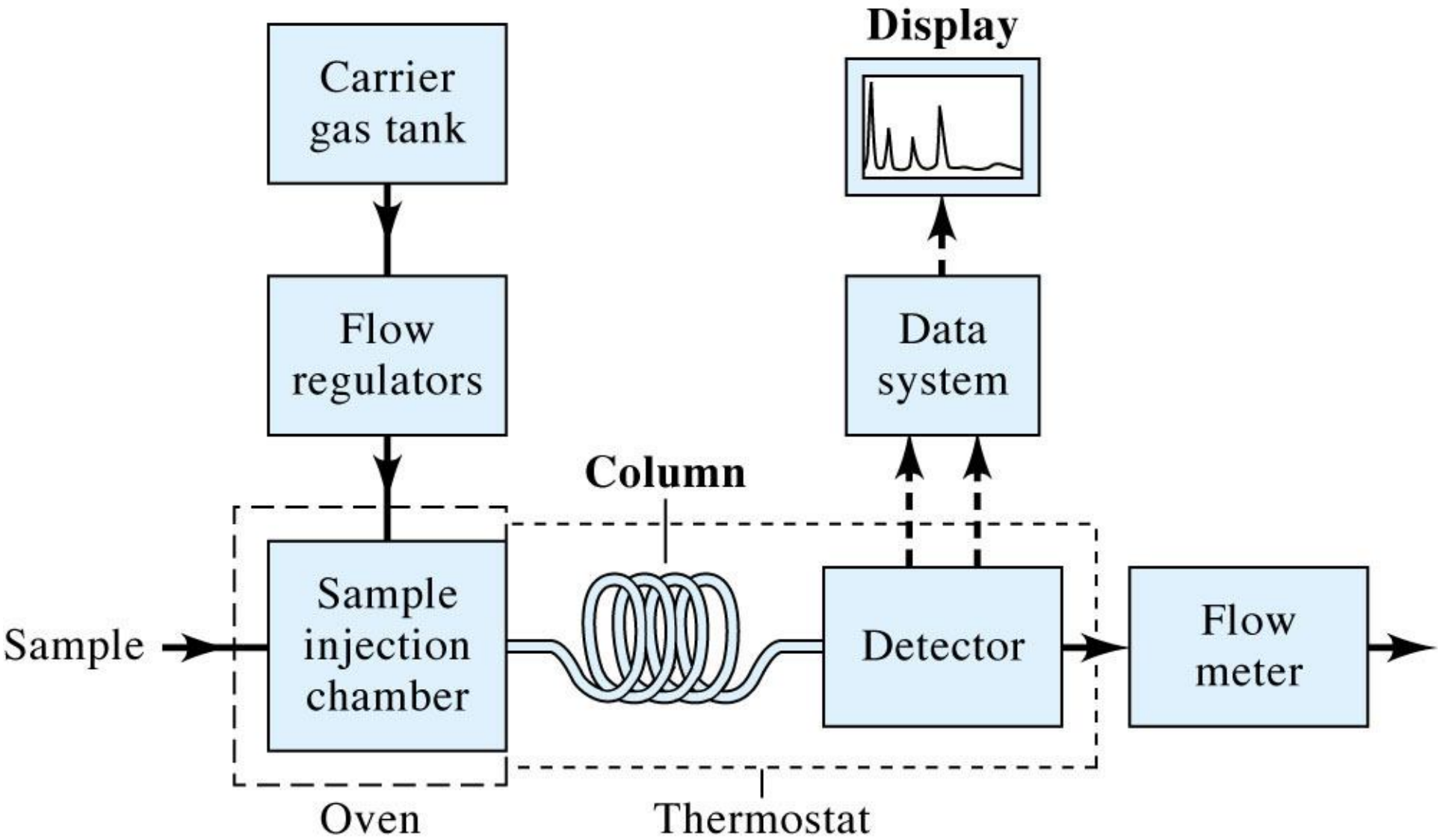
Gas Chromatography

Objective

- To study principle of Gas chromatography technique.
- To understand new technique of Gas Chromatography.
- To study instrumentation of Gas chromatography.
- To study application of Gas chromatography.

Gas Chromatography

- In gas chromatography (GC), the sample is vaporized and injected onto the head of a chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase.
- The mobile phase does not interact with molecule of the analyte; its only function is to transport the analyte through the column.
- Gas-liquid chromatography is based upon the partition of the analyte between a gaseous mobile phase and a liquid phase immobilized on the surface of an inert solid.



Principle of GC

- Involves partition between Gas & liquid
    1. Retention volume
    2. Relation ship between Vg & K
    3. Effect of mobile phase flow rate

1. Retention volume

- To know the effects of pressure and temperature in GC.

$$V_R = t_R F \;\&\; V_M = t_M F$$

Gas flow is not directly measured by a soap bubble meter

Average flow rate is F

$$F = \frac{Tc \;\; x \;\; (P - P_{H^2O})}{T \qquad\qquad P}$$

Both V_R & V_M d4epend upon average pressure within column (Pi = inlet pressure P = outlet pressure)

Pressure correction factor J used to account for the fact that pressure within n column is nonlinear function of Pi/P ratio

