…back to resolution

$\alpha = K_B/K_A$ = selectivity factor!　　　k' = capacity factor = $(t_r - t_m)/t_m$

$$R_s = \frac{t'_A - t'_B}{w_{avg}}$$

$$R_s = \frac{t_R^A - t_R^B}{t_R^B} \frac{\sqrt{N}}{4}$$

$$R_s = \frac{k'_B - k'_A}{1 + k'_B} \frac{\sqrt{N}}{4}$$

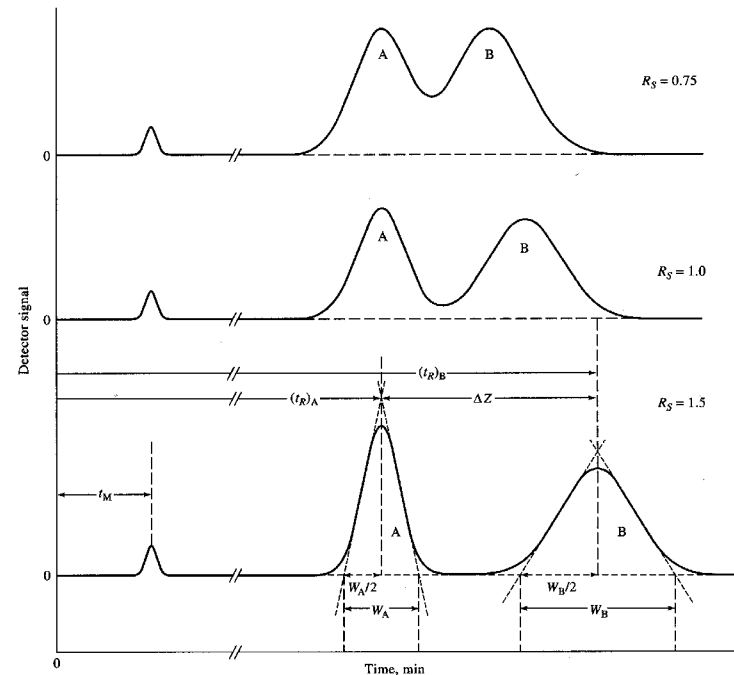$$R_s = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \frac{k'_B}{1 + k'_B}$$

Figure 26-11 Separations at three resolutions. Here, $R_s = 2\Delta Z/(W_A + W_B)$.

Here's the selectivity term again

General Elution Problem:
Resolution vs. Elution Time

(a) very slow elution

- last peaks are pretty broad
- all peaks base-line resolved

(b) fast separation

- all peaks are narrow
- 1,2 are not resolved

(c) the final compromise

- 1,2 barely resolved
- band widths are decent
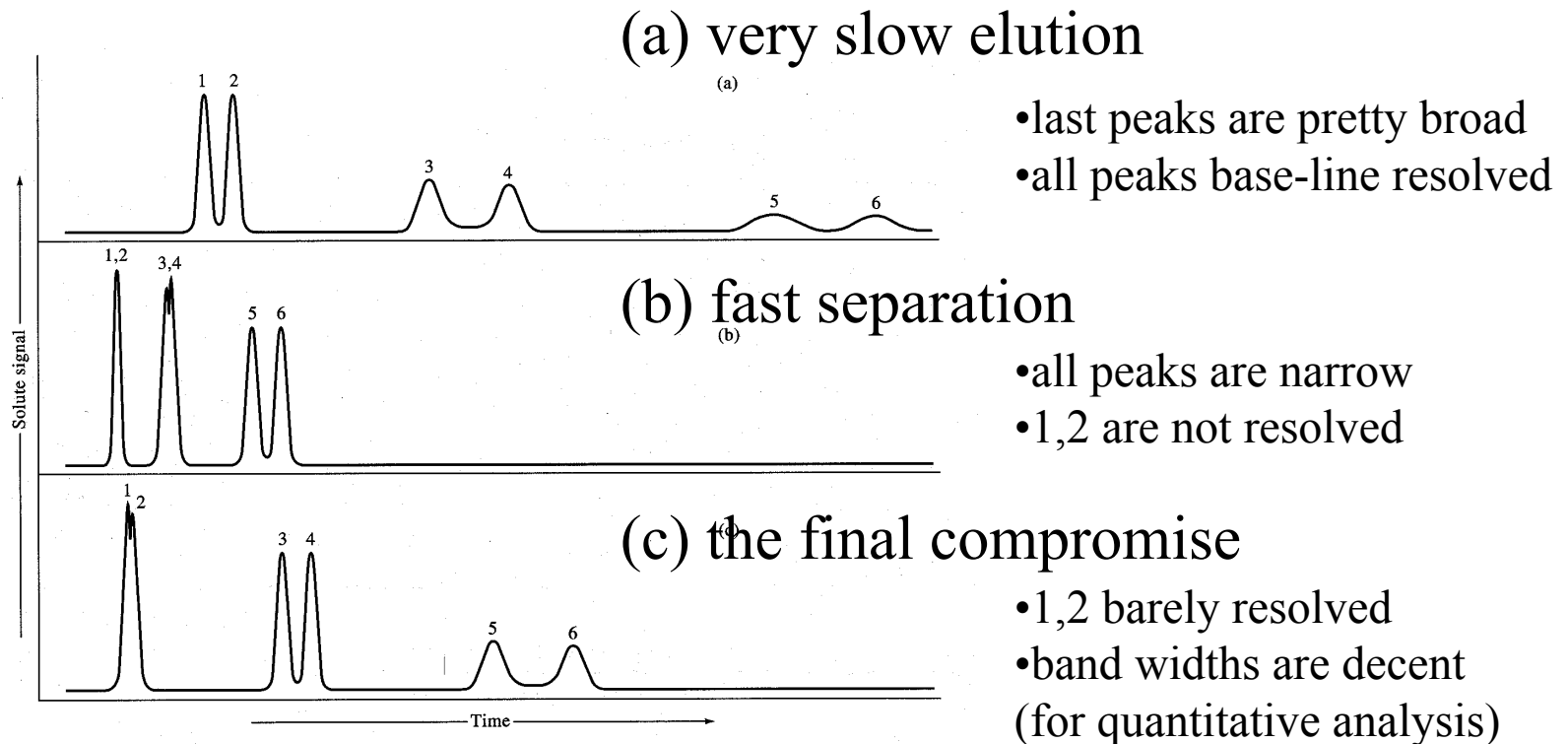(for quantitative analysis)

Figure 26-14 Illustration of the general elution problem in chromatography.

