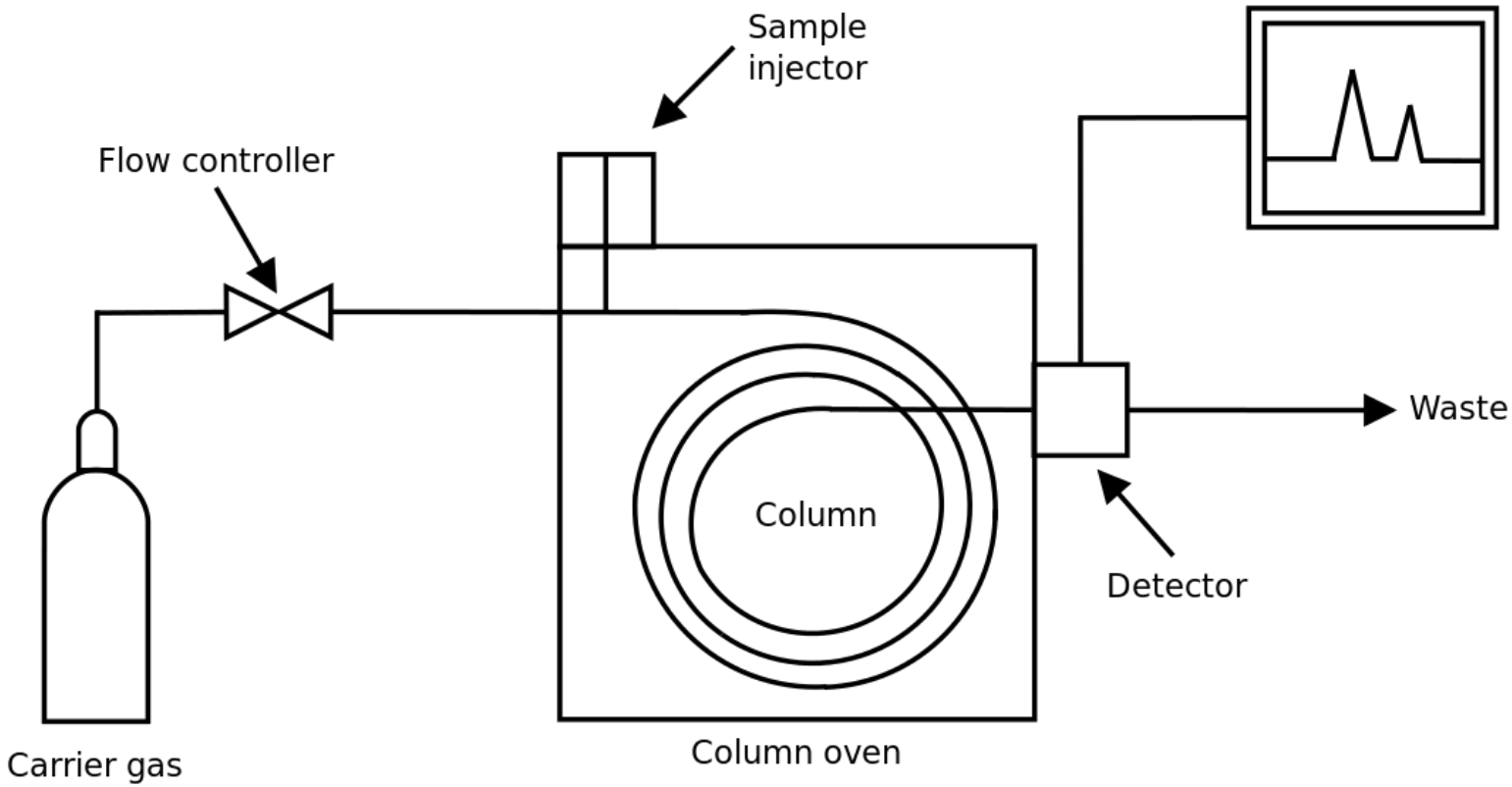
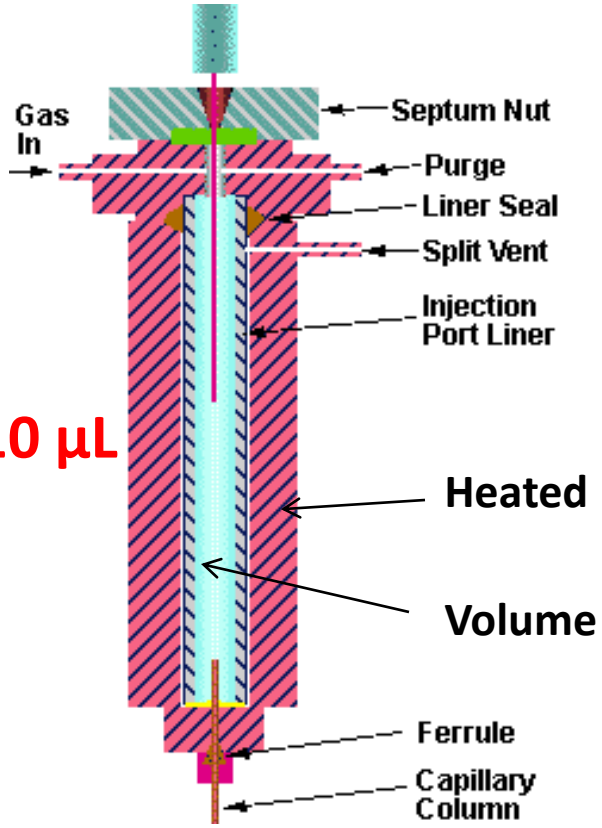
Gas Chromatograph

