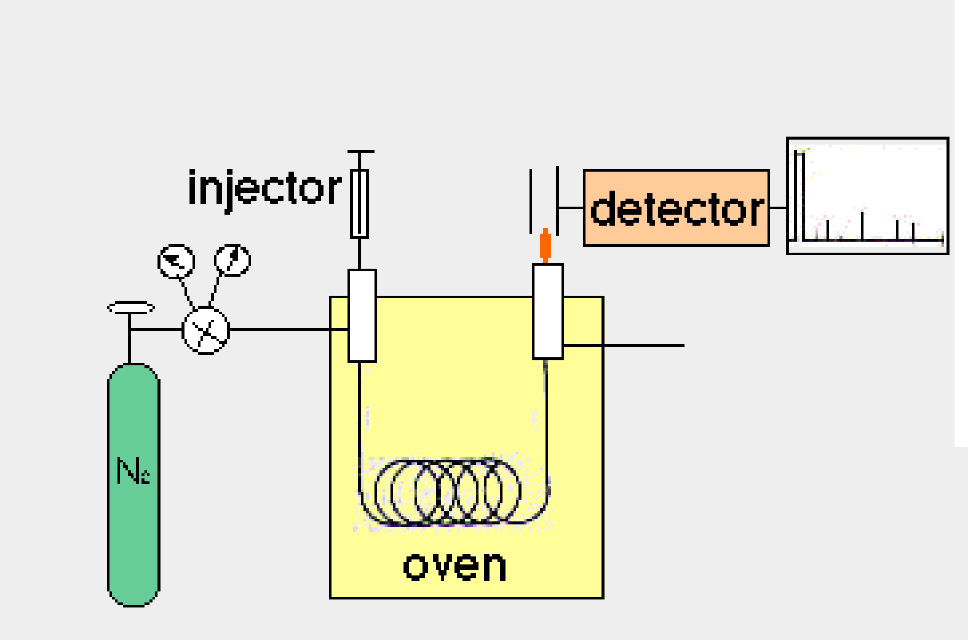
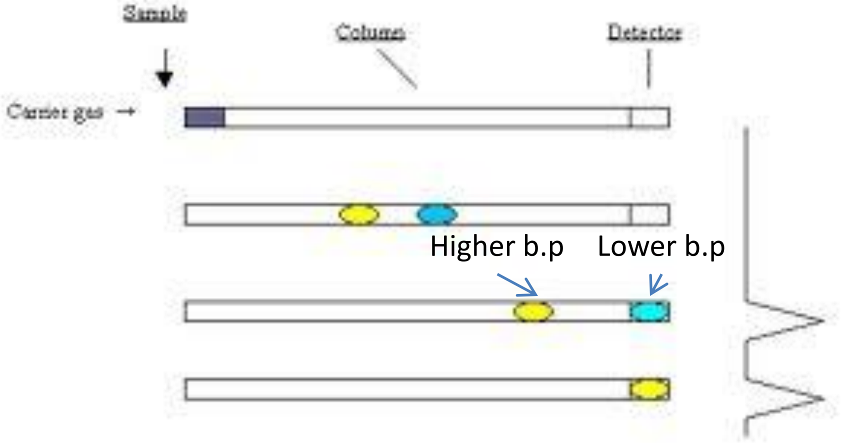
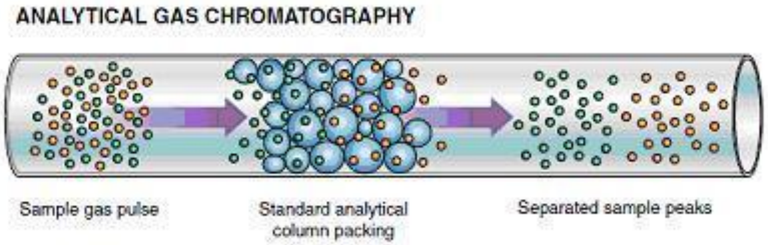
Chapter 22 - Gas Chromatography

Column separation (gas-liquid, gas-solid) used for separating and analyzing compounds that can be vaporized without decomposition.