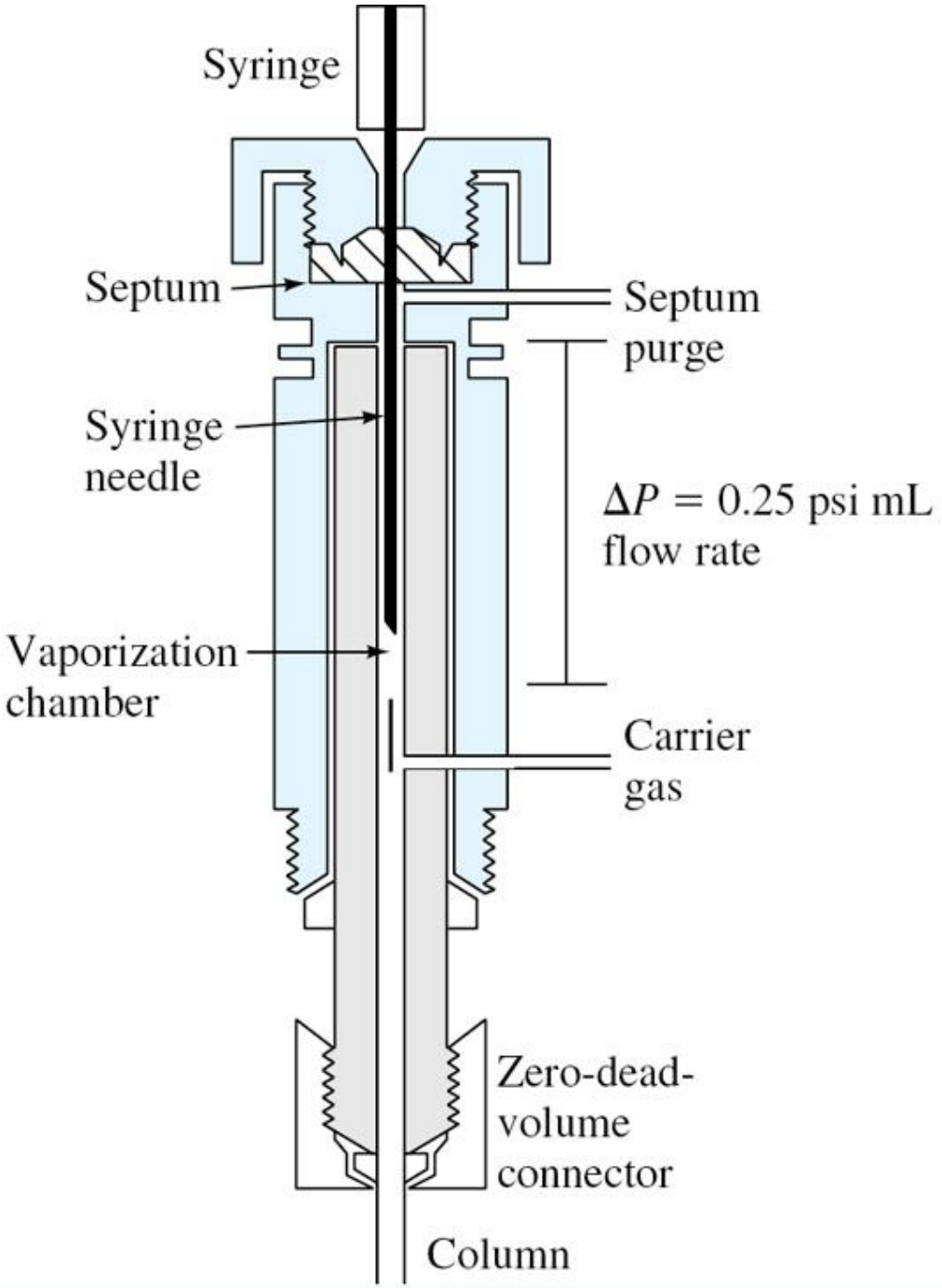
INSTRUMENTS FOR GC

Carrier Gas-Supply

Carrier gases, which must be chemically inert, include helium, nitrogen, and hydrogen. Associated with the gas supply are pressure regulators, gauges, and flow meters. In addition, the carrier gas system often contains a molecular sieve to remove water or other impurities.

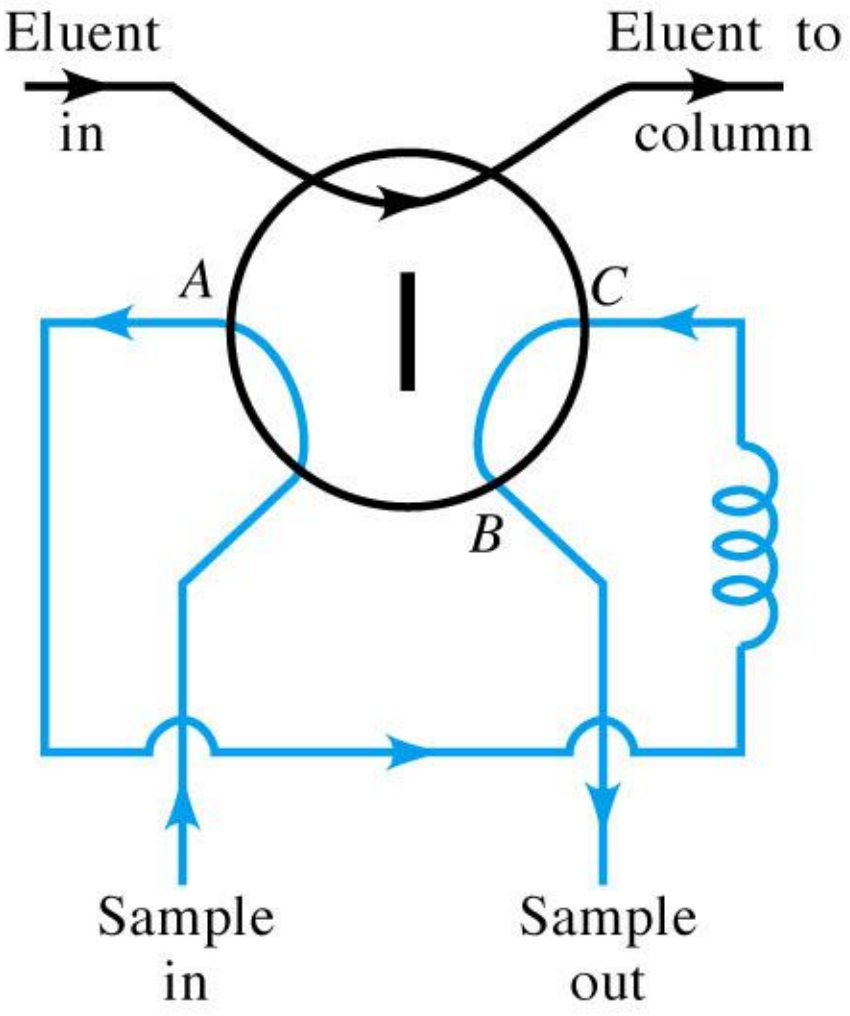
Sample Injection System

- 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.
- The most common method of sample injection involves the use of microsyringe 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^{o}C above the boiling point of the least volatile component of the sample).



Sample Injection System

- For quantitative work, more reproducible sample sizes for both liquids and gases are obtained by means of a rotary sample valve.
- Errors due to sample size can be reduced to 0.5% to 2% relative.
- 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.