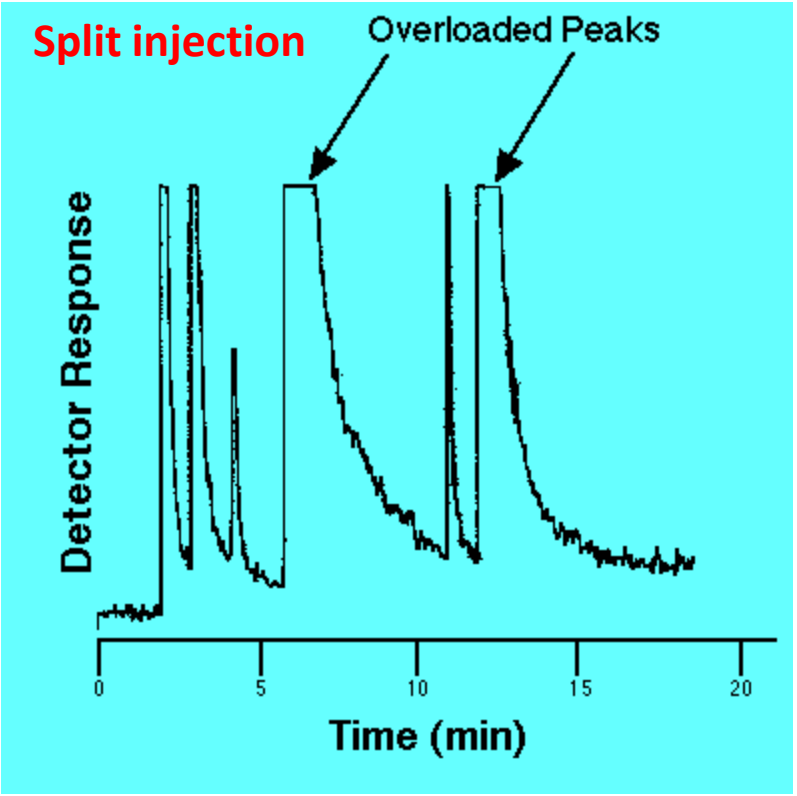
Temperature control of injection port and column are key.



Sample Injector



0.1 to 10 µL



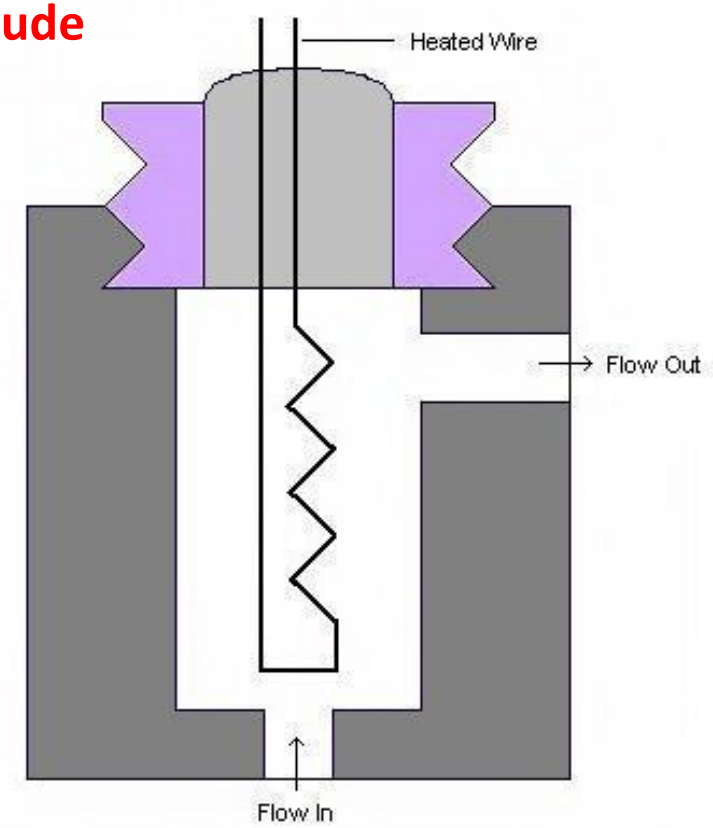
Must vaporize all of the analytes in sample. Often the injector temperature is about 50 °C the least volatile analyte.

Ideal Detector Characteristics

- Adequate sensitivity
- Good reproducibility and stability
- Dynamic range of 3-5 orders of magnitude
- Fast response time
- Stable to temperatures of 400 ^{o}C
- Nondestructive to the sample

