Gas Chromatography

- Vaporization of sample
  - Gas-solid
    - Physical absorption
  - Gas-liquid
    - Liquid immobilized on inert solid

- Principles
- Instrumentation
- Applications

Retention Volumes

- Volumes rather than times
  - Accounts for temperature and pressure effects (non linear)
    - High pressure at inlet
    - $V_R = t_R F$
    - $V_M = t_M F$
      - * F=average flow rate
        - ❷ Can be measured
      - * t=time
      - * R=retained species
      - * M=mobile species
        - ❷ Correction term j for pressure drop

Retention Volumes

- **Correct volumes**

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

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

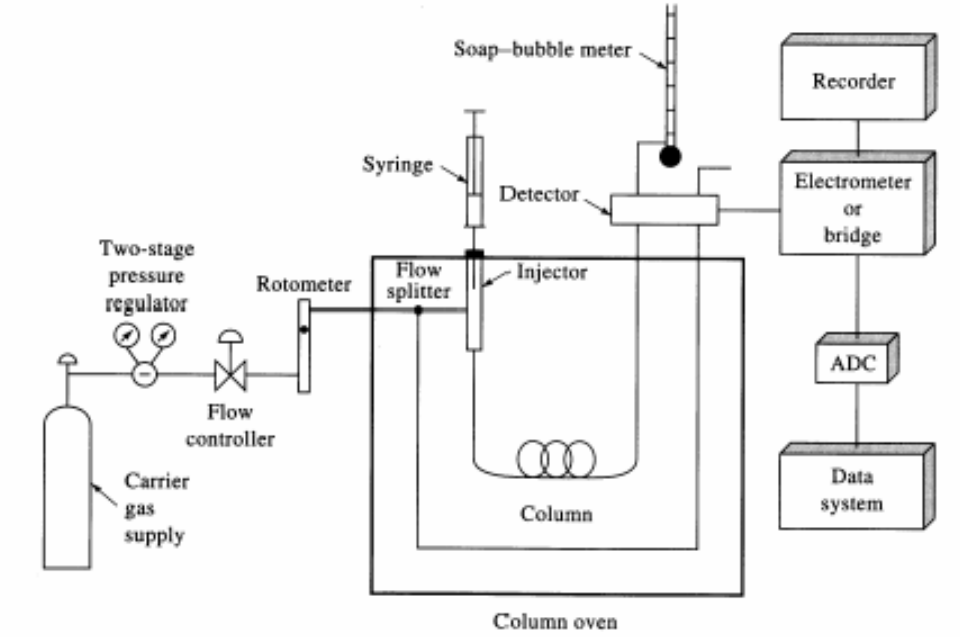
- **Specific retention volume**
  - **M_S = mass of stationary phase, T in K**

$$V_g = \frac{V_R^0 - V_M^0}{M_s} \times \frac{273}{T_{column}} \qquad V_g = \frac{K}{\rho_{stationary}} \times \frac{273}{T_{column}}$$

  - **V_g useful for species identification**
    - **term scales with vapor pressure**

