Ch. 23 Fundamentals of Analytical Separations

Separation

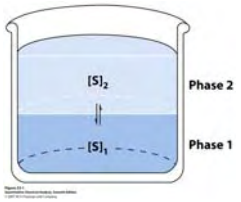
- Samples are usually complex mixtures. In order to identify and quantify the components of a mixture, we have to separate the components in the mixture.
- Separation methods
  - Extraction
  - Chromatography
  - Electrophoresis

Solvent Extraction

- The transfer of an analyte from one phase to a second based on the relative solubility of the analyte in two immiscible liquids.

$$K = \frac{[S]_2}{[S]_1} = \frac{(1-q)m/V_2}{qm/V_1}$$

$$q = \left(\frac{V_1}{V_1 + KV_2}\right)^n$$



At equilibrium: K: the partition coefficient for distribution of S between the two phases; q: the fraction of S remaining in phase 1; n: the # of extractions.

If q = 1/4, then 1/4 remains in phase 1 after one extraction

Extraction Efficiency

- A solute S has a partition coefficient of 3 between toluene and water. If you have 100 mL of a 0.010 M solution of S in water.(1)What fraction of the solute remains in H_2O after a 500 mL extraction with toluene? (2) What fraction of the solute remains in H_2O after a 5-100 mL extractions with toluene?

$$q = \frac{100}{100 + (3)(500)} = 0.062 \approx 6\%$$

$$q = \left(\frac{100}{100 + (3)(100)}\right)^5 = 0.00098 \approx 0.1\%$$

It is more efficient to do several small extractions than one big extraction.

pH Effects

- The charge changes of an acid or base is dependent on pH.
- Distribute coefficient (D): an alternate form of the partition coefficient.

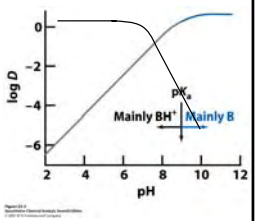
$$D = \frac{\text{Total conc. in phase 2}}{\text{Total conc. in phase 1}} = \frac{C_2}{C_1}$$

$$D = \frac{[B]_2}{[B]_1 + [BH^+]_1} = \frac{KKa}{Ka + [H^+]} = K\alpha_B$$

$$(Ka = \frac{[B]_1[H^+]}{[BH^+]_1}; K = \frac{[B]_2}{[B]_1})$$

$$D = \frac{[HA]_2}{[HA]_1 + [A^-]_1} = \frac{K[H^+]}{Ka + [H^+]} = K\alpha_{HA}$$

$$(Ka = \frac{[A^-]_1[H^+]}{[HA]_1}; K = \frac{[HA]_2}{[HA]_1})$$



α: fraction of the species (P.191)

pH Effects

- K for an amine B is 3.0 and the Ka for BH^+ is 1.08×10^{-9}. If 50.00 mL of 0.010 M aqueous amine is extracted with 100 mL of solvent, calculate the % remaining the in aqueous phase in M at (1) pH 10.00; (2) pH 8.00.

$$pH = 10.00: D = \frac{KKa}{Ka + [H^+]} = \frac{3.0\times1.0\times10^{-9}}{1.0\times10^{-9} + 1.0\times10^{-10}} = 2.73$$

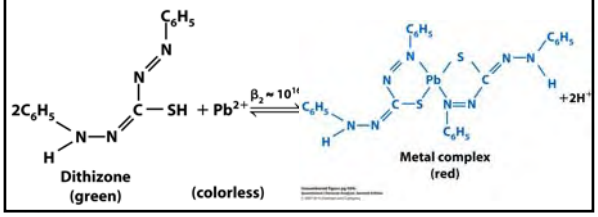
$$q = \frac{V_1}{V_1 + KV_2} = \frac{50}{50 + 2.73\times100} = 0.15 \Rightarrow 15\%$$

$$pH = 8.00: D = \frac{KKa}{Ka + [H^+]} = \frac{3.0\times1.0\times10^{-9}}{1.0\times10^{-9} + 1.0\times10^{-8}} = 0.273$$

$$q = \frac{V_1}{V_1 + KV_2} = \frac{50}{50 + 0.273\times100} = 0.65 \Rightarrow 65\%$$

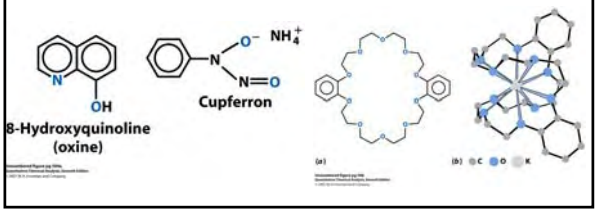
Extraction with a Metal Chelator

•Usually neutral complexes can be extracted into organic solvents. Charged complexes (e.g. $MEDTA^{2-}$) are not very soluble in organic solvents.
•Commonly used: dithizone, 8-hydroquinoline, and cupferron.



