CHAPTER 1

1-1. A transducer is a device that converts chemical or physical information into an electrical signal or the reverse. The most common input transducers convert chemical or physical information into a current, voltage, or charge, and the most common output transducers convert electrical signals into some numerical form.

1-2. The information processor in a visual color measuring system is the human brain.

1-3. The detector in a spectrograph is a photographic film or plate.

1-4. Smoke detectors are of two types: photodetectors and ionization detectors. The photodetectors consist of a light source, such as a light-emitting diode (LED) and a photodiode to produce a current proportional to the intensity of light from the LED. When smoke enters the space between the LED and the photodiode, the photocurrent decreases, which sets off an alarm. In this case the photodiode is the transducer.

In ionization detectors, which are the typical battery-powered detectors found in homes, a small radioactive source (usually Americium) ionizes the air between a pair of electrodes. When smoke enters the space between the electrodes, the conductivity of the ionized air changes, which causes the alarm to sound. The transducer in this type of smoke detector is the pair of electrodes and the air between them.

1-5. A *data domain* is one of the modes in which data may be encoded. Examples of data domain classes are the analog, digital and time domains. Examples of data domains are voltage, current, charge, frequency, period, number.

1-6. Analog signals include voltage, current, charge, and power. The information is encoded in the amplitude of the signal.

1-7.

Output Transducer	**Use**
LCD display	Alphanumeric information
Computer monitor	Alphanumeric information, text, graphics
Laser printer	Alphanumeric and graphical information
Motor	Rotates to change position of attached elements

1-8. A figure of merit is a number that provides quantitative information about some performance criterion for an instrument or method.

1-9. Let c_s= molar concentration of Cu^{2+} in standard = 0.0287 M

c_x = unknown Cu^{2+} concentration
V_s = volume of standard = 0.500 mL
V_x = volume of unknown = 25.0 mL
S_1 = signal for unknown = 23.6
S_2 = signal for unknown plus standard = 37.9

Assuming the signal is proportional to c_x and c_s , we can write

$$S_1 = Kc_x \quad \text{or} \quad K = S_1/c_x$$

After adding the standard

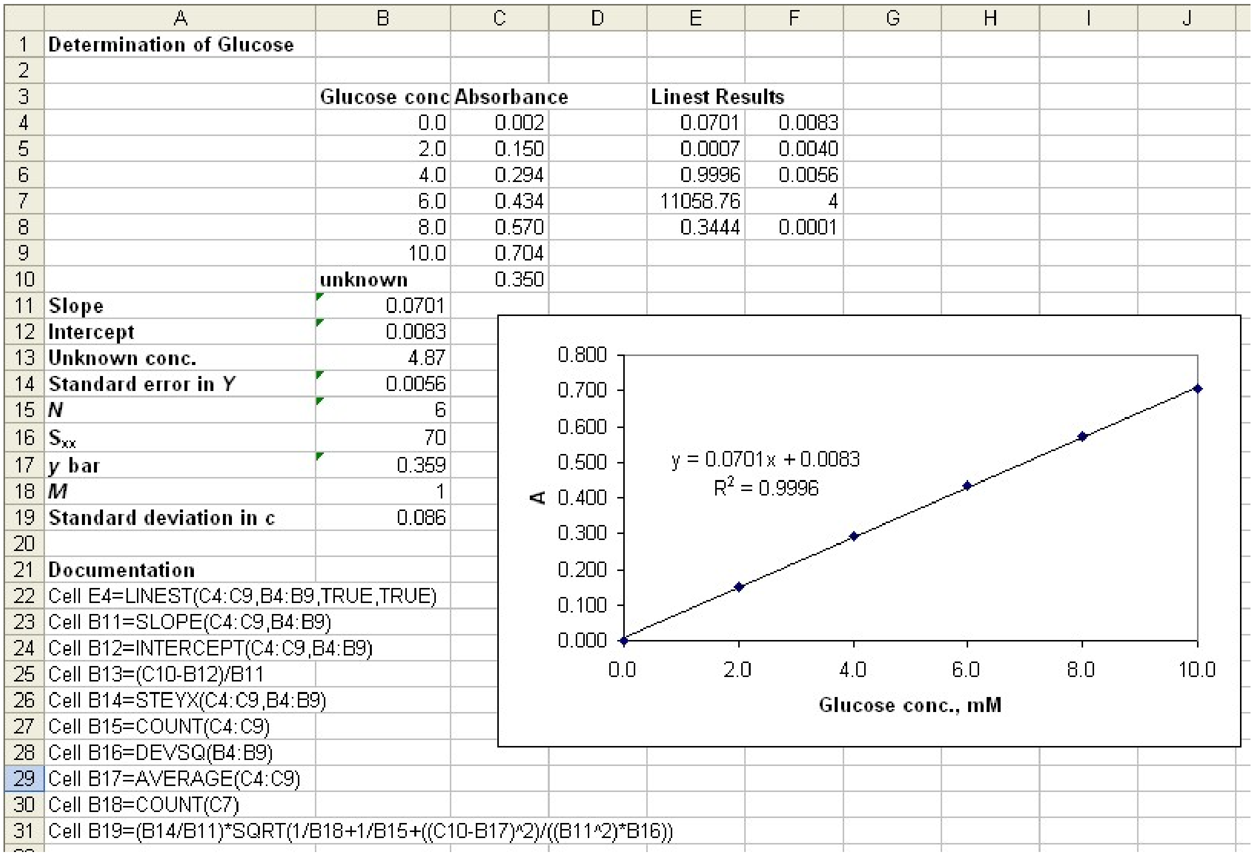
$$S_2 = K\left(\frac{V_x c_x + V_s c_s}{V_x + V_s}\right)$$

Substituting for K and rearranging gives,

$$c_x = \frac{S_1 V_s c_s}{S_2(V_x + V_s) - S_1 V_x}$$

$$c_x = \frac{23.6\times 0.500\ \text{mL}\times 0.0287\ \text{M}}{37.9(0.500\ \text{mL} + 25.0\ \text{mL}) - (23.6\times 25.0\ \text{mL})} = 9.00\times 10^{-4}\ \text{M}$$

1-10. The results are shown in the spreadsheet below.



	A	B	C	D	E	F	G	H	I	J
1	**Determination of Glucose**									
2										
3		**Glucose conc**	**Absorbance**		**Linest Results**					
4		0.0	0.002		0.0701	0.0083				
5		2.0	0.150		0.0007	0.0040				
6		4.0	0.294		0.9996	0.0056				
7		6.0	0.434		11058.76	4				
8		8.0	0.570		0.3444	0.0001				
9		10.0	0.704							
10		**unknown**	0.350							
11	**Slope**	0.0701								
12	**Intercept**	0.0083								
13	**Unknown conc.**	4.87								
14	**Standard error in *Y***	0.0056								
15	***N***	6								
16	**S_{xx}**	70								
17	***y* bar**	0.359								
18	***M***	1								
19	**Standard deviation in c**	0.086								
20										
21	**Documentation**									
22	Cell E4=LINEST(C4:C9,B4:B9,TRUE,TRUE)									
23	Cell B11=SLOPE(C4:C9,B4:B9)									
24	Cell B12=INTERCEPT(C4:C9,B4:B9)									
25	Cell B13=(C10-B12)/B11									
26	Cell B14=STEYX(C4:C9,B4:B9)									
27	Cell B15=COUNT(C4:C9)									
28	Cell B16=DEVSQ(B4:B9)									
29	Cell B17=AVERAGE(C4:C9)									
30	Cell B18=COUNT(C7)									
31	Cell B19=(B14/B11)*SQRT(1/B18+1/B15+((C10-B17)^2)/((B11^2)*B16))									

(a) Slope, $m = 0.0701$, intercept, $b = 0.0083$

(b) From LINEST results, SD slope, $s_m = 0.0007$, SD intercept, $s_b = 0.0040$

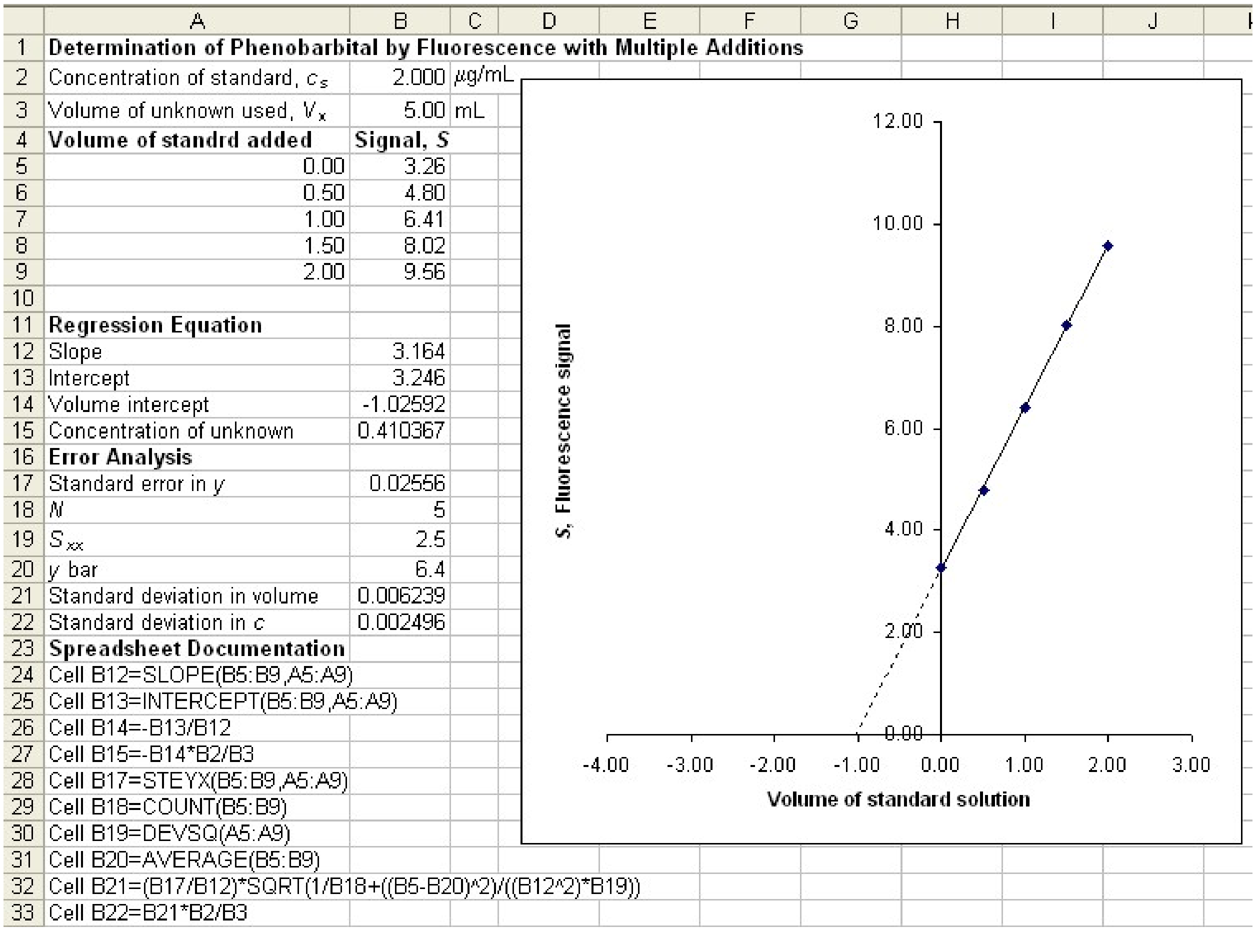
(c) 95% CI for slope m is $m \pm ts_m$ where t is the Student t value for 95% probability and $N - 2 = 4$ degrees of freedom = 2.78

$$95\%\ \text{CI for}\ m = 0.0701 \pm 2.78 \times 0.0007 = 0.0701 \pm 0.0019\ \text{or}\ 0.070 \pm 0.002$$

For intercept, 95% CI = $b \pm ts_b = 0.0083 \pm 2.78 \times 0.004 = 0.0083 \pm 0.011$ or 0.08 ± 0.01

(d) $c_u = 4.87 \pm 0.086$ mM or 4.87 ± 0.09 mM

1-11. The spreadsheet below gives the results



	A	B	C
1	**Determination of Phenobarbital by Fluorescence with Multiple Additions**		
2	Concentration of standard, c_s	2.000	µg/mL
3	Volume of unknown used, V_x	5.00	mL
4	**Volume of standrd added**	**Signal, *S***	
5	0.00	3.26	
6	0.50	4.80	
7	1.00	6.41	
8	1.50	8.02	
9	2.00	9.56	
10			
11	**Regression Equation**		
12	Slope	3.164	
13	Intercept	3.246	
14	Volume intercept	-1.02592	
15	Concentration of unknown	0.410367	
16	**Error Analysis**		
17	Standard error in *y*	0.02556	
18	*N*	5	
19	S_{xx}	2.5	
20	*y* bar	6.4	
21	Standard deviation in volume	0.006239	
22	Standard deviation in *c*	0.002496	
23	**Spreadsheet Documentation**		
24	Cell B12=SLOPE(B5:B9,A5:A9)		
25	Cell B13=INTERCEPT(B5:B9,A5:A9)		
26	Cell B14=-B13/B12		
27	Cell B15=-B14*B2/B3		
28	Cell B17=STEYX(B5:B9,A5:A9)		
29	Cell B18=COUNT(B5:B9)		
30	Cell B19=DEVSQ(A5:A9)		
31	Cell B20=AVERAGE(B5:B9)		
32	Cell B21=(B17/B12)*SQRT(1/B18+((B5-B20)^2)/((B12^2)*B19))		
33	Cell B22=B21*B2/B3		

(a) See plot in spreadsheet.

(b) $c_u = 0.410\ \mu\text{g/mL}$

(c) $S = 3.16V_s + 3.25$

(d) $$c_u = \frac{bc_s}{mV_u} = \frac{3.246 \times 2.000\ \mu\text{g/mL}}{3.164\ \text{mL}^{-1} \times 5.00\ \text{mL}} = 0.410\ \mu\text{g/mL}$$

(e) From the spreadsheet $s_c = 0.002496$ or $0.002\ \mu\text{g/mL}$

2-3. $V_{2.4} = 12.0 \times [(2.5 + 4.0) \times 10^3]/[(1.0 + 2.5 + 4.0) \times 10^3] = 10.4\ \text{V}$

With meter in parallel across contacts 2 and 4,

$$\frac{1}{R_{2,4}} = \frac{1}{(2.5 + 4.0)\ \text{k}\Omega} + \frac{1}{R_M} = \frac{R_M + 6.5\ \text{k}\Omega}{R_M \times 6.5\ \text{k}\Omega}$$

$R_{2,4} = (R_M \times 6.5\ \text{k}\Omega)/(R_M + 6.5\ \text{k}\Omega)$

(a) $R_{2,4} = (5.0\ \text{k}\Omega \times 6.5\ \text{k}\Omega)/(5.0\ \text{k}\Omega + 6.5\ \text{k}\Omega) = 2.83\ \text{k}\Omega$

$V_M = (12.0\ \text{V} \times 2.83\ \text{k}\Omega)/(1.00\ \text{k}\Omega + 2.83\ \text{k}\Omega) = 8.87\ \text{V}$

$$\text{rel error} = \frac{8.87\ \text{V} - 10.4\ \text{V}}{10.4\ \text{V}} \times 100\% = -15\%$$

Proceeding in the same way, we obtain (b) –1.7% and (c) –0.17%

2-4. Applying Equation 2-19, we can write

(a) $$-1.0\% = \frac{750\ \Omega}{(R_M - 750\ \Omega)} \times 100\%$$

$R_M = (750 \times 100 - 750)\ \Omega = 74250\ \Omega$ or $74\ \text{k}\Omega$

(b) $$-0.1\% = \frac{750\ \Omega}{(R_M - 750\ \Omega)} \times 100\%$$

$R_M = 740\ \text{k}\Omega$

2-5. Resistors R_2 and R_3 are in parallel, the parallel combination R_p is given by Equation 2-17

$R_p = (500 \times 200)/(500 + 200) = 143\ \Omega$

(a) This 143 Ω R_p is in series with R_1 and R_4. Thus, the voltage across R_1 is

$V_1 = (15.0 \times 100)/(100 + 143 + 1000) = 1.21\ \text{V}$

$V_2 = V_3 = 15.0\ \text{V} \times 143/1243 = 1.73\ \text{V}$

$V_4 = 15.0\ \text{V} \times 1000/1243 = 12.1\ \text{V}$

(b) $I_1 = I_5 = 15.0/(100 + 143 + 1000) = 1.21 \times 10^{-2}$ A

$I_2 = 1.73$ V/500 Ω= 3.5×10^{-3} A

$I_3 = I_4 = 1.73$ V /200 Ω = 8.6×10^{-3} A

(c) $P = IV = 1.73$ V× 8.6×10^{-3} A = 1.5×10^{-2} W

(d) Since point 3 is at the same potential as point 2, the voltage between points 3 and 4 V' is the sum of the drops across the 143 W and the 1000 W resistors. Or,

$V' = 1.73$ V + 12.1 V = 13.8 V. It is also the source voltage minus the V_1

$V' = 15.0 – 1.21 = 13.8$ V

2-6. The resistance between points 1 and 2 is the parallel combination or R_B and R_C

$R_{1,2} = 2.0$ kΩ × 4.0 kΩ/(2.0 kΩ + 4.0 kΩ) = 1.33 kΩ

Similarly the resistance between points 2 and 3 is

$R_{2,3} = 2.0$ kΩ × 1.0 kΩ/(2.0 kΩ + 1.0 kΩ) = 0.667 kΩ

These two resistors are in series with R_A for a total series resistance R_T of

$R_T = 1.33$ kΩ + 0.667 kΩ + 1.0 kΩ = 3.0 kΩ

$I = 24/(3000\ \Omega) = 8.0 \times 10^{-3}$ A

(a) $P_{1,2} = I^2R_{1,2} = (8.0 \times 10^{-3})^2 \times 1.33 \times 10^3 = 0.085$ W

(b) As above $I = 8.0 \times 10^{-3}$ A

(c) $V_A = IR_A = 8.0\times 10^{-3}$ A × 1.0×10^3 Ω = 8.0 V

(d) $V_D = 14 \times R_{2,3}/R_T = 24 \times 0.667/3.0 = 5.3$ V

(e) $V_{5,2} = 24 – V_A = 24 -8.0 = 16$ V

2-7. With the standard cell in the circuit,

$V_{\mathrm{std}} = V_b \times AC/AB$ where V_b is the battery voltage

$1.018 = V_b \times 84.3/AB$

With the unknown voltage V_x in the circuit,

$V_x = V_b \times 44.2/AB$

Dividing the third equation by the second gives,

$$\frac{1.018 \text{ V}}{V_x} = \frac{84.3 \text{ cm}}{44.3 \text{ cm}}$$

$$V_x = 1.018 \times 44.3 \text{ cm}/84.3 \text{ cm} = 0.535 \text{ V}$$

2-8. $E_r = -\dfrac{R_S}{R_M + R_S} \times 100\%$

For $R_S = 20\ \Omega$ and $R_M = 10\ \Omega$, $E_r = -\dfrac{20}{10+20} \times 100\% = -67\%$

Similarly, for $R_M = 50\ \Omega$, $E_r = -\dfrac{20}{50+20} \times 100\% = -29\%$

The other values are shown in a similar manner.

2-9. Equation 2-20 is $E_r = -\dfrac{R_{\text{std}}}{R_L + R_{\text{std}}} \times 100\%$

For $R_{\text{std}} = 1\ \Omega$ and $R_L = 1\ \Omega$, $E_r = -\dfrac{1\ \Omega}{1\ \Omega + 1\ \Omega} \times 100\% = -50\%$

Similarly for $R_L = 10\ \Omega$, $E_r = -\dfrac{1\ \Omega}{10\ \Omega + 1\ \Omega} \times 100\% = -9.1\%$

The other values are shown in a similar manner.

2-10. (a) $R_s = V/I = 1.00 \text{ V}/50 \times 10^{-6} \text{ A} = 20000\ \Omega$ or $20\text{ k}\Omega$

(b) Using Equation 2-19

$$-1\% = -\frac{20\text{ k}\Omega}{R_M + 20\text{ k}\Omega} \times 100\%$$

$R_M = 20\text{ k}\Omega \times 100 - 20\text{ k}\Omega = 1980\text{ k}\Omega$ or $\approx 2\text{ M}\Omega$

2–11. $I_1 = 90/(20 + 5000) = 1.793 \times 10^{-2}$ A

$I_2 = 90/(40 + 5000) = 1.786 \times 10^{-2}$ A

% change = $[(1.786 \times 10^{-2} - 1.793 \times 10^{-2}\text{ A})/\ 1.793 \times 10^{-2}\text{ A}] \times 100\% = -0.4\%$

2-12. $I_1 = 9.0/520 = 1.731 \times 10^{-2}$ A

$I_2 = 9.0/540 = 1.667 \times 10^{-2}$ A

% change = $[(1.667 \times 10^{-2} - 1.731 \times 10^{-2}\text{ A})/\ 1.731 \times 10^{-2}\text{ A}] \times 100\% = -3.7\%$

2-13. $i = I_{\text{init}}\, e^{-t/RC}$ (Equation 2-35)

$RC = 10 \times 10^6\ \Omega \times 0.2 \times 10^{-6}\text{ F} = 2.00\text{ s}$ $I_{\text{init}} = 24\text{V}/(10 \times 10^6\ \Omega) = 2.4 \times 10^{-6}$ A

$i = 2.4 \times 10^{-6}\, e^{-t/2.00}$ A or $2.4\, e^{-t/2.0}$ μA

***t*, s**	***i*, μA**
0.00	2.40
0.010	2.39
0.10	2.28

***t*, s**	***i*, μA**
1.0	1.46
10	0.0162

2-14. $v_C = V_C\, e^{-t/RC}$ (Equation 2-40)

$v_C/V_C = 1.00/100$ for discharge to 1%

$0.0100 = e^{-t/RC} = e^{-t/R \times 0.015 \times 10^{-6}}$

$\ln 0.0100 = -4.61 = -t/1.5 \times 10^{-8}R$

$t = 4.61 \times 1.5 \times 10^{-8}R = 6.90 \times 10^{-8}R$

(a) When $R = 10$ MΩ or $10 \times 10^6\ \Omega$, $t = 0.69$ s

(b) Similalry, when $R = 1$ MΩ, $t = 0.069$ s

(c) When $R = 1\ \text{k}\Omega$, $t = 6.9 \times 10^{-5}$ s

2-15. (a) When $R = 10\ \text{M}\Omega$, $RC = 10 \times 10^{6}\ \Omega \times 0.015 \times 10^{-6}\ \text{F} = 0.15$ s

(b) $RC = 1 \times 10^{6} \times 0.015 \times 10^{-6} = 0.015$ s

(c) $RC = 1 \times 10^{3} \times 0.015 \times 10^{-6} = 1.5 \times 10^{-5}$ s

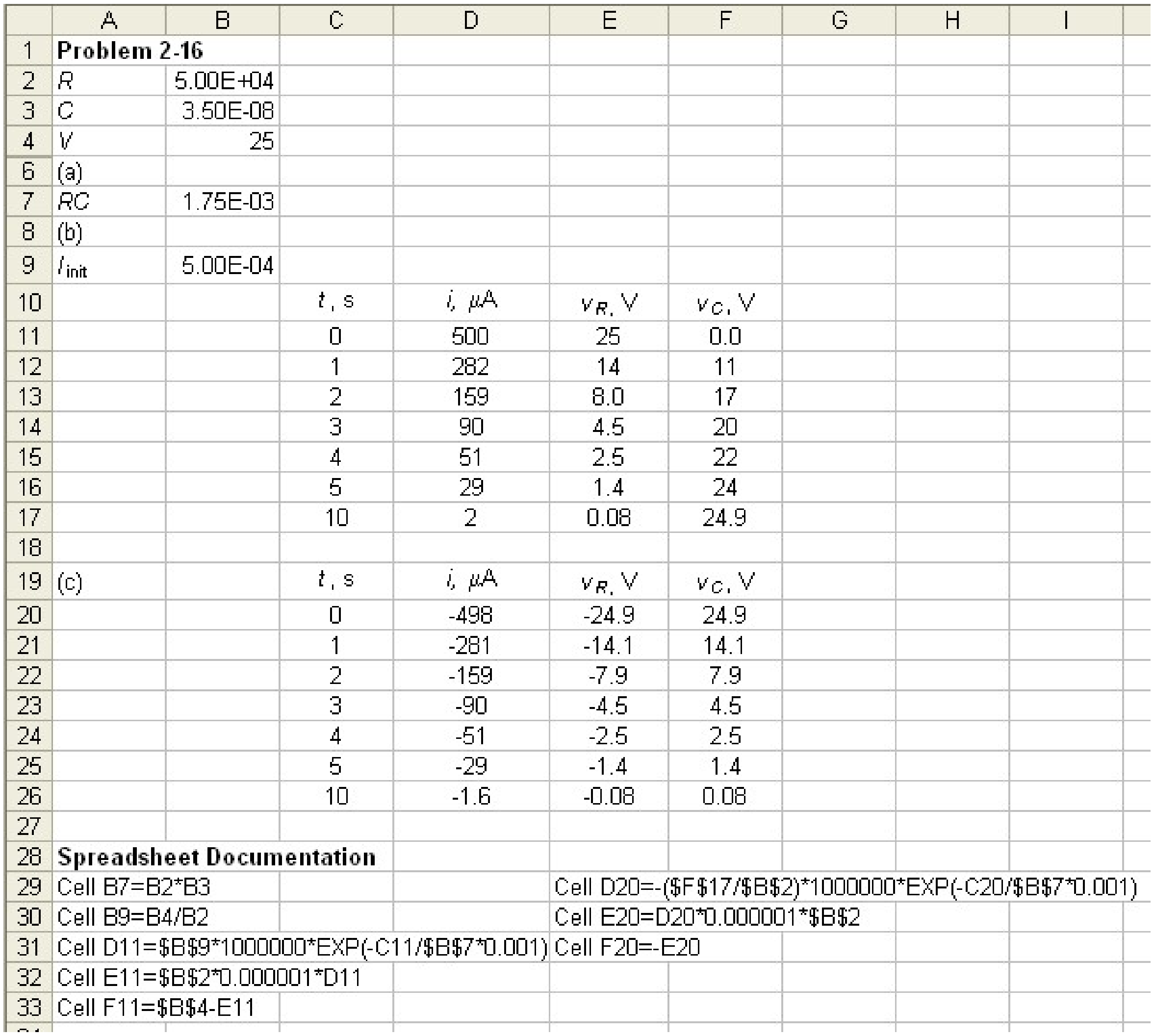
2-16. Parts (a) and (b) are given in the spreadsheet below. For part (c), we calculate the quantities from

$i = I_{\text{init}}\, e^{-t/RC}$, $v_R = iR$, and $v_C = 25 - v_R$

For part (d) we calculate the quantities from

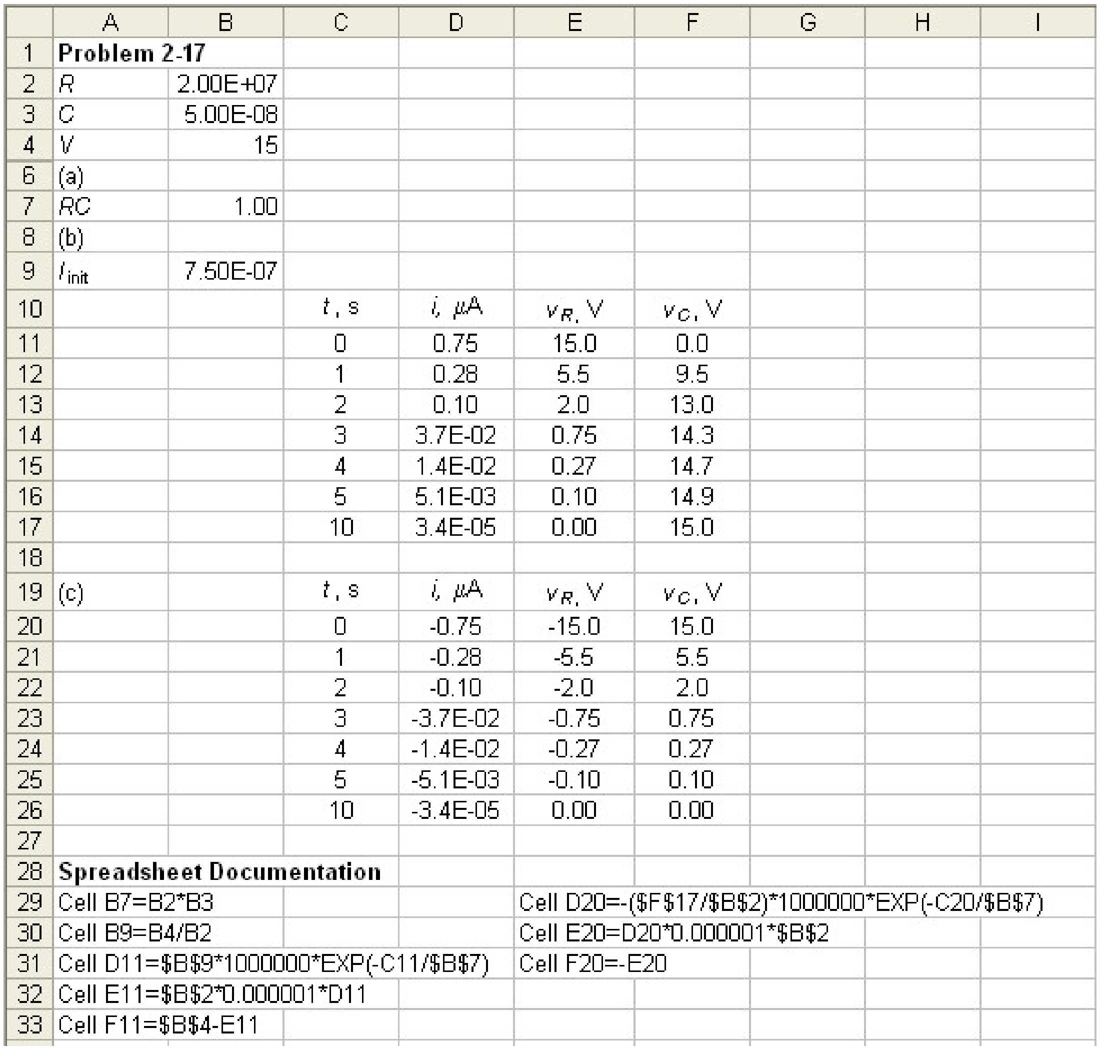
$$i = \frac{-v_C}{R} e^{-t/RC},\ v_R = iR, \text{ and } v_C = -v_R$$

The results are given in the spreadsheet.



