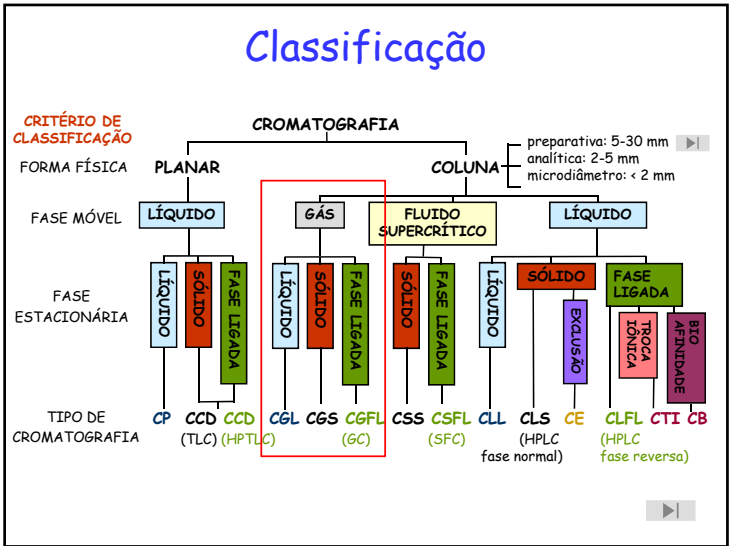


# Cromatografia a gás

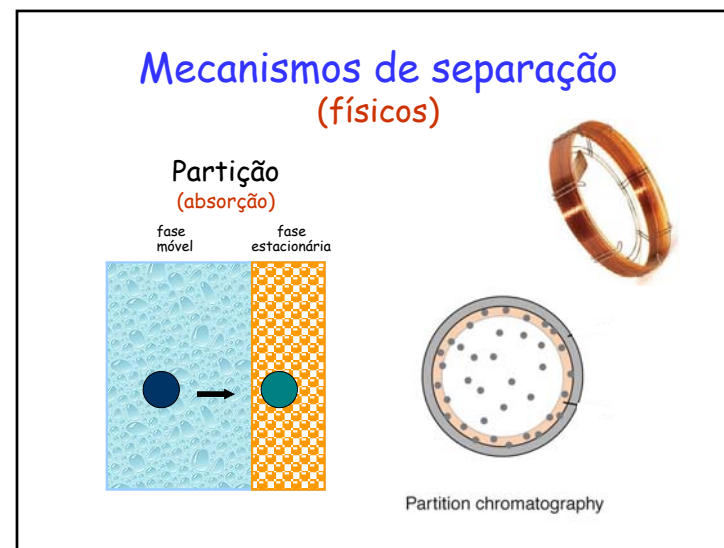
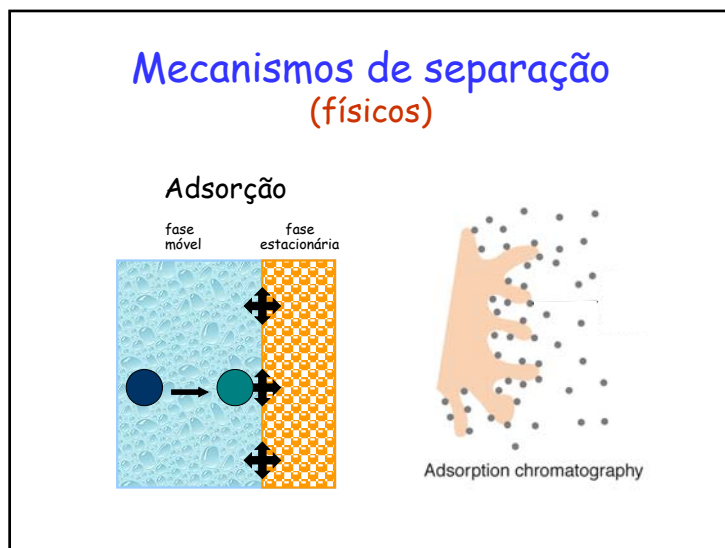
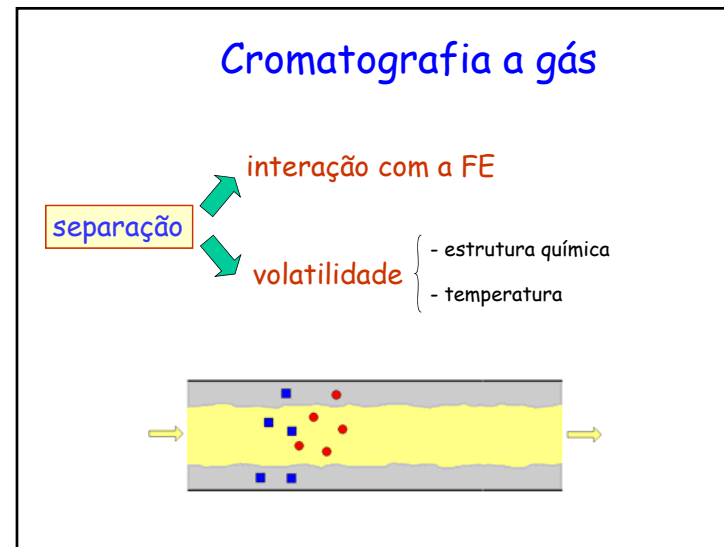
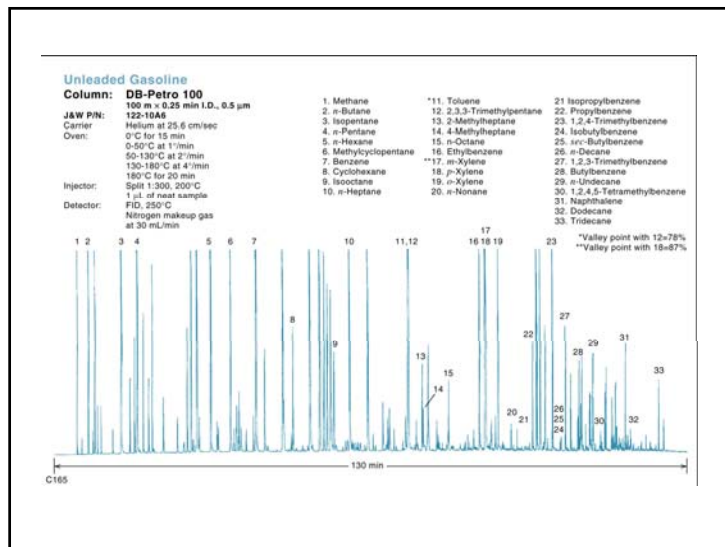
## Cromatografia - Princípio Básico

