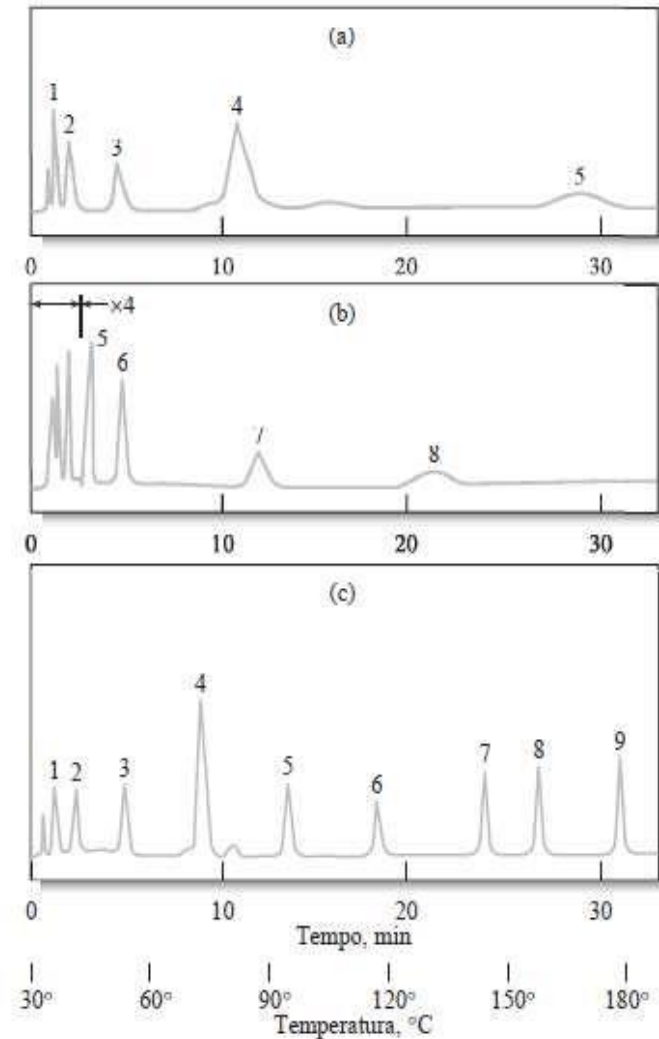


## ◎ COLUMN TEMPERATURE CONTROL

a) T isothermal column at 45°C

b) T column isothermal at 145 °C;

c) T column programmed from 30°C to 180°C



## ◎ DETECTORS

### IDEALLY

1. High sensitivity:  $10^{-8}$  to  $10^{-15}$  g of solute.
2. Good stability and reproducibility.
3. Linear response for solutes spanning several orders of magnitude.
4. Temperature range from ambient to at least  $400^{\circ}\text{C}$ .
5. Short response time.
6. Ease of use.
7. Response similarity for all solutes.
8. Non-destructive.