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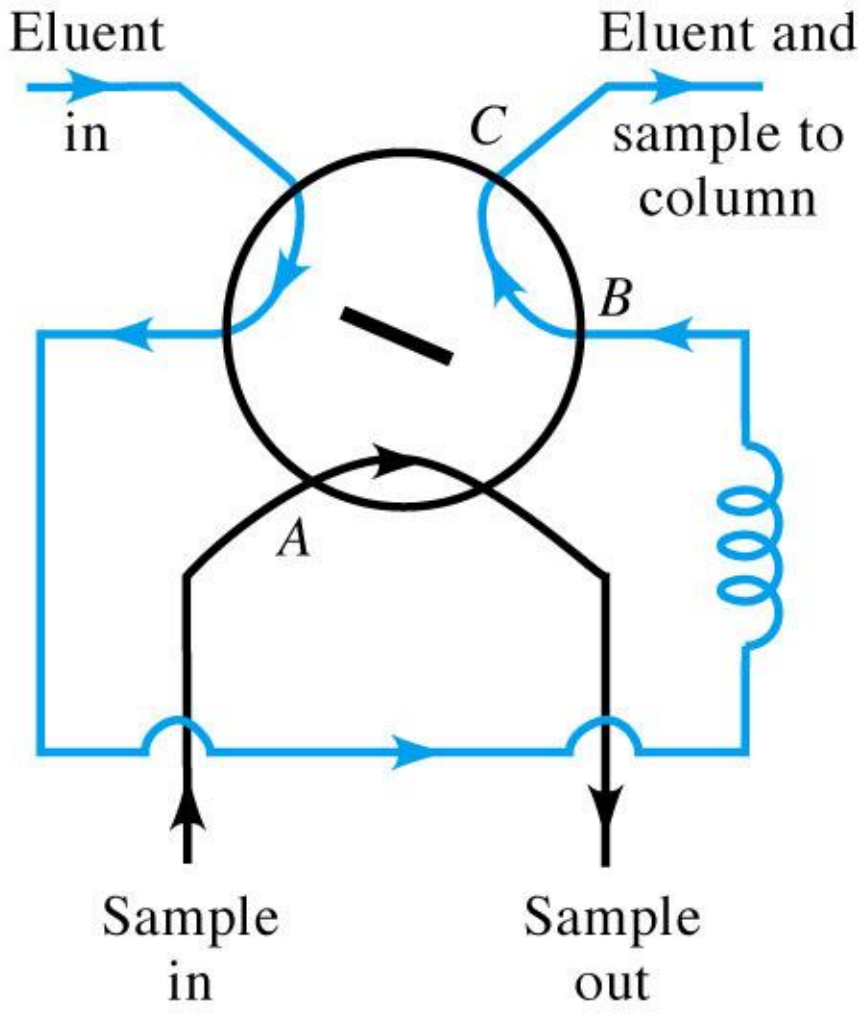


(b)

Column Configurations

- Two general types of columns are encountered in gas chromatography, **packed** and **open tubular**, or **capillary**.
- Chromatographic columns vary in length from less than 2 m to 50 m or more. They are constructed of stainless steel, glass, fused silica, or Teflon. In order to fit into an oven for thermostating, they are usually formed as coils having diameters of 10 to 30 cm.

Column Ovens

- Column temperature is an important variable that must be controlled to a few tenths of a degree for precise work. Thus, the column is ordinarily housed in a thermostated oven. 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.

Detection Systems

Characteristics of the Ideal Detector: The ideal detector for gas chromatography has the following characteristics:

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.

Characteristics of the Ideal Detector

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

The choice of detector will depend on the analyte and how the GC method is being used (i.e., analytical or preparative scale)

Flame Ionization Detectors (FID)

- Principle of operation:

  - measures the production of ions when a solute is burned in a flame.
  - ions are collected at an electrode to create a current

- FID most widely used and generally applicable detector for gas chromatography.
- 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.

Flame Ionization Detectors (FID)

- A potential of a few hundred volts is applied.
- The resulting current (~10^{-12} A) is then measured.
- FID exhibits a high sensitivity (~10^{-13} g/s), large linear response range (~10^{7}), and low noise.
- 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:
  - it is destructive of sample.

