Information given in these slides are, either in part or all, recollection from the followings:

http://bionmr.unl.edu/courses/chem421-821/lectures/chapter-2...

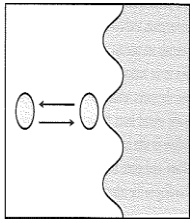
http://faculty.atu.edu/abhuiyan/Course/Chem 4414/Chapter 27.ppt

Principles of Instrumental Analysis, 6th Ed. Holler, Skoog & Crouch, 2007

Gas Chromatography

A) Introduction:

- ***Gas Chromatography (GC)*** is a chromatographic technique in which the ***mobile phase is a gas***.
- According to ***stationary phase,*** there two major types;



• Gas-solid chromatography: ***(GSC)***

stationary phase → solid,

retention mech. → physical ***adsorption***

rarely used ∴ severe tailing (non-linear nature of adsorption process)

• Gas-liquid chromatography: ***(GLC)***

stationary phase → immobilized liquid,

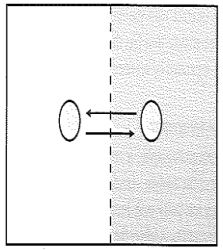
retention mech. → ***partition betw. MP and SP***

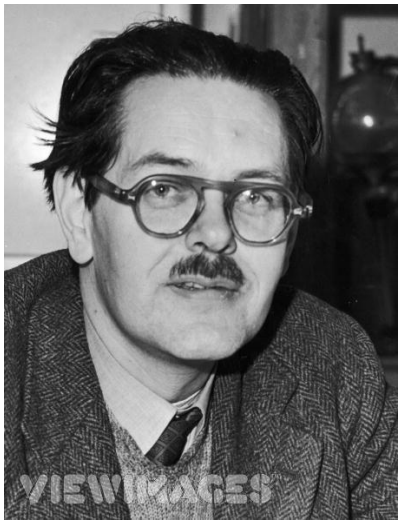
1941 by Martin & Synge

Nobel prize in 1952 for their work on partition chromatography

1955 first commercial GLC

GC is shortly used for GLC





➢GC is currently one of the most popular methods for separating and analyzing compounds.This is due to its;

- high resolution,
- low limits of detection,
- speed,
- accuracy and
- reproducibility.

➢ GC can be applied to the separation of any compound that is either;

- ***naturally volatile*** (i.e., readily goes into the gas phase) or
- can be converted to a ***volatile derivative***.

This makes GC useful in the separation of a number of small organic and inorganic compounds.

27A Principles of GLC

27A-1 Retention Volume

To take into account the effects of pressure and temperature in GC, it is often useful to use *retention volumes* rather than the *retention times*.

$V_R = t_R \times F$ retained

$V_M = t_M \times F$ non-retained

F: average volumetric flow rate (mL/min)

The flow rate within the column is not directly measurable. Instead, the rate of gas flow as it exits the column is determined experimentally with a flow meter, which is discussed in Section 27B. For popular soap-bubble type flow meters, which the gas is saturated with water, the average flow rate, *F is related to the measured flow rate* F_m *by*

$$F = F_m \times \frac{T_c}{T} \times \frac{(P - P_{H_2O})}{P}$$

T_c : column temperature (K),
T : temperature at the flow meter,
P : gas pressure at the end of the column. Usually P and T are the ambient pressure and temperature. The term involving the vapor pressure of water. P_{H_2O}, is a correction for the pressure used when the gas is saturated with water

➢ V_R and V_M depend on average pressure inside column. Column has resistance to flow

At inlet , P = high, F = low
At outlet, P = low, F = high

P ×F = constant

➢ Corrected retention volumes V_R^0 and V_M^0 *which correspond to volumes at* the average column pressure, are obtained from the relationships

$$V_R^0 = j \times t_R \times F \quad \text{and} \quad V_M^0 = j \times t_M \times F$$

➢ Pressure drop correction factor, j, used to calculate average pressure from inlet pressure P_{inlet} and outlet pressure P_{outlet}

$$j = \frac{3\,[\,P_i/P)^2 - 1\,]}{2\,[\,P_i/P)^3 - 1\,]}$$

27A-2 Relationship between V_g and K

➢ The Specific Retention Volume, V_g:

$$V_g = \frac{V_R^0 - V_M^0}{m_s} \times \frac{273}{T_c} = \frac{j\,F(t_R - t_M)}{m_s} \times \frac{273}{T_c}$$

m_s : mass of theSP

$$V_g = \frac{j\,F\,t_M\,k_A}{m_s} \times \frac{273}{T_c} = \frac{V_M^0\,k}{m_s} \times \frac{273}{T_c} = \frac{K\,V_s}{m_s} \times \frac{273}{T_c}$$

Distribution constant, k_A

$$k_A = \frac{t_R - t_M}{t_M}$$

$$V_M^0 = j \times t_M \times F$$

$$\rho_s = \frac{m_s}{V_s}$$

$$V_g = \frac{K}{\rho_s} \times \frac{273}{T_c}$$

Note that V_g at a given temperature; depends only on the distribution constant of the solute and the density of the liquid making up the stationary phase.

27 A-3 Effect of Mobile-Phase Flow Rate

Equation 26·23 The van Deemter equation

$$H = A + B/u + Cu$$
$$= A + B/u + (C_s + C_M)u$$

and the relationships shown in Table 26-3 are fully applicable to GC.

TABLE 26-3 Processes That Contribute to Band Broadening

Process	Term in Equation 26-23	Relationship to Column* and Analyte Properties
Multiple flow paths	A	$A = 2\lambda d_p$
Longitudinal diffusion	B/u	$\frac{B}{u} = \frac{2\gamma D_M}{u}$
Mass transfer to and from stationary phase	$C_S u$	$C_S u = \frac{f(k)d_f^2}{D_S}u$
Mass transfer in mobile phase	$C_M u$	$C_M u = \frac{f'(k)d_p^2}{D_M}u$

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The longitudinal diffusion term *(Blu) is more important in GLC,* because of the much larger diffusion rates in gases. (10^4 -10^5 times greater than liquids). As a result, the minima in curves relating plate height *H to flow rate (van* Deemter plots) are usually considerably broadened in GC (see Figure 26-8).

- *u, Ds, D_M,(diff. Coeff.) d_f, d_p (thickness of the coating on SP and diameter of packing particles*
- *k is retention factor, f(k) and f'(k) are functions of k, retention factors.*

λand γ are constants that depend on quality of the packing.

Carrier gas – main purpose of the gas in GC is to move the solutes along the column, mobile phase is often referred to as carrier gas.

- Inert, suitable for the detector, high purity, easily available, cheap

Common carrier gas: He, Ar, H_2, N_2

○ GC separates solutes based on their different interactions with the mobile and stationary phases.

-solute's retention is determined by its vapor pressure and volatility

-solute's retention is controlled by its interaction with the stationary phase

-gas mobile phase has much lower density and therefore;

- decreased chance for interacting with solute
- increased chance that stationary phase interacts with solute

○ Component more soluble in the S.P → travels slower
○ Component less soluble in the S.P → travels faster

Carrier Gas or Mobile phase does not affect solute retention, but does affect:

1.) Desired efficiency for the GC System
- low molecular weight gases (He, H_2) → larger diffusion coefficients
- low molecular weight gases → faster, more efficient separations

2.) Stability of column and solutes
- H_2 or O_2 can react with functional groups on solutes and stationary phase or with surfaces of the injector, connections and detector

3.) Response of the detector
- thermal conductor requires H_2 or He
- other detectors require specific carrier gas

