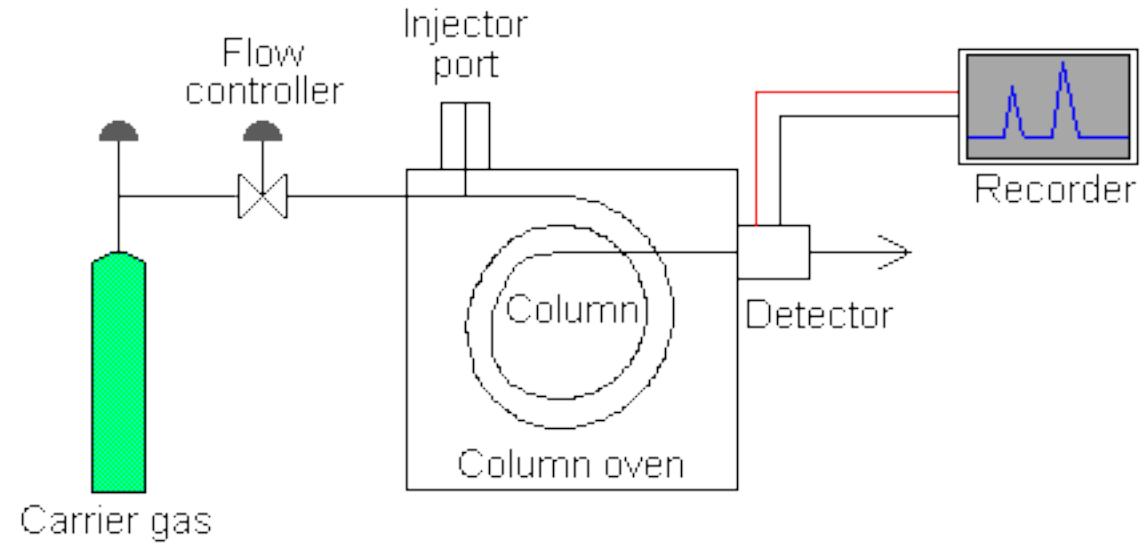
Chapter 27 – Introduction to Gas Chromatography

Read: pp. 701-721 Problems: 27-2,3,6,7,9,22

Gas chromatography involves a vaporized sample being injected into the head of a chromatographic column. Elution is brought about by the flow of an inert gas mobile phase. *In contrast to most other types of chromatography, the mobile phase does not interact with molecules of the analyte.* Its only function is to transport the analyte throught the column.

Two types: gas-solid and gas-liquid chromatography

Separation is based on differences in boiling points of the solutes and the solutes' interaction with the stationary phase.


Injector
port
Flow
controller
Recorder
Column
Detector
Column oven
Carrier gas

Volatile Organic Analysis in Soil

Inlet = 220 oC
Carrier = He
Flow = 1.5 ml/min
Column = 45 oC (2min) + 8 oC/min to 120 oC + 20 oC/ min to 150 oC

Table 1. Thirteen Aromatic Compounds and Two Internal Standards

Name	Name
Fluorobenzene(ISTD)	1,2-dichlorobenzene-D4(ISTD)
Benzene	1,3,5-Trimethylbenzene
Toluene	1,2,4-Trimethylbenzene
Ethyl benzene	pp-Isopropyltoluene
m-Benzene	n-Butylbenzene
Styrene	1,2,4-Trichlorobenzene
Bromobenzene	Naphthalene
	1,2,3-Trichlorobenzene

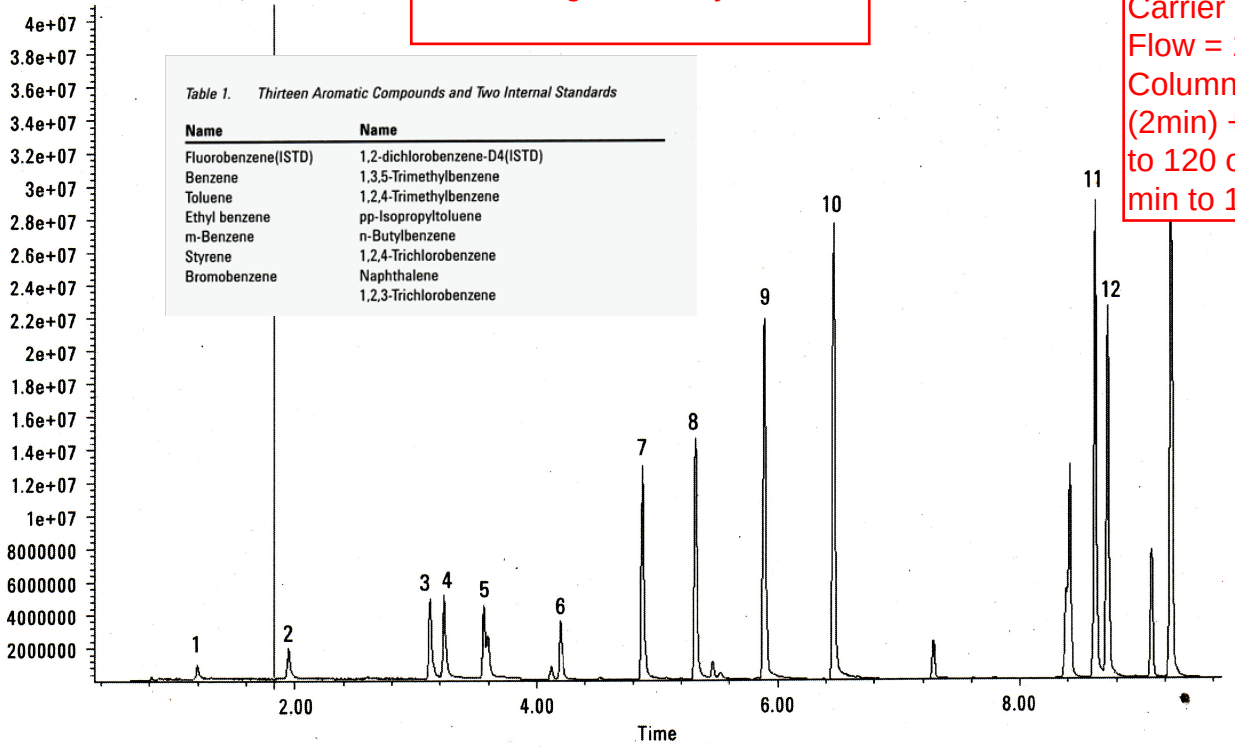


Figure 1. TIC of 13 volatile aromatic compounds, 20 µg/kg in soil; peak number is concurrent with Table 1.

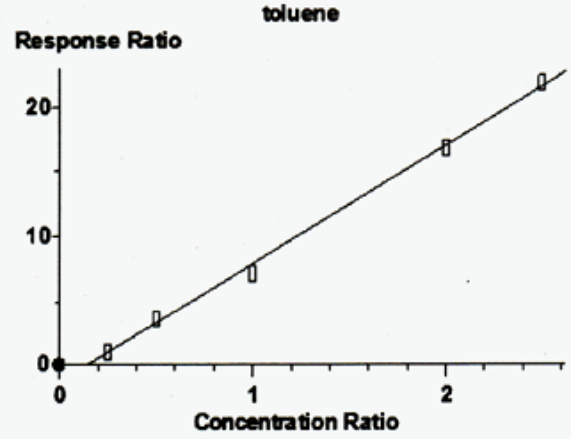


Figure 2. The linearity curve of toluene.

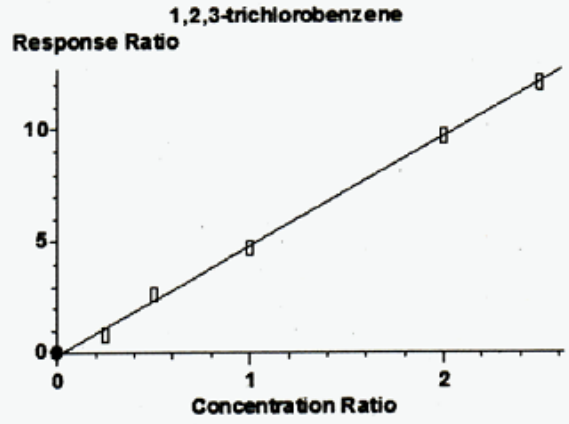


Figure 3. The linearity curve of 1,2,3-trichlorobenzene.