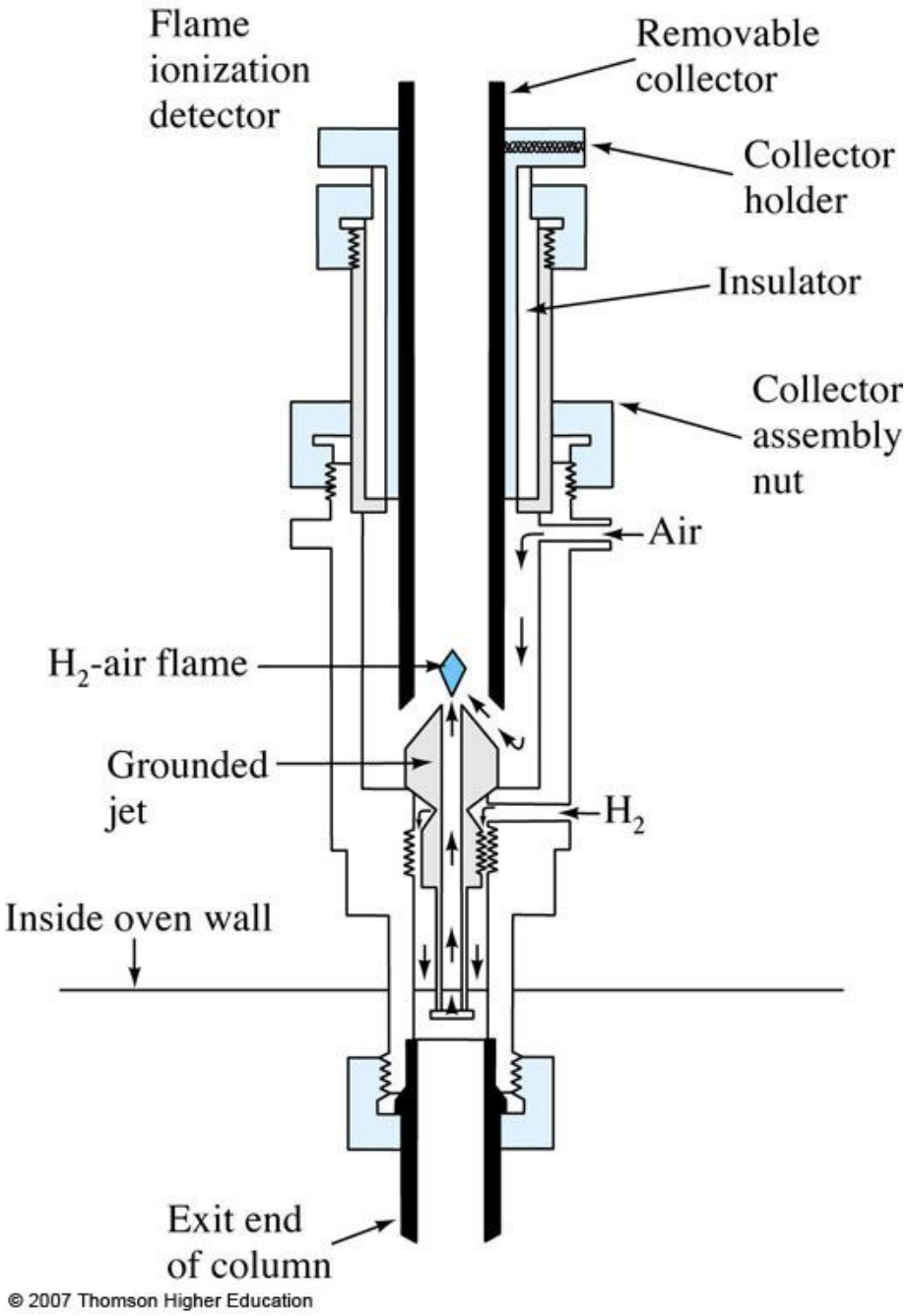


Fig: Flame Ionization Detector (FID)

Thermal Conductivity Detectors(TCD)

- A very early detector for GC,
- finds wide application, 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.

- Thermal conductivity changes with presence of other components in the mobile phase

Thermal Conductivity Detectors(TCD)

- Advantage:
  - simplicity,
  - large linear dynamic range(~10^5),
  - its general response to both organic and inorganic species, and
  - its nondestructive character, which permits collection of solutes after detection.
- A Limitation of the katharometer is its relatively low sensitivity (~10^{-8} g solute/mL carrier gas).
- detect mobile phase impurities
- sensitive to changes in flow-rates

Electron-Capture Detectors(ECD)

- widely used detectors for environmental samples because this detector selectivity detects halogen.
- Radioactive decay-based detector
- Selective for compounds containing electronegative atoms, such as halogens
- Principle of Operation
- Based on the capture of electrons by electronegative atoms in a molecule
- Electrons are produced by ionization of the carrier gas with a radioactive source such as ^{63}Ni (Nickel β emitter)
- In absence of solute, steady stream of these electrons is produced
- electrons go to collector electrode where they produce a current
- Compounds with electronegative atoms capture electrons, reducing current

Electron-Capture Detectors(ECD)

- Selective
- Highly sensitive to molecules containing electronegative functional groups such as halogens, peroxides, quinones, and nitro groups.
- It is insensitive to functional groups such as amines, alcohols, and hydrocarbons.
- An important application of ECD for detection and
  - -determination of chlorinated insecticides.
  - - detection of polynuclear aromatic carcinogens
  - - detection of organometallic compounds
- Selective for halogen- (I, Br, Cl, F), nitro-, and sulfur-containing compounds

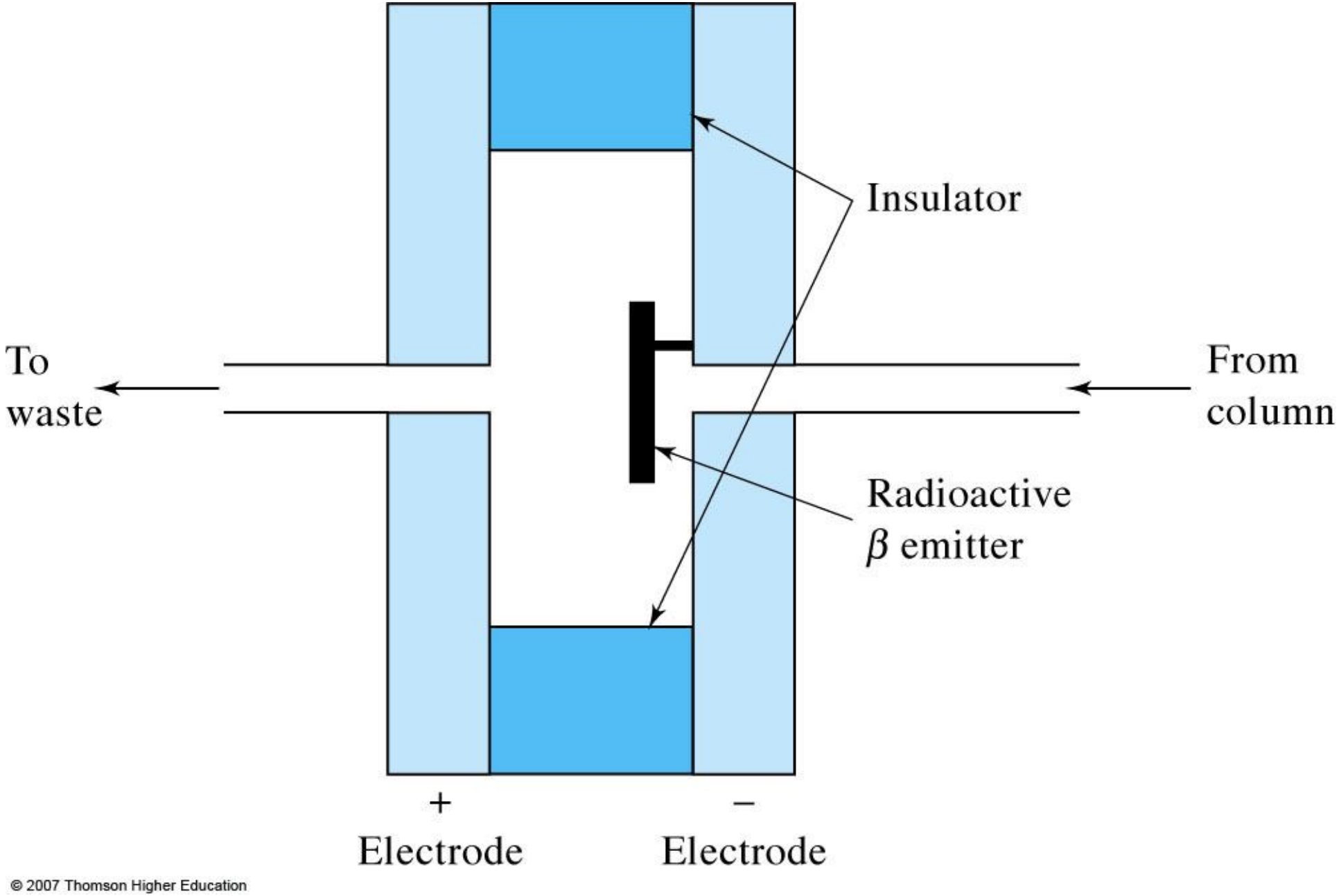


Fig: Electron Capture Detector (ECD)

Atomic Emission Detectors (AED)

- Selective for compounds containing sulfur and phosphorus (could be used for other elements by suitable changes in flame condition and filter)

- In this device the eluent is introduced into a microwave-energized helium plasma that is coupled to a diode array optical emission spectrometer. The plasma is sufficiently energetic to atomize all of the elements in a sample and to excite their characteristic atomic emission spectra.