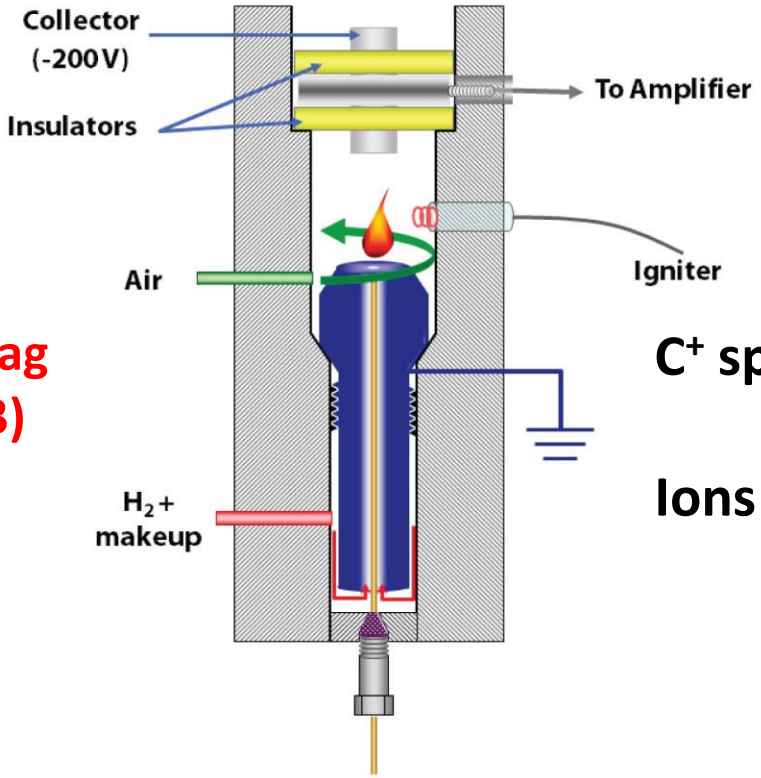
Thermal Conductivity Detector

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



Universal detector! Thermal conductivity of gas decreases with analyte present. Usually twin detectors used. One as a reference ahead of the column.

Flame Ionization Detector



LDR = 5-7 orders of mag
LOD = low ppb (S/N>3)
Destructive

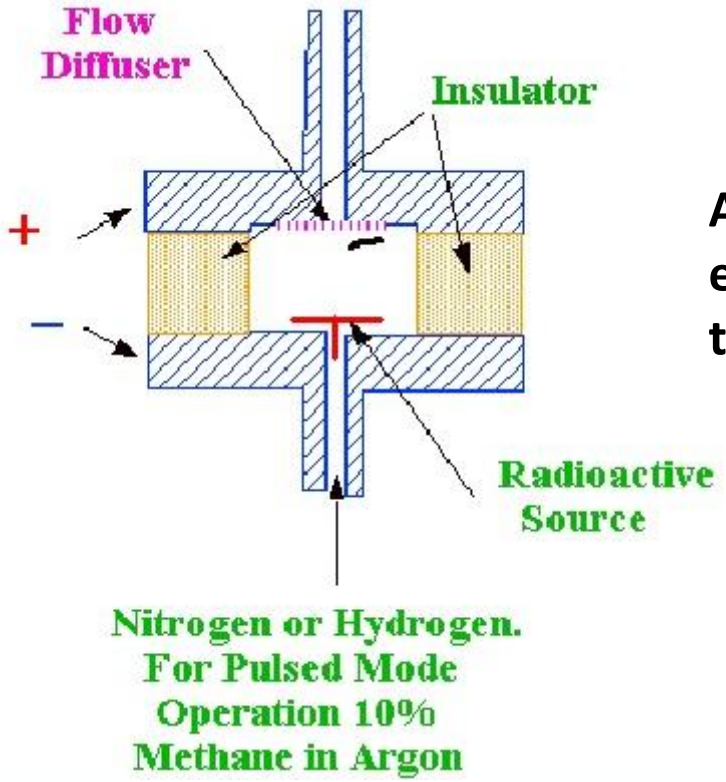
C^+ species produced.

Ions detected as a current

Excellent for <u>organic molecules</u>! Not responsive to H_2O, CO_2, SO_2, NO_x and some other non-combustible gases.

Electron Capture Detector

The electron capture detector contains a low energy beta-ray source, which is used to produce electrons for capturing by appropriate atoms/molecules.



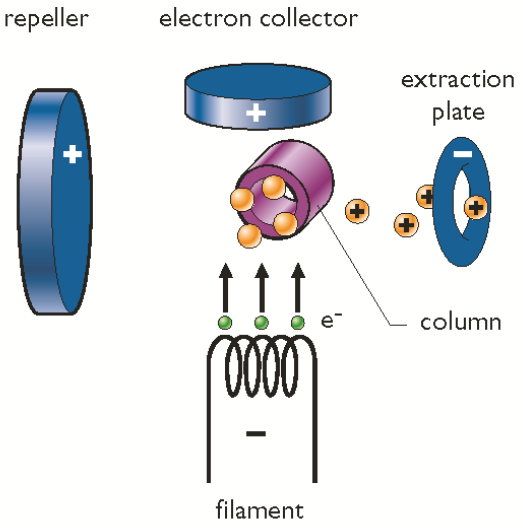
Analytes capture electrons and reduce the current.

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

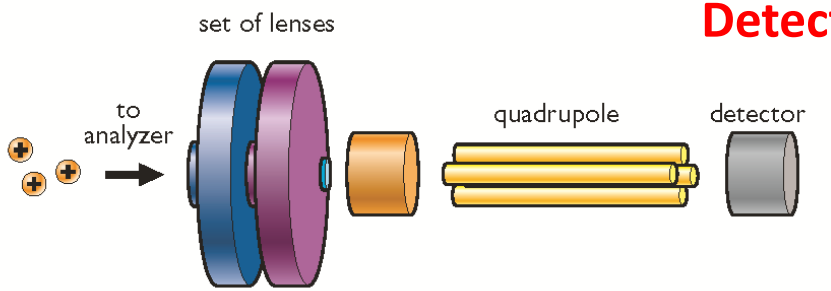
Compounds such as halogen-containing pesticides, peroxides, quinones, and nitro groups detected with high sensitivity.