27B- Instruments for GLC: Gas Chromatography

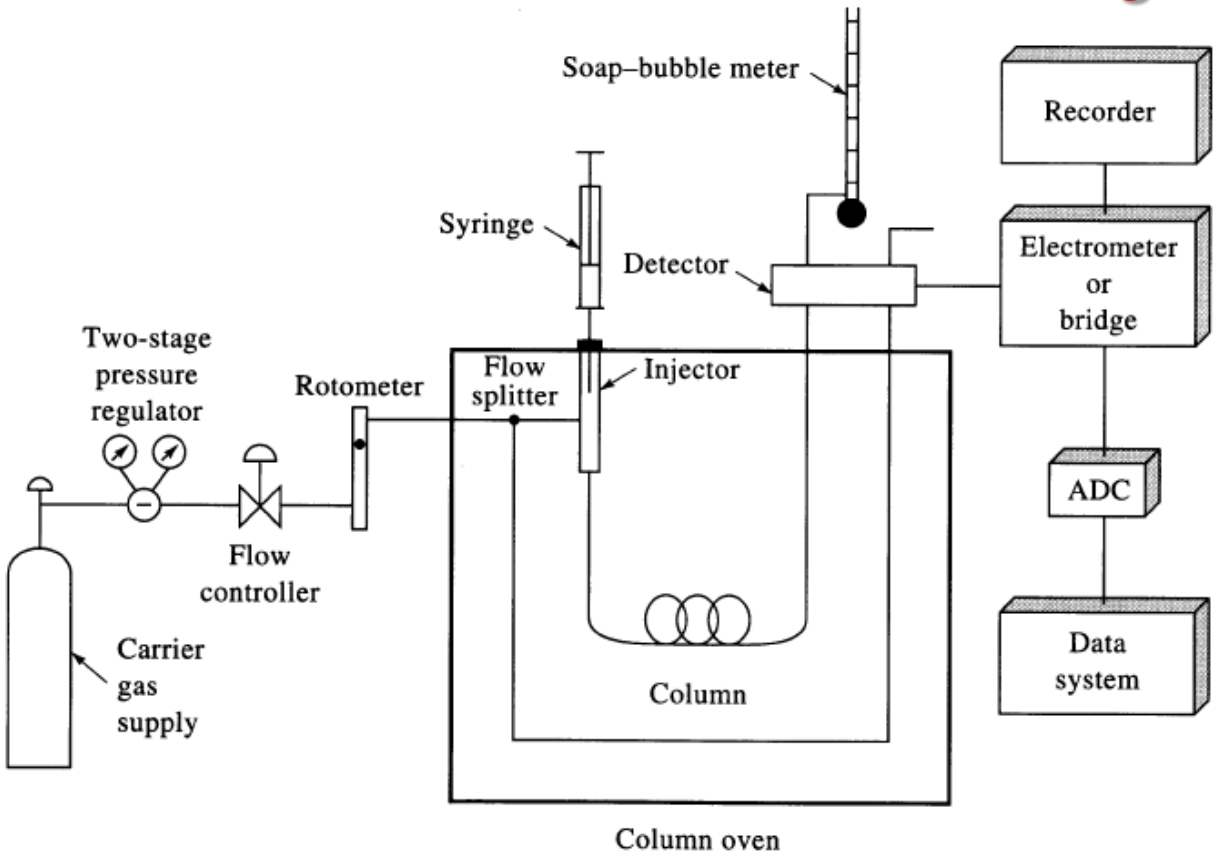
A simple GC system consists of:

1.Gas source (with pressure and flow regulators)

2. Injector or sample application system

3.Chromatographic column (with oven for temperature control)

4.Detector& computer or recorder



Carrier gas: He (common), N_2, H_2, Ar

P_{inlet} 10-50 psig

Flow = 25-150 mL/min packed column

Flow = 1-25 mL/min open tubular column

Column: 2-50 m coiled stainless steel/glass/Teflon

Oven: 0-400 °C ~ average boiling point of sample

Accurate to <1 °C

Detectors: FID, TCD, ECD, (MS)

27B-1 Carrier Gas system:

- Carrier gases are available in pressurized tanks. *Pressure regulators, gauges, and flow meters* are required to control the flow rate of the gas.

In addition, the carrier gas system often contains a *molecular sieve* to remove impurities and water.

• Inlet pressures usually range from 10 to 50 psi (lb/in^2) above room pressure, which lead to flow rates of

- 25 to 150 mL/min with *packed columns* and
- 1 to 25 mL/min for *open tubular capillary column*

• Generally, it is assumed that flow rates will be constant if the inlet pressure remains constant.

• Flow rates can be established by a rotometer at the column head; this device, however, is not as accurate as the simple soap-bubble meter which is located at the end of the column.

• A soap film is formed in the path of the gas when a rubber bulb containing an aqueous solution of soap or detergent is squeezed; the time required for this film to move between two graduations on the buret is measured and converted to volumetric flow rate. Many modern computer-controlled gas chromatographs are equipped with electronic flow meters that can be regulated.

27B-2 Sample Injection System:

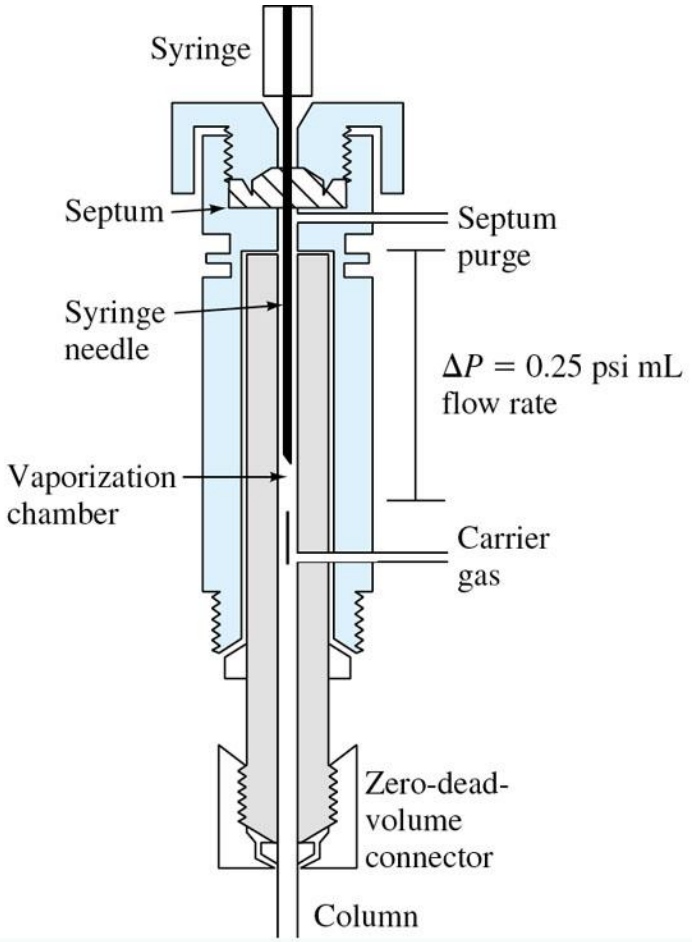
➢ Column efficiency requires that the sample be of suitable size and be introduced as a “plug” of vapor; slow injection of oversized samples causes band spreading and poor resolution.

➢ *Direct Injection:*

The most common method of sample injection involves the use of micro-syringe to inject a liquid or gaseous sample through a self-sealing, silicone-rubber diaphragm or septum into a flash vaporizer port located at the head of the column (the sample port is ordinarily about 50°C above the boiling point of the least volatile component of the sample).

- ➢ sample size (i) 1-20 μL packed column
  (ii) 10^{-3} μL capillary column

➢ a *sample splitter is often needed to deliver* a small known fraction (1 :50 to 1;500) of the injected sample, with the remainder going to waste.



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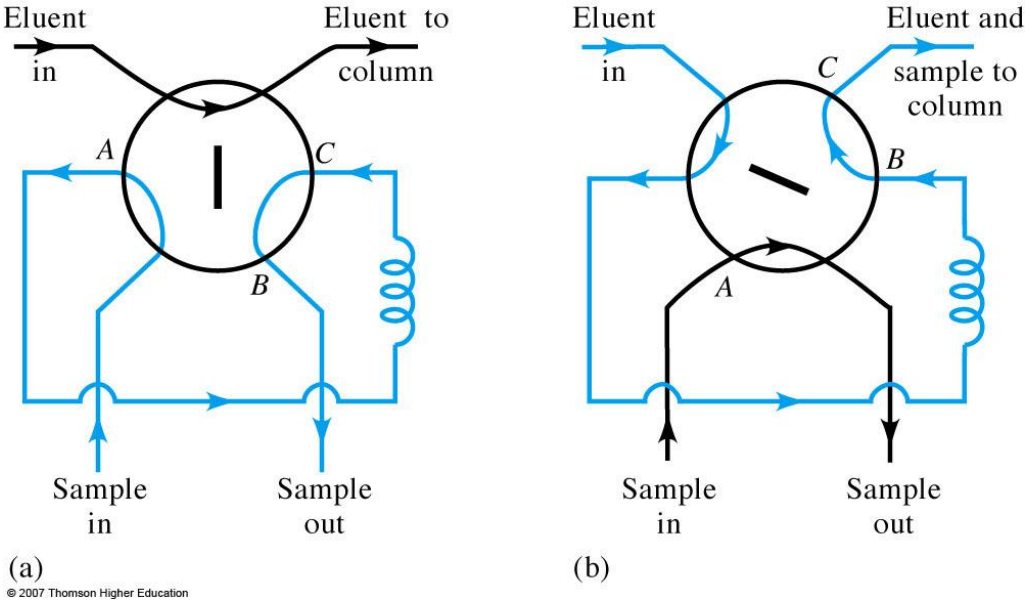
Split injection: routine method
0.1-1 % sample to column
remainder to waste

Splitless injection: all sample to column
best for quantitative analysis
only for trace analysis, low [sample]
risk of backflash

On-column injection: for samples that decompose above boiling point
no heated injection port
column at low temperature to condense sample in narrow band
heating of column starts chromatography

➢ *Injection with a rotary sample valve with sample loop*

➢ For quantitative work, more reproducible sample sizes for both liquids and gases are obtained by means of a rotary sample valve.