Gas Chromatography

- Mobile Phase: Gas
  - He, N_2 most common
- Stationary phase: Solid-Liquid
  - packed column--particles (GS) or liquid/polymer coated particles (GL)
  - glass column wall or, hydrocarbon solvent covalently bound to wall
- Applications:
  - small organic molecules (MW $< 10^3$)
  - research labs (industry, academia)
  - quality control, on-line process control
  - environmental

Like dissolves Like

- Chemical Principle: ionic or very polar solids are more soluble in polar (ionic) solvents (alcohols, acetone, acetonitrile)
- Weakly polar, nonpolar compounds are only soluble in apolar solvents (toluene, ether, hexane)
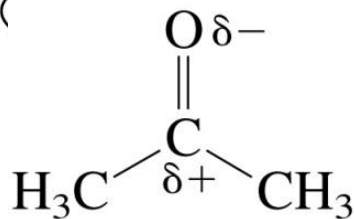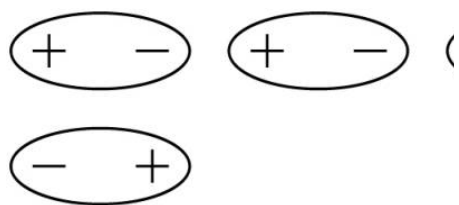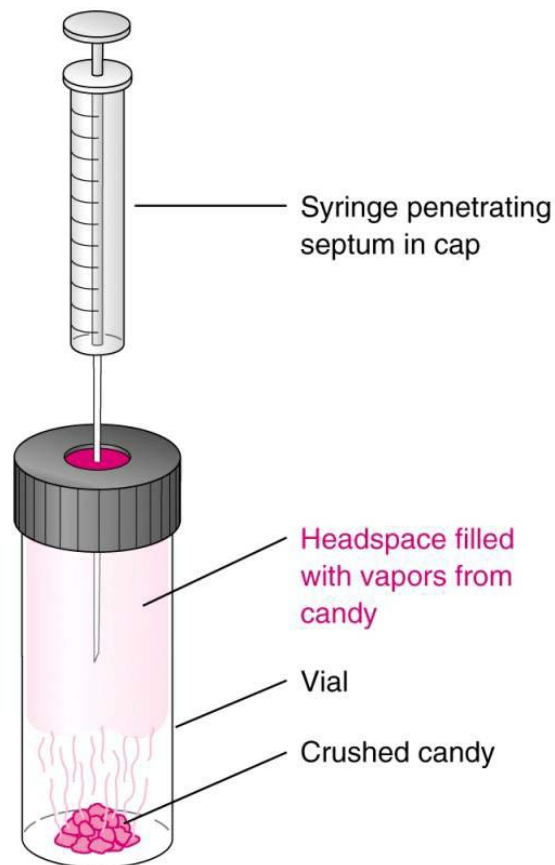

Acetone
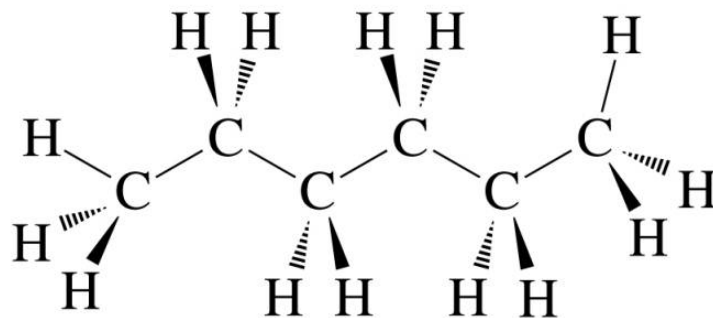
Hexane

Getting the Sample

- Volatile gases can be collected in a gas tight glass syringe

- small needle is inserted through a rubber septum (same septum is on the GC)

- Or (commonly) volatile liquids are injected

- solvent, (like acetone, acetonitrile) must not co-elute with any analyte of interest