Mass Spectrometric Detector

Qualitative and Quantitative Analysis!!! Universal Detector



Ionization



Detector

Analyzer

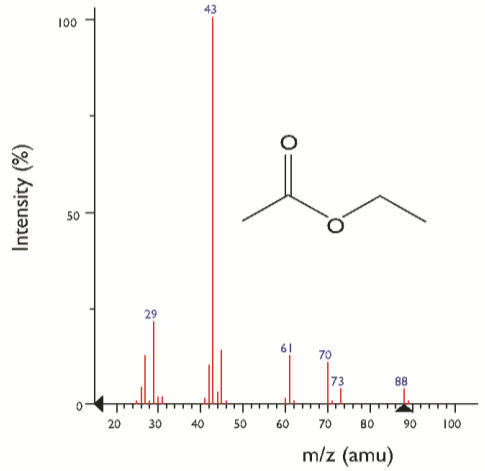
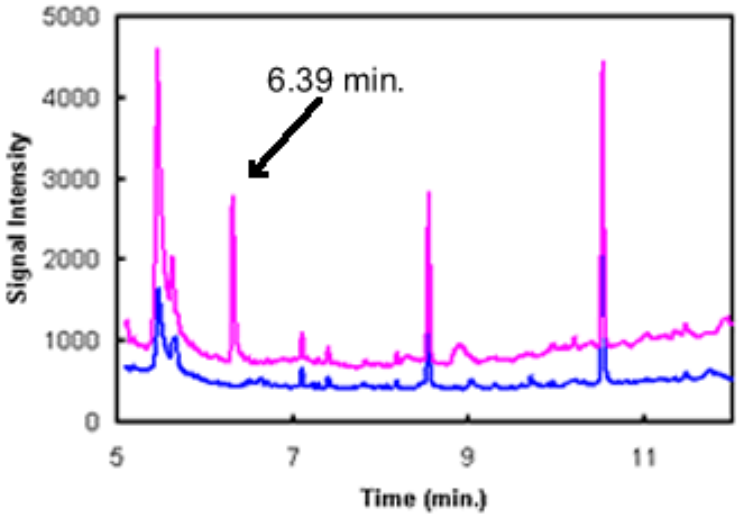
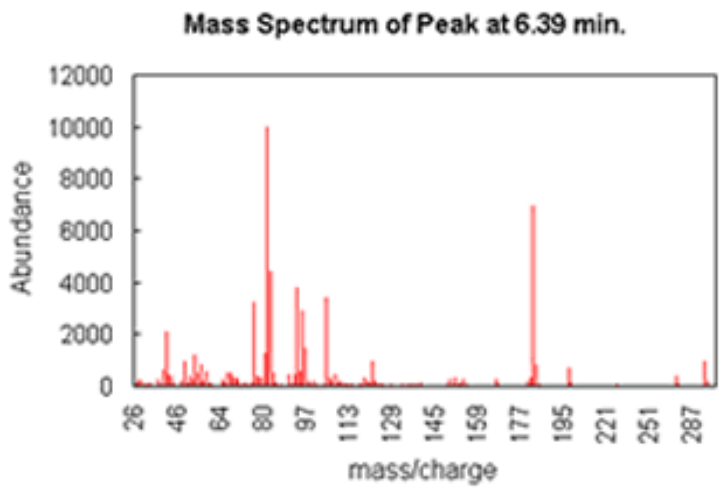


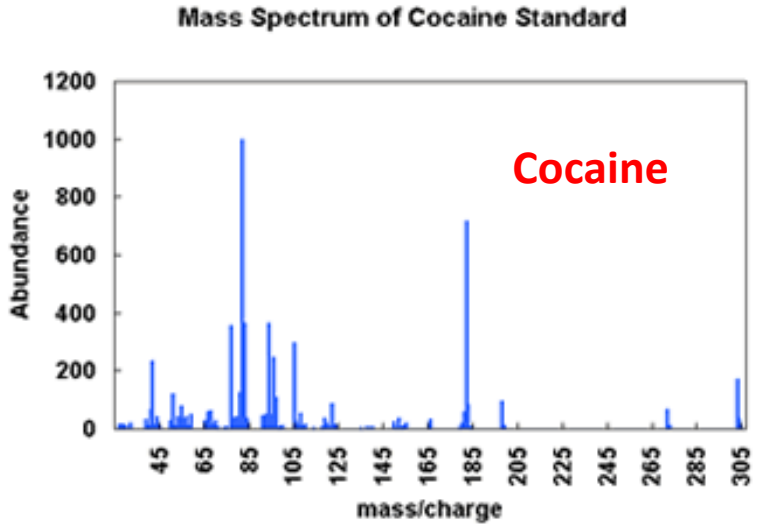
Fig. 2: Mass spectrum depicting the characteristic fragmentation pattern of ethyl acetate ($C_4H_8O_2$) with at M_w=88.05 g/mol the molecular (non-fragmented) ion.

LDR = 5-7 orders of mag
LOD = low ppb to high ppt range (S/N>3)