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➢ Errors due to sample size can be reduced to 0.5%

➢ The sampling loop is filled by injection of an excess of sample.

➢ Rotation of the valve by 45 deg then introduces the reproducible volume ACB into the mobile phase.

27B-3 Column Configurations and Column Ovens:

Two general types of columns are encountered in gas chromatography,

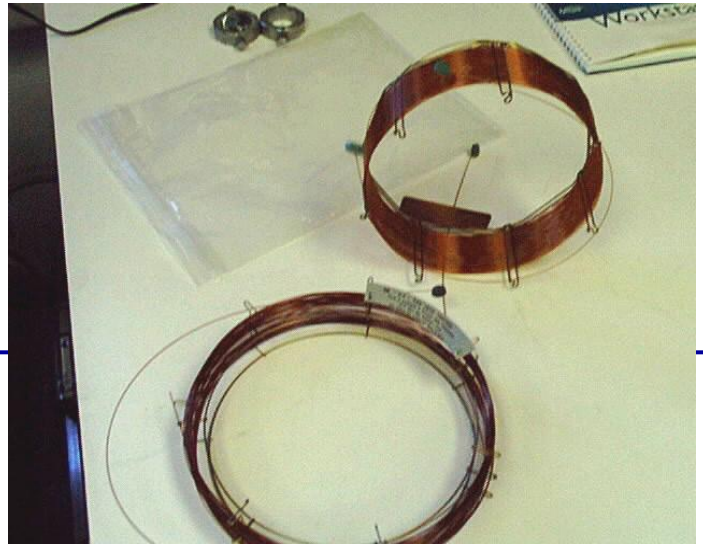
1) packed and
2) capillary (open tubular).

PACKED COLUMN:

- 1 - 4mm ID;
- 1 - 5 m length
- Glass / stainless steel coil
  (fused silica) / teflon)
- Packed solid particles either porous/non-porous coated with thin (1 μm) film of liquid
- To fit into an oven, they are usually formed as coils having diameters of 10 to 30 cm

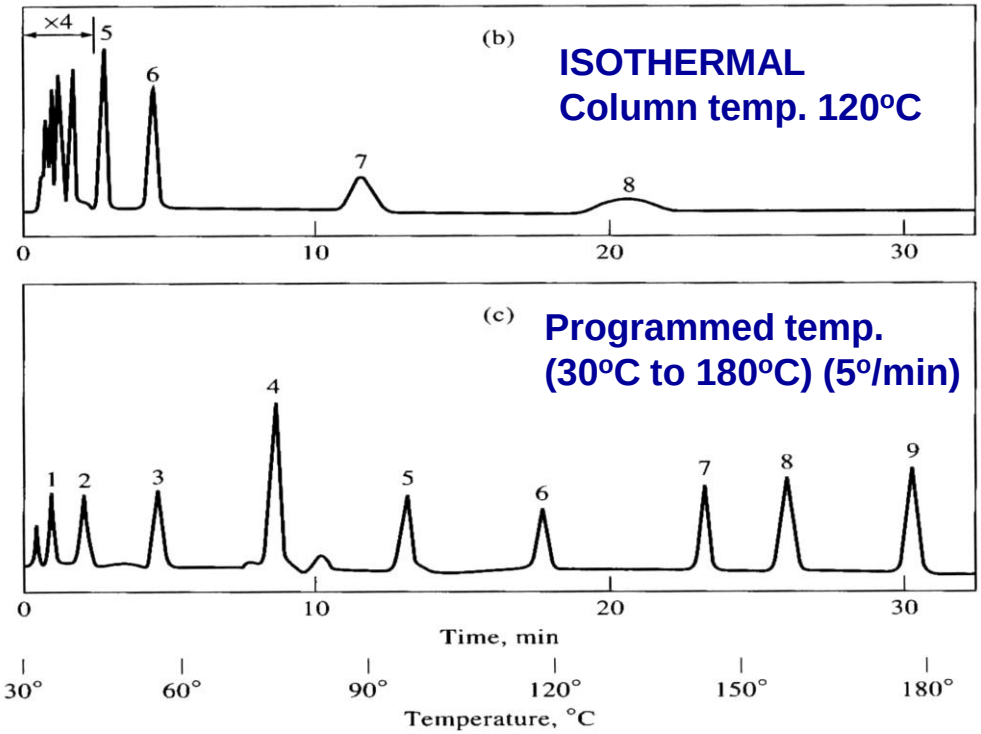
CAPILLARY COLUMN:

- 0.1 - 0.5 mm I.D.
- 2 - 100 m length
- Thin fused-silica.
- Inner wall coated with thin (0.1-5 μm) film of liquid (stationary phase)



Column Ovens:

- The column is ordinarily housed in a thermostated oven.
- Column temperature is an important variable that must be controlled to a few tenths of a degree for precise work.
- The optimum column temperature depends upon the boiling point of the sample and the degree of separation required.
- Roughly, a temperature equal to or slightly above the average boiling point of a sample results in a reasonable elution time (2 to 30 min).
- For samples with a broad boiling range, it is often desirable to employ temperature programming, whereby the column temperature is increased either continuously or in steps as the separation proceeds.



Temperature programming is usually done either in a stepwise change, a linear change or a combination of several linear changes. A single linear change or ramp is the most common

27B-4 Detection Systems:

Dozens of detectors have been investigated and used with GC separations.
The choice of detector will depend on the analyte and how the GC method is being used (i.e., analytical or preparative scale)
In some cases, gas chromatographs are coupled to spectroscopic instruments such as mass and infrared spectrometers.
With such systems, the spectral device not only detects the appearance of the analytes as they elute from the column but also helps to identify them.

Characteristics of the Ideal Detector:

1. Adequate sensitivity
2. Good stability and reproducibility.
3. A linear response to solutes that extends over several orders of magnitude.
4. A temperature range from room temperature to at least 400^{o}C.
5. A short response time that is independent of flow rate.
6. High reliability and ease of use.
7. Similarity in response toward all solutes or a highly selective response toward one or more classes of solutes.
8. Nondestructive of sample.

TABLE 27-1 Typical Gas Chromatographic Detectors

Type	Applicable Samples	Typical Detection Limit
Flame ionization	Hydrocarbons	1 pg/s
Thermal conductivity	Universal detector	500 pg/mL
Electron capture	Halogenated compounds	5 fg/s
Mass spectrometer (MS)	Tunable for any species	0.25 to 100 pg
Thermionic	Nitrogen and phosphorous compounds	0.1 pg/s (P), 1 pg/s (N)
Electrolytic conductivity (Hall)	Compounds containing halogens, sulfur, or nitrogen	0.5 pg Cl/s, 2 pg S/s, 4 pg N/s
Photoionization	Compounds ionized by UV radiation	2 pg C/s
Fourier transform IR (FTIR)	Organic compounds	0.2 to 40 ng

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1.) *Flame Ionization Detector (FID)*

- most common type of GC detector
- "universal" detector capable of measuring the presence of almost any organic and many inorganic compound

Process

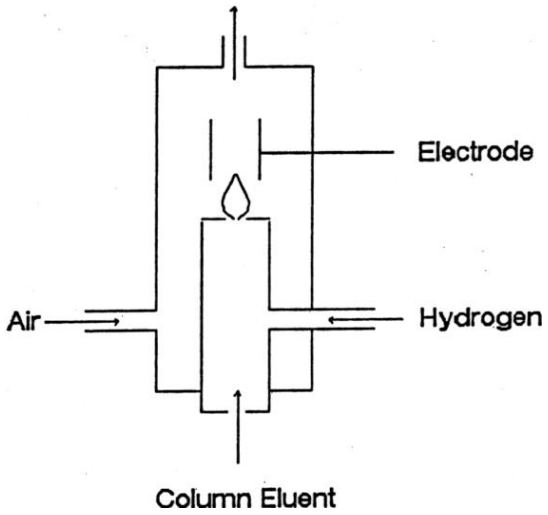
- The effluent from the column is mixed with hydrogen and air and then ignited electrically
- Most organic compounds, when pyrolyzed at the temperature of a hydrogen/air flame, produce ions and electrons that can conduct electricity through the flame.
- A potential of a few hundred volts is applied. The resulting current (~10^{-12} A) is then measured with a high impedence picoampermeter.
- The flame ionization detector exhibits a high sensitivity (~10^{-13} g/s), large linear response range (~10^{7}), and low noise
- it is a mass sensitive rather than concentration sensitive device because it responds to number of carbon atoms entering the detector per unit time

Advantages:

- universal detector for organics
  - doesn't respond to common inorganic compounds
- mobile phase impurities not detected
- carrier gases not detected
- limit of detection: FID is 1000x better than TCD
- linear and dynamic range better than TCD

Disadvantage:

- destroys the sample.