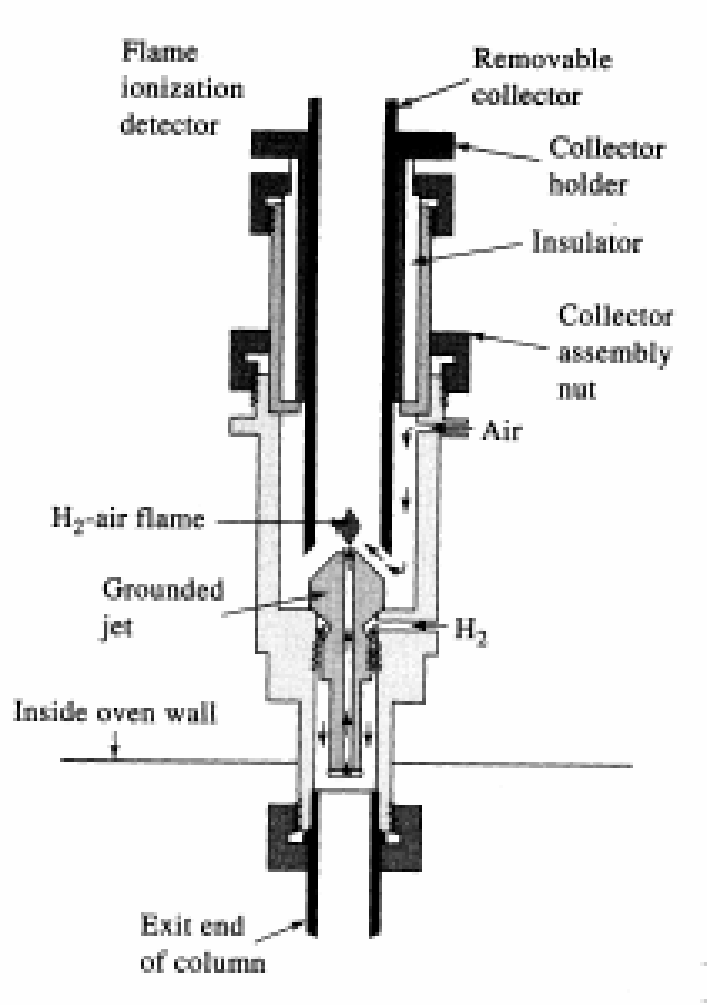
Instrumentation

- Carrier gas
  - He (common), N_2, H_2
  - 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
- Detectors
  - FID, TCD, ECD, (MS)



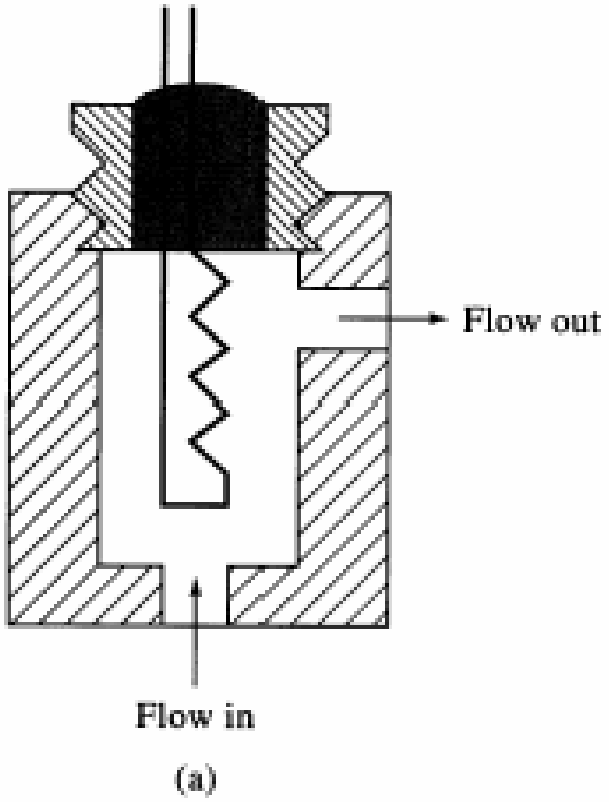
Flame Ionization Detector

- 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
  - carbonyl, amine, alcohol, amine groups
- • Not sensitive
  - H_2O, CO_2, SO_2, NOx
- Destructive technique