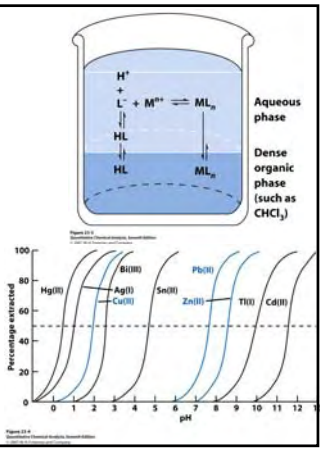
Extraction with a Metal Chelator

•Commonly used: dithizone, 8-hydroquinoline, and cupferron.
•Crown ethers can extract alkali metal ions and can bring them into non-polar solvents.



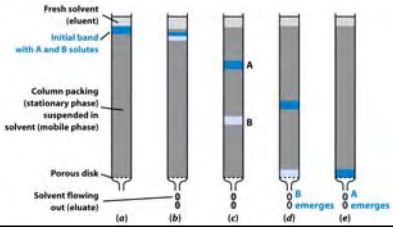
Extraction with a Metal Chelator

•Each ligand can be presented as a weak acid, HL.
•M^{n+} is in the aqueous phase and ML_n is in the organic phase
•The distribution coefficient (D) for metal ion extraction depends on pH and [ligand].
•By select a pH, you can bring the metal into either phase.



Chromatography

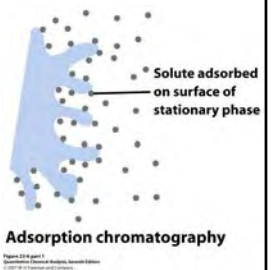
- A separation process based on the various partitioning coefficients of different solutes between the two phases.
- Involving the interaction of solute(s) and two phases
- **Mobile phase:** A gas or liquid that moves through the column.
- **Stationary phase:** A solid or liquid that remains in place.



Type of Chromatography

- Based on the mechanism of interaction of the solute with the stationary phase

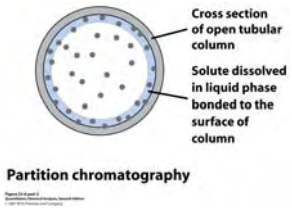
(1) Adsorption chromatography
- Solute is adsorbed on the surface of the stationary phase (solid).
- The stronger a solute adsorbs, the longer it takes to travel through the chromatography column



Type of Chromatography

- Based on the mechanism of interaction of the solute with the stationary phase

(2) Partition chromatography
- GC
- the partitioning of solutes between a mobile phase (gas) and bonded liquid stationary phase

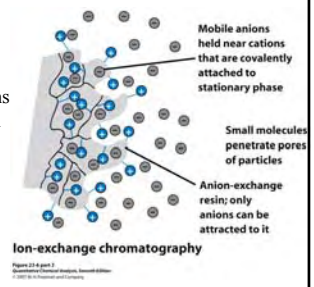


Type of Chromatography

- Based on the mechanism of interaction of the solute with the stationary phase

(3) Ion-exchange chromatography

- ionic interactions to separate ions
- a stationary phase of anions will separate cations and vice versa.



Type of Chromatography

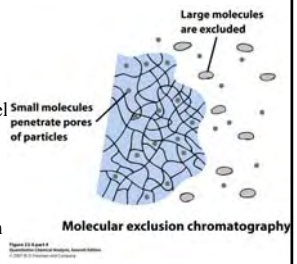
- Based on the mechanism of interaction of the solute with the stationary phase

(4) Molecular Size exclusion chromatography

-size exclusion, gel filtration, or gel permeation chromatography

-separate molecules by size

-large molecules pass through faster (they do not get caught up in pores)



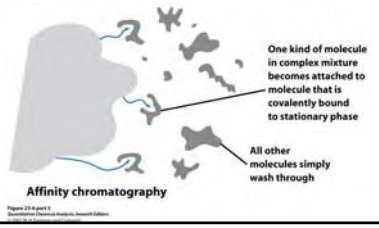
Type of Chromatography

- Based on the mechanism of interaction of the solute with the stationary phase

(5) Affinity chromatography

-Specific interactions of one kind of solute molecule to a second molecular that is covalently attached to the stationary phase

-Most selective (e.g. use antibodies to select out one protein from a mixture of hundreds)



The Chromatogram

•A plot of detector response with time.

•Volume flow rate (flow rate): vol. of solvent pass through the column

•Linear flow rate: the length of the column passed though by the solvent

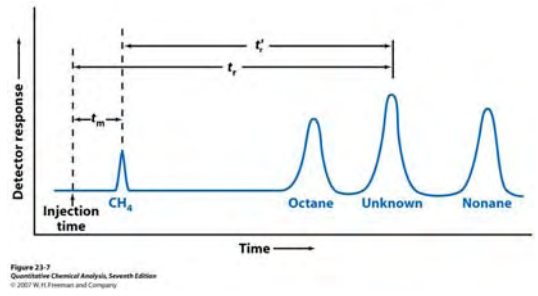
•t_m: unretained mobile phase travels through the column in the minimum possible time