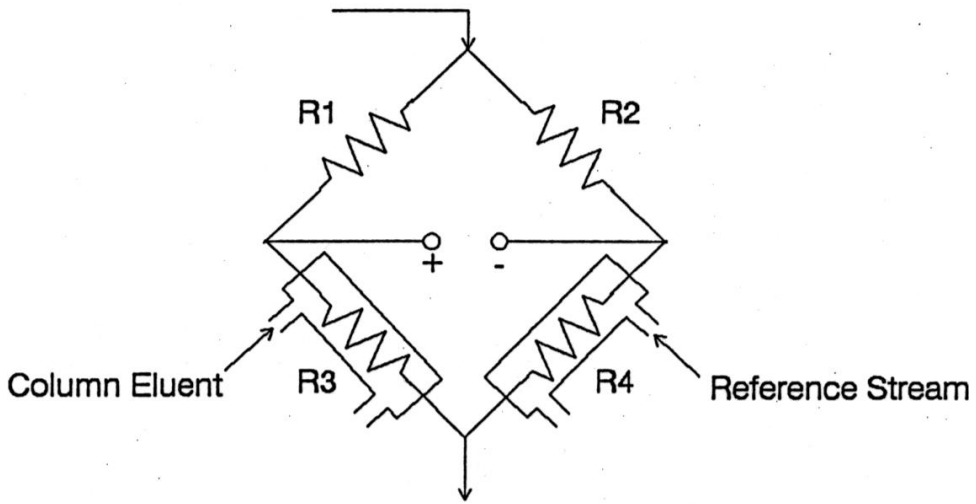


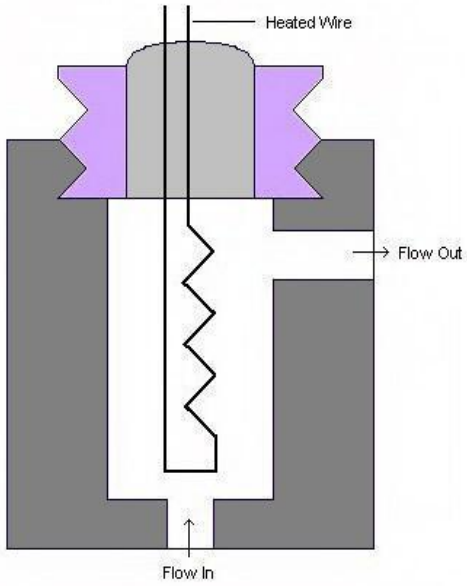
2.) *Thermal Conductivity Detector (TCD)*

- katherometer or hot-wire detector
- first universal detector developed for GC

Process

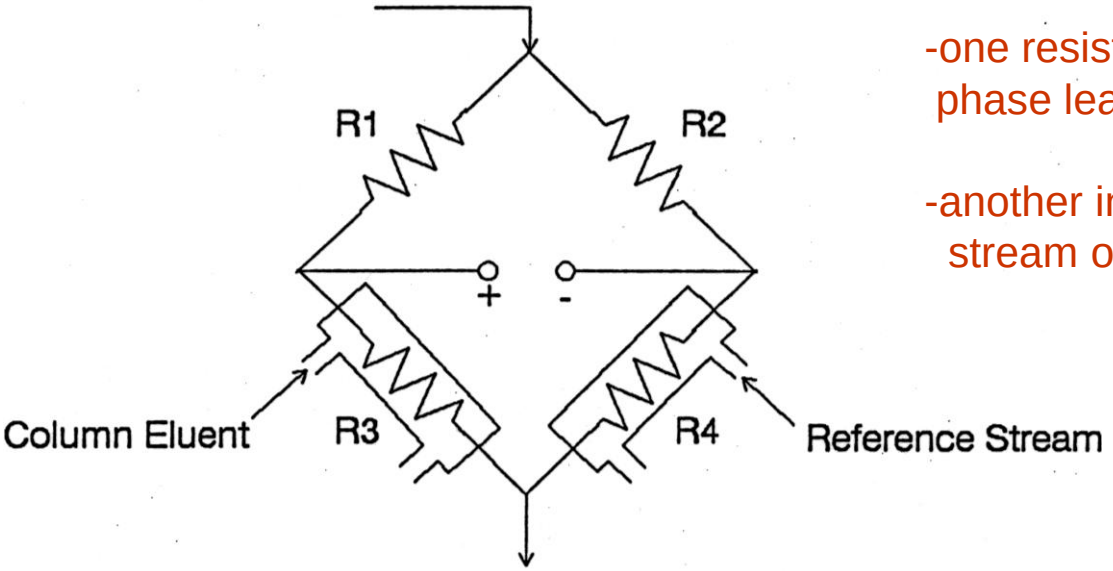
- is based upon changes in the thermal conductivity of the gas stream brought about by the presence of analyte molecules.
- The sensing element of TCD is an electrically heated element whose temperature at constant electrical power depends upon the thermal conductivity of the surrounding gas.
- The heated element may be a fine platinum, gold, or tungsten wire or a semiconducting thermistor.
- Difference in thermal conductivity between the carrier gas and sample gas causes a voltage output





Design

- based on electronic circuit known as a *Wheatstone bridge*.
- circuit consists of an arrangement of four resistors with a fixed current applied to them.
- thermal conductivity changes with presence of other components in the mobile phase.
- the voltage between points (+) and (-) will be zero as long as the resistances in the different arms of the circuit are properly balanced



-one resistor in contact with mobile phase leaving column

-another in contact with reference stream of pure mobile phase

as solute emerge from column:

change in thermal conductivity → change in amount of heat removed from resistor →change in resistor's temperature and resistance → change in voltage difference between points (+) and (-).

Considerations

- mobile phase must have a different thermal conductivity when solutes being separated
- most compounds separated in GC have thermal conductivity of about 1-4X10^{-5}.
- H_2 and He are carrier gases with significantly larger thermal conductivity values.

advantages:

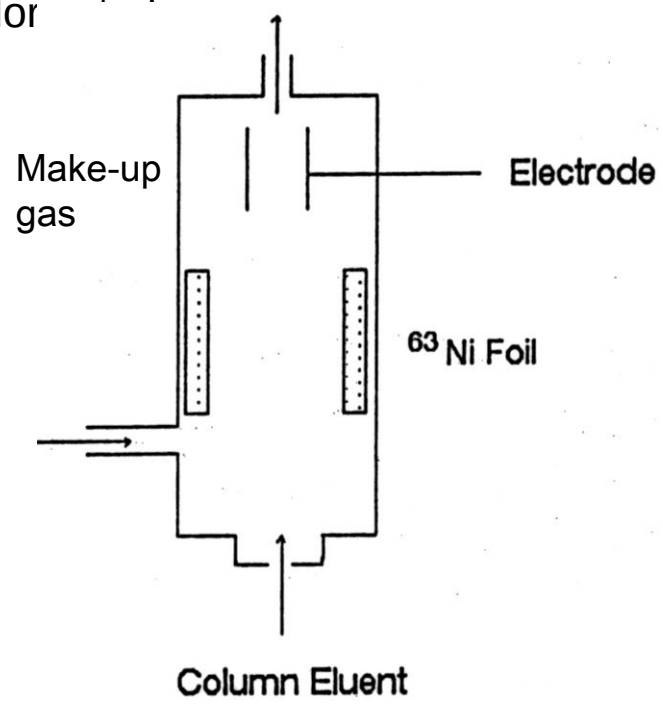
- truly universal detector
  - ② applicable to the detection of any compound in GC
- non-destructive
  - ② useful for detecting compounds from preparative-scale columns
  - ② useful in combination with other types of GC detectors
- large linear dynamic range (10^5)

disadvantage:

- detect mobile phase impurities
- sensitive to changes in flow-rates
- low sensitivity
  - ② ~ 10^{-8} g solute/mL carrier gas
  - ② other GC detectors are much higher
- due to its low sensitivity, can not be used with capillary columns where sample amounts are very small.

3.) *Electron Capture Detector (ECD)*

- radiation-based detector for environmental samples containing halogens such as, pesticides and polychlor biphenyls.