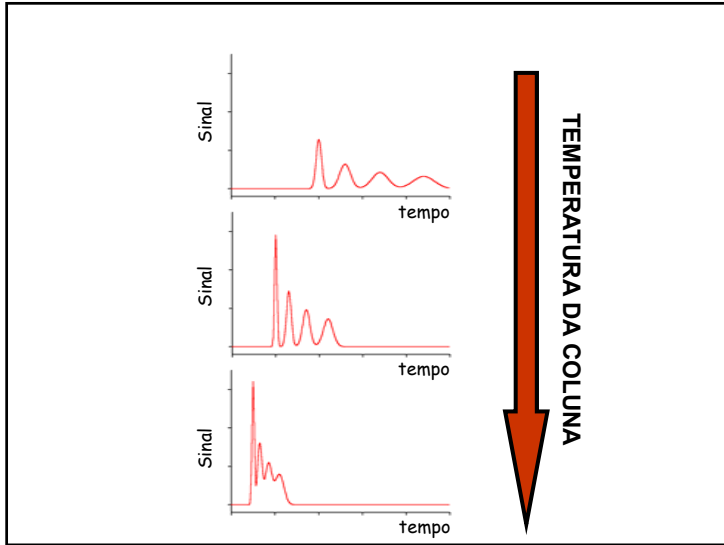
Separação de misturas por interação diferencial dos seus componentes entre uma **FASE ESTACIONÁRIA** (líquido ou sólido) e uma **FASE MÓVEL** (líquido ou gás).



## Cromatografia a gás

- Fase móvel ⇒ gás (de arraste)
- Fase estacionária ⇒ líquido ou sólido
- Aplicação
  - gases
  - compostos voláteis ( $T_e < 300\text{ °C}$ )
  - termicamente estáveis

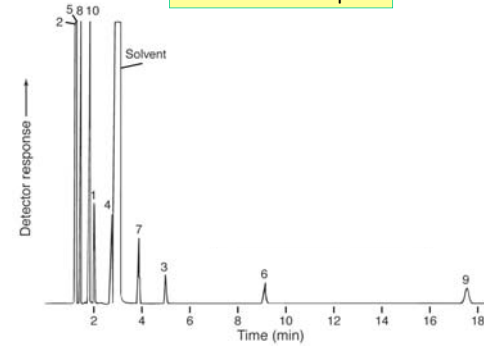




### Exercício

- hidrocarbonetos: pentano, hexano, heptano, octano
- álcoois: propanol, butanol, pentanol
- cetonas: propanona, metil-etil cetona, 3-pentanona

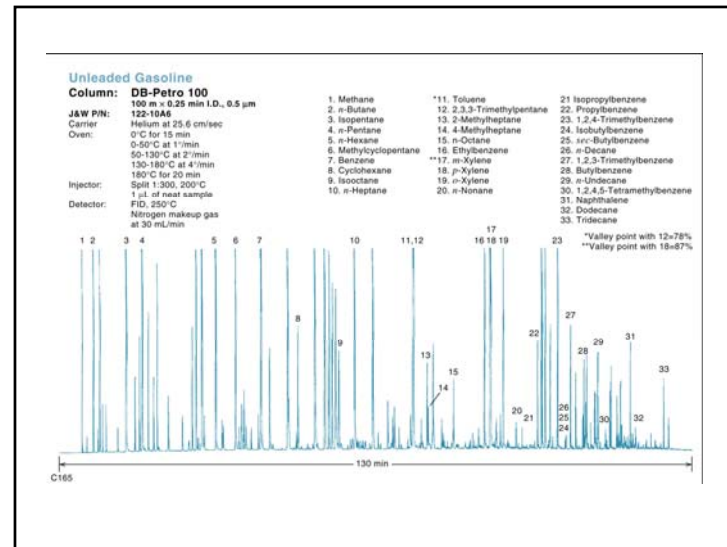
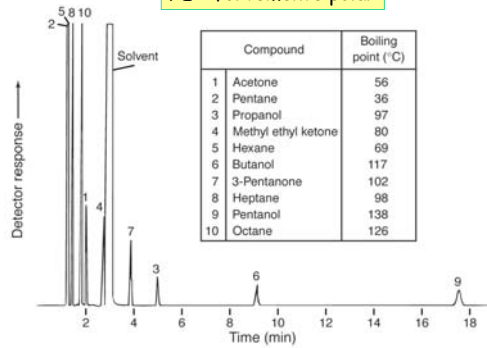
FE - fortemente polar