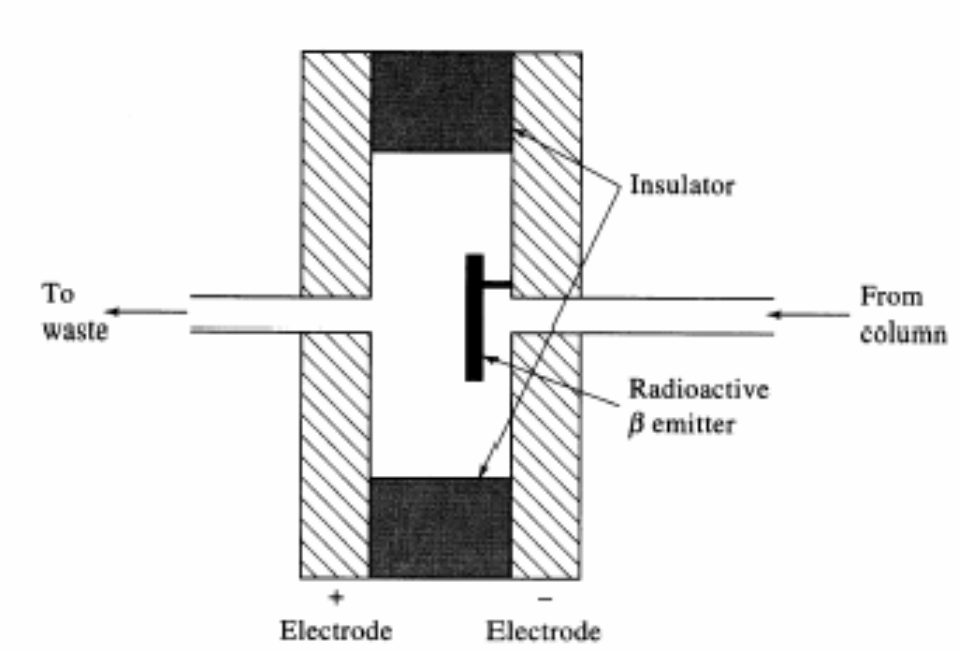
Thermal Conductivity Detector

- Change in gas thermal conductivity
  - Difference between carrier gas and analyte
  - Thermal conductivity of He, H_2 much larger than organics
    - Organics cause T rise in filament
  - Rugged
  - Wide dynamic range (10^5)
  - Nondestructive



Electron Capture Detector

- Electrons from radioactive source
- Organic molecules capture electrons and decrease current
- Simple and reliable
- Sensitive to electronegative groups
  - halogens, peroxides
- Insensitive to amines, alcohols
- Largely non-destructive
- Limited dynamic range (102)



Columns

- **Packed**
  - **liquid coated silica particles (<100-300 mm diameter) in glass tube**
  - **best for large scale but slow and inefficient**
- **Capillary/Open Tubular**
  - **wall-coated (WCOT) <1 mm thick liquid coating on inside of silica tube**
  - **support-coated (SCOT) 30 mm thick coating of liquid coated support on inside of silica tube**
  - **best for speed and efficiency but only small samples**