Mass Spectrometry - Data

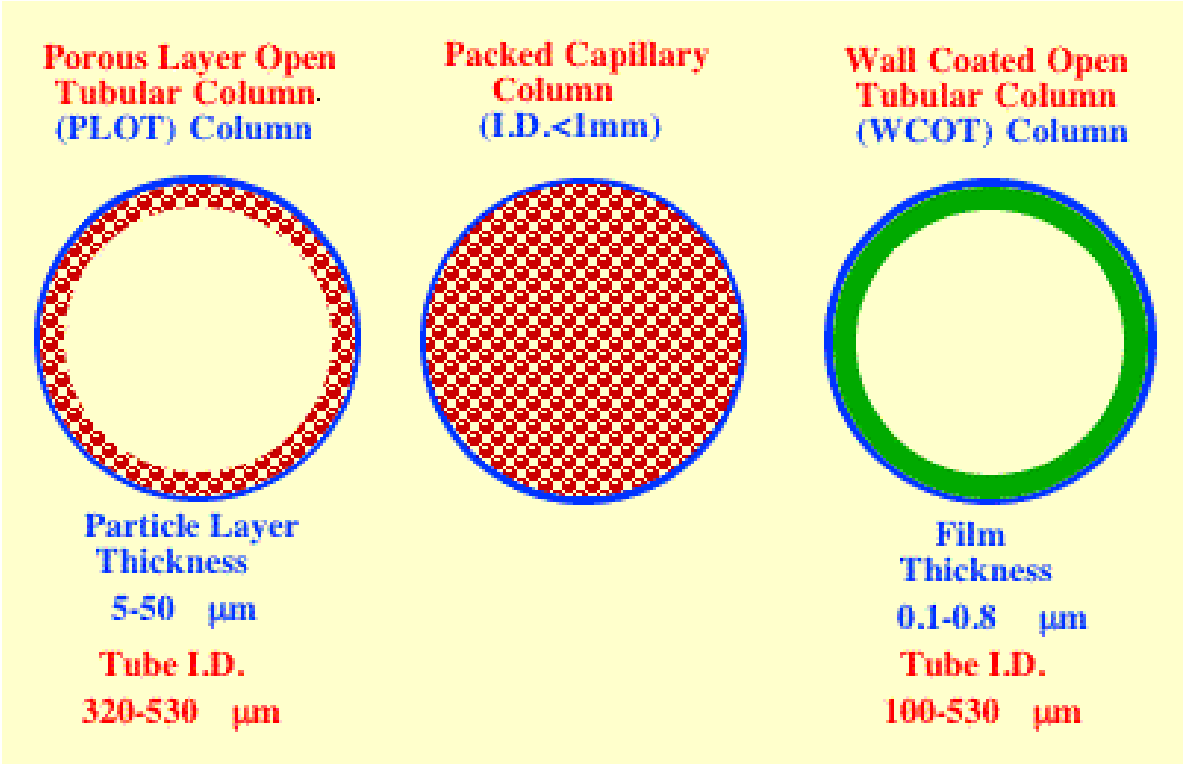




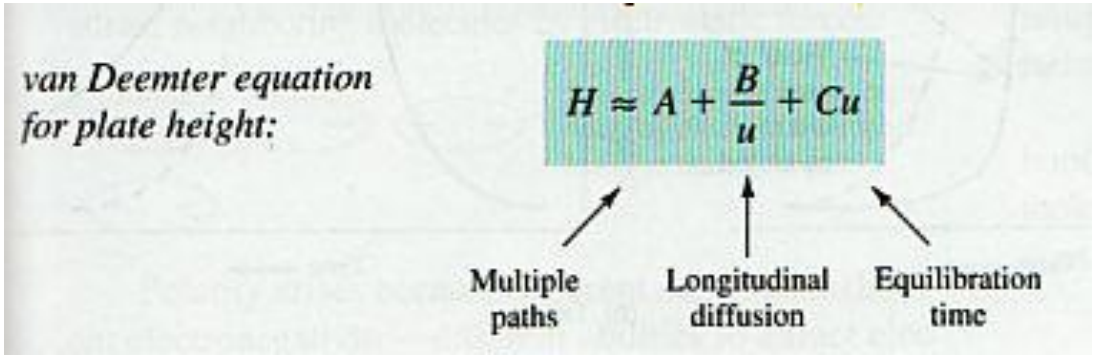


http://www2.kutztown.edu/academics/

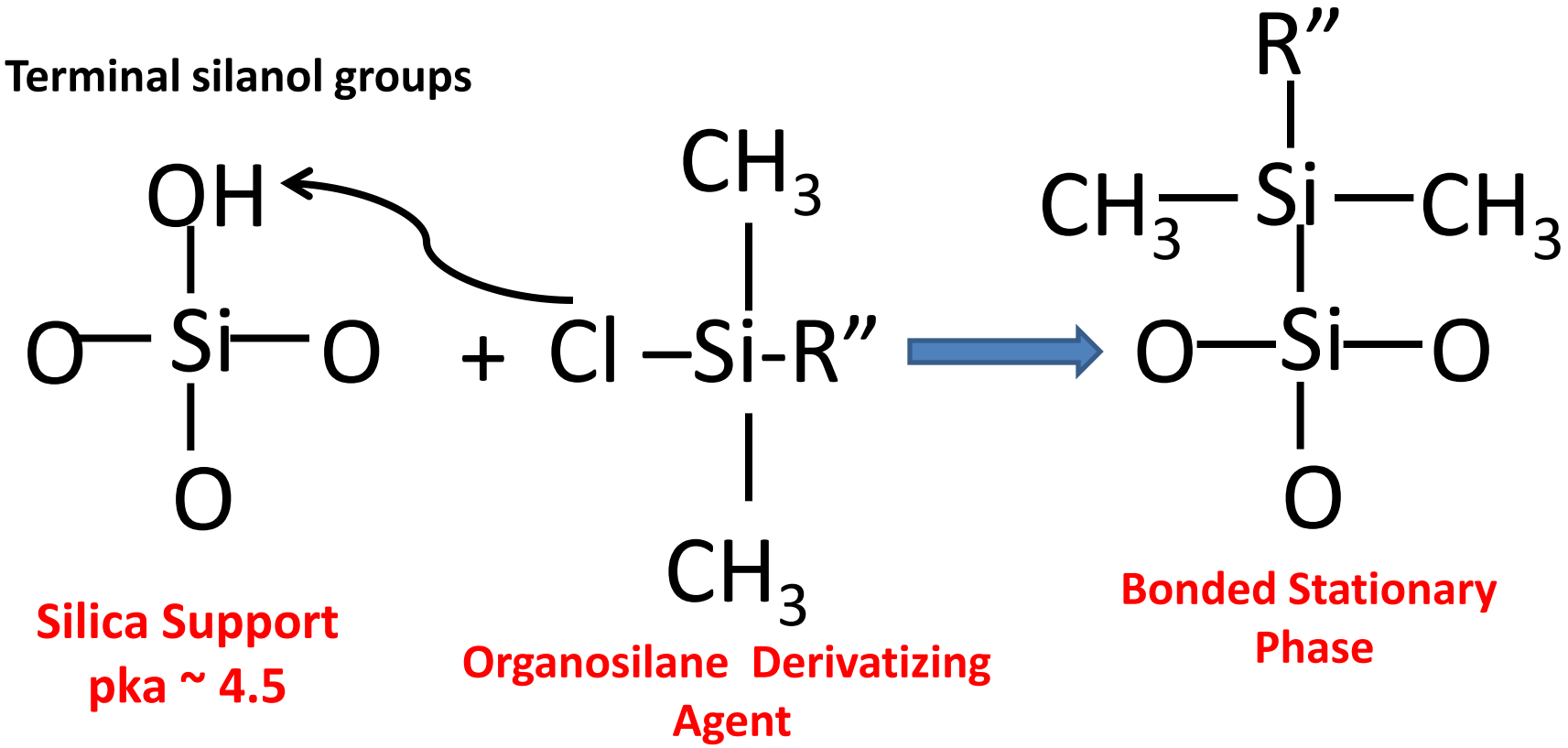
Column Types



N = L/H

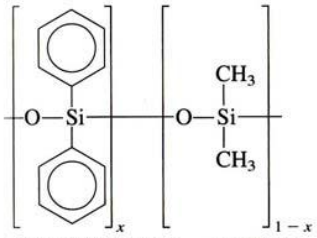
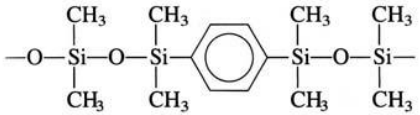
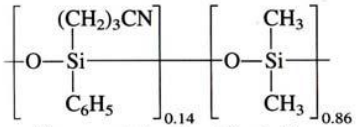
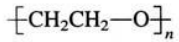
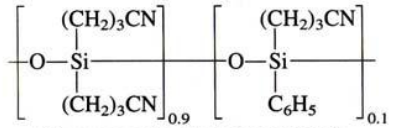


Bonded Stationary Phases



Stationary Phase Chemistry

Table 22-1 Common stationary phases in capillary gas chromatography

Structure	Polarity	Temperature range
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$ Nonpolar $x = 0.05$ Nonpolar $x = 0.35$ Intermediate polarity $x = 0.65$ Intermediate polarity	−60° to 360°C −60° to 360°C 0° to 300°C 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

Stationary Phase Chemistry

Table 1. Phase Polarity Based on Compound Polarity

Compound Polarity	Compound Examples	Recommended Phases
Non-polar		
C and H atoms only, C-C bonds	alkanes	Si-O-C_{18}
Polar		
C and H atoms, plus Br, Cl, F, N, O, P, and/or S	alcohols, acids, ethers, esters, amines, thiols	3.5% cyanopropyl, 3.5% phenyl, 93% methyl polysiloxane
Polarizable		
C and H atoms only, C=C or C=C bonds	alkenes, alkynes, aromatics	Si-O-C_3H_6-CN

Like interacts with like!!

Stationary Phase Retention Mechanisms