	A	B	C	D	E	F	G	H	I
1	**Problem 2-16**								
2	R	5.00E+04							
3	C	3.50E-08							
4	V	25							
6	(a)								
7	RC	1.75E-03							
8	(b)								
9	I_{init}	5.00E-04							
10			t, s	i, μA	v_R, V	v_C, V			
11			0	500	25	0.0			
12			1	282	14	11			
13			2	159	8.0	17			
14			3	90	4.5	20			
15			4	51	2.5	22			
16			5	29	1.4	24			
17			10	2	0.08	24.9			
18									
19	(c)		t, s	i, μA	v_R, V	v_C, V			
20			0	-498	-24.9	24.9			
21			1	-281	-14.1	14.1			
22			2	-159	-7.9	7.9			
23			3	-90	-4.5	4.5			
24			4	-51	-2.5	2.5			
25			5	-29	-1.4	1.4			
26			10	-1.6	-0.08	0.08			
27									
28	**Spreadsheet Documentation**								
29	Cell B7=B2*B3				Cell D20=-($F$17/$B$2)*1000000*EXP(-C20/$B$7*0.001)				
30	Cell B9=B4/B2				Cell E20=D20*0.000001*$B$2				
31	Cell D11=$B$9*1000000*EXP(-C11/$B$7*0.001)				Cell F20=-E20				
32	Cell E11=$B$2*0.000001*D11								
33	Cell F11=$B$4-E11								

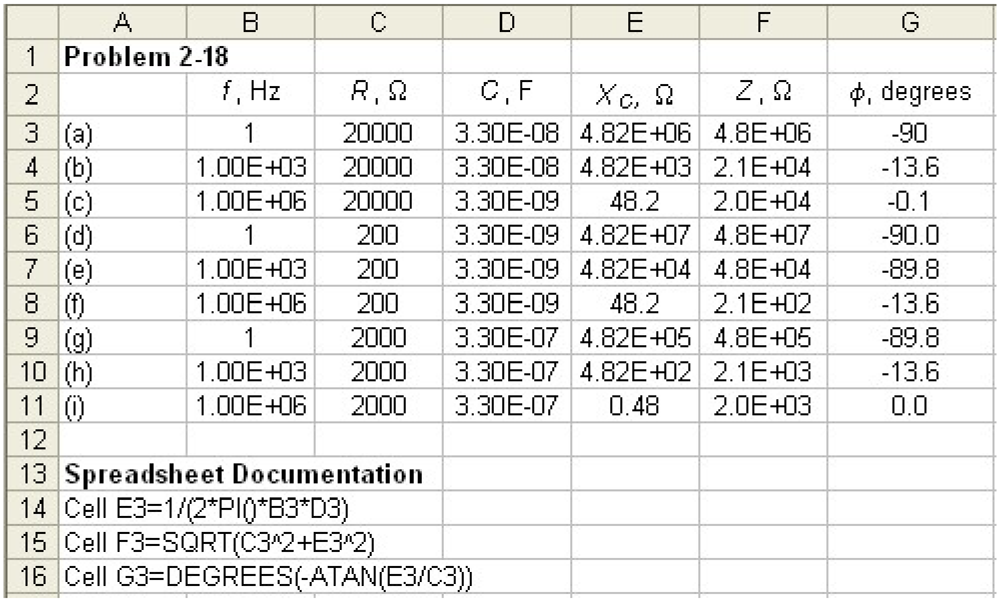
2-17. Proceeding as in Problem 2-16, the results are in the spreadsheet



	A	B	C	D	E	F	G	H	I
1	**Problem 2-17**								
2	*R*	2.00E+07							
3	*C*	5.00E-08							
4	*V*	15							
6	(a)								
7	*RC*	1.00							
8	(b)								
9	I_{init}	7.50E-07							
10			*t*, s	*i*, μA	v_R, V	v_C, V			
11			0	0.75	15.0	0.0			
12			1	0.28	5.5	9.5			
13			2	0.10	2.0	13.0			
14			3	3.7E-02	0.75	14.3			
15			4	1.4E-02	0.27	14.7			
16			5	5.1E-03	0.10	14.9			
17			10	3.4E-05	0.00	15.0			
18									
19	(c)		*t*, s	*i*, μA	v_R, V	v_C, V			
20			0	-0.75	-15.0	15.0			
21			1	-0.28	-5.5	5.5			
22			2	-0.10	-2.0	2.0			
23			3	-3.7E-02	-0.75	0.75			
24			4	-1.4E-02	-0.27	0.27			
25			5	-5.1E-03	-0.10	0.10			
26			10	-3.4E-05	0.00	0.00			
27									
28	**Spreadsheet Documentation**								
29	Cell B7=B2*B3				Cell D20=-($F$17/$B$2)*1000000*EXP(-C20/$B$7)				
30	Cell B9=B4/B2				Cell E20=D20*0.000001*$B$2				
31	Cell D11=$B$9*1000000*EXP(-C11/$B$7)				Cell F20=-E20				
32	Cell E11=$B$2*0.000001*D11								
33	Cell F11=$B$4-E11								

2-18. In the spreadsheet we calculate X_C, Z, and ϕ from

$$X_C = 2/2\pi fC,\ Z = \sqrt{R^2 + X_C^2}\text{, and } \phi = \text{arc tan}(X_C/R)$$



	A	B	C	D	E	F	G
1	**Problem 2-18**						
2		*f*, Hz	*R*, Ω	*C*, F	*X*_C, Ω	*Z*, Ω	*ϕ*, degrees
3	(a)	1	20000	3.30E-08	4.82E+06	4.8E+06	-90
4	(b)	1.00E+03	20000	3.30E-08	4.82E+03	2.1E+04	-13.6
5	(c)	1.00E+06	20000	3.30E-09	48.2	2.0E+04	-0.1
6	(d)	1	200	3.30E-09	4.82E+07	4.8E+07	-90.0
7	(e)	1.00E+03	200	3.30E-09	4.82E+04	4.8E+04	-89.8
8	(f)	1.00E+06	200	3.30E-09	48.2	2.1E+02	-13.6
9	(g)	1	2000	3.30E-07	4.82E+05	4.8E+05	-89.8
10	(h)	1.00E+03	2000	3.30E-07	4.82E+02	2.1E+03	-13.6
11	(i)	1.00E+06	2000	3.30E-07	0.48	2.0E+03	0.0
12							
13	**Spreadsheet Documentation**						
14	Cell E3=1/(2*PI()*B3*D3)						
15	Cell F3=SQRT(C3^2+E3^2)						
16	Cell G3=DEGREES(-ATAN(E3/C3))						

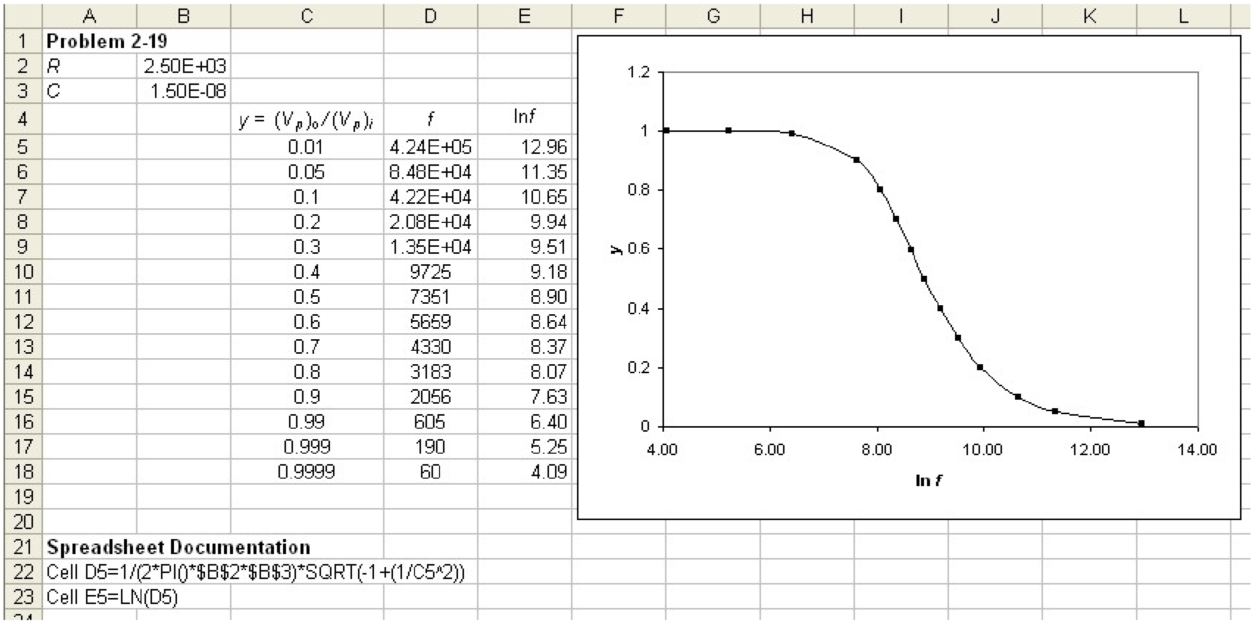
2-19. Let us rewrite Equation 2-54 in the form

$$y = \frac{(V_p)_o}{(V_p)_i} = \frac{1}{\sqrt{(2\pi fRC)^2 + 1}}$$

$$y^2(2\pi fRC)^2 + y^2 = 1$$

$$f = \frac{1}{2\pi \text{RC}}\sqrt{\frac{1}{y^2} - 1} = \frac{1}{2\pi \text{RC}}\sqrt{\frac{1 - y^2}{y^2}}$$

The spreadsheet follows



	A	B	C	D	E
1	**Problem 2-19**				
2	R	2.50E+03			
3	C	1.50E-08			
4			$y = (V_p)_o/(V_p)_i$	f	ln$f$
5			0.01	4.24E+05	12.96
6			0.05	8.48E+04	11.35
7			0.1	4.22E+04	10.65
8			0.2	2.08E+04	9.94
9			0.3	1.35E+04	9.51
10			0.4	9725	9.18
11			0.5	7351	8.90
12			0.6	5659	8.64
13			0.7	4330	8.37
14			0.8	3183	8.07
15			0.9	2056	7.63
16			0.99	605	6.40
17			0.999	190	5.25
18			0.9999	60	4.09
19					
20					
21	**Spreadsheet Documentation**				
22	Cell D5=1/(2*PI()*$B$2*$B$3)*SQRT(-1+(1/C5^2))				
23	Cell E5=LN(D5)				

2-20. By dividing the numerator and denominator of the right side of Equation 2-53 by R, we obtain

$$y = \frac{(V_p)_\text{o}}{(V_p)_i} = \frac{1}{\sqrt{1 + (1/2\pi fRC)^2}}$$

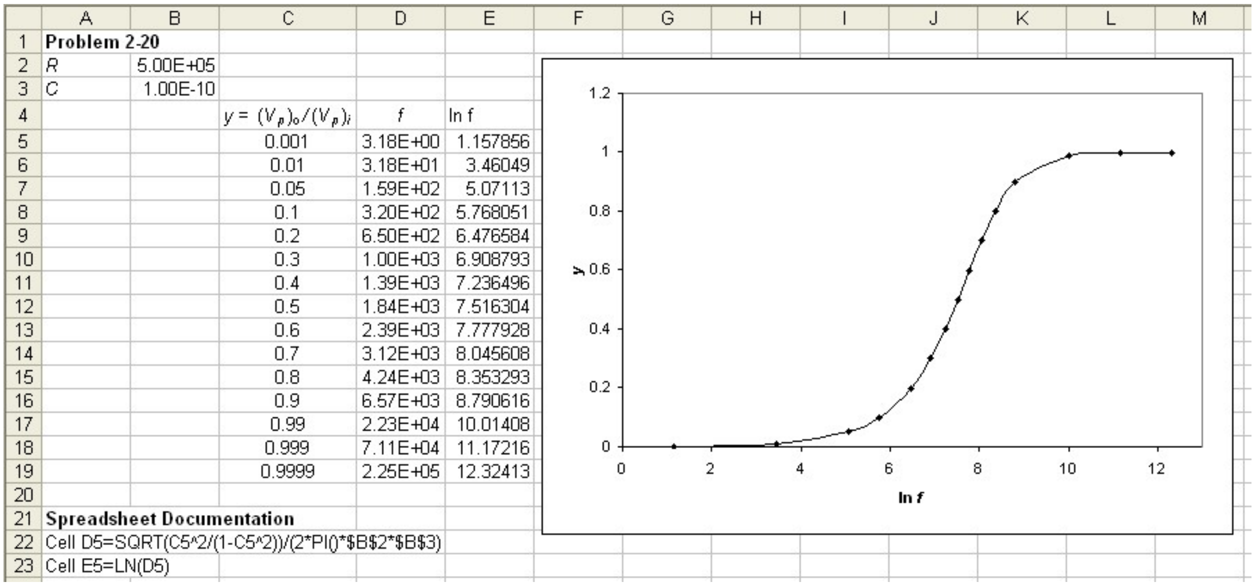
Squaring this equation yields

$$y^2 + y^2/(2\pi fRC)^2 = 1$$

$$2\pi fRC = \sqrt{\frac{y^2}{1-y^2}}$$

$$f = \frac{1}{2\pi RC}\sqrt{\frac{y^2}{1-y^2}}$$

The results are shown in the spreadsheet that follows.



	A	B	C	D	E
1	**Problem 2-20**				
2	*R*	5.00E+05			
3	*C*	1.00E-10			
4			$y = (V_p)_o/(V_p)_i$	*f*	ln f
5			0.001	3.18E+00	1.157856
6			0.01	3.18E+01	3.46049
7			0.05	1.59E+02	5.07113
8			0.1	3.20E+02	5.768051
9			0.2	6.50E+02	6.476584
10			0.3	1.00E+03	6.908793
11			0.4	1.39E+03	7.236496
12			0.5	1.84E+03	7.516304
13			0.6	2.39E+03	7.777928
14			0.7	3.12E+03	8.045608
15			0.8	4.24E+03	8.353293
16			0.9	6.57E+03	8.790616
17			0.99	2.23E+04	10.01408
18			0.999	7.11E+04	11.17216
19			0.9999	2.25E+05	12.32413
20					
21	**Spreadsheet Documentation**				
22	Cell D5=SQRT(C5^2/(1-C5^2))/(2*PI()*$B$2*$B$3)				
23	Cell E5=LN(D5)				

CHAPTER 3

3-1. $v_o = Av_s = A(v_+ - v_-)$ For + limit, $+13\text{ V} = A(v_+ - v_-)$ For – limit, $-14\text{ V} = A(v_+ - v_-)$

(a). If $A = 200{,}000$, for + limit, $(v_+ - v_-) = 13\text{ V}/200{,}000 = 65\ \mu\text{V}$. So v_+ must exceed v_- by 65 μV for + limit to be reached.

For – limit, $(v_+ - v_-) = -14\text{ V}/200{,}000 = -75\ \mu\text{V}$, so v_- must exceed v_+ by 75 μV.

(b). For + limit $(v_+ - v_-) = 13\text{ V}/500{,}000 = 26\ \mu\text{V}$. For – limit $(v_+ - v_-) = -14\text{ V}/500{,}000 = -28\ \mu\text{V}$.

(c). + limit, $(v_+ - v_-) = 13\text{ V}/1.5 \times 10^6 = 8.7\ \mu\text{V}$; – limit, $(v_+ - v_-) = -14\text{ V}/1.5 \times 10^6 = -9.3\ \mu\text{V}$

3-2. $\text{CMRR} = \dfrac{A_d}{A_{cm}}$ The difference gain, $A_d = 10\text{ V}/500\ \mu\text{V} = 2.0 \times 10^4$

The common mode gain, $A_{cm} = 1\text{ V}/500\text{ mV} = 2.0$

$\text{CMRR} = 2.0 \times 10^4/2.0 = 1.0 \times 10^4$ or in dB, $\text{CMRR} = 20\log(1.0 \times 10^4) = 80\text{ dB}$

3-3. For $v_s = 5.0\ \mu\text{V}$, $A = v_o/v_s = 13/5 \times 10^{-6} = 2.6 \times 10^6$.

3-4. (a). From Equation 3-2, $v_o = v_i\left(\dfrac{A}{1+A}\right) = 2.0 \times 1.0 \times 10^5/(1 + 1.0 \times 10^5) = 1.99998\text{ V}$

Error = $2.0 - 1.99998\text{ V} = 0.00002\text{ V}$ or 20 μV

Rel Error = $(20 \times 10^{-6}/2.0) \times 100\% = 0.001\%$

(b). Current drawn from the source, *i,* is $i = \dfrac{2.0\text{ V}}{(10^4 + 10^{12})\ \Omega} = 1.99999998 \times 10^{-12}\text{ A}$

The *IR* drop across the source resistance is $1.99999998 \times 10^{-12}\text{ A} \times 10^4\ \Omega = 20\text{ nV}$

Rel Error = (20 nV/2.0 V) × 100% = 1.0×10^{-6}%

3-5. Resistors R_1 and R_2 form a voltage divider. A fraction of the output voltage $\left(\frac{R_1}{R_1+R_2}\right)v_o$ is feedback to the inverting input. The amplifier maintains the voltage at the noninverting input, v_i equal to the voltage at the inverting input $\left(\frac{R_1}{R_1+R_2}\right)v_o$. Hence, if $v_i = \left(\frac{R_1}{R_1+R_2}\right)v_o$, it follows that $v_o = \left(\frac{R_1+R_2}{R_1}\right)v_i$. This is a voltage follower configuration, but since $(R_1 + R_2) > R_1$, there will be gain.

3-6. $R_1 + R_2 = 3.5 \times R_1 = 10.0 \times 10^3\ \Omega$. So, $R_1 = 10.0 \times 10^3\ \Omega/3.5 = 2.86 \times 10^3\ \Omega$ (2.9 kΩ).

$R_2 = 10.0 \times 10^3\ \Omega - R_1 = 10.0 \times 10^3 - 2.9 \times 10^3 = 7.1\ \text{k}\ \Omega$.

3-7. $v_o = -ix$ and $v_+ = v_- = 0$

$v_i = i(R - x)$

$$\frac{v_o}{v_i} = \frac{-ix}{i(R-x)} = -\frac{x}{R-x}$$

$$v_o = -\left(\frac{x}{R-x}\right)v_i$$

3-8. (a). The output voltage $v_o = -iR_f$. So $R_f = -v_o/I = 1.0\ \text{V}/10.0 \times 10^{-6}\ \text{A} = 1.0 \times 10^5\ \Omega$.

Use the circuit of Figure 3-6 with R_f = 100 kΩ.

(b). From Equation 3-5, $R_i = R_f/A = 100\ \text{k}\Omega/2 \times 10^5 = 0.5\ \Omega$.

(c). Equation 3-6 states $v_o = -R_f(i_i - i_b)\left(\frac{A}{1+A}\right)$

$$v_o = -100\ \text{k}\Omega\left(25\ \mu\text{A} - 2.5\ \text{nA}\right)\left(\frac{2\times10^5}{1+2\times10^5}\right) = 2.4997\ \text{V}$$

$$\text{Rel error} = \left(\frac{2.5000\ -\ 2.4997}{2.5000}\right)\times100\% = 0.01\%$$

3-9. (a). Gain = R_f/R_i so if R_i = 10 kΩ and the gain = 25, R_f= 25 × 10 kΩ = 250 kΩ.

Use the circuit of Figure 3-7, with R_f = 250 kΩ and R_i = 10 kΩ.

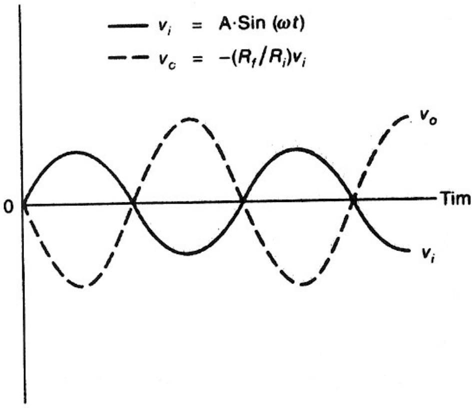
(b). $v_o = -\left(\frac{R_f}{R_i}\right)v_i$ so if v_o = ± 10 V, and gain = 25, $v_i = \frac{\pm\ 10\ \text{V}}{25} = \pm\ 0.40\ \text{V}$

(c). R_i is determined by the input resistor, so R_i = 10 kΩ.

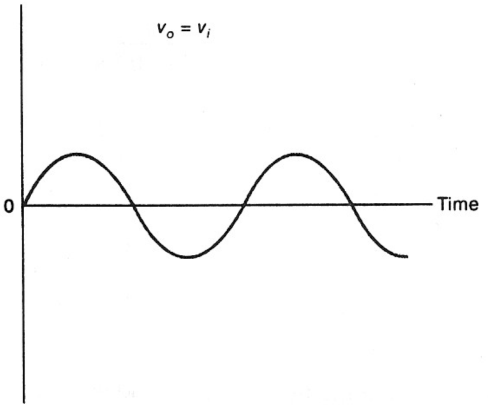
(d). Insert a voltage follower between the input voltage source and R_i as in Figure 3-11.

3-10.

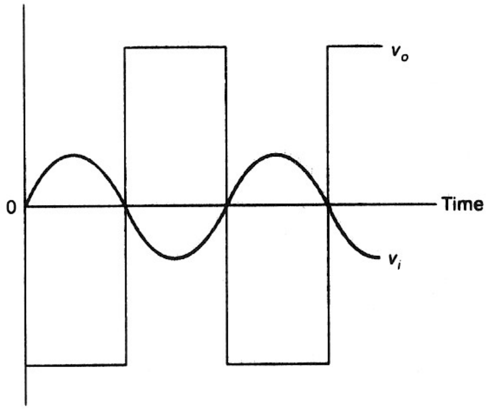
(a)


v_i = A·Sin (ωt)
v_c = −(R_f/R_i)v_i
v_o
0
Time
v_i

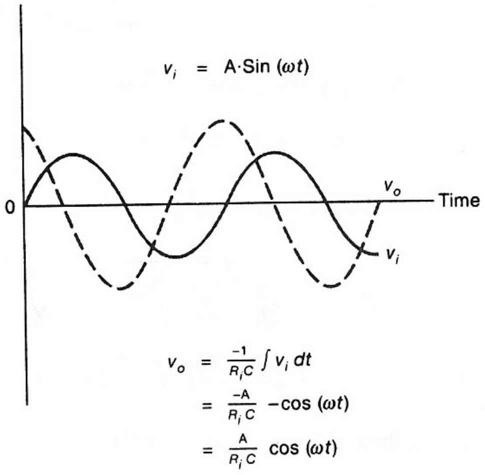
(b)


v_o = v_i
0
Time

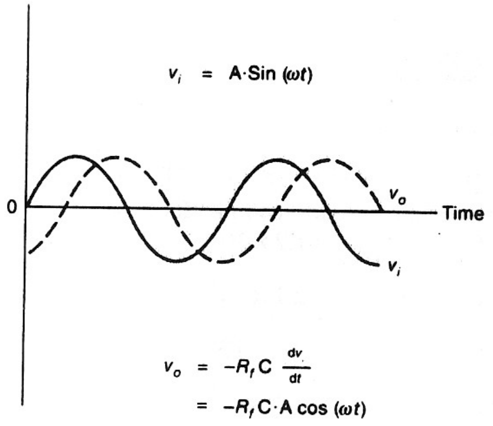
(c)


v_o
0
Time
v_i

(d)


v_i = A·Sin (ωt)
v_o
0
Time
v_i
v_o = −1/(R_iC) ∫ v_i dt
= −A/(R_iC) −cos (ωt)
= A/(R_iC) cos (ωt)

(e)

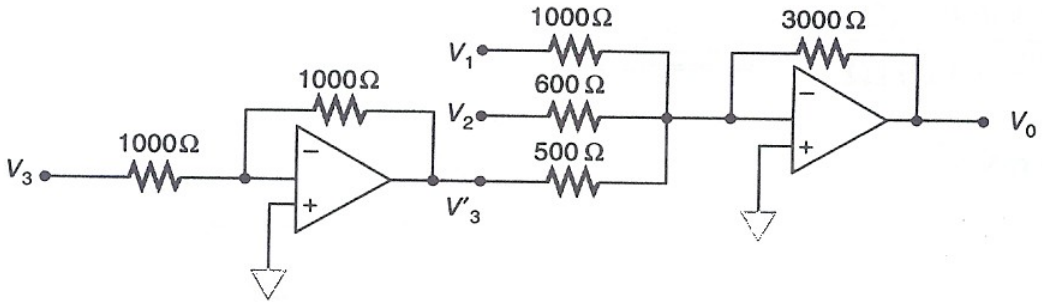

v_i = A·Sin (ωt)
0
v_o
Time
v_i
v_o = −R_f C dv/dt
= −R_f C·A cos (ωt)

3-11. The rise time t_r is given by Equation 3-9

$$t_r = \frac{1}{3\Delta f} = \frac{1}{3\times 50\times 10^6} = 6.7 \times 10^{-9} \text{ s} = 6.7 \text{ ns}$$

The slew rate is given by $\dfrac{\Delta v}{\Delta f} = \dfrac{10 \text{ V}}{6.7 \text{ ns}} = 1.5 \times 10^9$ V/s = 1500 V/μs

3-12. Several resistor combinations will work including the following

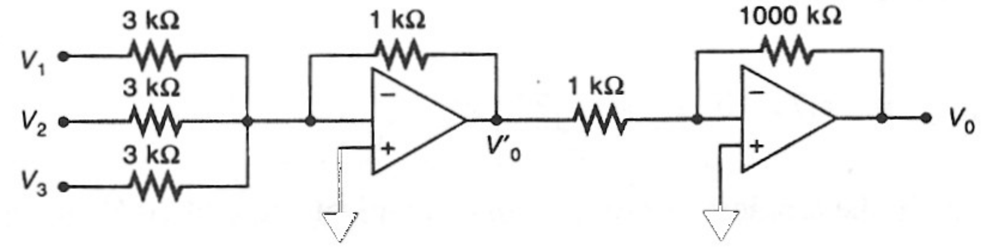


$$V_o = -R_f\left(\frac{V_1}{R_1}+\frac{V_2}{R_2}+\frac{V_3'}{R_3}\right) \qquad V_3' = -\frac{1000}{1000}V_3 = -V_3$$

$$V_o = -3000\left(\frac{V_1}{1000}+\frac{V_2}{600}+\frac{V_3'}{500}\right) = -3000\left(\frac{V_1}{1000}+\frac{V_2}{600}-\frac{V_3}{500}\right)$$

$V_o = -3V_1 - 5V_2 + 6V_3$

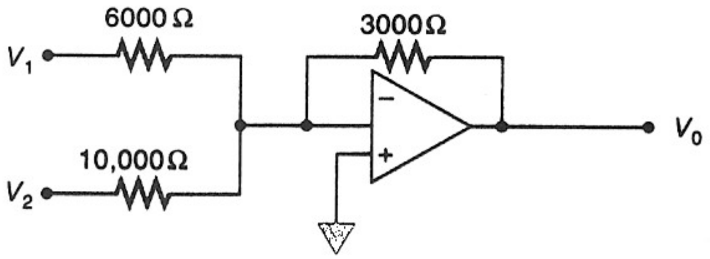
3-13. Several combinations will work, including the following



$$V_o{}' = -1\times\left(\frac{V_1}{3}+\frac{V_2}{3}+\frac{V_3}{3}\right)$$

$$V_o = -V_o{}'\times\frac{1000}{1} = 1000\left(\frac{V_1+V_2+V_3}{3}\right)$$

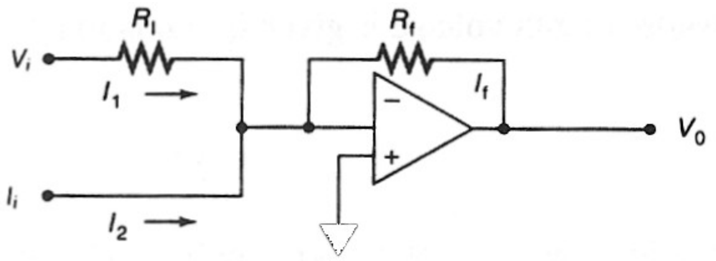
3-14. Several resistor combinations will work including



$$V_o = -R_f\left(\frac{V_1}{R_1}+\frac{V_2}{R_2}\right) = -3000\left(\frac{V_1}{6000}+\frac{V_2}{10000}\right) = -(0.500\ V_1 + 0.300\ V_2)$$

$$-V_o = \frac{1}{10}\left(5V_1+3V_2\right)$$

3-15. The circuit is shown below. Resistances values that work include $R_f = 1.00$ kΩ and $R_1 =$ 250 Ω



$I_1 + I_2 = I_f$ Note $I_2 = I_i$

$$\frac{V_1}{R_1} + I_i = -\frac{V_o}{R_f}$$

$$-V_o = \frac{V_1 R_f}{R_1} + I_i R_f \qquad \text{or } V_o = -\frac{V_1 R_f}{R_1} - I_i R_f$$

Substituting the vales of R_f and R_i gives

$$V_o = -\frac{V_1 \times 1000}{250} - 1000 I_i = -4V_1 - 1000 I_i$$

3-16. (a). Let v_x be the output from the first operational amplifier,

$$v_x = -\frac{v_1 R_{f1}}{R_1} - \frac{v_2 R_{f1}}{R_2}$$

and

$$v_o = -\frac{v_x R_{f2}}{R_4} = \frac{v_1 R_{f1} R_{f2}}{R_1 R_4} + \frac{v_2 R_{f1} R_{f2}}{R_2 R_4} - \frac{v_3 R_{f2}}{R_3}$$

(b). $$v_o = \frac{200 \times 400}{200 \times 400} v_1 + \frac{200 \times 400}{50 \times 400} v_2 - \frac{400}{10} v_3 = v_1 + 4v_2 - 40v_3$$

3-17. Let v_x be the output of the first operational amplifer,

$$v_x = -\frac{15}{3}v_1 - \frac{15}{5}v_2 = -5v_1 - 3v_2$$

$$v_o = -\frac{12}{6}v_x - \frac{12}{4}v_3 - \frac{12}{6}v_4 = -2v_x - 3v_3 - 2v_4 = 10v_1 + 6v_2 - 3v_3 - 2v_4$$

3-18. Operational amplifer 2 is an integrator whose output voltage is given by Equation 3-22.

