Gas Chromatography (Chapter 27)

Two major types

- Gas-solid chromatography

  (stationary phase: solid)

- Gas-liquid chromatography

  (stationary phase: immobilized liquid)

Retention Volume:

$$\underbrace{V_R = t_R \; F}_{\text{retained}} \qquad \underbrace{V_M = t_M \; F}_{\text{non-retained}}$$

average volumetric flow rate (mL/min)

F can be estimated by measuring flow rate exiting the column using soap bubble meter (some gases dissolving in soap solution)

but measured V_R and V_M depend on

- pressure inside column
- temperature of column

V_R and V_M depend on **average** pressure inside column

Column has resistance to flow

$$\begin{array}{l}\text{At inlet, } P = \text{high, } F = \text{low} \\ \text{At outlet, } P = \text{low, } F = \text{high}\end{array} \quad \Delta P \;\; F = \text{constant}$$

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

$$j = \frac{3\left[\left(P_{inlet} / P_{outlet}\right)^2 - 1\right]}{2\left[\left(P_{inlet} / P_{outlet}\right)^3 - 1\right]}$$

Corrected Retention Volume:

$$V_R^0 = j \;\; t_R \;\; F \qquad V_M^0 = j \;\; t_M \;\; F$$

Specific Retention Volume:

$$V_g = \frac{V_R^0 - V_M^0}{M_s} \times \underbrace{\frac{273}{T_{column}}}_{\begin{array}{c}\text{correction} \\ \text{for} \\ \text{temperature}\end{array}}$$

mass of stationary phase

partition ratio c_s/c_m

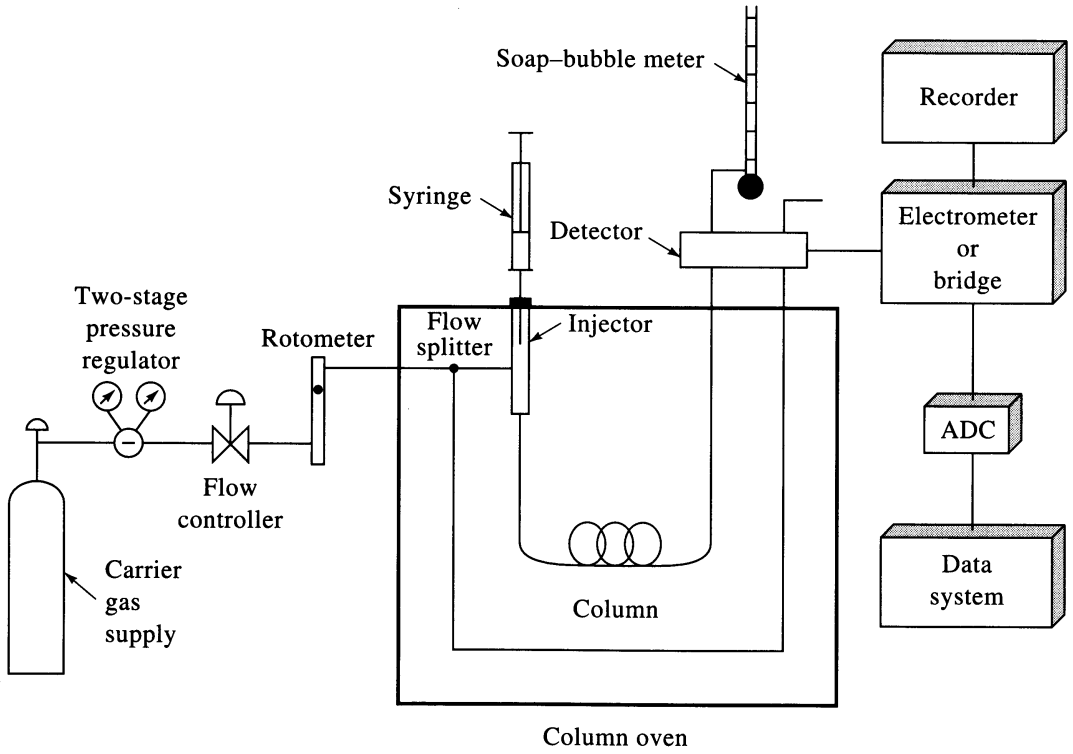
$$V_g = \frac{K}{\rho_{stationary}} \times \frac{273}{T_{column}}$$

density of stationary phase

V_g - semi-useful parameter for identifying species eluting

- often scales with vapor pressure (constant polarity analytes)

GC Instrumentation (Fig 27-1):



Carrier gas: He (common), N_2, H_2

P_{inlet} 10-50 psig

F=25-150 mL/min packed column

F=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)