Syringe penetrating septum in cap

Headspace filled with vapors from candy

Vial

Crushed candy

GC Instrument Schematic

Precise flow monitoring required, μ

Load sample here

Automation possible here
with sophisticated valves

Soap–bubble meter

Recorder

Syringe

Detector

Electrometer
or
bridge

Two-stage
pressure
regulator

Rotometer

Flow
splitter

Injector

ADC

Flow
controller

"inert" carrier
gas, e.g., He, N$_2$

Carrier
gas
supply
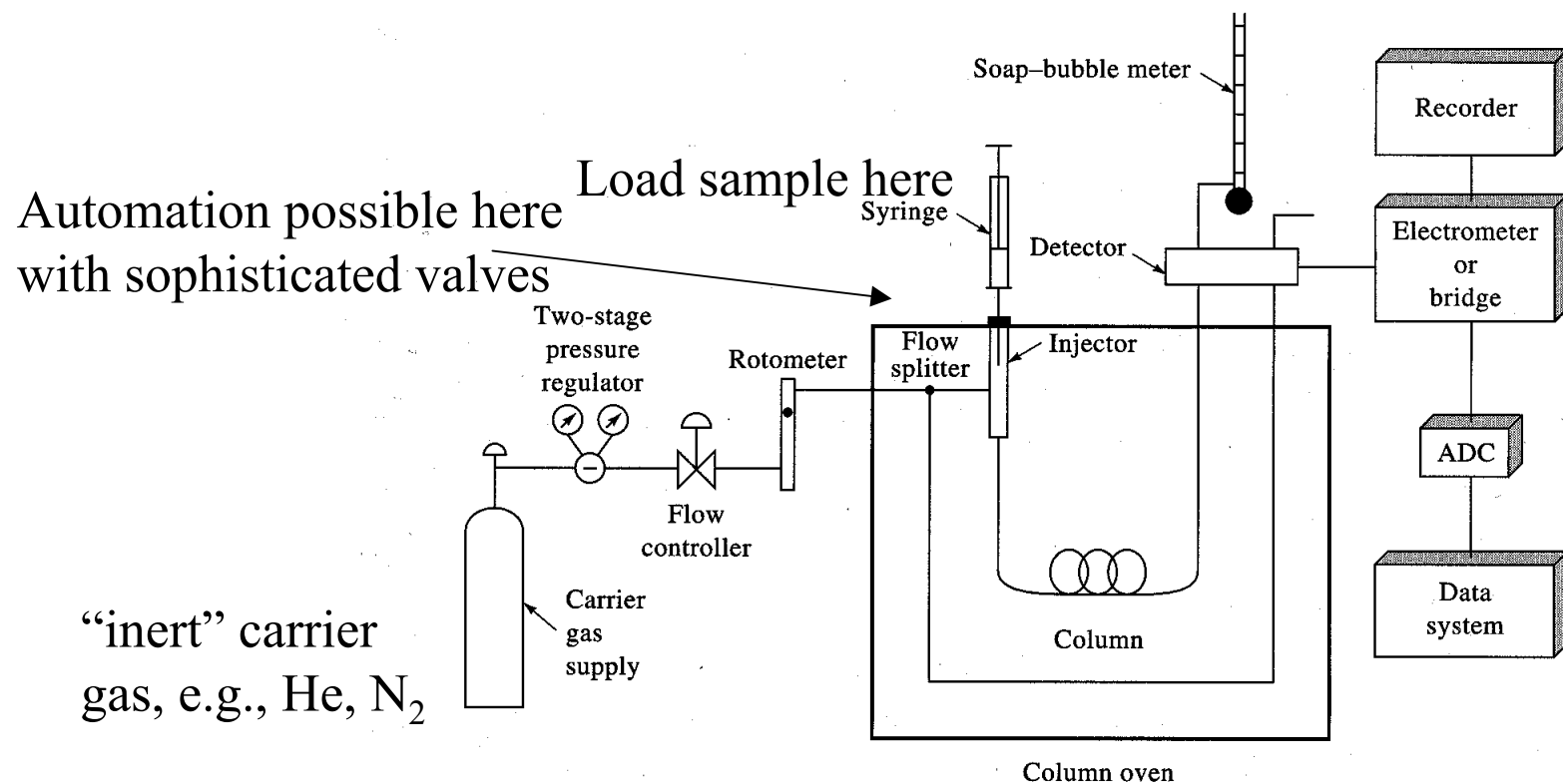
Column

Data
system

Column oven

Figure 27-1   Schematic of a gas chromatograph.

Temperature control very important
for optimized separations

Get the sample loaded

- Injection port designed to limit unwanted vapor from entering column

- typically 1-10 µL syringe used

- splitter diverts appr. 99% of the sample away from column
  - required by some very small capillaries

- chamber preheated to >50 ºC of the least volatile analyte carrier gas stream moves analyte onto the capillary

Syringe

Septum

Septum purge

Syringe needle

$\Delta P = 0.25$ psi mL^{-1} flow rate

Vaporization chamber

Carrier gas
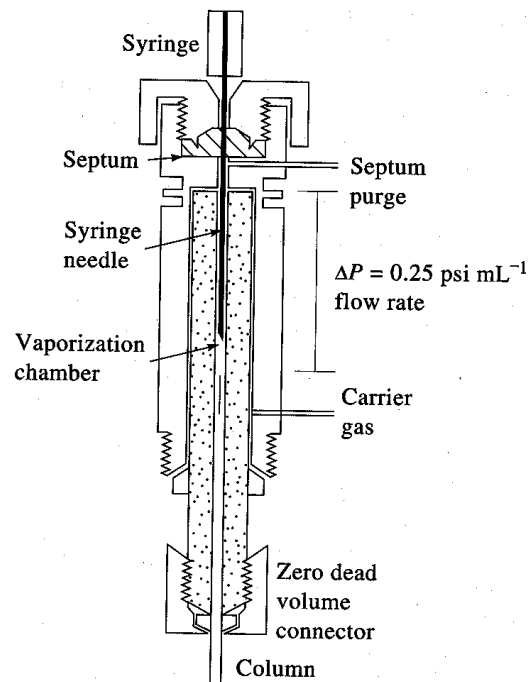
Zero dead volume connector

Column

Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

Temperature Programming

K_{part} in GC--depends on solute/stationary phase and temperature

Increase temperature during a separation--decreases K
a.k.a. temperature gradient, temperature ramp