Thus,

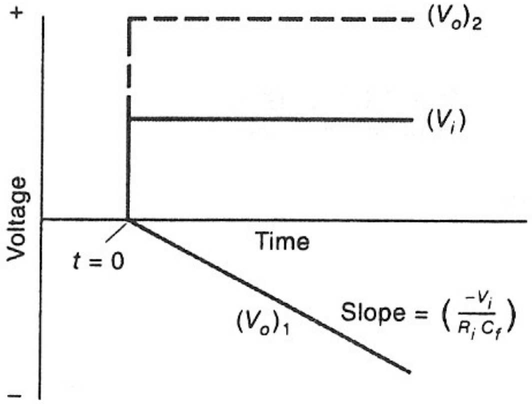
$$(v_o)_1 = -\frac{1}{R_i C_f}\int_0^t v_i dt = \left(\frac{-v_i}{R_i C_f}\right)t$$

Operational amplifier 2 is in the differentiator configuration where Equation 3-23 applies

$$(v_o)_2 = -R_f C_i \frac{d(v_o)_1}{dt} = -R_f C_i \frac{d}{dt}\left(\frac{-v_i}{R_i C_f}t\right)$$

$$(v_o)_2 = \frac{R_f C_i}{R_i C_f} v_i$$

In the sketch below, it is assumed that $R_f C_i / R_i C_f > 1$



3-19. $i_1 + i_2 = i_f$

$$\frac{V_1}{20\times10^6} + \frac{V_2}{5\times10^6} = -C\frac{dv_o}{dt} = -0.010\times10^6\frac{dv_o}{dt}$$

$$\frac{dv_o}{dt} = -\left(\frac{V_1}{0.20}+\frac{V_2}{0.05}\right)$$

$$v_o = -\left(5v_1+20v_2\right)\int_0^t dt$$

3-20. This circuit is analogous to that shown in Figure 3-13 with the added stipulation that

$R_1 = R_{k1} = R_2 = R_{k2}$

Equation 3-15 then applies and we can write

$$v_o = \frac{R_k}{R_i}\left(v_2 - v_1\right) = v_2 - v_1$$

3-21. $1.02 = V_o \times \overline{BC}/\overline{AB} = 3.00 \times \overline{BC}/100$

$\overline{BC}$ = 100 cm × 1.02/3.00 = 34.0 cm

3-22. Here we combine the outputs from two integrators (Figure 3-16c) with a summing amplifier (Figure 3-16b). If both integrators have input resistances of 10 MΩ and feedback capacitances of 0.1 μF, the outputs are

$$(v_o)_1 = -\frac{1}{10\times10^6\times0.1\times10^{-6}}\int_0^t v_1 dt = -1.0\int_0^t v_1 dt$$

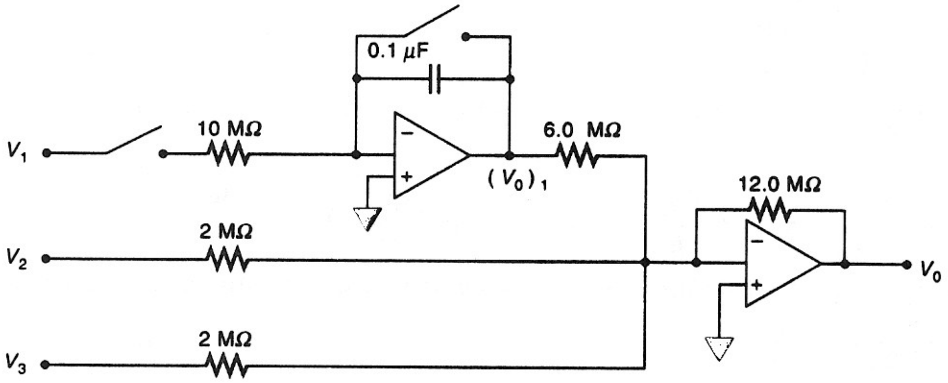
Similarly, $(v_o)_2 = -1.0\int_0^t v_2 dt$

If the summing amplifier has input resistances of 5.0 kΩ for integrator 1 and 4.0 kΩ for integrator 2 and a feedback resistance of 20 kΩ,

$$v_o = -20\left[\frac{(v_o)_1}{5.0} + \frac{(v_o)_2}{4.0}\right] = -4.0(v_o)_1 - 5.0(v_o)_2$$

$$v_o = +4.0\int_0^t v_1 dt + 5.0\int_0^t v_2 dt$$

3-23. The circuit is shown below with one possible resistance-capacitance combination



Here,

$$(v_o)_1 = -\frac{1}{10\times10^6\times0.1\times10^{-6}}\int_0^t v_1 dt = -1.0\int_0^t v_1 dt$$

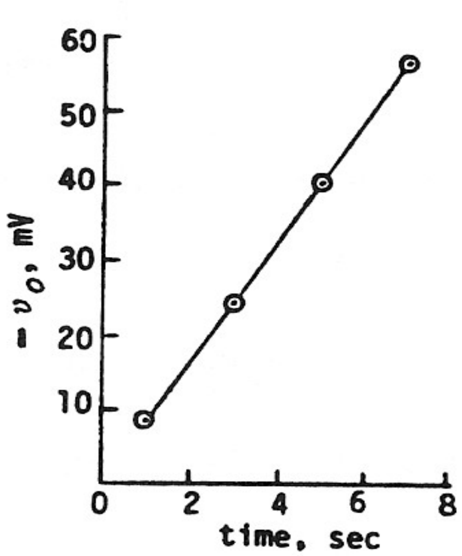
$$v_o = -12.0\left[\frac{(v_o)_1}{6} + \frac{v_2}{2} + \frac{v_3}{2}\right] = -2(v_o)_1 - 6(v_2 + v_3)$$

$$v_o = +2.0\int_0^t v_1 dt - 6(v_2 + v_3)$$

3-24. $$v_o = -\frac{1}{R_i C_f}\int_0^t v_1 dt = -\frac{1}{2\times10^6 \times 0.25\times10^{-6}}\int_0^t 4.0\times10^{-3} dt$$

$$v_o = -2\int_0^t 4.0\times10^{-3} dt = -8.0 \text{ mV } \times t$$

t, s	v_o, mV
1	–8.0
3	–24
5	–40
7	–56



CHAPTER 4

4-1. (a) For 24

$2^4 = 16 \quad 24 - 16 = 8$

$2^3 = 8 \quad 8 - 8 = 0$

binary $\underline{1 \qquad 1 \qquad 0 \qquad 0 \qquad 0 \qquad\qquad}$

$1 \times 2^4 + 1 \times 2^3 + 0 \times 2^2 + 0 \times 2^1 + 0 \times 2^0 = 24$

(b) For 91

$2^6 = 64 \quad 91 - 64 = 27$

$2^4 = 16 \quad 27 - 16 = 11$

$2^3 = 8 \quad 11 - 8 = 3$

$2^1 = 2 \quad 3 - 2 = 1$

$2^0 = 1 \quad 1 - 1 = 0$

binary $\underline{1 \qquad 0 \qquad 1 \qquad 1 \qquad 0 \qquad 1 \qquad 1 \qquad\qquad}$

$64 + 0 + 16 + 8 + 0 + 2 + 1 = 91$

In similar fashion we find,

(c) $135_{10} = 10000111_2$

(d) $396_{10} = 110001100_2$

4-2. (a) 24_{10} = 0010 1000 in BCD

(b) 91_{10} = 1001 0001 in BDC

(c) 135_{10} = 0001 0011 0101 in BCD

(d) 396_{10} = 0011 1001 0110 in BCD

4-3. Comparing 4-1c with 4-2c we see that in binary we need 8 bit to express 135_{10}, while in BCD we need12 bits. Likewise in 4-1d, we need 9 bits to express 396_{10} while in BCD, we need 12 bits. Hence, binary is more efficient. BCD is still very useful because it is much easier for humans to read and translate since it is closer to decimal.

4-4. (a) For 101_2, we have $1 \times 2^2 + 0 \times 2^1 + 1 \times 2^0 = 4 + 0 + 1 = 5_{10}$

(b) $10101_2 = 1 \times 2^4 + 0 \times 2^3 + 1 \times 2^2 + 0 \times 2^1 + 1 \times 2^0 = 16 + 0 + 4 + 0 + 1 = 21_{10}$

Similarly,

(c) $1110101_2 = 117_{10}$

(d) $1101011011_2 = 859_{10}$

4-5. (a) 0100 in BCD is 4_{10}

(b) 1000 1001 in BCD is 89_{10}

(c) 0011 0100 0111 in BCD is 347_{10}

(d) 1001 0110 1000 in BCD is 968_{10}

4-6. BCD is much easier to convert to decimal since we only have to read from 0 to 9 in each decade rather than counting powers of ten.

4-7. (a)

$$\begin{array}{r} 1\;0\;0\;1 \\ +\,0\;1\;1\;0 \\ \hline 1\;1\;1\;1 \end{array} \qquad \text{or} \qquad 8 + 4 + 2 + 1 = 15_{10}$$

(b) 341_2 is 101010101_2 29_2 is 11101_2. So

$$\begin{array}{r} 1\;0\;1\;0\;1\;0\;1\;0\;1 \\ 0\;0\;0\;0\;1\;1\;1\;0\;1 \\ \hline 1\;0\;1\;1\;1\;0\;0\;1\;0 \end{array} \qquad \text{or} \qquad 256 + 64 + 32 + 16 + 2 = 370_{10}$$

(c) Similarly, $47 + 16 = 111111_2 = 32 + 16 + 8 + 4 + 2 + 1 = 63_{10}$

(d) For 3 × 8 we have 011 × 1000

$$\begin{array}{r} 1000 \\ \underline{\times\ 11} \\ 1000 \\ \underline{1000} \\ \underline{11000} \end{array} \quad \text{or } 16 + 8 = 24_{10}$$

4-8. (a). $2^8 = 256$ so 10 V/256 = 0.039 V

(b) $2^{12} = 4096$ so 10 V/4096 = 0.0024 V

(c) $2^{16} = 65536$ so 10 V/65536 = 0.00015 V

4-9. (a) For the same full-scale range, the answers are identical to 4-8.

(b) If the 1-V signal is amplified to 10 V, the uncertainties are

for 8 bits 1 V/256 = 0.00309 V, for 12 bits, 1 V/4098 = 0.00024 V and for 16 bits,

1 V/65536 = 0.000015 V

4-10. Let us take the 8-bit converter as an example. For the 10V signal, the % error is

max %error = (0.039 V/10 V) × 100% = 0.39%

For 1-V, max %error = (0.039 V/1 V) × 100% = 3.9%. In each case, we have 10 times less error with the 10-V signal. If, however, we amplify the 1-V signal to 10 V, the % errors are identical

4-11. (a) 20 s/20 points = 1 s/point

$$\frac{1}{1\ \text{s/point}} = 1\ \text{point/s or } 1\ \text{Hz}$$

(b) 1 s/20 points = 0.05 s/point or 20 points/s = 20 Hz.

4-12. Conversion frequency = 1/8 μs = 125 kHz

According to the Nyquist criterion, the maximum signal frequency should be half the conversion frequency or 125 kHz/2 = 62.5 kHz.

CHAPTER 5

5-1. Frequency dependent noise sources: flicker and environmental noise.

Frequency independent sources: thermal and shot noise.

5-2. (a) Thermal noise.

(b) Certain types of environmental noise.

(c) Thermal andshot noise.

5-3. 10^3 to 10^5 Hz and 10^6 to 10^7 Hz, Enviromental noise is at a minimum in these regions (see Figure 5-3).

5-4. At the high impedance of a glass electrode, shielding is vital to minimize induced currents from power lines which can be amplified and can disturb the output.

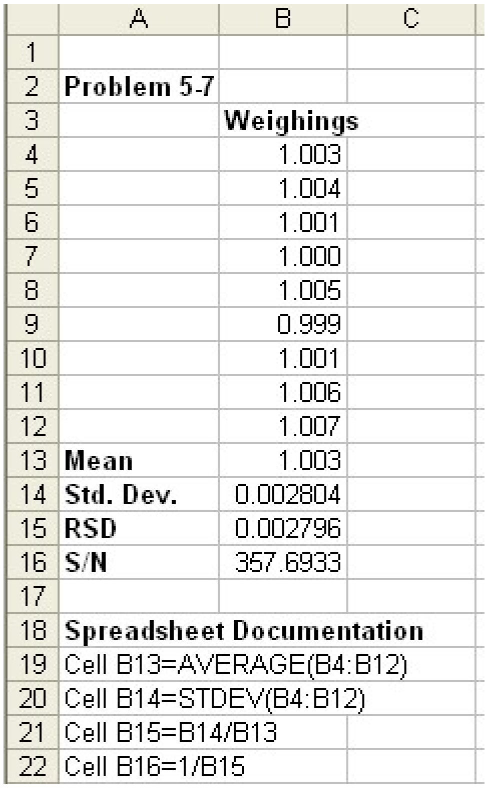
5-5. (a) High-pass filters are used to remove low frequency flicker noise from higher frequency analytical signals.

(b) Low-pass filters are used to remove high frequency noise from dc analytical signals.

5-6. We estimate the maximum and theminimum in the recorded signal (0.9×10^{-15} A) to be 1.5×10^{-15} and 0.4×10^{-15} A. The standard deviation of the signal is estimated to be one-fifth of the difference or 0.22×10^{-15} A. Thus,

$$\frac{S}{N} = \frac{0.9 \times 10^{-15}\ \text{A}}{0.22 \times 10^{-15}\ \text{A}} = 4$$

5-7. (a)



	A	B	C
1			
2	**Problem 5-7**		
3		**Weighings**	
4		1.003	
5		1.004	
6		1.001	
7		1.000	
8		1.005	
9		0.999	
10		1.001	
11		1.006	
12		1.007	
13	**Mean**	1.003	
14	**Std. Dev.**	0.002804	
15	**RSD**	0.002796	
16	**S/N**	357.6933	
17			
18	**Spreadsheet Documentation**		
19	Cell B13=AVERAGE(B4:B12)		
20	Cell B14=STDEV(B4:B12)		
21	Cell B15=B14/B13		
22	Cell B16=1/B15		

Hence, S/N = 358 for these 9 measurements

(b) $\frac{S}{N} = \frac{S_n}{N_n}\sqrt{n}$ (Equation 5-11). For the nine measurements,

$$358 = \frac{S_n}{N_n}\sqrt{9}$$

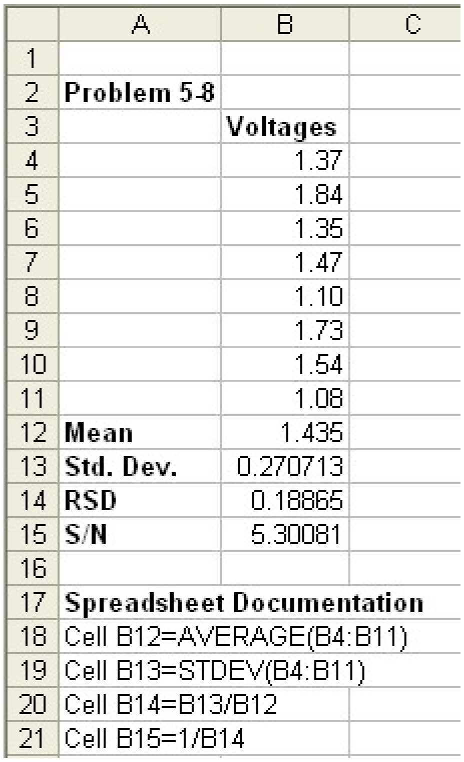
For the S/N to be 500 requires n_x measurements. That is,

$$500 = \frac{S_n}{N_n}\sqrt{n_x}$$

Dividing the second equation by the first gives, after squaring and rearranging,

$$n_x = \left(\frac{500}{358}\times 3\right)^2 = 17.6$$ or 18 measurements

5-8. (a)



	A	B	C
1			
2	**Problem 5-8**		
3		**Voltages**	
4		1.37	
5		1.84	
6		1.35	
7		1.47	
8		1.10	
9		1.73	
10		1.54	
11		1.08	
12	**Mean**	1.435	
13	**Std. Dev.**	0.270713	
14	**RSD**	0.18865	
15	**S/N**	5.30081	
16			
17	**Spreadsheet Documentation**		
18	Cell B12=AVERAGE(B4:B11)		
19	Cell B13=STDEV(B4:B11)		
20	Cell B14=B13/B12		
21	Cell B15=1/B14		

Thus $S/N = 5.3$

(b) Proceeding as in Solution 5-7, we obtain

$$n_x = \left(\frac{10}{5.3} \times \sqrt{8}\right) = 28.5 \quad \text{or 29 measurements}$$

5-9. $\bar{v}_{\text{rms}} = \sqrt{4kTR\Delta f} = \sqrt{4 \times 1.38 \times 10^{-23} \times 298 \times 1 \times 10^{6} \times 1 \times 10^{6}} = 1.28 \times 10^{-4}$ V

$\bar{v}_{\text{rms}} \propto \sqrt{\Delta f}$ So reducing Δf from 1 MHz to 100 Hz, means a reduction by a factor of

$10^6/10^2 = 10^4$ which leads to a reduction in $\bar{v}_{\text{rms}}$ of a factor of $\sqrt{10^4} = 100$.

5-10. To increase the S/N by a factor of 10 requires 10^2 more measurements. So $n = 100$.

5-11. The middle spectrum S/N is improved by a factor of $\sqrt{50} = 7.1$ over the top spectrum.

The bottom spectrum *S*/*N* is improved by a factor of $\sqrt{200} = 14.1$ over the top spectrum. The bottom spectrum is the result of 200/50 = 4 times as many scans so the *S*/*N* should be improved by a factor of $\sqrt{4} = 2$ over the middle spectrum

5-12. The magnitudes of the signals and the noise in the spectra in Figure 5-15 may be estimated directly from the plots. The results from our estimates are given in the table below. Baselines for spectra *A* and *D* are taken from the flat retions on the right side of the figure. Noise is calculated from one-fifth of the peak-to-peak excursions of the signal.

	A_{255}	A_{425}	A_b(peak)	A_b(valley)	A_b(mean)
Spectrum *A*	0.550	0.580	0.080	–0.082	0.001
Spectrum *D*	1.125	1.150	0.620	0.581	0.600

	S_{255}	S_{425}	$N = [A_b(\text{peak}) - A_b(\text{valley})]/5$	$(S/N)_{255}$	$(S/N)_{425}$
Spectrum *A*	0.549	0.579	0.0324	17	18
Spectrum *D*	0.525	0.550	0.0078	67	70

Note that the difference in *S*/*N* for the two peaks is due only to the difference in the peak heights.

So, at 255 nm, $(S/N)_D = 67/17(S/N)_A = 3.9(S/N)_A$; at 425 nm, $(S/N)_D = 79/18(S/N)_A = 3.9(S/N)_A$

CHAPTER 6

6-1. (a) Coherent radiation is radiation that is made up of wave trains having identical frequencies or sets of frequencies and phase relationships that are constant with time.

(b) Dispersion in a transparent medium is its variation in refractive index as a function of wavelength.

(c) Anomalous dispersion is the sharp change in refractive index of a substance in a wavelength region where absorption is occurring.

(d) The work function of a substance is a constant that measures the energy required to remove an electron from the surface of the substance.

(e) The photoelectric effect involves the emission of electrons from the surface of a substance brought about by a beam of radiation.

(f) The ground state of a molecule is its lowest energy state.

(g) Electronic excitation is the process by which electrons in a substance are promoted from their ground state to higher electronic states by absorption of energy.

(h) Blackbody radiation is the continuum radiation emitted by a solid when it is heated.

(i) Fluorescence is a type of emission which is brought about by irradiating atoms, ions, or molecules with electromagnetic radiation. Fluorescence involves a singlet-to-singlet transition. The lifetime of the excited state in fluorescence is very short (10^{-5} s or less).

(j) Phosphorescence is a type of emission brought about by irradiating a molecular system with electromagnetic radiation. Phosphorescence involves a triplet-to-singlet transition and the excited state lifetime is longer than that of a fluorescing species.

(k) Resonance fluorescence is a type of emission in which the radiation produced is of the same wavelength as that used to excite the fluorescence.

(l) A photon is a bundle or particle of radiant energy with a magnitude of $h\nu$, where h is Planck's constant and ν is the frequency of the radiation.

(m) Absorptivity a is defined by the equation $a = A/bc$, where A is the absorbance of a medium contained in a cell length of b and concentration c. The path length b is expressed in cm or another specifice unit of length. The concentration is expressed in units such as g/L.

(n) The wavenumber of radiation is the reciprocal of the wavelength in centimeters.

(o) Relaxation is a process whereby an excited species loses energy and returns to a lower energy state.

(p) The Stokes shift is the difference in wavelength between the incident radiation and the wavelength of fluorescence or scattering.

6-2. $$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\ \text{cm/s}}{6.24\ \text{Å} \times 10^{-8}\ \text{cm/Å}} = 4.80 \times 10^{17}\ \text{Hz}$$

$$E = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 4.80 \times 10^{17}\ \text{s}^{-1} = 3.18 \times 10^{-16}\ \text{J}$$

$$E = 3.18 \times 10^{-16}\ \text{J} \times 6.242 \times 10^{18}\ \text{s}^{-1} = 1.99 \times 10^{3}\ \text{ev}$$

6-3. $$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\ \text{cm/s}}{3.517\ \mu\text{m} \times 10^{-4}\ \text{cm/}\mu\text{m}} = 8.524 \times 10^{13}\ \text{s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{3.517 \times 10^{-4}\ \text{cm}} = 2843\ \text{cm}^{-1}$$

$$E = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 8.524 \times 10^{13}\ \text{s}^{-1} = 5.648 \times 10^{-20}\ \text{J}$$

6-4. $$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{10}\ \text{cm s}^{-1}}{368 \times 10^{6}\ \text{s}^{-1}} = 81.5\ \text{cm}$$

$$E = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 81.5\ \text{cm} = 5.40 \times 10^{-26}\ \text{J}$$

6-5. $$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\ \text{cm s}^{-1}}{589\ \text{nm} \times 10^{-7}\ \text{cm nm}^{-1}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

$$v_{\text{species}} = c/n_{\text{D}} = 2.998 \times 10^{10}\ \text{cm s}^{-1}/1.09 = 2.75 \times 10^{10}\ \text{cm s}^{-1}$$

$$\lambda_{\text{species}} = \frac{v_{\text{species}}}{\nu} = \frac{2.75 \times 10^{10}\ \text{cm s}^{-1}}{5.09 \times 10^{14}\ \text{s}^{-1}} \times 10^{7}\ \text{nm cm}^{-1} = 540\ \text{nm}$$

6-6. $$n_{\text{D}} = \frac{\sin 30}{\sin 11.9} = 2.42$$

6-7. $$E = h\nu = hc/\lambda = 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{10}\ \text{cm s}^{-1}/(779\ \text{nm} \times 10^{-7}\ \text{cm nm}^{-1})$$

$$= 2.55 \times 10^{-19}\ \text{J}$$

A photon with 3 times this energy has an energy, $E_3 = 3 \times 2.55 \times 10^{-19}\ \text{J} = 7.65 \times 10^{-19}\text{J}$

$$\lambda = hc/E = 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{10}\ \text{cm s}^{-1} \times 10^{7}\ \text{nm cm}^{-1}/7.65 \times 10^{-19}$$

$$= 260\ \text{nm}$$

6-8. $$E = 255\ \frac{\text{kJ}}{\text{mol}} \times \frac{10^{3}\ \text{J}}{\text{kJ}} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{photons}} = 4.24 \times 10^{-19}\ \text{J}$$

$$\nu = \frac{E}{h} = \frac{4.24 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 6.40 \times 10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998\quad 10^{10}\ \text{cm s}^{-1}}{6.40 \times 10^{14}\ \text{s}^{-1}} \times 10^{7}\ \frac{\text{nm}}{\text{cm}} = 469\ \text{nm}$$

6-9. (a) $$E_{660} = \frac{2.998 \quad 10^{10}\text{ cm s}^{-1}}{660\text{ nm} \times 10^{-7}\text{ cm nm}^{-1}} \times 6.626 \times 10^{-34}\text{ J s} = 3.01 \times 10^{-10}\text{ J}$$

$$E_{550} = \frac{2.998 \quad 10^{10}\text{ cm s}^{-1}}{550 \times 10^{-7}\text{ cm nm}^{-1}} \times 6.626 \times 10^{-34}\text{ J s} = 3.61 \times 10^{-19}\text{ J}$$

$E_{\max} = E_{550} - E_{660} = 3.61 \times 10^{-19} - 3.01 \times 10^{-19} = 6.02 \times 10^{-20}$ J

(b) The rest mass of the electron m is 9.11×10^{-31} kg. Letting v be the velocity of the photoelectron in meters/second, we may write

$E_{\max} = 6.02 \times 10^{-20}\text{ J} = \frac{1}{2}mv^2 = \frac{1}{2} \times 9.11 \times 10^{-31}\text{ kg } v^2$

$$v = \sqrt{\frac{2 \times 6.02 \times 10^{-20}\text{ kg m}^2\text{ s}^{-2}}{9.11 \times 10^{-31}\text{ kg}}} = 3.64 \times 10^5\text{ m s}^{-1}$$

6-10. From Figure 6-22, $\lambda_{\max}$ at 2000 K (Nernst glower) is estimated to be 1600 nm.

$k = T\lambda_{\max} = 2000\text{ K } 1600\text{ nm} = 3.2 \times 10^6\text{ K nm}$

At 1800 K,

$\lambda_{\max} = k/T = 3.2 \times 10^6\text{ K nm}/1800\text{ K} = 1.8 \times 10^3\text{ nm or } 1.8\ \mu\text{m}$

6-11. The wavelength in a medium different from air λ_m is given by

$\lambda_m = v_m/\nu$ (Equation 6-1)

where v_m is the velocity in the new medium. Letting n be the refractive index, we write

$v_m = c/n$ (Equation 6-11)

$\nu = c/\lambda_{air}$ (Equation 6-2)

Substituting into the first equation and rearranging, yields

$\lambda_m = \lambda_{air}/n$

(a) $\lambda_{hon} = 589\text{ nm}/1.50 = 393\text{ nm}$

(b) $\lambda_{quartz} = 694.3\text{ nm}/1.55 = 448\text{ nm}$

6-12. In entering an empty quartz cell, the beam must traverse an air-quartz interface, then a quartz-air interface. To get out of the cell, it must pass through an air-quartz interface and then a quartz-air interface.

The fraction reflected in passing from air into quartz is

$$\frac{I_{\mathrm{R1}}}{I_0} = \frac{(1.55\ -\ 1.00)^2}{(1.55 + 1.00)^2} = 0.0465$$

The intensity of the beam in the quartz, I_1 is

$I_1 = I_0 - 0.0465\ I_0 = 0.9535\ I_0$

The loss in pass from quartz to air is

$$\frac{I_{\mathrm{R2}}}{0.9535\ I_0} = 0.0465$$

$I_{\mathrm{R2}} = 0.0443\ I_0$

The intensity in the interior of the cell, I_2 is

$I_2 = 0.9535\ I_0 - 0.0443\ I_0 = 0.9092\ I_0$

The reflective loss in passing from the cell interior into the second quartz window is

$$\frac{I_{\mathrm{R3}}}{0.9092 I_0} = 0.0465$$

$I_{\mathrm{R3}}= 0.0423\ I_0$

and the intensity in the second quartz window I_3 is

$I_3 = 0.9092\ I_0 - 0.0423\ I_0 = 0.8669\ I_0$

Similarly, we found the intensity in passing from quartz to air $I_4 = 0.8266\ I_0$

The total loss by reflection is then $I_{\mathrm{Rt}} = 1 - 0.8266 = 0.173$ or 17.3%

6-13. The wave model of radiation requires that the radiation from a beam be evenly distributed over any surface it strikes. Under these circumstances, no single electron could gain sufficient energy rapidly enough to be ejected from the surface and thus provide an instantaneous current.