•t_r: retention time, the time for each component needed after injection of the mixture onto the column until that component reaches the detector

•t_r': adjusted retention time, $t_r' = t_r - t_m$

•Vr: retention volume, volume of mobile phase required to elute a solute to a maximum from a column. Vr= t_r*flow rate

The Chromatogram



Retention Parameters

- **Adjusted retention time**
  - Time spent in the stationary phase (or t_s)

$$t_r' = t_r - t_m$$

- **Relative retention**
  - ratio of adjusted retention times for any two components
  - the greater the relative retention, the greater the separation

$$\alpha = \frac{t_{r2}'}{t_{r1}'}$$

- **Capacity factor** (or retention factor):
  - the longer a component is retained by the column, the greater is the capacity factor.

$$k' = \frac{t_r - t_m}{t_m}$$

- Example: Calculate the adjusted retention time and capacity factor for benzene and toluene in the GC experiment? Methane (as a solvent) peak is at 42 s; benzene at 251 s and toluene at 333 s.

For Benzene

$$t_r' = t_r - t_m = 251 - 42 = 209\ \text{s}$$

$$k' = \frac{t_r - t_m}{t_m} = \frac{251 - 42}{42} = 5.0$$

For Toluene

$$t_r' = t_r - t_m = 333 - 42 = 291\ \text{s}$$

$$k' = \frac{t_r - t_m}{t_m} = \frac{333 - 42}{42} = 6.9$$

Retention Time and Partition Coefficient

- The capacity factor is equivalent to the time the solute spends in the stationary phase over the mobile phase and can be related to the partition coefficient:

$$k' = \frac{C_s V_s}{C_m V_m} = K\frac{V_s}{V_m} \Leftrightarrow k' = \frac{t_r - t_m}{t_m} = \frac{t_r'}{t_m} = \frac{V_r - V_m}{V_m}$$

- Relative retention can be related to retention time, capacity factor, and/or partition coefficient

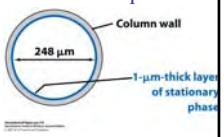
$$\alpha = \frac{t_{r2}'}{t_{r1}'} = \frac{k_2'}{k_1'} = \frac{K_2}{K_1}$$

- Physical basis of chromatography: the greater the ratio of partition coefficients between mobile and stationary phases, the greater the separation between two components of a mixture

- Example: If use the open tubular chromatography column, where methane (as a solvent) peak is at 42 s and benzene peak at 251 s. Calculate the partition coefficient (K) for benzene between stationary and mobile phases and the fraction of the time benzene spends in the mobile phase.

Cross - sectional area of column

$$V_m = \pi r_1^2 = \pi(124)^2 = 4.83\times10^4\ \mu\text{m}^2$$



Cross - sectional area of coating

$$V_s = 2\pi r_2 \times \text{thickness} = 2\pi(124.5)\times1 = 7.8\times10^2\ \mu\text{m}^2$$

$$k' = \frac{t_r - t_m}{t_m} = \frac{251 - 42}{42} = 5.0 = K\frac{V_s}{V_m} \Rightarrow K = 310$$

$$k' = \frac{t_r - t_m}{t_m} = \frac{t_r'}{t_m} \Rightarrow t_r' = k' t_m$$

Fraction of time in mobile phase:

$$\frac{t_m}{t_r' + t_m} = \frac{t_m}{k' t_m + t_m} = \frac{1}{k' + 1} = \frac{1}{5.0 + 1} = 0.17$$

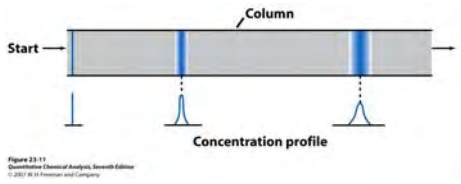
Scaling Up

- Analytical and preparative
- Keep column length constant
- Cross-sectional area of column ~ mass of analyte ~ volume flow rate (if maintain constant linear flow rate) ~ sample volume applied to column
- If change the column length, then the mass of sample can be increased in proportion to the increase in length

Scaling equation:

$$\frac{\text{Mass 2}}{\text{Mass 1}} = \left(\frac{\text{Radius 2}}{\text{Radius 1}}\right)^2$$

Diffusion

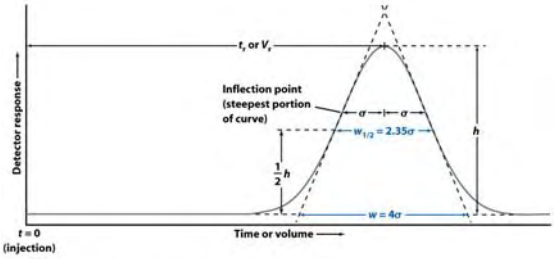


- One main cause of band broadening is diffusion.
- Diffusion coefficient (D): measures the rate at which a substance moves randomly from a region of high concentration to a region of lower concentration.
- Std deviation of diffusive band spreading: $\sigma = \sqrt{2Dt}$