Bromobenzene

Naphthalene

1,2,3-Trichlorobenzene

Instrumentation

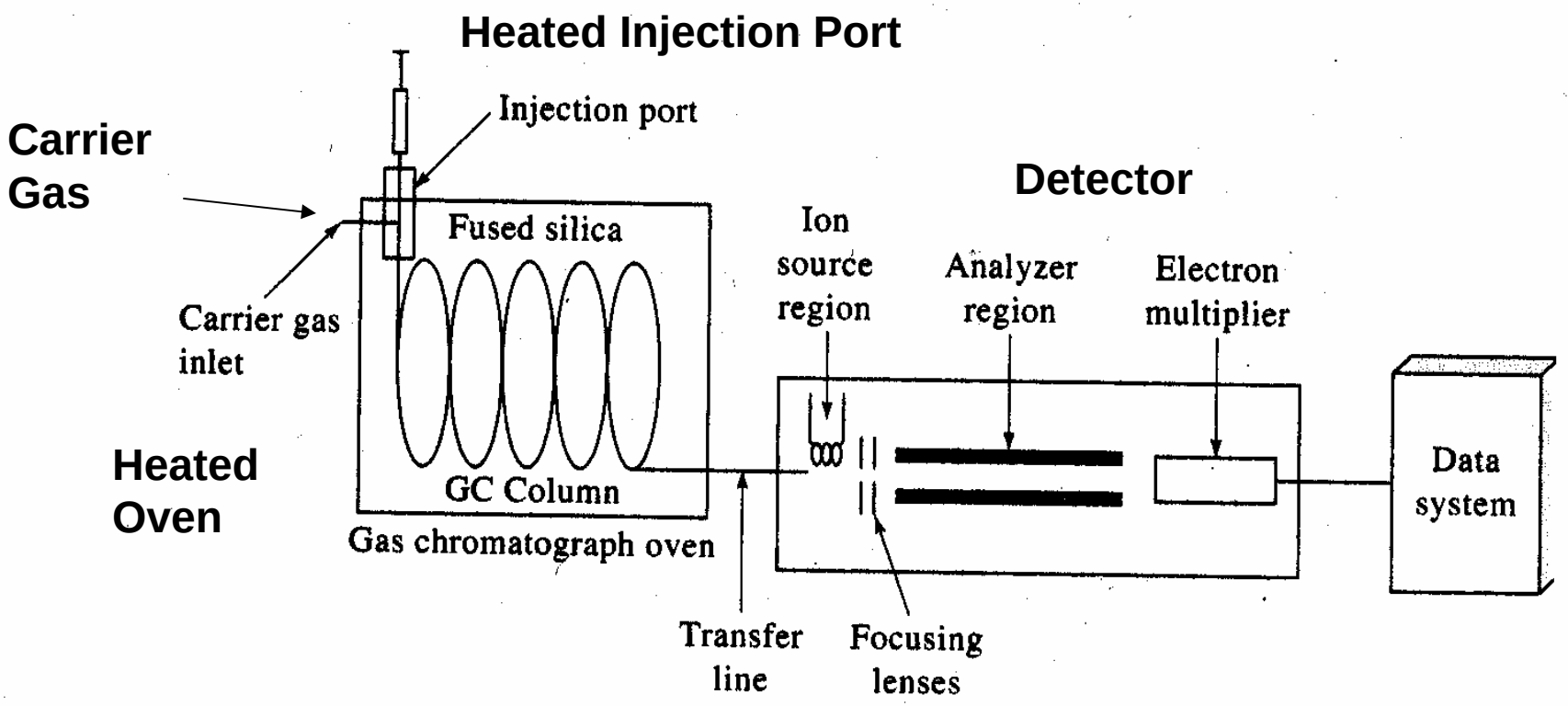
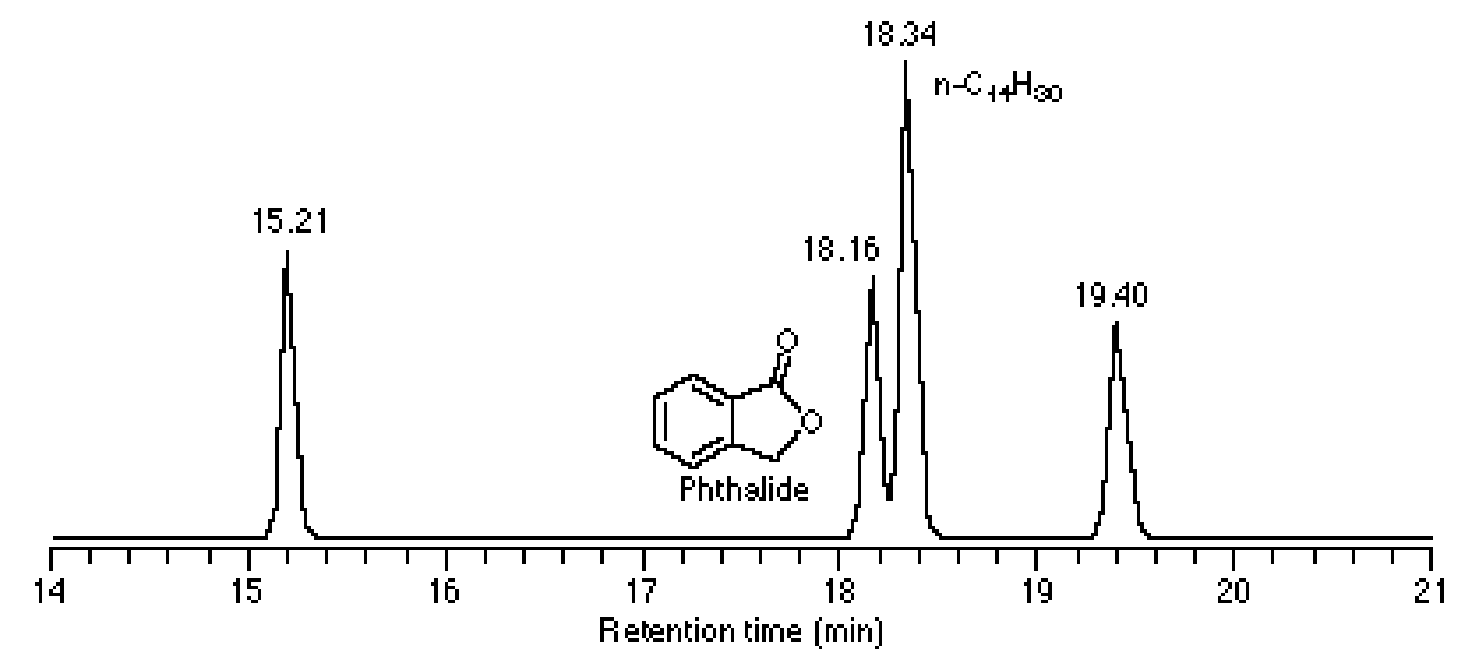
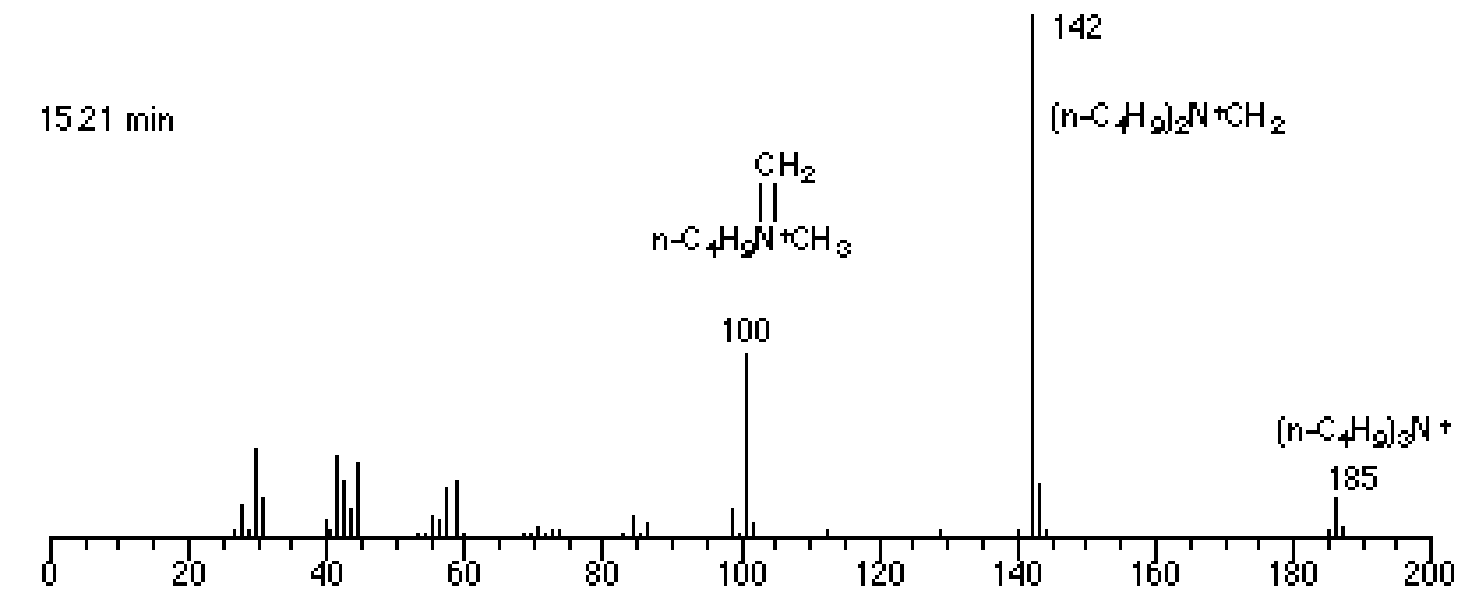
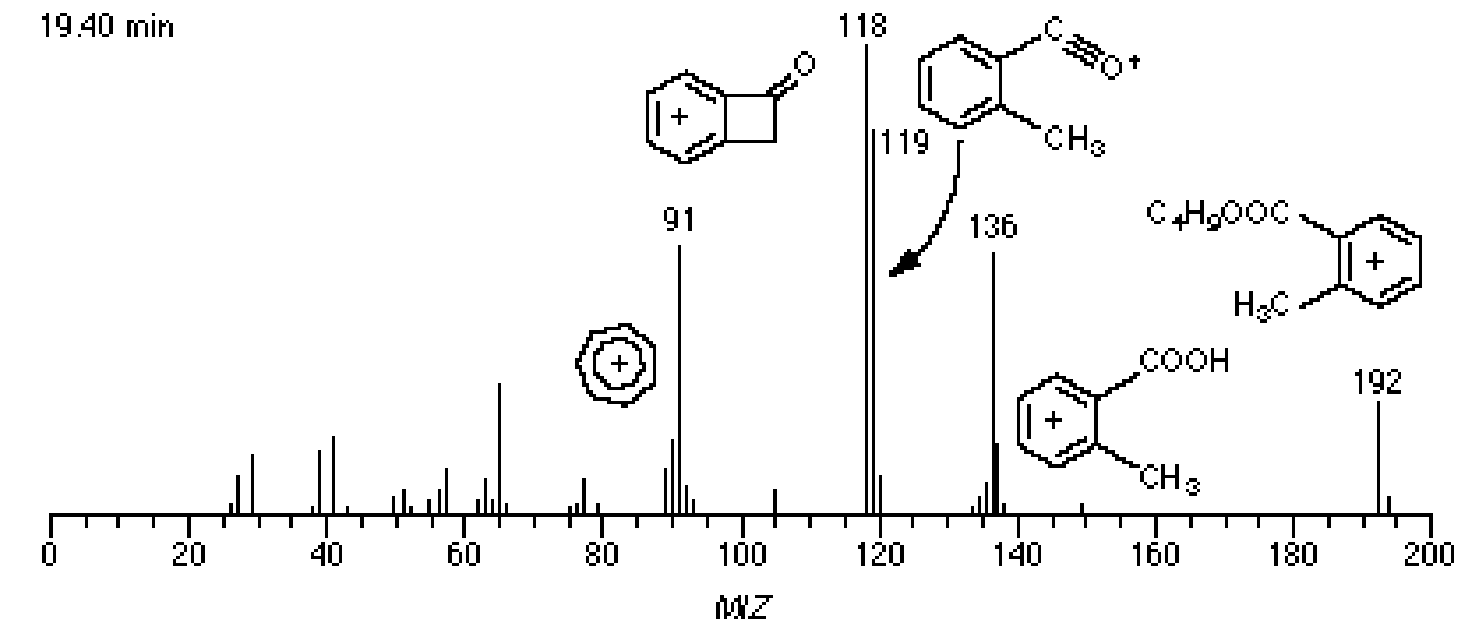