6-14. (a) T = antilog (–0.278) = 0.527 or 52.7%. Similarly, (b) 3.17%, and (c) 91.4%

6-15. (a) $A = -\log(29.9/100) = 0.524$. Similarly (b) 0.065, and (c) 1.53

6-16. (a) $A = 0.278/2 = 0.139$. $T = \text{antilog}(-0.139) = 0.726$ or 72.6%

(b) $A = 1.499/2 = 0.7495$. $T = \text{antilog}(-0.7495) = 0.178$ or 17.8%

(c) $A = 0.039/2 = 0.0195$. $T = \text{antilog}(-0.0195) = 0.956$ or 95.6%

6-17. (a) $T = 0.299/2 = 0.1495$. $A = -\log(0.1495) = 0.825$

(b) $T = 0.861/2 = 0.4305$. $A = 0.366$

(c) $T = 0.0297/2 = 0.1485$. $A = 1.83$

6-18. $A_1 = -\log(0.212) = 0.674 = \varepsilon b c_1 = \varepsilon \times 2.00 \times 3.78 \times 10^{-3}$

$$\varepsilon = \frac{0.674}{2.00 \times 3.78 \times 10^{-3}} = 89.109$$

$A_2 = -\log(0.212 \times 3) = 0.4437 = \varepsilon b c_2 = 89.109 \times 1.00 \times c_2$

$$c_2 = \frac{0.4437}{89.109} = 4.98 \times 10^{-3}\ \text{M}$$

6-19. $A = -\log(9.53/100) = 1.021$

$c = A/(\varepsilon b) = 1.021/(3.03 \times 10^3\ \text{L mol}^{-1}\ \text{cm}^{-1} \times 2.50\ \text{cm}) = 1.35 \times 10^{-4}\ \text{M}$

CHAPTER 7

7-1. Equation 7-17 can be written $w = \Delta\lambda_{\text{eff}}/D^{-1}$. For a prism monochromator the linear dispersion D decreases continuously with increasing wavelength. The reciprocal linear dispersion D^{-1} thus increases as the wavelength becomes longer. Hence, if $\Delta\lambda_{\text{eff}}$ is to remain constant, w, the slit width, must be decreased accordingly. For a grating instrument, D^{-1} is essentially constant over a considerable wavelength range. Thus, w does not need to be varied with a grating monochromator.

7-2. For qualitative analysis, it is important to resolve as many absorption bands as possible for identification purposes. This consideration often means that slit widths should be as narrow as possible. On the other hand, for quantitative methods, better signal-to-noise ratios, and hence higher precision, can be obtained with wider slit widths.

7-3. (a) $\lambda_{\text{max}} = 2.90 \times 10^3/T = 2.90 \times 10^3/5000\text{ K} = 0.58\ \mu\text{m}$ or 580 nm

(b) $\lambda_{\text{max}} = 2.90 \times 10^3/3000\text{ K} = 0.967\ \mu\text{m}$ or 967 nm

(c) $\lambda_{\text{max}} = 2.90 \times 10^3/1500\text{ K} = 1.93\ \mu\text{m}$

7-4. (a) $E_t = \alpha T^4 = 5.69 \times 10^{-8}\text{ W m}^{-2}\text{ K}^{-4} \times (5000\text{ K})^4 = 3.56 \times 10^7\text{ W m}^{-2}$

(b) $E_t = 5.69 \times 10^{-8}\text{ W m}^{-2}\text{ K}^{-4} \times (3000\text{ K})^4 = 4.61 \times 10^6\text{ W m}^{-2}$

(c) $E_t = 5.69 \times 10^{-8}\text{ W m}^{-2}\text{ K}^{-4} \times (1500\text{ K})^4 = 2.88 \times 10^5\text{ W m}^{-2}$

7-5. (a) $\lambda_{\text{max}} = 2.90 \times 10^3/T = 2.90 \times 10^3/2870 = 1.01\ \mu\text{m}$ or 1010 nm

$\lambda_{\text{max}} = 2.90 \times 10^3/3500 = 0.829\ \mu\text{m}$ or 829 nm

(b) $E_t = 5.69 \times 10^{-8}\text{ W m}^{-2}\text{ K}^{-4} \times (2870\text{ K})^4 = 3.86 \times 10^6\text{ W m}^{-2} \times 10^{-4}\text{ m}^2/\text{cm}^2$

$= 3.86 \times 10^2\text{ W cm}^{-2}$

$$E_t = 5.69 \times 10^{-8}\ \text{W m}^{-2}\ \text{K}^{-4} \times (3500\ \text{K})^4 = 8.54 \times 10^6\ \text{W m}^{-2} \times 10^{-4}\ \text{m}^2\text{cm}^{-2}$$

$$= 8.54 \times 10^2\ \text{W cm}^{-2}$$

7-6. Spontaneous emission occurs when a species loses all or part of its excess energy in the form of fluorescence or phosphorescence radiation. Because the process is random and can occur in any direction, the radiation is incoherent.

Stimulated emission is brought about by interaction of excited species with externally produced photons that have energies exactly matching the energy of a transition. The photons produced are in phase with those stimulating the emission, and coherent radiation is the result.

7-7. A four-level laser system has the advantage that population inversion is achieved more easily than with a three-level system. In a four-level system, it is only necessary to maintain a number of excited species that exceeds the number in an intermediate energy level that is higher in energy than the ground state. If the lifetime of the intermediate state is brief, a relatively few excited species is required for population inversion.

7-8. The effective bandwidth of a filter is the width in wavelength units of the band transmitted by the filter when measured at one-half the peak height.

7-9. (a) $\lambda = \dfrac{1}{\bar{\nu}} = \dfrac{2dn}{\mathbf{n}}$ (Equation 7-5)

$$d = \frac{\mathbf{n}}{2n\bar{\nu}} = \frac{1}{2 \times 1.34 \times 1537\ \text{cm}^{-1}} = 2.43 \times 10^{-4}\ \text{cm} \times 10^4\ \mu\text{m cm}^{-1} = 2.43\ \mu\text{m}$$

For second-order, $\lambda_2 = 2 \times 2.43\ \mu\text{m} \times 1.34/2 = 3.48\ \mu\text{m}$

For third-order, $\lambda_3 = 2 \times 2.43\ \mu\text{m} \times 1.34/3 = 2.17\ \mu\text{m}$, etc.

7-10. From Equation 7-5, $d = \lambda \mathbf{n}/2n$. If first-order interference is used, one end of the wedge would have a thinckness d of

$$d = 700 \text{ nm} \times 1/(2 \times 1.32) = 265 \text{ nm or } 0.265\ \mu\text{m}.$$

This thickness would also transmit second-order radiation of 700/2 = 350 nm, which would be absorbed by the glass plates supporting the wedge.

The other end of the wedge should have a thickness of

$$d = 400 \times 1/(2 \times 1.32) = 1.52 \text{ nm or } 0.152\ \mu\text{m}$$

Thus, a layer should be deposited with is 0.265 μm on one end and which tapers linearly over 10.0 cm to 0.152 μm at the other end.

7-11. The dispersion of glass for visible radiation is considerably greater than that for fused silica or quartz (see Figure 6-9).

7-12. $\mathbf{n}\lambda = d\,(\sin i + \sin r)$ (Equation 7-6)

$d = \mathbf{n}\lambda/(\sin i + \sin r) = 1 \times 400 \text{ nm}/(\sin 45 + \sin 5) = 400 \text{ nm}/(0.707 + 0.087) = 503.7 \text{ nm}$

$$\text{lines/mm} = \frac{1 \text{ line}}{503.7 \text{ nm}} \times 10^6 \frac{\text{nm}}{\text{mm}} = 1985$$

7-13. For first-order diffraction, Equation 7-13 takes the form

$$\lambda/\Delta\lambda = \mathbf{n}N = 1 \times 15.0 \text{ mm} \times 84.0 \text{ lines/mm} = 1260$$

In order to obtain the resolution in units of cm^{-1}, we differentiate the equation $\lambda = 1/\bar{\nu}$

$$\frac{d\lambda}{d\bar{\nu}} = \frac{1}{\bar{\nu}^2} \quad \text{or} \quad \frac{\Delta\lambda}{\Delta\bar{\nu}} = \frac{1}{\bar{\nu}^2}$$

Thus,

$$\Delta\lambda = \Delta\bar{\nu}/\bar{\nu}^2$$

Substituting for λ and $\Delta\lambda$ in the first equation gives

$$-\frac{1/\bar{\nu}}{\Delta\bar{\nu}/\bar{\nu}^2} = -\frac{\bar{\nu}}{\Delta\bar{\nu}} = 1260$$

$$\Delta\bar{\nu} = -\frac{\bar{\nu}}{1260} = -\frac{1200\ \text{cm}^{-1}}{1260} = -0.95\ \text{cm}^{-1}$$

Note that here the minus sign has no significance.

7-14. $\mathbf{n}\lambda = d(\sin i + \sin r)$ (Equation 7-6)

where d = 1 mm/84.0 lines = 0.0119 mm/line or 11.9 μm/line

For $\mathbf{n} = 1$

(a) $\lambda = 11.9[\sin 45 + \sin 25] = 13.4$ μm

for $\mathbf{n} = 2$, $\lambda = 6.7$ μm

Similarly,

(b) 8.4 μm and 4.2 μm

7-15.

	Source	Wavelength Selector	Container	Transducer	Signal Processor/Readout
(a)	W lamp	Grating	Glass window	Photomultiplier	Computer
(b)	Globar	None (Michelson interferometer)	KBr window	Pyroelectric	Computer
(c)	W lamp	Filter	Pyrex test tube	Photodiode or photovoltaic cell	Amplifier and meter
(d)	Nichrome wire	Filter	TlBr or TlI window	Thermocouple	Amplifier and meter
(e)	Flame	Grating	Flame	Photomultiplier	Computer
(f)	Argon lamp	Grating	KBr window	Photomultiplier	Computer
(g)	W lamp	Grating	Glass window	Photoconductivity	

7-16. $F = f/d$ (Equation 7-14)

F = 17.6 cm/5.4 cm = 3.26

7-17. $F = 16.8/37.6 = 0.45$

$$\frac{\text{Light gathering power of } F\,0.45 \text{ lens}}{\text{Light gathering power of } F\,3.26 \text{ lens}} = \frac{(3.26)^2}{(0.45)^2} = 52.5$$

7-18. (a) $R = \mathbf{n}N = 1 \times 1500\ \frac{\text{lines}}{\text{mm}} \times 10\ \frac{\text{mm}}{\text{cm}} \times 3.0\text{ cm} = 4.50 \times 10^4$

(b) $D^{-1} = \frac{d}{\mathbf{n}f} = \frac{(1\text{ mm}/1500\text{ lines}) \times 10^6\text{ nm/mm}}{1 \times 1.6\text{ m} \times 10^3\text{ mm/m}} = 0.42\text{ nm/mm}$

For $\mathbf{n} = 2$, $D^{-1} = 0.42/2 = 0.21$ nm/mm

7-19. (a) $D^{-1} = \frac{(1\text{ mm}/2500\text{ lines}) \times 10^6\text{ nm/mm}}{1 \times 0.78\text{ m} \times 10^3\text{ mm/m}} = 0.51\text{ nm/mm}$

(b) $R = \mathbf{n}N = 1 \times 2500\text{ lines/mm} \times 2.0\text{ cm} \times 10\text{ mm/cm} = 5.0 \times 10^4$

(c) $\lambda/\Delta\lambda = R = 5.0 \times 10^4 = 430/\Delta\lambda$

$\Delta\lambda = 430/5.0 \times 10^4 = 8.6 \times 10^{-3}$ nm

7-20. A silicon photodiode transducer is a *pn* junction device operated under reverse bias conditions. Photons striking the depletion layer create electrons and holes that can be attracted across the junction giving rise to a current proportional to the flux of photons.

7-21. (a) A spectroscope is an optical instrument for visual identification of spectra. It is a device with an entrance slit, a dispersing element, and an eyepiece that can be moved along the focal plane.

(b) A spectrograph is a device with an entrance slit, a dispersing element, and a large aperture ext that allows a wide range of wavelengths to strike a multichannel detector in the focal plane.

(c) A spectrophotometer is an instrument with a monochromator or polychromator and photodetector arranged to allow the ratio of two beams to be obtained.

7-22. $f = 2\,v_M/\lambda$ (Equation 7-23)

(a) $f = \dfrac{2 \times 2.75 \text{ cm/s}}{350 \text{ nm} \times 10^{-7} \text{ cm/nm}} = 1.6 \times 10^{5} \text{ Hz}$

(b) $f = 5.5/(575 \times 10^{-7}) = 9.6 \times 10^{4}$ Hz

(c) $f = 5.5/(5.5 \times 10^{-4}) = 1.0 \times 10^{4}$ Hz

(d) $f = 5.5/(25 \times 10^{-4}) = 2.2 \times 10^{3}$ Hz

7-23. $\bar{\nu}_2 - \bar{\nu}_1 = \dfrac{1}{\delta}$ (Equation 7-33)

(a) $\bar{\nu}_2 - \bar{\nu}_1 = 500.6 - 500.4 = 0.2 \text{ cm}^{-1}$ and $\delta = 1/0.2 = 5$ cm

length of drive = 5.0/2 = 2.5 cm

(b) $\bar{\nu}_2 - \bar{\nu}_1 = 4008.8 - 4002.1 = 6.7 \text{ cm}^{-1}$ $\delta = 1/6.7 = 0.149$ cm

length of drive = 0.149/2 = 0.075 cm

CHAPTER 8

8-1. The emission or absorption spectrum for calcium in a low-temperature flame is broad because the calcium is largely present as the molecule CaOH, which has many vibrational and rotational states and thus many excited energy levels. Hence, a broad molecular band spectrum is observed. Barium, in contrast is present largely as atoms and these absorb or emit at only a few discrete wavelengths.

8-2. Resonance fluorescence is a type of fluorescence in which the emitted radiation has the same wavelength as the radiation used to excite the fluorescence.

8-3. Fluorescence will occur at a longer wavelength (the Stokes shift) than the excitation wavelength when relaxation to a lower energy excited state takes place prior to emission.

8-4. Natural line widths in atomic spectroscopy are the widths of lines when only the uncertainty principle, and not Doppler or pressure broadening, contribute to the broadening. The width is then determined by the lifetime of the excited state.

8-5. In the presence of KCl, ionization of sodium is suppressed because of the high concentration of electrons from the ionization of potassium. In the absence of KCl, some of the sodium atoms are ionized, which leads to a lower emission intensity for atomic Na.

8-6. The energy needed to promote a ground state *s* electron to the first excited *p* state is so high for Cs that only a fraction of the Cs atoms are excited at the low temperature of a natural gas flame. At the higher temperature of a H_2/O_2 flame, a much larger fraction of the atoms is excited and a more intense Cs emission line results.

8-7. A continuous type of atomizer is an inductively coupled plasma. A noncontinuous type is a electrothermal furnace atomizer. The plasma produces an output that is essentially constant with time, whereas the furnace produces a transient signal that rises to a maxium and then decreases to zero.

8-8. (a) $\nu = \sqrt{8kT/\pi m}$

where Boltzmann's constant $k = 1.38 \times 10^{-23}$ kg m^2 s^{-2} K^{-1}

$$\text{Thus, } \nu = \sqrt{\frac{8 \times 1.38 \times 10^{-23}\ \text{kg m}^2\ \text{s}^{-2}\ \text{K}^{-1} \times 2100\ \text{K}}{\pi \times 6.941 \times 10^{-3}\ \text{kg Li/mol/(6.02} \times 10^{23}\ \text{particles Li/mol}}}$$

$\nu = 2.53 \times 10^3$ m/s

$$\frac{\Delta\lambda}{\lambda_0} = \frac{\nu}{c} \qquad \text{so } \Delta\lambda = \frac{\nu\lambda_0}{c} = \frac{2.53 \times 10^3\ \text{m s}^{-1} \times 670.776\ \text{nm} \times 10^{-9}\ \text{m/nm}}{3.00 \times 10^8\ \text{m s}^{-1}}$$

$\Delta\lambda = 5.66 \times 10^{-12}$ m or 5.7×10^{-3} nm (0.057 Å)

(b) Proceeding in the same way, at 3150 K, we find $\Delta\lambda = 6.9 \times 10^{-3}$ nm (0.069 Å)

8-9. The energies of the 3*p* states can be obtained from the emission wavelengths shown in Figure 8-1. For Na, we will use an average wavelength of 5893 Å and for Mg$^+$, 2800 Å. For Na, the energy of the excited state is

$$E_{3p,Na} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^8\ \text{m s}^{-1}}{5893\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 3.37 \times 10^{-19}\ \text{J}$$

For Mg$^+$

$$E_{3p,\text{Mg}^+} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^8\ \text{m s}^{-1}}{2800\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 7.10 \times 10^{-19}\ \text{J}$$

(a) Substituting into Equation 8-1, gives at 1800 K

$$\left(\frac{N_j}{N_0}\right)_{\text{Na}} = 3\exp\left(-\frac{3.37 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1800\ \text{K}}\right) = 3.85 \times 10^{-6}$$

$$\left(\frac{N_j}{N_0}\right)_{\text{Mg}^+} = 3\exp\left(-\frac{7.10 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1800\ \text{K}}\right) = 1.16 \times 10^{-12}$$

Proceeding in the same wave we obtain for Na and Mg^+

(b) $N_j/N_0 = 7.6 \times 10^{-4}$ and 8.0×10^{-8}

(c) $N_j/N_0 = 0.10$ and 2.5×10^{-3}

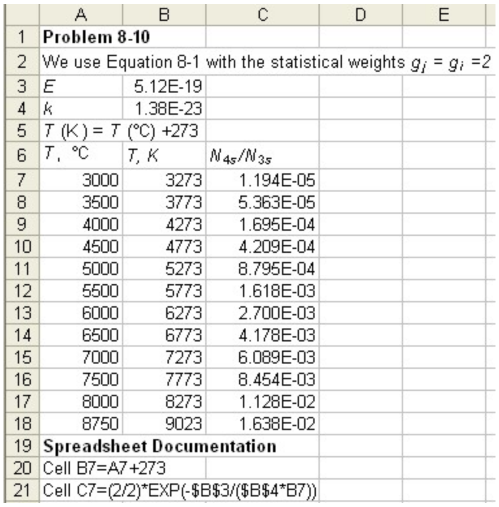
8-10. The energy difference between the 3*p* and 3*s* states was shown in Solution 8-9 to be $E = 3.37 \times 10^{-19}$ J. The energy difference between the 4*s* and 3*p* states *E´* can be calculated from the wavelength of the emission lines at 1139 nm

$$E' = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{1139\ \text{nm} \times 10^{-9}\ \text{m/nm}} = 1.75 \times 10^{-19}\ \text{J}$$

The energy difference between the 4*s* and 3*s* state is then

$$E'' = 3.37 \times 10^{-19} + 1.75 \times 10^{-19} = 5.12 \times 10^{-19}\ \text{J}$$

The ratio of N_{4s}/N_{3p} is calculated in the spreadsheet every 500 °C from 3000 to 8750°C



	A	B	C	D	E
1	**Problem 8-10**				
2	We use Equation 8-1 with the statistical weights $g_j = g_i = 2$				
3	*E*	5.12E-19			
4	*k*	1.38E-23			
5	*T* (K) = *T* (°C) +273				
6	*T* , °C	*T*, *K*	N_{4s}/N_{3s}		
7	3000	3273	1.194E-05		
8	3500	3773	5.363E-05		
9	4000	4273	1.695E-04		
10	4500	4773	4.209E-04		
11	5000	5273	8.795E-04		
12	5500	5773	1.618E-03		
13	6000	6273	2.700E-03		
14	6500	6773	4.178E-03		
15	7000	7273	6.089E-03		
16	7500	7773	8.454E-03		
17	8000	8273	1.128E-02		
18	8750	9023	1.638E-02		
19	**Spreadsheet Documentation**				
20	Cell B7=A7+273				
21	Cell C7=(2/2)*EXP(-$B$3/($B$4*B7))				

8-11. This behavior would result from ionization of U. At low concentrations, the fraction of U that is ionized is greater giving a nonlinear relationship between concentration and absorbance. The alkali metal salt suppresses the ionization of U.

CHAPTER 9

9-1. (a) A releasing agent is a cation that preferentially reacts with a species that would otherwise react with the analyte to cause a chemical interference.

(b) Protective agents prevent interference by forming stable and volatile products with the analyte.

(c) An ionization suppressor is more easily ionized than the analyte and provides a high concentration of electrons in the flame or plasma. These electrons suppress the ionization of the analyte.

(d) Atomization is the process by which a sample is vaporized and decomposed into atoms usually by heat.

(e) Pressure broadening refers to the broadening of atomic lines due to collisions with other species.

(f) A hollow-cathode lamp (Figure 9-11) has a tungsten anode and a cylindrical-shaped cathode containing the element of interest. The element is sputtered from the cathode into the gas phase. This process excites some of the gaseous atoms, which then emit characteristic radiation as they return to the ground state.

(g) Sputtering is the process in which gaseous cations bombard a cathode surface and eject atoms from the surface into the gas phase.

(h) Self-absorption refers to the absorption of emitted radiation by unexcited atoms in the gas phase of a hollow-cathode lamp, flame, or plasma.

(i) A spectral interference is encountered when the absorption or emission of a nonanalyte species overlaps a line being used for the determination of the analyte.

(j) A chemical interference is the result of any chemical process which decreases or increases the absorption or emission of the analyte.

(k) A radiation buffer is a substance added in excess to both sample and standards which swamps the effect of the sample matrix on the analyte emission or absorption.

(l) Doppler broadening arises because atoms moving toward or away from the monochromator give rise to absorption or emission lines at slightly different frequencies.

9-2. The absorbance of Cr decreases with increasing flame height because chromium oxides are formed to a greater and greater extent as the Cr rises through the flame. The Ag absorbance increases as the silver becomes more atomized as it rises through the flame. Silver oxides are not readily formed. Magnesium exhibits a maximum as a result of the two above effects opposing each other.

9-3. The electrothermal atomizer is a more efficient atomizer. It requires much less sample and keeps the atomic vapor in the beam for a longer time than does a flame.

9-4. The continuum radiation from the D_2 lamp is passed through the flame alternately with the hollow-cathode beam. Since the atomic lines are very narrow, the D_2 lamp is mostly absorbed by the background, wherase the hollow-cathode radiation is absorbed by the atoms. By comparing the radiant power of the two beams, the atomic absorption can be corrected for any backbround absorption.

9-5. Source modulation is employed to distinguish between atomic absorption (an ac signal) and flame emission (a dc signal).

9-6. The alcohol reduces the surface tension of the solution leading to smaller droplets. It may also add its heat of combustion to the flame leading to a slightly higher temperature compared to water which cools the flame. Alcohol also changes the viscosity of the solution which may increase the nebulizer uptake rate. All of these factors can lead to a great number of Ni atoms in the viewing region of the flame.

9-7. At hih currents, more unexcited atoms are formed in the sputtering process. These atoms generally have less kinetic energy than the excited atoms. The Doppler broadening of their absorption lines is thus less than the broadening of the emission lines of the faster moving excited atoms. Hence, only the center of the line is attenuated by self-absorption.

9-8. (1) Employ a higher temperature flame (oxyacetylene). (2) Use a solvent that contains ethanol or another organic substance. (3) Add a releasing agent, a protective agent, or an ionization suppressor.

9-9. The population of excited atoms from which emission arises is very sensitive to the flame temperature and other conditions. The population of ground state atoms, from which absorption and fluorescence originate, is not as sensitive to these conditions since it is a much larger fraction of the total population.

9-10. Nebulization: Aqueous solution containg $MgCl_2$ is converted to an aqueous aerosol.

Desolvation. The solvent is evaporated leaving solid particles.

Volatilization. The remaining water is evaporated and the particles are vaporized.

Atomization. Mg atoms are produced

Excitation of Mg to Mg*

Ionization of Mg to Mg^+

Reaction of Mg to form MgOH and MgO

9-11. $R = \dfrac{\lambda}{\Delta\lambda} = \mathbf{n}N = \dfrac{500\ \text{nm}}{0.002\ \text{nm}} = 2.5 \times 10^5 = 1 \times N$

N = no. of blazes = 2.5×10^5

Size of grating = $\dfrac{2.5 \times 10^5\ \text{grooves}}{2400\ \text{grooves/mm}} = 104\ \text{mm}$

9-12. The flame temperature at the four heights are estimated to be 1700, 1863, 1820, and 1725 °C or 1973, 2136, 2092, and 1998 K. To obtain E_j in Equation 8-1, we use Equation 6-19. Then,

$$E_j = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^8\ \text{m s}^{-1}}{766.5 \times 10^{-9}\ \text{m}} = 2.59 \times 10^{-19}\ \text{J}$$

Substituting into Equation 8-1 with the first temperature (1973 K) gives

$$\frac{N_j}{N_0} = 3\exp\left(-\frac{2.59 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1973\ \text{K}}\right) = 2.2 \times 10^{-4}$$

In the same way, we find

	Height	**T**	**$N_j/N_0 \times 10^4$**	**I_x/I_y**
(a)	2.0	1973	2.22	1.00
(b)	3.0	2136	4.58	2.06
(c)	4.0	2092	3.81	1.72
(d)	5.0	1998	2.50	1.13

9-13. (a) Sulfate ion forms complexes with Fe(III) that are not readily atomized. Thus, the concentration of iron atoms in the flame is less in the presence of sulfate ions.

(b) Sulfate interference could be overcome by (1) adding a releasing agent that forms more stable complexes with sulfate than does iron, (2) adding a protective agent, such as EDTA, that forms highly stable but volatile complexes with Fe(III), and (3) using a higher flame temperature (oxyacetylene or nitrous oxide-acetylene).

9-14. The energies of the 3*p* states can be obtained from the emission wavelengths shown in Figure 8-1. For Na, we will use an average wavelength of 5893 Å and for Mg^+, 2800 Å. For Na, the energy of the excited state is

$$E_{3p,Na} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{5893\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 3.37 \times 10^{-19}\ \text{J}$$

For Mg^+

$$E_{3p,\text{Mg}^+} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{2800\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 7.10 \times 10^{-19}\ \text{J}$$

(a) Substituting into Equation 8-1, gives at 2100 K

$$\left(\frac{N_j}{N_0}\right)_{\text{Na}} = 3\ \exp\left(-\frac{3.37 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 2100\text{K}}\right) = 2.67 \times 10^{-5}$$

$$\left(\frac{N_j}{N_0}\right)_{\text{Mg}^+} = 3\ \exp\left(-\frac{7.10 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 2100\ \text{K}}\right) = 6.87 \times 10^{-11}$$

Proceeding in the same wave we obtain for Na and Mg^+

(b) $N_j/N_0 = 6.6 \times 10^{-4}$ and 5.9×10^{-8}

(c) $N_j/N_0 = 0.051$ and 5.7×10^{-4}

9-15. The energy difference between the 3*p* and 3*s* states was shown in Solution 8-9 to be $E = 3.37 \times 10^{-19}$ J. The energy difference between the 4*s* and 3*p* states E' can be calculated from the wavelength of the emission lines at 1139 nm

$$E' = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{1139\ \text{nm} \times 10^{-9}\ \text{m/nm}} = 1.75 \times 10^{-19}\ \text{J}$$

The energy difference between the 4*s* and 3*s* state is then

$$E'' = 3.37 \times 10^{-19} + 1.75 \times 10^{-19} = 5.12 \times 10^{-19}\ \text{J}$$

(a) At 3000°C = 3273 K

$$\frac{N_{4s}}{N_{3s}} = \frac{2}{2}\exp\left(-\frac{5.12 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 3273}\right) = 1.2 \times 10^{-5}$$

(b) At 9000°C = 9273 K,

$$\frac{N_{4s}}{N_{3s}} = \frac{2}{2}\exp\left(-\frac{5.12 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 9273}\right) = 1.8 \times 10^{-2}$$

9-16. The absorbances of the three standards are estimated to be 0.32, 0.18, and 0.09. The unknown absorbance was approximately 0.09. From a least-squares treatment of the data, the equation for the line is y = 1.5143x + 0.02. From the analysis, the concentration of the unknown is 0.046 ± 0.009 µg Pb/mL.

9-17. During drying and ashing, volatile absorbing species may have been formed. In addition, particulate matter would appear as smoke during ashing, which would scatter source radiation and reduce its intensity.

9-18. This behavior results from the formation of nonvolatile complexes between calcium and phosphate. The suppressions levels off after a stoichiometric amount of phosphate has been added. The interference can be reduced by adding a releasing agent which ties up the phosphate when added in excess.

9-19. When an internal standard is used, the ratio of intensity of the analyte line to that of the internal standard is plotted as a function of the analyte concentration (see Figure 1-12). If the internal standard and the analyte species are influenced in the same way by variation in the aspiration rate and the flame temperature, and if the internal standard is present at approximately the same concentration in the standards and the unknown, the intensity ratio should be independent of these variables.