Sample injection:

- direct injection into *heated* port (>T_{oven}) using microsyringe

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

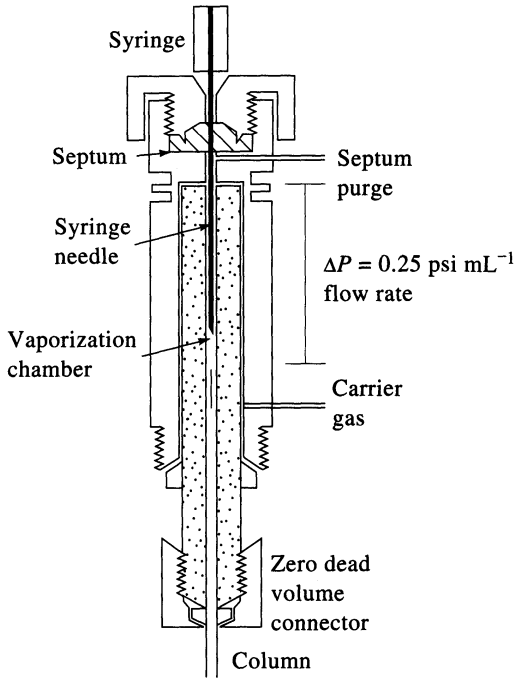


Fig 27-3

- rotary sample valve with sample loop

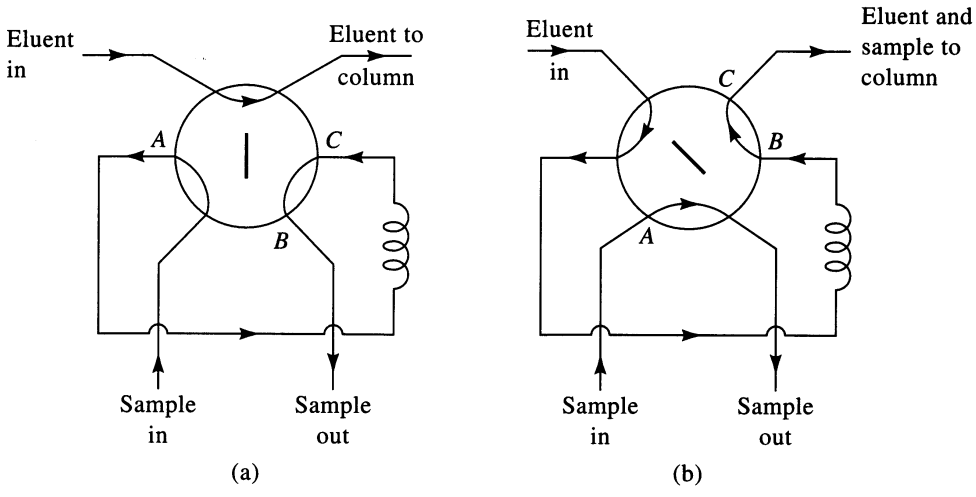


Fig 27-4

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]
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

GC Detectors:

Need

- Sensitive (10^{-8}-10^{-15} g solute/s)
- Operate at high T (0-400 °C)
- Stable and reproducible
- Linear response

Desire

- Wide dynamic range
- Fast response
- Simple (reliable)
- Nondestructive
- Uniform response to all analytes

Flame Ionization Detector (FID):

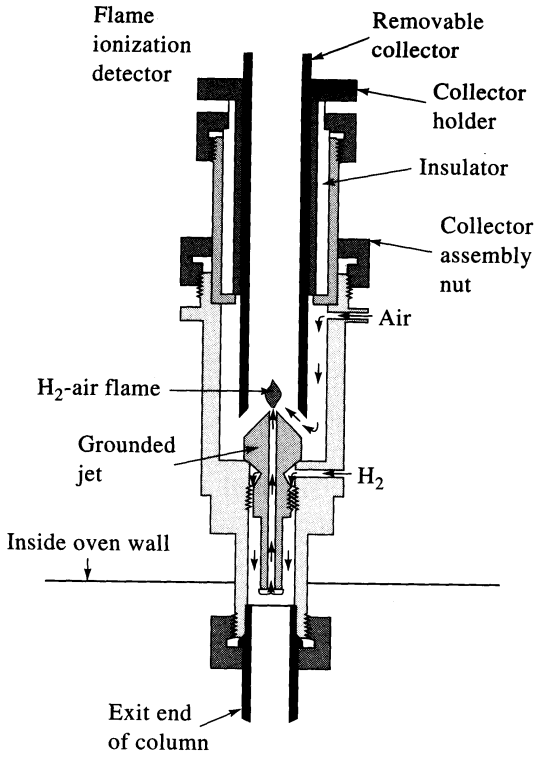


Fig 27-6

- Rugged
- Sensitive (10^{-13} g/s)
- Wide dynamic range (10^7)
- Signal depends on # C atoms in organic analyte - mass sensitive not concentration sensitive
- Weakly sensitive to carbonyl, amine, alcohol, amine groups
- Not sensitive to non-combustibles - H_2O, CO_2, SO_2, NO_x
- Destructive