Separations based on differences in boiling points!



Conditions

- Carrier gas (mobile phase) does NOTHING in GC but transport the compounds. Not involved in separation mechanism (H_2 and He common).

- Injection volume (0.1 – 10 µL generally). Temperature of injector is 50 ^{o}C greater than least volatile (highest boiling point compound). All compounds must be vaporized before transport onto column.

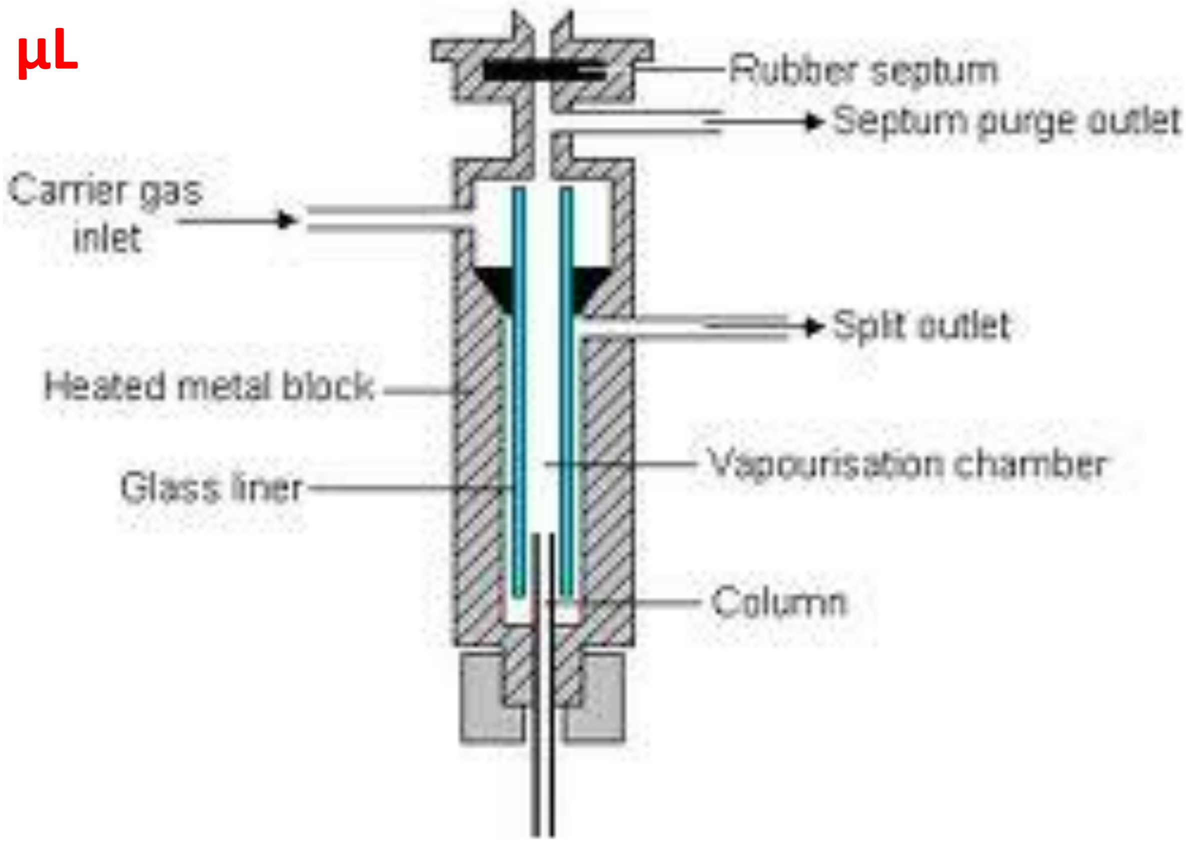
- Carrier gas is often dried by passage over molecular sieves as they strongly retain water. Activated by heating to 300 ^{o}C in vacuum.