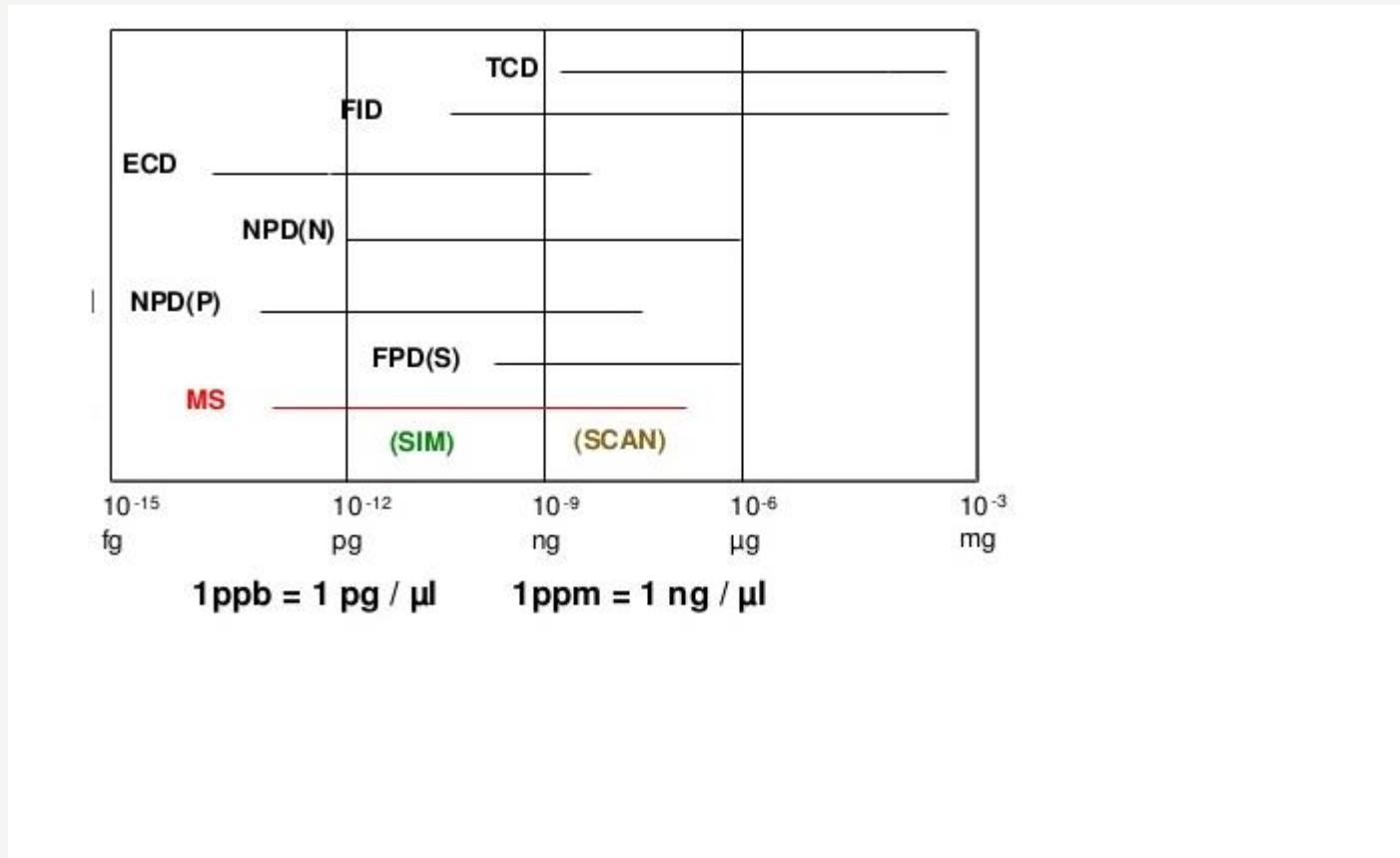
## ◎ DETECTORS

- **Thermal Conductivity (TCD)**: Variation of the thermal conductivity of the carrier gas.  
FM = helium. Universal answer. Non-destructive.
- **Flame Ionization (FID)**: Ions generated during the burning of eluates in a flame of H<sub>2</sub> + air.  
FM = hydrogen. High sensitivity, almost universal response (any substance containing C-H bonds). Destructive.
- **Electron Capture (ECD)**: Current suppression caused by the absorption of electrons by highly electrophilic compounds.  
FM = nitrogen. Selective for organic halogens, nitriles, nitrates and organometallics. Non-destructive.
- **Nitrogen Phosphorus Detector (NPD) or Thermionic Detector (TSD)**: The eluent burned in the flame of H<sub>2</sub> + air passes through a rubidium silicate surface where ions of molecules with N and P are formed. Selective for compounds that contain N and P.
- **Mass Spectrometry (MS)**: Universal response. Hyphenated method.

