Lecture 10

Gas Chromatography

Column Resolution

$$R_s = \frac{\Delta Z}{W_A/2 + W_B/2} = \frac{2\Delta Z}{W_A + W_B} = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B} \qquad (26\text{-}20)$$

stationary phase can be improved by lengthening the column, thus increasing the number of plates. An adverse consequence of the added plates, however, is an increase in the time required for the separation.

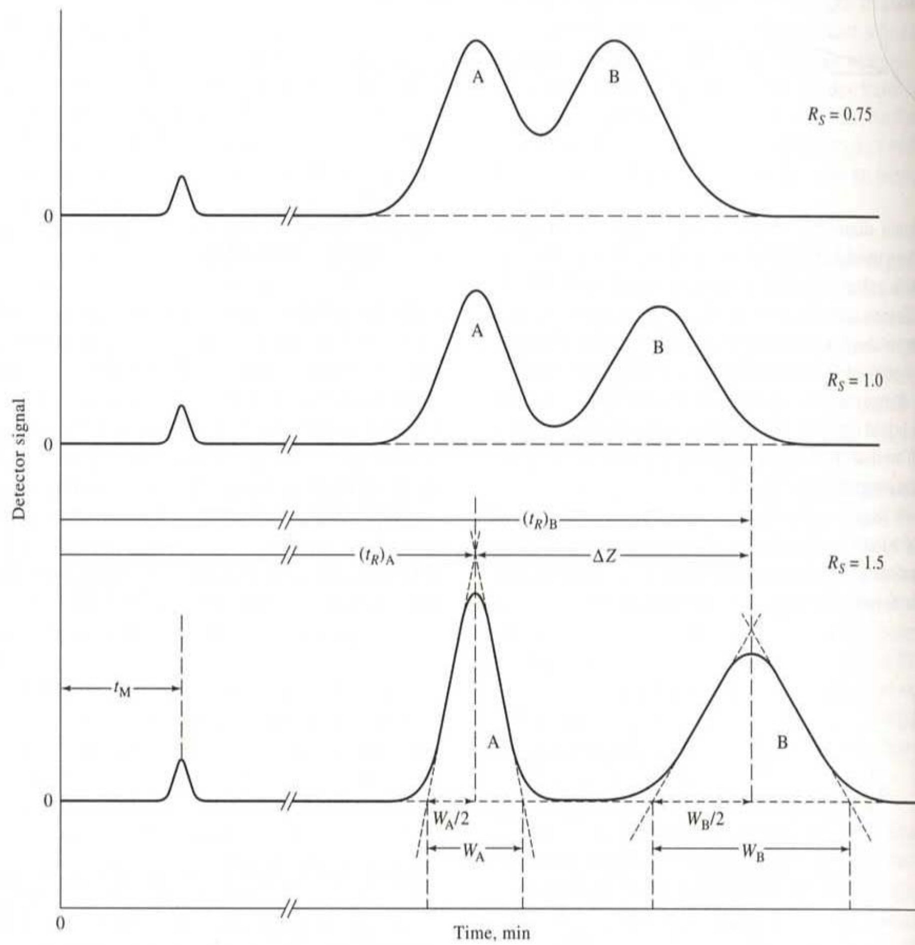

Figure 26-11 Separations at three resolutions. Here, $R_s = 2\Delta Z/(W_A + W_B)$.

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Summary – The General Elution Problem