- Retention mechanisms of non-polar columns are primarily dispersive, meaning that they are governed by Van der Waals forces. These are intermolecular attractions that increase with the size of the compound. Thus, larger compounds with higher boiling points have longer retention. Elution order generally follows the boiling points of the compounds.

- Retention mechanisms of intermediate polar columns and polar columns are strongly dispersive. Moderate amounts of hydrogen bonding and basic interactions are also possible. Phases with phenyl functional groups can also undergo π - π, dipole-dipole, and dipole-induced dipole interactions. Separations are determined by differences in the overall effects of these mechanisms.

- Retention mechanisms of highly polar columns and extremely polar columns are strongly dispersive, very strongly dipole-dipole, and very strongly dipole-induced dipole. Moderately basic interactions are also possible. Separations are determined by differences in the overall effects of these mechanisms.

Separation Mechanisms

Different compounds have different ***retention times***. For a particular compound, the retention time will vary depending on:

The boiling point of the compound. A compound which boils at a temperature higher than the column temperature is going to spend nearly all of its time condensed as a liquid at the beginning of the column. So high boiling point means a long retention time.

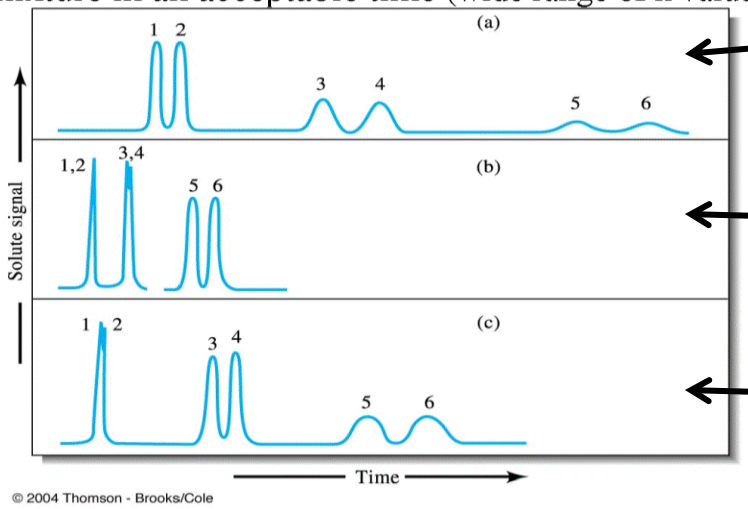
The solubility in the liquid phase. The more soluble a compound is in the liquid phase, the less time it will spend being carried along by the gas. High solubility in the liquid phase means a high retention time.