## ⊙ DETECTORES MAIS COMUNS EM CG

Tipo	Amostras a que são aplicáveis
Flame ionization (FID)	Hydrocarbons / compounds with C-H bonds
Thermal Conductivity (TCD)	Universal Detector
Electron capture (ECD)	Halogen compounds
Mass spectrometer (MS)	Adjustable to any species
Nitrogen-Phosphorus Detector (NPD)	Nitrogen and phosphorus compounds

## ◎ MOST COMMON DETECTORS IN GC



## Exercise 1 - Internal Standard Method

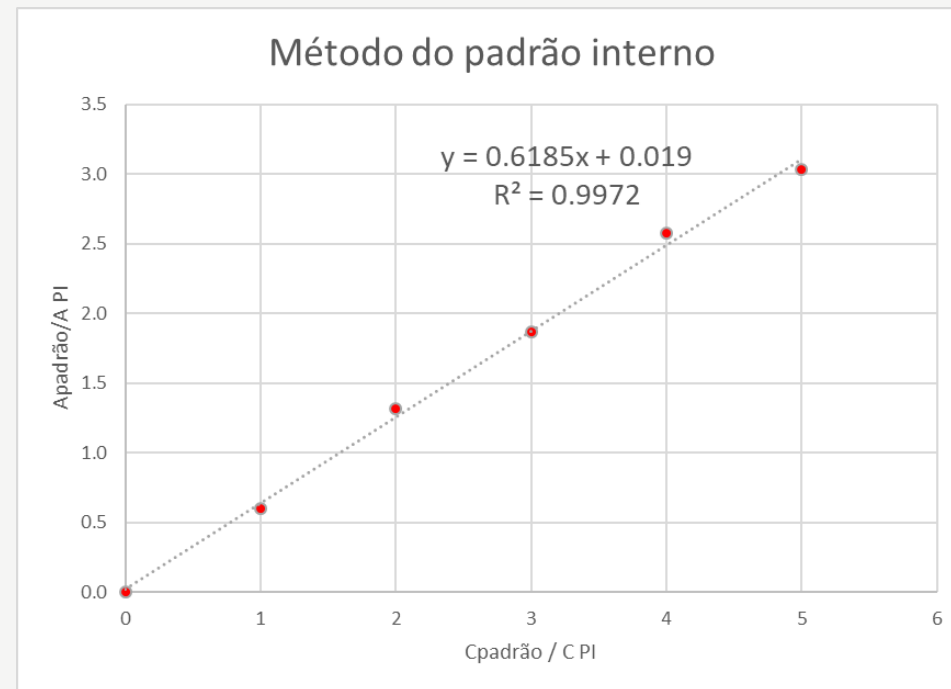
In determining the concentration of species X in a sample, using gas chromatography, the values for the standard and internal standard areas were obtained.

Determine the concentration and associated error of the sample using the internal standard (IS) method. Compare with the method of calibration curve (CC).

$C_{pj}$	$A_x$	$A_{PI}$
0	0	34583
1	26981	44958
2	39534	30087
3	74242	39770
4	68635	26629
5	117449	38733
amostra	72541	33826

## Exercise 1 - Internal Standard Method

Cpadrão/C PI	Apadrão	Apadrão interno (PI)	Apadrão/A PI
0	0	34585	0.0000000
1	26981	44958	0.6001379
2	39534	30087	1.3139894
3	74242	39770	1.8667840
4	68635	26629	2.5774532
5	117449	38733	3.0322722
Area Amostra	72541	33826	2.1445338
C Amostra / C PI	3.436888		
C PI	constante		