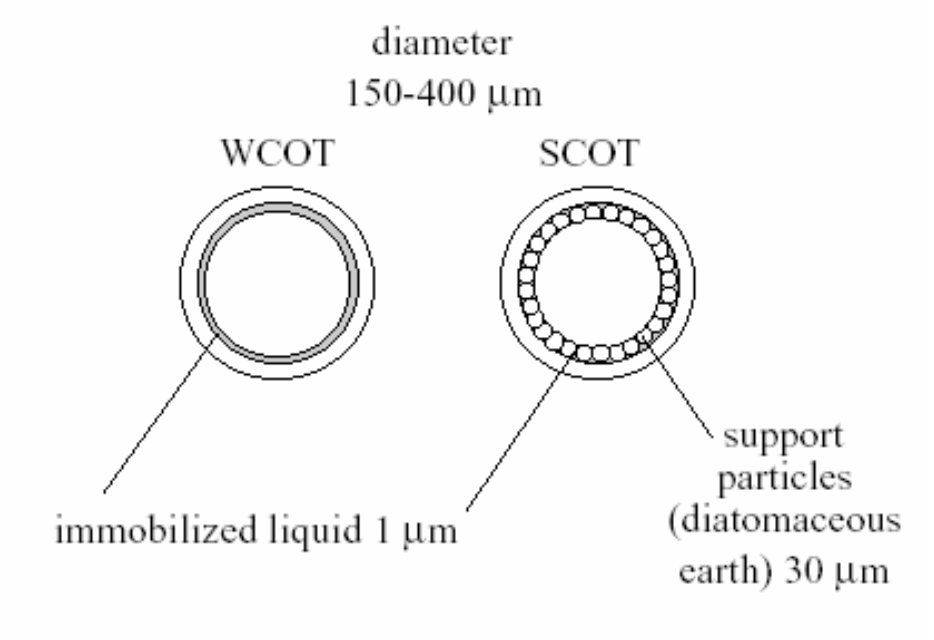
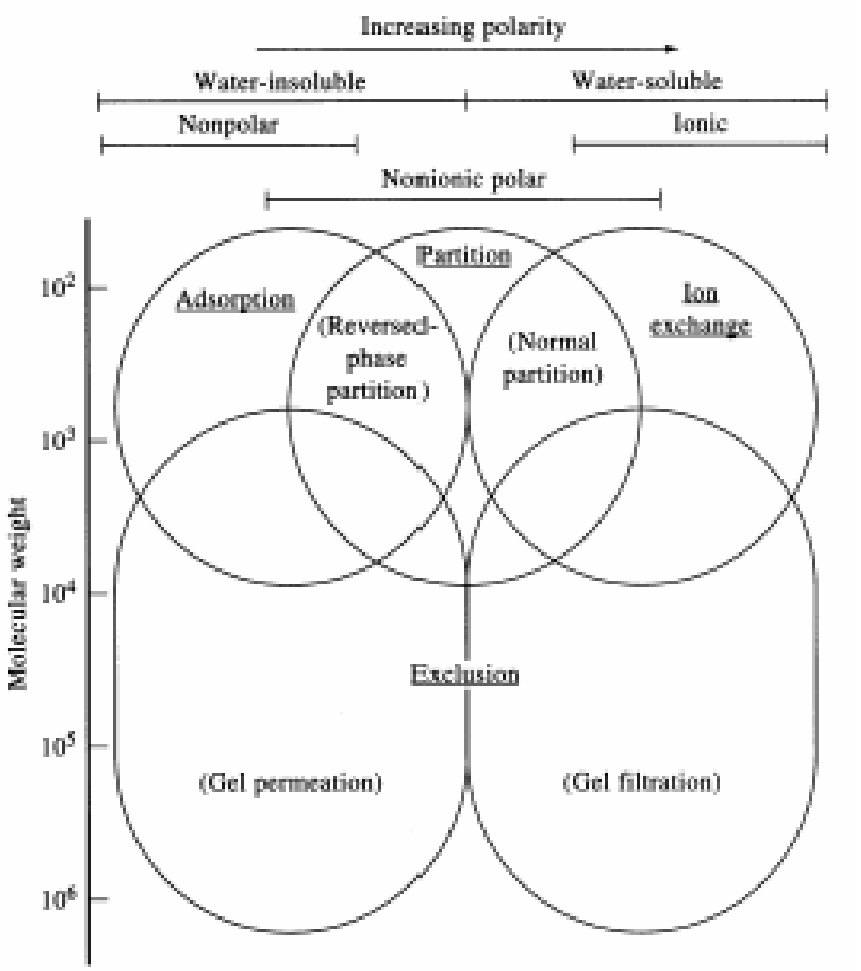