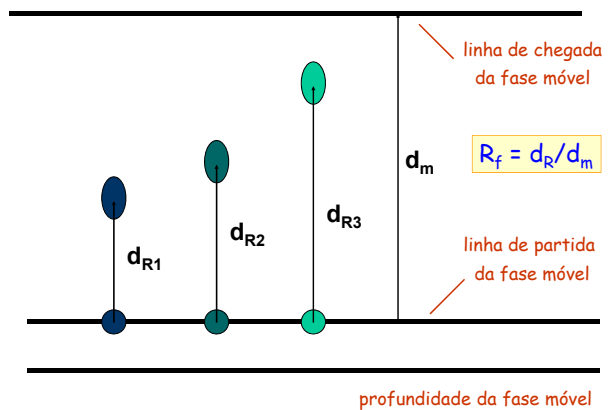
### Exercício

- hidrocarbonetos: pentano, hexano, heptano, octano
- álcoois: propanol, butanol, pentanol
- cetonas: propanona, metil-etil cetona, 3-pentanona

FE - fortemente polar

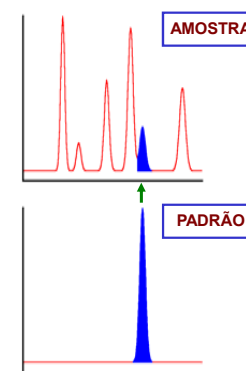


## Cromatografia planar

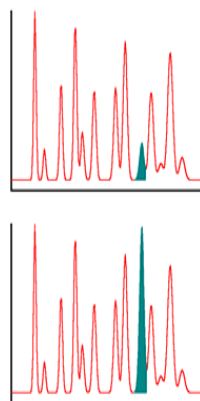


## Identificação dos picos

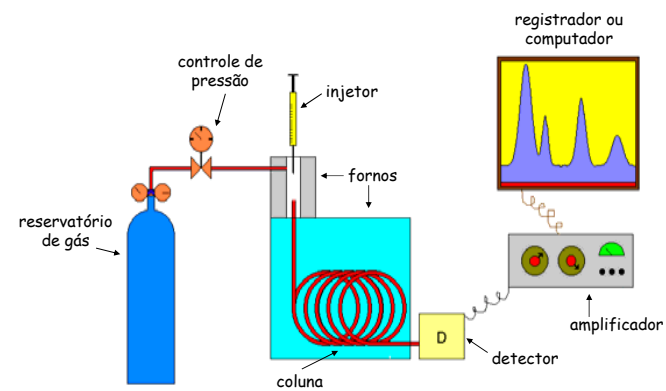
Comparação de  $t_R'$

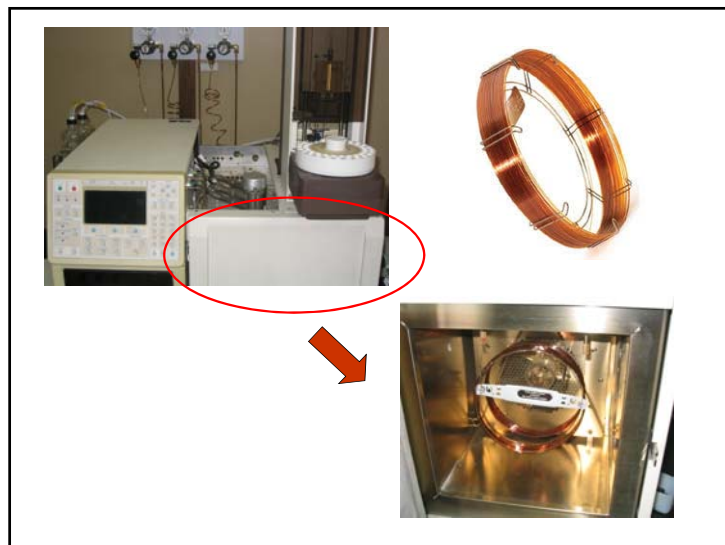


## Identificação dos picos (spiking)



## Instrumentação básica





## Gás de arraste

- Inerte

- Puro

$H_2O, O_2$  → oxida / hidroliza algumas FE  
incompatíveis com DCE

hidrocarbonetos → ruído no sinal de DIC

- Custo