typically 2°-10°/minute, today even faster
ovens are very stable and uniform

Premise: vapor pressure strongly dependent on temperature

$$\ln p = \frac{\Delta_v H}{RT} + const$$

Clausius-Clapeyron equation
$\Delta_v H$. Partial molar enthalpy of vaporization

partitioning of give solute between gas and solid/liquid phase
depends on energy of interaction (solvation, adsorption) and
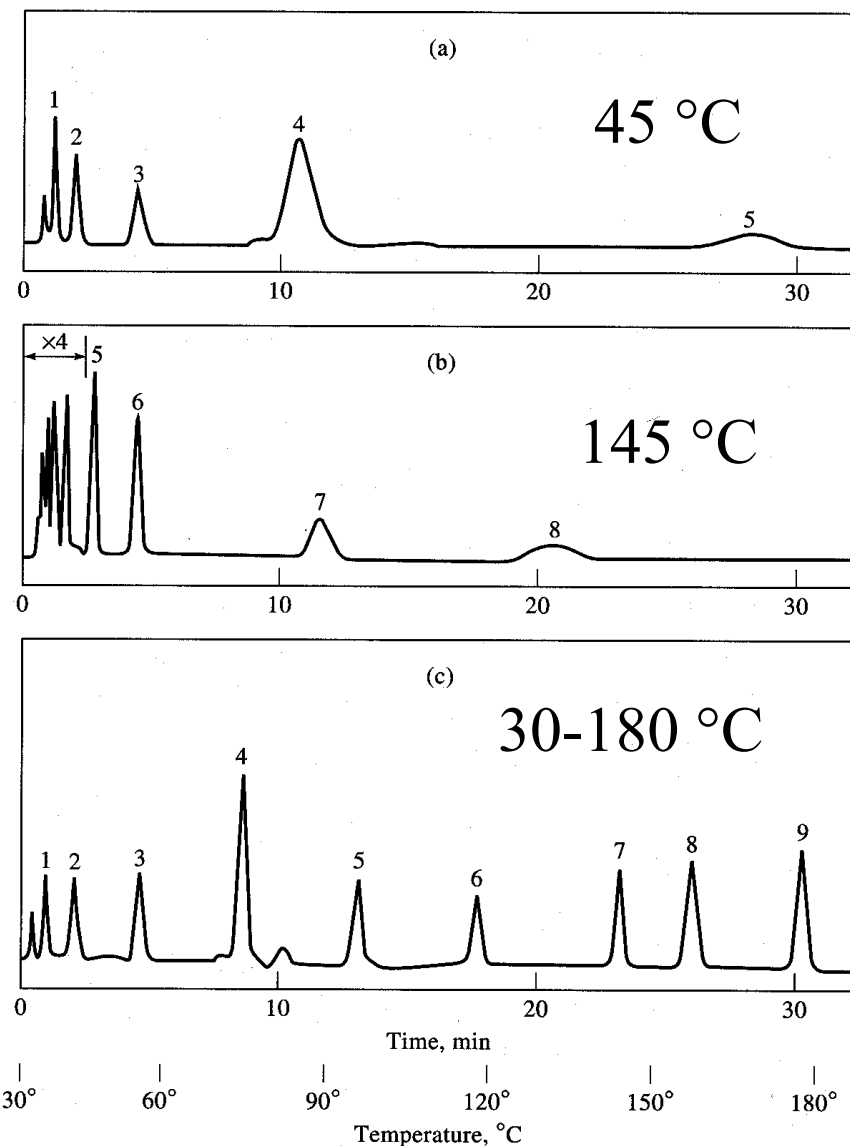its vapor pressure! Temperature changes cause change in p