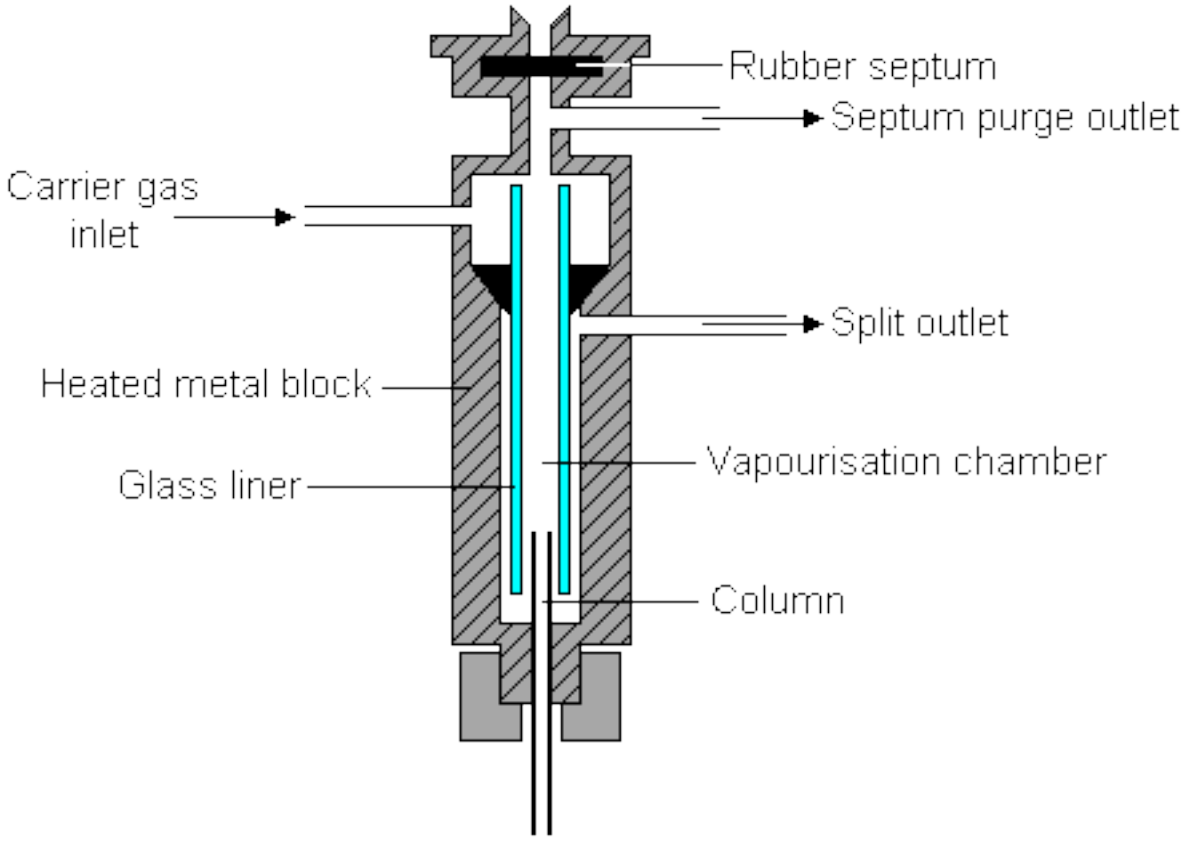
Figure 27-13 Schematic of a typical capillary gas chromatography/mass spectrometer.


