Print version

Gas Chromatography

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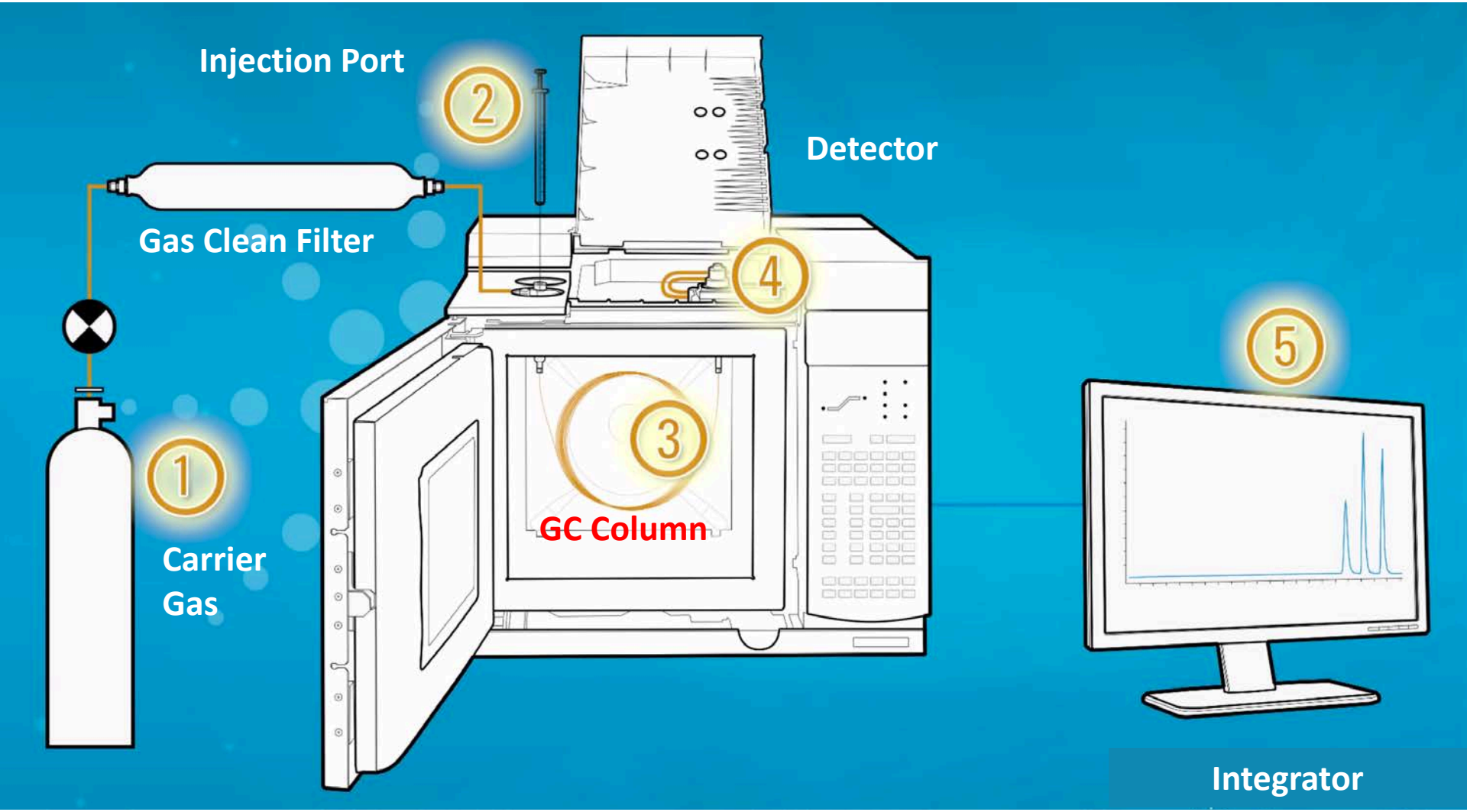
CEE772 Instrumental Methods in Environmental Analysis

Contents

- The primary components to a GC system
  1. **Carrier Gas System (including Gas Clean Filters)**
     - The concept of theoretical plates and *van Deemter* curves
     - Selection of proper carrier gas
  2. **Sample Introduction System**
     - Split & splitless injection
  3. **Column (most critical component)**
     - Column configurations: packed vs. open tubular/capillary
     - Stationary phase
  4. **Detection System/GC Detectors**
     - Types of detectors and their specific applications
  5. **Computer ChemStation/Integrator**

The Basic Components to a GC System



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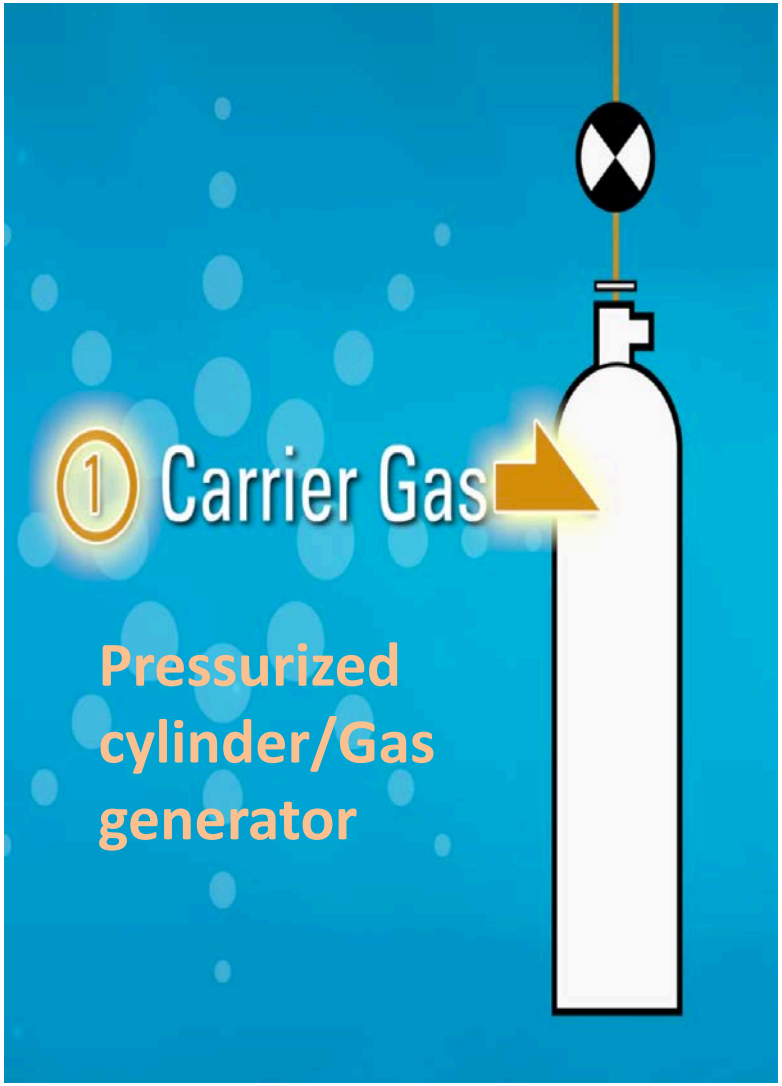
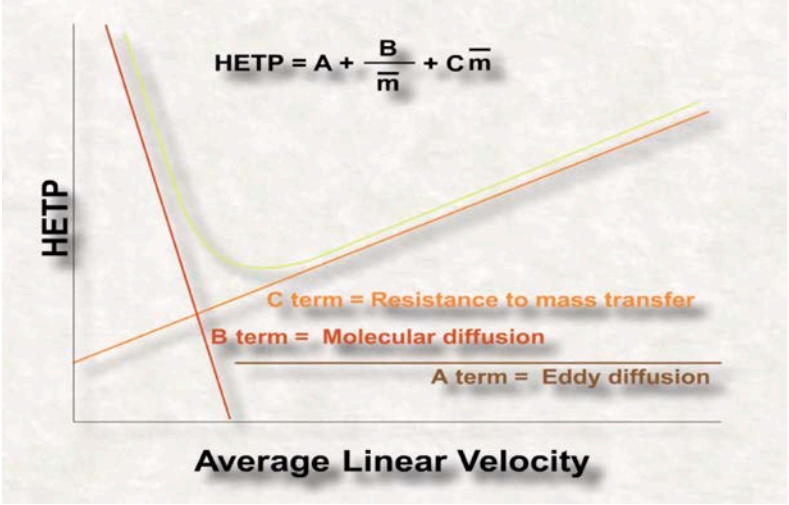
I. Carrier Gas System

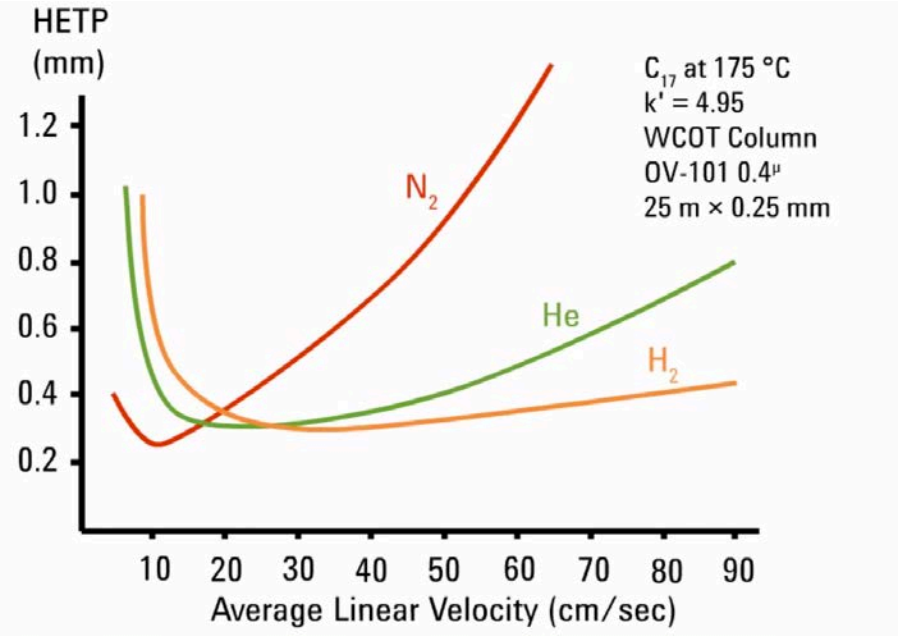


- Type of carrier gas effect on column efficiency and resolution
  - ✧ H_2/He/N_2
- Selection of carrier gas linear velocity/column flow rate

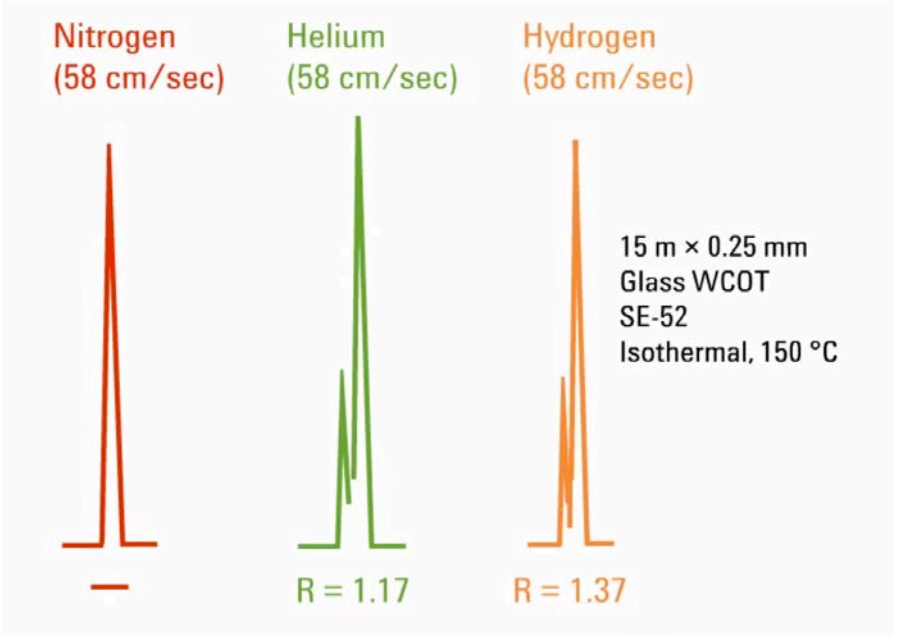


- Gas clean filter

Type of Carrier Gas Effect on Column Efficiency and Resolution



Efficiency curves for a 25 m × 0.25 mm id WCOT column with 0.4 um of OV-101



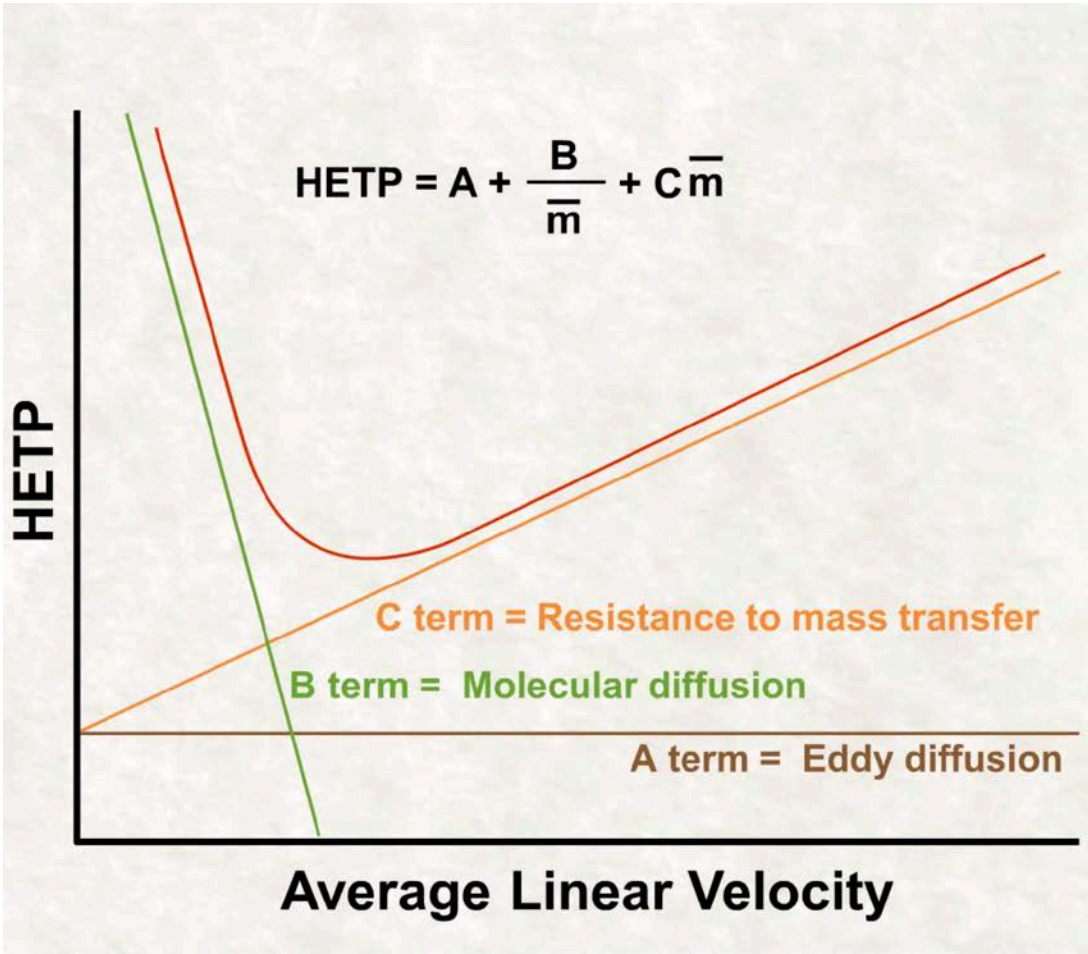
Effect of carrier gas on the resolution of n-heptadecane and pristane

Selection of carrier gas:

H_2 > He > N_2 (> Argon)

H_2 should be applied with safety precautions

Optimizing Linear Velocity/Flow Rate for High Column Efficiency



Efficiency is a function of the carrier gas linear velocity or flow rate.