- Gaseous mobile phase carries gaseous compounds (analytes) through a long column with a stationary phase.

Injector

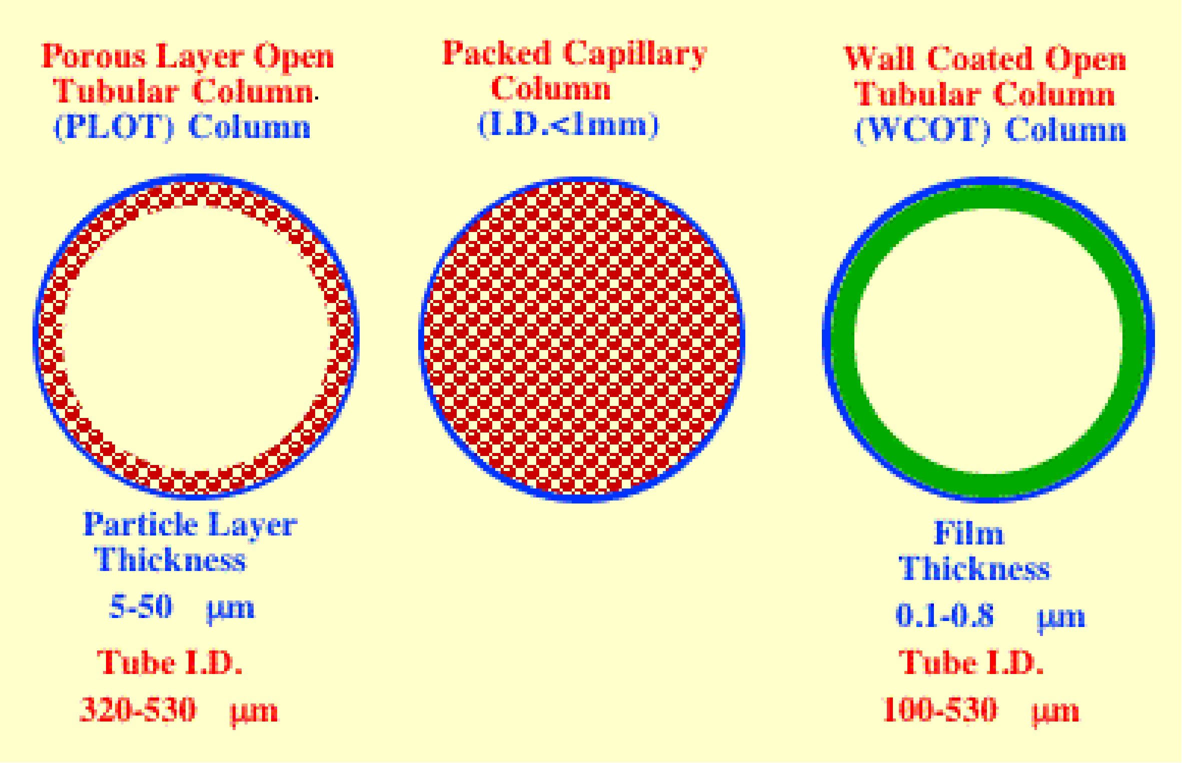
The split / splitless injector

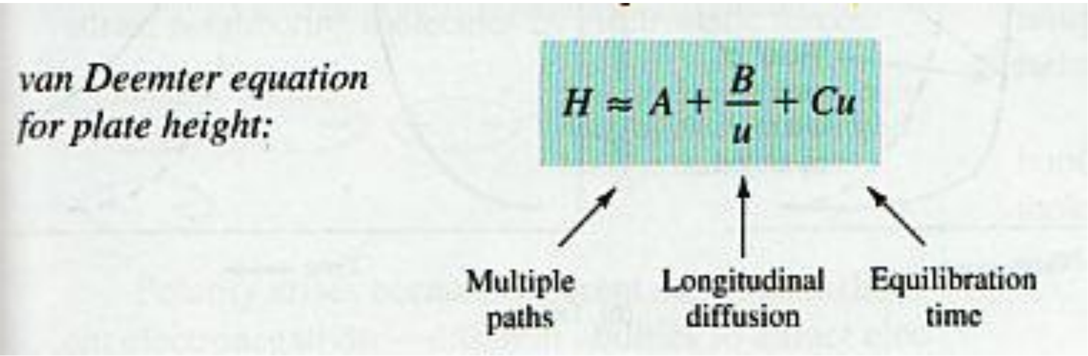
0.1 to 10 µL



Must vaporize all of the analytes in sample. Often the injector temperature is about 50 ^{o}C the least volatile analyte.

Column Types





van Deemter equation for plate height:

$$H \approx A + \frac{B}{u} + Cu$$

N = L/H

Stationary Phase Chemistry

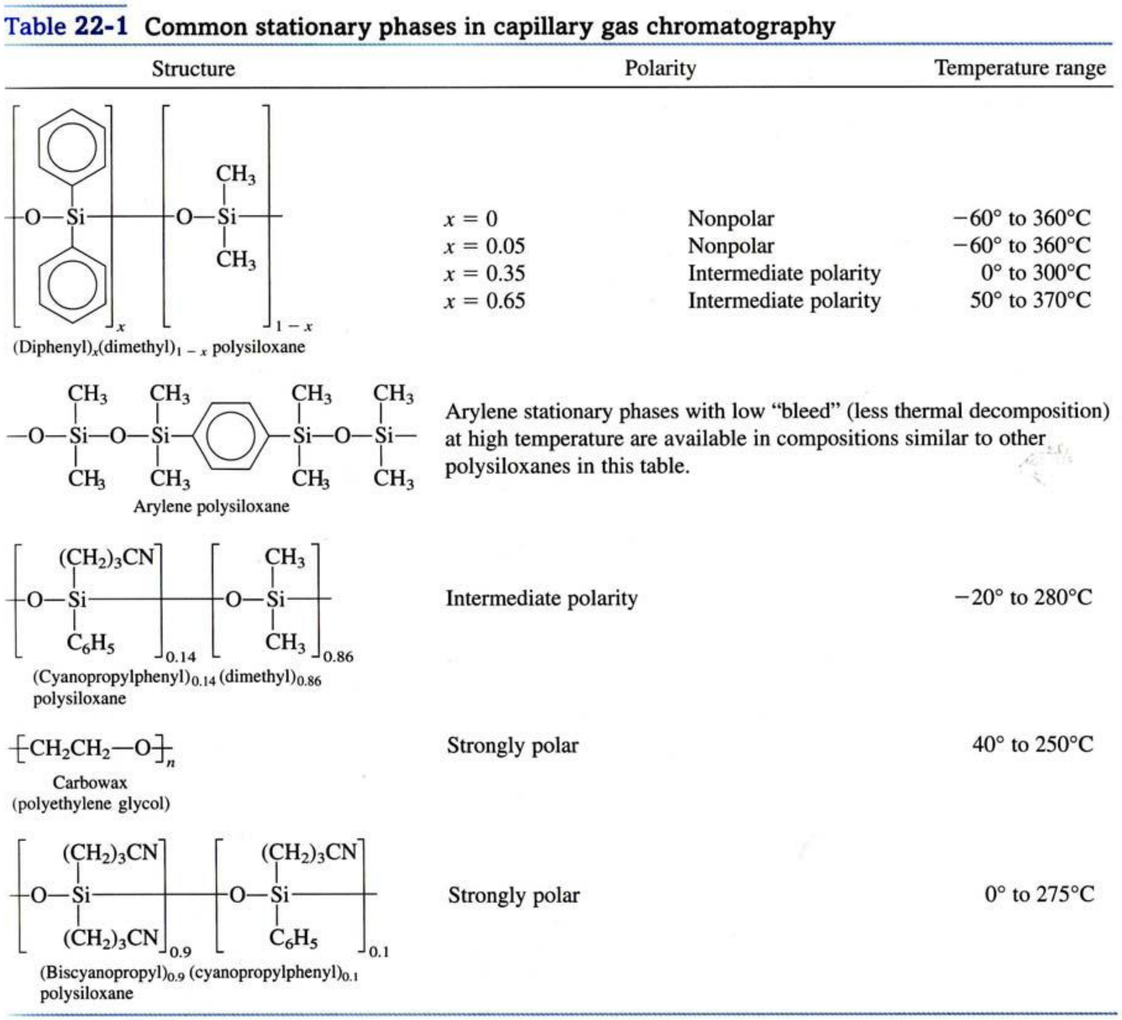


Table 22-1 **Common stationary phases in capillary gas chromatography**

Structure		Polarity	Temperature range
(Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$	Nonpolar	−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