Principle of Operation

- Decompose of analytes using H_2/Air flame
- Products emit bands of radiation

$$S_2^* \rightarrow S2 + h\nu\,(394\text{ nm})$$

Excited state S2* species could result from several two or three body collision reactions:

$$H + H + S_2 \rightarrow S_2^*$$

$$S + S \rightarrow S_2^*$$

$$S + S + M \rightarrow S_2^* + M \text{ (third body)}$$

For P

$$PO + H + M \rightarrow HPO^* + M$$

$$PO + OH + H_2 \rightarrow HPO^* + H2O$$

526 nm is given due to HPO*

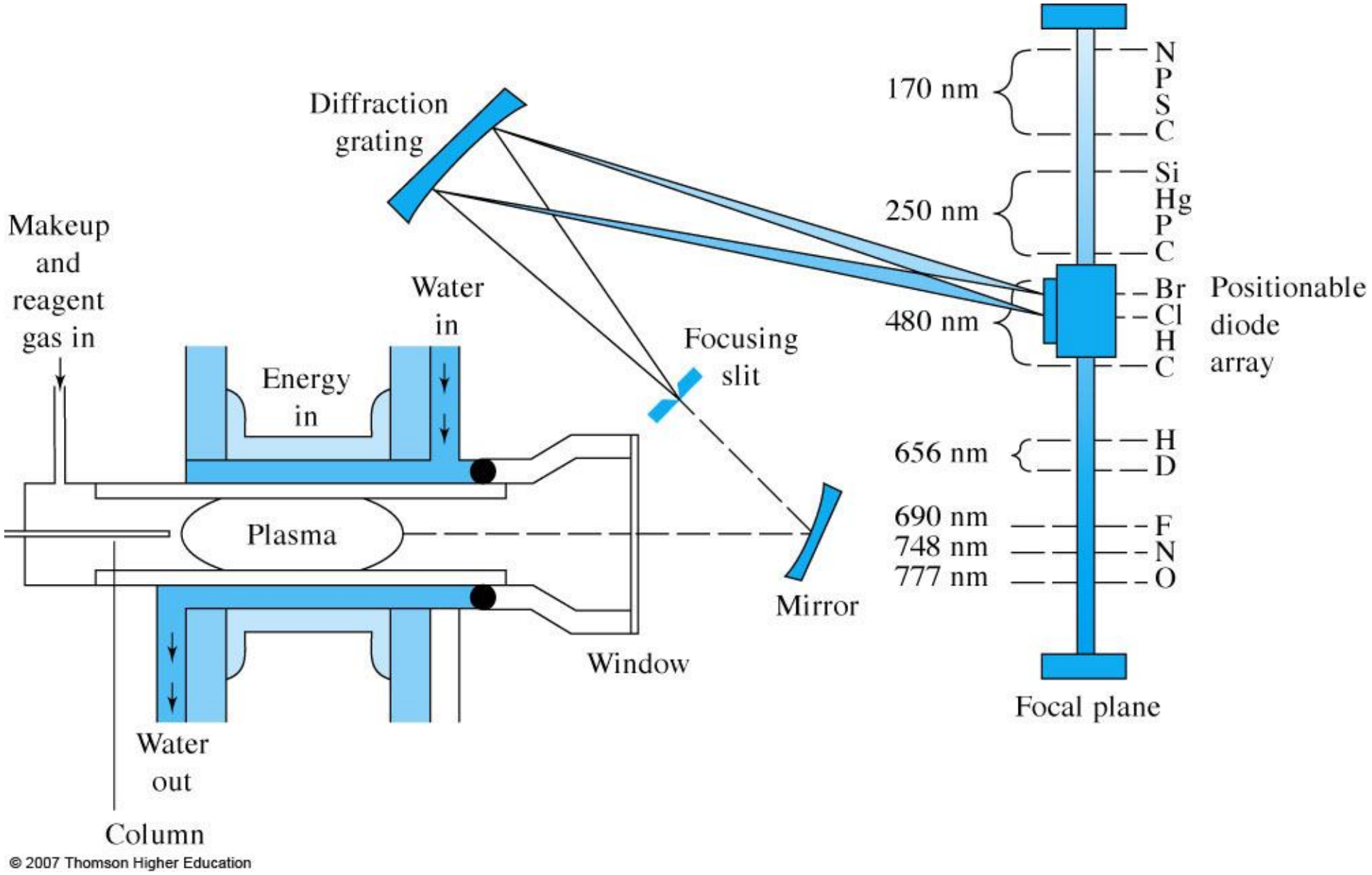


Fig: Atomic Emission Detectors (AED)

Thermionic Detectors (TID)

- also known as *Nitrogen-Phosphorus Detector (NPD)*
- selective toward organic compounds containing phosphorus and nitrogen.
- Its response to a phosphorus atom is approximately ten times greater than to a nitrogen atom and 10^4 to 10^6 larger than a carbon atom.
- more sensitive to phosphorus-containing compounds than FID and 50 times more sensitive to nitrogen bearing species.
- These properties make TCD particularly useful for detecting and determining the many phosphorus-containing pesticides.

Principle of Operation

- same basic principal as FID
- measures production of ions when a solute is burned in a flame
- ions are collected at an electrode to create a current
- contains a small amount of alkali metal vapor in the flame
- enhances the formation of ions from nitrogen- and phosphorus- containing compounds

Advantages:

- useful for environmental testing

detection of organophosphate pesticides

- useful for drug analysis

determination of amine-containing or basic drugs

- Like FID, does not detect common mobile phase impurities or carrier gases

- limit of detection: TID/NPD is **500**x better than FID in detecting nitrogen- and phosphorus- containing compounds

- TID/NPD more sensitive to other heterocompounds, such as sulfur-, halogen-, and arsenic- containing molecules

Disadvantages:

- Destructive detector
- TID/NPD is less sensitive to organic compounds compared to FID

GAS CHROMATOGRAPHIC COLUMNS

Open tubular Columns

Open tubular, or capillary, columns are of two basic types,

1. Wall—Coated Open Tubular (WCOT):

   simply capillary tubes coated with a thin layer of the stationary phase.