HETP (height equivalent to theoretical plates) is defined as the length of the column divided by the number of theoretical plates (L/N).

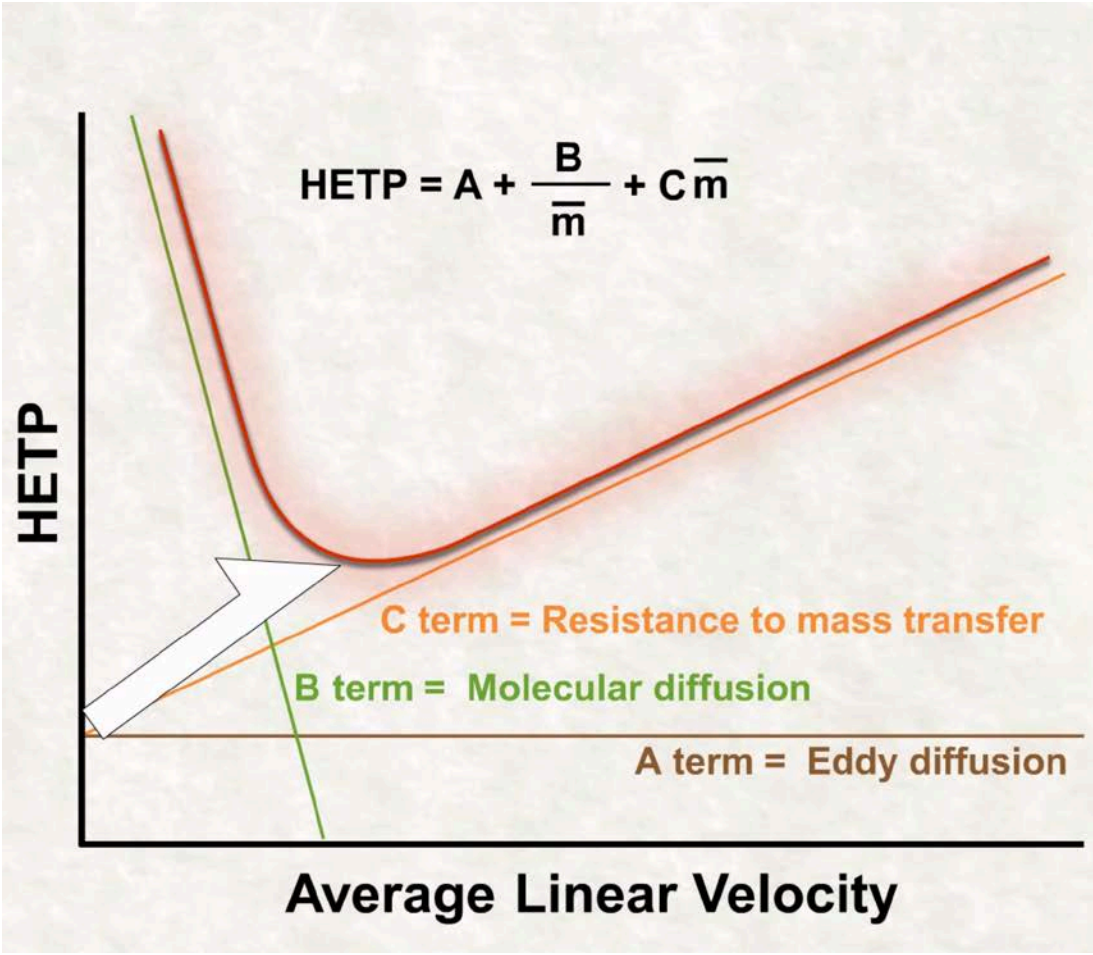
Plot of HETP vs. linear velocity is know as the Van Deemter plot.

The minimum of the curve represents the smallest HETP (or largest plates per meter) and thus the best efficiency.

The linear velocity value at the minimum of the curve is the optimum value for achieving the best efficiency.

***van Deemter* Plot**

Optimizing Linear Velocity/Flow Rate for High Column Efficiency



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***van Deemter* Plot**

Gas Clean Filter

- Significant damages can be done to the column if it is heated above 70℃ with even trace amounts of O_2 in the column
- Use carrier gas that meets the 99.9995% specification (UHP grade)
- Use O_2 & moisture traps

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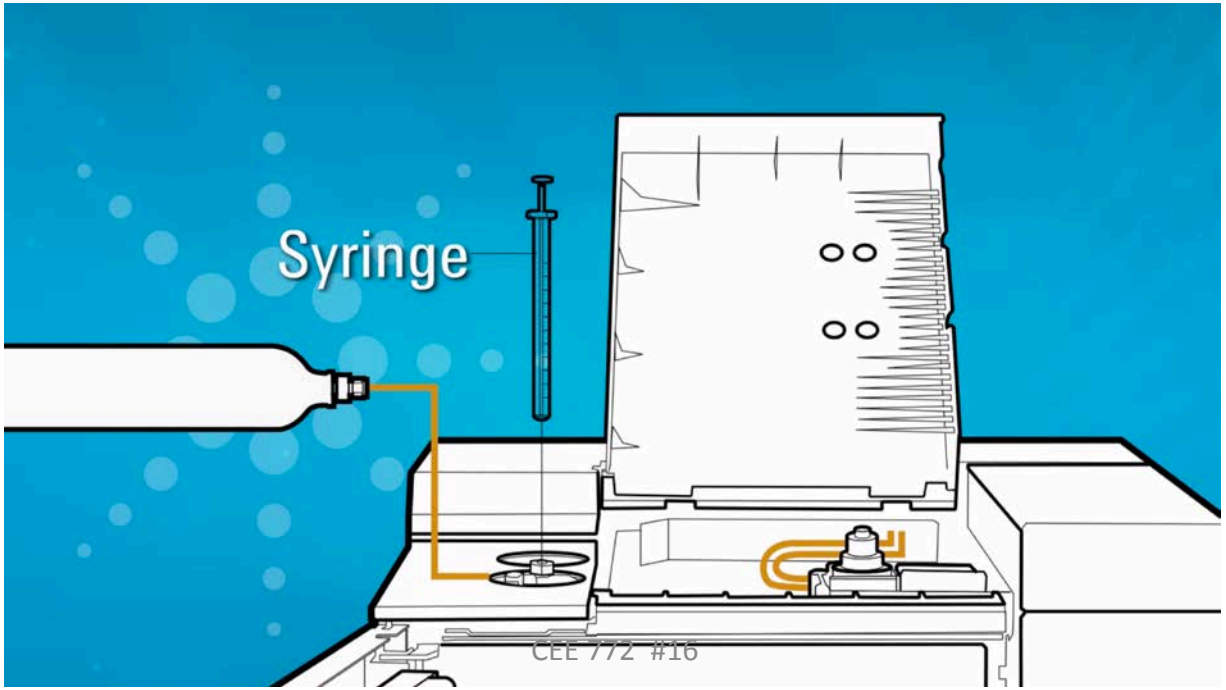
II. Sample Introduction

- The sample must be of a ***suitable size*** (especially for WCOT/capillary columns) and introduced ***instantaneously*** as a **PLUG OF VAPOR**