Table 23-1 Representative diffusion coefficients at 298 K

Solute	Solvent	Diffusion coefficient (m^2/s)
H_2O	H_2O	2.3×10^{-9}
Sucrose	H_2O	0.52×10^{-9}
Glycine	H_2O	1.1×10^{-9}
CH_3OH	H_2O	1.6×10^{-9}
Ribonuclease (FM 13 700)	H_2O (293 K)	0.12×10^{-9}
Serum albumin (FM 65 000)	H_2O (293 K)	0.059×10^{-9}
I_2	Hexane	4.0×10^{-9}
CCl_4	Heptane	3.2×10^{-9}
N_2	CCl_4	3.4×10^{-9}
$CS_2(g)$	Air (293 K)	1.0×10^{-5}
$O_2(g)$	Air (273 K)	1.8×10^{-5}
H^+	H_2O	9.3×10^{-9}
OH^-	H_2O	5.3×10^{-9}
Li^+	H_2O	1.0×10^{-9}
Na^+	H_2O	1.3×10^{-9}
K^+	H_2O	2.0×10^{-9}
Cl^-	H_2O	2.0×10^{-9}
I^-	H_2O	2.0×10^{-9}

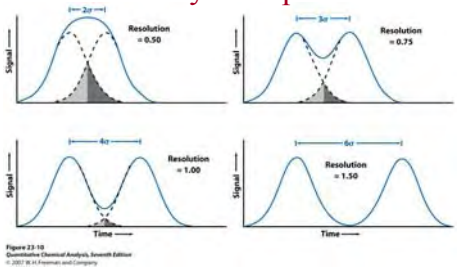
Efficiency of Separation



Solutes moving through a column can spread into a Gaussian distribution with a standard deviation, σ (K is a constant). Resolution of two peaks:

$$\text{Resolution} = \frac{\Delta t_r}{w_{av}} = \frac{\Delta V_r}{w_{av}} = \frac{0.589\Delta t_r}{w_{1/2,av}}$$

Efficiency of Separation



A resolution of 1.5 gives an essentially complete separation of A and B.

$$\text{Resolution} = \frac{\Delta t_r}{w_{av}} = \frac{\Delta V_r}{w_{av}} = \frac{0.589\Delta t_r}{w_{1/2,av}}$$

Column Efficiency-Theoretical Plates (N)

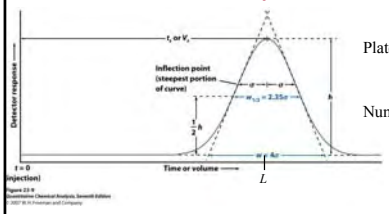


Plate Height $H = \frac{\sigma^2}{L}$

Number of Theoretical Plates $N = \frac{L}{H}$

$$N = \frac{L}{H} = \frac{Lx}{\sigma^2} = \frac{16L^2}{w^2}$$

L=x

σ =w/4

$$N = \frac{16t_r^2}{w^2} = \frac{t_r^2}{\sigma^2} = \frac{5.55t_r^2}{w_{1/2}^2}$$

- Martin & Synge (1941): Treated a chromatographic column as if it were similar to a distillation column made up of numerous discrete but contiguous narrow layers (theoretical plates).

- Example: A solute with a retention time of 407 s has a base width of 13 s on a 12.2 m column. Find the plate height and number of plates.

$$N = \frac{16t_r^2}{w^2} = \frac{(16)(407)^2}{13^2} = 1.57\times10^4$$

$$H = \frac{L}{N} = \frac{12.2\text{ m}}{1.57\times10^4} = 0.78\text{ mm}$$

Factors Affecting Resolution

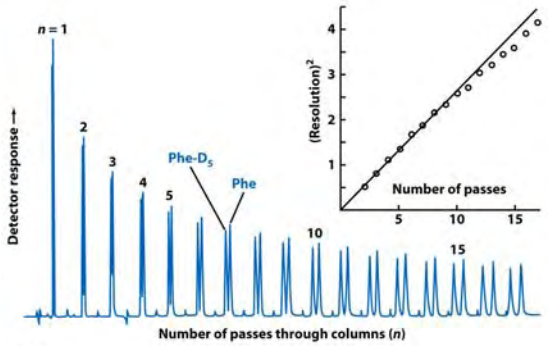
$$\text{Resolution} = \left(\frac{\sqrt{N}}{4}\right)(\gamma - 1)$$

γ : separation factor

Increase resolution:

- Increase column length (Square root of *N*)
- Change phase interaction
- Increase capacity factor (Increase fraction of time solute spends in stationary phase)