18.34
n-C14H30
15.21
18.16
19.40
Phthalide
14
15
16
17
18
19
20
21
Retention time (min)


15.21 min
142
(n-C4H9)2N+CH2
CH2
n-C4H9N+CH3
100
(n-C4H9)3N+
185
0
20
40
60
80
100
120
140
160
180
200


19.40 min
118
119
91
136
C4H9OOC
H3C
COOH
CH3
192
0
20
40
60
80
100
120
140
160
180
200
M/Z

The split / splitless injector



Injector

Function is to introduce a plug of vapor.

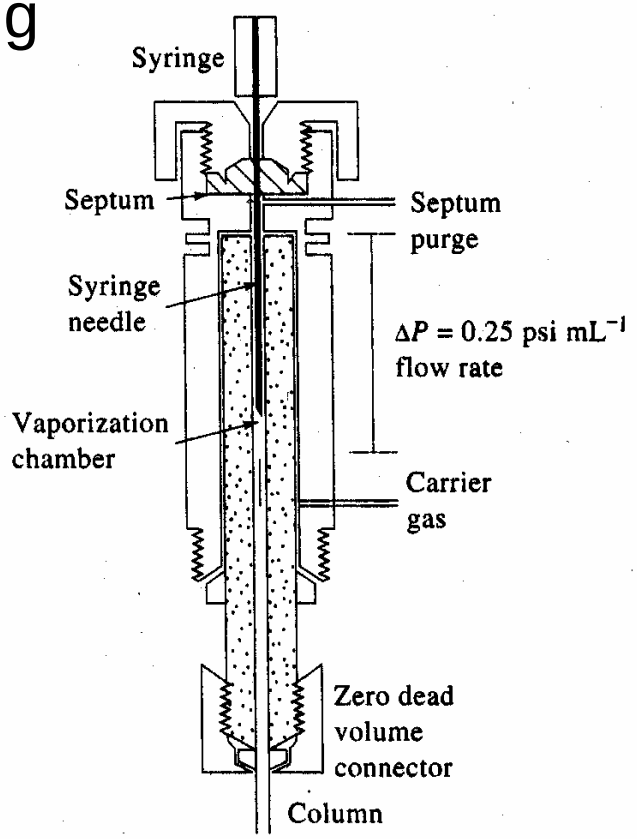


Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

20-50 μL volume for normal size columns.

Ordinarily about 50 °C above the least volatile component in the sample.

Capillary columns require injection volumes of a few nL.

Column Types

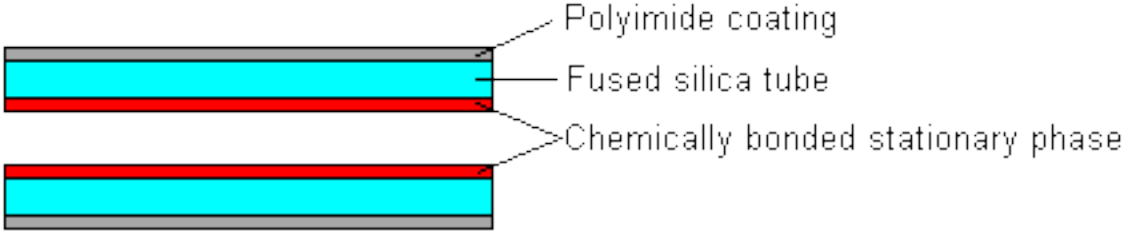
There are three general types of columns used in modern day separations:

1. Packed (filled with a “pseudospherical” support material that the stationary phase material is bonded to)
2. Open tubular (inner walls of the tube are coated with a liquid or solid stationary phase material)
3. Capillary columns

Packed columns are most often used. 1-10 m length, 2-4 mm in diameter, particle size 1-10 μm.

The optimum column temperature depends on the boiling point of the sample and the degree of separation required.

Cross section of a Fused Silica Open Tubular Column



Columns

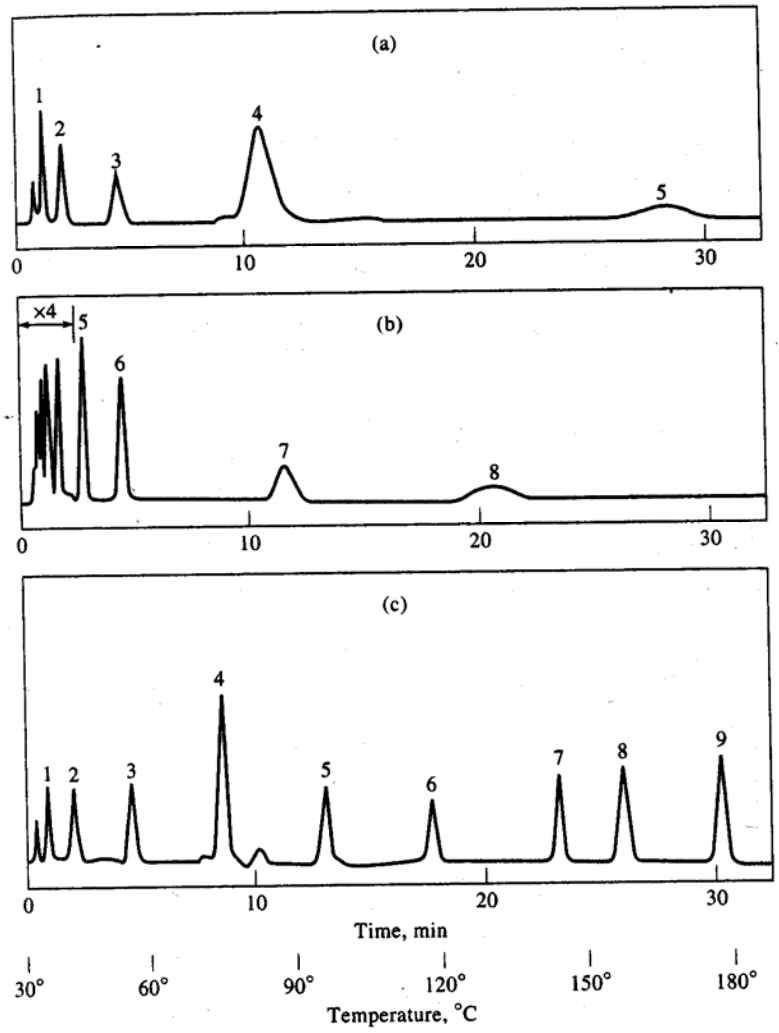


Figure 27-5 Effect of temperature on gas chromatograms: (a) isothermal at 45°C; (b) isothermal at 145°C; (c) programmed at 30° to 180°C. *(From W. E. Harris and H. W. Habgood,* Programmed Temperature Gas Chromatography, *p. 10. New York: Wiley, 1966. Reprinted by permission of John Wiley & Sons, Inc.)*

A separation temperature roughly above the average boiling point of the sample results in a 2-30 min elution time.

*****Temperature programming*****

Optimum resolution is associated with minimal temperature. The cost of lowered temperature is an increase in the elution time and therefore the time required to complete the analysis.