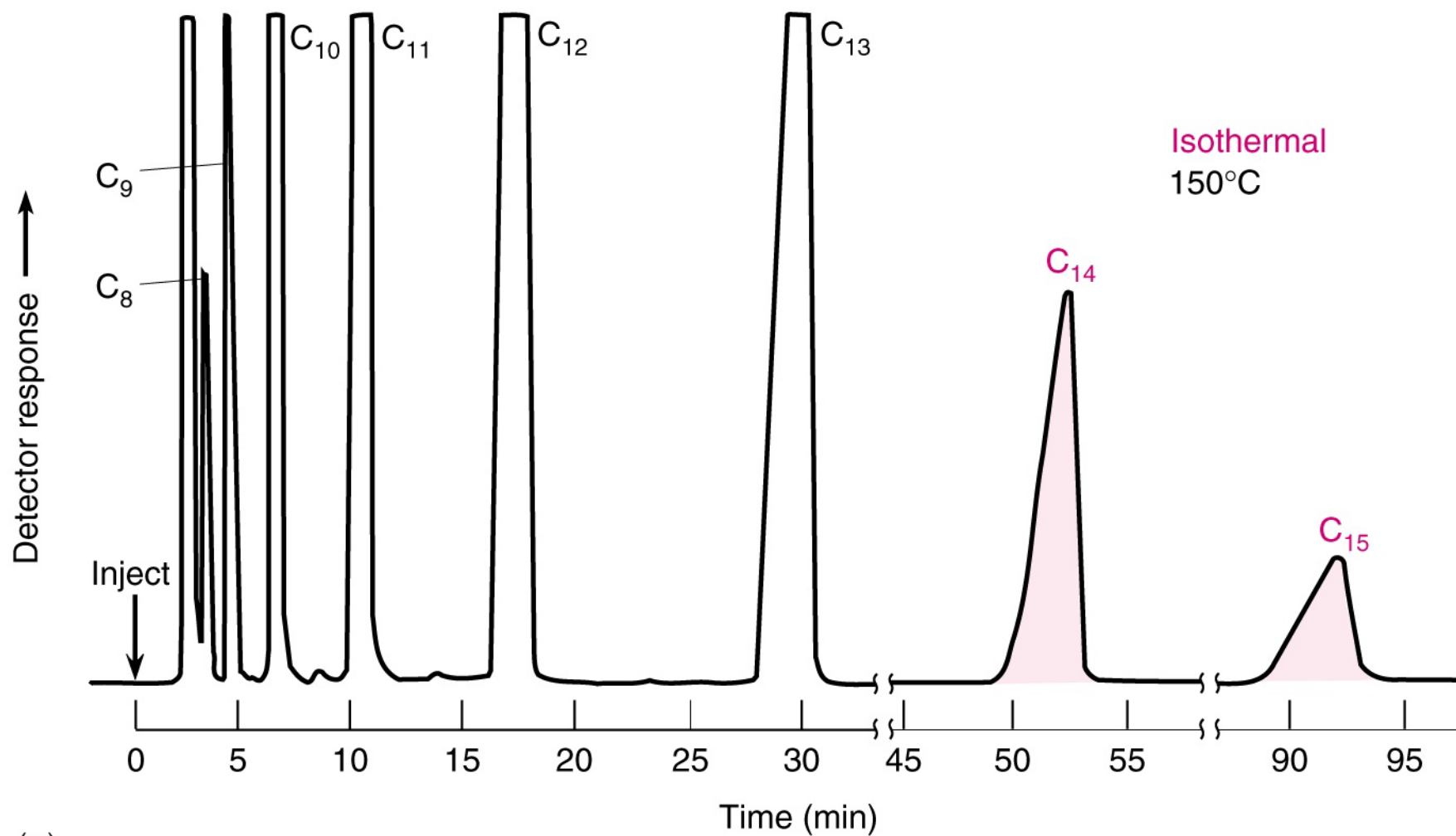# Separations at Various Temperatures

Recall the "general elution problem"
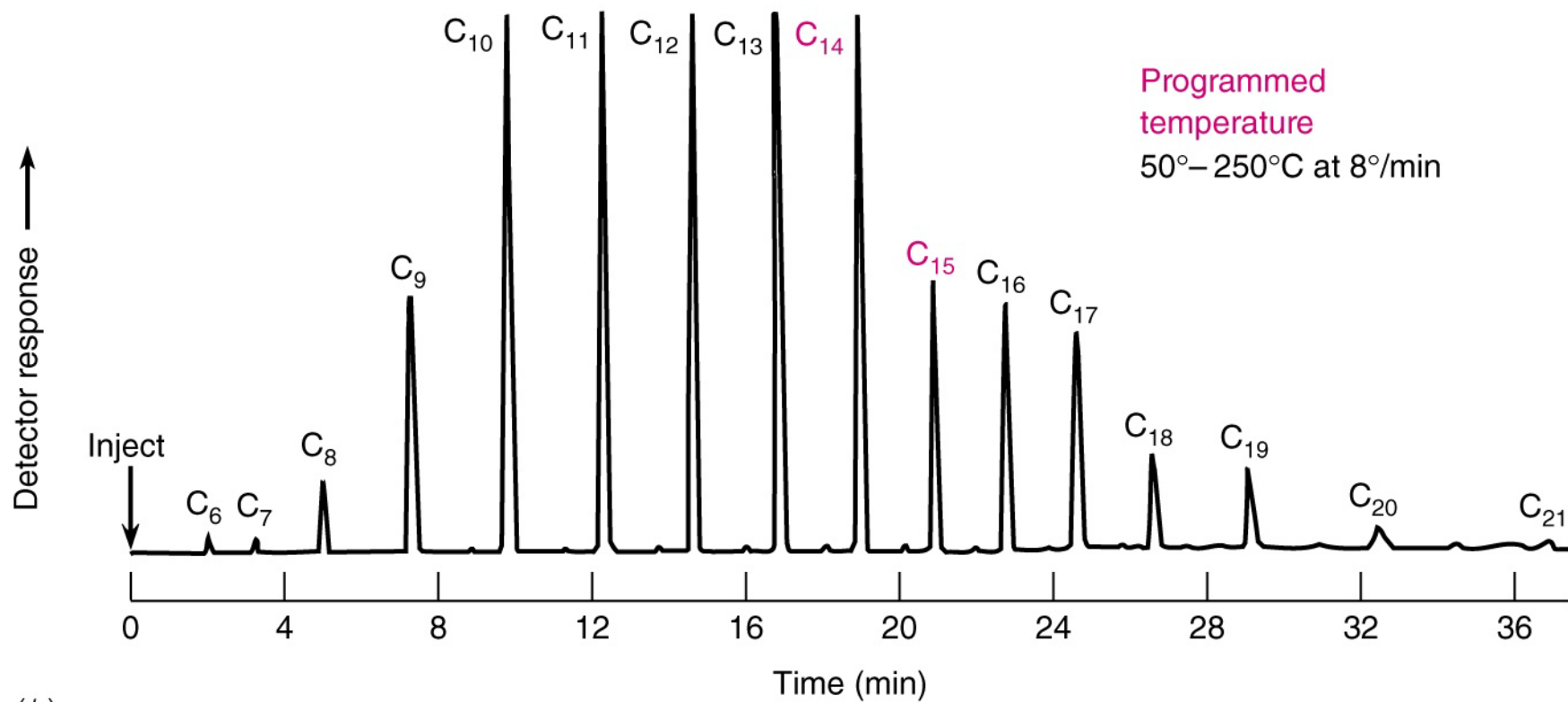• either poor separations or really long experiment times

Demonstrates the improved performance of a linear temperature ramp.
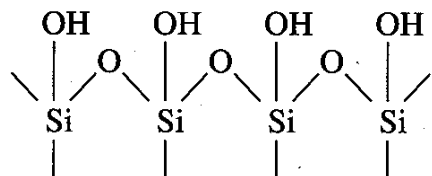note, better selectivity, better peak widths. (both used to calculate resolution)

(a)

(b)

Stationary Phases--example

Normal surface of quartz
column (hydrophylic)

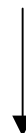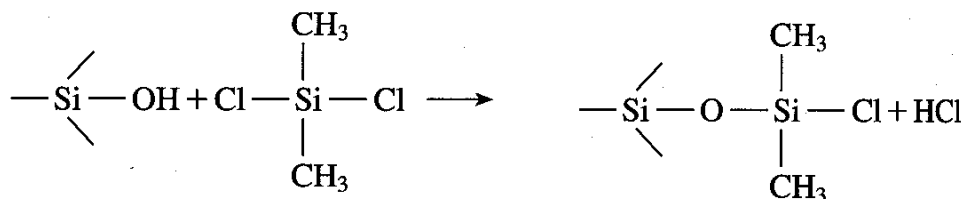1) functionalize with
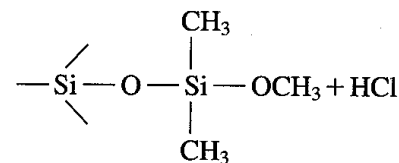dimehtylchlorosilane

is

Variations:
- phenyl instead of methyl
- more non-polar
- propyl or trifluoropropyl
- at step 2) use glycol
  - polyethylene glycol
  - great for alcohols, acids

2) add an alcohol

3) add more DMCS (repeat)
- results in polydimethylsiloxane film
the all-purpose GC column