Factors Affecting Resolution - Column Length



Doubling the column length increases resolution by $(2)^{1/2}$

Table 23-2 Summary of chromatography equations

Quantity	Equation	Parameters
Partition coefficient	$K = C_s/C_m$	C_s = concentration of solute in stationary phase C_m = concentration of solute in mobile phase
Adjusted retention time	$t_r' = t_r - t_m$	t_r = retention time of solute of interest t_m = retention time of unretained solute
Retention volume	$V_r = t_r \cdot u_x$	u_x = volume flow rate = volume/unit time
Capacity factor	$k' = t_r'/t_m = KV_s/V_m$	V_s = volume of stationary phase V_m = volume of mobile phase
	$k' = \frac{t_s}{t_m}$	
t_s = time solute spends in stationary phase		t_m = time solute spends in mobile phase
Relative retention	$\alpha = \frac{t_{r2}'}{t_{r1}'} = \frac{k_2'}{k_1'} = \frac{K_2}{K_1}$	Subscripts 1 and 2 refer to two solutes
Separation factor	$\gamma = t_2/t_1\ (\gamma > 1)$	t_2 = retention time of solute 2 t_1 = retention time of solute 1
Number of plates	$N = \frac{16t_r^2}{w^2} = \frac{5.55t_r^2}{w_{1/2}^2}$	w = width at base $w_{1/2}$ = width at half-height
Plate height	$H = \frac{\sigma^2}{x} = \frac{L}{N}$	σ = standard deviation of band x = distance traveled by center of band L = length of column N = number of plates on column
Resolution	Resolution $= \frac{\Delta t_r}{w_{av}} = \frac{\Delta V_r}{w_{av}}$	Δt_r = difference in retention times ΔV_r = difference in retention volumes w_{av} = average width measured at baseline in same units as numerator (time or volume)
	Resolution $= \frac{1}{4}\sqrt{N}(\gamma - 1)$	N = number of plates γ = separation factor ($\gamma > 1$)

Table 23-2
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Column Efficiency- van Deemter Equation

- van Deemter (Dutch, 1956):

$$H \approx A + \frac{B}{u_x} + Cu_x$$

- H is plate height
- u is the flow rate through the column
- A, Multiple paths (Eddy diffusion)
- B/*u*, Longitudinal diffusion (molecular diffusion)
- C*u*, Equilibration time (resistance to mass transfer)

Multiple Paths (Eddy Diffusion)

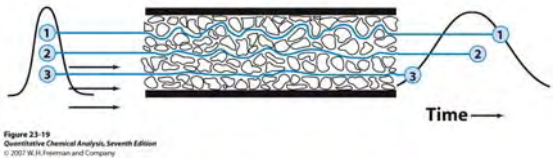

Figure 23-19
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In a packed column, analyte can diffuse through many different paths around the stationary phase.

Longitudinal Diffusion

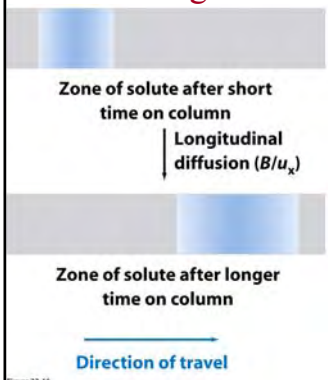

Figure 23-16
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- Solute diffuses from the high concentration within the band to regions of lower concentration on the edges of the band.
- Is inversely proportional with flow rate

Equilibration Time

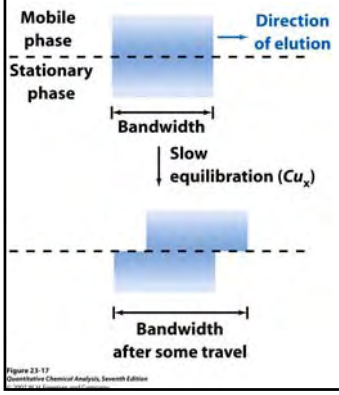


Figure 23-17
Quantitative Chemical Analysis, Seventh Edition

- Some solute is stuck in the stationary phase, which falls behind the solute in the moving forward mobile phase.
- Resulting in spreading the overall zone of solute
- Is propotional to flow rate

Van Deemter Plot for Gas Chromatography

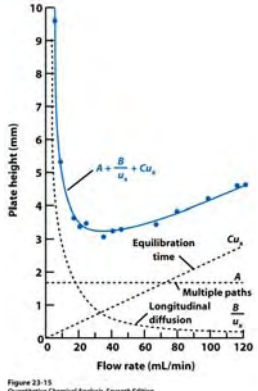


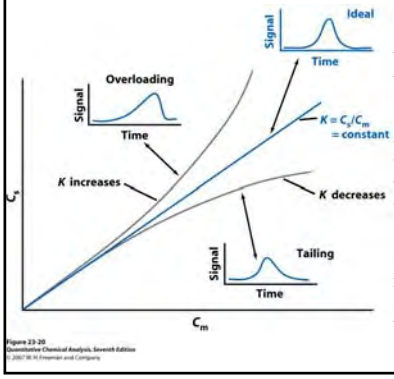
Figure 23-15
Quantitative Chemical Analysis, Seventh Edition

- A minimal plate height of ~3 mm is obtained with flow rate of ~35 mL/min.
- Because longitudinal diffusion in a gas is much faster than diffusion in a liquid, the optimum linear flow rate in gas chromatography is higher than in liquid chromatography.