9-20. Setting up two equations in two unknowns

$0.599 = 0.450m + b$

$0.396 = 0.250m + b$

Subtracting the second equation from the first gives

$0.203 = 0.200\, m$

or the slope $m = 0.203/0.200 = 1.015$

Then using this value in the first equation gives

$b = 0.599 - 0.450 \times 1.015 = 0.14225$

The unknown Pb concentration is then $x = (0.444 - 0.14225)/1.015 = 0.297$ ppm Pb

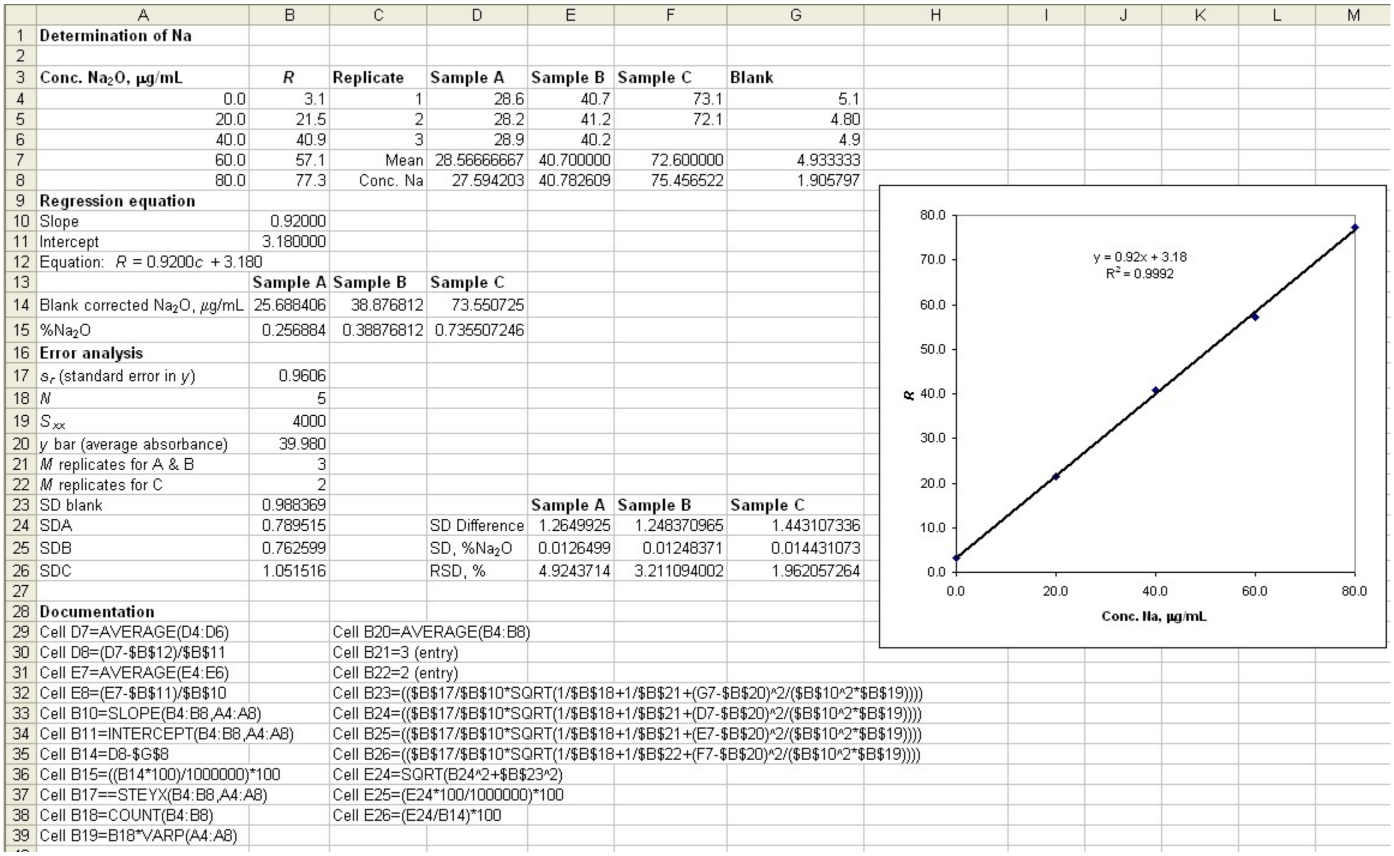
9-21. In the spreadsheet below we first calculate the equation for the line in cells B10 and B11.

$y = 0.920\, x + 3.180$

The mean readings for the samples and blanks are calculated in cells D7:G7, and the mean Na concentrations in cell D8:G8. These values are uncorrected for the blank. The blank corrections are made in Cells B14:D14. These are then converted to %Na_2O in cells B15:D15 by the following equation

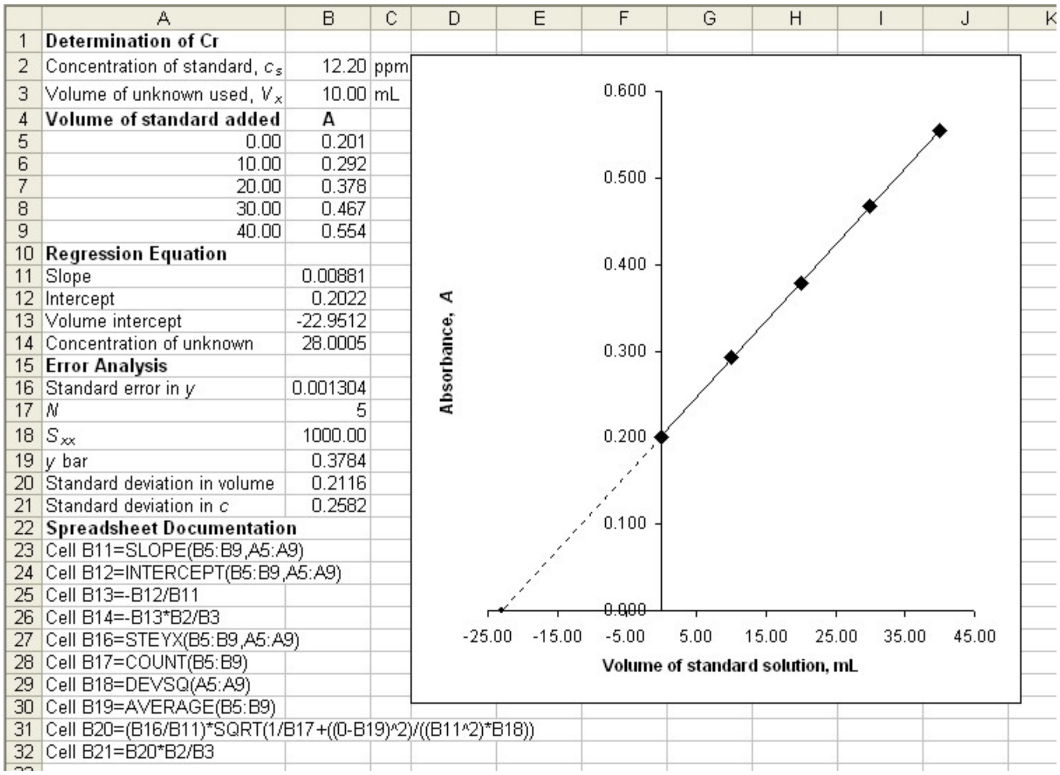
$$\%\text{Na}_2\text{O} = \frac{\text{conc. Na}_2\text{O in } \mu\text{g/mL} \times 100.0 \text{ mL}}{1.0 \text{ g} \times 10^6 \ \mu\text{g/g}} \times 100\%$$

The error analysis shows the calculations of the 4 standard deviations by the equations in Appendix 1, Section a1-D2. Since the final result is obtained by subtracting the blank reading, the standard deviations must be calculated from the difference in cells E24:G24 by $s_d = \sqrt{s_A^2 + s_{bl}^2}$ where s_A is the standard deviation for the concentration of A and s_{bl} is the standard deviation of the blank. These are then converted to absolute and relative standard deviations of %Na_2O in cells E25:G26.



	A	B	C	D	E	F	G
1	**Determination of Na**						
2							
3	**Conc. Na_2O, µg/mL**	*R*	**Replicate**	**Sample A**	**Sample B**	**Sample C**	**Blank**
4	0.0	3.1	1	28.6	40.7	73.1	5.1
5	20.0	21.5	2	28.2	41.2	72.1	4.80
6	40.0	40.9	3	28.9	40.2		4.9
7	60.0	57.1	Mean	28.56666667	40.700000	72.600000	4.933333
8	80.0	77.3	Conc. Na	27.594203	40.782609	75.456522	1.905797
9	**Regression equation**						
10	Slope	0.92000					
11	Intercept	3.180000					
12	Equation: $R = 0.9200c + 3.180$						
13		**Sample A**	**Sample B**	**Sample C**			
14	Blank corrected Na_2O, µg/mL	25.688406	38.876812	73.550725			
15	%Na_2O	0.256884	0.38876812	0.735507246			
16	**Error analysis**						
17	s_r (standard error in *y*)	0.9606					
18	*N*	5					
19	S_{xx}	4000					
20	*y* bar (average absorbance)	39.980					
21	*M* replicates for A & B	3					
22	*M* replicates for C	2					
23	SD blank	0.988369			**Sample A**	**Sample B**	**Sample C**
24	SDA	0.789515		SD Difference	1.2649925	1.248370965	1.443107336
25	SDB	0.762599		SD, %Na_2O	0.0126499	0.01248371	0.014431073
26	SDC	1.051516		RSD, %	4.9243714	3.211094002	1.962057264
27							
28	**Documentation**						
29	Cell D7=AVERAGE(D4:D6)		Cell B20=AVERAGE(B4:B8)				
30	Cell D8=(D7-$B$12)/$B$11		Cell B21=3 (entry)				
31	Cell E7=AVERAGE(E4:E6)		Cell B22=2 (entry)				
32	Cell E8=(E7-$B$11)/$B$10		Cell B23=(($B$17/$B$10*SQRT(1/$B$18+1/$B$21+(G7-$B$20)^2/($B$10^2*$B$19))))				
33	Cell B10=SLOPE(B4:B8,A4:A8)		Cell B24=(($B$17/$B$10*SQRT(1/$B$18+1/$B$21+(D7-$B$20)^2/($B$10^2*$B$19))))				
34	Cell B11=INTERCEPT(B4:B8,A4:A8)		Cell B25=(($B$17/$B$10*SQRT(1/$B$18+1/$B$21+(E7-$B$20)^2/($B$10^2*$B$19))))				
35	Cell B14=D8-$G$8		Cell B26=(($B$17/$B$10*SQRT(1/$B$18+1/$B$22+(F7-$B$20)^2/($B$10^2*$B$19))))				
36	Cell B15=((B14*100)/1000000)*100		Cell E24=SQRT(B24^2+$B$23^2)				
37	Cell B17==STEYX(B4:B8,A4:A8)		Cell E25=(E24*100/1000000)*100				
38	Cell B18=COUNT(B4:B8)		Cell E26=(E24/B14)*100				
39	Cell B19=B18*VARP(A4:A8)						

9-22.



	A	B	C
1	**Determination of Cr**		
2	Concentration of standard, c_s	12.20	ppm
3	Volume of unknown used, V_x	10.00	mL
4	**Volume of standard added**	**A**	
5	0.00	0.201	
6	10.00	0.292	
7	20.00	0.378	
8	30.00	0.467	
9	40.00	0.554	
10	**Regression Equation**		
11	Slope	0.00881	
12	Intercept	0.2022	
13	Volume intercept	-22.9512	
14	Concentration of unknown	28.0005	
15	**Error Analysis**		
16	Standard error in *y*	0.001304	
17	*N*	5	
18	S_{xx}	1000.00	
19	*y* bar	0.3784	
20	Standard deviation in volume	0.2116	
21	Standard deviation in *c*	0.2582	
22	**Spreadsheet Documentation**		
23	Cell B11=SLOPE(B5:B9,A5:A9)		
24	Cell B12=INTERCEPT(B5:B9,A5:A9)		
25	Cell B13=-B12/B11		
26	Cell B14=-B13*B2/B3		
27	Cell B16=STEYX(B5:B9,A5:A9)		
28	Cell B17=COUNT(B5:B9)		
29	Cell B18=DEVSQ(A5:A9)		
30	Cell B19=AVERAGE(B5:B9)		
31	Cell B20=(B16/B11)*SQRT(1/B17+((0-B19)^2)/((B11^2)*B18))		
32	Cell B21=B20*B2/B3		

CHAPTER 10

10-1. An internal standard is a substance that responds to uncontrollable variables in a similar way as the analyte. It is introduced into or is present in both standards and samples in a fixed amount. The ratio of the analyte signal to the internal standard signal then serves as the analytical reading.

10-2. Flame atomic absorption requires a separate lamp for each element, which is not convenient when multiple elements are to be determined.

10-3. The temperature of a high-voltage spark is so high (~40,000 K) that most atoms present become ionized. In a lower temperature arc (~4000 K) only the lighter elements are ionized to any significant exten. In a plasma, the high concentration of electrons suppresses extensive ionization of the analyte.

10-4. $D^{-1} = (2d \cos\beta)/\mathbf{n}f$ (Equation 7-16)

(a) $$D^{-1} = \frac{2 \times \dfrac{1\text{ mm}}{120\text{ grooves}} \times \dfrac{10^7\text{ Å}}{\text{mm}} \times \cos 63^{\circ}26'}{30 \times 0.85\text{ m} \times 10^3\text{ mm/m}} = 2.9\text{ Å/mm}$$

(b) $$D^{-1} = \frac{2 \times \dfrac{1\text{ mm}}{120\text{ grooves}} \times \dfrac{10^7\text{ Å}}{\text{mm}} \times \cos 63^{\circ}26'}{90 \times 0.85\text{ m} \times 10^3\text{ mm/m}} = 0.97\text{ Å/mm}$$

10-5. In the presence of air and with graphite electrodes, strong cyanogens (CN) bands render the wavelength region of 350 to 420 nm of little use. By excluding nitrogen with an inert gas, the intensities of these bands are greatly reduced making possible detection of several elements with lines in this region.

10-6. By Nebulization, by electrothermal vaporization, and by laser ablation.

10-7. The advantages of the ICP over the DCP are higher sensitivity for several elements and freedom from some interferences and maintainence problems. No electrodes need to be replaced in the ICP, whereas in the DCP, the graphite electrodes must be replaced every few hours. Advantages of the DCP include lower argon consumption and simpler and less expensive equipment.

10-8. Ionization interferences are less severe in the ICP than in flame emission because argon plasmas have a high concentration of electrons (from ionization of the argon) which represses ionization of the analyte.

10-9. Advantages of plasma sources include:

1. Lower interferences
2. Emission spectra for many elements can be obtained with one set of excitation conditions.
3. Spectra can be obtained for elements that tend to form refractory compounds.
4. Plasma sources usually have a linearity range that covers several decades in concentration.

10-10. The internal standard method is often used in preparing ICP calibration curves to compensate for random instrumental errors that arise from fluctuations in the output of the plasma source.

CHAPTER 11

11-1. Three types of mass spectrometers are used in atomic mass spectrometry: (1) quadrupole mass analyzers, (2) time-of-flight mass spectrometers, and (3) double-focusing mass spectrometers. The quadrupole mass spectrometer separates ions of different mass based on selective filtering of ions during their passage through four parallel rods that serve as electrodes. One pair of rods is attached to a positive dc voltage and the other to a negative dc voltage. In addition, variable radio frequency ac voltages that are 180° out of phase are applied to each pair of rods . The ions to be separated are then accelerated between the rods. Only ions having a limited range of m/z values are able to pass through the rods. All others are annihilated by stiking the rods. By varying the dc and ac voltages simultaneously, separation of ions of different masses occurs.

In the time-of-flight mass spectrometer, ions are accelerated periodically into a field-free drift tube. Their velocity in the tube is determined by their mass-to-charge ratio so that they arrive at a detector at different times depending on their mass

In a double-focusing mass spectrometer, ions are accelerated into a curved electrostatic field and then into an electromagnetic field. The lightest ions are deflected to a greater extent than are heavier ions, and thus are dispersed on a plane where they are detected.

11-2. The ICP torch in an ICPMS instrument causes atomization and ionization of the species which can then be separated by the mass spectrometer.

11-3. The ordinate (y-axis) in a mass spectrum is usually the relative abundances or intensities of the ions. The abscissa (x-axis) is usually the mass-to-charge ratio.

11-4. ICPMS has become an important tool for elemental analysis because of its high sensitivity, its high degree of selectivity, and its good precision for determining many elements in the periodic table.

11-5. The interface consists of a water-cooled metal cone with a tiny orifice in its center. The region behind the cone is maintained at a pressure of about 1 torr by pumping. The hot gases from the ICP impinge on the cone, and a fraction of these gases pass through the orifice where they are cooled by expansion. A fraction of the cooled gas then passes through a second orifice into a region that is maintained at the pressure of the mass spectrometer. Here, the positive analyte ions are separated from electrons and negative ions by a suitable field and are accelerated into the mass spectrometer itself.

11-6. Lasers are used for sampling in ICPMS by exposing a solid sample to an intense, pulsed laser beam, which rapidly vaporizes (ablates) the sample. The resulting vapor is carried into the ICP torch where atomization and ionization occurs. The resulting gaseous mixture then enters the mass spectrometer for ion analysis.

11-7. Isobaric interferences are encountered when the isotopes of two elements have the same mass. A second type of spectroscopic interference occurs from molecular species that have the same mass as that of an analyte ion. A third type of interference is from matrix species that combine with the analyte and reduce the analyte signal as a result.

11-8. An internal standard is often used in preparing calibration curves for ICPMS in order to compensate for random error from instrument drift and noise, torch instabilities, and some matrix effects. The internal standard chosen should be an element that is normally absent from the sample, but one that has an atomic mass and ionization potential close to that of the analyte.

11-9. In an isotope dilution experiment, a known weight of the analyte that has been prepared from a non-naturally occurring isotope of one of the elements in the analyte is added to the sample to be analyzed and mixed thoroughly until homogenization is assured. A known weight of the sample is then taken and a fraction of the highly purified analyte is isolated and weighed. The amount of enriched analyte is then determined by a mass spectrometric measurement. As shown in Section 32 D-1, these data then permit the calculation of the percentage of the analyte in the original sample.

11-10. In a glow-discharge mass spectrometric analysis, the sample is made part of the cathode of a glow-discharge atomizer, such as that shown in Figure 8-12. Here, the solid sample is bombarded by a stream of argon ions that have been accelerated through a potential of 5 to 15 kV. Analyte atoms are sputtered from the cathode surface and converted by collisions with electrons and argon ions into positive ions. These are then passes into the mass spectrometer for analysis.

11-11. In secondary-ion mass spectrometry, the sample is bombarded with a stream of 5- to 20-eV positive ions, such as Ar^+ or Cs^+. The ion beam is formed in an ion gun. The impact of the beam on the surface of the sample results in secondary ion formation containing analyte ions, which then pass into the mass spectrometer for analysis.

CHAPTER 12

12-1. $\lambda_0 = 12398/V$ Equation 12-2

$\lambda_0 = 12398/(90 \times 10^3) = 0.138$ Å

12-2. Equation 12-2 gives the minimum voltage needed to produce an emission line of wavelength λ.

Thus, solving for V_{min}

$$V_{\text{min}} = 12398/\lambda$$

(a) For U, Kβ_1 = 0.111 Å and Lβ_1 = 0.720 Å Table 12-1

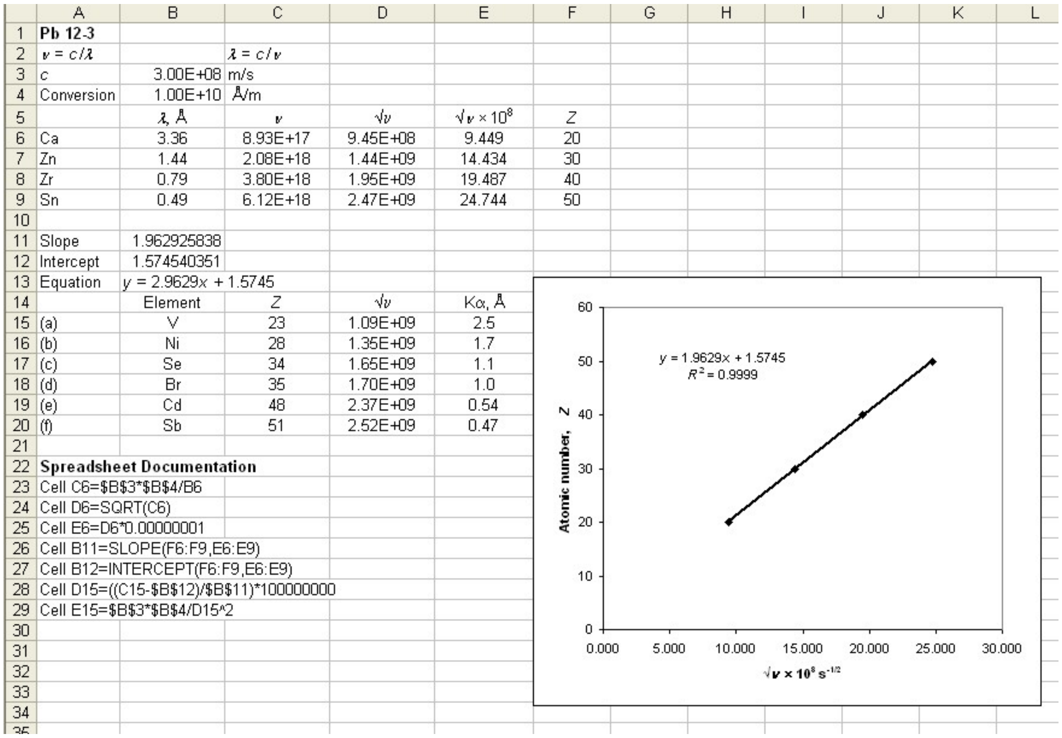
For U Kβ_1 $V_{\text{min}} = 12398/0.111 = 1.12 \times 10^5$ V or 112 kV

For U L β_1 $V_{\text{min}} = 12398/0.720 = 17.2$ kV

Similarly,

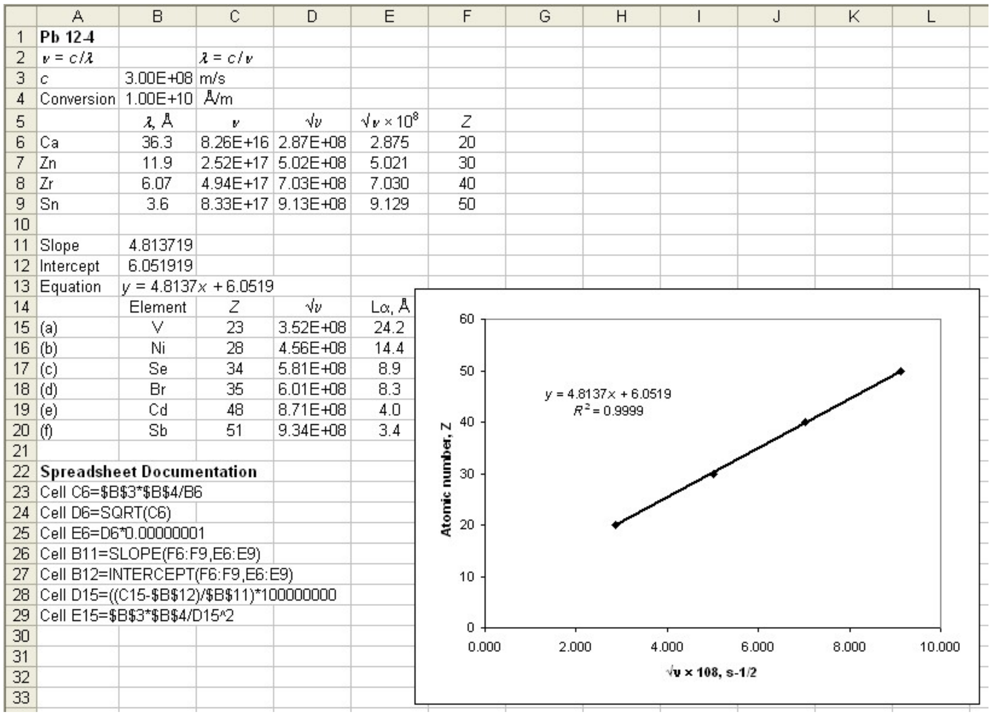
		λ for Kβ_1, Å	**V_{min} for Kβ_1, kV**	**λ for Lβ_1, Å**	**V_{min} for Lβ_1, kV**
(a)	For U	0.111	112	0.720	17.2
(b)	For K	3.454	3.59	No Lβ_1 line	----
(c)	For Rb	0.829	15.0	7.075	1.75
(d)	For W	0.184	67.4	1.282	9.67

12-3. Here we assume that a linear relationship exists between the atomic number Z for the elements in question and the square root of the frequency ν of their Kα lines (see Figure 12-3). This linear relationship can then be used to determine the frequencies and wavelengths of the other elements as shown in the spreadsheet.



	A	B	C	D	E	F
1	**Pb 12-3**					
2	$\nu = c/\lambda$		$\lambda = c/\nu$			
3	c	3.00E+08	m/s			
4	Conversion	1.00E+10	Å/m			
5		λ, Å	ν	$\sqrt{\nu}$	$\sqrt{\nu} \times 10^8$	Z
6	Ca	3.36	8.93E+17	9.45E+08	9.449	20
7	Zn	1.44	2.08E+18	1.44E+09	14.434	30
8	Zr	0.79	3.80E+18	1.95E+09	19.487	40
9	Sn	0.49	6.12E+18	2.47E+09	24.744	50
10						
11	Slope	1.962925838				
12	Intercept	1.574540351				
13	Equation	$y = 2.9629x + 1.5745$				
14		Element	Z	$\sqrt{\nu}$	Kα, Å	
15	(a)	V	23	1.09E+09	2.5	
16	(b)	Ni	28	1.35E+09	1.7	
17	(c)	Se	34	1.65E+09	1.1	
18	(d)	Br	35	1.70E+09	1.0	
19	(e)	Cd	48	2.37E+09	0.54	
20	(f)	Sb	51	2.52E+09	0.47	
21						
22	**Spreadsheet Documentation**					
23	Cell C6=$B$3*$B$4/B6					
24	Cell D6=SQRT(C6)					
25	Cell E6=D6*0.00000001					
26	Cell B11=SLOPE(F6:F9,E6:E9)					
27	Cell B12=INTERCEPT(F6:F9,E6:E9)					
28	Cell D15=((C15-$B$12)/$B$11)*100000000					
29	Cell E15=$B$3*$B$4/D15^2					

12-4. Proceeding as in Pb. 12-3, we construct the following spreadsheet:



	A	B	C	D	E	F
1	**Pb 12-4**					
2	$\nu = c/\lambda$		$\lambda = c/\nu$			
3	c	3.00E+08	m/s			
4	Conversion	1.00E+10	Å/m			
5		λ, Å	ν	$\sqrt{\nu}$	$\sqrt{\nu} \times 10^8$	Z
6	Ca	36.3	8.26E+16	2.87E+08	2.875	20
7	Zn	11.9	2.52E+17	5.02E+08	5.021	30
8	Zr	6.07	4.94E+17	7.03E+08	7.030	40
9	Sn	3.6	8.33E+17	9.13E+08	9.129	50
10						
11	Slope	4.813719				
12	Intercept	6.051919				
13	Equation	$y = 4.8137x + 6.0519$				
14		Element	Z	$\sqrt{\nu}$	Lα, Å	
15	(a)	V	23	3.52E+08	24.2	
16	(b)	Ni	28	4.56E+08	14.4	
17	(c)	Se	34	5.81E+08	8.9	
18	(d)	Br	35	6.01E+08	8.3	
19	(e)	Cd	48	8.71E+08	4.0	
20	(f)	Sb	51	9.34E+08	3.4	
21						
22	**Spreadsheet Documentation**					
23	Cell C6=$B$3*$B$4/B6					
24	Cell D6=SQRT(C6)					
25	Cell E6=D6*0.00000001					
26	Cell B11=SLOPE(F6:F9,E6:E9)					
27	Cell B12=INTERCEPT(F6:F9,E6:E9)					
28	Cell D15=((C15-$B$12)/$B$11)*100000000					
29	Cell E15=$B$3*$B$4/D15^2					

12-5. $\ln P_0/P = \mu_M \rho x$ Equation 12-3

$\ln (1/0.478) = 49.2\ \text{cm}^2/\text{g} \times 8.9\ \text{g/cm}^3 \times x$

$x = 0.738/(49.2 \times 8.9) = 1.69 \times 10^{-3}$ cm

12-6. $\mu_M = W_K\mu_K + W_I\mu_I + W_H\mu_H + W_O\mu_O$ Equation 12-4

(a)

$$\mu_M = \frac{11.00}{100.00}\left(\frac{39.1}{166.0} \times 16.7 + \frac{126.9}{166.0} \times 39.2\right) + \frac{89.00}{100.00}\left(0 + \frac{16.0}{18.0} \times 1.50\right)$$

$= 4.92\ \text{cm}^2/\text{g}$

12-7. $\ln P_0/P = (1/0.965) = \mu_M \rho x = 2.74 \times 2.70x$

$x = 0.0356/(2.74 \times 2.70) = 4.82 \times 10^{-3}$ cm

12-8. $\ln P_0/P = \ln(1/0.273) = \mu_M \rho x = \mu_M \times 0.794 \times 1.50$

$\mu_M = 1.298/(0.794 \times 1.50) = 1.09$

(a) $\mu_M = 1.09 = 2 \times 39.2 W_{I_2}$

$W_{I_2} = 0.0139$ or 1.39% I_2

(b) $\mu_M = 1.09 = 2 \times 39.2 W_{I_2} + W_{ETOH}\left(\frac{24}{46} \times 0.70 + 0.00 + \frac{16}{46} \times 1.50\right)$

$1.09 = 78.4 W_{I_2} + 0.887 W_{ETOH}$

$W_{I_2} + W_{ETOH} = 1$

Solving the two equations yields

$W_{I_2} = 2.62 \times 10^{-3}$ or 0.262%

12-9. $\mathbf{n}\lambda = 2d \sin \theta$ Equation 12-6

(a) For topaz, $d = 1.356$ Å

For Fe Kα at 1.76 Å $1 \times 1.76 = 2 \times 1.346 \sin \theta$

$\theta = 40.46°$ and $2\theta = 80.9°$

The following data were obtained in the same way.