- Compatível com o detector

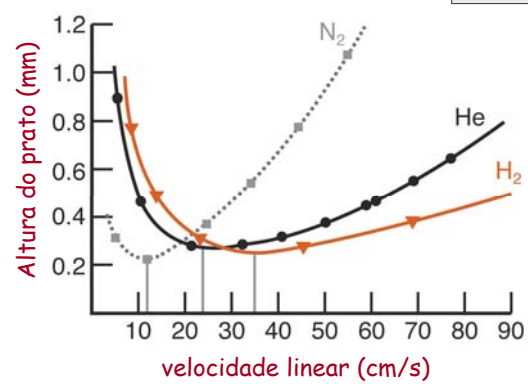
DCT → He,  $H_2$

DIC →  $N_2, H_2$

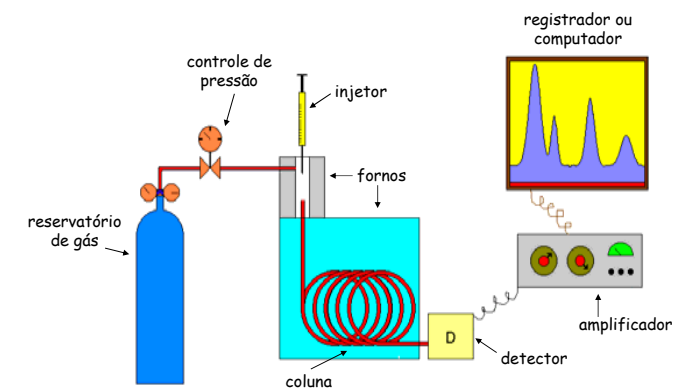
DCE →  $N_2, Ar + 5\% CH_4$

## Gás de arraste

$$\sigma^2 = H L$$



## Instrumentação básica



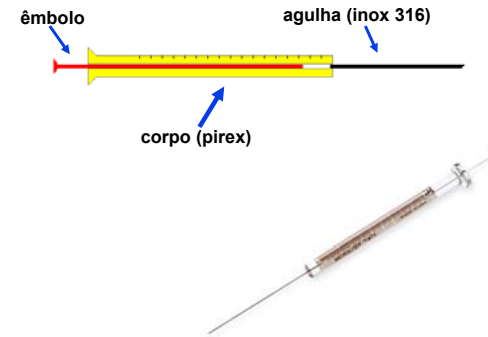
## Injeção de amostras

- Introdução instantânea de amostra
- Aquecimento ( $T > T_e$ )
- Volume injetado

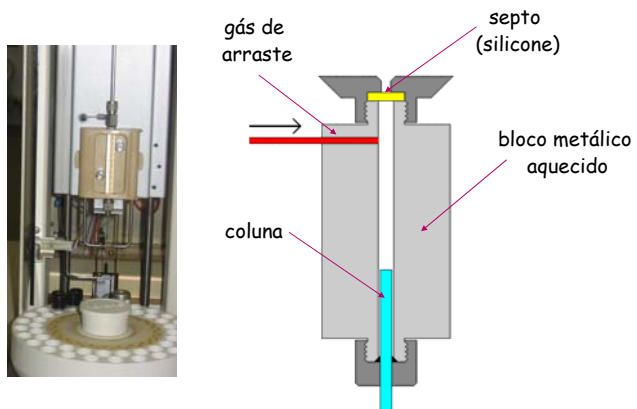
COLUNA	Amostras Líquidas	Amostras Gasosas
recheada $\varnothing = 3,2 \text{ mm } (1/8")$	$0,2 \mu\text{L} \dots 20 \mu\text{L}$	$0,1 \text{ mL} \dots 50 \text{ mL}$
capilar $\varnothing = 0,25 \text{ mm}$	$0,01 \mu\text{L} \dots 3 \mu\text{L}$	$0,001 \text{ mL} \dots 0,1 \text{ mL}$