GC Instrument Design

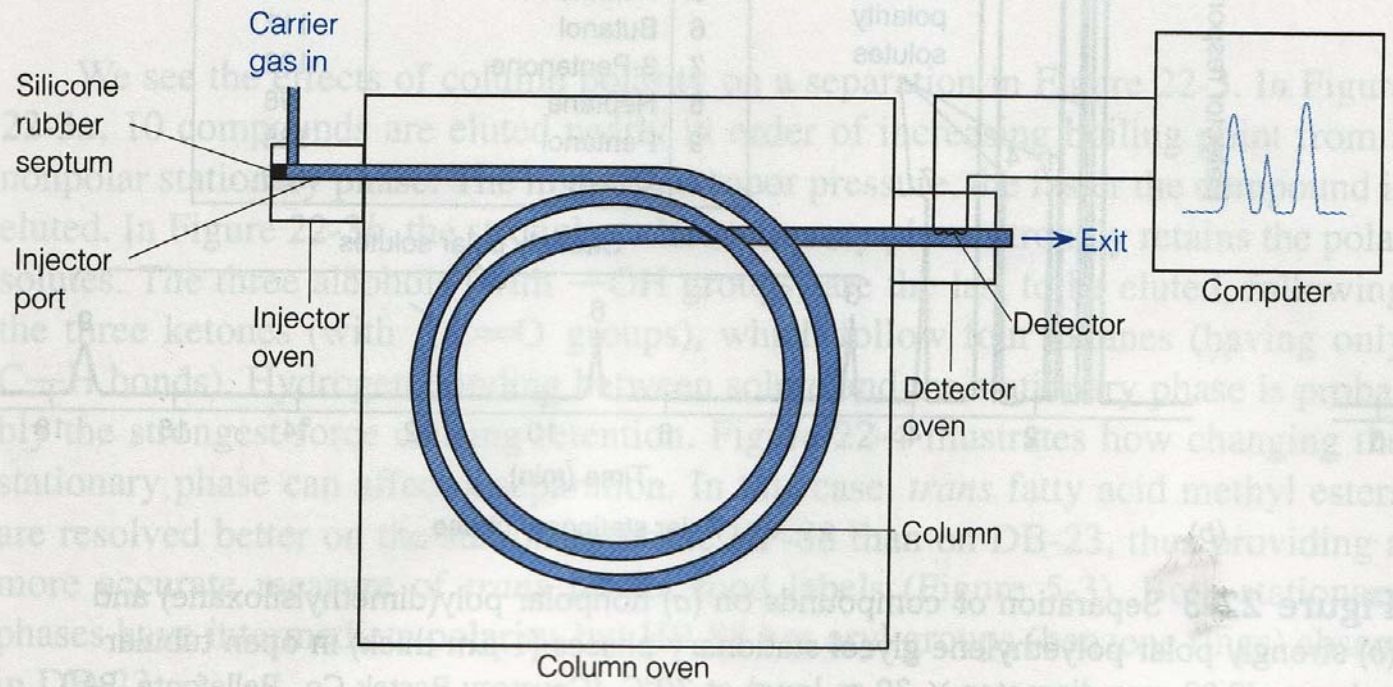


Figure 22-1 Schematic representation of a gas chromatograph.

Price paid for higher speed is reduced resolving power and reduced peak capacity.

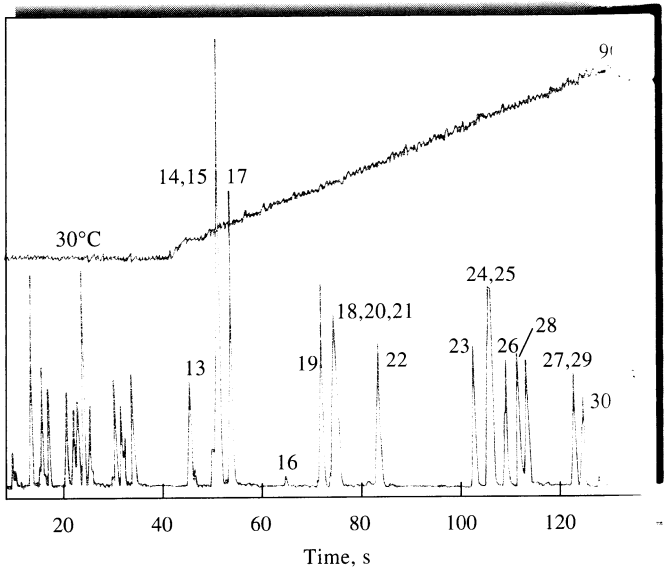


FIGURE 27-19 High-speed chromatogram obtained with isothermal operation (30°C) for 37 s followed by a 35°C/min temperature ramp to 90°C. (From H. Smith and R. D. Sacks, *Anal. Chem.*, **1998**, *70*, 4960. Copyright 1998 American Chemical Society.)

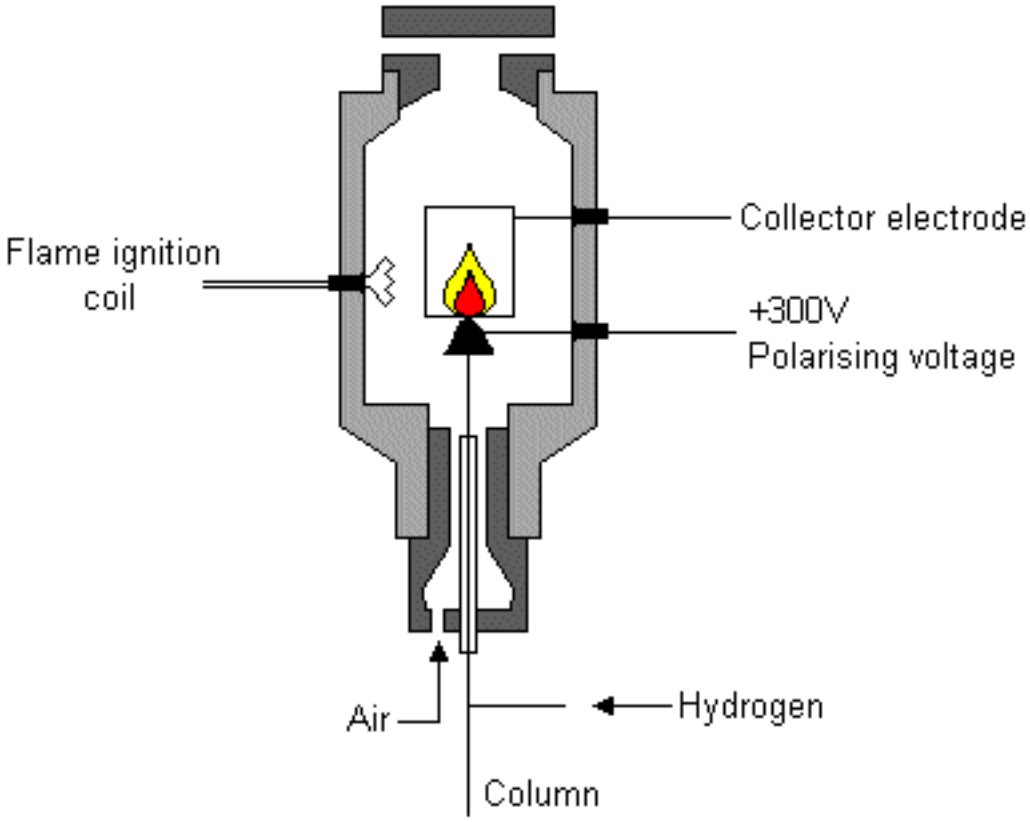
Separations at a higher speed albeit at the expense of some selectivity and resolution

Detectors

Ideal Detector Properties

1. Adequate sensitivity (slope of the response curve)
2. Good stability and reproducibility
3. A linear dynamic range 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. Highly reproducible and easy to use
7. A predictable response toward all solutes
8. Nondestructive to the sample

The Flame Ionisation Detector



Detectors

Flame Ionization Detector

100's V applied

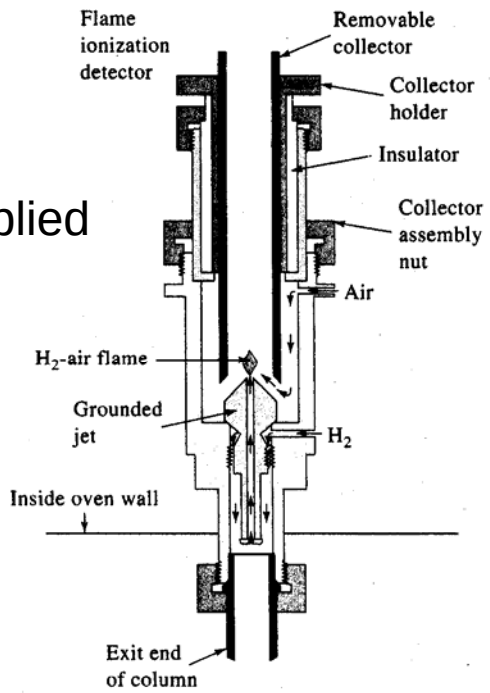


Figure 27-6 A typical flame ionization detector. *(Courtesy of Hewlett-Packard Company.)*

Widely used and generally applicable.