  Slow injection/oversize causes peak broadening and poor resolution

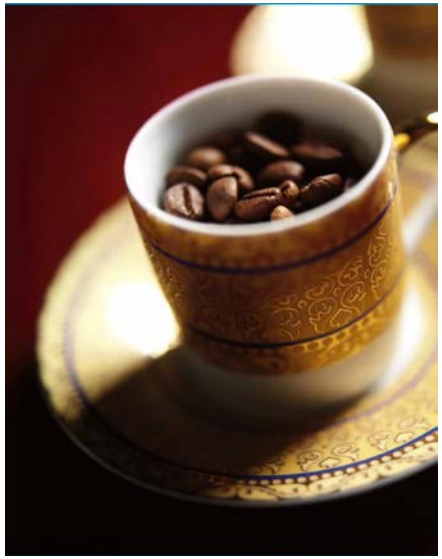


Types of GC samples and injection methods

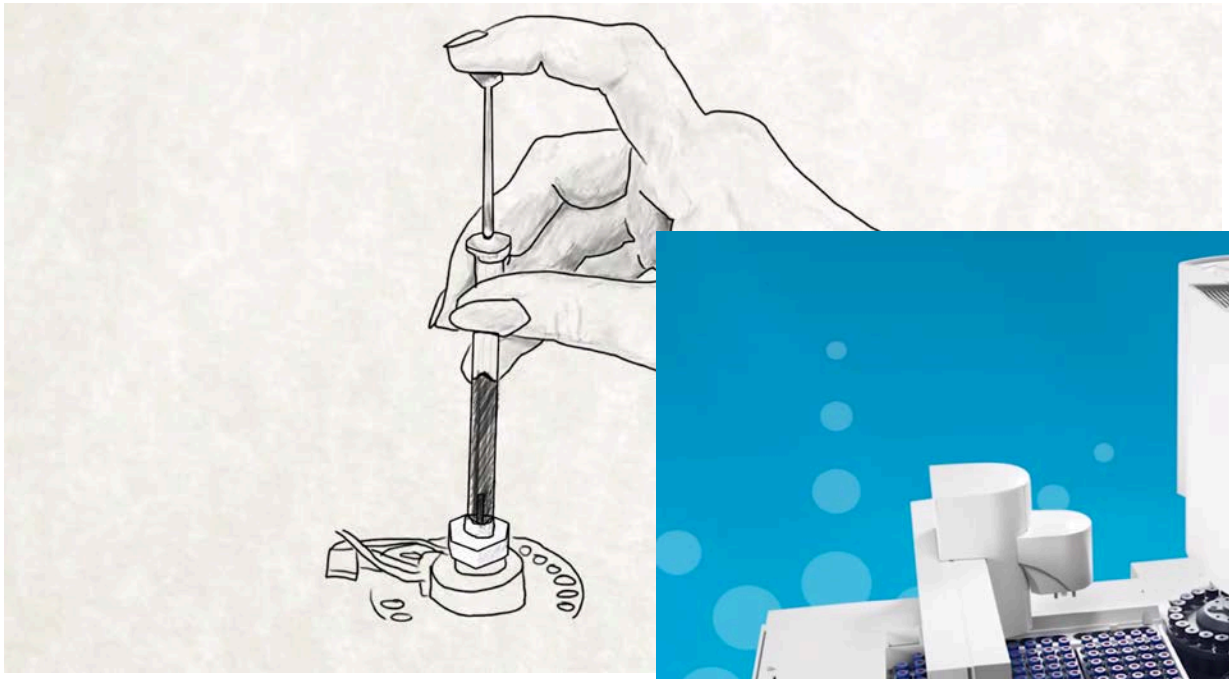
Liquid

Gas

Solid

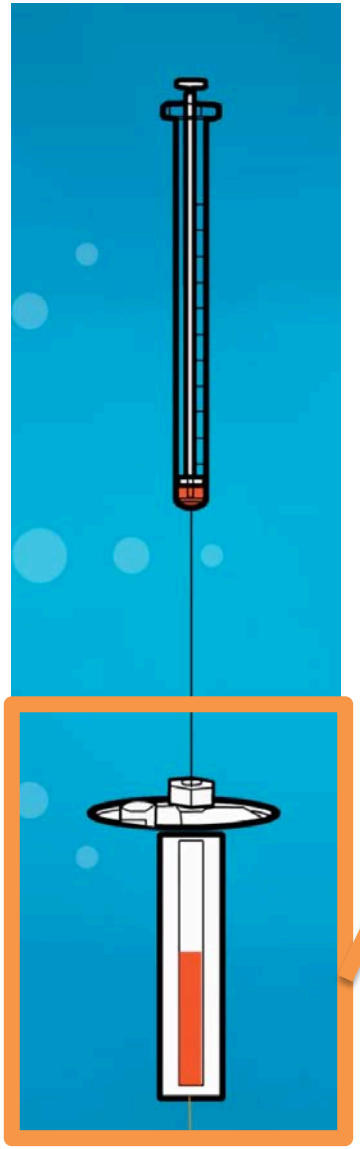


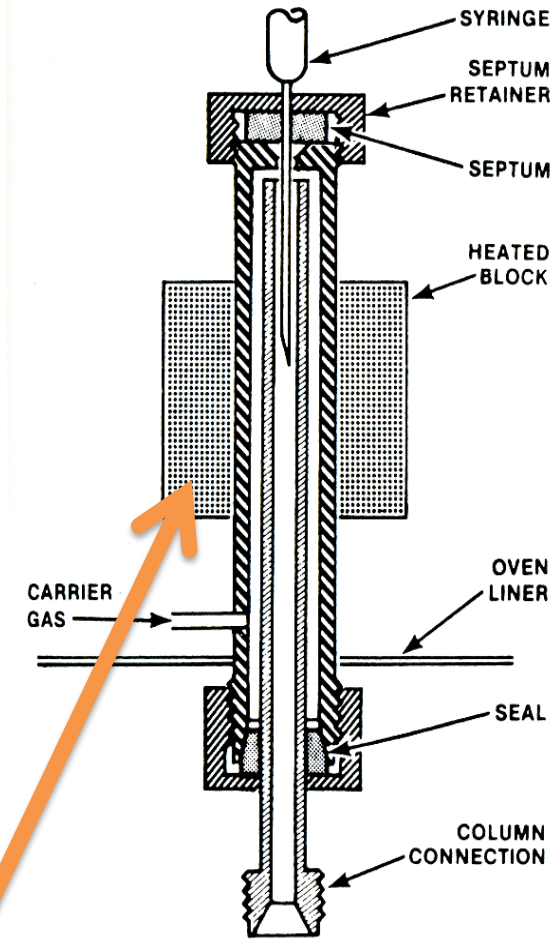
Auto Sampler

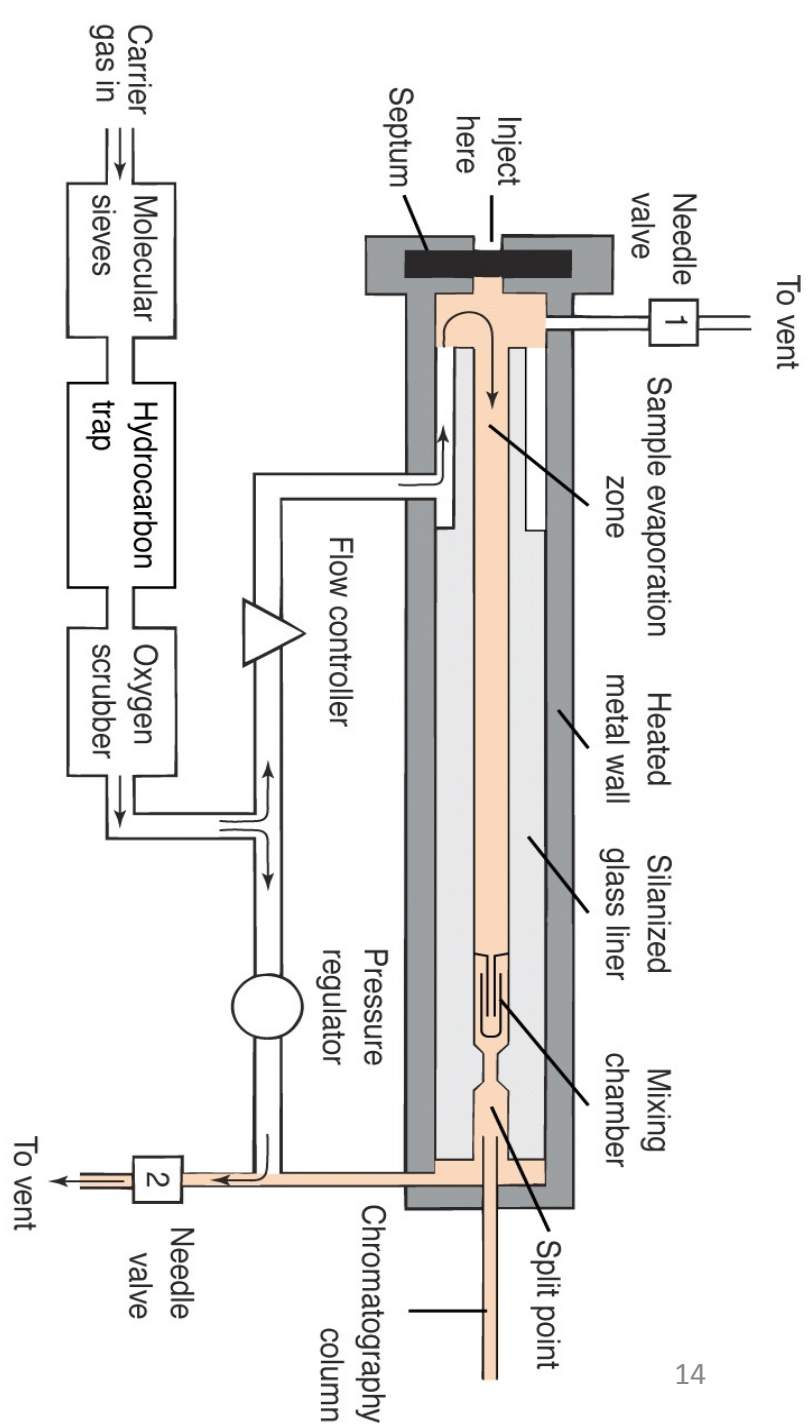


- Automation
- Up to 150 samples
- Instantaneous injection
- Same amount of sample injected every time

Injection Port







Packed Column Injector

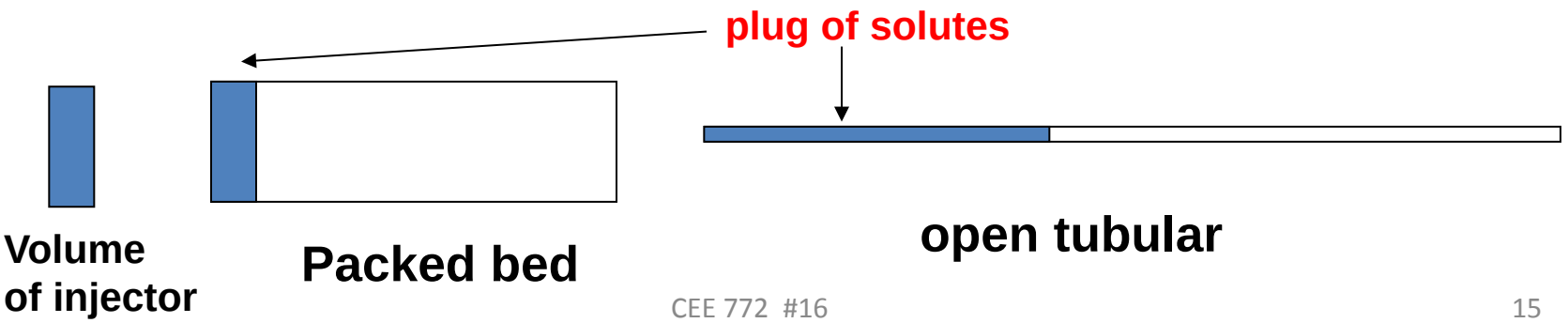
Split vs. Splitless Injection

- Splitless injection

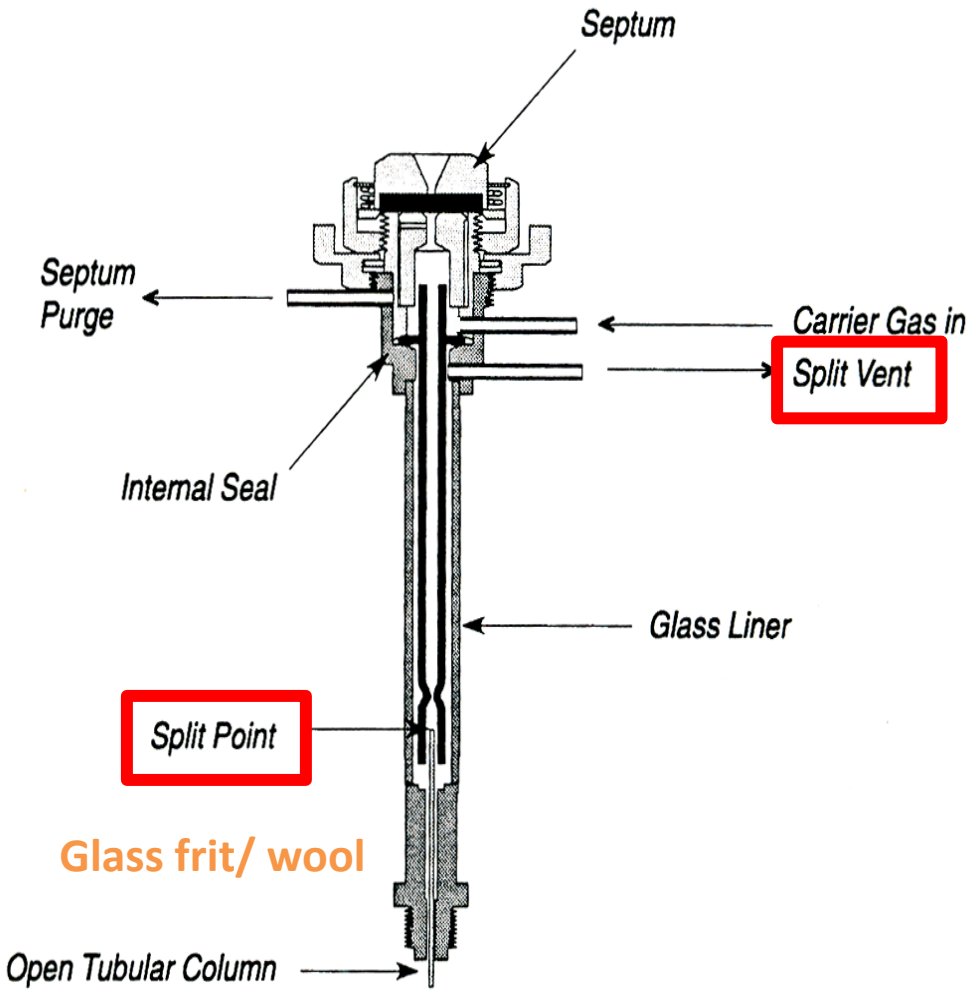
  For example, a liquid sample is injected into the port, it is quickly volatilized at the end of the microsyringe and at the head of the column; the solutes are then taken by the carrier gas into the column

- Split injection

  Open tubular/capillary columns usually have a much smaller cross-section area than that of packed columns. This makes them more subject to extra-column band-broadening, requiring that special low volume injection techniques be used with them.



Sample Splitter



- The sample is first placed into the injection port and is vaporized
- As the sample leaves the inject port, only a small portion of the vaporized samples is applied to the column (usually 1/50 to 1/500), with the remainder going to waste (by opening the purge valve/split vent).

* Cold On-Column Injector

- Cold on-column injectors involves **direct injection** of a sample **onto a column** at **low temperature.**

- No heated injection port is used. The low initial column temperature increases the retention of all solutes and concentrates them at the top of the column in a narrow plug. The column temperature is then increased, allowing the solutes to volatilize and be separated.

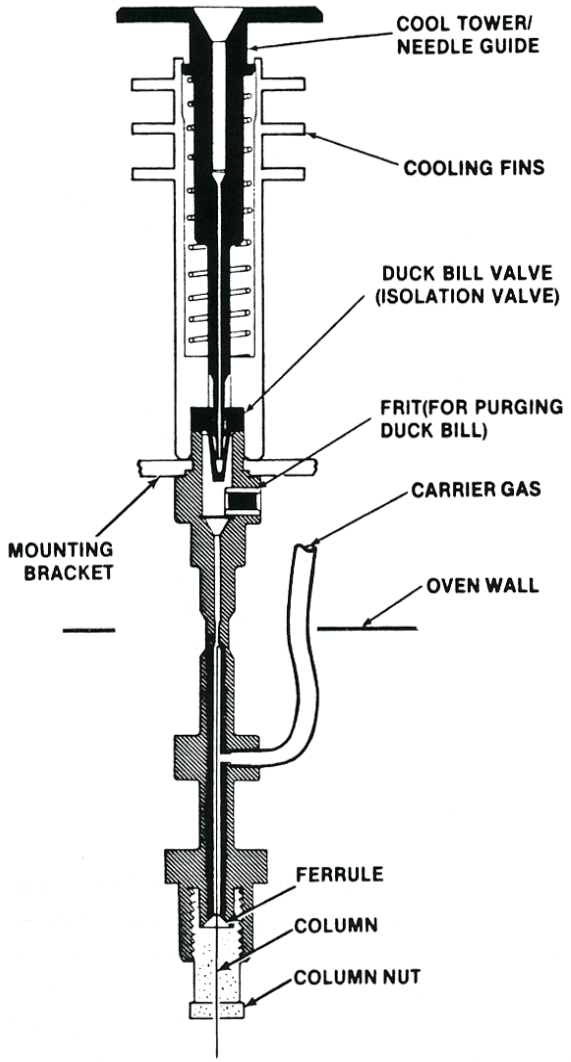


Figure 3.8. Cold-on column injector with a duckbill valve sealing mechanism (©Hewlett-Packard Co.).

*Programmed temperature vaporizer (PTV)

- **A programmed temperature vaporize involves placing sample into a cold injection port, where it is then heated and applied to column at any desired temperature.**

- **A *"universal" injector* for open-tubular columns since it temperature program may be changed so that it can be used either in cold injectors, splitless injectors, or split injectors.**

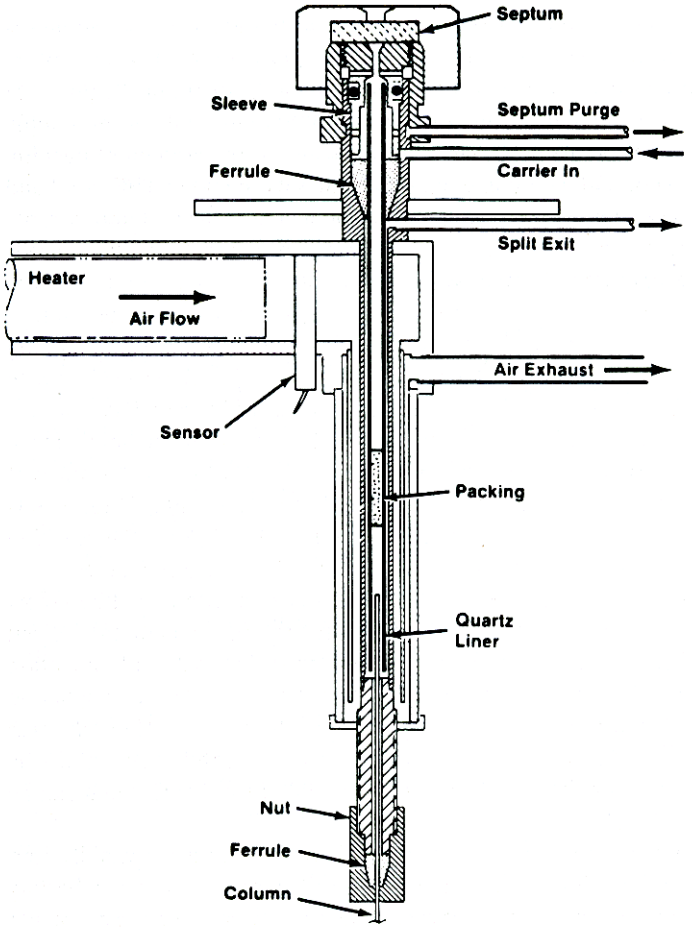


Figure 3.6. Schematic diagram of a PTV type injector. (From ref. [66]; ©Wiley-VCH).