Thermal Conductivity Detector (TCD)

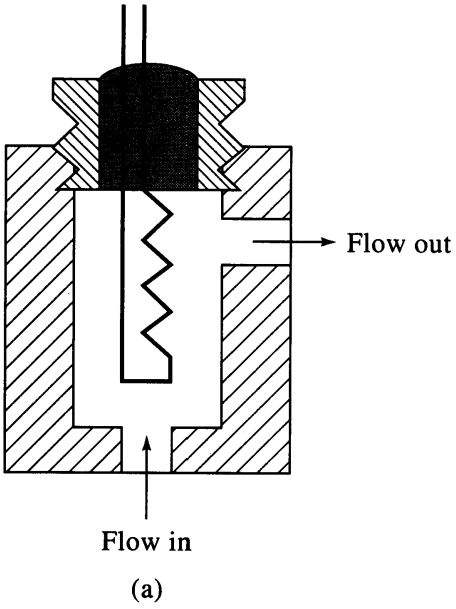


Fig 27-7

Thermal conductivity of He, H_2 much larger than organics

Organics cause T rise in filament

- Rugged
- Wide dynamic range (10^5)
- Nondestructive
- Insensitive (10^{-8} g/s) - non-uniform

Electron Capture Detector (ECD):

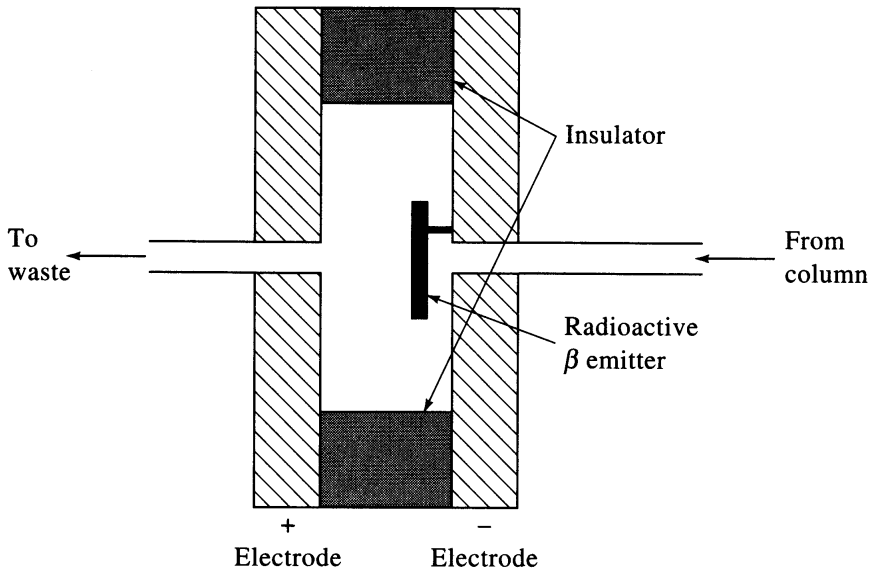


Fig 27-8

Electrons from β-source ionize carrier gas

Organic molecules capture electrons and decrease current

- Simple and reliable
- Sensitive (10^{-15} g/s) to electronegative groups (halogens, peroxides)
- Largely non-destructive
- Insensitive to amines, alcohols and hydrocarbons
- Limited dynamic range (10^2)

Important Other Detectors:

- AES, AAS, chemiluminescent reaction (S), mass spectrometer, FTIR

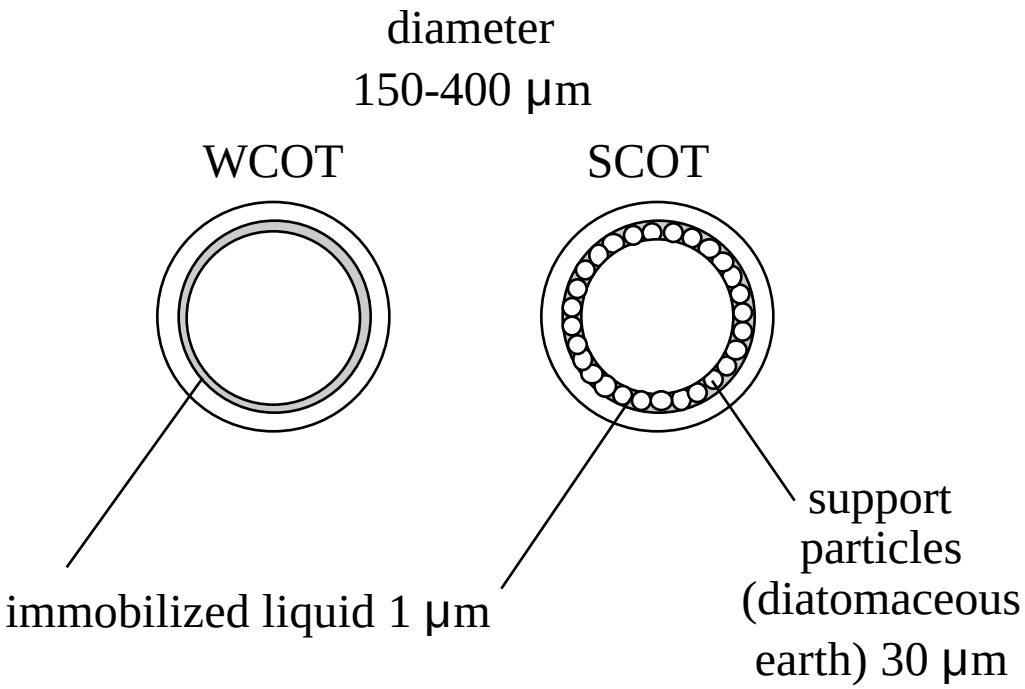
Column Stationary Phases:

Packed

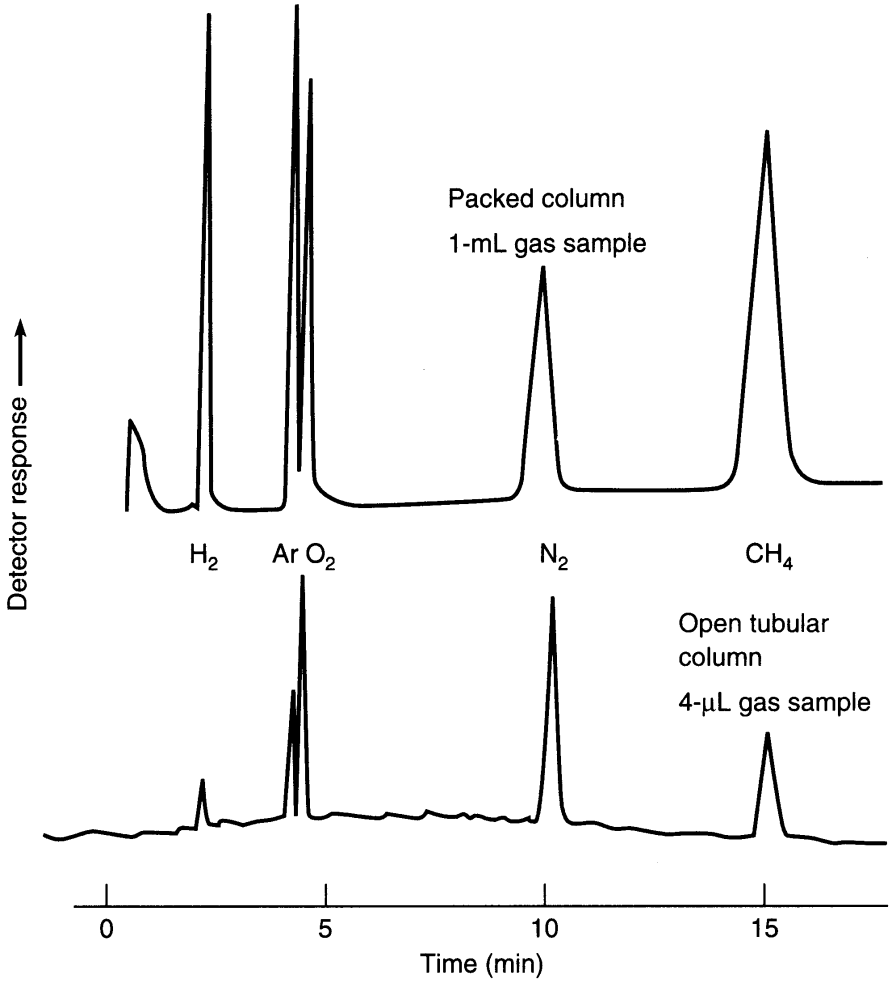
- liquid coated silica particles (<100-300 μm diameter) in glass tube
- best for large scale but slow and inefficient