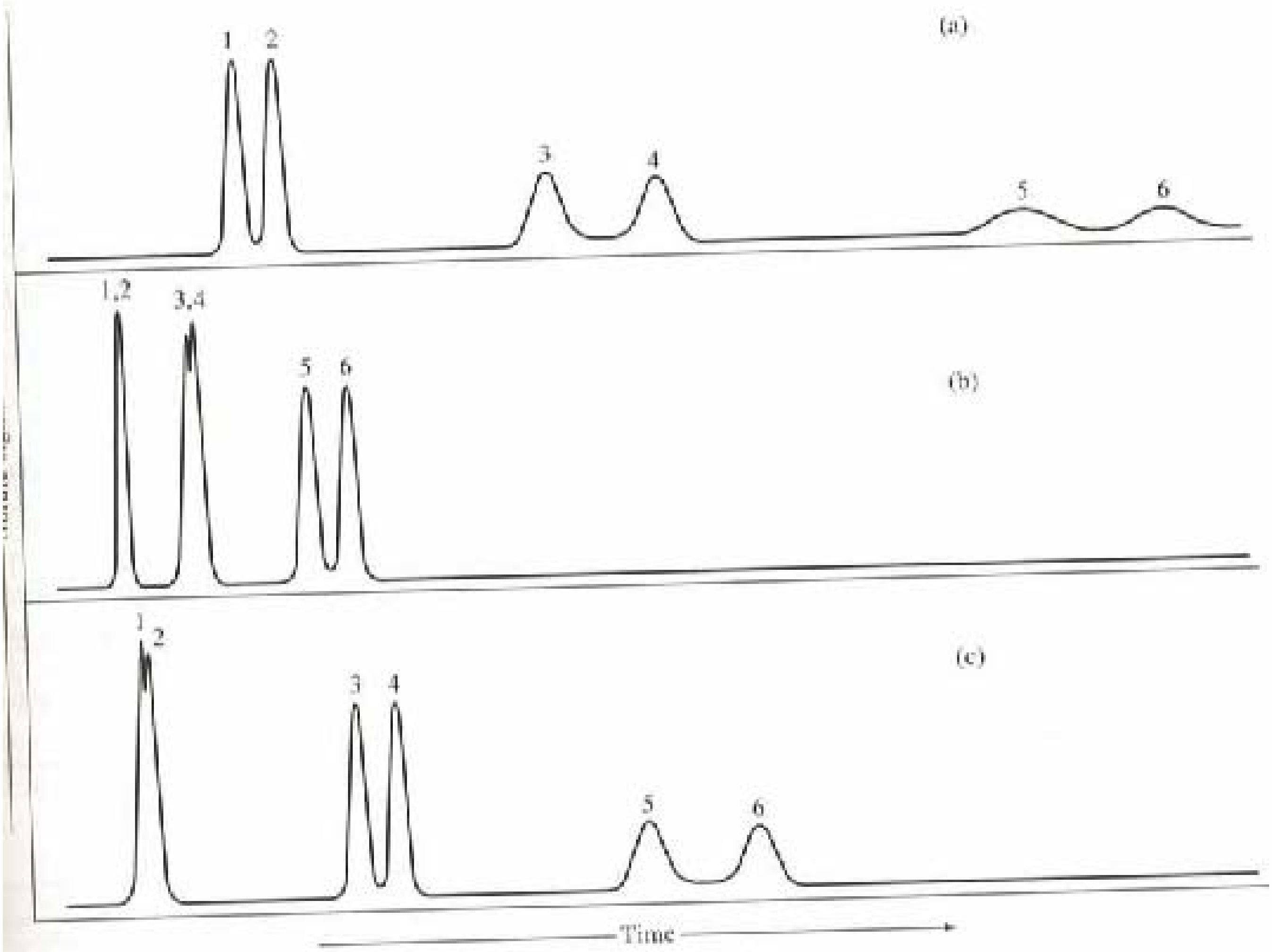

Figure 26-14 Illustration of the general elution problem in chromatography.

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TABLE 26-4 Important Chromatographic Experimental Quantities and Relationships

Name	Symbol of Experimental Quantity	Determined From
Migration time, nonretained species	t_M	Chromatogram (Figure 26-6)
Retention times, species A and B	$(t_R)_A$, $(t_R)_B$	Chromatogram (Figure 26-6)
Adjusted retention time, species A	$(t_R')_A$	$(t_R')_A = (t_R)_A - t_M$
Peak widths, species A and B	W_A, W_B	Chromatogram (Figure 26-6)
Length of column packing	L	Direct measurement
Flow rate	F	Direct measurement
Volume of stationary phase	V_S	Packing preparation data
Concentration of analyte in mobile and stationary phases	c_M, c_S	Analysis and preparation data