Process

-based on the capture of electrons by electronegative atoms in a molecule

-electrons are produced by ionization of the carrier gas (nitrogen) with a radioactive source ^{63}Ni

- electrons go to collector electrode where they produce a current

- in absence of solute organic species, a constant standing current is produced,

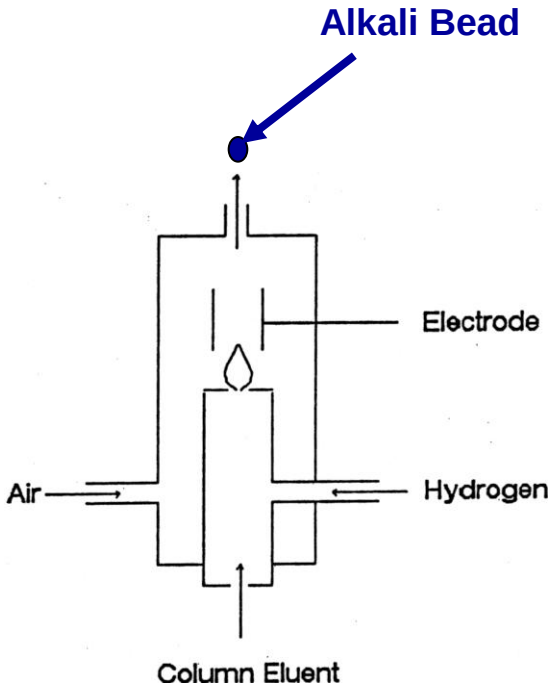
- compounds with electronegative atoms capture electrons, and reduce the current.

advantages:

- useful for environmental testing
  - ➢ detection of chlorinated pesticides or herbicides, polynuclear aromatic carcinogens, organometallic compounds, anhydrides and conjugated carbonyls
- selective for halogen- (I, Br, Cl, F), nitro-, and sulfur-containing compounds
- *insensitive* to functional groups such as amines, alcohols, and hydrocarbons

4.) Thermionic Detectors: *Nitrogen-Phosphorus Detector (NPD)*

- for detecting nitrogen- or phosphorus containing organic compounds
- also known as *alkali* flame ionization detector or thermionic detector



Process

- same basic principal as FID
- The column effluent is mixed with hydrogen, passes through the flame tip assembly, and is ignited.
- The hot gas then flows around an electrically heated Rubidium silicate bead, which is maintained at about 180 V with respect to the collector.
- The heated bead forms a plasma having a temperature of 600°C-800°C. ions are collected at an electrode to create a current
- Exactly what occurs in the plasma to produce unusually large numbers of ions from phosphorus- or nitrogen-containing molecules is not fully understood; but large ion currents result, which are useful for determining compounds containing these two elements.

4.) Thermionic Detectors: *Nitrogen-Phosphorus Detector (NPD)*

advantages:

- useful for environmental testing
  - ② detection of organophosphate pesticides
- useful for drug analysis
  - ② determination of amine-containing or basic drugs
- Like FID, does not detect common mobile phase impurities or carrier gases
- limit of detection: NPD is 500x better than FID in detecting nitrogen- and phosphorus- containing compounds
- NPD more sensitive to other heterocompounds, such as sulfur-, halogen-, and arsenic- containing molecules

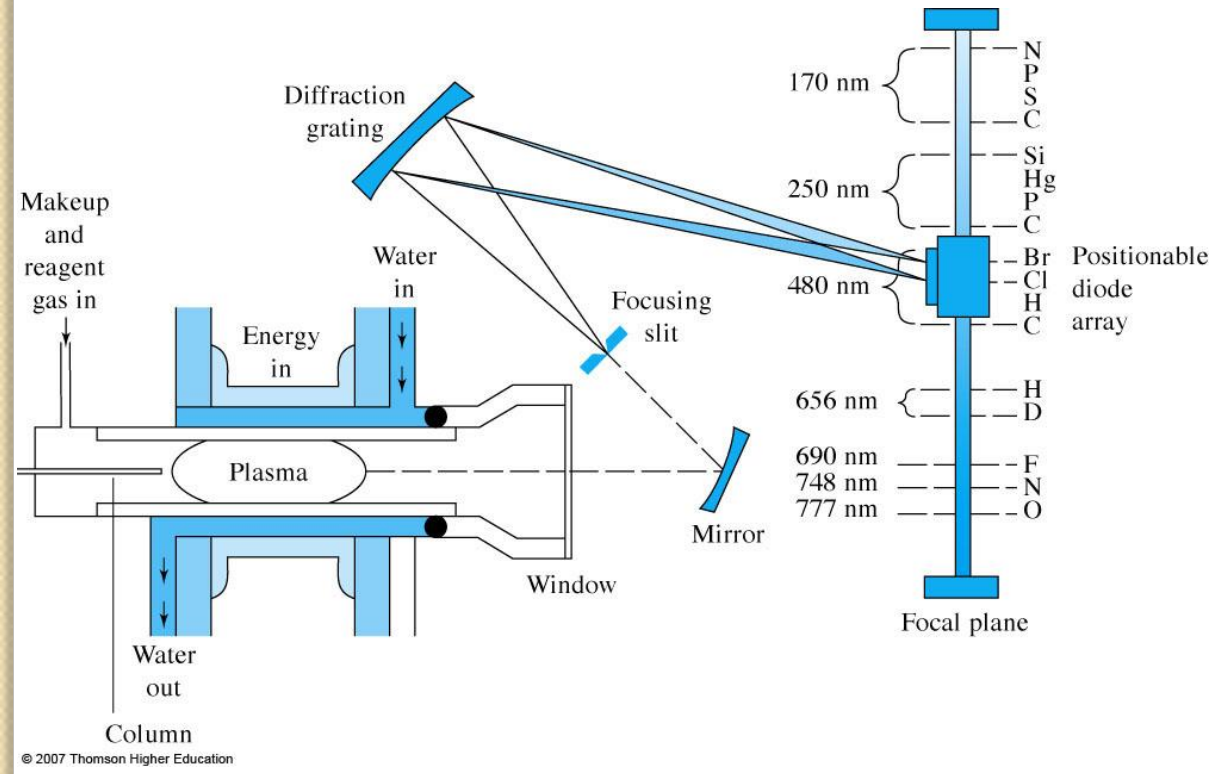
disadvantage:

- destructive detector
- NPD is less sensitive to organic compounds compared to FID

Photoionization Detector:

-Effluents are photoionized by UV radiation from H_2 (10.2 eV) or / Ar lamp (11.7 eV)
- Ions and electrons produced by photoionization are collected at a pair of biased electrodes
- Most sensitive for aromatic hydrocarbons, organosulfur or organophosphorous compounds that are easily photo ionized.
-Linear range 10^7

Atomic Emission Detector



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- Effluent from the column introduced into MIP, ICP, DCP
- The MIP has been most widely used and is available commercially.
- The MIP is used in conjunction with a diode array or charge-coupled device atomic emission spectrometer, multielement analysis.

Interfacing Gas Chromatography with Spectroscopic Methods

Gas chromatography is often coupled with the selective techniques of spectroscopy, thus giving so-called hyphenated methods that provide the chemist with powerful tools for identifying the components of complex mixtures.