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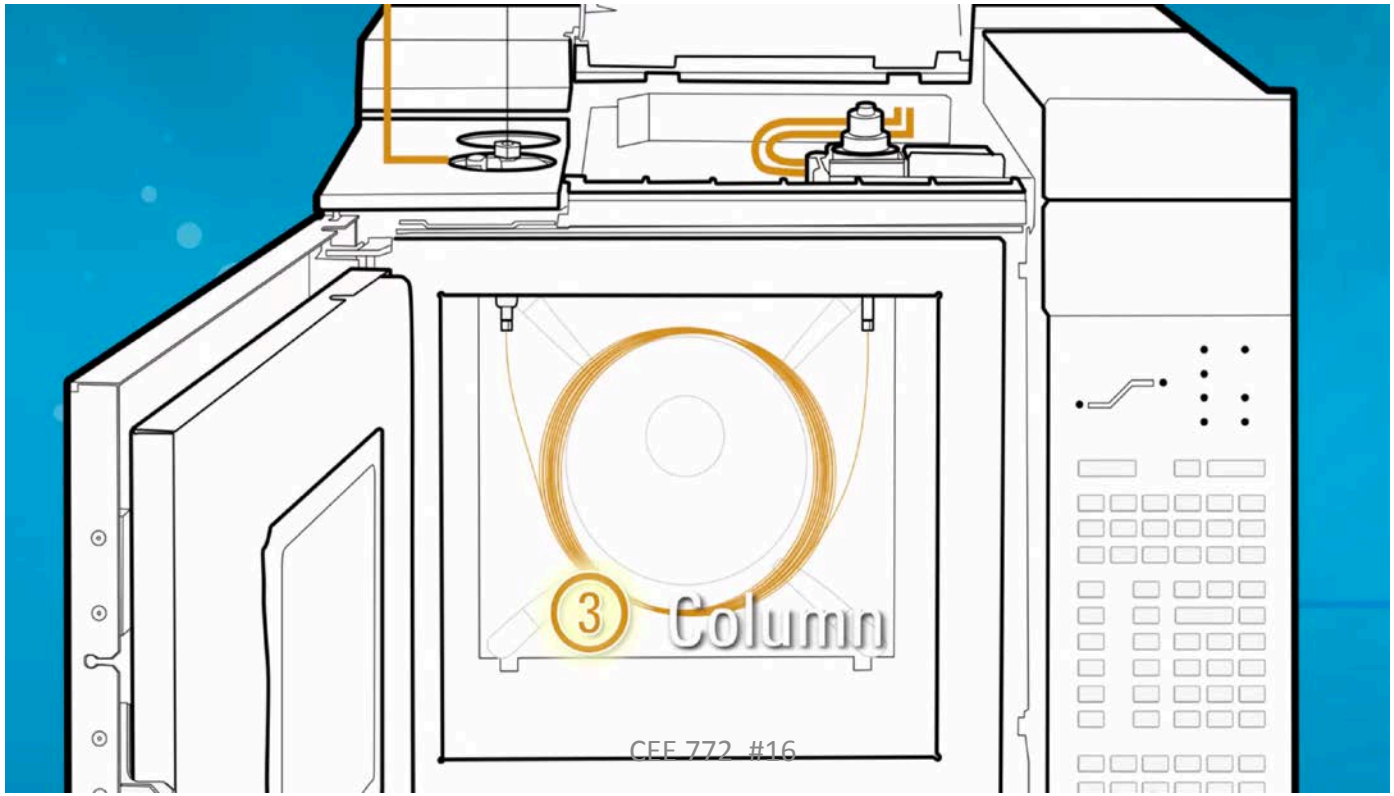
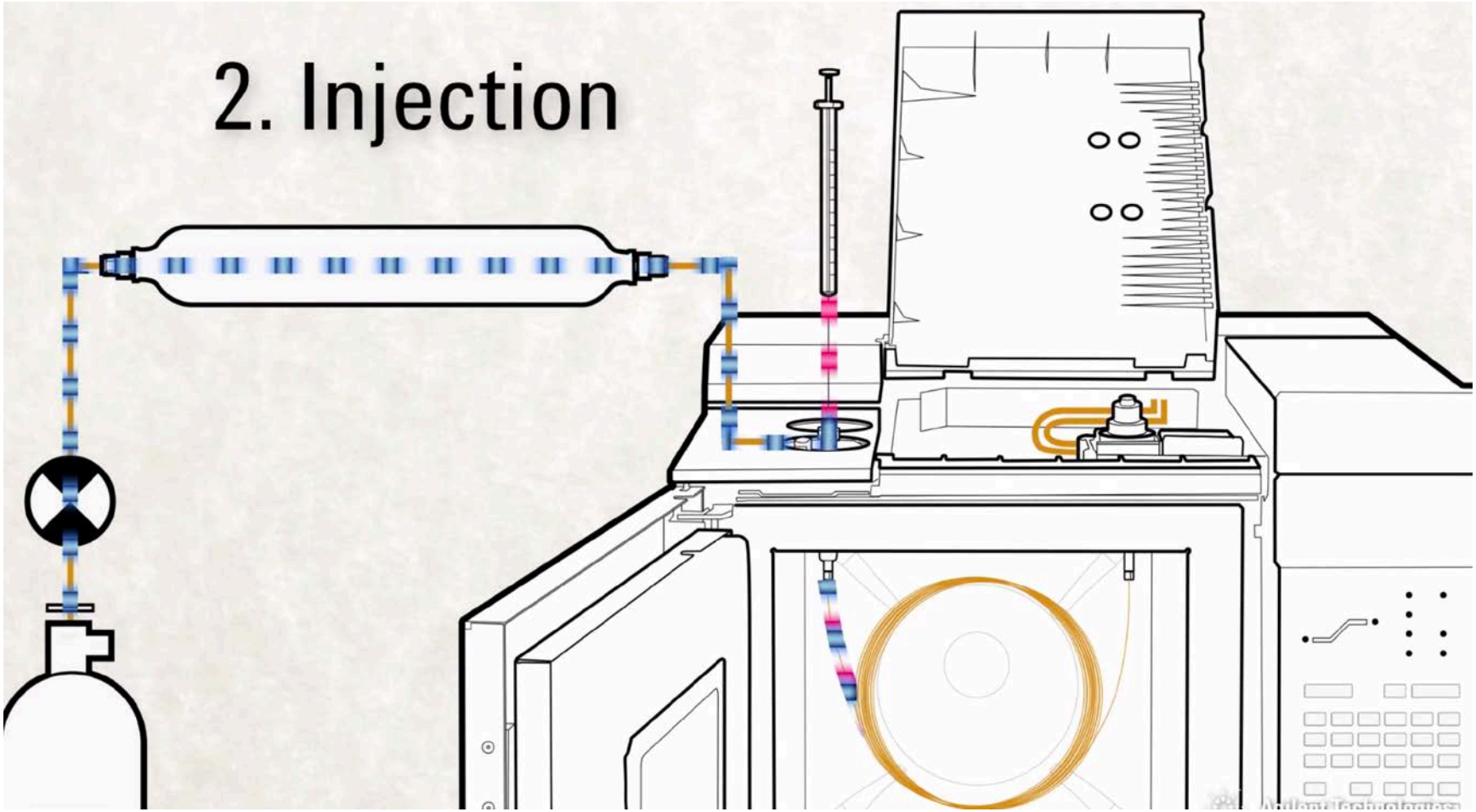
III. GC Column (heart of a GC system)

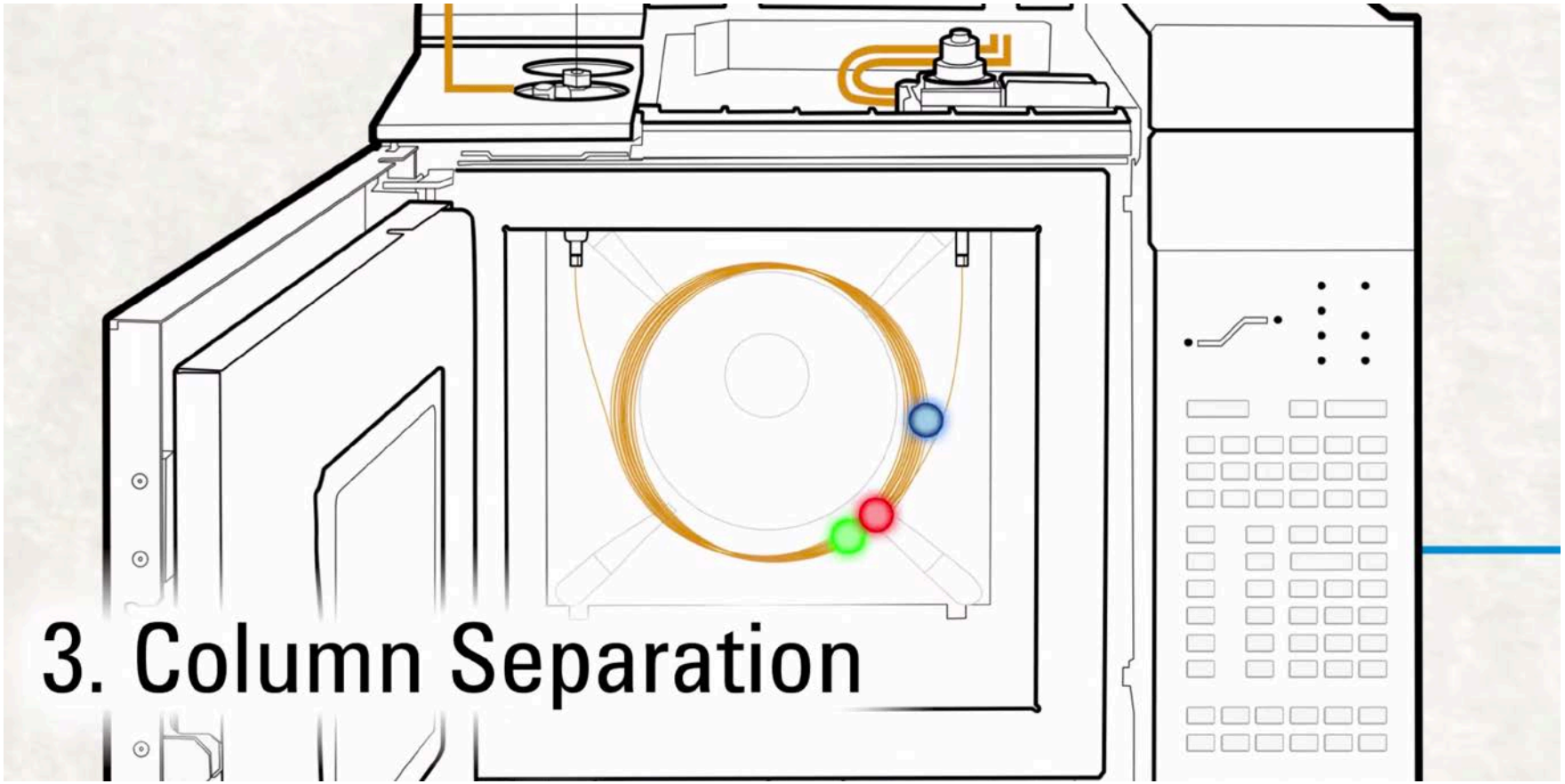
- Column configurations: packed vs. open tubular/capillary columns
- Stationary phase
- Film thickness and column efficiency