Carrier gas in

Silicone rubber septum

Injector port

Injector oven

Column oven

Detector

Detector oven

Exit

Computer or recorder

Column

Stationary liquid phase
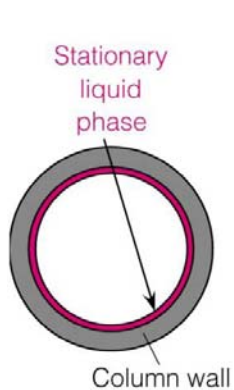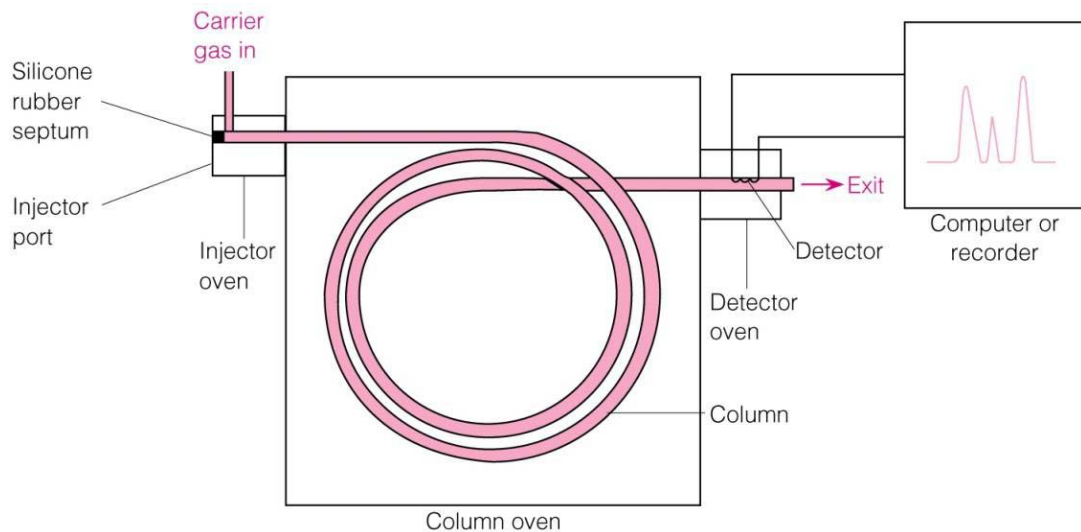
Column wall

Wall-coated open tubular column (WCOT)

Solid support coated with stationary liquid phase
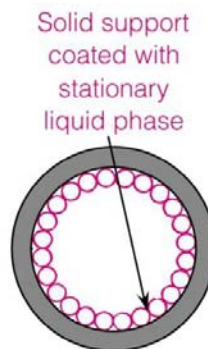
Support-coated open tubular column (SCOT)

Stationary solid-phase particles
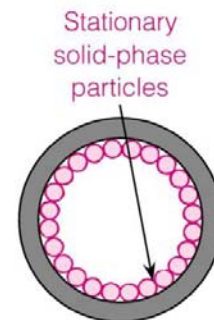
Porous-layer open tubular column (PLOT)

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

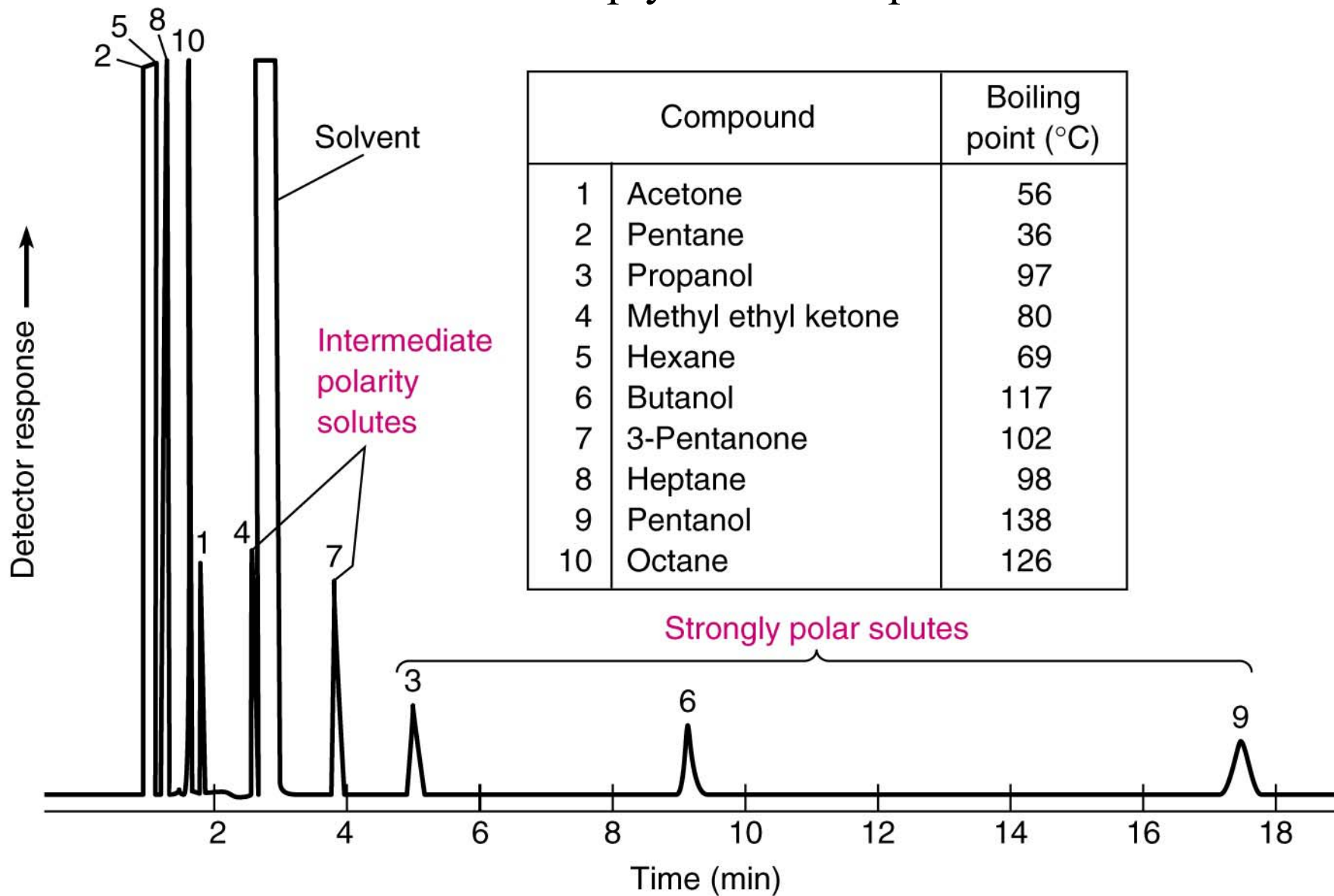| Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs
Poly(phenylmethyldimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters; 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