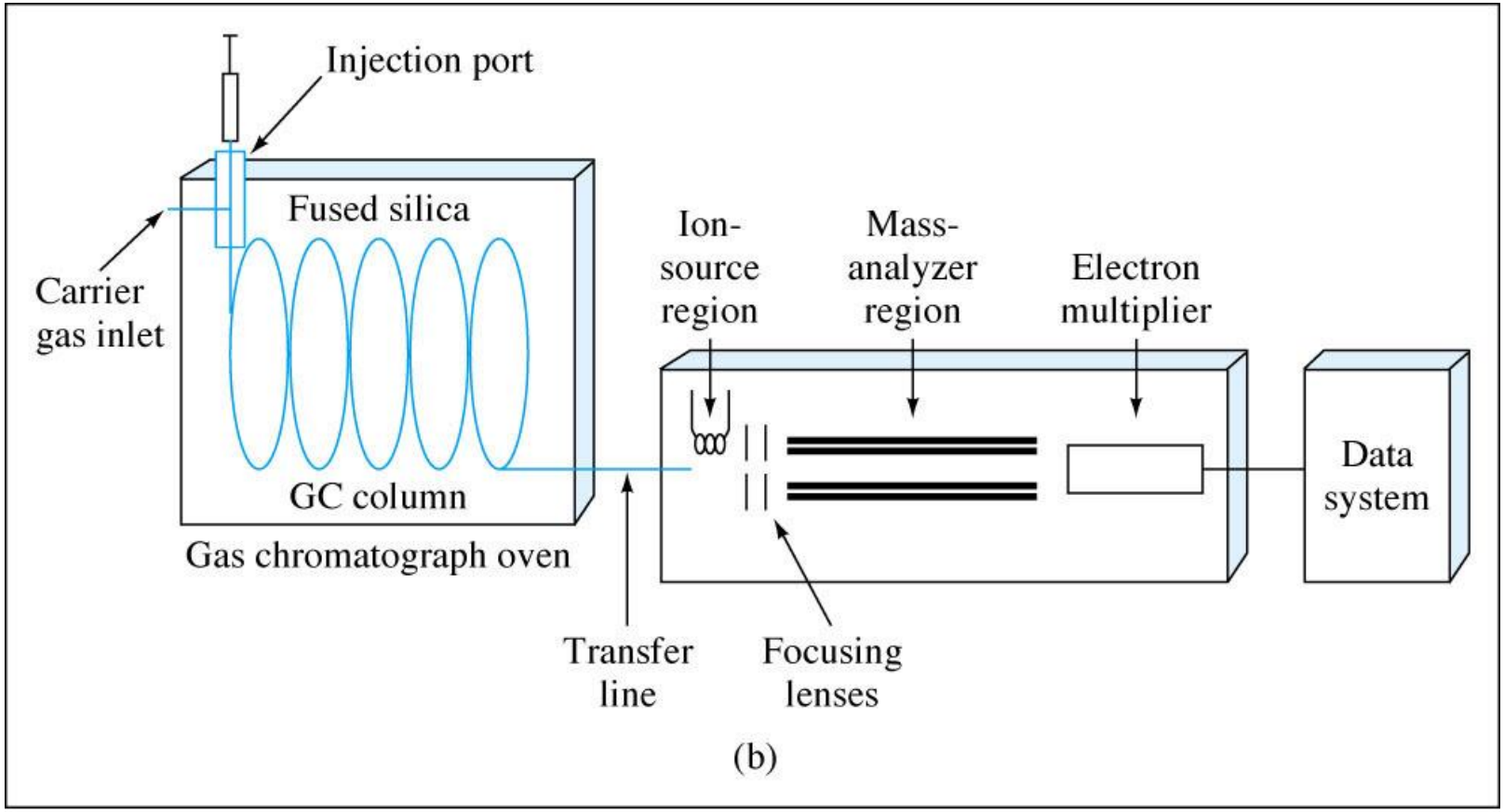
GC-MS

GC-FTIR

Gas Chromatography/Mass Spectrometry (GC/MS)

The flow rate from capillary columns is generally low enough that the column output can be fed directly into the ionization chamber of the mass spectrometer. For packed columns and megabore capillary columns however, a jet separator must be employed to remove most of the carrier gas from the analyte.

GC/MS



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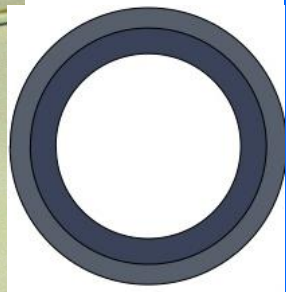
27 C- GAS CHROMATOGRAPHIC COLUMNS

1- Open tubular, Capillary Columns



Open tubular column (capillary column)

- 0.1 - 0.5 mm I.D.
- 2 - 100 m length
- Thin fused-silica.
- Inner wall coated with thin (0.1-5 μm) film of liquid (stationary phase)
- higher efficiency
- smaller sample size
- analytical applications

2- Packed Columns

Packed column

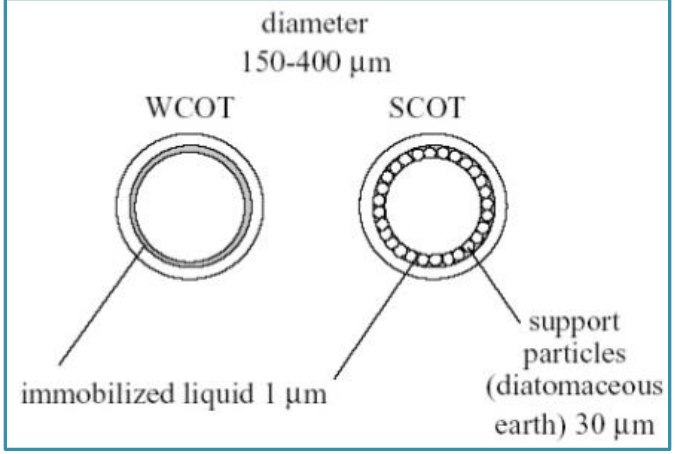
- 1 - 4mm ID;
- 1 - 5 m length
- Glass / stainless steel coil (fused silica) / teflon)
- Packed solid particles either porous /non-porous coated with thin (1 μm) film of liquid
- large sample capacity
- good for preparative work
- To fit into an oven, they are usually formed as coils having diameters of 10 to 30 cm

27 C1- Open tubular Columns

- Open tubular (capillary) columns –
  - wall—coated open tubular (WCOT)
  - support-coated open tubular (SCOT).

Wall-coated open tubular, WCOT,
-simply capillary tubes coated with a thin layer of the stationary phase
- Early WCOT columns were constructed of stainless steel, aluminum, copper, or plastic. Later, glass columns began to be used.
- the glass etched with HCl acid, or KHF to give a rough surface on to which the stationary phase is bonded more tightly. - The most widely used capillary columns are *fused-silica wall-coated (FSWC) open tubular columns. Offer advantages like: physical strength, much lower reactivity toward sample components, and flexibility.*

Support-coated open tubular, SCOT,
- the inner surface of the capillary is lined with a thin film (~30 μm) of a support material, diatomaceous earth.
- This type of column holds several times as much stationary phase as does a wall-coated column and thus has a greater sample capacity.



Generally, the efficiency of a SCOT column is less than that of a WCOT column but significantly greater than that of a packed column.

27 C2- Packed Columns

Solid Support Materials

- The packing, or solid support in a packed column, holds the liquid stationary phase in place so that as large a surface area as possible is exposed to the mobile phase.
- The ideal support consists of small, uniform, spherical particles with good mechanical strength and a specific surface area of at least $1 m^2/g$.
- the material should be inert at elevated temperatures and be uniformly wetted by the liquid phase. No material is yet available that meets all of these criteria perfectly.
- The earliest, and still the most widely used packing is prepared from naturally occurring *diatomaceous earth*, which is made up of the skeletons of thousands of species of single-celled plants (diatoms) that once inhabited ancient lakes and seas.
- Such plants received their nutrients and disposed of their wastes via molecular diffusion through their pores. As a consequence, their remains are well-suited as support materials because gas chromatography is also based upon the same kind of molecular diffusion.

Packed Columns

Particle Size of Supports

- The efficiency of a gas-chromatographic column increases rapidly with decreasing particle diameter of the packing.
- The pressure difference required to maintain a given flow rate of carrier gas, however, varies inversely as the square of the particle diameter
- Usual support particles are 60-80 mesh (250-170 microns) or 80-100 mesh (170-149 microns)

TABLE 27-2 Properties and Characteristics of Typical GC Columns

	Type of Column			
	FSWC*	**WCOT†**	**SCOT‡**	**Packed**
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.3	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Sample size, ng	10–75	10–1000	10–1000	$10–10^6$
Relative pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Flexibility?	Yes	No	No	No
Chemical inertness	Best →			Poorest

*Fused silica, wall-coated open tubular column.

†Wall-coated open tubular metal, plastic, or glass columns.

‡Support-coated open tubular column (also called porous-layer open tubular, or PLOT).