Capillary/Open Tubular

- wall-coated (WCOT) <1 μm thick liquid coating on inside of silica tube
- support-coated (SCOT) 30 μm thick coating of liquid-coated support on inside of silica tube
- best for speed and efficiency but only small samples



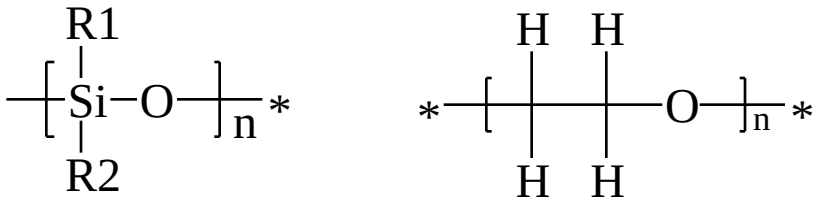
(Fig 17-5; Harris)



Immobilized Liquid Stationary Phases:

- low volatility
- high decomposition temperature
- chemically inert (reversible interactions with solvent)
- chemically attached to support (prevent "bleeding")
- appropriate k' and α for good resolution

Many based on polysiloxanes or polyethylene glycol (PEG):



(Table 27-2)

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

Stationary phases usually bonded and/or cross-linked

- bonding - covalent linking of stationary phase to support
- cross-linking - polymerization reactions after bonding to join individual stationary phase molecules

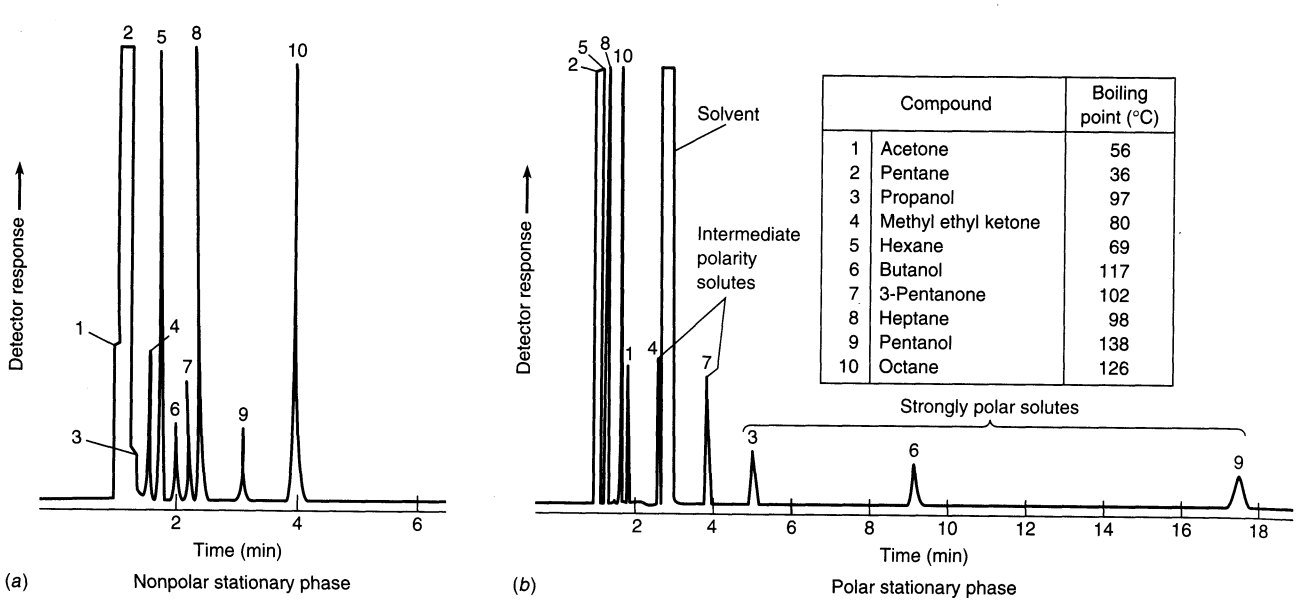
Non-polar stationary phases best for non-polar analytes

non-polar analytes retained preferentially

Polar stationary phases best for polar analytes

polar analytes retained preferentially

(Fig 17-4; Harris)



	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

- Film thickness (0.1-5 μm) affects retention and resolution - thicker films for volatile analytes, poorer resolutions
- Chiral phases being developed for enantiomer separation (pharmaceuticals)

Temperature Programming:

- As column temperature raised, vapor pressure analyte increases, eluted faster
- Raise column temperature **during** separation - temperature programming - separates species with wide range of polarities or vapor pressures

(Fig 17-6; Harris)