TABLE 26-5 Important Derived Quantities and Relationships

Name	Calculation of Derived Quantities	Relationship to Other Quantities
Linear mobile-phase velocity	$u = L/t_M$	
Volume of mobile phase	$V_M = t_M F$	
Retention factor	$k' = (t_R - t_M)/t_M$	$k' = \frac{KV_S}{V_M}$
Distribution constant	$K = \frac{k'V_M}{V_S}$	$K = \frac{c_S}{c_M}$
Selectivity factor	$\alpha = \frac{(t_R)_B - t_M}{(t_R)_A - t_M}$	$\alpha = \frac{k_B'}{k_A'} = \frac{K_B}{K_A}$
Resolution	$R_s = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$	$R_s = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_B'}{1 + k_B'}\right)$
Number of plates	$N = 16\left(\frac{t_R}{W}\right)^2$	$N = 16R_s^2\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{1 + k_B'}{k_B'}\right)^2$
Plate height	$H = L/N$	
Retention time	$(t_R)_B = \frac{16R_s^2 H}{u}\left(\frac{\alpha}{\alpha - 1}\right)^2 \frac{(1 + k_B')^3}{(k_B')^2}$	

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Instrumentation-
Basic Gas Chromatography

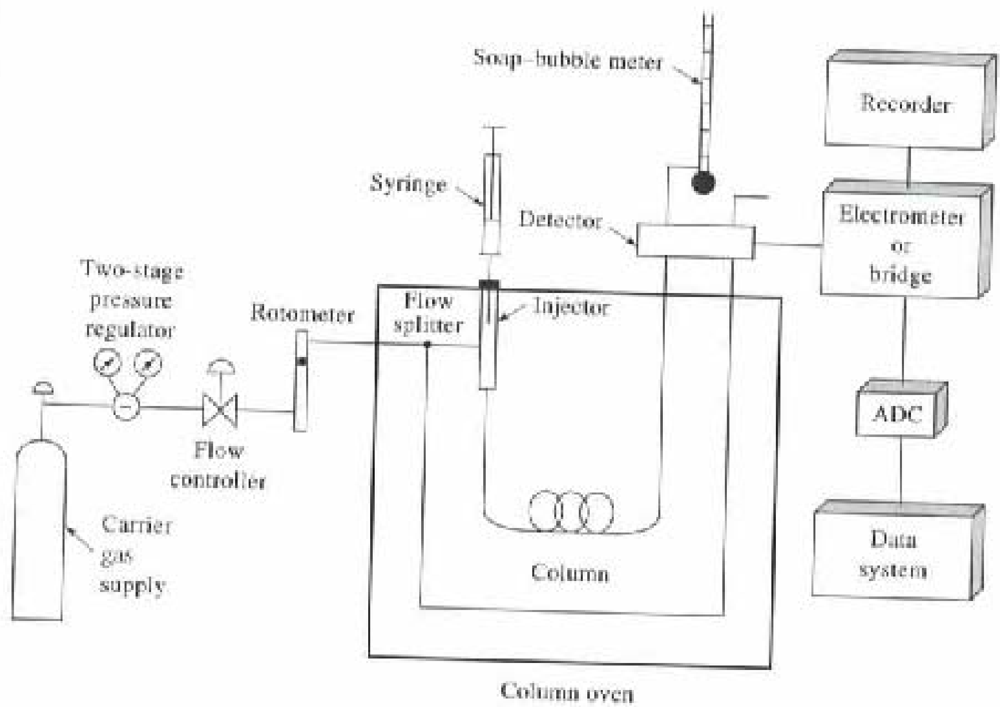

Figure 27-1 Schematic of a gas chromatograph.

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Sample Injection System

-Liquid or Gas
-Important! Slow injection causes band spreading, poor resolution
-Sample is 0.1 to 20 microliters, typical packed column GC or.0001 microliters for capillary GC