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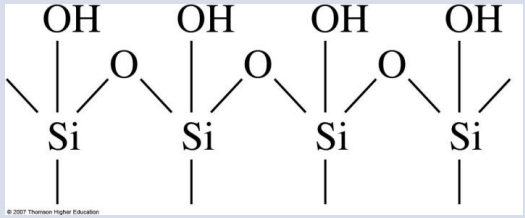
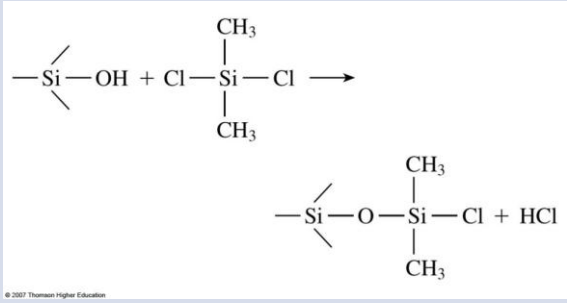
27 C3- Adsorption on Column Packings or Capillary Walls

PROBLEM: the physical adsorption of polar or polarizable analyte species, such as alcohols or aromatic hydrocarbons, on the silicate surfaces of column packings or capillary walls.
RESULTS: distorted peaks, which are broadened and often exhibit a tail

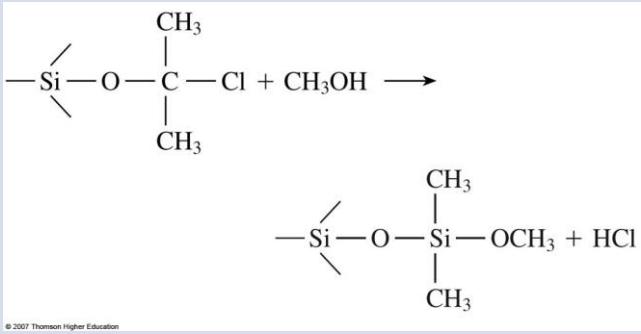
REASON: Adsorption occurs with silanol groups that form on the surface of silicates by reaction with moisture. Thus, a fully hydrolyzed silicate surface has the structure



SOLUTION: The SiOH groups on the support surface have a strong affinity for polar organic molecules and tend to retain them by adsorption.
Support materials can be deactivated by *silanization with dimethylchlorosilane (DMCS)*



When the support is washed with methanol, the second chloride is replaced by a methoxy group. Acid washing prior to silanization removes the impurities.



27 C4- The Stationary Phase

✓ The proper choice of SP is often crucial to the success of a separation.

✓ Desirable properties for the immobilized liquid phase in a GLC column:

- *low volatility (ideally, the boiling point of the liquid should be at 100^{o}C higher than the maximum operating temperature for the column);*
- *thermal stability;*
- *chemical inertness;*
- *solvent characteristics such that k and α values for the solutes to be resolved fall within a suitable range.*

✓ Many liquids have been proposed as stationary phases in the development of GLC. Qualitative guidelines for stationary-phase selection can be based on a literature review, an internet search, prior experience, or advice from a vendor of chromatographic equipment and supplies.

✓ The retention time for a solute on a column depends upon its distribution constant which in turn is related to the chemical nature of the stationary phase. To separate various sample components, their distribution constants must be sufficiently different to accomplish a clean separation. At the same time, these constants must not be extremely large or extremely small because large distribution constants lead to prohibitively long retention times and small constants produce such short retention times that separations are incomplete.

The Stationary Phase cont'

- To have a reasonable residence time in the column, a species must show some degree of compatibility (solubility) with the stationary phase. Here, the principle of "like dissolves like" applies, where "like" refers to the polarities of the solute and the immobilized liquid.
- Polar stationary phases contain functional groups such as
  - –CN, --CO and –OH.
  - Hydrocarbon-type stationary phase and dialkyl siloxanes are nonpolar, whereas polyester phases are highly polar.
  - Polar solutes include alcohols, acids, and amines; solutes of medium polarity include ethers, ketones, and aldehydes.

Generally, when the polarity of the stationary phase matches that of the sample components the order of elution is determined by the boiling point of the eluents.

Some Widely used Stationary Phases (Liquid)

TABLE 27-3 Some Common Liquid Stationary Phases for GLC

Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase, hydrocarbons, polynuclear aromatics, steroids, PCBs
5% Phenyl-polydimethyl siloxane	OV-3, SE-52	350	Fatty acid methyl esters, alkaloids, drugs, halogenated compounds
50% Phenyl-polydimethyl siloxane	OV-17	250	Drugs, steroids, pesticides, glycols
50% Trifluoropropyl-polydimethyl siloxane	OV-210	200	Chlorinated aromatics, nitroaromatics, alkyl substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids, alcohols, ethers, essential oils, glycols
50% Cyanopropyl-polydimethyl siloxane	OV-275	240	Polyunsaturated fatty acids, rosin acids, free acids, alcohols

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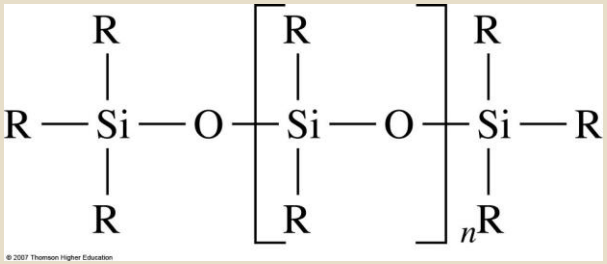
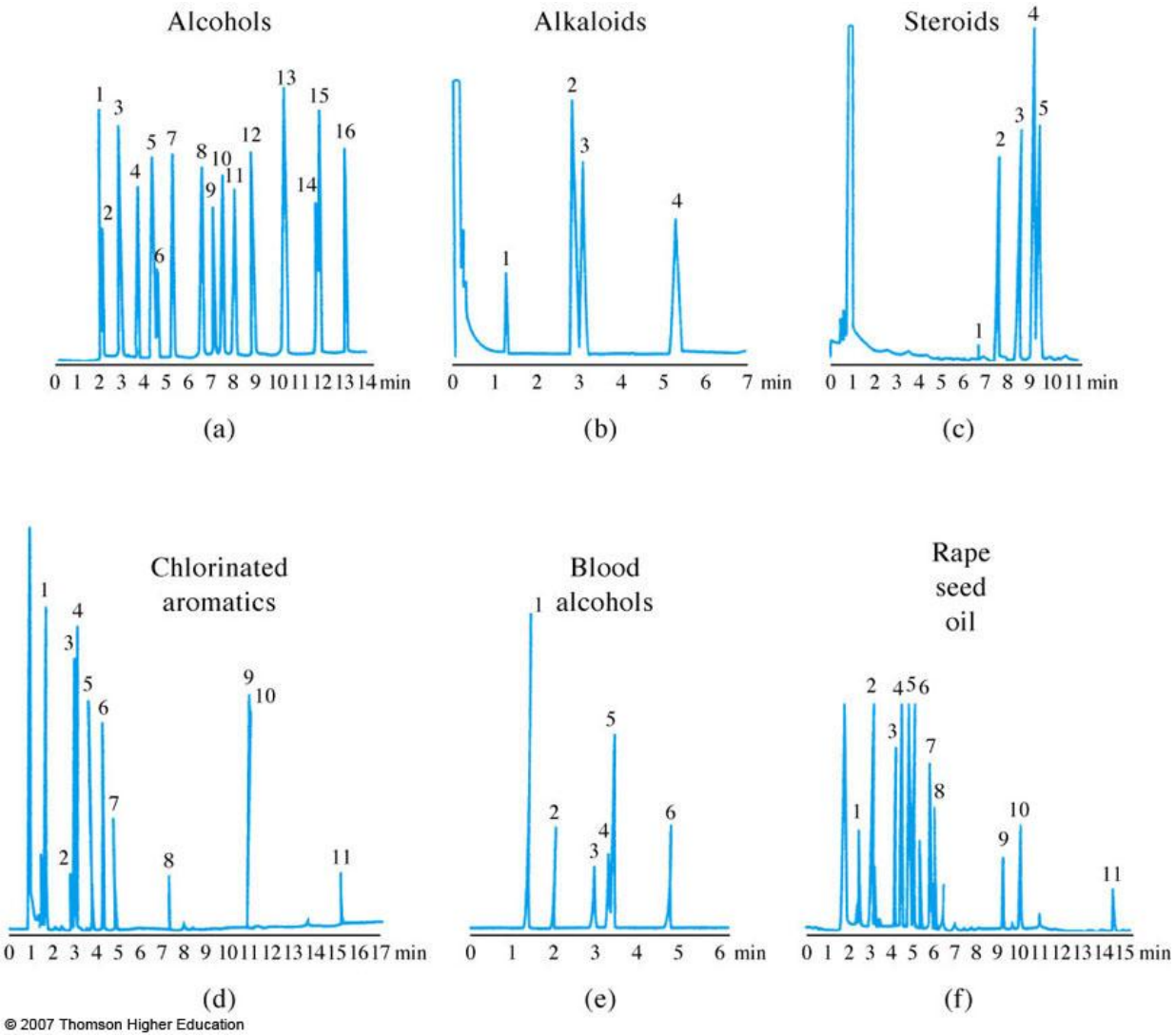
polydimethyl siloxanes



polyethylene glycol

HO-CH2-CH2-(O-CH2-CH2)n -OH

#1- polydimethyl siloxane, the – R groups are all –CH3 giving a liquid that is relatively nonpolar.
#2,3,4,6 - the other polysiloxanes, a fraction of the methyl groups are replaced by functional groups such as phenyl ($-C_6H_5$), cyanopropyl ($-C_3H_6CN$), and trifloropropyl ($-C_3H_6CF_3$). The percentage description in each case gives the amount of substitution of the named group for methyl groups on the polysiloxane backbone. These substitutions increase the polarity of the liquids to various degrees.
#5- is a polyethylene glycol, It finds widespread use for separating polar species.