$-[CH_2CH_2-O]_n-$ Carbowax (polyethylene glycol)		Strongly polar	40° to 250°C
(Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane		Strongly polar	0° to 275°C

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.

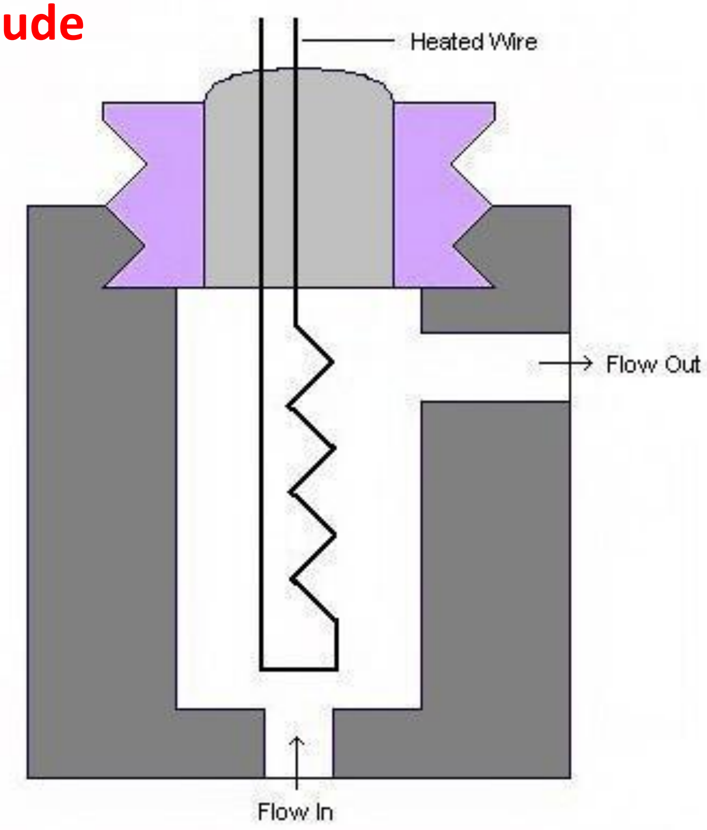
The temperature of the column. A higher temperature will tend to excite molecules into the gas phase - because they evaporate more readily.