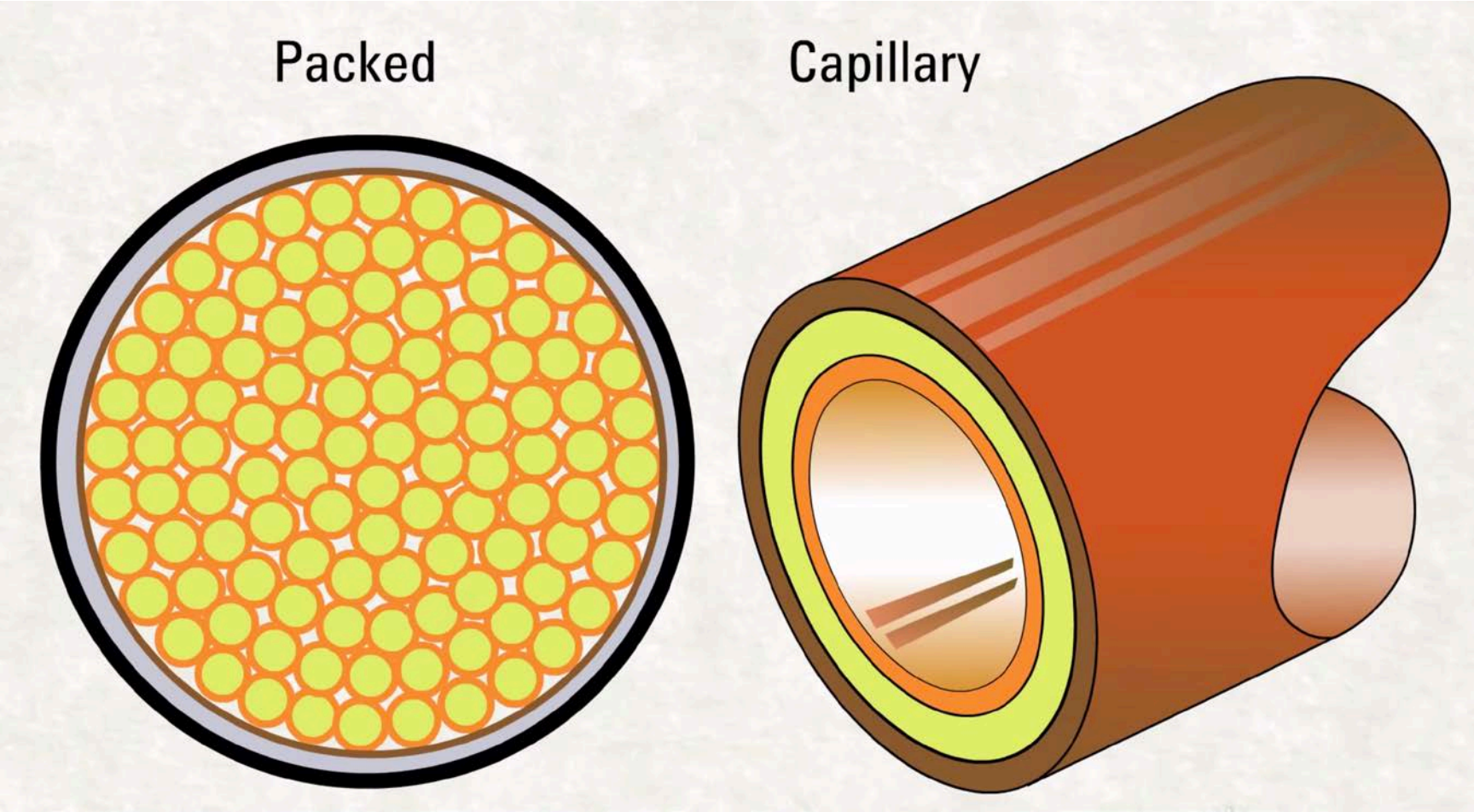
The Heart of GC



The Heart of GC



1. Types of GC columns (GLC)



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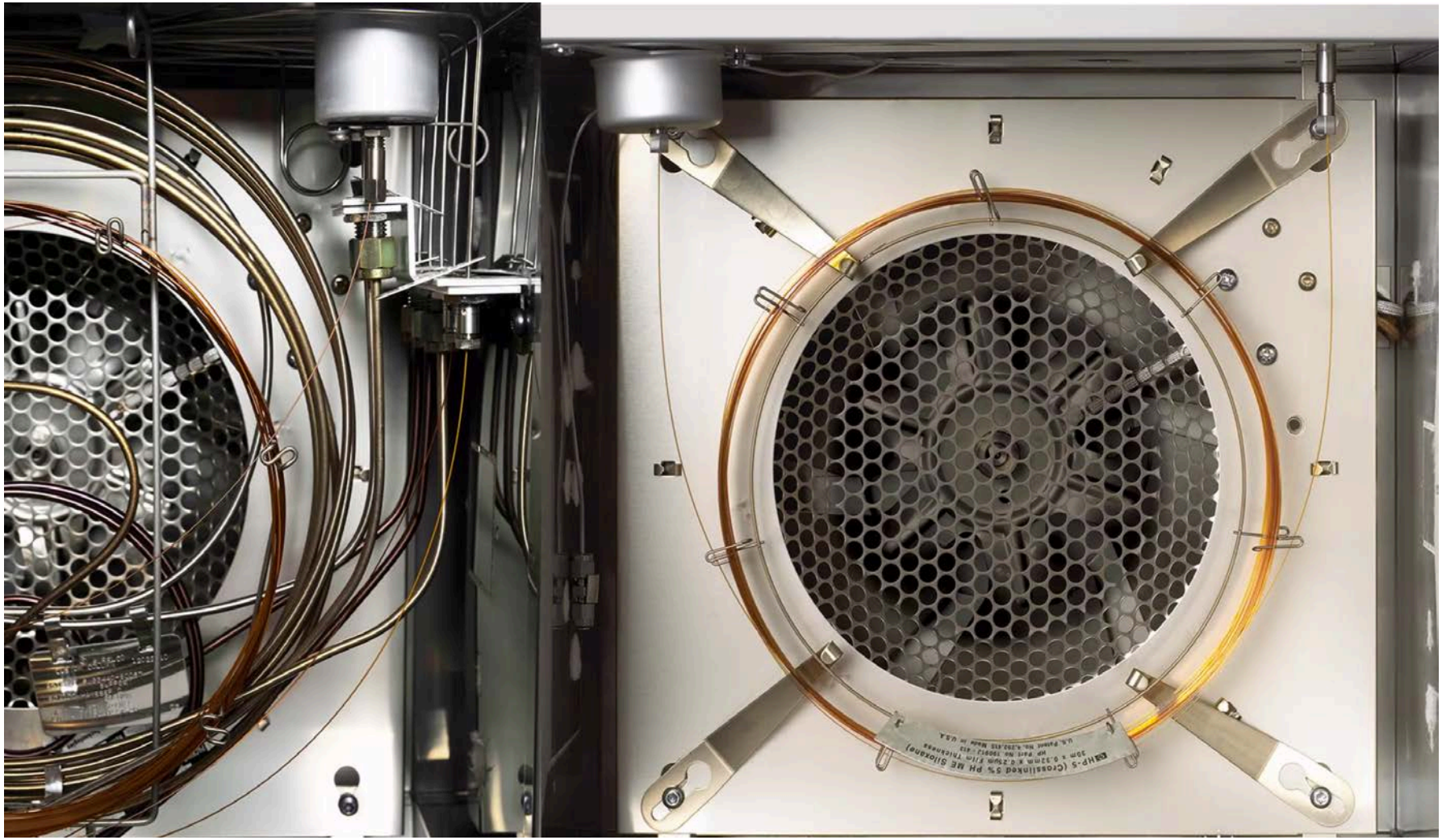
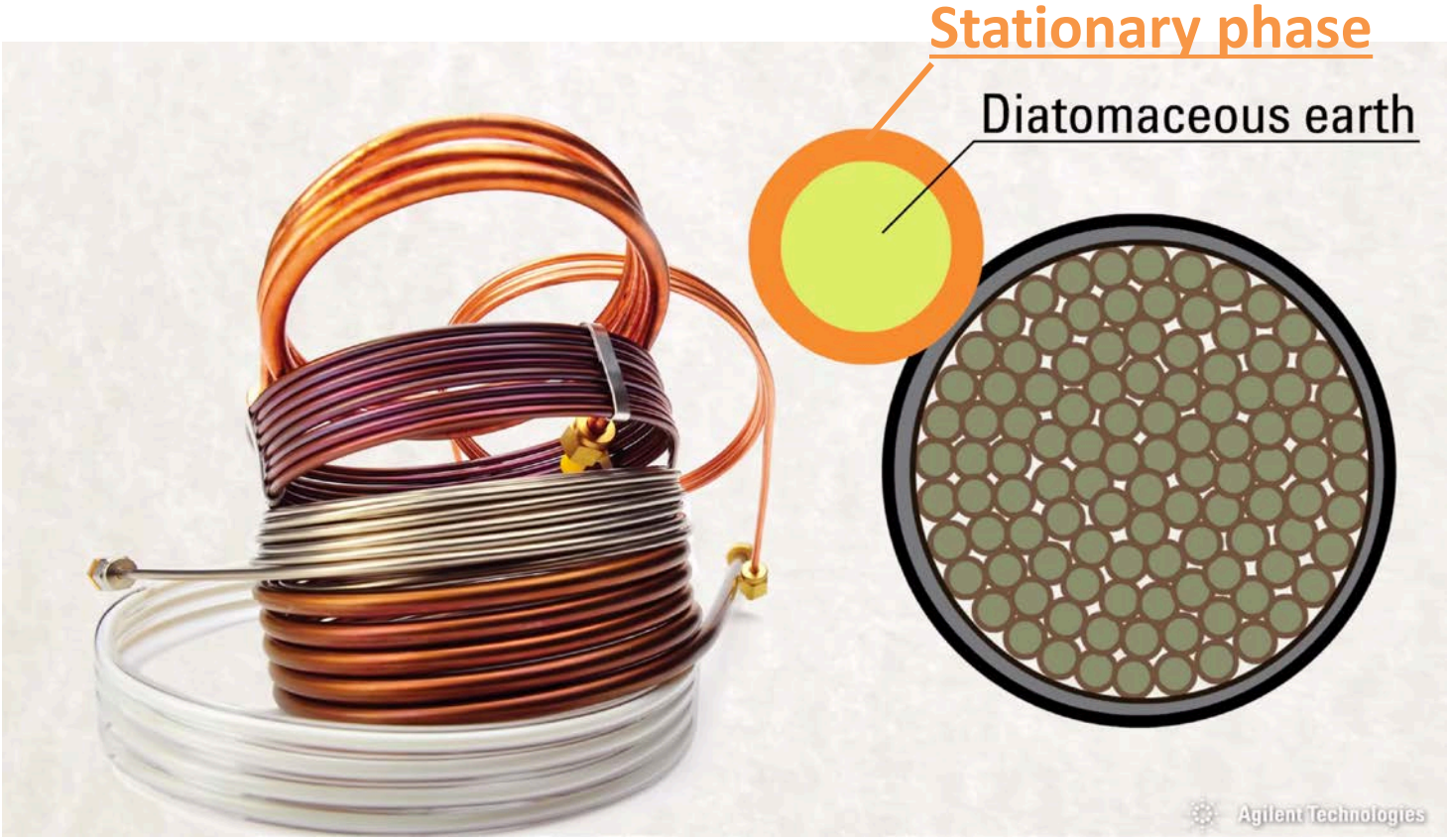


Packed GC Columns



- Less ubiquitous application: fixed gas analysis
- Lower column efficiency than that of capillary columns (smaller in length)
- Larger sample capacity

Particle Size of Supports

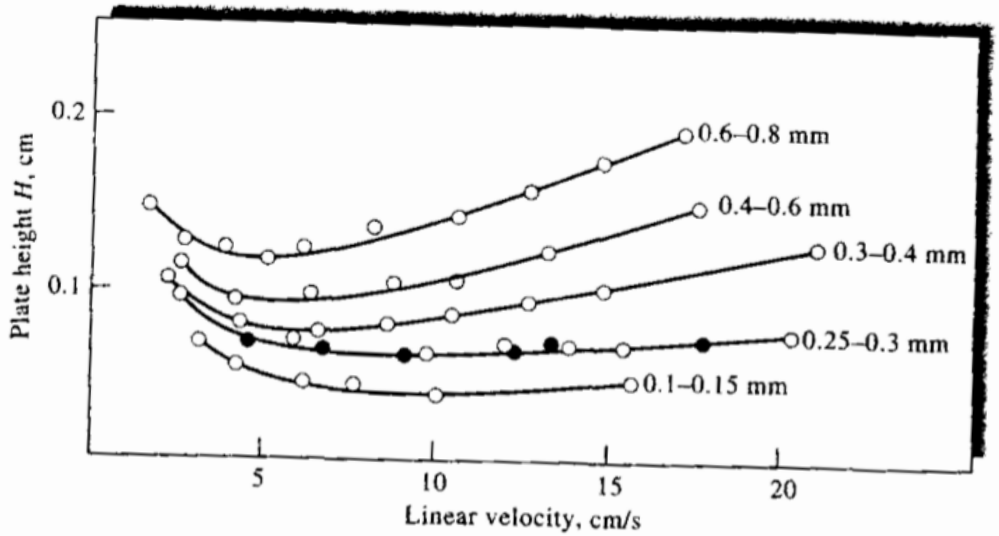
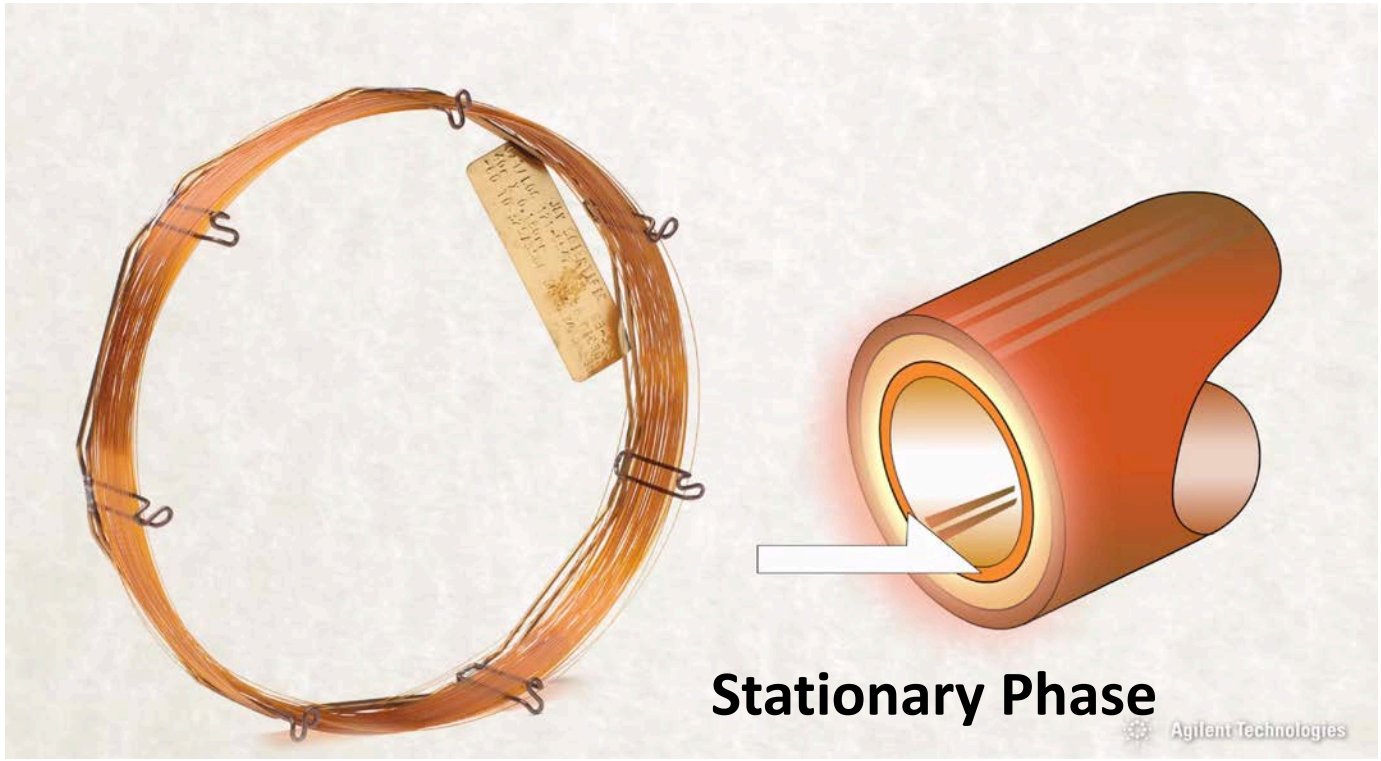


FIGURE 26-11 Effect of particle size on plate height for a packed GC column. The numbers to the right of each curve are particle diameters. (From J. Boheman and J. H. Purnell, in *Gas Chromatography 1958*, D. H. Desty, ed., New York: Academic Press, 1958. With permission.)

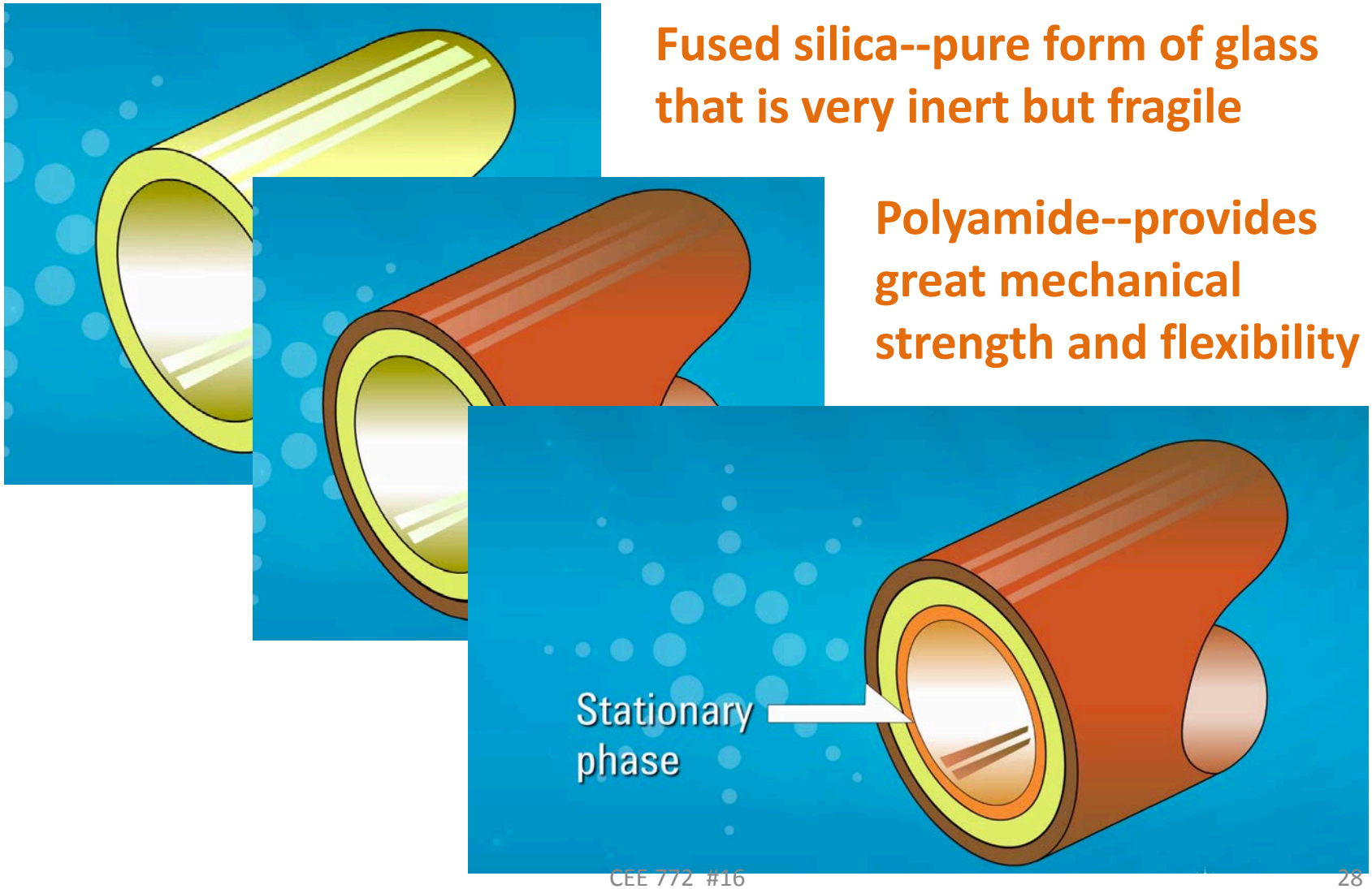
The efficiency of a gas chromatographic column increases rapidly with decreasing particle diameter of the packing. The pressure difference (head loss) required to maintain an acceptable flow rate of carrier gas, however, varies inversely as the square of the particle diameter; the latter relationship has placed lower limits on the size of particles used in GC because it is not convenient to use pressure differences that are greater than 50 psi.