Asymmetric Bandshapes

- Theoretically, the band coming off a column should be Gaussian but this is not always the case
- This usually occurs when the partition coefficient, K (C_s/C_m) changes during the run
  - K can become either bigger or smaller
  - K becomes bigger when too much solute has been put into the column (**overloading**)-so much solute is dissolved that the stationary phase acts like the solute
  - K becomes smaller due to **tailing**-this is when the solute binds strongly to some sites on the column

Asymmetry and K



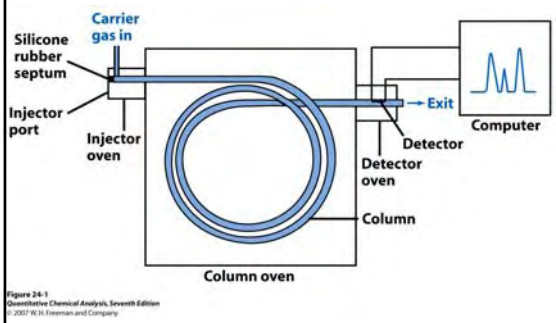
- Isotherm: a graph of Cs vs Cm at a given temperature
- Overloading produces a gradual rise and an abrupt fall of the chromatographic peak (load less solute).
- A long tail occurs when some sites retain solute more strongly than other sites (silanization to block –OH).

Ch. 24 Gas Chromatography (GC)

GC Process

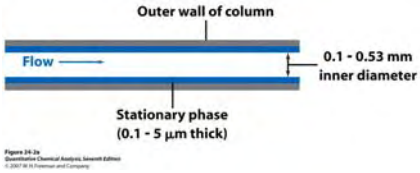
- In **gas chromatography**, vapor-phase analyte is swept through the column by a gaseous mobile phase (**carrier gas**)
  - Gas-liquid chrom (liquid stationary phase)
  - Gas-solid chrom (solid stationary phase)
  - The mobile phase is usually He, N_2, or H_2 depending on the application
- The analyte is a volatile liquid or gas that is injected through a **septum** (rubber disk)

Schematic Diagram of GC



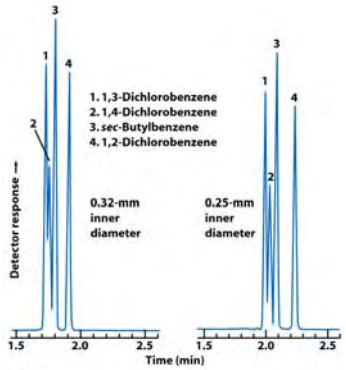
Gaseous analyte is transported through the column by a gaseous mobile phase.

Open Tubular Columns

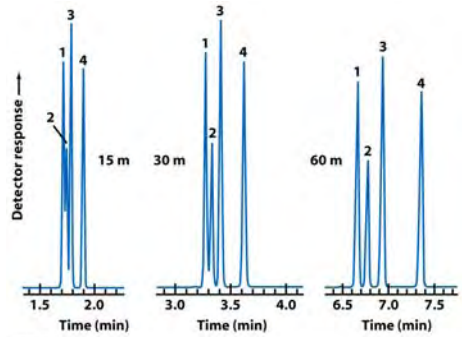


- Fused silica (SiO_2) coated with a polyimide that can withstand 350˚C.
- Typically, inner diameters are 0.10-0.53 mm and lengths are 15-100 m.
- Compared to packed columns: give higher resolution, shorter analysis time, greater sensitivity, lower sample capacity

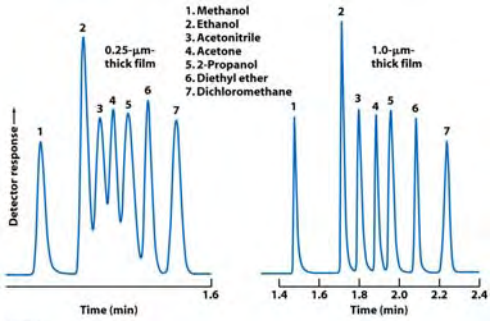
Effect of Inner Diameter on Resolution



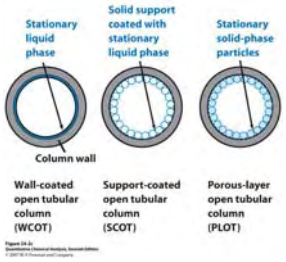
Effect of Column Length on Resolution



Effect of Stationary Phase Thickness on Resolution



Open Tubular Columns



- Wall-coated: liquid stationary phase on inside wall of column
- Supported-coated: liquid stationary phase coated on solid support attached to inside wall of column
- Porous-layer: solid stationary phase on inside wall of column (higher surface area, handle larger samples)

Stationary Phases

- Chosen based on the rule that "like dissolves like".
- The silica backbone and the polarity.
- Strongly polar columns are best for strongly polar solute.
- As a column ages, stationary phase bakes off and Si-OH groups become exposed (tailing peaks).