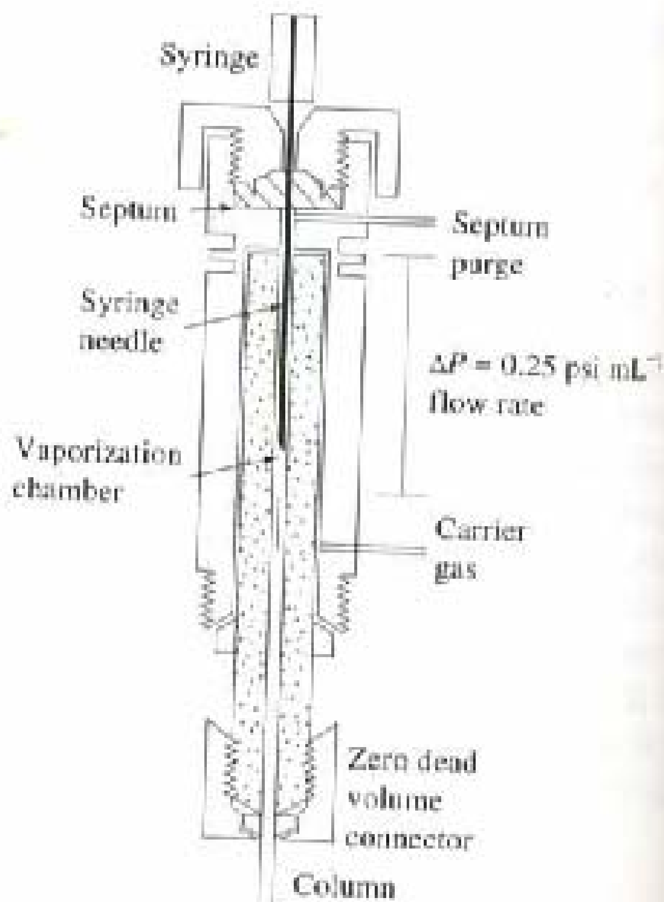

Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

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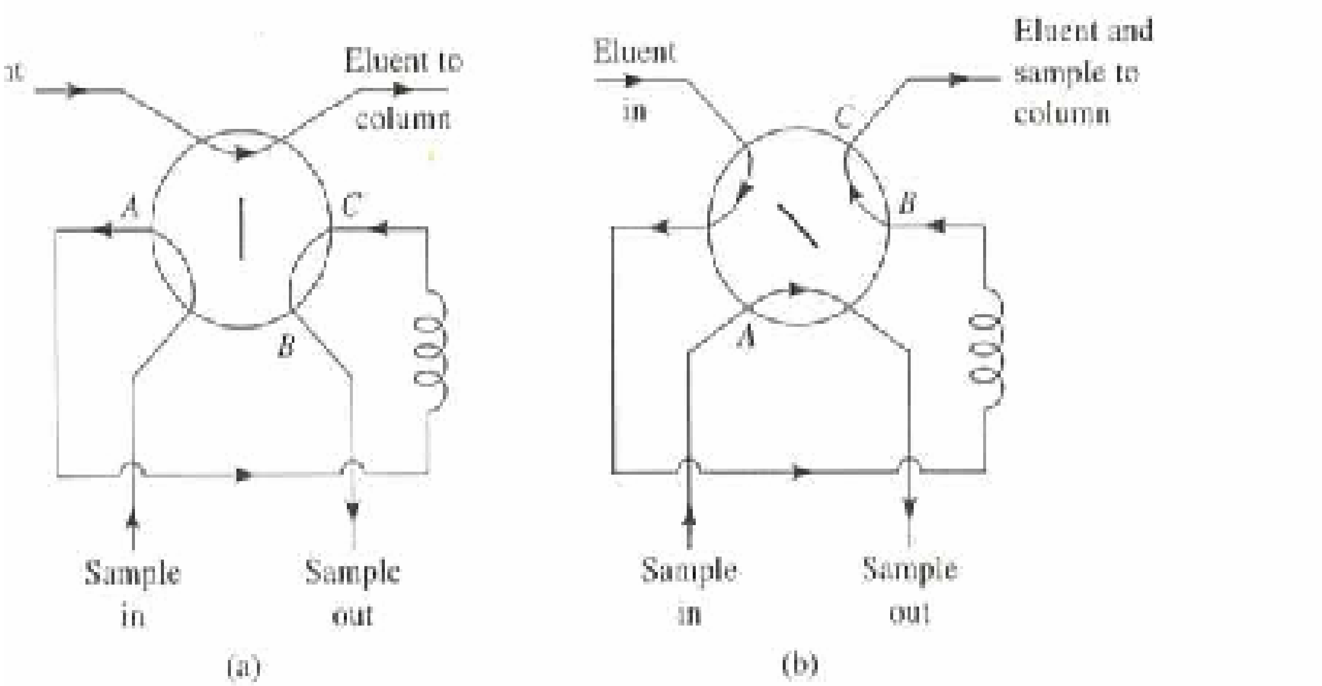
Rotary Sample Valve
A. Fill sample loop



ure 27-4 A rotary sample valve: valve position (a) for filling sample loop *ACB*
(b) for introduction of sample into column.

