EXAM FOUR – TUESDAY APRIL 20th

Thursday April 22nd – no class – individual meetings with students

Daniel C. Harris

Quantitative Chemical Analysis

Seventh Edition

On line quiz for chapter 23 - due by 11:59 PM on 4/16/10 - questions 1-12 only!

Chapter 24

Gas Chromatography

Sections 24-1, 24-3

Suggested problems: Chapter 23: 1, 2, 8, 15, 16, 27, 30,
Chapter 24: 1a, 3a, 5a,b,c, 6,
Chapter 25: 1a, 15
Chapter 26: 25, 28

Schematic of a gas chromatograph

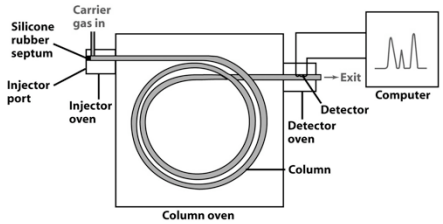

Figure 24-1
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Open tubular (capillary) columns for GC

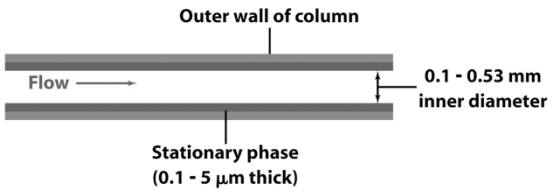

Figure 24-2a
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Effect of column diameter on resolution

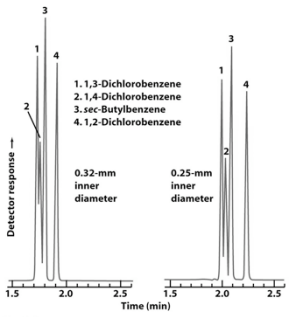

Figure 24-4
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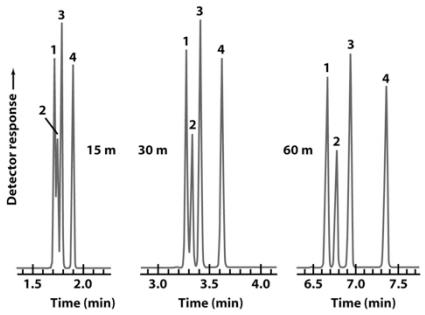
Effect of column length on resolution



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Effect of stationary film thickness on column performance

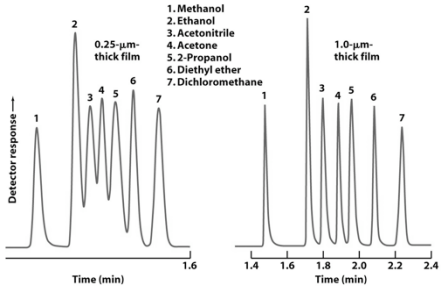

Figure 24-6
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Stationary phases for capillary GC

Table 24-1 Common stationary phases in capillary gas chromatography

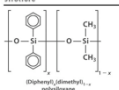
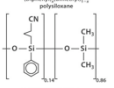
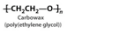
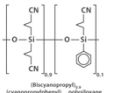
Structure	Polarity		Temperature range (°C)
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$	Nonpolar	−60°–320°
	$x = 0.05$	Nonpolar	−60°–320°
	$x = 0.35$	Intermediate polarity	0°–300°
	$x = 0.65$	Intermediate polarity	50°–320°
 (Cyanopropylphenyl)$_{0.14}$ (dimethyl)$_{0.86}$ polysiloxane	Intermediate polarity		−20°–280°
 Carbowax (polyethylene glycol)	Strongly polar		40°–250°
 (Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar		0°–275°

Table 24-1
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Polarity of solutes…

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).

Table 24-2
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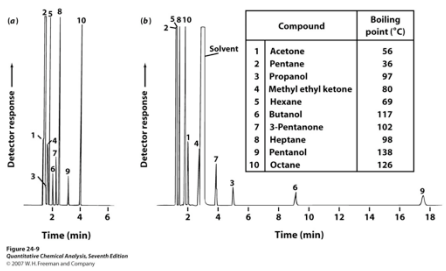
Effect of stationary phase polarity and separation



	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 24-9
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a) non-polar poly(dimethoxysiloxane) and b) strongly polar poly(ethylene glycol)

Retention indices - choosing the right column

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

	Retention index[a]				
Phase	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
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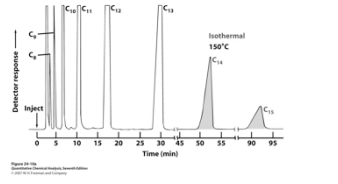
Temperature programming and the general elution problem



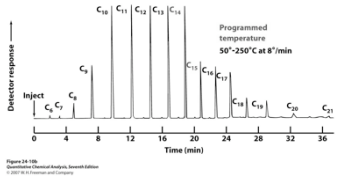


Figure 24-10b
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Detectors for gas chromatography

- Wide linear dynamic range
- Low limit of detection
- Low dead volume
- Non-destructive
- Rapid response
- Universal versus selective response

Thermal conductivity detector

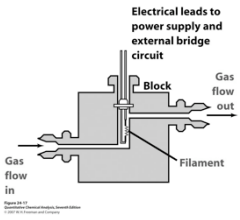

Figure 24-17
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Table 24-4 Thermal conductivity at 273 K and 1 atm

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.

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Linear range > 10^5

LOD 400 pg/mL

Flame ionization detector

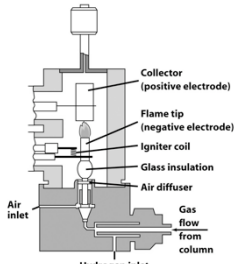

Figure 24-18
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Linear range > 10^7

LOD 2 pg/s

Electron capture detector

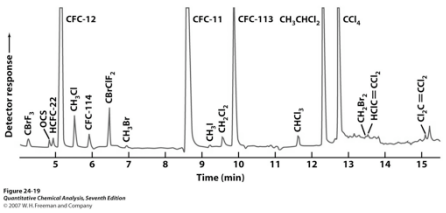

Figure 24-19
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Halogenated compounds in air at 800 m 1400 km south of New Zealand

Linear range > 10^4

LOD 5 fg/s

Performance characteristics for some GC detectors

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.*

Table 24-5
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FID vs SCD for natural gas analysis

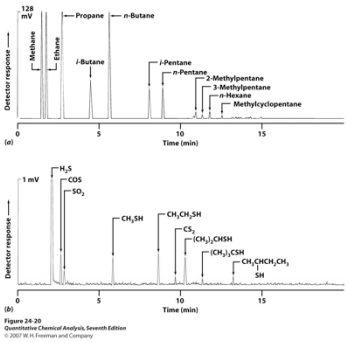

Figure 24-20
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