Effluent from column is mixed with H_2 and air and ignited electrically.

Organic compounds, when pyrolyzed, produce ions and electrons.

Number of ions produced is a function of the number of carbon atoms in the molecule. Good for the analysis of most organics.

Detector insensitive toward noncombustible gases, such as H_2O, CO_2, SO_2 and NOx.

LDR = 4-7 orders of magnitude
LOD = low ppb range (S/N>3)
Destructive to the sample!

Detectors

Thermal Conductivity Detector

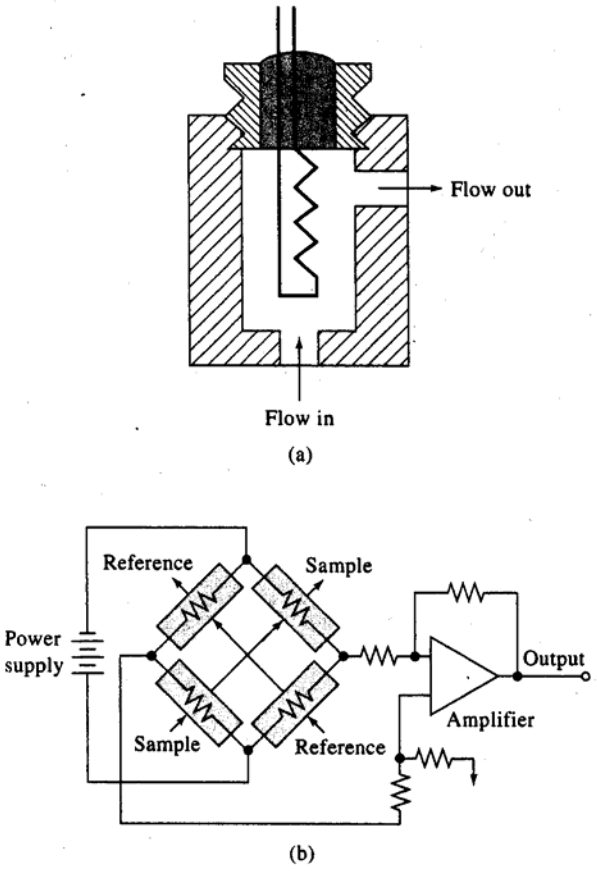


Figure 27-7 Schematic of (a) a thermal conductivity detector cell, and (b) an arrangement of two sample detector cells and two reference detector cells. *(From J. V. Hinshaw, LC-GC, 1990, 8, 298. With permission.)*

A very general or universal detector.

Response results from changes in the thermal conductivity of a gas stream brought about by the presence of an analyte.

Thermal conductivity of He and H_2 (carrier gases) is roughly 10x greater than that for most organic molecules.

Filament heated resistively to a constant temperature. The electrical power needed to maintain a constant temperature depends on the thermal conductivity of the surrounding gas. Small amount of analyte produces a big temperature change (increase) in the filament.

LDR = 3-5 orders of magnitude
LOD = ppm range (S/N>3)

Detectors

Electron Capture Detector

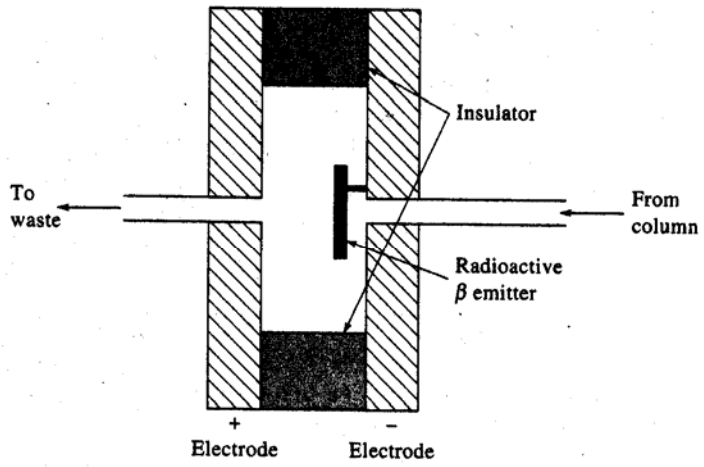


Figure 27-8 A schematic of an electron-capture detector.

Widely used for environmental analysis.

Very good for detecting halogenated compounds, like pesticides and polychlorinated biphenyls.

Electron from a β-emitter ionizes the carrier gas, often N_2, and produces a burst of electrons. A constant current is measured in the absence of any analyte.

Analytes that capture electrons reduce the current.

LDR = 3-5 orders of magnitude
LOD = low ppb to high ppt levels (S/N>3)

Detector Summary

Gas chromatography detectors:

- *flame ionization:* responds to compounds with C—H
- *thermal conductivity:* responds to everything, but not sensitive enough for columns <0.53 mm in diameter
- *electron capture:* halogens, conjugated C=O, —C≡N, $—NO_2$
- *flame photometer:* P and S
- *alkali flame:* P and N
- *sulfur chemiluminescence:* S
- *mass spectrometer:* responds to everything

Stationary Phases

There are three general types of columns/stationary phases:

1. **Packed columns** - (stationary phase supported on small particles).

2. **Open tubular columns** – wall-coated (thin layer of stationary phase material, 30 μm thick) and support-coated (diatomaceous earth support coated on the wall, and stationary phase bonded to this).

3. **Fused silica open tubular columns** – chemically modified inner wall. Direct bonding to the wall surface (100-500 μm diam.).

N values can be 100,000 to 500,000 plates for OT format.

Types of Columns

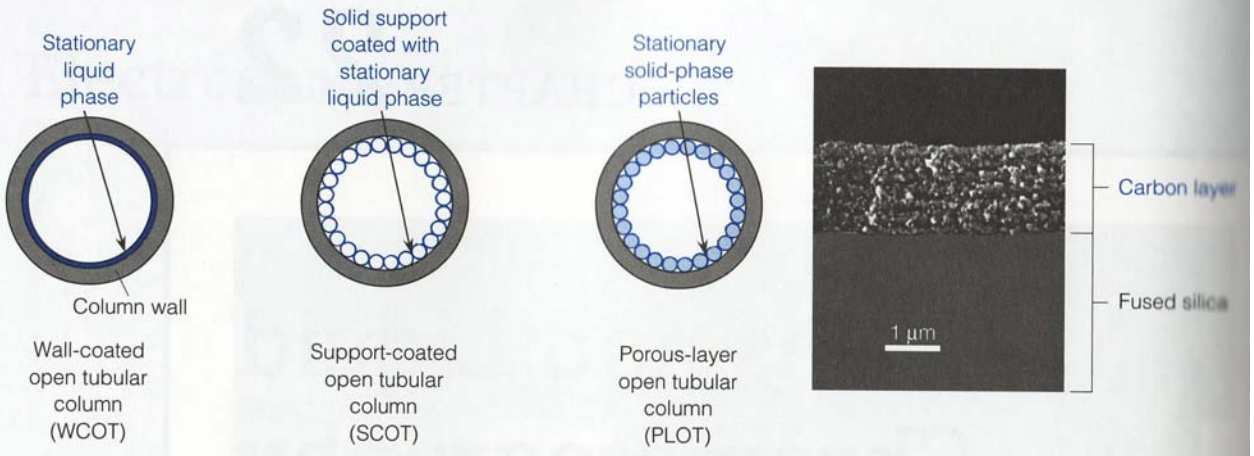
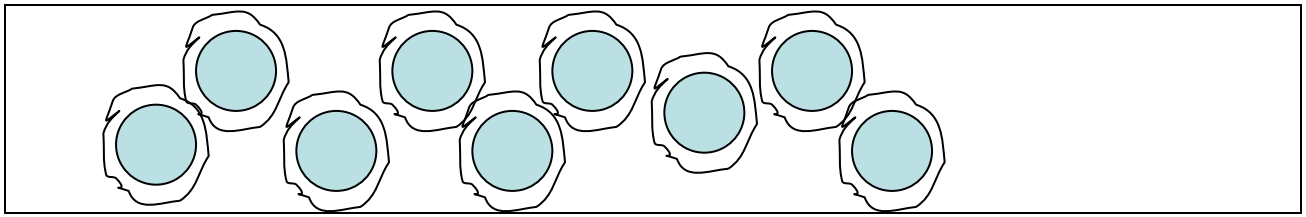