2. Support-Coated Open Tubular (SCOT):

   the inner surface of the capillary is lined with a thin film (~30 μm) of a support material, such as diatomaceous earth. WCOT column holds several times as much stationary phase & has a greater sample capacity.

Packed Columns

- fabricated from glass, metal (stainless steel, copper, aluminum), or Teflon tubes that
- lengths of 2 to 3 m and inside diameters of 2 to 4 mm.
- densely packed with a uniform, finely divided packing material, or solid support, that is coated with a thin layer (0.05 to μm) of the stationary liquid phase.
- In order to fit in a thermostating oven, the tubes are formed as coils having diameters of roughly 15 cm.

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).

Solid Support Materials

The most widely used support material is prepared from naturally occurring diatomaceous earth, which is made up of the skeletons of thousands of species of single-celled plants (diatoms) that 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.

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.

The Stationary Phase

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

(1) low volatility (ideally, the boiling point of the liquid should be at 100^{o}C higher than the maximum operating temperature for the column);

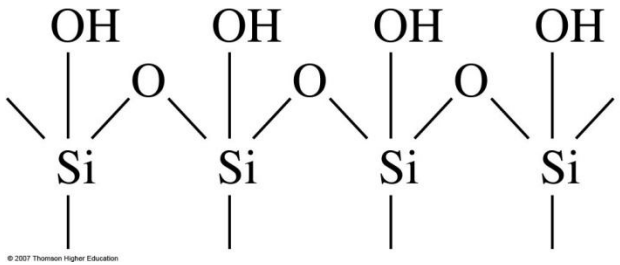
(2) thermal stability;

(3) chemical inertness;

(4) solvent characteristics such that k` and α values for the solutes to be resolved fall within a suitable range.

The retention time for a solute on a column depends upon its distribution constant (K) which in turn is related to the chemical nature of the stationary phase.

Silanol groups have strong affinity for polar organic molecules.



Support materials can be deactivated by silanization with dimethylchlorosilane (DMCS).

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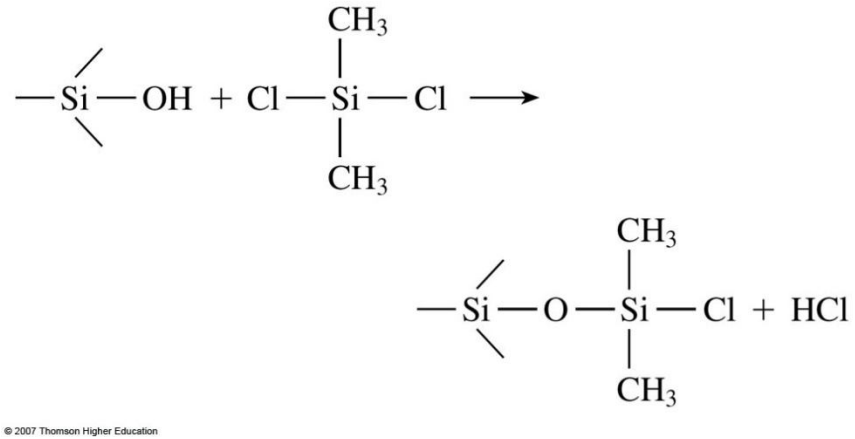

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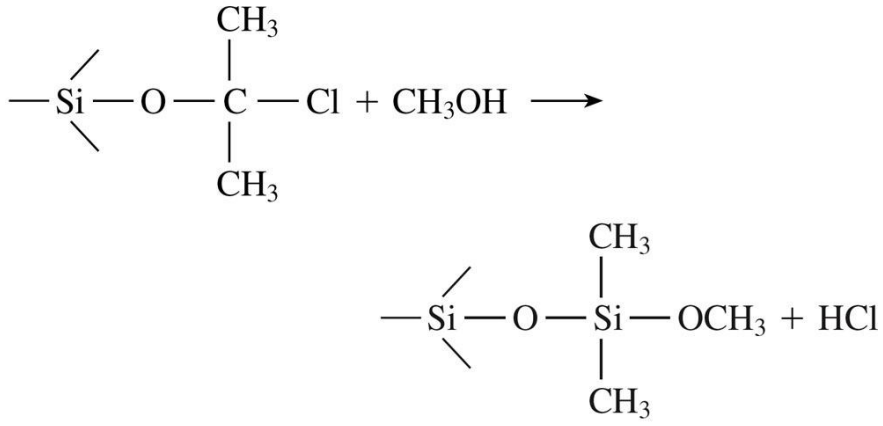


The Stationary Phase

- 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.
- Low volatility
- Thermal stability
- Chemical inertness