TABLE 27-2 Some Common Stationary Phases for Gas-Liquid Chromatography

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

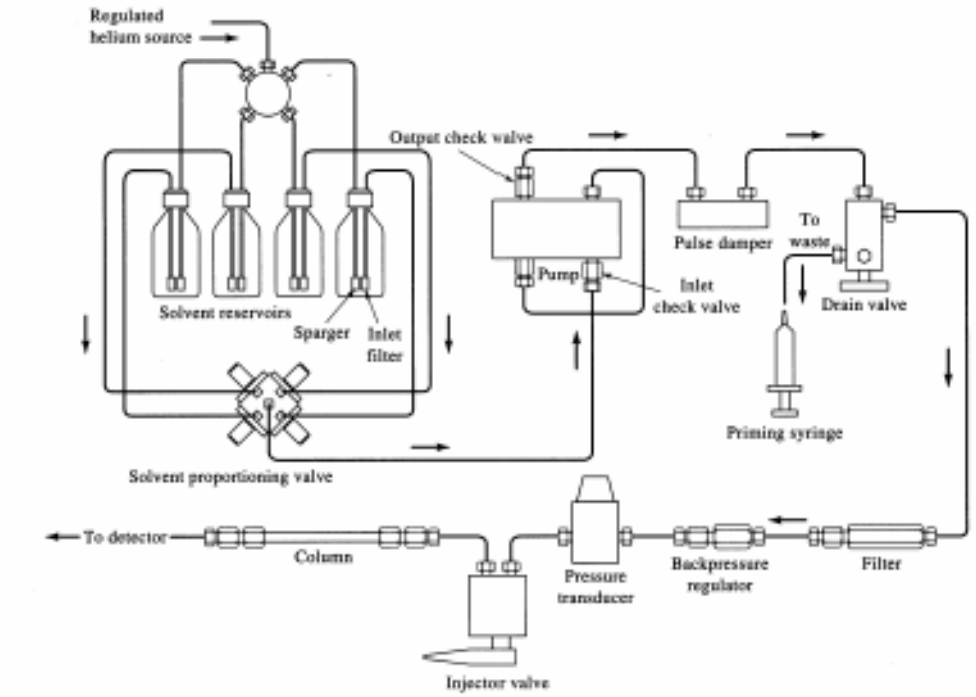
High Performance Liquid Chromatography

- **Mobile phase is liquid**
  - **Four types**
    - **partition**
    - **adsorption (liquid-solid)**
    - **ion exchange**
    - **size exclusion or gel**



Instrumentation

- For reasonable analysis times, moderate flow rate required but small particles (1-10 mm)
  - Solvent forced through column 1000-5000 psi - more elaborate instrument than GC
  - Solvents degassed - "sparging“
  - High purity solvents
- Single mobile phase composition
  - isocratic elution
- Programmed mobile phase composition
  - gradient elution
- Sample introduced without depressurization



Instrumentation

- **HPLC Columns:**
  - **Stainless steel**
  - **10-30 cm long**
  - **4-10 mm internal diameter**
  - **1-10 mm particle size - 40,000-60,000 plates/m**
- **High Speed Isocratic Separation**
  - **100,000 plates/m**
- **Variation in solvent changes elution**
  - **polarity**

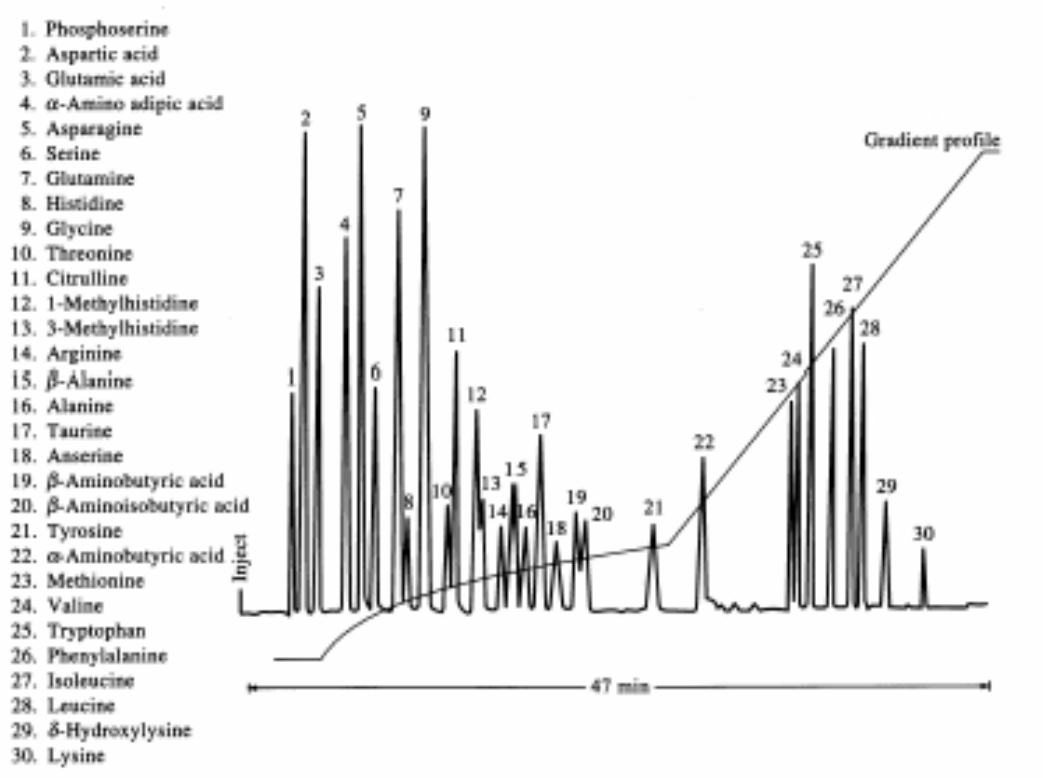
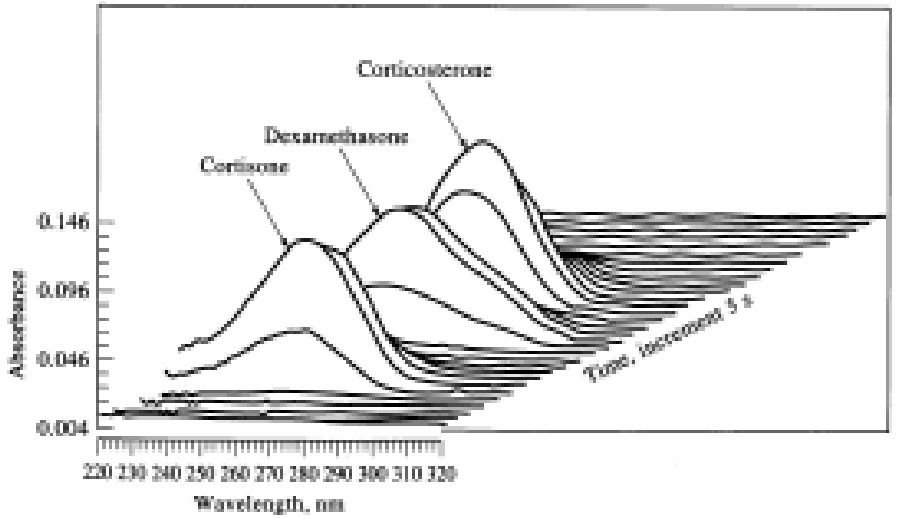