## Injeção de amostras

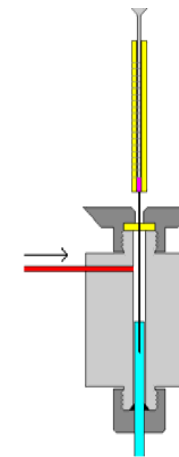
Microseringas - 1, 5, 10  $\mu\text{L}$

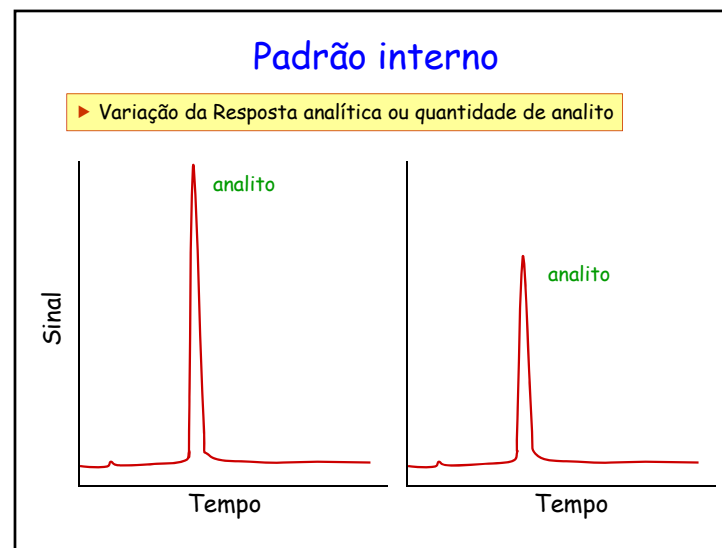
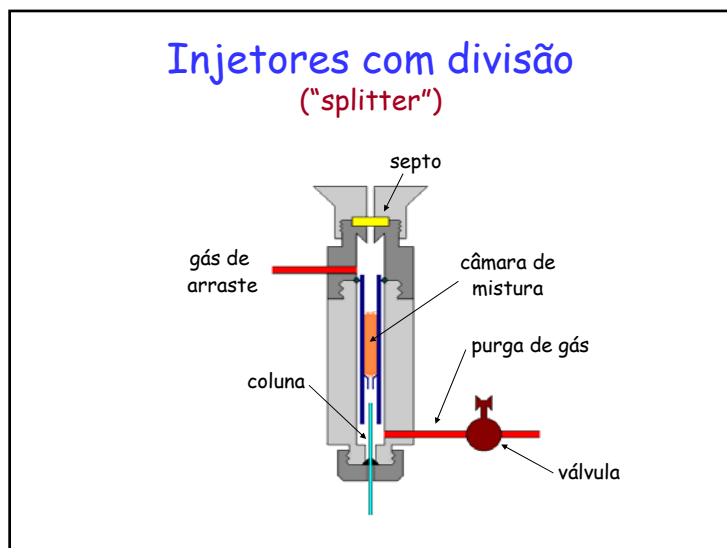
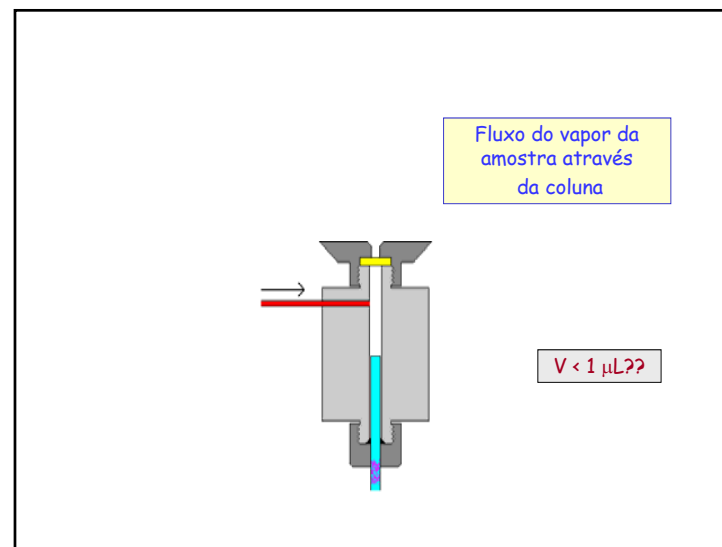
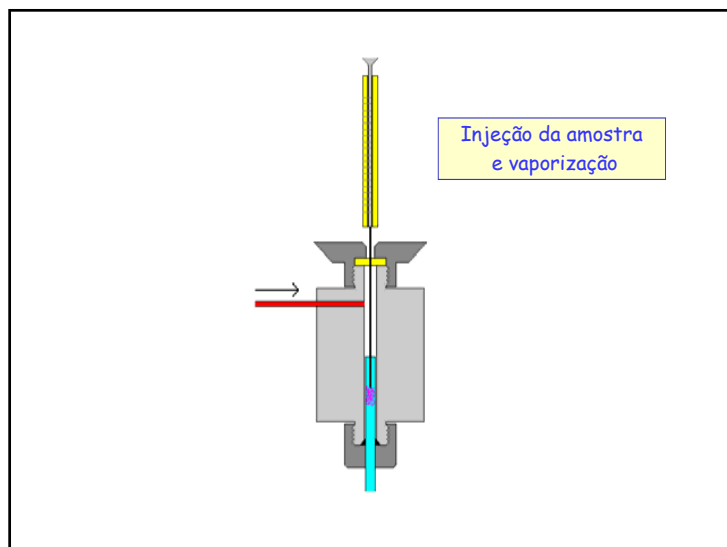