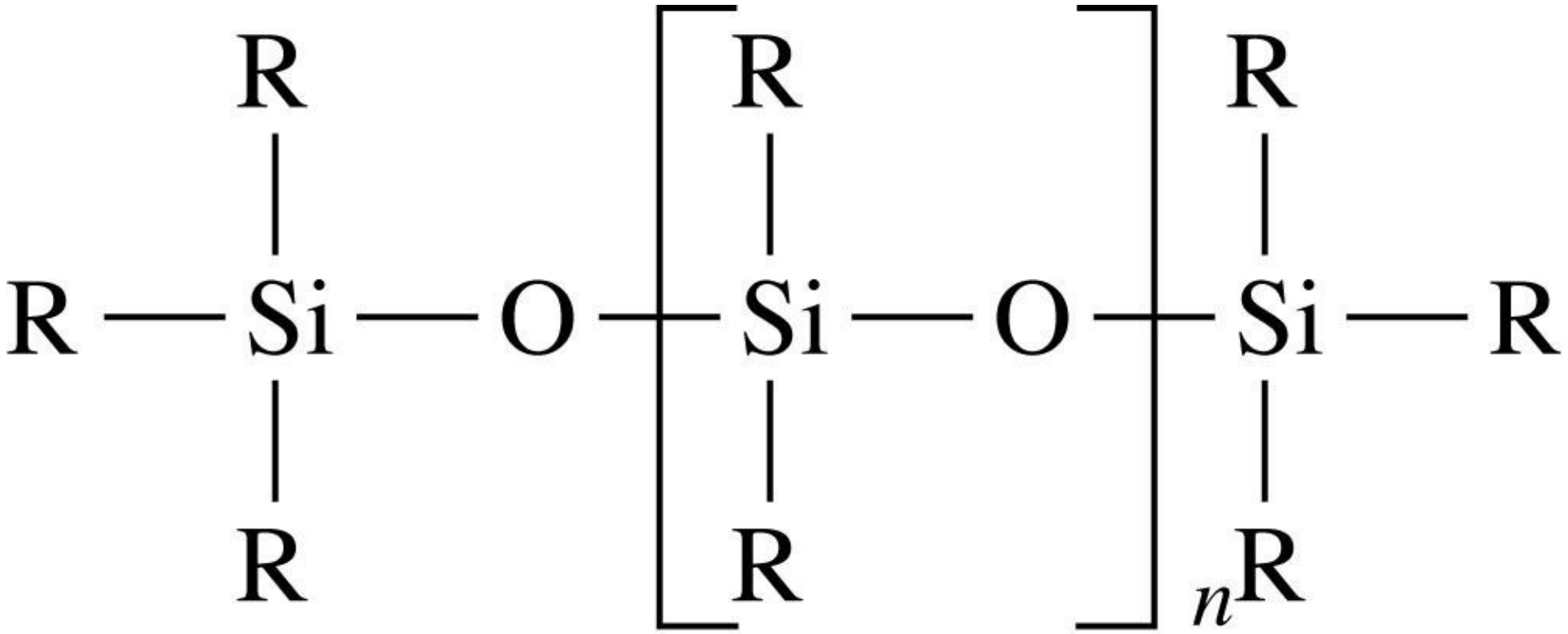
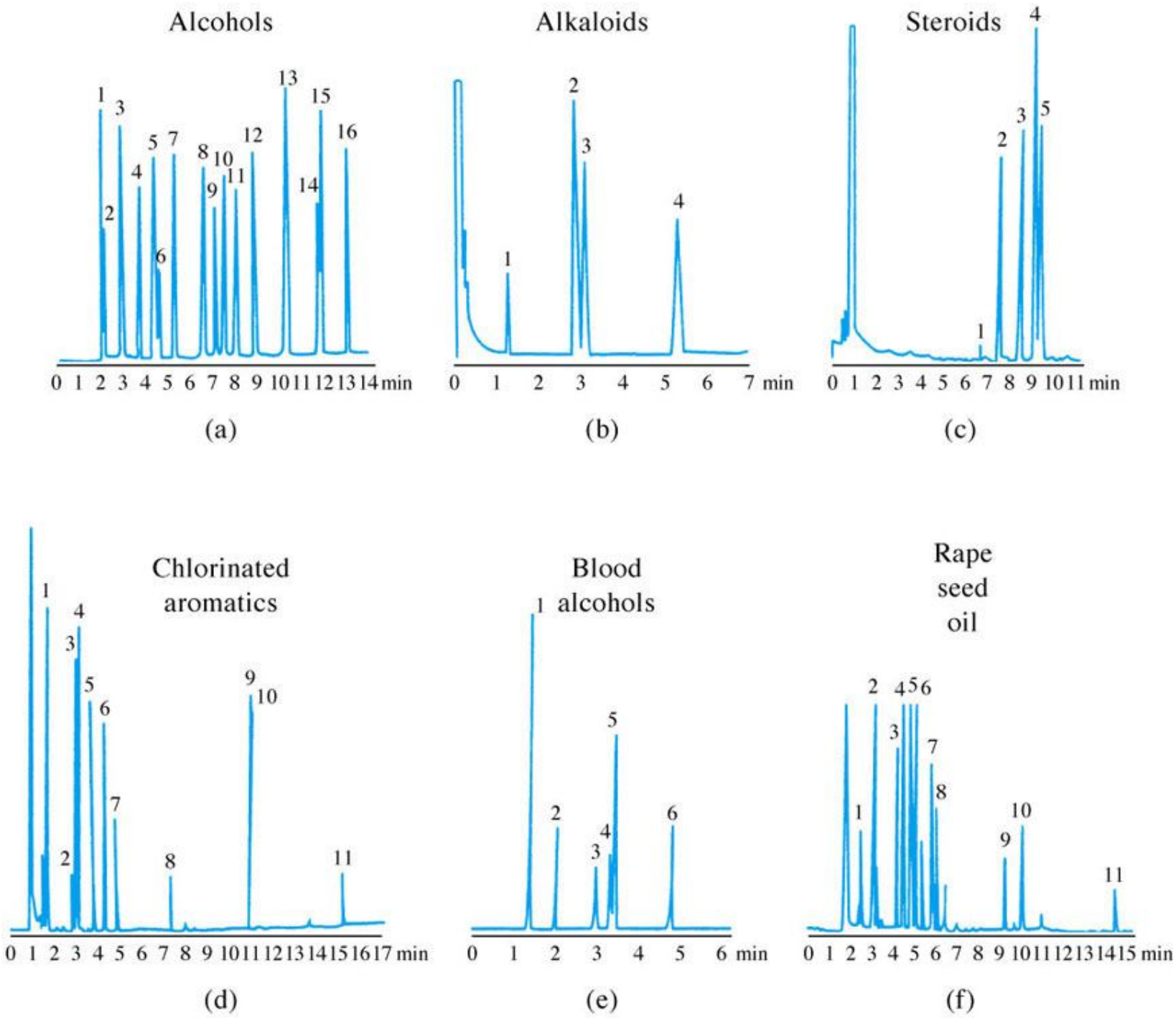


TABLE 27-3 Some Common Liquid Stationary Phases for GLC

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

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.