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

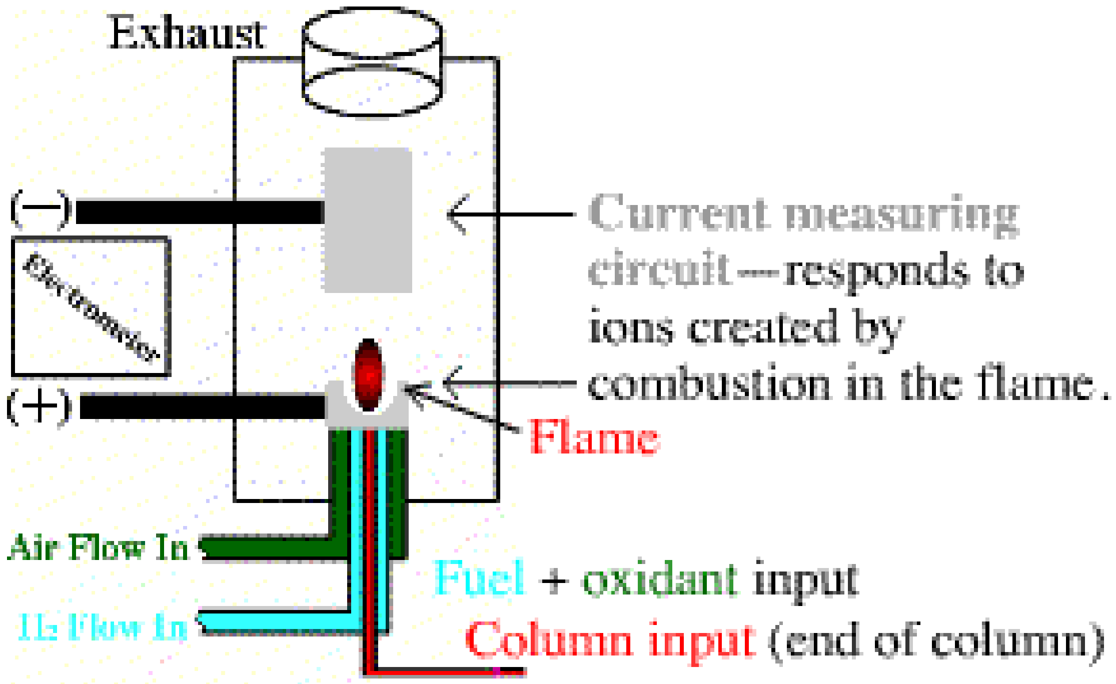
Thermal Conductivity Detector

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



Universal detector!   Thermal conductivity of gas decreases with analyte present.

Flame Ionization Detector (FID)



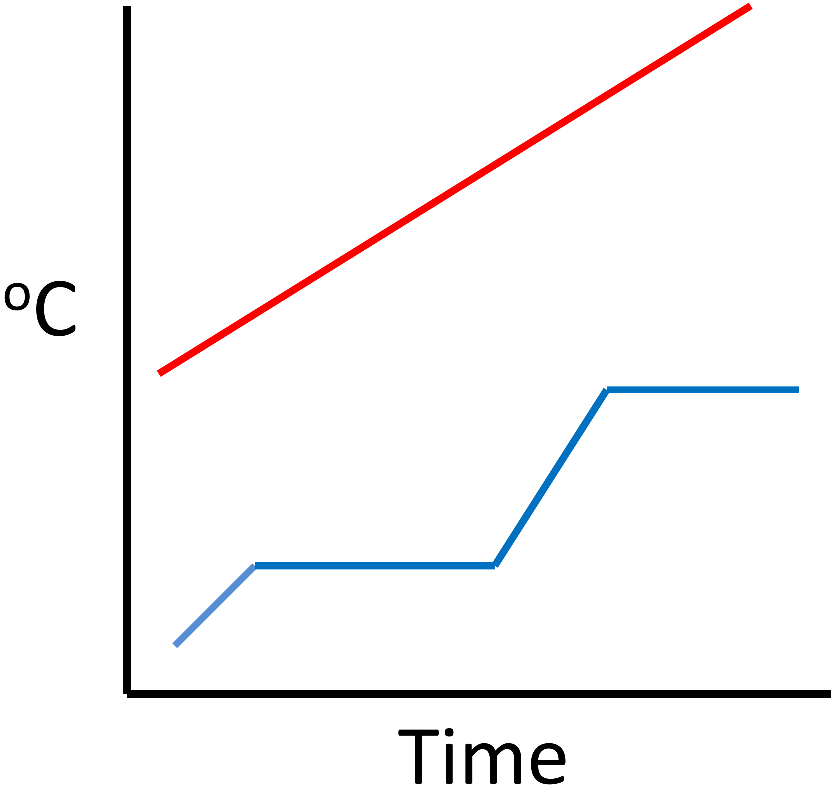
Excellent for organic molecules! Not responsive to H_2O, CO_2, SO_2, NO_x.