Figure 22-2 Cross-sectional view of wall-coated, support-coated, and porous-layer columns. Micrograph shows porous carbon stationary phase on inside wall of a fused-silica open tubular column.

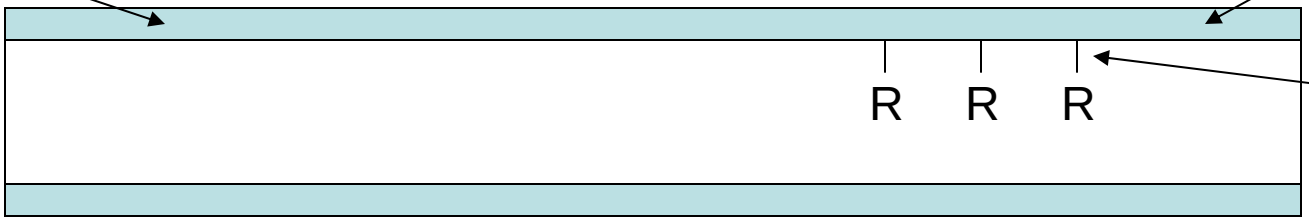
Stationary Phases



Packed Column

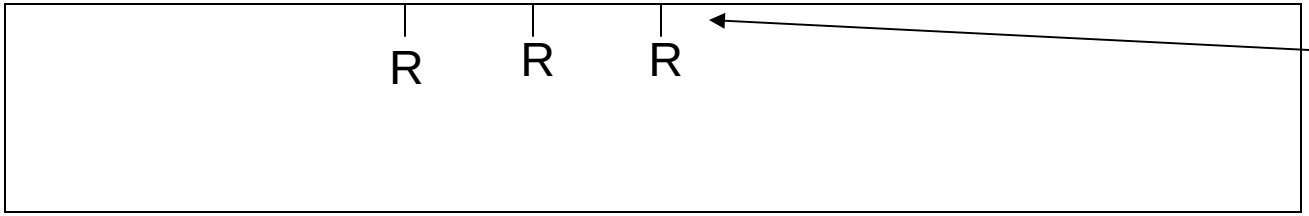
Stationary Phase

Support



Bonded Stat. Phase

Open Tubular Column



Bonded Stat. Phase

Fused Silica Open Tubular Column

Stationary Phases

TABLE 27-1 Properties and Characteristics of Typical Gas-Chromatographic Columns

	Type of Column*			
	FSOT	WCOT	SCOT	Packed
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.53	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Total plates	$(20–400) \times 10^3$	$(10–400) \times 10^3$	$(6–120) \times 10^3$	$(1–10) \times 10^3$
Sample size, ng	10–75	10–1000	10–1000	$10–10^6$
Relative back pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Chemical inertness	Best →			Poorest
Flexible?	Yes	No	No	No

*FSOT: Fused-silica, open tubular column.
WCOT: Wall-coated, open tubular column.
SCOT: Support-coated open tubular column.

Stationary Phases

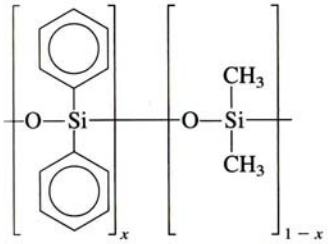
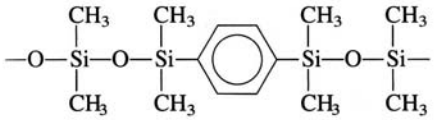
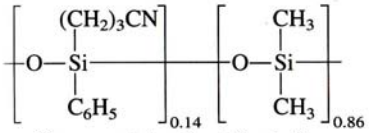
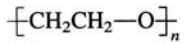
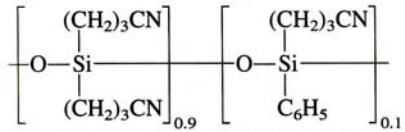
TABLE 27-2 Some Common Stationary Phases for Gas-Liquid Chromatography

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

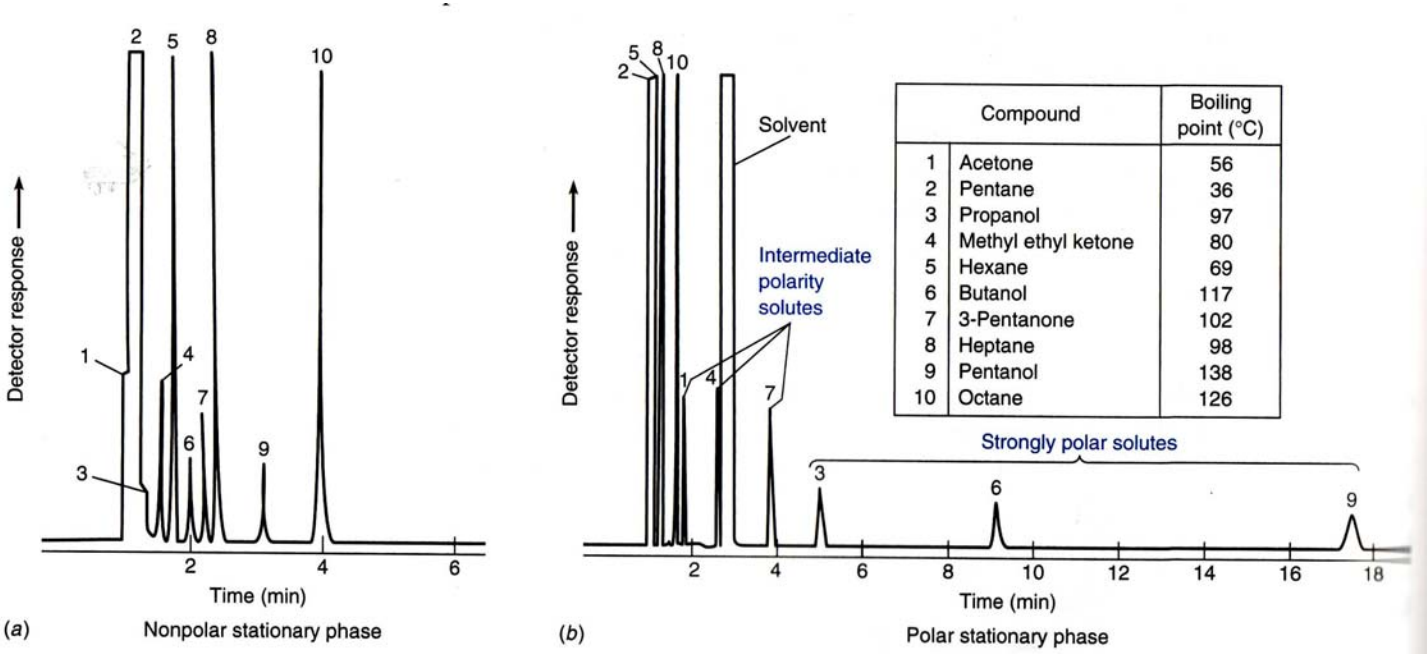
Like interacts with like!!!