	(a) Topaz **(*d* = 1.356 Å)**	**(b) LiF** **(*d* = 2.014 Å)**	**(c) NaCl** **(*d* = 2.820 Å)**
Fe (1.76 Å)	80.9	51.8	36.4
Se (0.992 Å)	42.9	28.5	20.3
Ag (0.497 Å)	21.1	14.2	10.1

12.10. Using the same method used in Solution 12-9, we find

(a) $2\theta = 135°$ (b) 99.5°

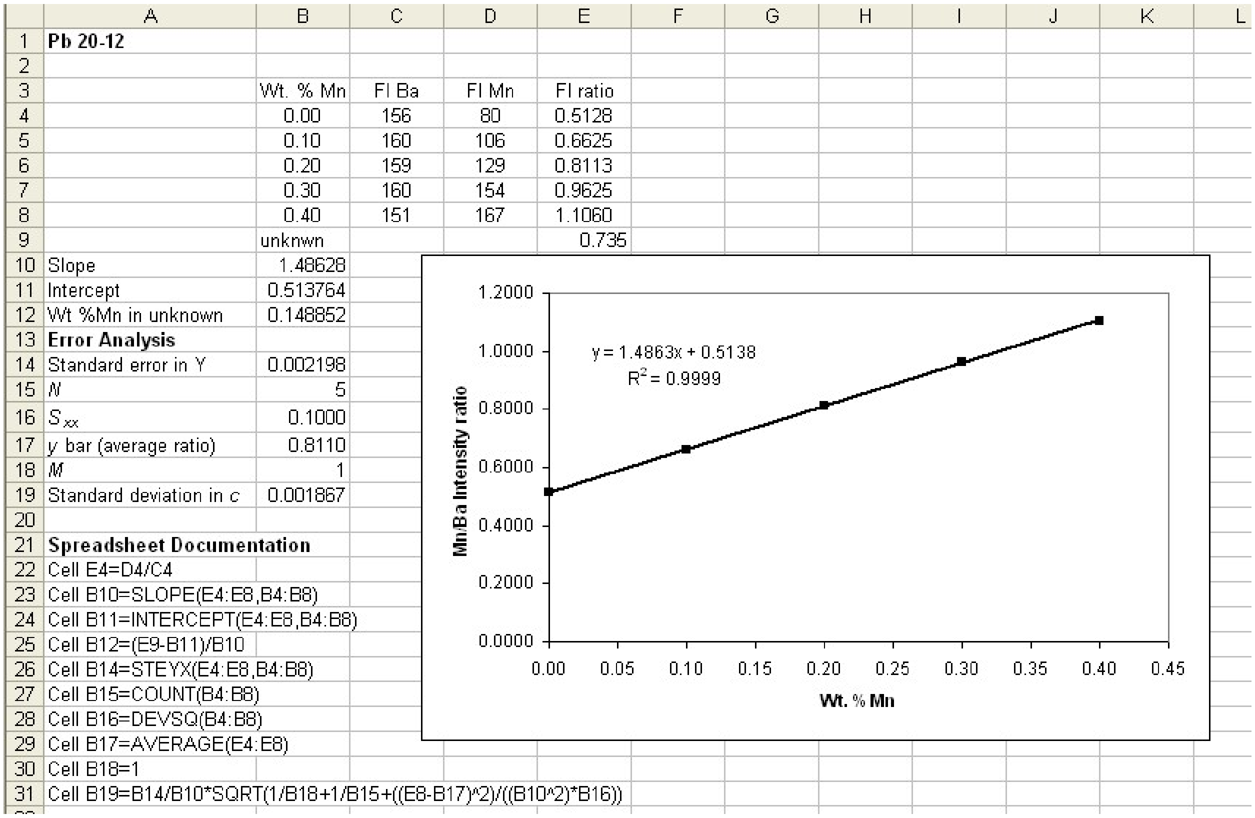
12-11. $V_{\text{min}} = 12398/\lambda$ Equation 12-2

(a) $V_{\text{min}} = 12398/3.064 = 4046$ V or 4.046 kV

Likewise for the others,

(b) 1.323 kV (c) 20.94 kV (d) 25.00 kV

12-12. Following the least-squares procedure outlined in Appendix 1, Section a1D, the spreadsheet shown was constructed. The unknown was found to contain 0.149 ± 0.002 %Mn



	A	B	C	D	E
1	**Pb 20-12**				
2					
3		Wt. % Mn	FI Ba	FI Mn	FI ratio
4		0.00	156	80	0.5128
5		0.10	160	106	0.6625
6		0.20	159	129	0.8113
7		0.30	160	154	0.9625
8		0.40	151	167	1.1060
9		unknwn			0.735
10	Slope	1.48628			
11	Intercept	0.513764			
12	Wt %Mn in unknown	0.148852			
13	**Error Analysis**				
14	Standard error in Y	0.002198			
15	*N*	5			
16	S_{xx}	0.1000			
17	*y* bar (average ratio)	0.8110			
18	*M*	1			
19	Standard deviation in *c*	0.001867			
20					
21	**Spreadsheet Documentation**				
22	Cell E4=D4/C4				
23	Cell B10=SLOPE(E4:E8,B4:B8)				
24	Cell B11=INTERCEPT(E4:E8,B4:B8)				
25	Cell B12=(E9-B11)/B10				
26	Cell B14=STEYX(E4:E8,B4:B8)				
27	Cell B15=COUNT(B4:B8)				
28	Cell B16=DEVSQ(B4:B8)				
29	Cell B17=AVERAGE(E4:E8)				
30	Cell B18=1				
31	Cell B19=B14/B10*SQRT(1/B18+1/B15+((E8-B17)^2)/((B10^2)*B16))				

CHAPTER 13 PROBLEM SOLUTIONS

13-1. (a) $\%T = 10^{-A} \times 100\% = 10^{-0.038} \times 100\% = 91.6\%$

Proceeding in the same way, we obtain

(b) 11.0% (c) 39.9% (d) 57.4% (e) 36.7% (f) 20.3%

13-2. (a) $A = -\log T = -\log (15.8/100) = 0.801$

Proceeding in the same way, we obtain

(b) 0.308 (c) 0.405 (d) 0.623 (e) 1.07 (f) 1.27

13-3 (a) $\%T = 10^{-0.038/2} \times 100\% = 95.7\%$

Similarly,

(b) 33.2% (c) 63.2% (d) 75.8% (e) 60.6% (f) 45.1%

13-4. (a) $A = -\log (2 \times 15.8/100) = 0.500$

Similarly,

(b) 0.007 (c) 0.103 (d) 0.322 (e) 0.770 (f) 0.968

13-5. $$c = \frac{6.23\ \cancel{\text{mg KMnO}_4}}{\text{L}} \times \frac{10^{-3}\ \cancel{\text{g KMnO}_4}}{\cancel{\text{mg KMnO}_4}} \times \frac{1\text{ mol KMnO}_4}{158.034\ \cancel{\text{g KMnO}_4}} = 3.942 \times 10^{-5}\text{ M}$$

$A = -\log T = -\log 0.195 = 0.710$

$\varepsilon = A/(bc) = 0.710/(1.00 \times 3.942 \times 10^{-5}) = 1.80 \times 10^{4}\text{ L mol}^{-1}\text{ cm}^{-1}$

13-6. $$c = \frac{5.24\ \cancel{\text{mg A}}}{100\ \cancel{\text{mL}}} \times \frac{10^{-3}\ \cancel{\text{g A}}}{\cancel{\text{mg A}}} \times \frac{1000\ \cancel{\text{mL}}}{\text{L}} \times \frac{1\text{ mol A}}{335\ \cancel{\text{g A}}} = 1.564 \times 10^{-4}\text{ M}$$

$A = -\log T = -\log 0.552 = 0.258$

$\varepsilon = A/(bc) = 0.258/(1.50 \times 1.564 \times 10^{-4}) = 1.10 \times 10^{3}\text{ L mol}^{-1}\text{ cm}^{-1}$

13-7. (a) $A = \varepsilon bc = 9.32 \times 10^3$ L mol^{-1} cm^{-1} × 1.00 cm × 3.79×10^{-5} M = 0.353

(b) $\%T = 10^{-A} \times 100\% = 10^{-0.353} \times 100\% = 44.4\%$

(c) $c = A/\varepsilon b = 0.353/(9.32 \times 10^3 \times 2.50) = 1.52 \times 10^{-5}$ M

13-8. (a) $A = \varepsilon bc = 7.00 \times 10^3$ L mol^{-1} cm^{-1} × 1.00 cm × 3.49×10^{-5} M = 0.244

(b) $A = \varepsilon bc = 7.00 \times 10^3$ L mol^{-1} cm^{-1} × 2.50 cm × $3.49 \times 10^{-5}/2$ M = 0.305

(c) For (a), $\%T = 10^{-0.244} \times 100\% = 57.0\%$; For (b) $\%T = 10^{-0.305} \times 100\% = 49.5\%$

(d) $A = -\log T = -\log(0.570/2) = 0.545$

13-9. $\varepsilon = 7.00 \times 10^3$ L mol^{-1} cm^{-1}

$$c_{\text{Fe}} = 7.9\frac{\cancel{\text{mg Fe}}}{\text{L}} \times 10^{-3}\frac{\text{g Fe}}{\cancel{\text{mg Fe}}} \times \frac{1\ \text{mol Fe}}{55.85\ \cancel{\text{g Fe}}} \times \frac{2.50\ \cancel{\text{mL}}}{50\ \cancel{\text{mL}}} = 7.073 \times 10^{-6}\ \text{M}$$

$A = \varepsilon bc = 7.00 \times 10^3$ L mol^{-1} cm^{-1} × 2.50 cm × 7.073×10^{-6} M = 0.124

13-10. $c_{\text{ZnL}} = 1.59 \times 10^{-4}$ M $A = 0.352$

(a) $\%T = 10^{-0.352} \times 100\% = 44.5\%$

(b) $A = 2.50 \times 0.352 = 0.880$ $\%T = 10^{-0.880} \times 100\% = 13.2\%$

(c) $\varepsilon = A/(bc) = 0.352/(1.00 \times 1.59 \times 10^{-4}) = 2.21 \times 10^3$ L mol^{-1} cm^{-1}

13-11. $[\text{H}_3\text{O}^+][\text{In}^-]/[\text{HIn}] = 8.00 \times 10^{-5}$ $[\text{H}_3\text{O}^+] = [\text{In}^-]$ $[\text{Hin}] = c_{\text{Hin}} - [\text{In}^-]$

(a) At $c_{\text{HIn}} = 3.00 \times 10^{-4}$

$$\frac{[\text{In}^-]^2}{(3.00 \times 10^{-4}) - [\text{In}^-]} = 8.00 \times 10^{-5}$$

$$[\text{In}^-]^2 + 8.00 \times 10^{-5}[\text{In}^-] - 2.40 \times 10^{-8} = 0$$

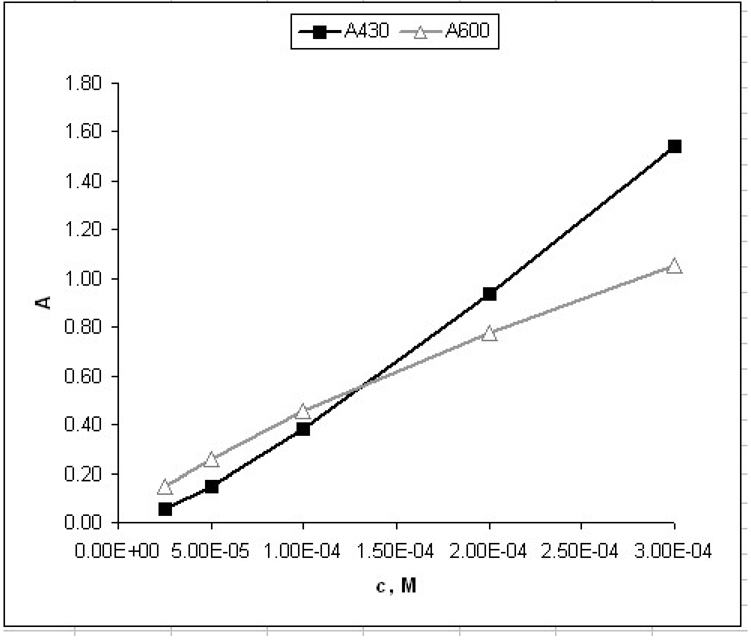
$[\text{In}^-] = 1.20 \times 10^{-4}$ M $[\text{HIn}] = 3.00 \times 10^{-4} - 1.20 \times 10^{-4} = 1.80 \times 10^{-4}$ M

$A_{430} = 1.20 \times 10^{-4} \times 0.775 \times 10^3 + 1.80 \times 10^{-4} \times 8.04 \times 10^3 = 1.54$

$$A_{600} = 1.20 \times 10^{-4} \times 6.96 \times 10^{3} + 1.80 \times 10^{-4} \times 1.23 \times 10^{3} = 1.06$$

The remaining calculations are done the same way with the following results.

c_{ind}, M	$[\text{In}^-]$	[HIn]	A_{430}	A_{600}
3.00×10^{-4}	1.20×10^{-4}	1.80×10^{-4}	1.54	1.06
2.00×10^{-4}	9.27×10^{-5}	1.07×10^{-4}	0.935	0.777
1.00×10^{-4}	5.80×10^{-5}	4.20×10^{-5}	0.383	0.455
0.500×10^{-4}	3.48×10^{-5}	1.52×10^{-5}	0.149	0.261
0.200×10^{-4}	2.00×10^{-5}	5.00×10^{-6}	0.056	0.145



13-12.
$$\frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2[\text{H}^+]^2} = 4.2 \times 10^{14}$$

$$[\text{H}^+] = 10^{-5.60} = 2.512 \times 10^{-6}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = c_{\text{K}_2\text{Cr}_2\text{O}_7} - \frac{[\text{CrO}_4^{2-}]}{2}$$

$$\frac{c_{\text{K}_2\text{Cr}_2\text{O}_7} - \frac{[\text{CrO}_4^{2-}]}{2}}{[\text{CrO}_4^{2-}]^2 \times (2.512 \times 10^{-6})^2} = 4.2 \times 10^{14}$$

$$c_{\mathrm{K_2Cr_2O_7}} - 0.500[\mathrm{CrO_4^{2-}}] = 2.65 \times 10^3[\mathrm{CrO_4^{2-}}]^2$$

$$[\mathrm{CrO_4^{2-}}]^2 + 1.887 \times 10^{-4}[\mathrm{CrO_4^{2-}}] - 3.774 \times 10^{-4}c_{\mathrm{K_2Cr_2O_7}} = 0$$

When $c_{\mathrm{K_2Cr_2O_7}} = 4.00 \times 10^{-4}$

$$[\mathrm{CrO_4^{2-}}]^2 + 1.887 \times 10^{-4}[\mathrm{CrO_4^{2-}}] - 1.510 \times 10^{-7} = 0$$

$$[\mathrm{CrO_4^{2-}}] = 3.055 \times 10^{-4}\ \mathrm{M}$$

$$[\mathrm{Cr_2O_7^{2-}}] = 4.00 \times 10^{-4} - 3.055 \times 10^{-4}/2 = 2.473 \times 10^{-4}\ \mathrm{M}$$

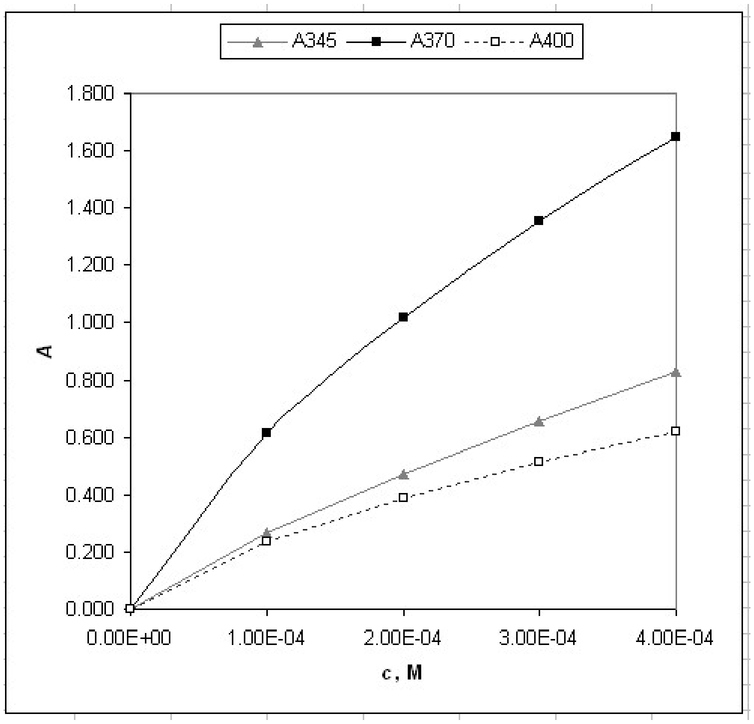
$$A_{345} = 1.84 \times 10^3 \times 3.055 \times 10^{-4} + 10.7 \times 10^2 \times 2.473 \times 10^{-4} = 0.827$$

$$A_{370} = 4.81 \times 10^3 \times 3.055 \times 10^{-4} + 7.28 \times 10^2 \times 2.473 \times 10^{-4} = 1.649$$

$$A_{400} = 1.88 \times 10^3 \times 3.055 \times 10^{-4} + 1.89 \times 10^2 \times 2.473 \times 10^{-4} = 0.621$$

The following results were obtained in the same way

$c_{\mathrm{K_2Cr_2O_7}}$	$[\mathrm{CrO_4^{2-}}]$	$[\mathrm{Cr_2O_7^{2-}}]$	A_{345}	A_{370}	A_{400}
4.00×10^{-4}	3.055×10^{-4}	2.473×10^{-4}	0.827	1.649	0.621
3.00×10^{-4}	2.551×10^{-4}	1.725×10^{-4}	0.654	1.353	0.512
2.00×10^{-4}	1.961×10^{-4}	1.019×10^{-4}	0.470	1.018	0.388
1.00×10^{-4}	1.216×10^{-4}	3.920×10^{-5}	0.266	0.613	0.236



13-13. (a) *Hydrogen* and *deuterium lamps* differ only in the gases that are used in the discharge. Deuterium lamps generally produce higher intensity radiation.

(b) *Filters* provide low resolution wavelength selection often suitable for quantitative work, but not for qualitative analysis or structural studies. *Monochromators* produce high resolution (narrow bandwidths) for both qualitative and quantitative work.

(c) A *phototube* is a vacuum tube equipped with a photoemissive cathode and a collection anode. The photo electrons emitted as a result of photon bombardment are attracted to the positively charged anode to produce a small photocurrent proportional to the photon flux. A *photovoltaic cell* consists of a photosensitive semiconductor sandwiched between two electrodes. An incident beam of photons causes production of electron-hole pairs which when separated produce a voltage related to the photon flux.

Phototubes are generally more sensitive and have a greater wavelength range. Photocells are in general simpler, cheaper and more rugged. Photocells do not require external power supplies.

(d) A *photodiode* consists of a photo-sensitive *pn*-junction diode that is normally reverse-biased. An incident beam of photons causes a photocurrent proportional to the photon flux. A *photomultiplier tube* is a vacuum tube consisting of a photoemissive cathode, a series of intermediate electrodes called dynodes, and a collection anode. Each photoelectron emitted by the photocathode is accelerated in the electric field to the first positively charged dynode where it can produce several secondary electrons. These are, in turn, attracted to the next positively charge dynode to give rise to multiple electrons. The result is a cascade multiplication of 10^6 or more electrons per emitted photoelectron. Photomultipliers are more sensitive than photodiodes, but require a high voltage power supply compared to the low voltage supplies required by photodiodes. Photomultipliers are larger and require extensive shielding. Photodiodes are better suited for small, portable instruments because of their size and ruggedness.

(e) Both types of spectrophotometers split the beam into two portions. One travels through the reference cell and one through the sample cell. With the *double-beam-in-space* arrangement, both beams travel at the same time through the two cells. They then strike two separate photodetectors where the signals are processed to produce the absorbance. With the *double-beam-in-time* arrangement, the two beams travel at different times through the cells. They are later recombined to strike one photodetector at different times. The double-beam-in-time arrangement is a little more complicated mechanically and electronically, but uses one photodetector. The double-beam-in-space arrangement is simpler, but requires two matched photodetectors.

(f) *Spectrophotometers* have monochromators or spectrographs for wavelength selection. Photometers generally have filters are use an LED source for wavelength selection. The spectrophotometer can be used for wavelength scanning or for multiple wavelength selection. The photometer is restricted to one or a few wavelengths.

(g) A *single-beam* spectrophotometer employs one beam of radiation that irradiates one cell. To obtain the absorbance, the reference cell is replaced with the sample cell containing the analyte. With a *double-beam instrument*, the reference cell and sample cell are irradiated simultaneously or nearly so. Double-beam instruments have the advantages that fluctuations in source intensity are cancelled as is drift in electronic components. The double-beam instrument is readily adapted for spectral scanning. Single-beam instruments have the advantages of simplicity and lower cost. Computerized versions are useful for spectral scanning.

(h) *Multichannel spectrophotometers* detect the entire spectral range essentially simultaneously and can produce an entire spectrum in one second or less. They do not use mechanical means to obtain a spectrum. *Conventional spectrophotometers* use mechanical methods (rotation of a grating) to scan the spectrum. An entire spectrum requires several minutes to procure. Multichannel instruments have the advantage of speed and long-term reliability. Conventional spectrophotometers can be of higher resolution and have lower stray light characteristics.

13-14. (a) $\%T = P/P_0 \times 100\% = I/I_0 \times 100\% = 41.6\ \mu\text{A}/63.8\ \mu\text{A} = 65.2\%$

(b) $A = -\log T = 2 - \log \%T = 2 - \log(65.2) = 0.186$

(c) $A = 0.186/3 = 0.062$; $T = 10^{-A} = 10^{-0.062} = 0.867$

(d) $A = 2 \times 0.186 = 0.372$ $T = 10^{-0.372} = 0.425$

13-15. (a) $\%T = P/P_0 \times 100\% = I/I_0 \times 100\% = 256 \text{ mV}/498 \text{ mV} \times 100\% = 51.4\%$
$A = 2 - \log \%T = 2 - \log(51.4) = 0.289$

(b) $A = 0.289/2 = 0.144$ $T = 10^{-A} = 10^{-0.144} = 0.717$

(c) $A = 2 \times 0.289 = 0.578$ $T = 10^{-0.578} = 0.264$

13-16. In a deuterium lamp, the lamp energy from the power source produces an excited deuterium molecule that dissociates into two atoms in the ground state and a photon of radiation. As the excited deuterium relaxes, its quantized energy is distributed between the energy of the photon and the energies of the two atoms. The latter can vary from nearly zero to the energy of the excited molecule. Therefore, the energy of the radiation, which is the difference between the quantized energy of the excited molecule and the kinetic energies of the atoms, can also vary continuously over the same range. Consequently, the emission spectrum is a spectral continuum.

13-17. Photons from the infrared region of the spectrum do not have enough energy to cause photoemission from the cathode of a photomultiplier tube.

13-18. *Tungsten/halogen lamps* often include a small amount of iodine in the evacuated quartz envelope that contains the tungsten filament. The iodine prolongs the life of the lamp and permits it to operate at a higher temperature. The iodine combines with gaseous tungsten that sublimes from the filament and causes the metal to be redeposited, thus adding to the life of the lamp.

13-19. Shot noise has its origin in the random emission of photons from a source and the random emission of electrons from the electrodes in phototubes and photomultiplier tubes. When shot noise is the most important source of noise, the relative concentration uncertainty, s_c/c goes through a minimum as the concentration increases.

13-20. (a) The *dark current* is the small current that exists in a radiation transducer in the absence of radiation. It has its origin in the thermal emission of electrons at the photocathode, in ohmic leakage, and in radioactivity.

(b) A *transducer* is a device that converts a physical or chemical quantity into an electrical signal.

(c) *Scattered radiation* is unwanted radiation that reaches the exit slit of a monochromator as a result of reflections and scattering. Its wavelength is usually different from that of the radiation reaching the slit directly from the dispersive device.

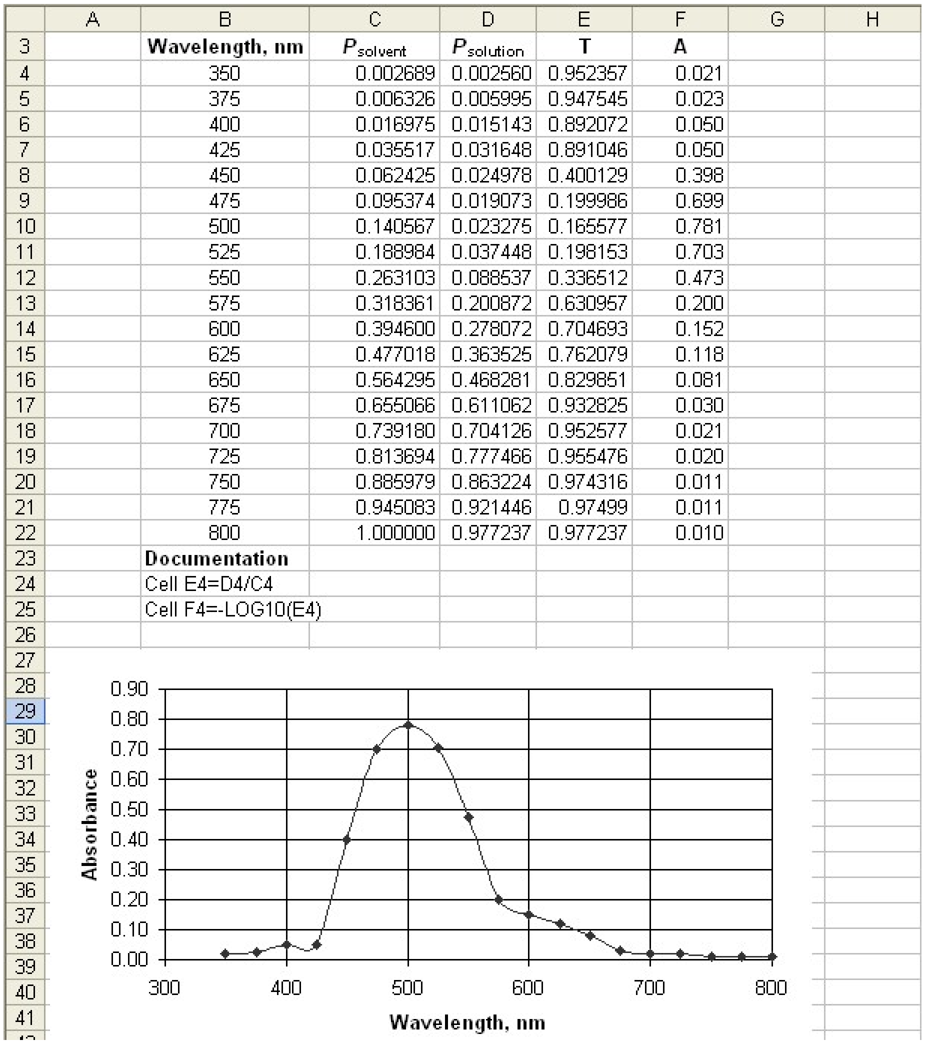
(d) *Source flicker noise* is caused by variations in experimental variables that control the source intensity, such as power supply voltages and temperature. It can also be caused by mechanical variations such as vibrations.

(e) *Cell positioning uncertainty* is caused by our inability to position the cell in the same exact place each time. A random variation is introduced because the incident beam is imaged onto slightly different portions of the cell walls each time causing differences in the reflection, transmission and scattering characteristics of the cell.

(f) A *beam splitter* is a device that causes an incident beam to divide into two beams at its output. It can be made from mirrors, rotating choppers, or optical materials that cause a beam to be split into two beams.

13-21. A monochromator is a dispersive instrument with an entrance slit and an exit slit. It is designed to isolate a single band of wavelengths. A spectrograph has an entrance slit, but no exit slit. It is designed to image an entire spectrum at its focal plane. Spectrographs are used with multichannel detectors like CCD arrays and diode arrays. A spectrophotometer is an instrument with a monochromator or spectrograph designed to obtain the ratio of two beam intensities to calculate absorbances and transmittances in absorption spectroscopy.

13-22.



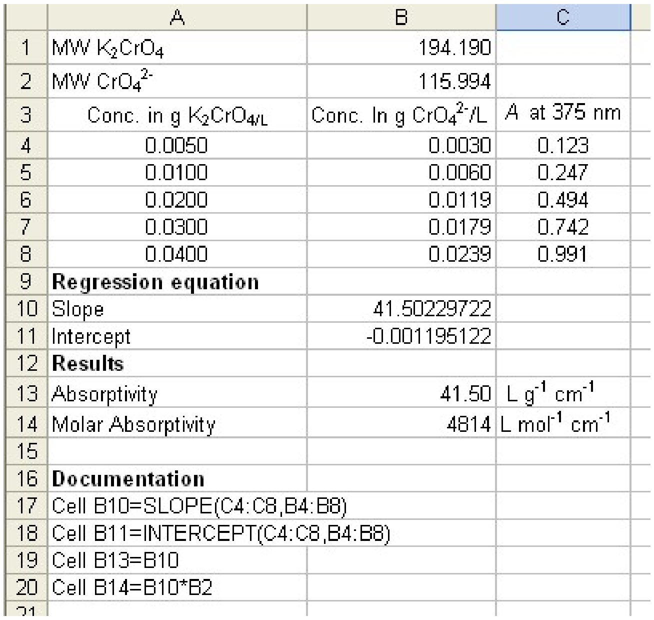
	A	B	C	D	E	F	G	H
3		**Wavelength, nm**	$P_{solvent}$	$P_{solution}$	**T**	**A**		
4		350	0.002689	0.002560	0.952357	0.021		
5		375	0.006326	0.005995	0.947545	0.023		
6		400	0.016975	0.015143	0.892072	0.050		
7		425	0.035517	0.031648	0.891046	0.050		
8		450	0.062425	0.024978	0.400129	0.398		
9		475	0.095374	0.019073	0.199986	0.699		
10		500	0.140567	0.023275	0.165577	0.781		
11		525	0.188984	0.037448	0.198153	0.703		
12		550	0.263103	0.088537	0.336512	0.473		
13		575	0.318361	0.200872	0.630957	0.200		
14		600	0.394600	0.278072	0.704693	0.152		
15		625	0.477018	0.363525	0.762079	0.118		
16		650	0.564295	0.468281	0.829851	0.081		
17		675	0.655066	0.611062	0.932825	0.030		
18		700	0.739180	0.704126	0.952577	0.021		
19		725	0.813694	0.777466	0.955476	0.020		
20		750	0.885979	0.863224	0.974316	0.011		
21		775	0.945083	0.921446	0.97499	0.011		
22		800	1.000000	0.977237	0.977237	0.010		
23		**Documentation**						
24		Cell E4=D4/C4						
25		Cell F4=-LOG10(E4)						

13-23. Quantitative analysis can usually tolerate rather wide slits because measurements are often made on an absorption maximum where there is little change in absorptivity over the bandwidth. Wide slit widths are desirable because the radiant powers will be larger and the signal-to-noise ratio will be higher. On the other hand, qualitative analysis requires narrow slit widths so that fine structure in the spectrum will be resolved.