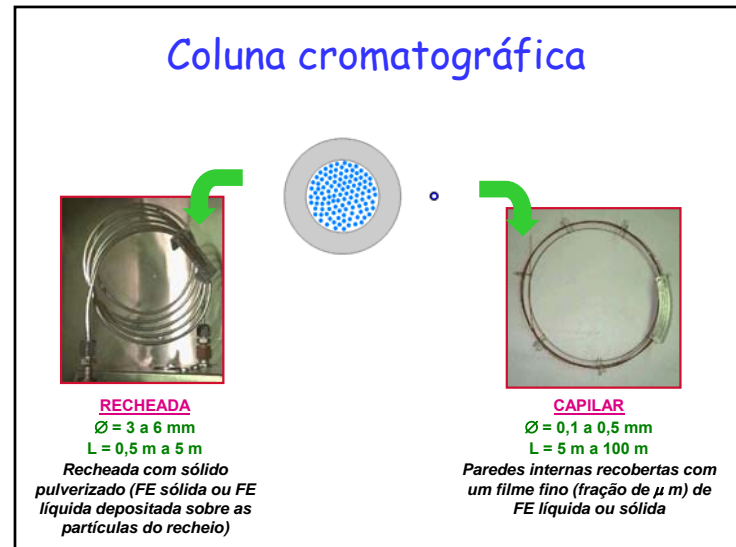
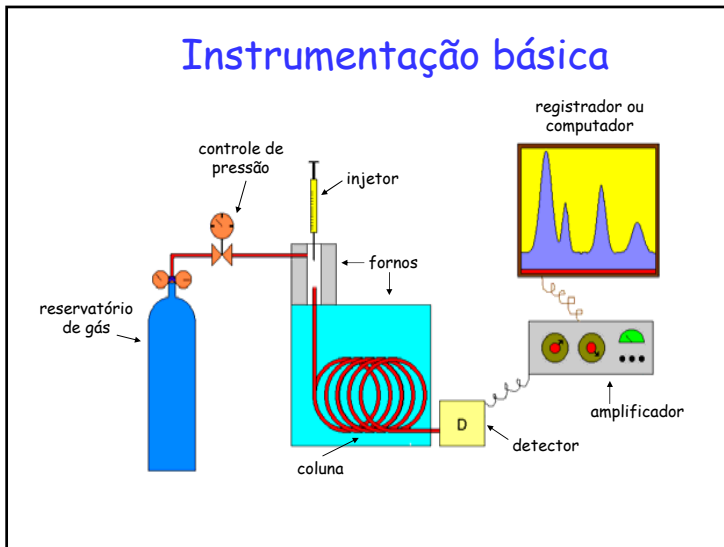
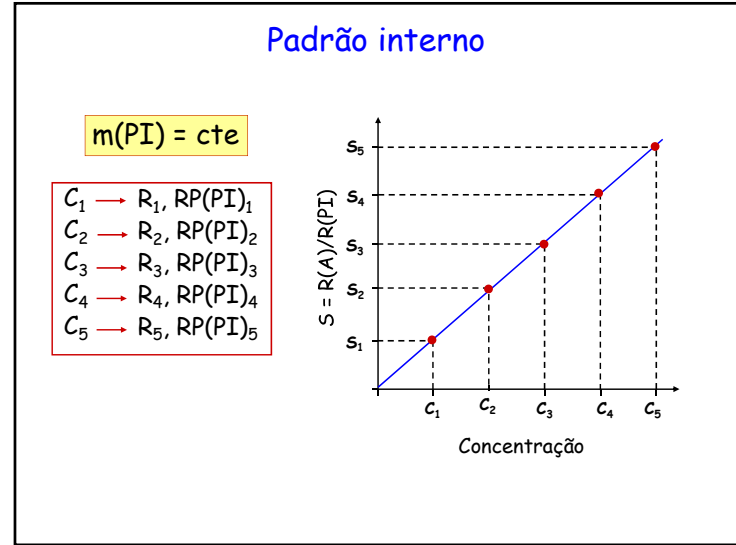
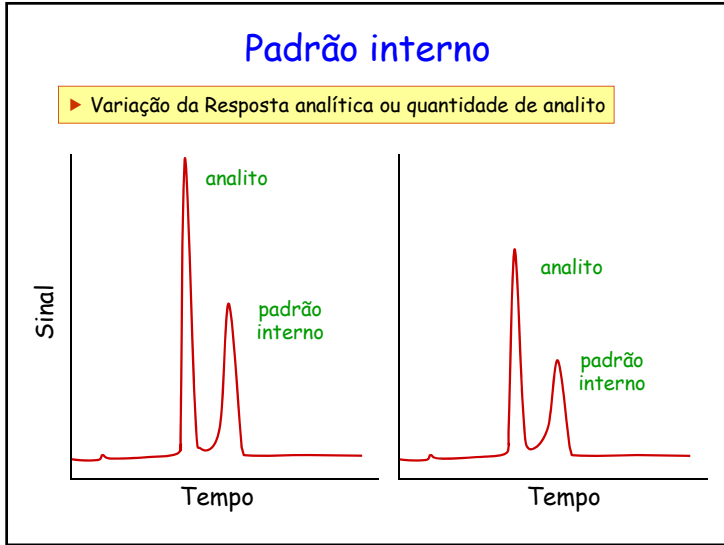
## Injetor convencional



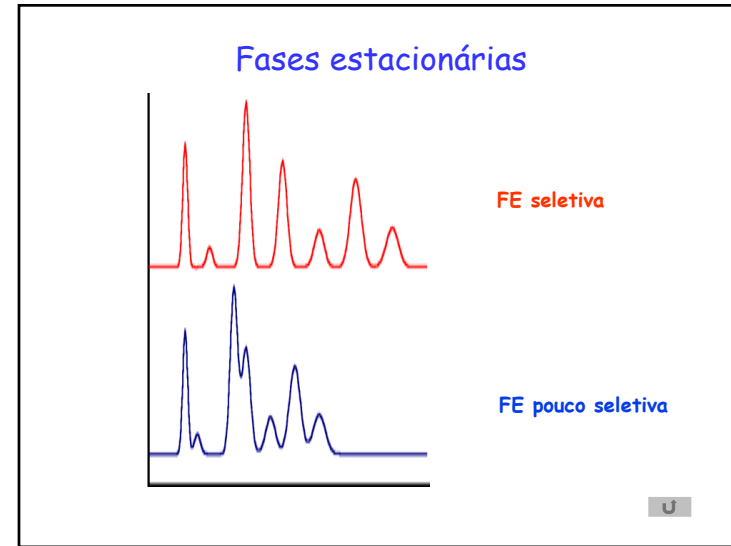
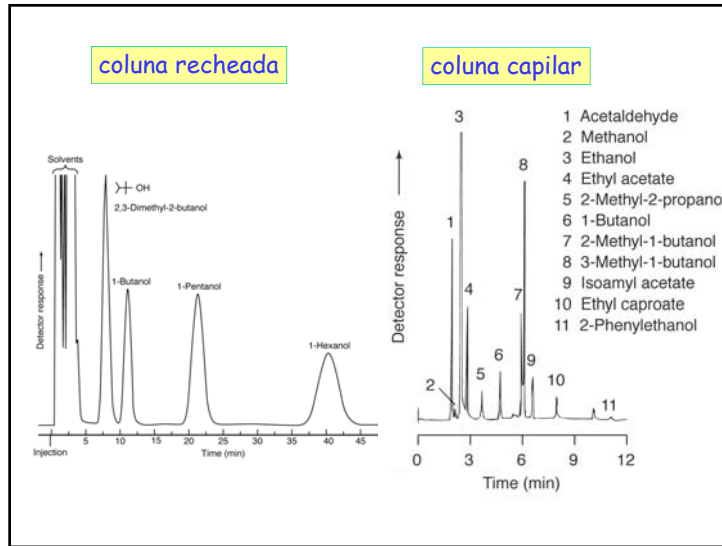
Introdução da agulha da microseringa