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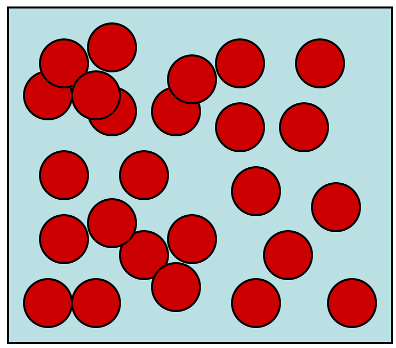
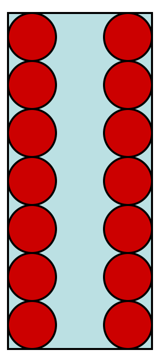
Column Configurations

Length 2-50 m

1. Packed



2. Open tubular or capillary



3. Temperature

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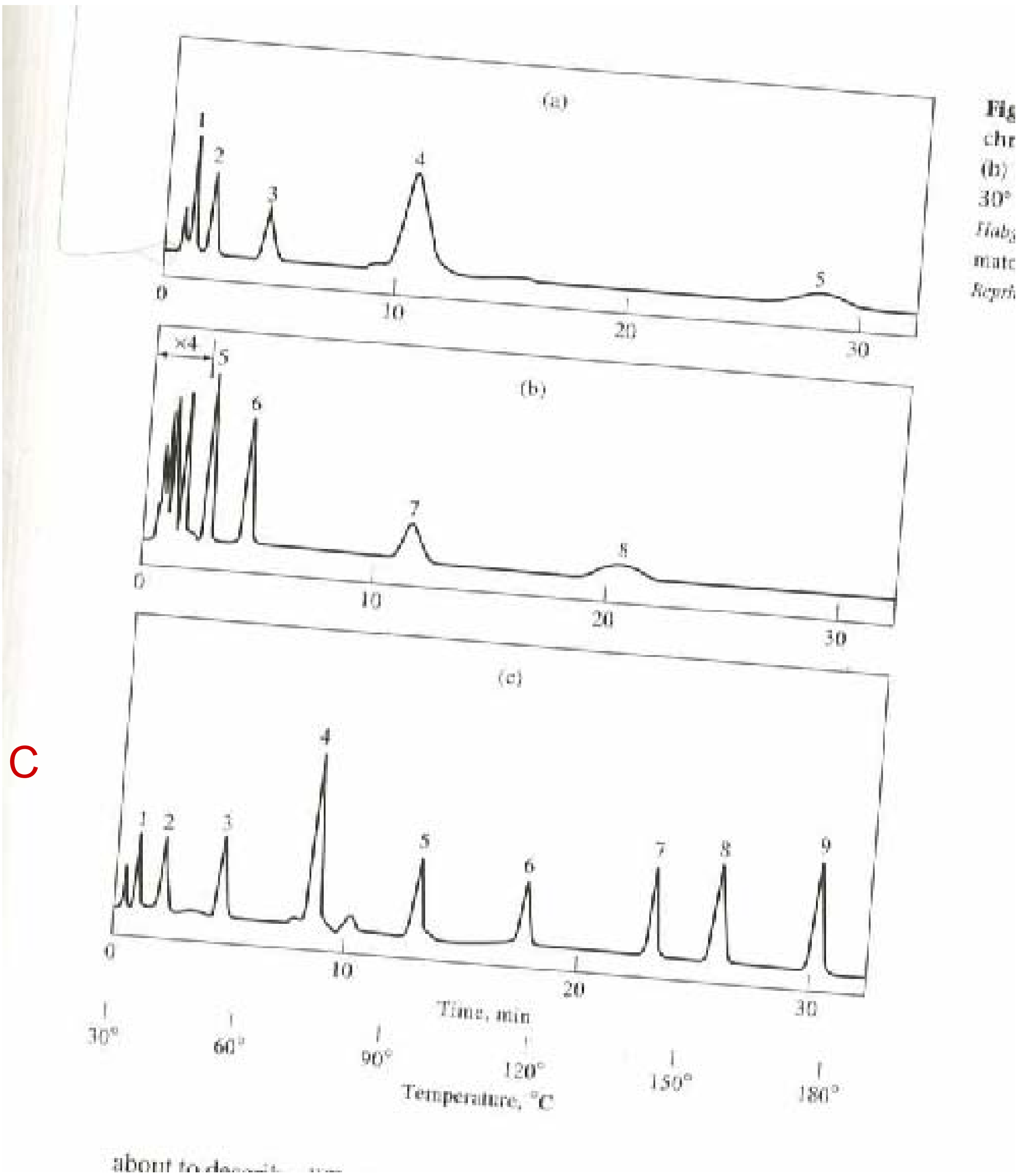
Temperature Programming

45 C

145 C

30-180 C



Many choices for Stationary Phase (for packed and tubular columns)

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

Many Choices!