LDR = 5-7 orders of magnitude

LOD = low ppb (S/N>3)

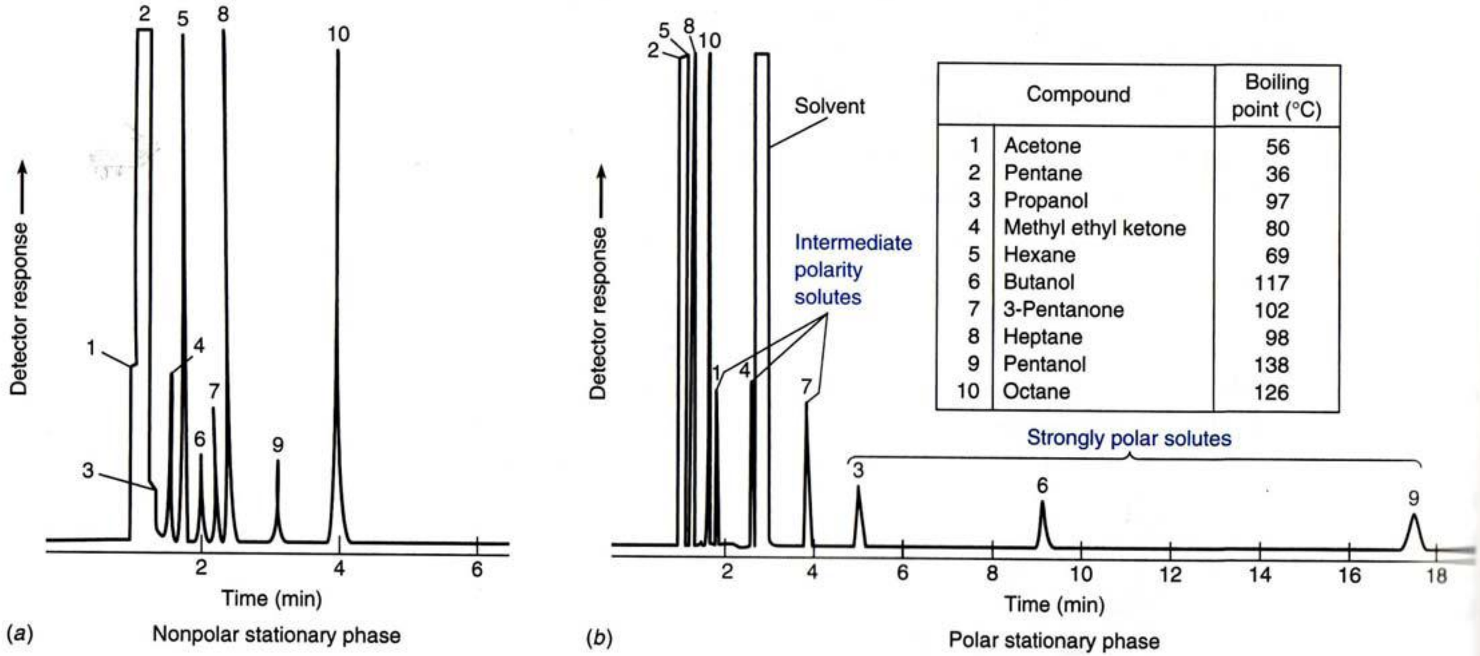
Temperature Programming

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



Fixed temperature separation = *isothermal* separation

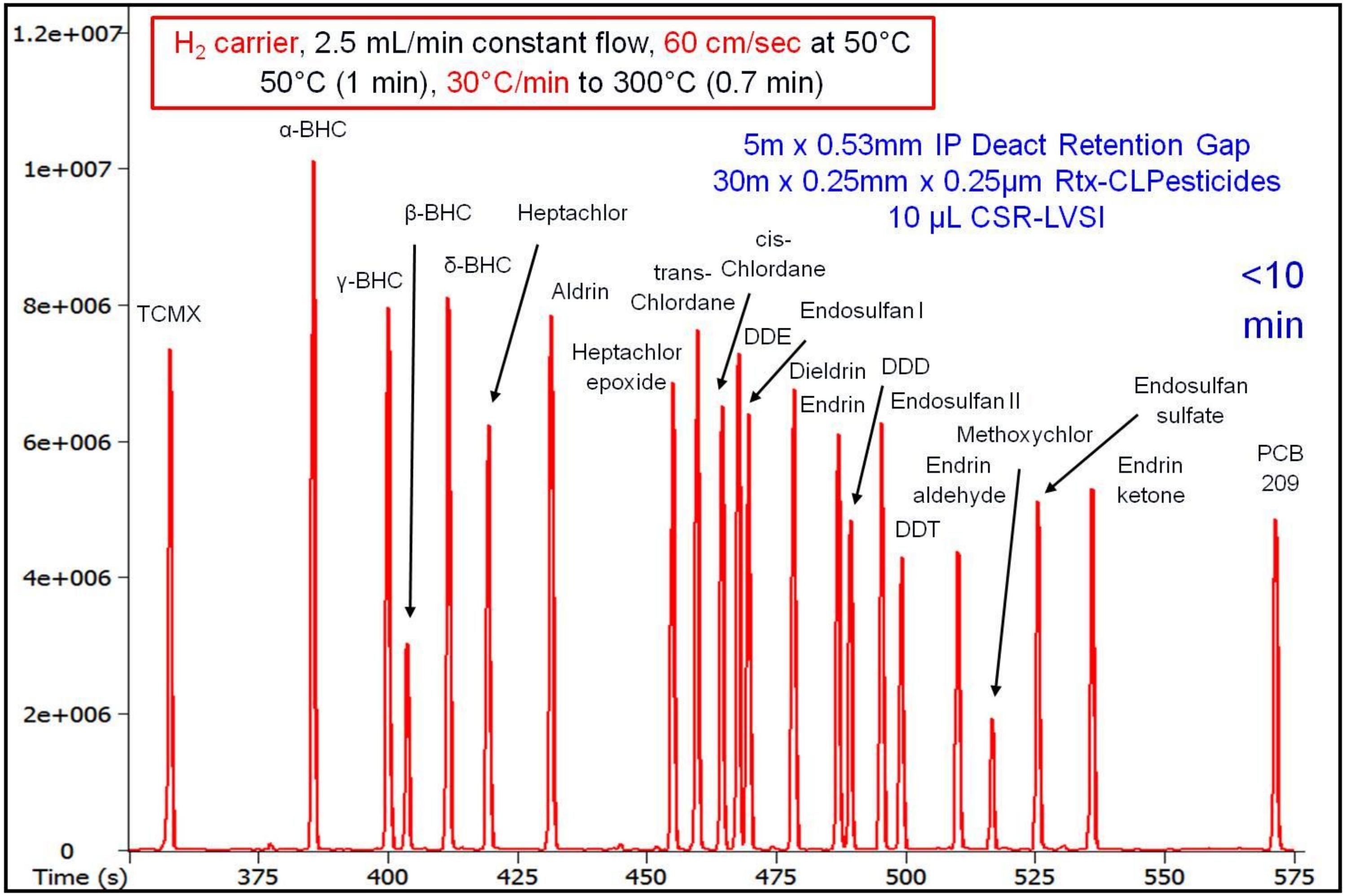
Real Separation



	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.]

Real Separation



H_2 carrier, 2.5 mL/min constant flow, 60 cm/sec at 50°C
50°C (1 min), 30°C/min to 300°C (0.7 min)

5m x 0.53mm IP Deact Retention Gap
30m x 0.25mm x 0.25µm Rtx-CLPesticides
10 µL CSR-LVSI

<10 min