The temperature of the column. A higher temperature will tend to excite molecules into the gas phase - because they evaporate more readily.

The General Elution Problem

The "general" elution problem:

a single set of conditions is often unsatisfactory for good separation of all components in a complex mixture in an acceptable time (wide range of k values)



Early eluting components well separated

Late eluting components well separated

Some combination of the conditions leads to separation of all components

a) all components separated but time is long and peak widths are broad at long times

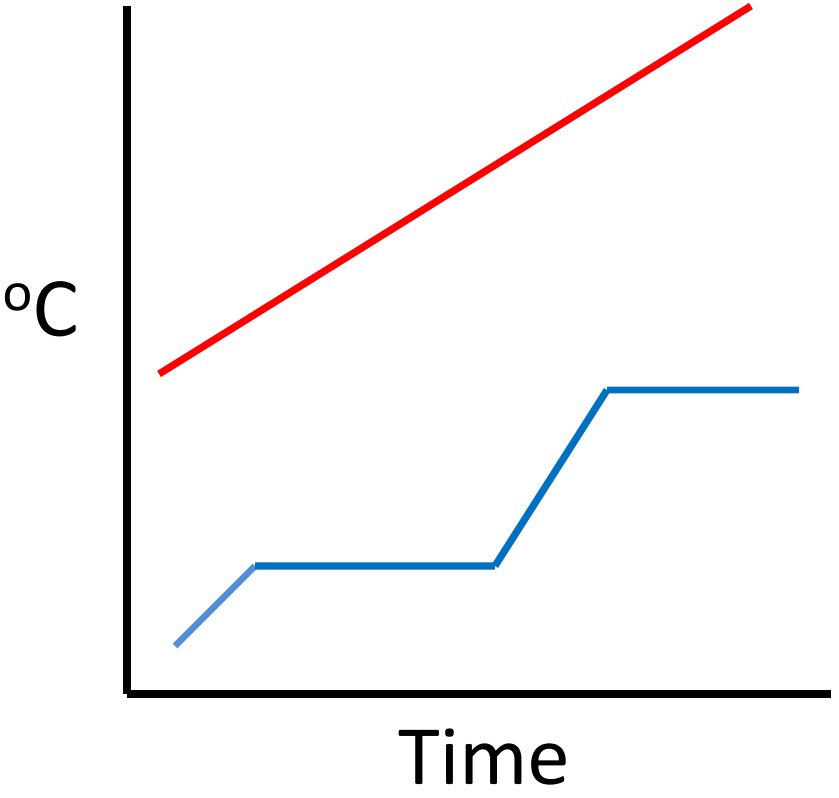
b) a faster separation and good peak shapes for 5,6 but 1,2 and 3,4 are not resolved

c) intermediate case where 1,2 still not resolved

common solution: change separation conditions dynamically – e.g. temperature gradient, solvent gradient

Temperature Programming – Solution to General Elution Problem

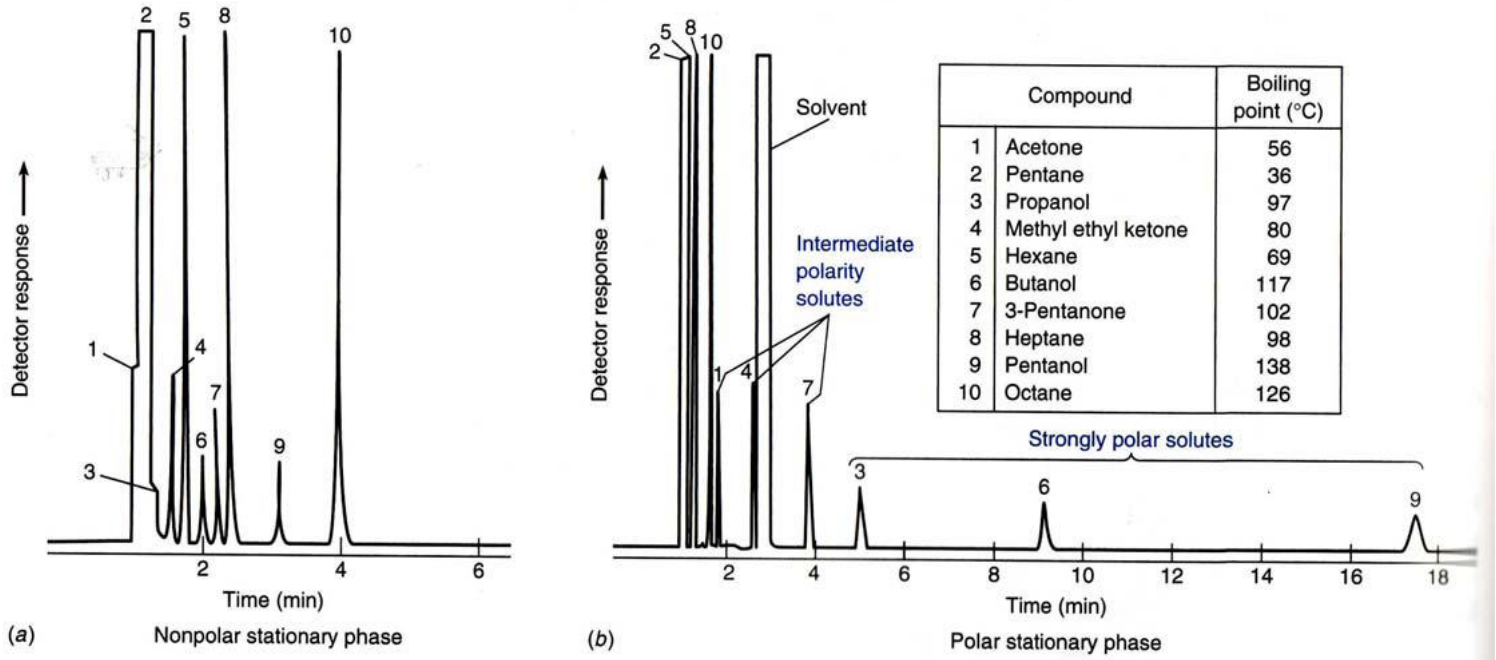
- Raising column temp. decreases retention times.
- Sharpens peaks
- **<u>Necessary</u>** for separating compounds with a wide range of boiling points or polarities