TABLE 27-1 Properties and Characteristics of Typical Gas-Chromatographic Columns

	Type of Column*			
	FSOT	WCOT	SCOT	Packed
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.53	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Total plates	$(20–400) \times 10^3$	$(10–400) \times 10^3$	$(6–120) \times 10^3$	$(1–10) \times 10^3$
Sample size, ng	10–75	10–1000	10–1000	$10–10^6$
Relative back pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Chemical inertness	Best →			→ Poorest
Flexible?	Yes	No	No	No

*FSOT: Fused-silica, open tubular column.
WCOT: Wall-coated, open tubular column.
SCOT: Support-coated open tubular column.

... with methanol, the second chloride is re-

perature for the column); (2) *thermal stability*; (3) ... (4) *solvent characteristics* such that

Open Tubular Columns

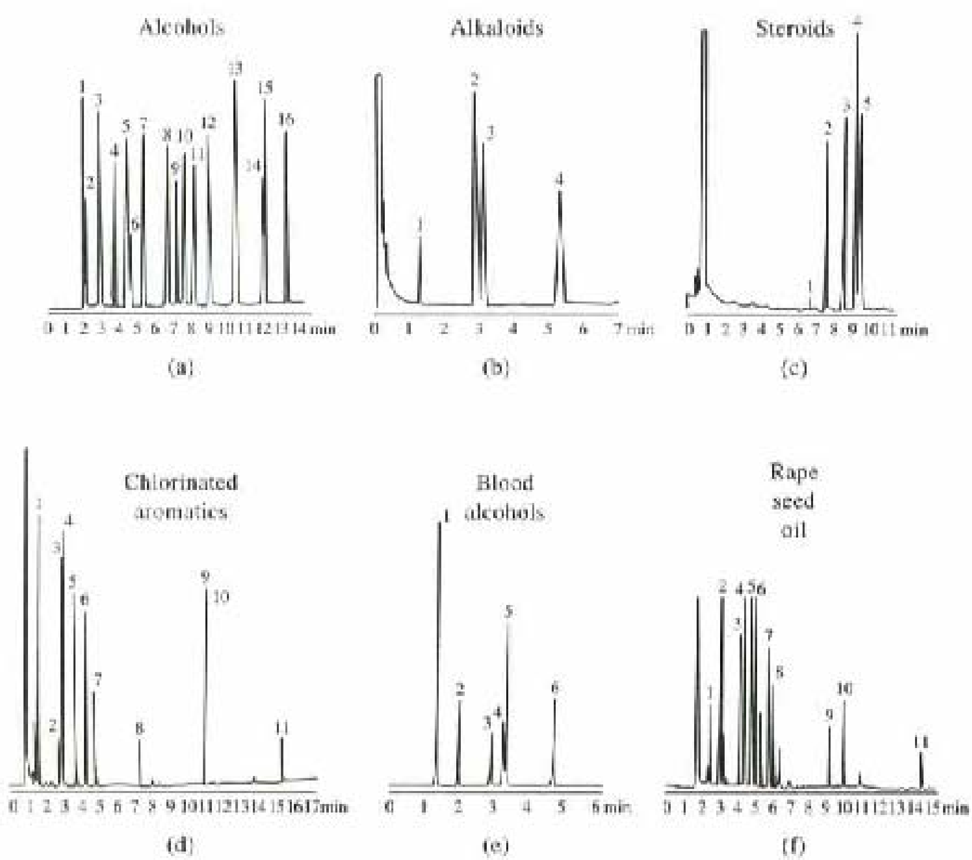


Figure 27-11 Typical chromatograms from open tubular columns coated with (a) poly-dimethyl siloxane; (b) 5(phenylmethyldimethyl) siloxane; (c) 50(phenylmethyldimethyl) siloxane; (d) 50% poly(trifluoropropyl-dimethyl) siloxane; (e) polyethylene glycol; (f) 50% poly(cyanopropyl-dimethyl) siloxane. *(Courtesy of J & W Scientific.)*