TABLE 28-1 Performances of LC Detectors

LC Detector	Commercially Available	Mass LOD (commercial detectors)[a]	Mass LOD (state of the art)[b]
Absorbance	Yes[c]	100 pg–1 ng	1 pg
Fluorescence	Yes[c]	1–10 pg	10 fg
Electrochemical	Yes[c]	10 pg–1 ng	100 fg
Refractive index	Yes	100 ng–1 μg	10 ng
Conductivity	Yes	500 pg–1 ng	500 pg
Mass spectrometry	Yes[d]	100 pg–1 ng	1 pg
FT–IR	Yes[d]	1 μg	100 ng
Light scattering[e]	Yes	10 μg	500 ng
Optical activity	No	—	1 ng
Element selective	No	—	10 ng
Photoionization	No	—	1 pg–1 ng



Partition Chromatography

- Most popular method
- Low molecular weight (mw<3000) analytes
- Polar or non-polar
- Bonded stationary phase column
  - liquid chemically bonded to support particles
- 3, 5 or 10 mm hydrolyzed silica particles coated with siloxanes
- Normal phase HPLC
  - nonpolar solvent/polar columı
- Reversed phase HPLC
  - polar solvent/nonpolar columı

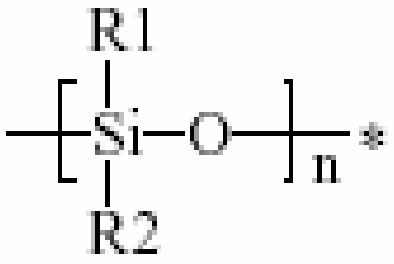


TABLE 28-2 Properties of Common Chromatographic Mobile Phases

Solvent	Refractive Index[a]	Viscosity, cP[b]	Boiling Point, °C	Polarity Index, P'	Eluent Strength,[c] ϵ^0
Fluoroalkanes[d]	1.27–1.29	0.4–2.6	50–174	< -2	−0.25
Cyclohexane	1.423	0.90	81	0.04	−0.2
n-Hexane	1.372	0.30	69	0.1	0.01
1-Chlorobutane	1.400	0.42	78	1.0	0.26
Carbon tetrachloride	1.457	0.90	77	1.6	0.18
i-Propyl ether	1.365	0.38	68	2.4	0.28
Toluene	1.494	0.55	110	2.4	0.29
Diethyl ether	1.350	0.24	35	2.8	0.38
Tetrahydrofuran	1.405	0.46	66	4.0	0.57
Chloroform	1.443	0.53	61	4.1	0.40
Ethanol	1.359	1.08	78	4.3	0.88
Ethyl acetate	1.370	0.43	77	4.4	0.58
Dioxane	1.420	1.2	101	4.8	0.56
Methanol	1.326	0.54	65	5.1	0.95
Acetonitrile	1.341	0.34	82	5.8	0.65
Nitromethane	1.380	0.61	101	6.0	0.64
Ethylene glycol	1.431	16.5	182	6.9	1.11
Water	1.333	0.89	100	10.2	Large

[a] At 25°C.
[b] The centipoise is a common unit of viscosity; in SI units, 1 cP = 1 mN · s · m^{-2}.
[c] On Al_2O_3. Multiplication by 0.8 gives ϵ^0 on SiO_2.
[d] Properties depend upon molecular weight. Range of data given.