Elution not simply based on bp values!!!

	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

Detector response

Solvent

Intermediate polarity solutes

Strongly polar solutes

Time (min)

(b)

Polar stationary phase

poly(ethylene) glycol phase

poly(dimethyl)siloxane phase
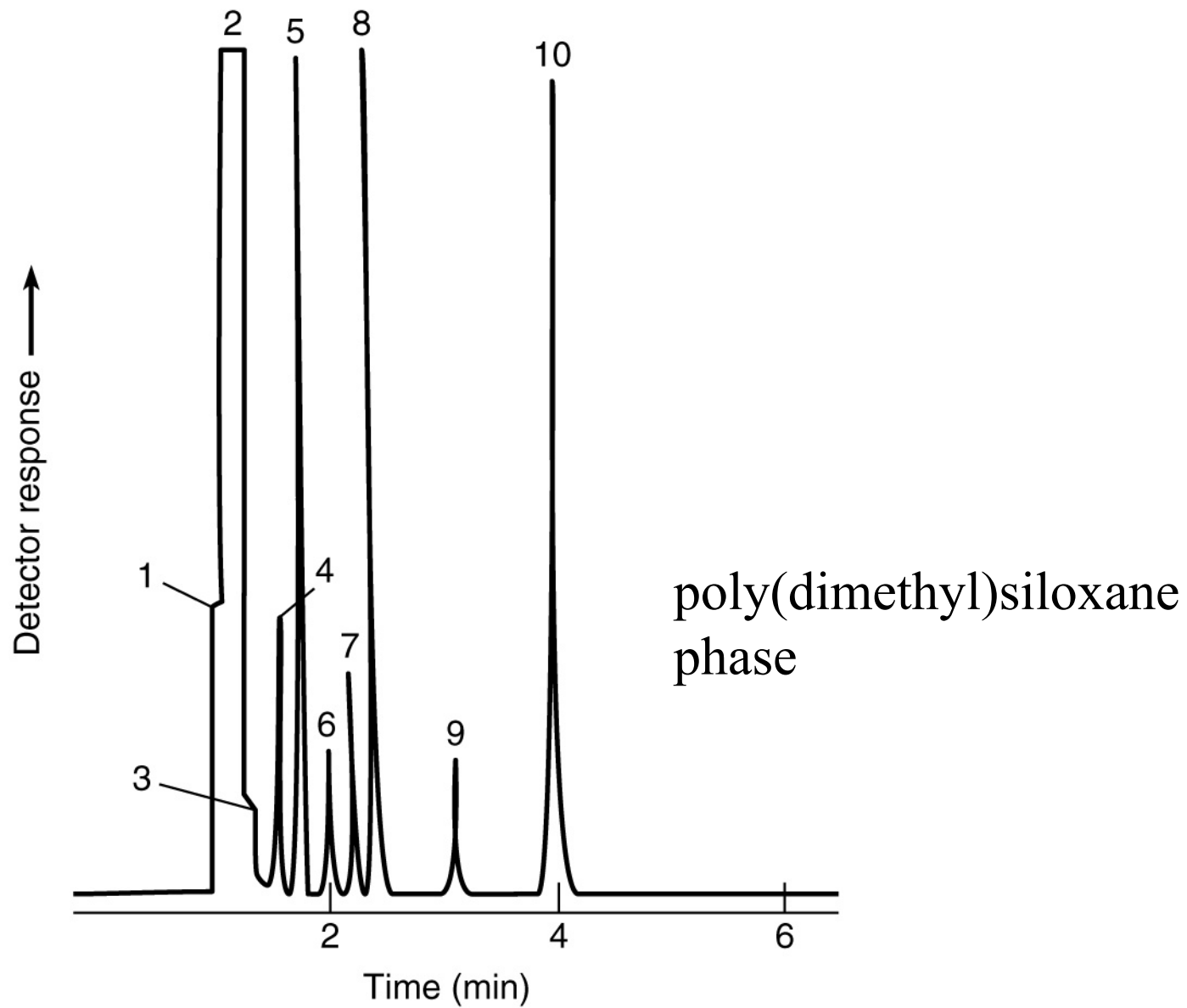
(*a*)   Nonpolar stationary phase