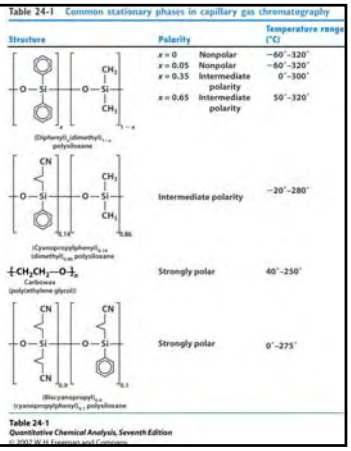
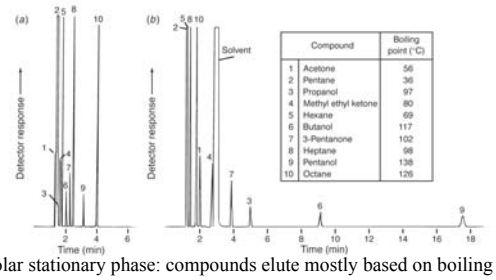


Table 24-2 Polarity of solutes

Nonpolar	Weak intermediate polarity
Saturated hydrocarbons	Ethers
Olefinic hydrocarbons	Ketones
Aromatic hydrocarbons	Aldehydes
Halocarbons	Esters
Mercaptans	Tertiary amines
Sulfides	Nitro compounds (without α-H atoms)
CS_2	Nitriles (without α-atoms)
Strong intermediate polarity	**Strongly polar**
Alcohols	Polyhydroxyalcohols
Carboxylic acids	Amino alcohols
Phenols	Hydroxy acids
Primary and secondary amines	Polyprotic acids
Oximes	Polyphenols
Nitro compounds (with α-H atoms)	
Nitriles (with α-H atoms)	

SOURCE: Adapted from H. M. McNair and E. J. Bonelli, Basic Gas Chromatography (Palo Alto, CA: Varian Instrument Division, 1968).

Retention Time



Non-polar stationary phase: compounds elute mostly based on boiling point.

Polar stationary phase: strongly retains the polar solutes (alcohols are strongly retained).

The Kovats Retention Index (I)

- Retention index relates the retention time of a solute to the retention times of linear alkanes
- For a linear alkane, $I = 100\times$# of C atoms (ex. for octane I=800; for nonane, I=900)

$$I = 100\left[n + (N-n)\frac{\log t_r'(\text{unknown}) - \log t_r'(n)}{\log t_r'(N) - \log t_r'(n)} \right]$$

N: # of carbon atoms in larger alkane
n: # of carbon atoms in smaller alkane

Table 24-3 Retention indexes for several compounds on common stationary phases

Phase	Retention index* Benzene b.p. 80°C	Butanol b.p. 117°C	2-Pentanone b.p. 102°C	1-Nitropropane b.p. 132°C	Pyridine b.p. 116°C
Poly(dimethylsiloxane)	657	648	670	708	737
(Diphenyl)$_{0.05}$(dimethyl)$_{0.95}$-polysiloxane	672	664	691	745	761
(Diphenyl)$_{0.35}$(dimethyl)$_{0.65}$-polysiloxane	754	717	777	871	879
(Cyanopropylphenyl)$_{0.14}$-(dimethyl)$_{0.86}$polysiloxane	726	773	784	880	852
(Diphenyl)$_{0.65}$(dimethyl)$_{0.35}$-polysiloxane	797	779	824	941	943
Poly(ethylene glycol)	956	1 142	987	1 217	1 185
(Biscyanopropyl)$_{0.9}$-(cyanopropylphenyl)$_{0.1}$-polysiloxane	1 061	1 232	1 174	1 409	1 331

a. For reference, boiling points (b.p.) for various alkanes are hexane, 69°C; heptane, 98°C; octane, 126°C; nonane, 151°C; decane, 174°C; undecane, 196°C. Retention indexes for the straight-chain alkanes are fixed values and do not vary with the stationary phase: hexane, 600; heptane, 700; octane, 800; nonane, 900; decane, 1 000; undecane, 1 100.

SOURCE: Restek Chromatography Products Catalog, 1993–94, Bellefonte, PA.

Table 24-3
Quantitative Chemical Analysis, Seventh Edition
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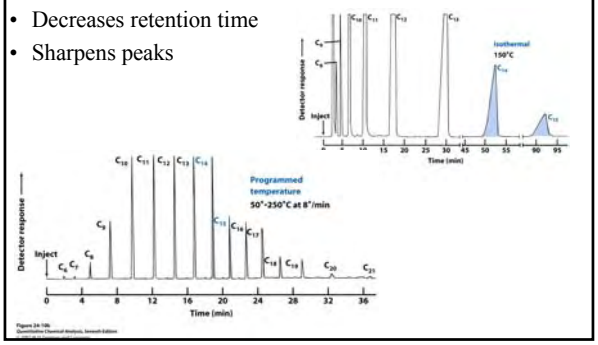
- Example: If retention times for methane, octane, and nonane in a GC run are 0.5, 14.3, and 18.5 minutes respectively, what is the retention index for an unknown that elutes at 15.7 minutes?