Open Tubular/Capillary GC Columns



- Most widely used
- High column efficiency (large number of theoretical plates due to long column length, up to 100 m)
- Small sample capacity (split sample inside inlet)

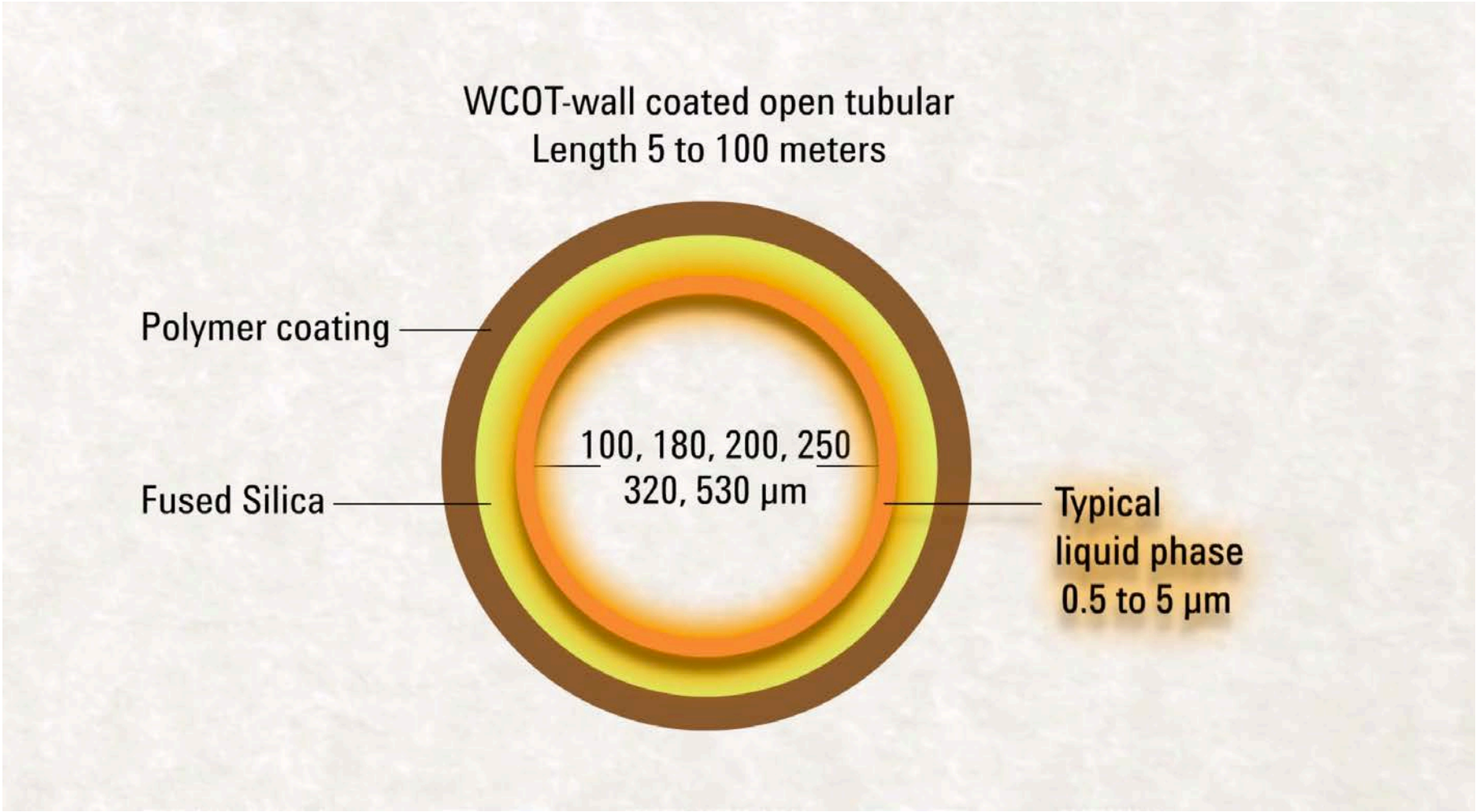
Open Tubular/Capillary GC Columns



Fused silica--pure form of glass that is very inert but fragile

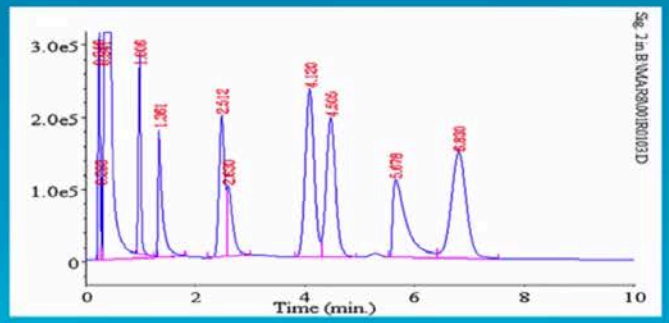
Polyamide--provides great mechanical strength and flexibility

Open Tubular/Capillary Columns

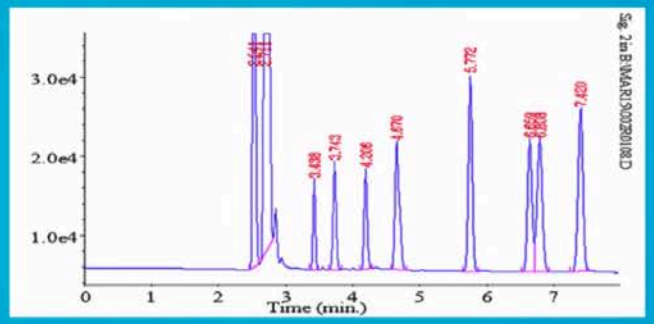


Packed vs. Capillary

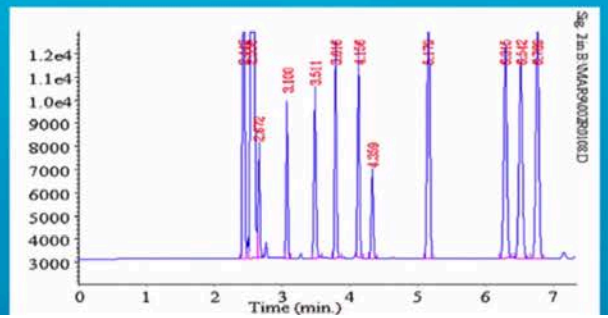
Packed Column Analysis:
5% OV101
on 80/100 Chromosorb



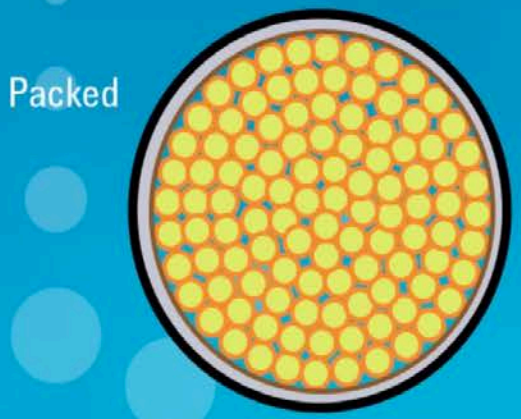
Capillary Column Analysis:
30 m × 0.53 mm × 0.88 µm



Capillary Column Analysis:
30 m × 0.32 mm × 0.25 µm



Packed vs. Capillary



		Capillary		
	Packed	**Megabore**	**WCOT (wide)**	**WCOT (narrow)**
Length (meters)	0.5–10	5–100	5–100	5–100
I.D. (mm)	2–4	0.530	0.25–0.32	0.05–0.2
Flow Rate (ml/min.)	10–60	4–30	1–15	0.3–8.0
Operating Pressure	10–90 PSI	5–15 PSI	5–40 PSI	10–90 PSI
Sample Capacity	100 ng/peak	10 ng/peak	1 ng/peak	<1 ng/peak

2. Stationary Phase

Important Attributes

1. Low volatility (boiling point at least 100 °C higher than max. column operating temperature)
2. Thermo stability (wide temperature operating range)
3. Chemical inertness (non-reactive to both solutes and carrier gas)
4. Solvent characteristics (differential solvent for different components)

Phase	Applications	Polarity	Temperature range °C
DB1–Methyl Silicone	Hydrocarbons, amines, pesticides, PCB's	Non-Polar	-60–325
DB5–5% Phenyl Methyl Silicone	Hydrocarbons, alkaloids, drugs, FAME's	Slightly polar	-60–325
DB 1701	Aroclors, herbicides, pesticides–for confirmation	Intermediate	-20–280
DB Wax	Alcohols, glycols, aromatics	Polar	40–240

Qualitative Guidelines for Stationary Phase Selection

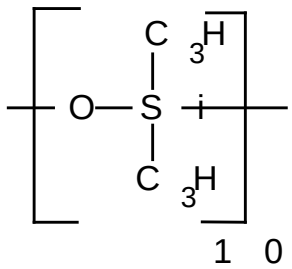
- **Sources:**

  Literature review, Internet search, prior experience, advice from a vendor of chromatographic equipment and supplies

- **General rule:** ***"like dissolves like"***
  - "Like" refers to the **POLARITIES** of the analyte and the immobilized liquid
  - The polarity of a molecule, as indicated by its dipole moment, is a measure of the electric field produced by separation of charge within the molecule
  - **Polar functional groups**: -CN, -CO, -OH, -COOH, $-NH_2$, -CHO, -X, etc.

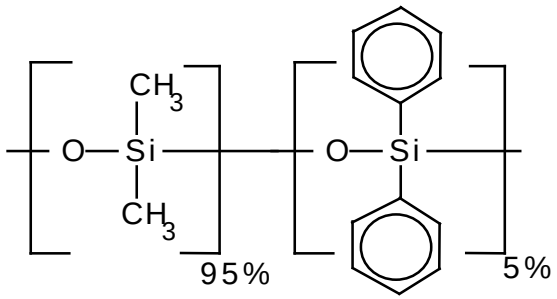
    Nonpolar function groups: saturated alkane –CH, etc.

Types and Polarities of Stationary Phase



"X"- 1

Polydimethyl siloxane backbone

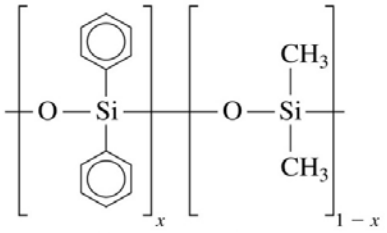
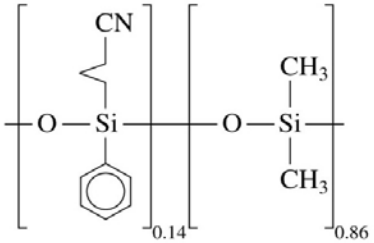
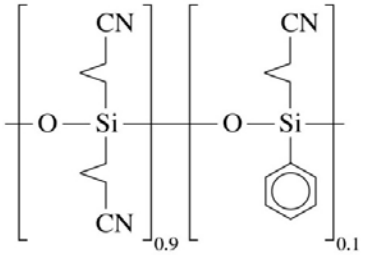


"X"- 5

Phenyl substitution of methyl groups

Polarity

Table 24-1 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°
$+CH_2CH_2-O+_n$ Carbowax (poly(ethylene glycol))	Strongly polar	40°−250°
 (Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar	0°–275°

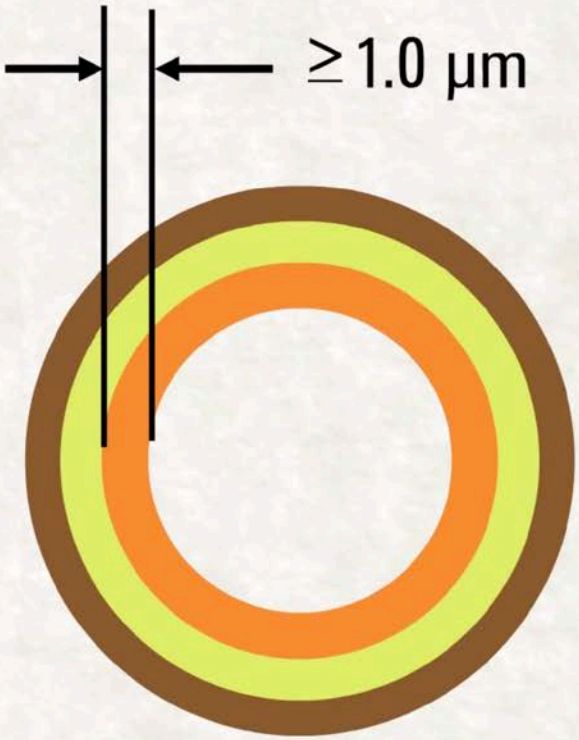
Types and Polarities of Stationary Phase

Table 2.4
Characteristic properties of some poly(siloxane) liquid phases used for packed column gas chromatography

Name	Structure	Viscosity (cP)	Average molecular weight	Temperature operating range (°C) Minimum	Maximum
OV-1	Dimethylsiloxane	gum	$> 10^6$	100	350
OV-101	Dimethylsiloxane	1500	30,000	<20	350
OV-7	Phenylmethyldimethylsiloxane 80 % methyl and 20 % phenyl	500	10,000	<20	350
OV-17	Phenylmethylsiloxane 50 % methyl and 50 % phenyl	1300	40,000	<20	350
OV-25	Phenylmethyldiphenylsiloxane 25 % methyl and 75 % phenyl	>100,000	10,000	<20	300
OV-210	Trifluoropropylmethylsiloxane 50 % methyl and 50 % 3,3,3-trifluoropropyl	10,000	200,000	<20	275
OV-225	Cyanopropylmethylphenylmethylsiloxane 50 % methyl, 25 % phenyl and 25 % 3-cyanopropyl	9000	8,000	<20	250
Silar 7CP	Cyanopropylphenylsiloxane 75 % 3-cyanopropyl and 25 % phenyl			50	250
OV-275	Di(cyanoalkyl)siloxane 70 % 3-cyanopropyl and 30 % 2-cyanoethyl	20,000	5,000		250
Silar 10CP	Di(3-Cyanopropyl)siloxane			50	250

3. Effect of Film Thickness on Column Efficiency

Stationary phase–thick films



Advantages:

Increased retention for volatiles

Increased capacity for GC/MS, GC/IR

Disadvantages:

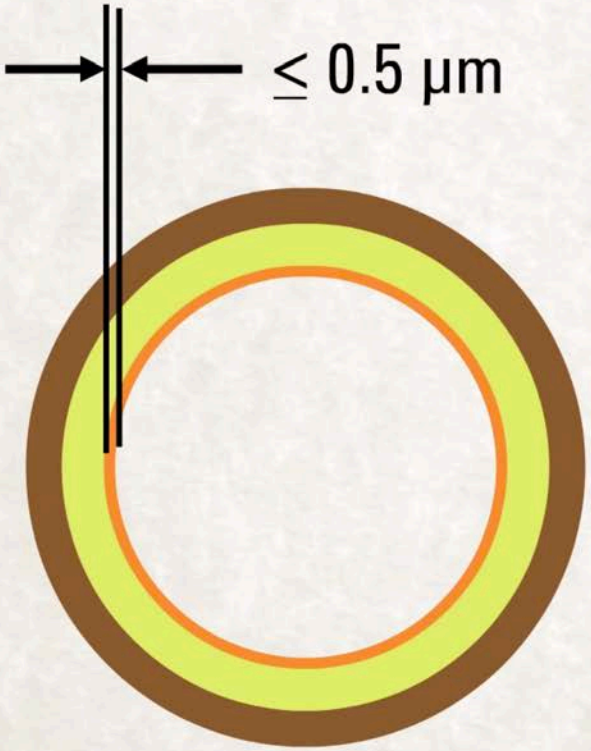
Less efficient

Higher temperatures required–Leads to noise

Higher bleed

3. Effect of Film Thickness on Column Efficiency

Stationary phase–thin films

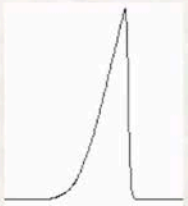


Advantages:

- Highest efficiency
- Lower elution temperature (less bleed)
- Fast analysis

Disadvantages:

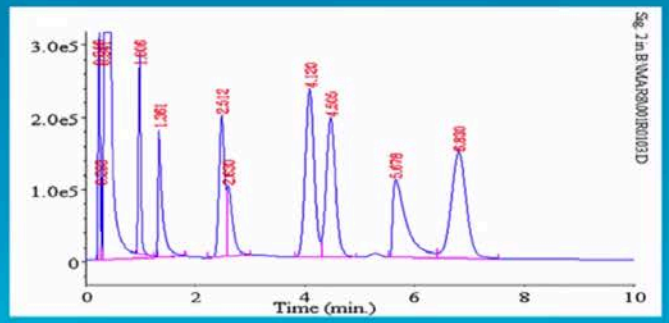
- Low capacity
- Limited trace analysis



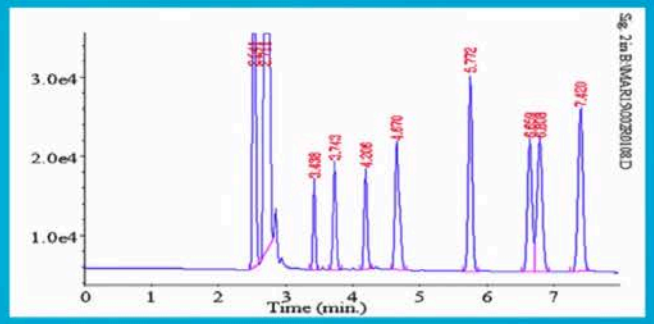
Peak Fronting

Packed vs. Capillary

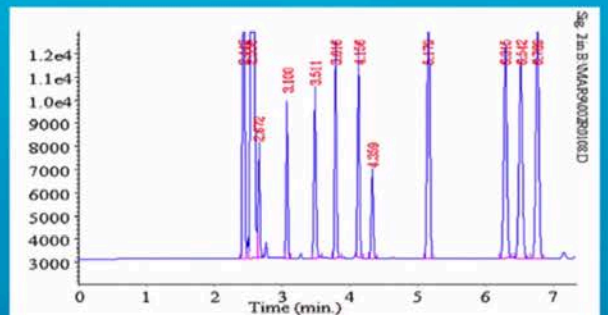
Packed Column Analysis:
5% OV101
on 80/100 Chromosorb



Capillary Column Analysis:
30 m × 0.53 mm × 0.88 µm



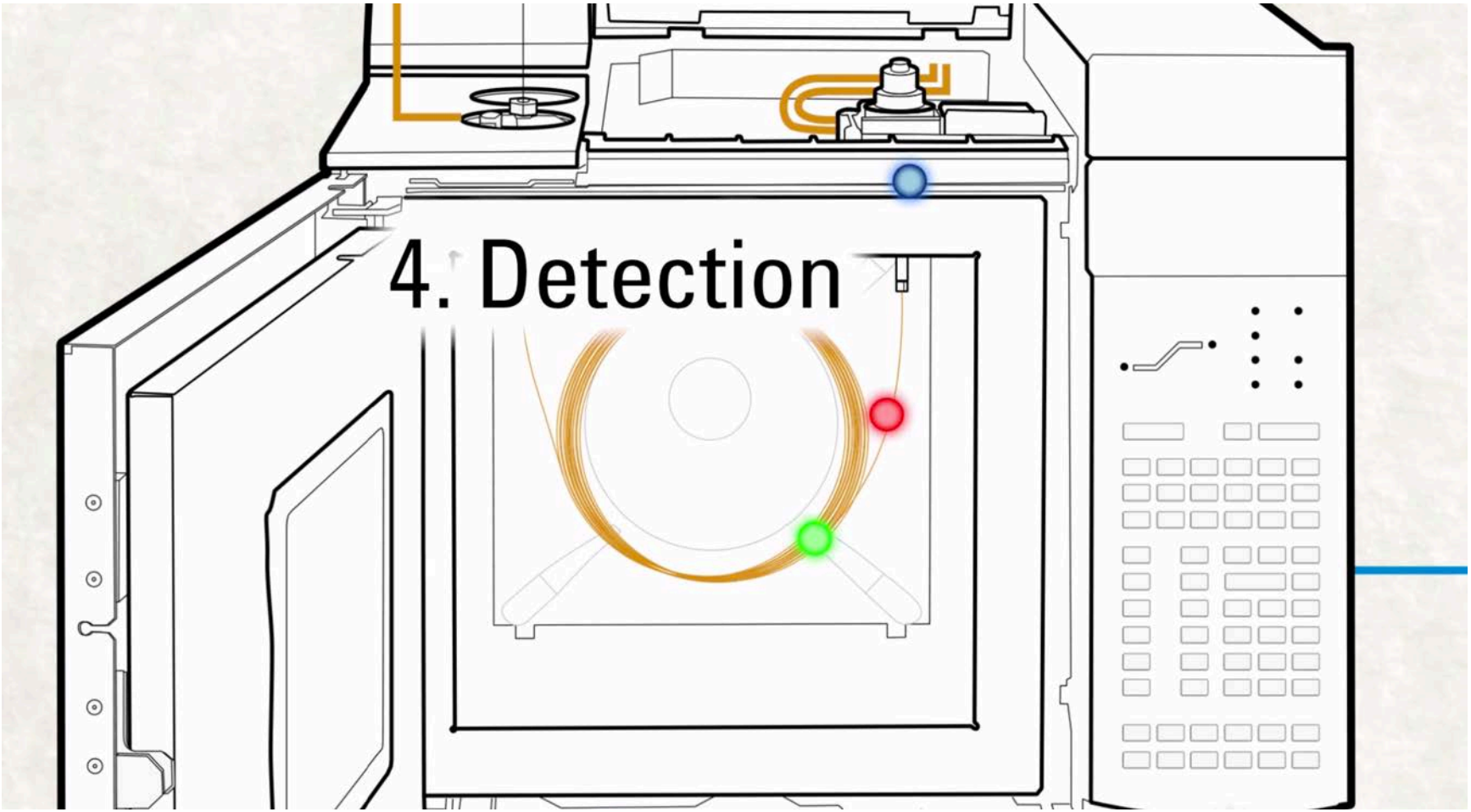
Capillary Column Analysis:
30 m × 0.32 mm × 0.25 µm



Contents

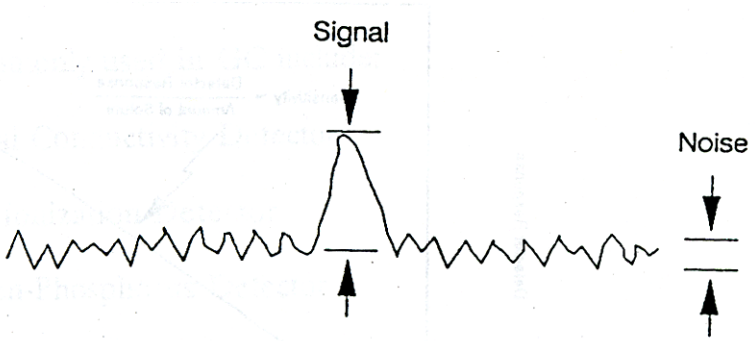
- The primary components to a GC system
  1. **Carrier Gas System (including Gas Clean Filters)**
     - The concept of theoretical plates and *van Deemter* curves
     - Selection of proper carrier gas
  2. **Sample Introduction System**
     - Split & splitless injection
  3. **Column (most critical component)**
     - Column configurations: packed vs. open tubular/capillary
     - Stationary phase
  4. **Detection System/GC Detectors**
     - Types of detectors and their specific applications
  5. **Computer ChemStation/Integrator**

IV. GC Detection Systems/Detectors



Characteristics of the Ideal Detector

1. Adequate sensitivity (application specific, i.e. adequate for certain tasks)



S/N >3

1. Good stability and reproducibility
2. A linear response to solutes that extends over several orders of magnitude (calibration purposes)
3. A wide temperature range
4. A short response time independent of flow rate
5. High reliability and ease of use (unfortunately, usually not the case ☹)
6. Similarity in response toward all solutes/most classes of solutes
7. The detector should be nondestructive

Typical GC Detectors

Table 15.5 Properties of Selected Gas Chromatography Detectors

Type	Approximate limit of detection ($g\ s^{-1}$)	Approximate linear range	Comments
Thermal conductivity (TCD)	10^{-5}–10^{-6}	10^{3}–10^{4}	Universal detector Measures changes in heat conduction
Flame ionization (FID)	10^{-12}	10^{6}–10^{7}	Universal detector Measures ion currents from pyrolysis
Electron capture (EC or ECD)	10^{-14}	10^{2}–10^{3}	Selective detector for compounds containing atoms with high electron affinities
Flame photometric (FPD)	10^{-13}	10^{2}	Selective detector for compounds containing S, P
Nitrogen-phosphorus	10^{-8}–10^{-14}	10^{5}–10^{7}	Selective for N, P containing compounds
Photoionization (PID)	10^{-8}–10^{-12}	10^{5}	Universal (some selectivity due to to identity of gas in lamp)
Hall Detector	10^{-11}	10^{5}	Specific detector for compounds which contain halogen, S, or N
Mass spectrometer (MS)	10^{-12}	*a*	Universal detector
Fourier-transform infrared (FTIR)	10^{-10}	10^{2}	Polar molecules

a. Varies, depending on the type of mass spectrometer as well as the kinds of compounds being analyzed.

Universal detectors

1. Flame Ionization Detector (FID)

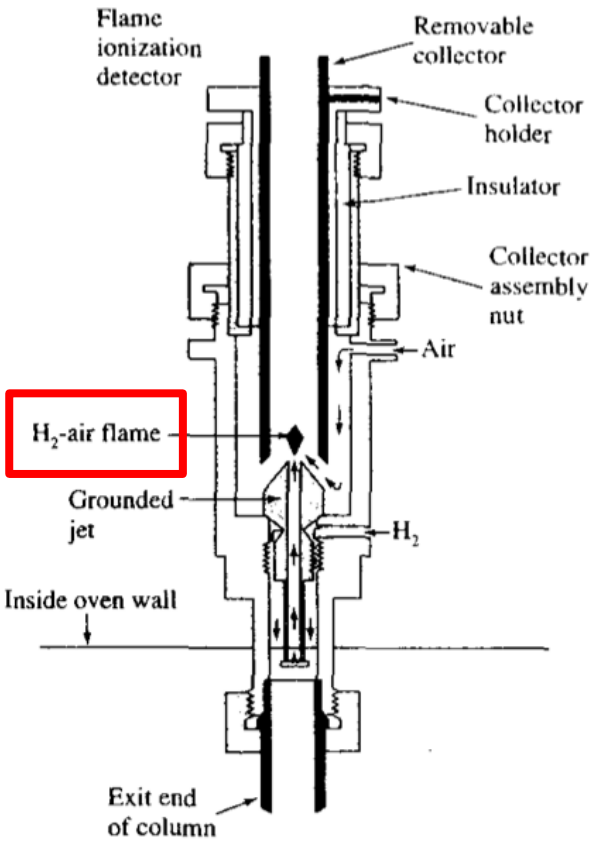


FIGURE 27-8 A typical flame ionization detector. (Courtesy of Agilent Technologies.)

- Most common detector for GC
- In an FID, effluent from the column is directed into a small air-hydrogen flame. Most carbon atoms (except C=O) produce radicals (CHO^+) in the flame:

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

- Electrons are used to neutralize the CHO^+ atoms and the ions are collected at an electrode to create a current to be measured. This current is proportional to the number of molecules present.
- The ionization of carbon compounds in the FID is not fully understood, although the number of ions produced is roughly proportional to the number of reduced carbon atoms in the flame.

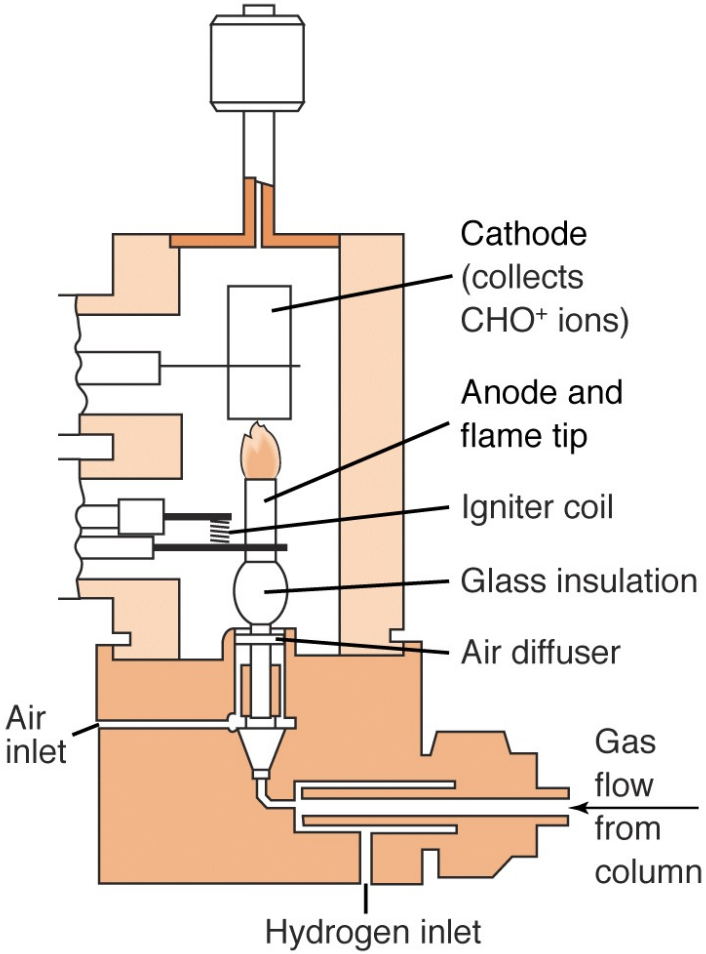
Pros and Cons of FID

- **Advantages:**

  1. universal detector for organics
  2. does not respond to common inorganic compounds
  3. mobile phase impurities not detected
  4. carrier gases not detected
  5. limit of detection: FID is 1000x better than TCD
  6. linear and dynamic range better than TCD

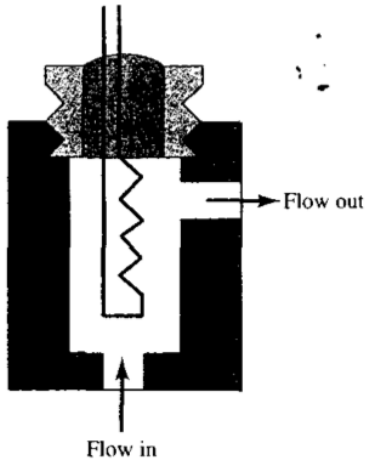
- **Disadvantage:**

  destructive detector



2. Thermal Conductivity Detector (TCD)

Temp.-sensitive element



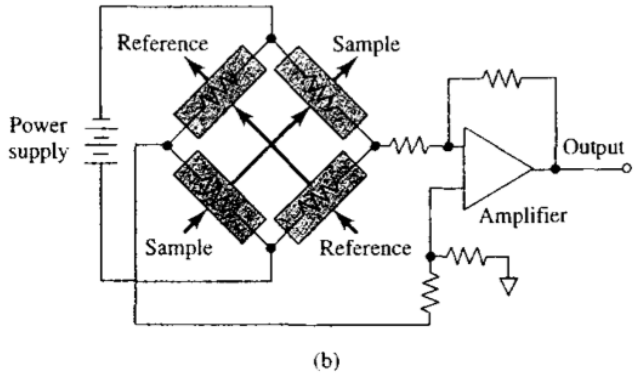
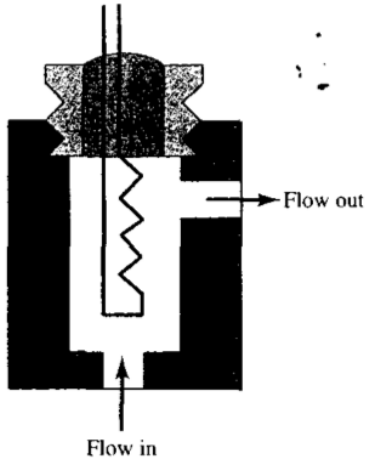


FIGURE 27-9 Schematic of (a) a TCD cell, and (b) an arrangement of two sample detector cells and two reference detector cells. (From J. Hinshaw, *LC-GC*, **1990**, *8*, 298. With permission.)