Example Application

- Kovats' Retention Indices
- Qualitative Analysis
- based on adjusted retention time, t_s'
- derived for normal alkane series
- extrapolate values for highly branched or unsaturated compounds
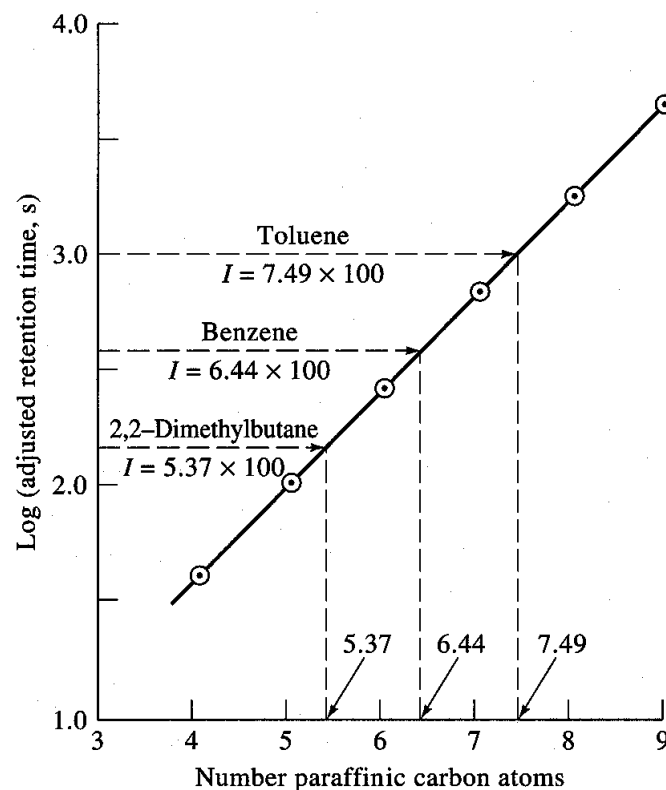

Figure 27-12 Graphical illustration of the method for determining retention indexes for three compounds. Stationary phase: squalane. Temperature: 60°C.

Thermal Conductivity Detector

- Sensitive to both hydrocarbons and inorganic species

- temperature response of a wire filament as column flow passes by

- carrier gas is either H_2 or He
  - 5-6 times the thermal conductivity of most other analytes

- inexpensive; non-destructive

- Detection limit .3 ng/ml (slower response)
- linear response 10^4

hot wire
(Au, Pt, W)
constant voltage

Flow out

Flow in

(a)
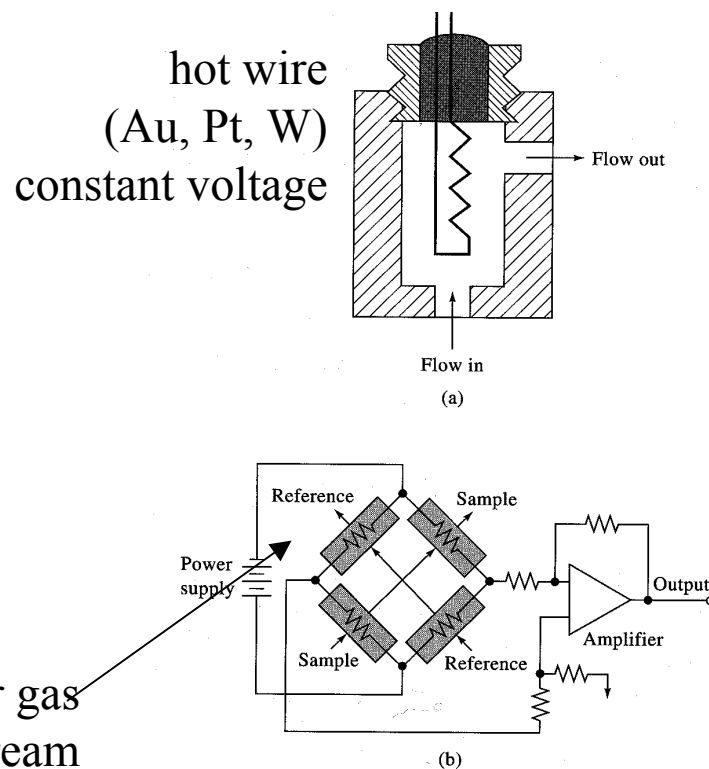
Resistance of element in carrier gas compared to column eluent stream

Reference   Sample

Power supply

Output

Amplifier

Sample   Reference

(b)

Figure 27-7 Schematic of (a) a thermal conductivity detector cell, and (b) an arrangement of two sample detector cells and two reference detector cells. *(From J. V. Hinshaw, LC-GC, 1990, 8, 298. With permission.)*

Temp of wire changes---as organic species elute --this changes resistance of wire!

Flame Ionization Detector

•Detection limit 4 pg/s

•linear over 10^7

- the most common detector

- good for most hydrocarbons
  - oxygen, nitrogen, sulfur functional groups reduced response

- Analyte is burned in an oxygen/hydrogen flame

- Ions produced are detected as current on the collector electrode

- rugged and easy to operate

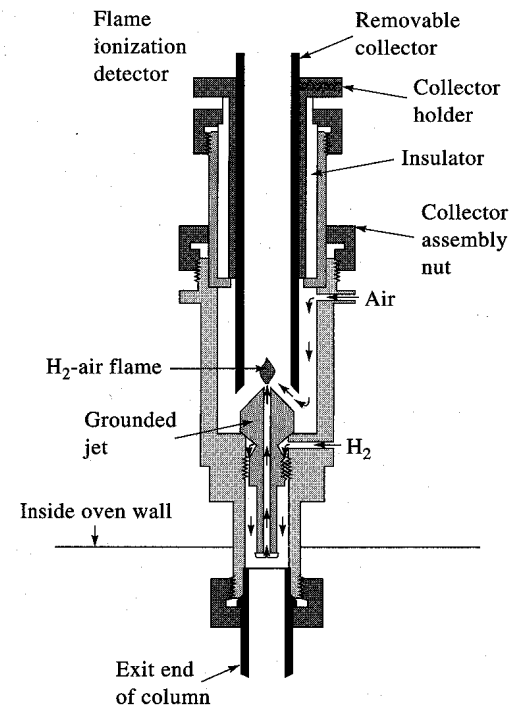- no background non-ionized species like water

Flame ionization detector

Removable collector

Collector holder

Insulator

Collector assembly nut

Air

H_2-air flame

Grounded jet

H_2

Inside oven wall

Exit end of column

Igure 27-6 A typical flame ionization detector. *(Coursy of Hewlett-Packard Company.)*

$i \propto nC$ (mass not concentration) except C=O C=N, C≡N

Cathode (collects CHO⁺ ions)

Anode and flame tip

Glass insulation

Air diffuser

Igniter coil

Air inlet

Hydrogen inlet

Gas flow from column