13-24. Note: To find the absorptivity of the chromate ion, we must convert the concentration of K_2CrO_4 in g/L to the concentration of CrO_4^{2-} in g/L. Hence, we write for *x* g/L K_2CrO_4,

$$c_{\mathrm{CrO_4^{2-}}}\text{, g/L} = \frac{x\ \cancel{\mathrm{g\ K_2CrO_4}}}{\mathrm{L}} \times \frac{1\ \cancel{\mathrm{mol\ K_2CrO_4}}}{194.190\ \cancel{\mathrm{g\ K_2CrO_4}}} \times \frac{115.994\ \mathrm{g\ CrO_4^{2-}}}{\cancel{\mathrm{mol\ CrO_4^{2-}}}} \times \frac{1\ \cancel{\mathrm{mol\ CrO_4^{2-}}}}{\cancel{\mathrm{mol\ K_2CrO_4}}} = \frac{x \times 115.994}{194.190}$$

A plot of absorbance vs. the concentration of CrO_4^{2-} in g/L will give the absorptivity in L g^{-1} cm^{-1} as the slope. To convert this to the molar absorptivity, we multiply by the molecular mass of CrO_4^{2-}, 115.995 g mol^{-1}.



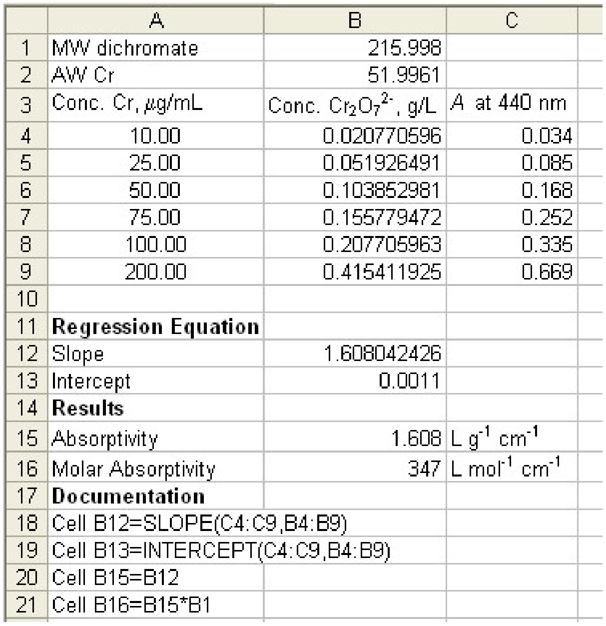
	A	B	C
1	MW K_2CrO_4	194.190	
2	MW CrO_4^{2-}	115.994	
3	Conc. in g $K_2CrO_{4/L}$	Conc. In g CrO_4^{2-}/L	*A* at 375 nm
4	0.0050	0.0030	0.123
5	0.0100	0.0060	0.247
6	0.0200	0.0119	0.494
7	0.0300	0.0179	0.742
8	0.0400	0.0239	0.991
9	**Regression equation**		
10	Slope	41.50229722	
11	Intercept	-0.001195122	
12	**Results**		
13	Absorptivity	41.50	L g^{-1} cm^{-1}
14	Molar Absorptivity	4814	L mol^{-1} cm^{-1}
15			
16	**Documentation**		
17	Cell B10=SLOPE(C4:C8,B4:B8)		
18	Cell B11=INTERCEPT(C4:C8,B4:B8)		
19	Cell B13=B10		
20	Cell B14=B10*B2		

13-25. To obtain the absorptivity of dichromate, we must first convert the concentration of Cr in μg/mL to the concentration of $Cr_2O_7^{2-}$ in g/L. We write for x μg Cr/mL,

$$c_{Cr_2O_7^{2-}},\ \text{g/L} = \frac{x\ \cancel{\mu\text{g Cr}}}{\cancel{\text{mL}}} \times \frac{10^{-6}\ \text{g}\ \cancel{\text{Cr}}}{\cancel{\mu\text{g Cr}}} \times \frac{10^{3}\ \cancel{\text{mL}}}{\text{L}} \times \frac{215.988\ \text{g}\ Cr_2O_7^{2-}}{\cancel{\text{mol}\ Cr_2O_7^{2-}}} \times \frac{\cancel{\text{mol Cr}}}{51.9961\ \cancel{\text{g Cr}}} \times \frac{1\ \cancel{\text{mol}\ Cr_2O_7^{2-}}}{2\ \cancel{\text{mol Cr}}}$$

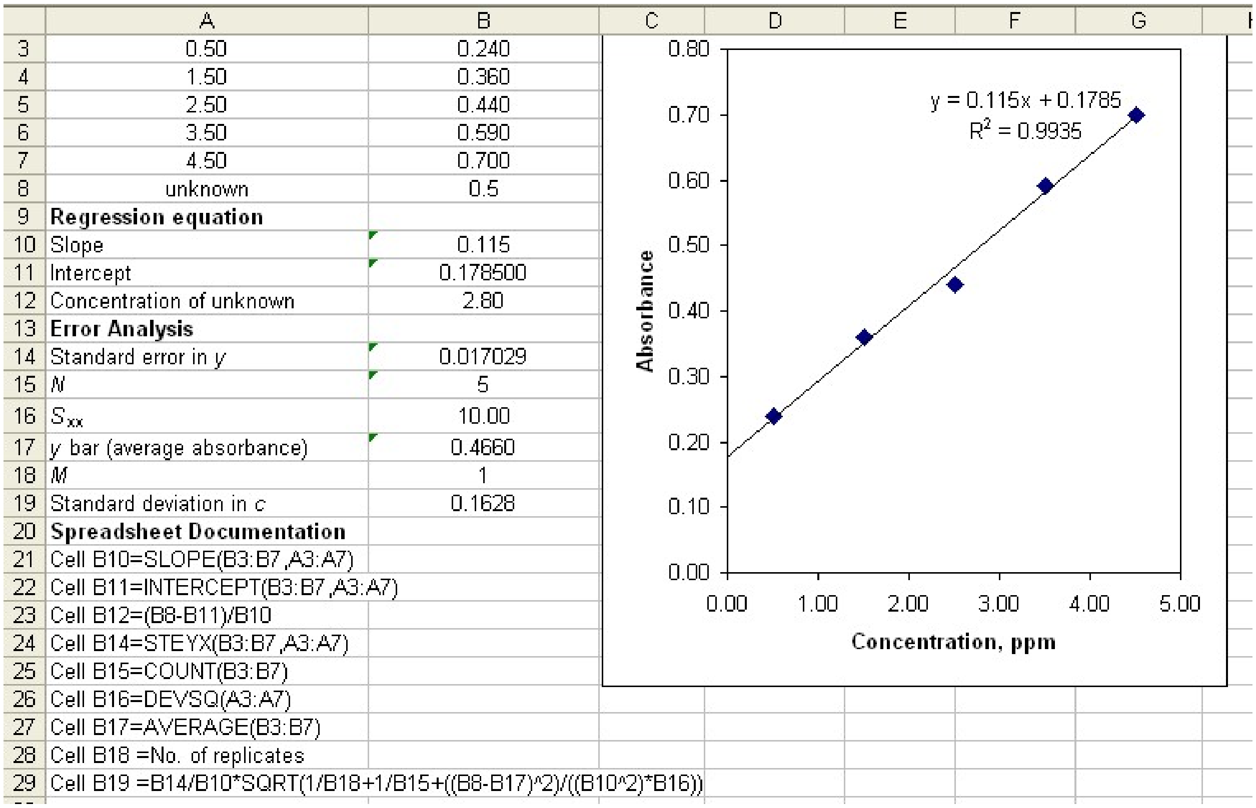
$$= \frac{0.215998\,x}{2\,\times\,51.9961}$$

A plot of absorbance vs. the concentration of $Cr_2O_7^{2-}$ in g/L will give the absorptivity in L g^{-1} cm^{-1} as the slope. To convert this to the molar absorptivity, we multiply by the molecular mass of $Cr_2O_7^{2-}$, 215.988 g mol^{-1}.



	A	B	C
1	MW dichromate	215.998	
2	AW Cr	51.9961	
3	Conc. Cr, μg/mL	Conc. $Cr_2O_7^{2-}$, g/L	A at 440 nm
4	10.00	0.020770596	0.034
5	25.00	0.051926491	0.085
6	50.00	0.103852981	0.168
7	75.00	0.155779472	0.252
8	100.00	0.207705963	0.335
9	200.00	0.415411925	0.669
10			
11	**Regression Equation**		
12	Slope	1.608042426	
13	Intercept	0.0011	
14	**Results**		
15	Absorptivity	1.608	L g^{-1} cm^{-1}
16	Molar Absorptivity	347	L mol^{-1} cm^{-1}
17	**Documentation**		
18	Cell B12=SLOPE(C4:C9,B4:B9)		
19	Cell B13=INTERCEPT(C4:C9,B4:B9)		
20	Cell B15=B12		
21	Cell B16=B15*B1		

13-26.



	A	B
3	0.50	0.240
4	1.50	0.360
5	2.50	0.440
6	3.50	0.590
7	4.50	0.700
8	unknown	0.5
9	**Regression equation**	
10	Slope	0.115
11	Intercept	0.178500
12	Concentration of unknown	2.80
13	**Error Analysis**	
14	Standard error in *y*	0.017029
15	*N*	5
16	S_{xx}	10.00
17	*y* bar (average absorbance)	0.4660
18	*M*	1
19	Standard deviation in *c*	0.1628
20	**Spreadsheet Documentation**	
21	Cell B10=SLOPE(B3:B7,A3:A7)	
22	Cell B11=INTERCEPT(B3:B7,A3:A7)	
23	Cell B12=(B8-B11)/B10	
24	Cell B14=STEYX(B3:B7,A3:A7)	
25	Cell B15=COUNT(B3:B7)	
26	Cell B16=DEVSQ(A3:A7)	
27	Cell B17=AVERAGE(B3:B7)	
28	Cell B18 =No. of replicates	
29	Cell B19 =B14/B10*SQRT(1/B18+1/B15+((B8-B17)^2)/((B10^2)*B16))	

CHAPTER 14

14-1. Letting the subscript x stand for the unknown solution, $x + s$ stand for the unknown plus standard, and V_t the total volume of solution, we can write

$$A_x = \varepsilon b c_x V_x / V_t$$

$$A_{x+s} = \varepsilon b(c_x V_x + c_s V_s) / V_t$$

Dividing the first equation by the second and rearranging gives

$$c_x = \frac{A_x c_s V_s}{(A_{x+s} - A_x)V_x} = \frac{0.656 \times 25.7 \times 10.0}{(0.976 - 0.656) \times 25.0} = 21.1 \text{ ppm}$$

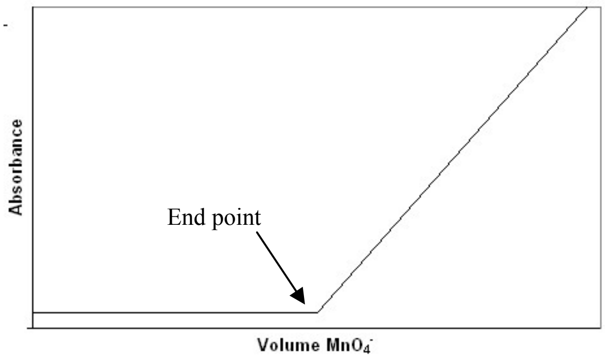
14-2. Using the equation developed in problem 14-1, we can write

$$c_{\text{Cu}^{2+}} = \frac{0.723 \times 2.75 \times 1.00}{(0.917 - 0.723) \times 5.00} = 2.0497 \text{ ppm}$$

For dilute solutions, 1 ppm = 1 mg/L, so

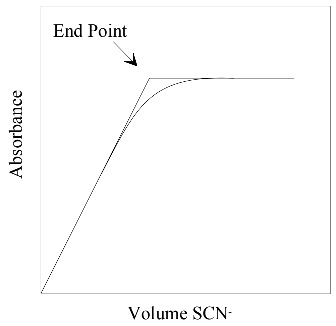
$$\text{Percent Cu} = 200 \text{ mL} \times 2.0497 \frac{\cancel{\text{mg}}}{\cancel{\text{L}}} \times 10^{-3} \frac{\text{g}}{\cancel{\text{mg}}} \times 10^{-3} \frac{\cancel{\text{L}}}{\text{mL}} \times \frac{100\%}{0.599 \text{ g}} = 0.0684\%$$

14-3.



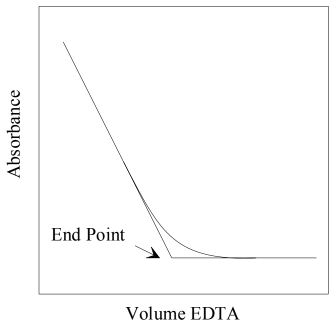
There should be little or no absorbance until the end point after which the absorbance should increase approximately linearly. A green filter should be used because the red permanganate solution absorbs green light.

14-4.



A green filter is used because the red $Fe(SCN)^{2+}$ absorbs green light.

14-5.



The absorbance should decrease approximately linearly with titrant volume until the end point. After the end point the absorbance becomes independent of titrant volume.

14-6. The data must be corrected for dilution so

$$A_{\mathrm{corr}} = A_{500} \times \frac{10.00\ \mathrm{mL} + V}{10.00\ \mathrm{mL}}$$

For 1.00 mL

$$A_{\mathrm{corr}} = 0.147 \times \frac{10.00\ \mathrm{mL} + 1.00\ \mathrm{mL}}{10.00\ \mathrm{mL}} = 0.162$$

A_{corr} is calculated for each volume in the same way and the following results are obtained.

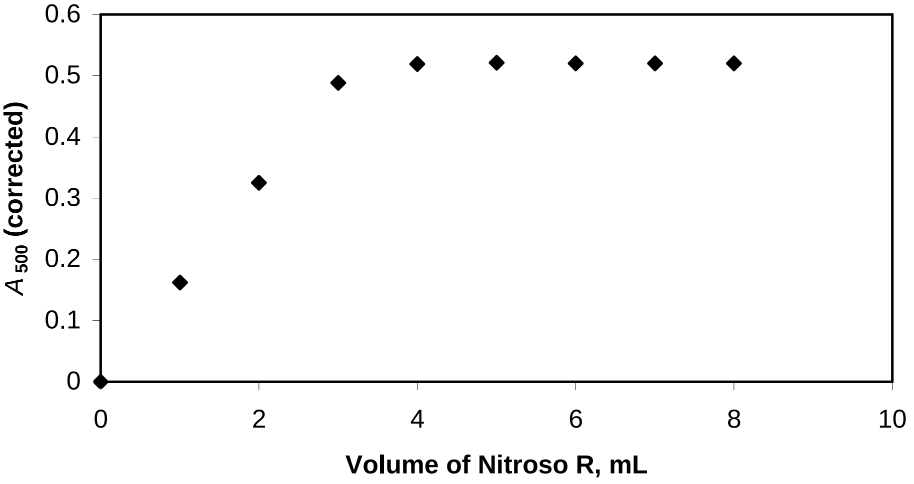
Vol, mL	**A_{500}**	**A_{corr}**	**Vol, mL**	**A_{500}**	**A_{corr}**
0	0	0	5.00	0.347	0.521
1.00	0.147	0.162	6.00	0.325	0.520
2.00	0.271	0.325	7.00	0.306	0.520
3.00	0.375	0.488	8.00	0.289	0.520
4.00	0.371	0.519			

These data are plotted below. The point of intersection of the linear portion of the plot can be determined graphically or evaluated by performing least-squares on the linear portions and solving the two linear simultaneous equations. Least-squares analysis gives the following results.

Points 1 to 4	Points 5 to 9
b_1 = slope = 1.626×10^{-1}	$b_2 = 1.300 \times 10^{-4}$
a_1 = intercept = 3.000×10^{-4}	$a_2 = 5.1928 \times 10^{-1}$
$y = a_1 + b_1 x$	$y = a_2 + b_2 x$

$$x = \frac{a_2 - a_1}{b_1 - b_2} = 3.19 \text{ mL}$$

$$\frac{3.19 \text{ mL} \times 2.44 \times 10^{-4} \dfrac{\text{mmol Nitroso R}}{\text{mL}} \times \dfrac{1 \text{ mmol Pd(II)}}{2 \text{ mmol Nitroso R}}}{10.00 \text{ mL solution}} = 3.89 \times 10^{-5} \text{ M}$$



14-7. From Problem 14-1, $c_x = \dfrac{A_x c_s V_s}{(A_{x+s} - A_x)V_x}$

Substituting numerical values gives $c_x = \dfrac{0.276 \times 4.25 \times 5.00}{(0.491 - 0.276) \times 25.00}$ = 1.0912 ppm Co

$$\text{Percent Co} = 500\text{ mL} \times 1.0912\ \frac{\cancel{\text{mg}}}{\cancel{\text{L}}} \times 10^{-3}\frac{\text{g}}{\cancel{\text{mg}}} \times 10^{-3}\frac{\cancel{\text{L}}}{\text{mL}} \times \frac{100\%}{3.65\text{ g}} = 0.0149\%$$

14-8. (a) $A_{365} = 0.426 = 3529 \times 1.00 \times c_{\text{Co}} + 3228 \times 1.00 \times c_{\text{Ni}}$

$A_{700} = 0.026 = 428.9 \times 1.00 \times c_{\text{Co}} + 10.2 \times 1.00 \times c_{\text{Ni}}$

Rearranging the second equation gives

$c_{\text{Co}} = (0.026 - 10.2c_{\text{Ni}})/428.9$

$= 6.062 \times 10^{-5} - 2.378 \times 10^{-2}c_{\text{Ni}}$

Substituting into the first equation gives

$0.426 = 3529(6.062 \times 10^{-5} - 2.378 \times 10^{-2}c_{\text{Ni}}) + 3228c_{\text{Ni}}$

$0.426 = 0.2139 - 83.91c_{\text{Ni}} + 3228c_{\text{Ni}}$

$c_{\text{Ni}} = 6.75 \times 10^{-5}$ M

Substituting into the equation for c_{Co} gives

$c_{\mathrm{Co}} = 6.062 \times 10^{-5} - 2.378 \times 10^{-2} c_{\mathrm{Ni}} = 6.062 \times 10^{-5} - 2.378 \times 10^{-2} \times 6.75 \times 10^{-5}$

$= 5.90 \times 10^{-5}$ M

(b) Proceeding in the same way, we obtain

$c_{\mathrm{Co}} = 1.88 \times 10^{-4}$M and $c_{\mathrm{Ni}} = 3.99 \times 10^{-5}$ M

14-9. At 475 nm, $\varepsilon_{\mathrm{A}} = 0.155/7.50 \times 10^{-5} = 2067$; $\varepsilon_{\mathrm{B}} = 0.702/4.25 \times 10^{-5} = 16518$

At 700 nm $\varepsilon_{\mathrm{A}} = 0.755/7.50 \times 10^{-5} = 10067$; $\varepsilon_{\mathrm{B}} = 0.091/4.25 \times 10^{-5} = 2141$

(a) $2067c_{\mathrm{A}} + 16518c_{\mathrm{B}} = 0.439/2.5 = 0.1756$

$10067c_{\mathrm{A}} + 2141c_{\mathrm{B}} = 1.025/2.5 = 0.410$

Solving the two equations simultaneously gives,

$c_{\mathrm{A}} = 3.95 \times 10^{-5}$ M and $c_{\mathrm{B}} = 5.69 \times 10^{-6}$ M

(b) In the same way,

$c_{\mathrm{A}} = 2.98 \times 10^{-5}$ M and $c_{\mathrm{B}} = 1.23 \times 10^{-6}$ M

14-10. (a) At 485 nm, $\varepsilon_{\mathrm{In}} = 0.075/5.00 \times 10^{-4} = 150$ $\varepsilon_{\mathrm{HIn}} = 0.487/5.00 \times 10^{-4} = 974$

At 625, $\varepsilon_{\mathrm{In}} = 0.904/5.00 \times 10^{-4} = 1808$ $\varepsilon_{\mathrm{HIn}} = 0.181/5.00 \times 10^{-4} = 362$

(b) To obtain $[\mathrm{In}^-]$ and [HIn], we write

$150[\mathrm{In}^-] + 974[\mathrm{HIn}] = 0.567$

$1808[\mathrm{In}^-] + 362[\mathrm{HIn}] = 0.395$

Solving these equations simultaneously, we get

$[\mathrm{In}^-] = 1.05 \times 10^{-4}$ M and $[\mathrm{HIn}] = 5.66 \times 10^{-4}$ M

Since $[\mathrm{H}^+] = 1.00 \times 10^{-5}$,

$$K_a = \frac{[H^+][In^-]}{[HIn]} = \frac{1.00\times10^{-5}\times 1.05\times10^{-4}}{5.66\times10^{-4}} = 1.86\times10^{-6}$$

(c) $150[In^-] + 974[HIn] = 0.492$

$1808[In^-] + 362[HIn] = 0.245$

Solving these equations gives

$[In^-] = 3.55\times10^{-5}$ M and $[HIn] = 5.00\times10^{-4}$ M

$$\frac{[H^+]\times3.55\times10^{-5}}{5.00\times10^{-4}} = 1.86\times10^{-6}$$

$[H^+] = 2.62\times10^{-5}$ M and pH = 4.58

(d) $150[In^-] + 974[HIn] = 0.333$

$1808[In^-] + 362[HIn] = 0.655$

Solving these equations gives

$[In^-] = 3.03\times10^{-4}$ M and $[HIn] = 2.95\times10^{-4}$ M

We then calculate H^+ from K_a

$$\frac{[H^+]\times3.03\times10^{-4}}{2.95\times10^{-4}} = 1.86\times10^{-6}$$

$[H^+] = 1.81\times10^{-6}$ and pH = 5.74

In the half-neutralized solution of HX, we assume that $[HX] = [X^-]$ and

$$\frac{[H^+][X^-]}{[HX]} = K_a = 1.81\times10^{-6}$$

(e) At $[H^+] = 1.00\times10^{-6}$ M,

$[In^-]/[HIn] = 1.86\times10^{-6}/1.00\times10^{-6} = 1.858$

But,

$$[\text{In}^-] + [\text{HIn}] = 2.00 \times 10^{-4}$$

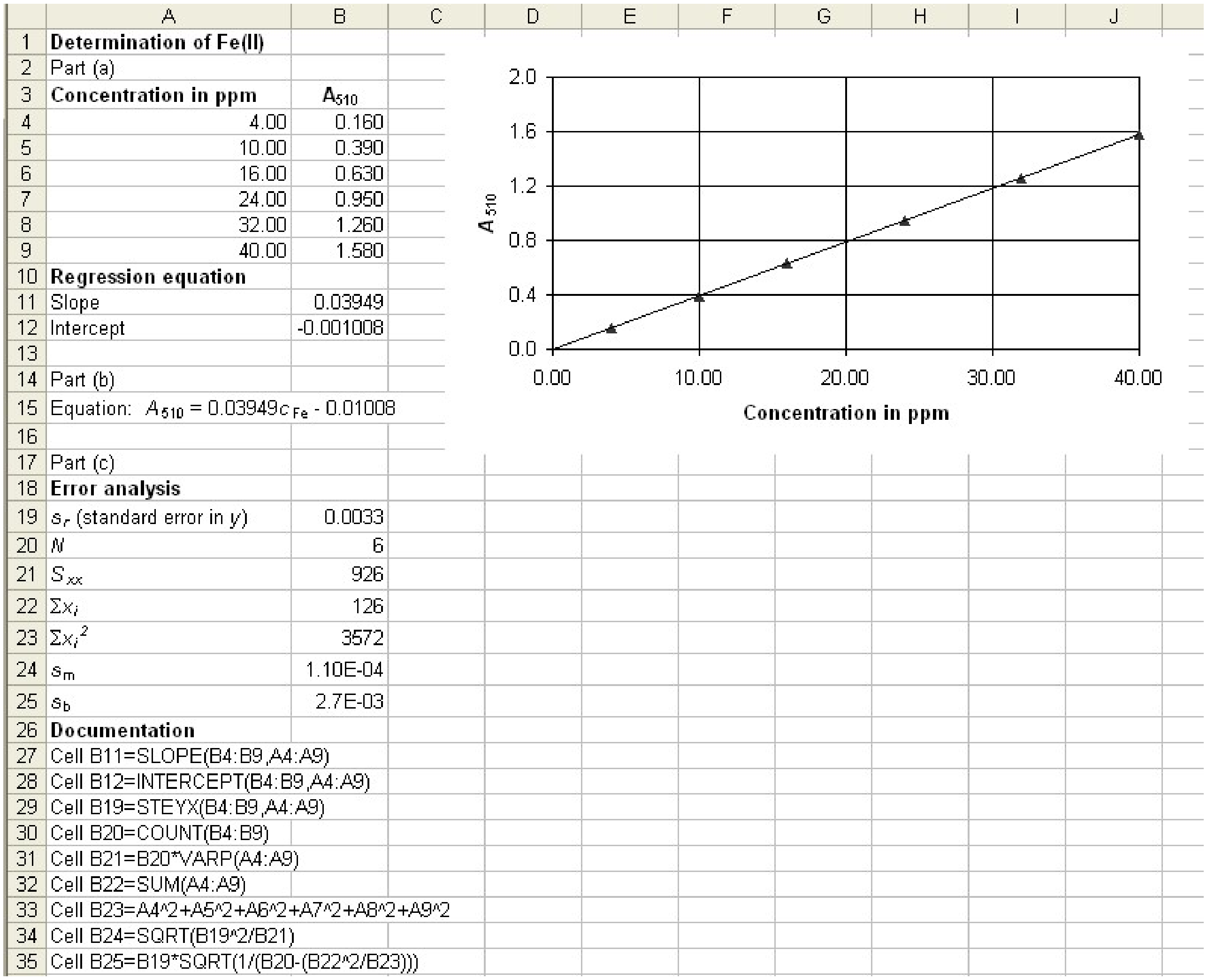
$$1.858[\text{HIn}] + [\text{HIn}] = 2.00 \times 10^{-4}$$

$$[\text{HIn}] = 7.00 \times 10^{-5}\ \text{M} \qquad \text{and } [\text{In}^-] = 2.00 \times 10^{-4} - 7.00 \times 10^{-5} = 1.30 \times 10^{-4}\ \text{M}$$

$$A_{485} = 150 \times 1.50 \times 1.30 \times 10^{-4} + 974 \times 1.50 \times 7.00 \times 10^{-5} = 0.131$$

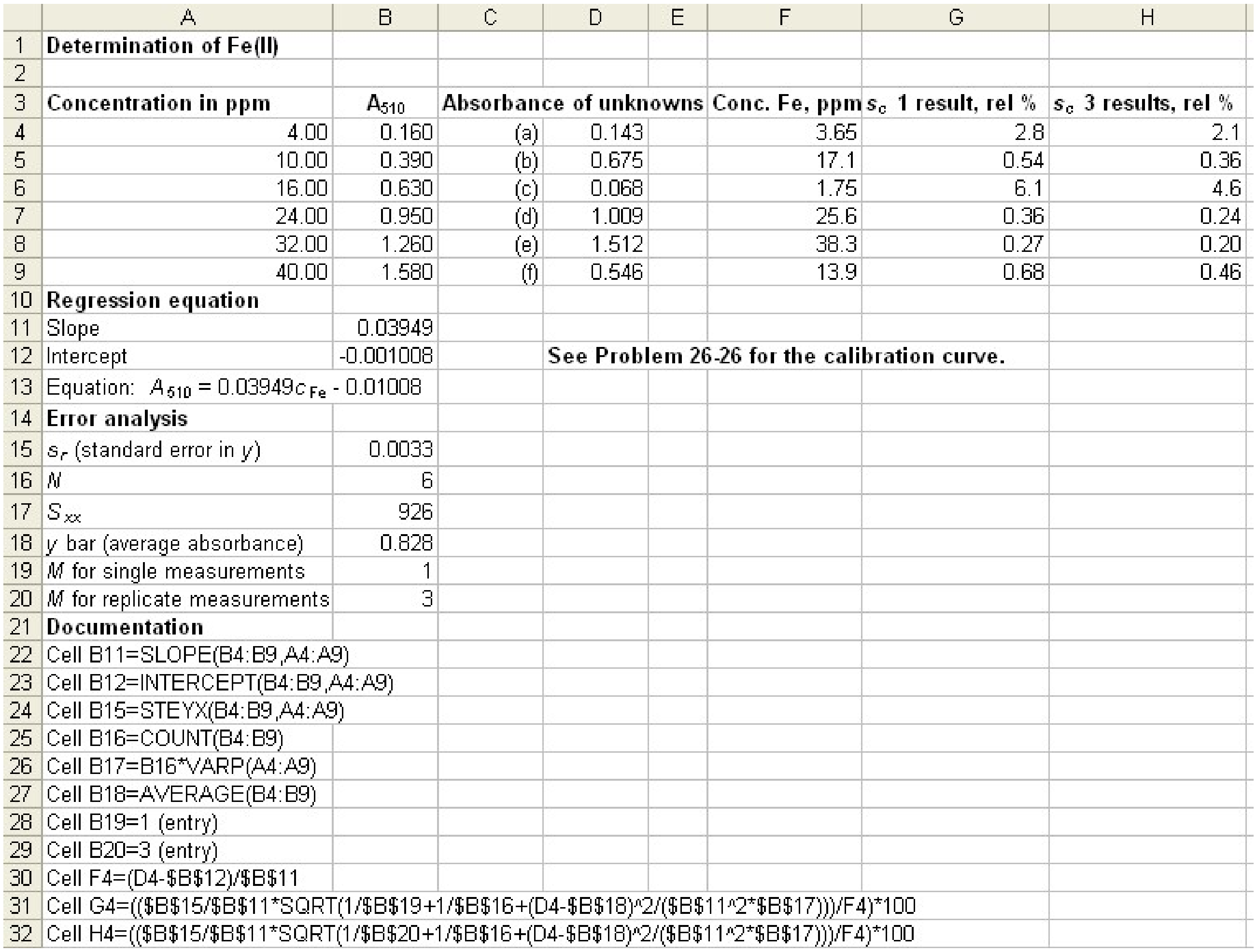
$$A_{625} = 1808 \times 1.50 \times 1.30 \times 10^{-4} + 362 \times 1.50 \times 7.00 \times 10^{-5} = 0.391$$

14-11.