- One of the earliest detectors of GC
- The device contains an electrically heated source whose temperature at constant electrical power depends on the thermal conductivity of the surrounding gas.
- Twin detectors are usually used, one being located ahead of the sample-injection chamber and the other immediately beyond the column. The bridge (Wheatstone bridge) circuit is arranged so that the thermal conductivity of the carrier gas is canceled.

2. Thermal Conductivity Detector (TCD)



Twin detectors

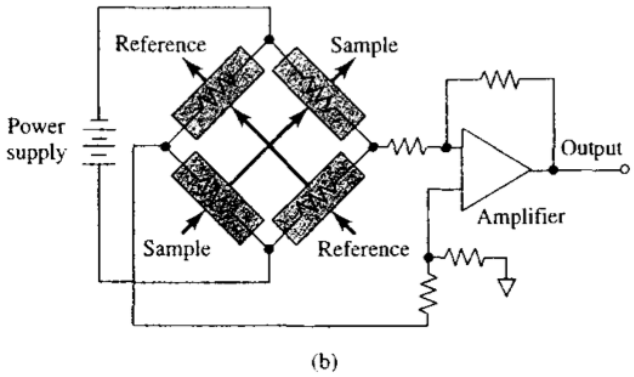


FIGURE 27-9 Schematic of (a) a TCD cell, and (b) an arrangement of two sample detector cells and two reference detector cells. (From J. Hinshaw, *LC-GC*, **1990**, *8*, 298. With permission.)

- The thermal conductivities of helium and hydrogen (commonly used carrier gases for TCD) are roughly 6~10 times greater than those of most organic compounds. Thus, even small amounts of organic species cause relatively large ***decreases in the thermal conductivity*** of the column effluent, which results in a marked ***rise in the temperature*** of the detector.
- **Advantages:**
  Simplicity, large linear dynamic range, nondestructive
- **Disadvantages:**
  Low sensitivity (precludes their use with WCOT columns with small amounts of sample)

3. Electron Capture Detector (ECD)

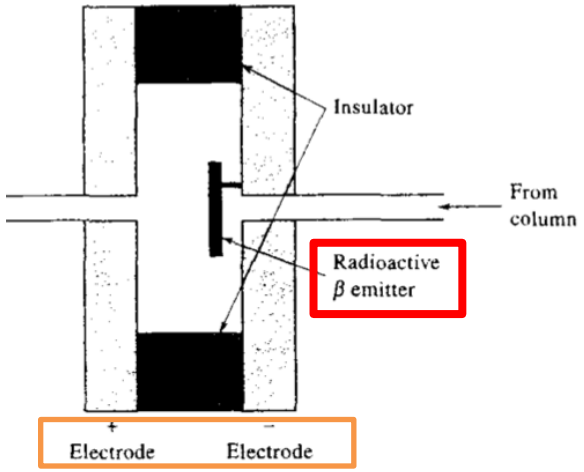


FIGURE 27-10 Schematic diagram o

- **Radioactive decay-based** detector
- Selective for compounds containing **electronegative atoms**, such as halogens, peroxides, quinones, and nitro groups
- The sample effluent from a column is passed over a ***radioactive β emitter***, usually ^{63}Ni. An electron from the emitter causes **ionization of the carrier gas** (often N_2) and the production of a burst of electrons.
- In the absence of organic species, a **constant standing current** between a pair of electrode results from this ionization process. The **current decreases significantly in the presence of organic molecules** containing electron negative functional groups that tend to capture electrons.

3. Electron Capture Detector (ECD)

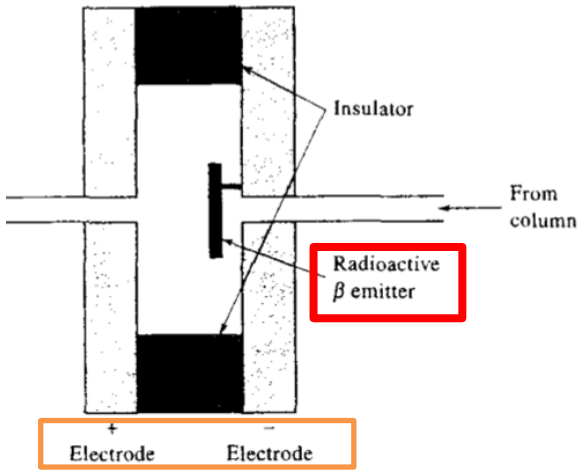


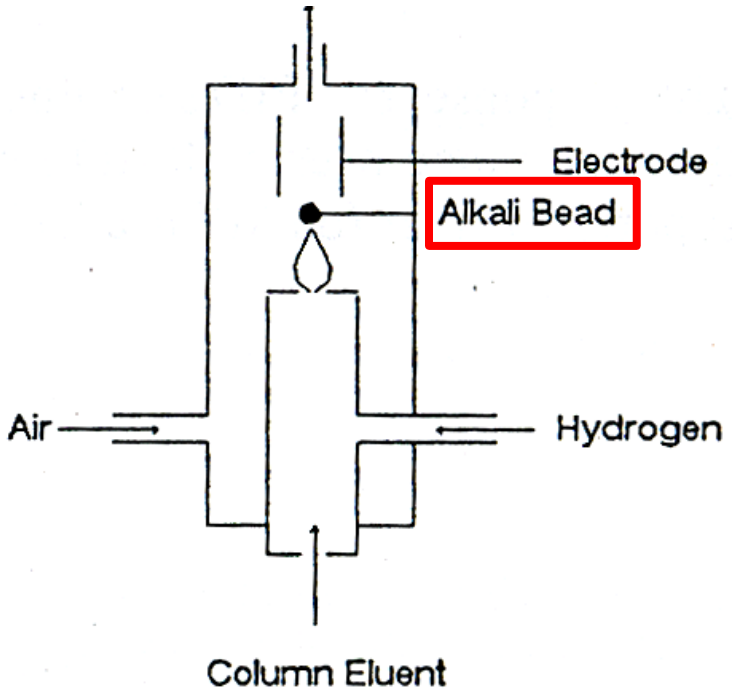
FIGURE 27-10 Schematic diagram o

- **Ionization of carrier gases:**

  $N_2 + \beta^- \rightarrow N_2^+ + e^-$ $\qquad$ $Ar_2 + \beta^- \rightarrow Ar_2^+ + e^-$

- **Advantages:**
  - useful for environmental testing
    detection of chlorinated pesticides or herbicides; polynuclear aromatic carcinogens, organometallic compounds
  - selective for halogen- (I, Br, Cl, F), nitro-, and sulfur-containing compounds
  - detects polynuclear aromatic compounds, anhydrides and conjugated carbonyl compounds
- **Disadvantages:**
  - could be affected by the flow rate

4. Thermionic Detector/Nitrogen-Phosphorous Detector (NPD)



- A NPD is based on the same basic principles as an FID.
- However, a small amount of alkali metal vapor in the flame, which greatly enhances the formation of ions from nitrogen and phosphorus-containing compounds.
- The NPD is about 500-fold more sensitive that an FID in detecting phosphorous-containing compounds, and 50-fold more sensitive to nitrogen-containing compounds
- Applications:
  Organophosphate in pesticides and in drug analysis for determination of amine-containing or basic drugs

5. Electrolytic Conductivity Detector

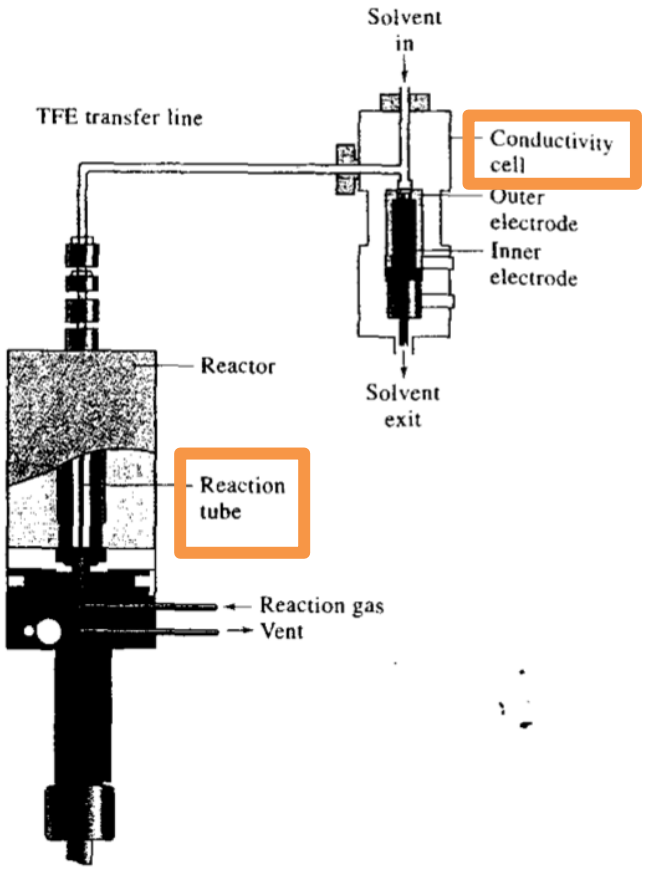


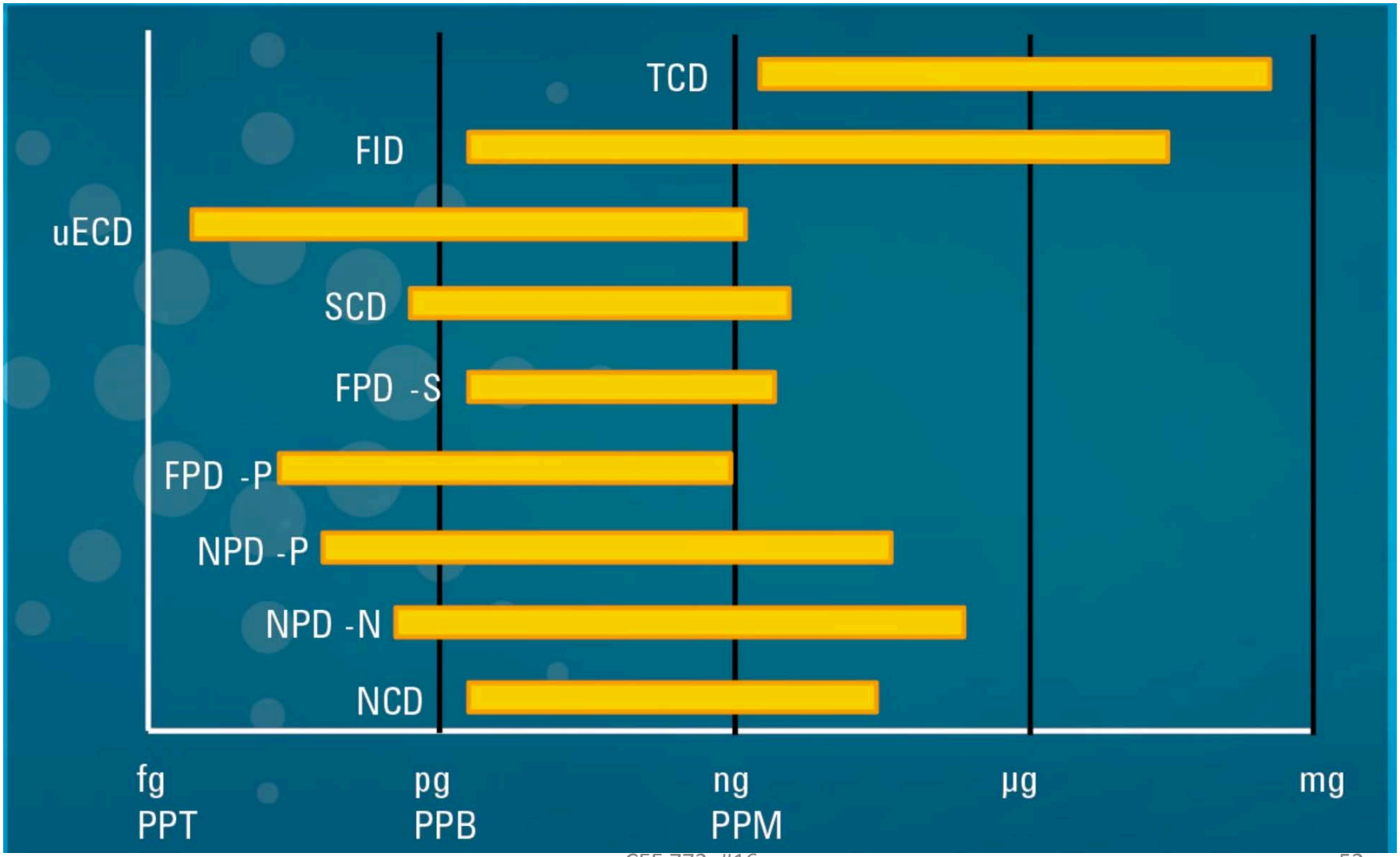
FIGURE 27-11 Diagram of a Hall electrolytic conductivity detector. (Courtesy of ThermoElectron Corp.)

- Element-selective detector for halogen-, sulfur- and nitrogen-containing compounds
- Compounds containing halogens, sulfur, or nitrogen are mixed with a reaction gas in a small reactor tube, usually made of Ni. The products from the reaction tube are then dissolved in a liquid, which produces a conductive solution. The change in conductivity as a result of the ionic species is then measured.

Other GC Detectors

- **Photoionization Detector**
  - aromatic hydrocarbons
  - organosulfur/organophosphorous
- **Atomic Emission Detector**
  - element-selective detector
- **Flame Photometric Detector**
  - sulfur and phosphorous containing compounds

Comparison of GC Detector Sensitivity and Dynamic Range



*Mass Spectrometry Detector (MS)

- One of the most powerful detectors for gas chromatography

- SAVE FOR LATER

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V. Quantitative Chromatographic Analysis

- **Quantitative Analysis**

  Based on a comparison of either the height or the area of the analyte peak with that of one or more standards

- **Peak height vs. Peak area**

  Peak heights are inversely related to peak width. Thus, accurate results are obtained with peak heights only if variations in column conditions do not alter the peak width during the period required to obtain chromatograms for samples and standards.

  Peak areas are independent of broadening effects, which are usually the preferred method of quantitation.

  * most modern chromatographic instruments are equipped with computers or digital electronic integrators that permit precise estimation of peak areas

Questions?

Rosa Yu

Email: victorosa1212@gmail.com

- To next lecture