**Table 24-2 Polarity of solutes**

Nonpolar	Weak intermediate polarity
Saturated hydrocarbons	Ethers
Olefinic hydrocarbons	Ketones
Aromatic hydrocarbons	Aldehydes
Halocarbons	Esters
Mercaptans	Tertiary amines
Sulfides	Nitro compounds (without $\alpha$ -H atoms)
CS <sub>2</sub>	Nitriles (without $\alpha$ -atoms)
Strong intermediate polarity	Strongly polar
Alcohols	Polyhydroxyalcohols
Carboxylic acids	Amino alcohols
Phenols	Hydroxy acids
Primary and secondary amines	Polyprotic acids
Oximes	Polyphenols
Nitro compounds (with $\alpha$ -H atoms)	
Nitriles (with $\alpha$ -H atoms)	

SOURCE: Adapted from H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography* (Palo Alto, CA: Varian Instrument Division, 1968).

### Principal FE líquida

⇒ **Polisiloxanos**

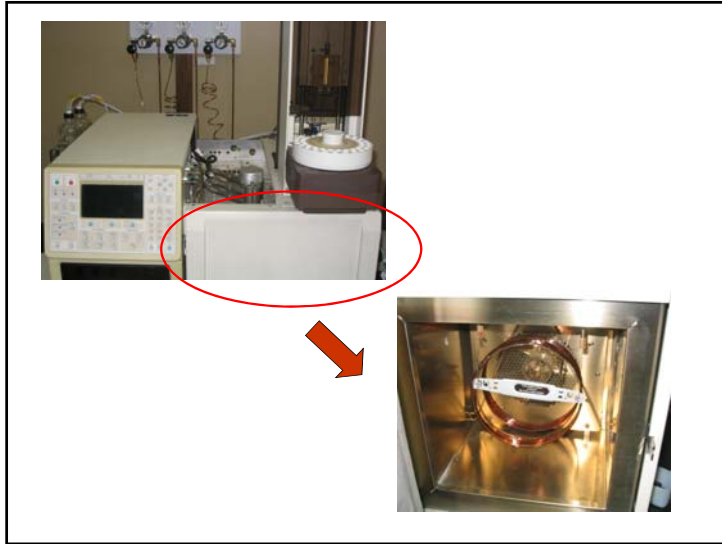
- FE mais empregadas em GC
- elevada estabilidade térmica e química
- fabricação em larga escala

$$\text{H}_3\text{C}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{O}-\text{Si}\left(\begin{array}{c} \text{R} \\ | \\ \text{R} \end{array}\right)-\text{O} \\ | \\ \text{CH}_3 \end{array}\right)_n-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{O}-\text{Si}\left(\begin{array}{c} \text{R} \\ | \\ \text{R} \end{array}\right)-\text{O} \\ | \\ \text{CH}_3 \end{array}\right)_n-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{O}-\text{Si}\left(\begin{array}{c} \text{R} \\ | \\ \text{R} \end{array}\right)-\text{O} \\ | \\ \text{CH}_3 \end{array}\right)_n-\text{CH}_3$$

R = -CH<sub>3</sub> → apolar

R = -C<sub>6</sub>H<sub>5</sub>  
-C<sub>3</sub>H<sub>6</sub>CN  
-C<sub>3</sub>H<sub>6</sub>CF<sub>3</sub> → polar

**polidimetil-fenil-siloxano (5%)**



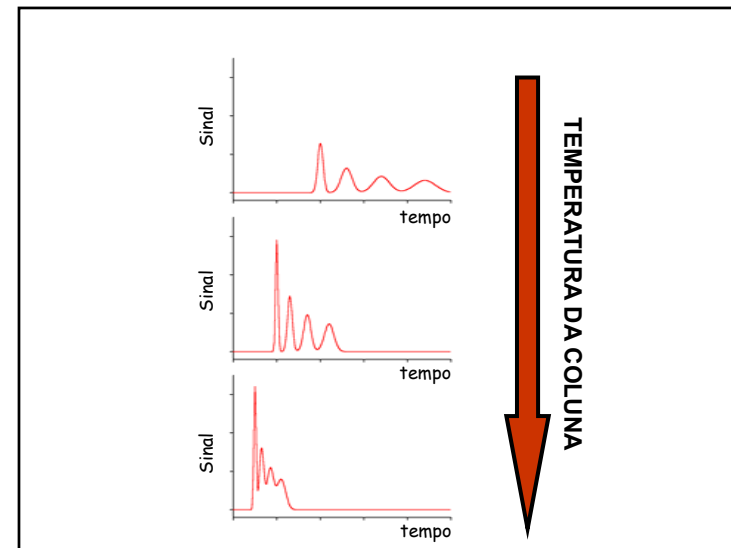
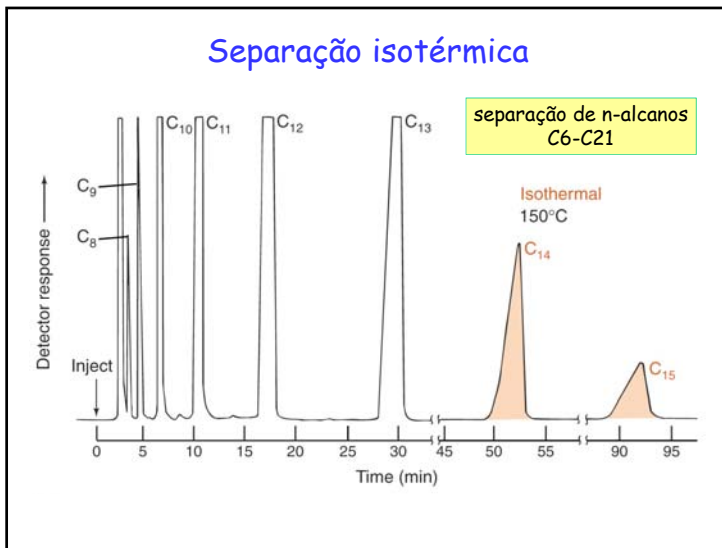
## Forno da coluna