## Exercise 1 - Internal Standard Method

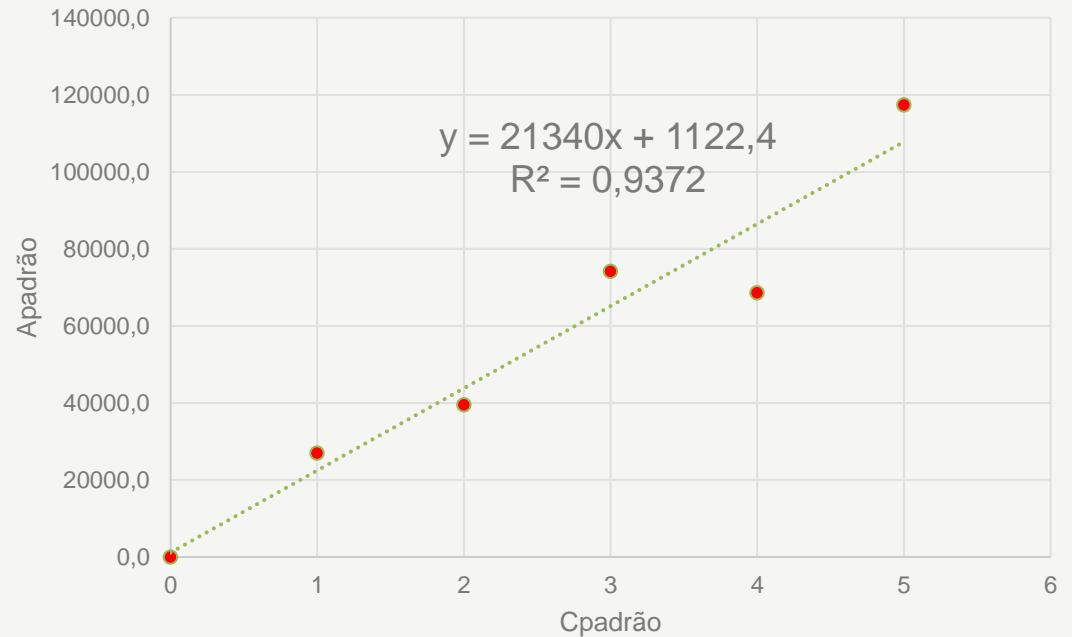
SUMÁRIO DOS RESULTADOS								
<i>Estatística de regressão</i>								
R múltiplo	0.998614365							
Quadrado	0.997230651							
Quadrado	0.996538314							
Erro-padrão	0.068169752							
Observação	6							
ANOVA								
	<i>gl</i>	<i>SQ</i>	<i>MQ</i>	<i>F</i>	<i>p significância</i>			
Regressão	1	6.693624	6.693624	1440.383	2.88E-06			
Residual	4	0.018588	0.004647					
Total	5	6.712213						
	<i>Coefficientes</i>	<i>Erro-padrão</i>	<i>Stat t</i>	<i>valor P</i>	<i>15% inferior</i>	<i>5% superior</i>	<i>inferior 95.0%</i>	<i>Superior 95.0%</i>
Intercepta	0.018956018	0.049338	0.38421	0.720374	-0.11803	0.155939	-0.11803	0.155939278
Variável X	0.618460041	0.016296	37.95237	2.88E-06	0.573216	0.663704	0.573216	0.663704123

**Camosta (method IS) =  $3.4 \pm 0.1$ ; relative error (%) = 3**

## Exercise 1 - Calibration Curve Method

Cpadrão	Apadrão
0	0
1	26981
2	39534
3	74242
4	68635
5	117449
Area Amostra	72541
C Amostra	3.346632482

Reta da calibração



## Exercise 1 - Calibration Curve Method

SUMÁRIO DOS RESULTADOS								
<i>estatística de regressão</i>								
R múltiplo	0.968099							
Quadrado	0.937215							
Quadrado	0.921519							
Erro-padrão	11553.14							
Observação	6							
ANOVA								
	<i>gl</i>	<i>SQ</i>	<i>MQ</i>	<i>F</i>	<i>e significância</i>			
Regressão	1	7.97E+09	7.97E+09	59.70957	0.00151			
Residual	4	5.34E+08	1.33E+08					
Total	5	8.5E+09						
	<i>Coefficientes</i>	<i>erro-padrão</i>	<i>Stat t</i>	<i>valor P</i>	<i>95% inferior</i>	<i>5% superior</i>	<i>95.0% inferior</i>	<i>95.0% superior</i>
Intercepta	1122.429	8361.552	0.134237	0.899699	-22093	24337.82	-22093	24337.82
Variável X	21340.43	2761.73	7.727197	0.00151	13672.64	29008.22	13672.64	29008.22

**Camosta (Method CC) =  $3.3 \pm 0.6$ ; relative error (%) = 18**



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# EXERCISE 2

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In a separation of phenolic compounds by gas chromatography 3 peaks A, B and C were obtained with very close retention times under the following experimental conditions:

Length column 5 m; inside diameter, 2 mm; filling particle diameter 0.1mm, eluent pressure 25 psi; column temperature 500°C, boiling temperature of A, and C between 100 and 200°C; boiling temperature of the liquid phase 600°C.

Suggest the simplest change to achieve better separation.

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# PROBLEM SOLVING

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As such a high temperature is being used, the solutes elute quickly and are not separated. Therefore, the elution must be carried out at a programmed temperature (and not constant).