Gel Permeation Size Exclusion

- Used for large mw compounds
  - proteins and polymers
- Separation mechanism is sieving not partitioning
- Stationary phase porous silica or polymer particles
  - polystyrene, polyacrylamide) (5-10 mm)
- well-defined pore sizes (40-2500 Å)
- Large molecules excluded from pores
  - not retained, first eluted (exclusion limit - terms of mw)
- Intermediate molecules
  - retained, intermediate elution times
- Small molecules permeate into pores
  - strongly retained, last eluted (permeation limit - terms of mw)

TABLE 28-6 Properties of Typical Commercial Packings for Size-Exclusion Chromatography

Type	Particle Size, μm	Average Pore Size, Å	Molecular Weight Exclusion Limit[a]
Polystyrene-divinylbenzene	10	10^2	700
		10^3	$(0.1 \text{ to } 20) \times 10^4$
		10^4	$(1 \text{ to } 20) \times 10^4$
		10^5	$(1 \text{ to } 20) \times 10^5$
		10^6	$(5 \text{ to } > 10) \times 10^6$
Silica	10	125	$(0.2 \text{ to } 5) \times 10^4$
		300	$(0.03 \text{ to } 1) \times 10^5$
		500	$(0.05 \text{ to } 5) \times 10^5$
		1000	$(5 \text{ to } 20) \times 10^5$

[a]Molecular weight above which no retention occurs.

Retention related to size (and shape) of molecule

$$\underbrace{V_t}_{\text{total}} = \underbrace{V_g}_{\text{gel or solid}} + \underbrace{V_i}_{\text{inside pores}} + \underbrace{V_o}_{\text{outside pores/ free–space}}$$

V_o retention volume for non-retained (large) molecules

(V_o+V_i) retention volume for retained (small) molecules

(V_o+KV_i) retention volume for intermediate molecules ($K=c_s/c_m$)

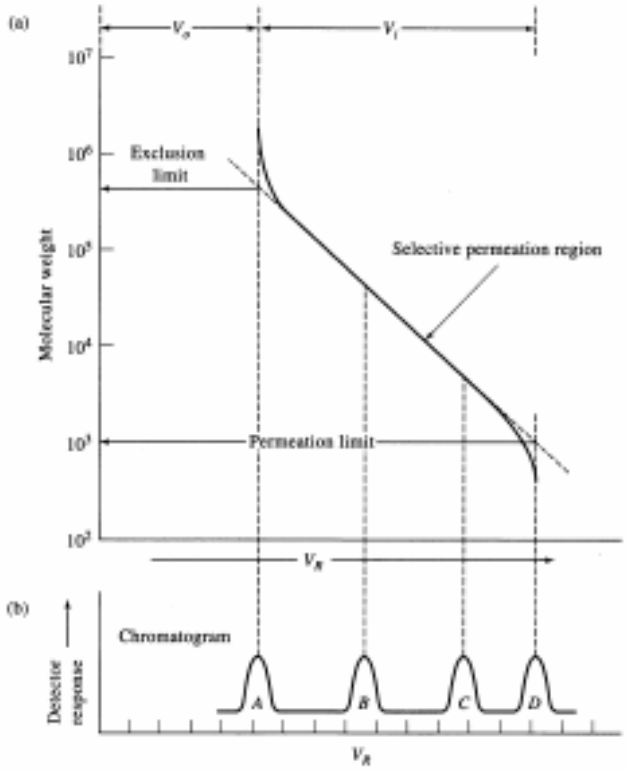


Fig 28-27

- Separation of proteins/peptides, sugars, determination of polymer molecular weight distribution