Fixed temperature separation = *isothermal* separation

Real Separation

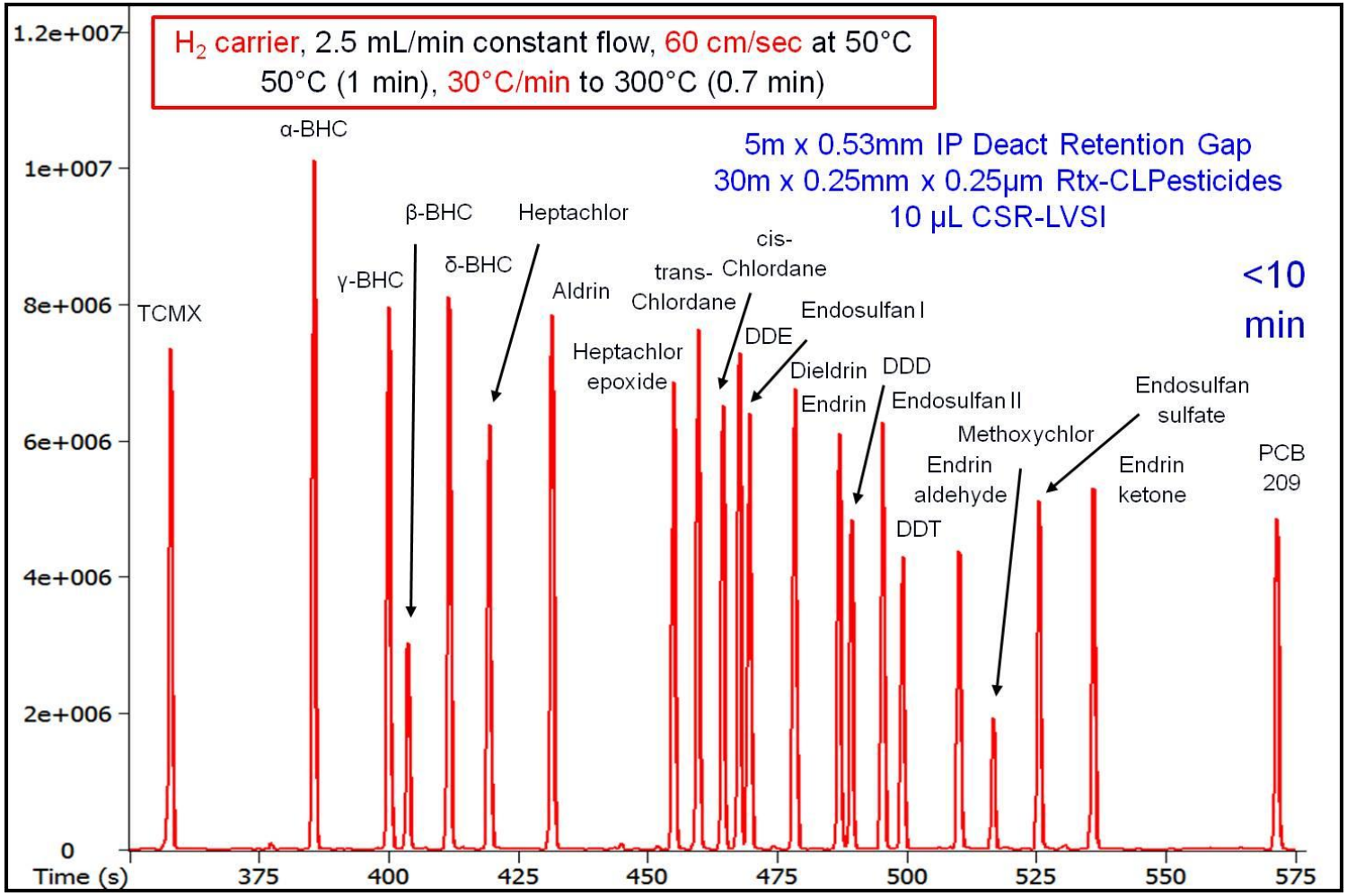
Non-polar stat phase **Polar stat phase**



	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.]

Real Separation



Separation Strategy

- It is often found that by controlling the capacity factor, *k′*, separations can be greatly improved. This can be achieved by changing the temperature (in Gas Chromatography) or the composition of the mobile phase (in Liquid Chromatography).

- The selectivity factor, α, can also be manipulated to improve separations. When α is close to unity, optimizing *k′* and increasing *N* is not sufficient to give good separation in a reasonable time.

- In these cases, *k′* is optimized first, and then α is increased by one of the following procedures:

1. Changing mobile phase composition (LC)
2. Changing column temperature (GC)
3. Changing composition of stationary phase
4. Using special chemical effects (such as incorporating a species which complexes with one of the solutes into the stationary phase)