### ⇒ Temperatura

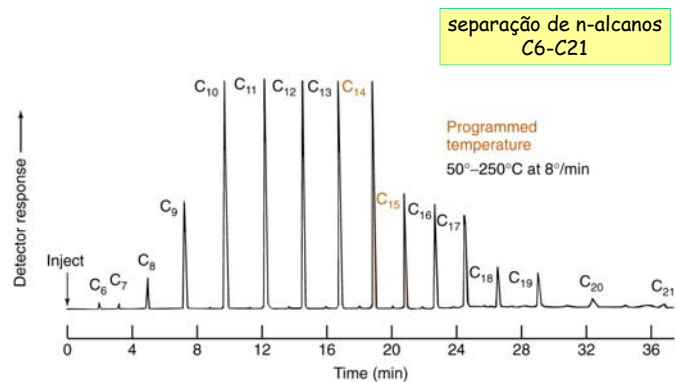
- estável e reprodutível - precisão de  $\pm 0,1^\circ\text{C}$
- uniforme
- ampla faixa
- independente dos demais módulos

### ⇒ Fácil acesso à coluna

### ⇒ Aquecimento e resfriamento rápido



## Separação com programa de temperatura



## Detectores

- ⇒ Classificação
- universal
  - seletivo
  - específico
- ⇒ Resposta rápida
- ⇒ Sensibilidade
- ⇒ Faixa de resposta

## Detectores

~ 60 detectores já usados em CG

~ 15 equipam cromatógrafos comerciais

4 respondem pela maior parte das aplicações

**DCT TCD**  
Detector por  
condutividade  
térmica

**DCE ECD**  
Detector por  
captura de  
elétrons

**DIC FID**  
Detector por  
ionização em  
chama

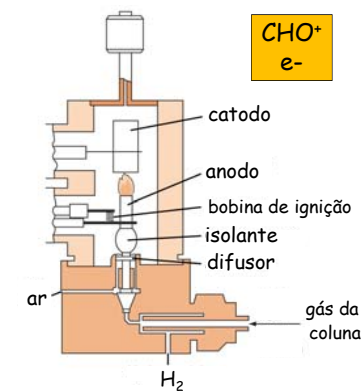
**EM MS**  
Espectrômetro  
de massas

## Detector de ionização em chama (FID)

### PRINCÍPIO

Formação de íons  
quando um composto é  
queimado em chama  
ar/H<sub>2</sub>

- LQ = 10-100 pg
- linearidade de 10<sup>7</sup> e 10<sup>8</sup> (pg a mg)



## Espectrômetro de massas (MS)

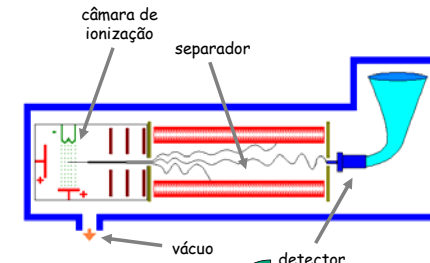
⇒ Informações quali e quantitativas

⇒ Sensibilidade

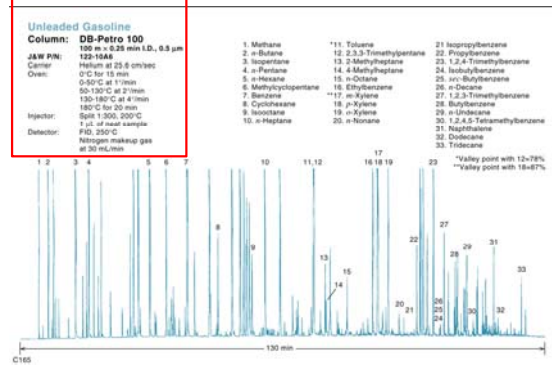
⇒ Princípio

- fragmentação e ionização
  - impacto eletrônico
  - ionização química
- separação razão massa/carga
- detecção

## Espectrômetro de massas



- LQ = 25 fg - 100 pg
- linearidade de  $10^5$



### Unleaded Gasoline

**Column: DB-Petro 100**  
**100 m x 0.25 mm I.D., 0.5 µm**  
**J&W P/N: 122-10A6**  
**Carrier:** Helium at 25.6 cm/sec  
**Oven:** 0°C for 15 min  
 0-50°C at 1°/min  
 50-130°C at 2°/min  
 130-180°C at 4°/min  
 180°C for 20 min  
**Injector:** Split 1:300, 200°C  
 1 µL of neat sample  
**Detector:** FID, 250°C  
 Nitrogen makeup gas at 30 mL/min