Qualitative Analysis

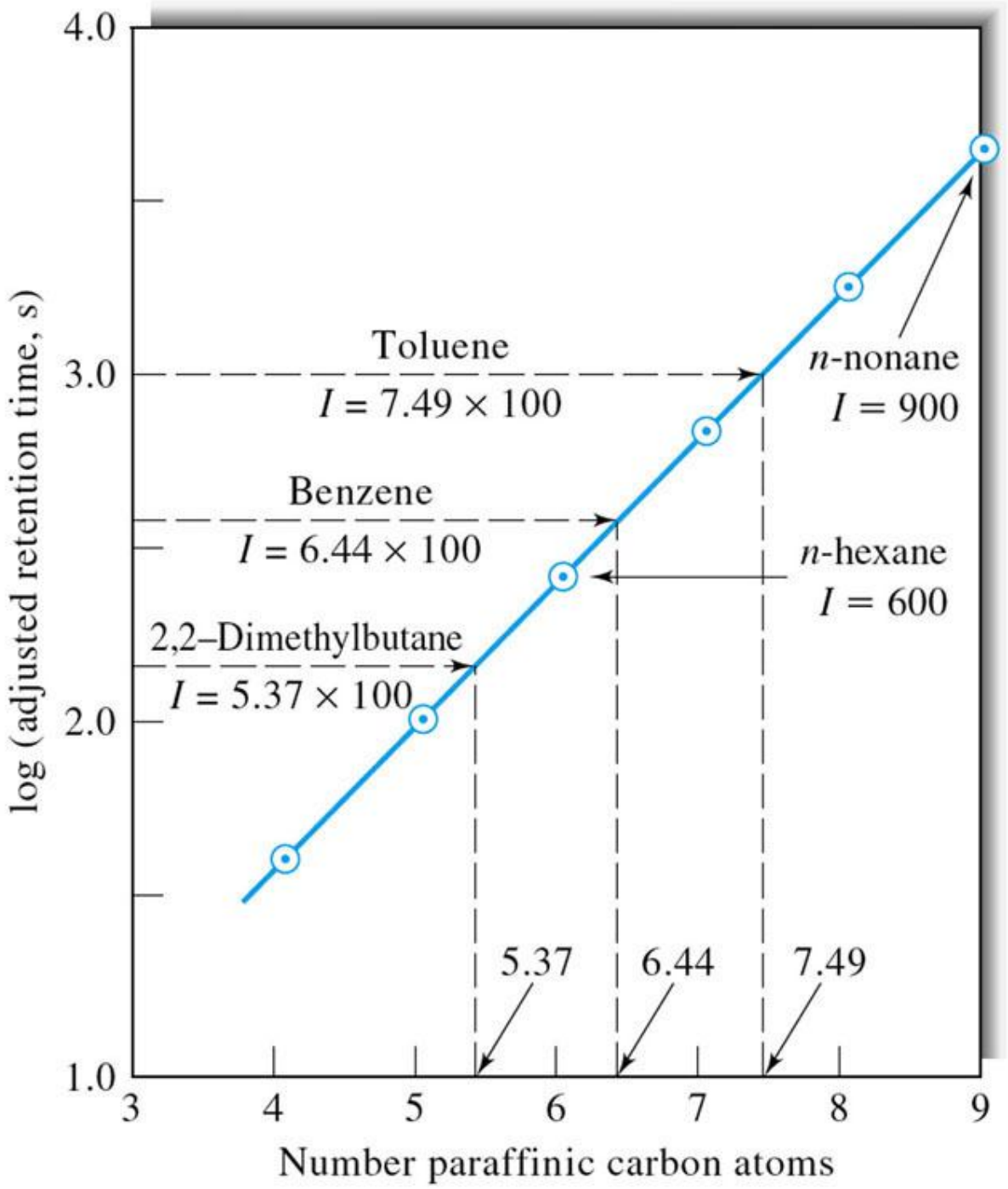
Gas chromatograms are widely used as criteria of purity for organic compounds. Contaminants, if present, are revealed by the appearance of additional peaks; the areas under these peaks provide rough estimates of the extent of contamination. The technique is also useful for evaluating the effectiveness of purification procedures. Retention times should be useful for the 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.

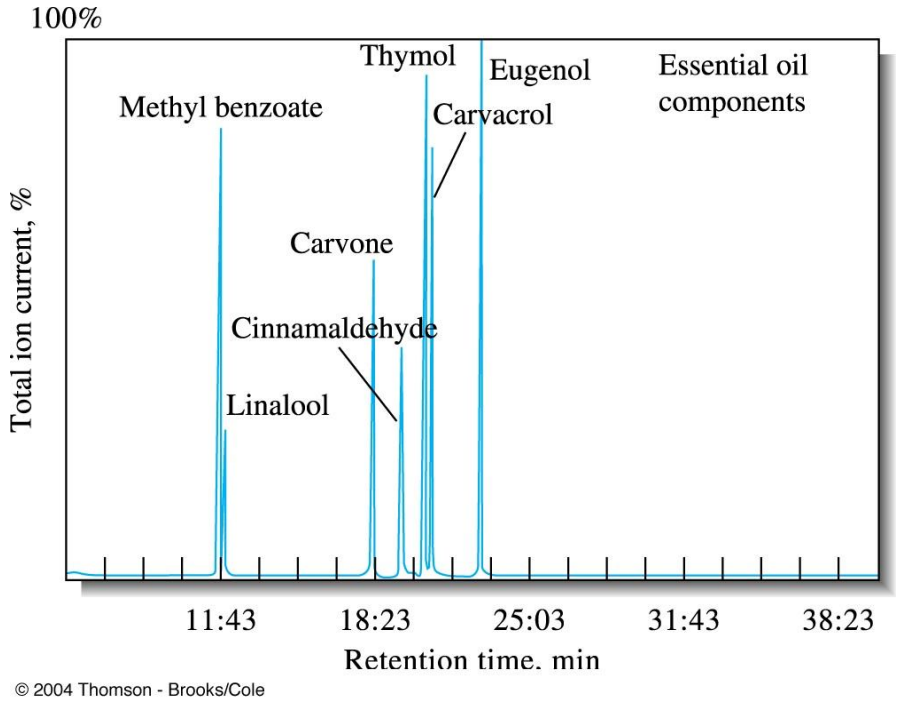
Quantitative Analysis

The detector signal from a gas-liquid chromatographic column has had wide use for quantitative and semiquantitative 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.



A Gas Chromatogram

Gas Chromatogram of Essential Oils with Mass Spectrometric Detection



Qualitative Information

Identity of eluted solutes may be based on

- Retention time
- Spectral information obtained for eluted peak

Quantitative Information is based on peak areas

Application:

- **Petroleum industry**
- **Herbicides & pesticides**
- **Food industry**
- **Biochemical & clinical field**
- **Cosmetics & Perfumes**
- **Pharmaceutical**
  - Analysis of solvent
  - Determination of alkyl & acryl resin
  - Determination of latex
- **Miscellaneous**
  - Determination of functional group
  - Determination of gas
  - Determination coal tar products
  - Determination of fertilizers
  - Determination of air pollutants
  - Determination of rubber & rubber products
  - Determination of soap & detergent
  - Water 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.

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.