Common Stationary Phases

Table 22-1 Common stationary phases in capillary gas chromatography

Structure	Polarity	Temperature range
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$	Nonpolar	−60° to 360°C
	$x = 0.05$	Nonpolar	−60° to 360°C
	$x = 0.35$	Intermediate polarity	0° to 300°C
	$x = 0.65$	Intermediate polarity	50° to 370°C
 Arylene polysiloxane	Arylene stationary phases with low "bleed" (less thermal decomposition) at high temperature are available in compositions similar to other polysiloxanes in this table.	
 (Cyanopropylphenyl)$_{0.14}$(dimethyl)$_{0.86}$ polysiloxane	Intermediate polarity	−20° to 280°C
 Carbowax (polyethylene glycol)	Strongly polar	40° to 250°C
 (Biscyanopropyl)$_{0.9}$(cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar	0° to 275°C

Example Separation



	Compound	Boiling point (°C)
1	Acetone	56
2	Pentane	36
3	Propanol	97
4	Methyl ethyl ketone	80
5	Hexane	69
6	Butanol	117
7	3-Pentanone	102
8	Heptane	98
9	Pentanol	138
10	Octane	126

Figure 22-3 Separation of compounds on (*a*) nonpolar poly(dimethylsiloxane) and (*b*) strongly polar polyethylene glycol stationary phases (1 μm thick) in open tubular columns (0.32 mm diameter × 30 m long) at 70°C. [Courtesy Restek Co., Bellefonte, PA.]

Why is the Efficiency, N, so Different?

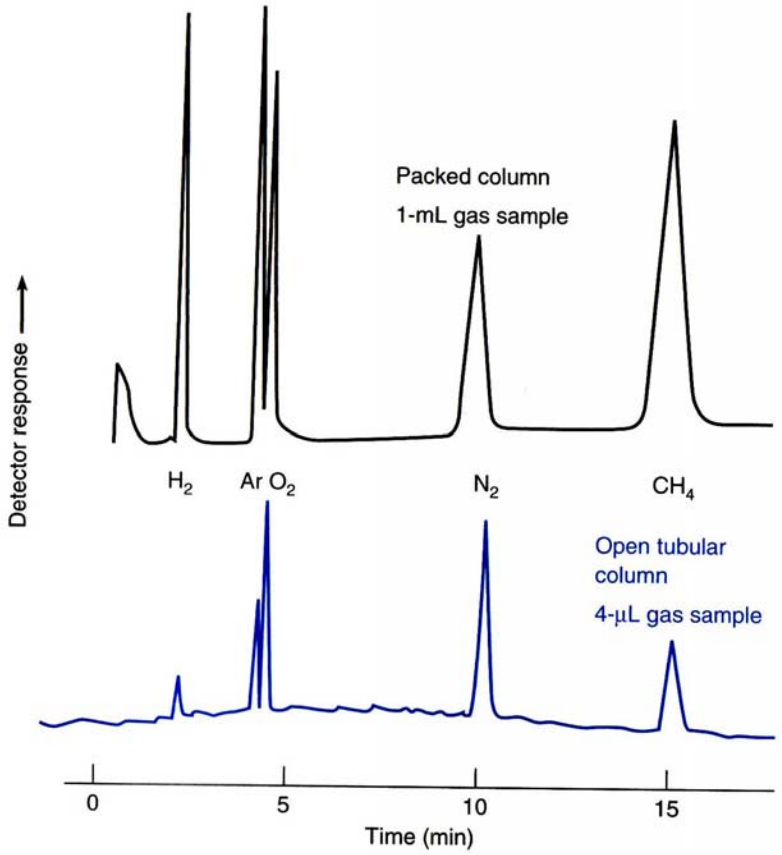


Figure 22-5 Gas chromatography with 5A molecular sieves. Upper chromatogram was obtained with a packed column (3.2 mm diameter × 4.6 m long) at 40°C, by using 1 mL of sample containing 2 ppm (by volume) of each analyte in He. Lower chromatogram was obtained with an open tubular column (0.32 mm diameter × 30 m long) at 30°C, by using 4 μL of the same sample. [From J. Madabushi, H. Cai, S. Steams, and W. Wentworth, *Am. Lab.* October 1995, p. 21.]

Examples of Separations

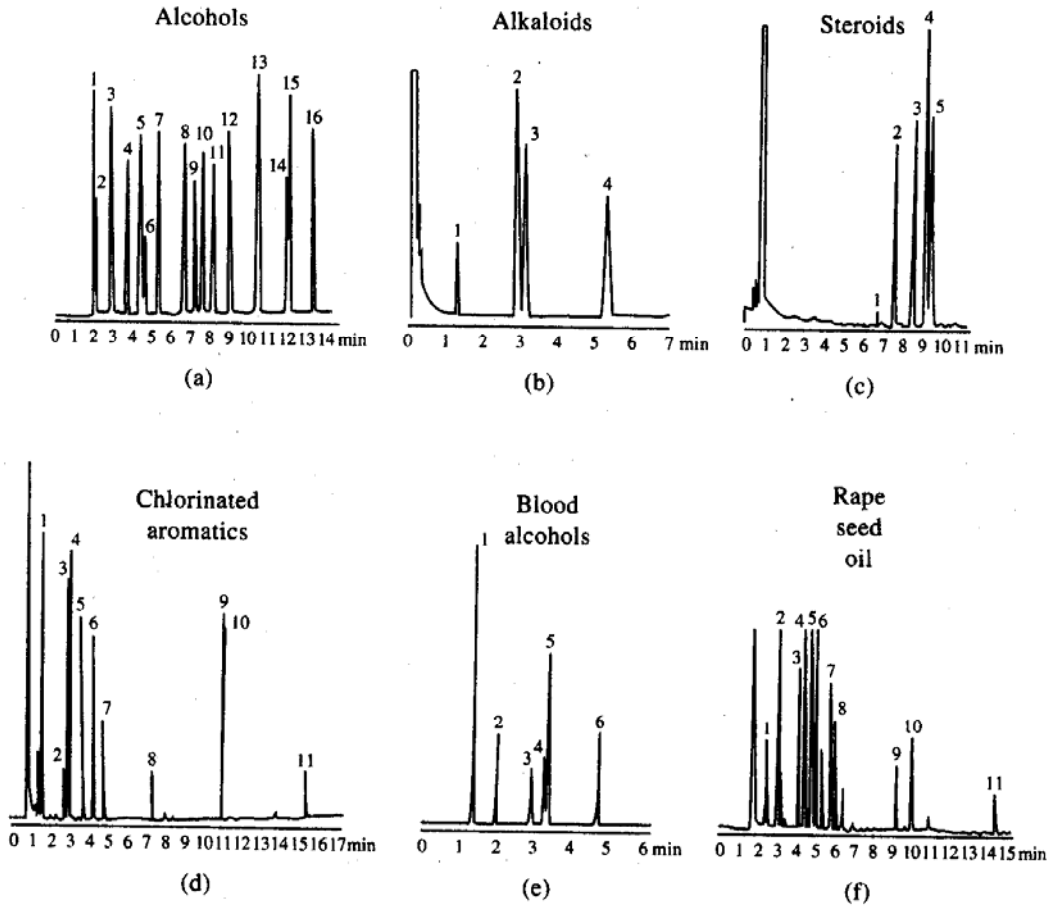


Figure 27-11 Typical chromatograms from open tubular columns coated with (a) polydimethyl siloxane; (b) 5(phenylmethyldimethyl) siloxane; (c) 50(phenylmethyldimethyl) siloxane; (d) 50% poly(trifluoropropyl-dimethyl) siloxane; (e) polyethylene glycol; (f) 50% poly(cyanopropyl-dimethyl) siloxane. *(Courtesy of J & W Scientific.)*