$$I = 100\left[8 + (9-8)\frac{\log 15.2 - \log 13.8}{\log 18.0 - \log 13.8} \right] = 836$$

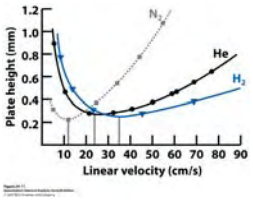
Temperature Programming

- The temperature of the column is raised during the separation to increase solute vapor pressure
- Decreases retention time
- Sharpens peaks

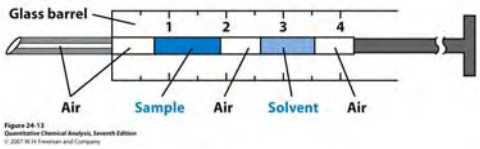


Carrier Gas

- Helium is the most common carrier gas.
- The choice is mostly dependent on the type of detector used.
- H_2 provides the fastest separations and a better resolution, but limited by it's reactivity



Sample Injection

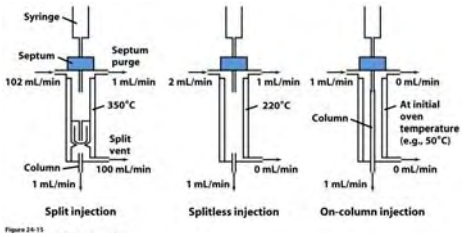


•"Sandwich" injection technique

•The air bubble before the sample: preventing sample from volatilizing in the injector oven before you inject it.

•The air bubble behind the sample: prevent sample and solvent from mixing.

Sample Injection



•Split injection: analytes are > 0.1% of the sample; impurities do not get onto the column in large concentrations.

•Splitless injection: trace analyses < 0.01% of the sample.

•On-column injection: go straight onto the column rather than through an injector oven; for samples that thermally decompose.

Detectors

- Most common:
  - Thermal conductivity detector (TCD)
  - Flame ionization detector (FID)
- Other detectors:
  - Mass spectrometer (MSD)
  - Infrared spectrometer (IRD)
  - Electron capture (ECD)
  - Nitrogen-phosphorous (NPD)
  - Atomic emission (AED)

Thermal Conductivity Detector (TCD)

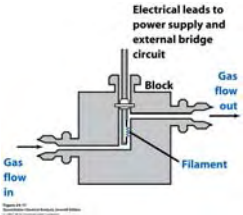
Table 24-4 Thermal conductivity at 273 K and 1 atm

Gas	Thermal conductivity J/(K • m • s)
H_2	0.170
He	0.141
NH_3	0.021 5
N_2	0.024 3
C_2H_4	0.017 0
O_2	0.024 6
Ar	0.016 2
C_3H_8	0.015 1
CO_2	0.014 4
Cl_2	0.007 6

The energy per unit area per unit time flowing from a hot region to a cold region is given by

$$\text{Energy flux } (J/m^2 \cdot s) = -\kappa(dT/dx)$$

where κ is the thermal conductivity [units = J/(K • m • s)] and dT/dx is the temperature gradient (K/m). Thermal conductivity is to energy flux as the diffusion coefficient is to mass flux.



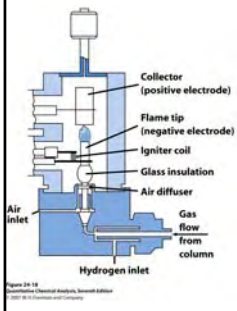
•Measures how much a substance can transport heat from a hot to cold region.

•Helium is the commonly used carrier gas (has a 2nd highest thermal conductivity after H_2)

•When an analyte emerges from the column with it, conductivity will decrease.

•Response to all analytes, but sensitivity is not very good.

Flame Ionization Detector (FID)



•The most common detector for GC

•Response nearly all analytes (insensitive to nonhydrocarbons)

•Has greater sensitivity than a TCD.

•Eluate is burned in a mixture of H_2 and air. Most carbon atoms (except C=O) produce radicals that produce CHO^+ in the flame:

$$CH + O \rightarrow CHO^+ + e^-$$

•Measure the electron current produced, which is proportional to the number of molecules present.

Detector Figures of Merit

Table 24-5 Detection limits and linear ranges of gas chromatography detectors

Detector	Approximate detection limit	Linear range
Thermal conductivity	400 pg/mL (propane)	$>10^5$
Flame ionization	2 pg/s	$>10^7$
Electron capture	As low as 5 fg/s	10^4
Flame photometric	<1 pg/s (phosphorus)	$>10^4$
	<10 pg/s (sulfur)	$>10^3$
Nitrogen-phosphorus	100 fg/s	10^5
Sulfur chemiluminescence	100 fg/s (sulfur)	10^5
Photoionization	25 pg to 50 pg (aromatics)	$>10^5$
Fourier transform infrared	200 pg to 40 ng	10^4
Mass spectrometric	25 fg to 100 pg	10^5

SOURCE: Most data are from D. G. Westmoreland and G. R. Rhodes, "Detectors for Gas Chromatography," Pure Appl. Chem. 1989, 61, 1147.