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Typical chromatograms from open tubular columns coated with
(a) polydimethylsiloxane;
(b) 5% (phenyl methyldimethyl)siloxane;
(c)50% (phenyl methyldimethyl)siloxane;
(d)50% poly(trifluoropropyl-dimethyl)siloxane;
(e) polyethylene glycol;
(f)50% poly(cyanopropyl-dimethyl)siloxane

Bonded and Cross-Linked Stationary Phases

-Commercial columns are advertised as having bonded or cross-linked stationary phases.

- The purpose of bonding and cross-linking is to provide a longer-lasting stationary phase that is not disrupted at elevated temperatures or during temperature programming.

- With use, untreated columns slowly lose their stationary phase because of *"bleeding" in which a small amount of immobilized liquid is carried out of the column during the elution process.*

- Such columns are also recommended for on-column injection where a large solvent volume is used. Indeed, cross-linked or bonded columns may be backflushed to remove contaminants without significant loss of stationary phase.

- Bonding involves attaching a monomolecular layer of the stationary phase to the silica surface of the column by a chemical reaction. For commercial columns, the nature of the reaction is usually proprietary (Privately owned and controlled).

- Cross-linking is carried out *in situ after a column is coated with one of the polymers listed in Table 27-3. One way of cross-linking is to incorporate a peroxide into the original liquid. When the film is heated, reaction between the methyl groups in the polymer chains is initiated by a free radical mechanism.*

- The polymer molecules are then cross-linked through carbon-to-carbon bonds. The resulting films are less extractable and have considerably greater thermal stability than do untreated films. Cross-linking has also been initiated by exposing the coated columns to gamma radiation.

Film Thickness

✓Commercial columns are available having stationary phases that vary in thickness from 0.1 to 5μm.

✓Film thickness primarily affects the retentive character and the capacity of a column.

✓Thick films are used with highly volatile analytes because such films retain solutes for a longer time, thus providing a greater time for separation to take place.

✓Thin films are useful for separating species of low volatility in a reasonable length of time.

✓ For most applications with 0.26- or 0.32-mm columns, a film thickness of 0.26 μm is recommended. With megabore columns, 1- to 1.5 μm films are often used.

Chiral Stationary Phases

✓ In recent years, much effort has been devoted to developing methods for the separation of *enantiomers by gas or liquid chromatography.*

✓ Two approaches have been used.

- ✓ One is based on *forming derivatives of the analyte with an optically active reagent that forms a pair of diastereomers that can be separated on an achiral column.*
- ✓ The alternative method is *to use a chiral liquid as the stationary phase. A number of amino acid-derived chiral phases have been developed for this purpose, and others are becoming available commercially.*

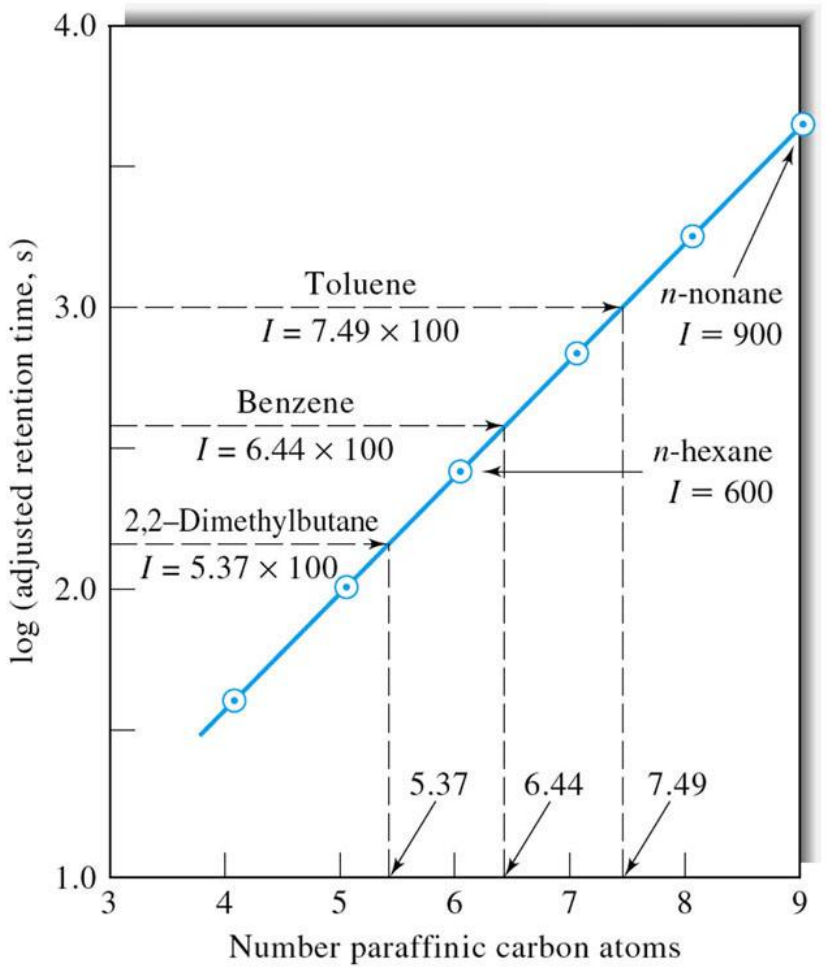
27 D Applications of GC

Qualitative Analysis

✓ Gas chromatograms are widely used as criteria of purity for organics.
✓ Contaminants, if present, are revealed by the appearance of additional peaks; the areas under these peaks provide rough estimates of the extent of contamination.
✓ The technique is also useful for evaluating the effectiveness of purification procedures.
✓ Retention times or volumes are useful for qualitative identification of components in mixtures.
✓ Gas chromatography provides an excellent means of confirming the presence or absence of a suspected compound in a mixture.

The Retention Index

- The retention index I was first proposed by Kovats for identifying solutes from chromatograms.
- The retention index for any given solute can be derived from a chromatogram of a mixture of that solute with at least two normal alkanes having retention times that bracket that of the solute.
- That is, normal alkanes are the standards upon which the retention index scale is based.
- The retention index for a normal alkane is equal to 100 times the number of carbons in the compound regardless of the column packing, the temperature, or other chromatographic conditions.
- Within a homologous series, a plot of the logarithm of adjusted retention time $t`_R$ ($t`_R = t_R - t`_M$) versus the number of carbon atoms is linear.



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Quantitative Analysis

✓ The peak height or peak area of an eluate from a GC column has been widely used for quantitative and semi-quantitative analyses.
✓ An accuracy of 1% relative is attainable under carefully controlled conditions.
✓ Reliability is directly related to the control of variables; the nature of the sample also plays a part in determining the potential accuracy.

27.C- Stationary Phases:

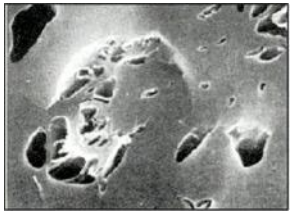
Stationary phase in GC is the main factor determining the selectivity and retention of solutes.

There are three types of stationary phases used in GC:

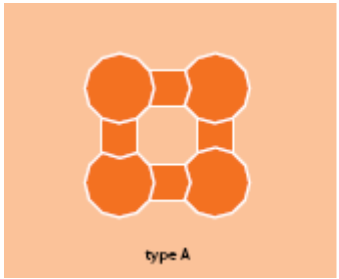
- Solid adsorbents
- Liquids coated on solid supports
- Bonded-phase supports

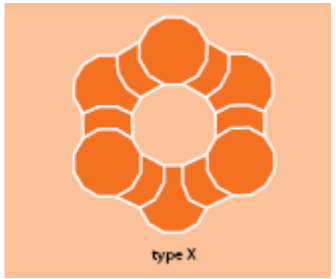
1.) *Gas-solid chromatography (GSC)*

- same material is used as <u>both</u> the stationary phase and support material
- common adsorbents include:
  - ② alumina
  - ② molecular sieves (**crystalline aluminosilicates [zeolites] and clay)**
  - ② silica
  - ② active carbon



Magnified Pores in activated carbon





Gas-solid chromatography (GSC):

advantages:

- long column lifetimes
- ability to retain and separate some compounds not easily resolved by other GC methods
  - ② geometrical isomers
  - ② permanent gases

disadvantage:

- very strong retention of low volatility or polar solutes
- catalytic changes that can occur on GSC supports
- strong retention of the analytes result with severe tailing in elution peaks
- GSC supports have a range of chemical and physical environments
  - ② different strength retention sites
  - ② non-symmetrical peaks
  - ② variable retention times