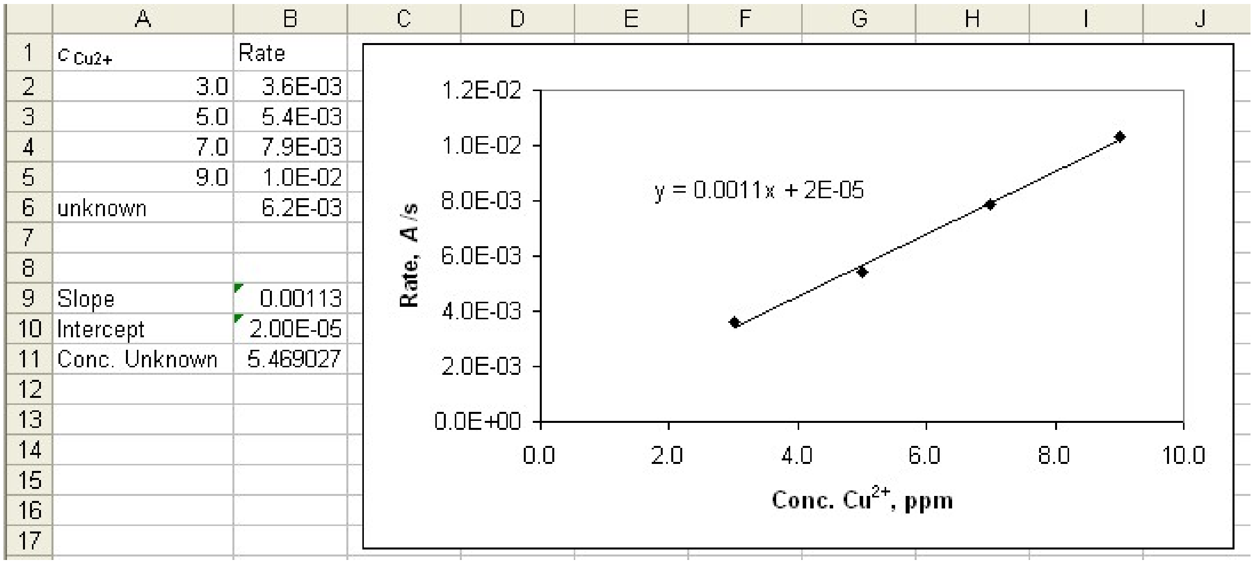
	A	B
1	**Determination of Fe(II)**	
2	Part (a)	
3	**Concentration in ppm**	**A_{510}**
4	4.00	0.160
5	10.00	0.390
6	16.00	0.630
7	24.00	0.950
8	32.00	1.260
9	40.00	1.580
10	**Regression equation**	
11	Slope	0.03949
12	Intercept	-0.001008
13		
14	Part (b)	
15	Equation: $A_{510} = 0.03949c_{\text{Fe}}$ - 0.01008	
16		
17	Part (c)	
18	**Error analysis**	
19	s_r (standard error in y)	0.0033
20	N	6
21	S_{xx}	926
22	Σx_i	126
23	Σx_i^2	3572
24	s_m	1.10E-04
25	s_b	2.7E-03
26	**Documentation**	
27	Cell B11=SLOPE(B4:B9,A4:A9)	
28	Cell B12=INTERCEPT(B4:B9,A4:A9)	
29	Cell B19=STEYX(B4:B9,A4:A9)	
30	Cell B20=COUNT(B4:B9)	
31	Cell B21=B20*VARP(A4:A9)	
32	Cell B22=SUM(A4:A9)	
33	Cell B23=A4^2+A5^2+A6^2+A7^2+A8^2+A9^2	
34	Cell B24=SQRT(B19^2/B21)	
35	Cell B25=B19*SQRT(1/(B20-(B22^2/B23)))	

14-12.



	A	B	C	D	E	F	G	H
1	**Determination of Fe(II)**							
2								
3	**Concentration in ppm**	**A_{510}**	**Absorbance of unknowns**			**Conc. Fe, ppm**	**s_c 1 result, rel %**	**s_c 3 results, rel %**
4	4.00	0.160	(a)	0.143		3.65	2.8	2.1
5	10.00	0.390	(b)	0.675		17.1	0.54	0.36
6	16.00	0.630	(c)	0.068		1.75	6.1	4.6
7	24.00	0.950	(d)	1.009		25.6	0.36	0.24
8	32.00	1.260	(e)	1.512		38.3	0.27	0.20
9	40.00	1.580	(f)	0.546		13.9	0.68	0.46
10	**Regression equation**							
11	Slope	0.03949						
12	Intercept	-0.001008		**See Problem 26-26 for the calibration curve.**				
13	Equation: $A_{510} = 0.03949c_{\text{Fe}} - 0.01008$							
14	**Error analysis**							
15	s_r (standard error in y)	0.0033						
16	N	6						
17	S_{xx}	926						
18	y bar (average absorbance)	0.828						
19	M for single measurements	1						
20	M for replicate measurements	3						
21	**Documentation**							
22	Cell B11=SLOPE(B4:B9,A4:A9)							
23	Cell B12=INTERCEPT(B4:B9,A4:A9)							
24	Cell B15=STEYX(B4:B9,A4:A9)							
25	Cell B16=COUNT(B4:B9)							
26	Cell B17=B16*VARP(A4:A9)							
27	Cell B18=AVERAGE(B4:B9)							
28	Cell B19=1 (entry)							
29	Cell B20=3 (entry)							
30	Cell F4=(D4-$B$12)/$B$11							
31	Cell G4=(($B$15/$B$11*SQRT(1/$B$19+1/$B$16+(D4-$B$18)^2/($B$11^2*$B$17)))/F4)*100							
32	Cell H4=(($B$15/$B$11*SQRT(1/$B$20+1/$B$16+(D4-$B$18)^2/($B$11^2*$B$17)))/F4)*100							

14-13.



	A	B
1	c_{Cu2+}	Rate
2	3.0	3.6E-03
3	5.0	5.4E-03
4	7.0	7.9E-03
5	9.0	1.0E-02
6	unknown	6.2E-03
7		
8		
9	Slope	0.00113
10	Intercept	2.00E-05
11	Conc. Unknown	5.469027
12		
13		
14		
15		
16		
17		

14-14.

$$\text{rate} = 1.74\, c_{\text{Al}} - 0.225 \qquad c_{\text{Al}} = (\text{rate} + 0.225) / 1.74$$

$$c_{\text{Al}} = (0.76 + 0.225) / 1.74 = 0.57\ \mu\text{M}$$

14-15.

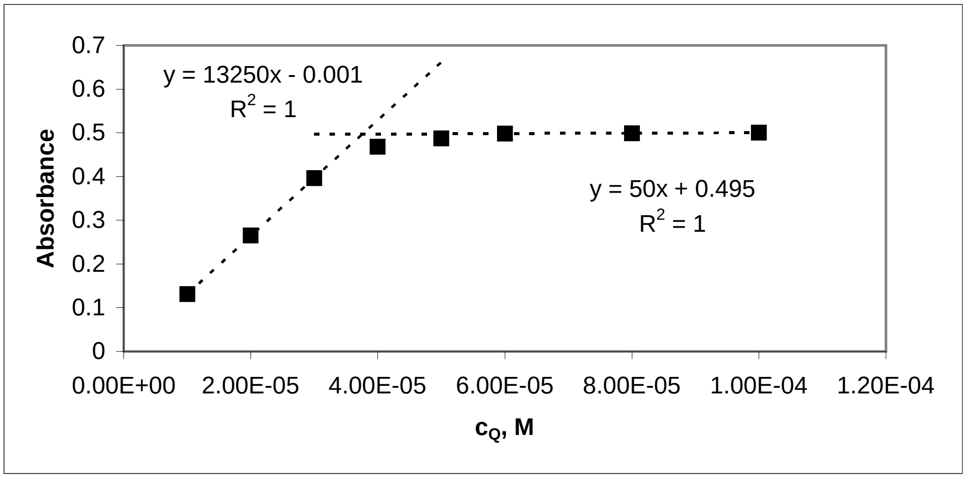
$$\text{Rate} = R = \frac{k_2[\text{E}]_0[\text{tryp}]}{[\text{tryp}] + K_\text{m}}$$

Assume $K_m >> [\text{tryp}]$

$$R = \frac{\nu_{\max}[\text{tryp}]}{K_\text{m}} \qquad \text{and} \qquad [\text{tryp}] = R\,K_m / \nu_{\max}$$

$$[\text{tryp}] = (0.18\ \mu\text{M/min})(4.0\times10^{-4}\ \text{M}) / (1.6\times10^{-3}\ \mu\text{M/min}) = 4.5 \times 10^{-2}\ \text{M}$$

14-16. Plotting the data provided in the question gives,

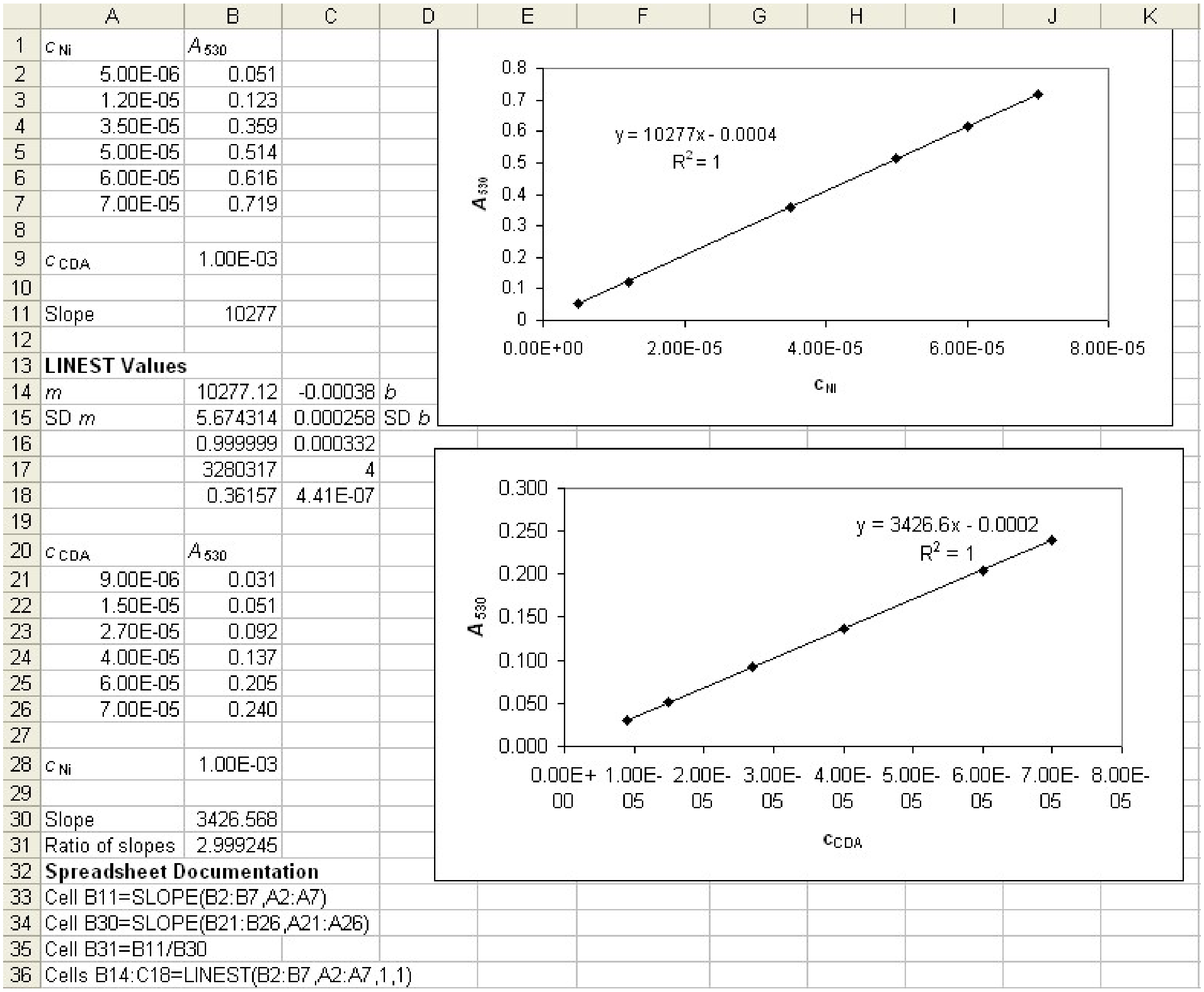


Solving for the crossing point by using the 2 best fit equations gives, $c_Q = 3.76 \times 10^{-5}$ M.

(a) Since $c_{Al} = 3.7\times10^{-5}$ M and complex formation is saturated when $c_Q = 3.76\times10^{-5}$ M, the complex must be 1:1, or AlQ^{2+}.

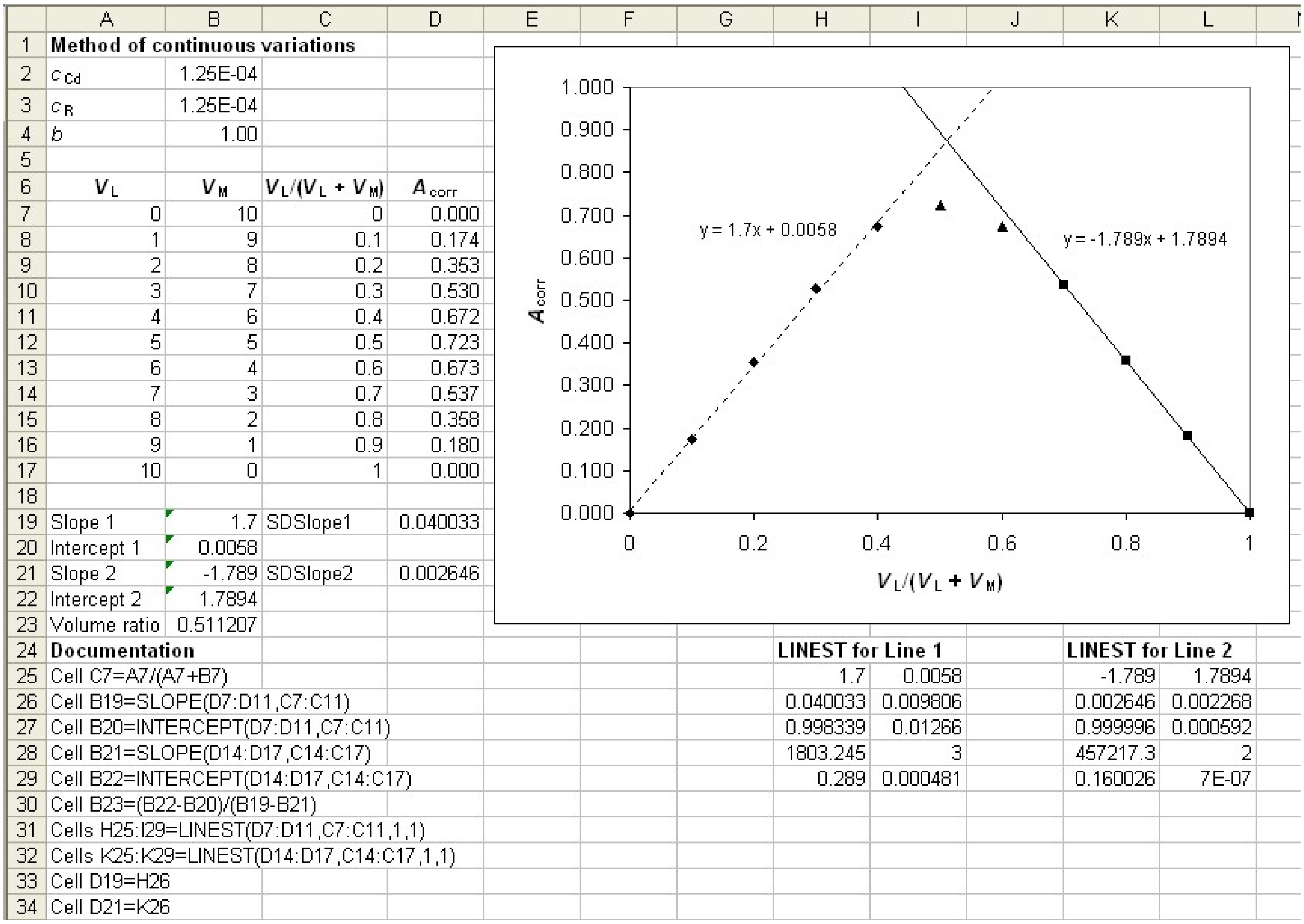
(b) $\varepsilon_{AlQ^{2+}} = (0.500)/(3.7\times10^{-5}) = 1.4\times10^4$

14-17.



	A	B	C	D
1	c_{Ni}	A_{530}		
2	5.00E-06	0.051		
3	1.20E-05	0.123		
4	3.50E-05	0.359		
5	5.00E-05	0.514		
6	6.00E-05	0.616		
7	7.00E-05	0.719		
8				
9	c_{CDA}	1.00E-03		
10				
11	Slope	10277		
12				
13	**LINEST Values**			
14	*m*	10277.12	-0.00038	*b*
15	SD *m*	5.674314	0.000258	SD *b*
16		0.999999	0.000332	
17		3280317	4	
18		0.36157	4.41E-07	
19				
20	c_{CDA}	A_{530}		
21	9.00E-06	0.031		
22	1.50E-05	0.051		
23	2.70E-05	0.092		
24	4.00E-05	0.137		
25	6.00E-05	0.205		
26	7.00E-05	0.240		
27				
28	c_{Ni}	1.00E-03		
29				
30	Slope	3426.568		
31	Ratio of slopes	2.999245		
32	**Spreadsheet Documentation**			
33	Cell B11=SLOPE(B2:B7,A2:A7)			
34	Cell B30=SLOPE(B21:B26,A21:A26)			
35	Cell B31=B11/B30			
36	Cells B14:C18=LINEST(B2:B7,A2:A7,1,1)			

14-18.



	A	B	C	D
1	**Method of continuous variations**			
2	c_{Cd}	1.25E-04		
3	c_R	1.25E-04		
4	b	1.00		
5				
6	V_L	V_M	$V_L/(V_L + V_M)$	A_{corr}
7	0	10	0	0.000
8	1	9	0.1	0.174
9	2	8	0.2	0.353
10	3	7	0.3	0.530
11	4	6	0.4	0.672
12	5	5	0.5	0.723
13	6	4	0.6	0.673
14	7	3	0.7	0.537
15	8	2	0.8	0.358
16	9	1	0.9	0.180
17	10	0	1	0.000
18				
19	Slope 1	1.7	SDSlope1	0.040033
20	Intercept 1	0.0058		
21	Slope 2	-1.789	SDSlope2	0.002646
22	Intercept 2	1.7894		
23	Volume ratio	0.511207		
24	**Documentation**			
25	Cell C7=A7/(A7+B7)			
26	Cell B19=SLOPE(D7:D11,C7:C11)			
27	Cell B20=INTERCEPT(D7:D11,C7:C11)			
28	Cell B21=SLOPE(D14:D17,C14:C17)			
29	Cell B22=INTERCEPT(D14:D17,C14:C17)			
30	Cell B23=(B22-B20)/(B19-B21)			
31	Cells H25:I29=LINEST(D7:D11,C7:C11,1,1)			
32	Cells K25:K29=LINEST(D14:D17,C14:C17,1,1)			
33	Cell D19=H26			
34	Cell D21=K26			

	H	I	K	L
24	**LINEST for Line 1**		**LINEST for Line 2**	
25	1.7	0.0058	-1.789	1.7894
26	0.040033	0.009806	0.002646	0.002268
27	0.998339	0.01266	0.999996	0.000592
28	1803.245	3	457217.3	2
29	0.289	0.000481	0.160026	7E-07

(a) From the spreadsheet, the lines intersect at $V_M / (V_M + V_L) = 0.511$, thus the Cd^{2+} to R ratio is 1 to 1.

(b) Using the slope of the data for solutions 0 through 4

$\varepsilon = \text{Slope}/c_{Cd} = 1.7/1.25 \times 10^{-4} = 13600$ with a standard deviation of $0.040/1.25 \times 10^{-4} = 320$

Using the slope of the results for solutions 7 through 10

$\varepsilon = -\text{Slope}/c_R = 1.789/1.25 \times 10^{-4} = 14312$, standard deviation $0.00265/1.25 \times 10^{-4} = 21$

$\varepsilon_{avg} = (13600+14312)/2 = 13956$ $\quad$ $\text{SD} = \sqrt{(\text{SD1})^2 + (\text{SD2})^2} = 320$

$\varepsilon_{\text{avg}} = 14000 \pm 300$

(c) The absorbance at a 1:1 volume ratio where the lines intersect is $A = 0.723$. Thus,

$[\text{CdR}] = (0.723)/(14000) = 5.16 \times 10^{-5}$ M

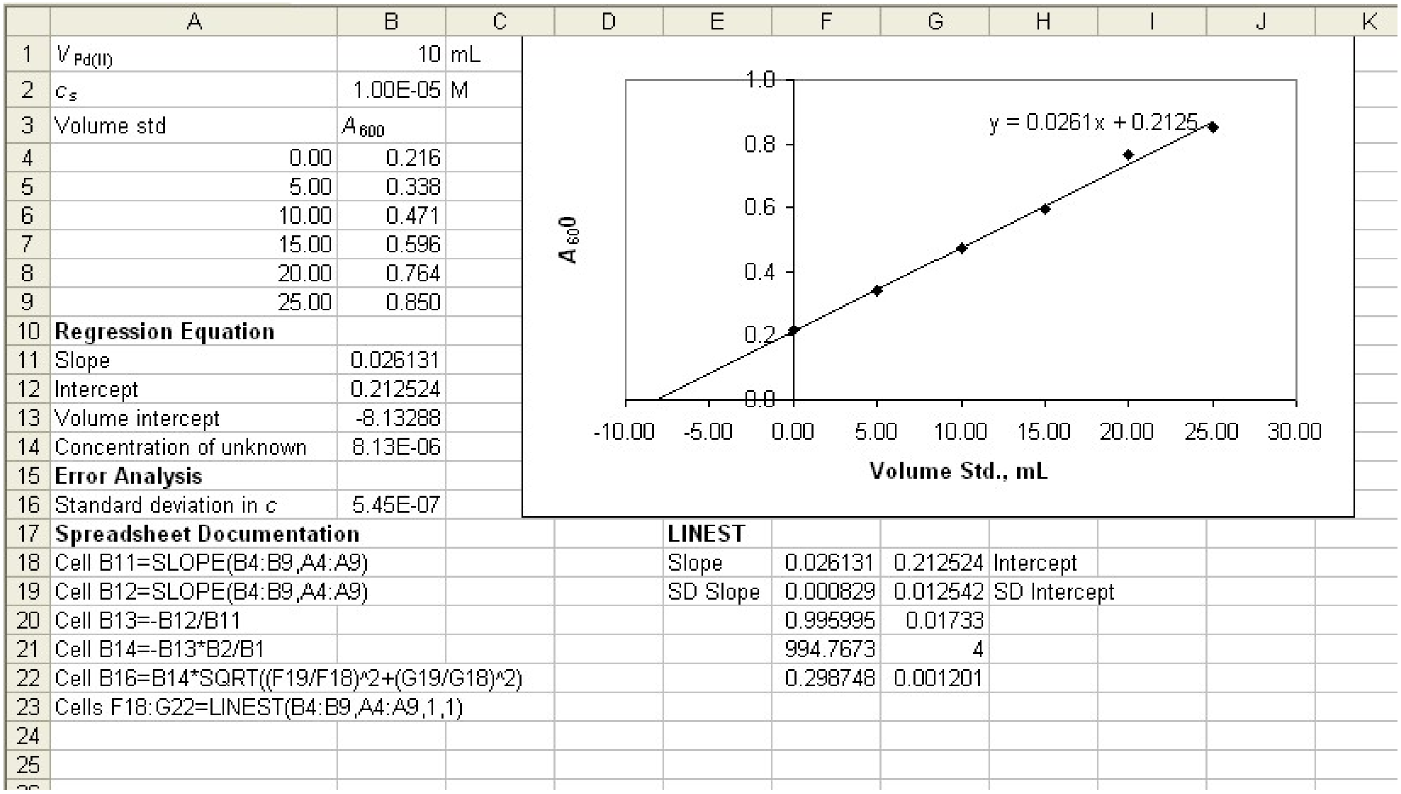
$[\text{Cd}^{2+}] = [(5.00 \text{ mL})(1.25 \times 10^{-4} \text{ mmol/mL}) - (10.00 \text{ mL})(5.16 \times 10^{-5} \text{ mmol/mL})]/(10.00 \text{ mL})$

$= 1.09 \times 10^{-5}$ M

$[\text{R}] = [\text{Cd}^{2+}] = 1.09 \times 10^{-5}$ M

$$K_f = \frac{[\text{CdR}]}{[\text{Cd}^{2+}][\text{R}]} = \frac{5.16\times10^{-5}}{(1.09\times10^{-5})^2} = 4.34 \times 10^5$$

14-19. (a)



	A	B	C	D	E	F	G	H	I	J	K
1	$V_{\text{Pd(II)}}$	10	mL								
2	c_s	1.00E-05	M								
3	Volume std	A_{600}									
4	0.00	0.216									
5	5.00	0.338									
6	10.00	0.471									
7	15.00	0.596									
8	20.00	0.764									
9	25.00	0.850									
10	**Regression Equation**										
11	Slope	0.026131									
12	Intercept	0.212524									
13	Volume intercept	-8.13288									
14	Concentration of unknown	8.13E-06									
15	**Error Analysis**										
16	Standard deviation in *c*	5.45E-07									
17	**Spreadsheet Documentation**				**LINEST**						
18	Cell B11=SLOPE(B4:B9,A4:A9)				Slope	0.026131	0.212524	Intercept			
19	Cell B12=SLOPE(B4:B9,A4:A9)				SD Slope	0.000829	0.012542	SD Intercept			
20	Cell B13=-B12/B11					0.995995	0.01733				
21	Cell B14=-B13*B2/B1					994.7673	4				
22	Cell B16=B14*SQRT((F19/F18)^2+(G19/G18)^2)					0.298748	0.001201				
23	Cells F18:G22=LINEST(B4:B9,A4:A9,1,1)										
24											
25											

(b). From the spreadsheet, $m = 0.02613$ and $b = 0.2125$

(c). From LINEST, $s_m = 0.000829$, $s_b = 0.01254$

(d) From the spreadsheet, $c_{\mathrm{Pd(II)}} = 8.13 \times 10^{-6}$ M

(e) $$s_c = c_x\sqrt{\left(\frac{s_m}{m}\right)^2 + \left(\frac{s_b}{b}\right)^2} = 8.13 \times 10^{-6}\sqrt{\left(\frac{0.000829}{0.026130}\right)^2 + \left(\frac{0.01254}{0.2125}\right)^2} = 5.45 \times 10^{-7}\ \mathrm{M}$$

14-20. If a small amount of Cu^{2+} is added to the analyte solution, no absorption will occur until all of the Fe^{2+} has been used up forming the more stable Y^{4-} complex. After the equivalence point, the absorbance will increase linearly until the Cu^{2+} is used up.

14-21. $\varepsilon = 0.759/2.15 \times 10^{-4} = 3.53 \times 10^3$

$[\mathrm{CuA_2^{2-}}] = 0.654/3.53 \times 10^3 = 1.8526 \times 10^{-4}$ M

$[\mathrm{Cu^{2+}}] = 2.15 \times 10^{-4} - 1.8526 \times 10^{-4} = 2.974 \times 10^{-5}$ M

$[\mathrm{A^{2-}}] = 4.00 \times 10^{-4} - 2 \times 1.8526 \times 10^{-4} = 2.9486 \times 10^{-5}$ M

$$K_f = \frac{[\mathrm{CuA_2^{2-}}]}{[\mathrm{Cu^{2+}}][\mathrm{A^{2-}}]^2} = \frac{1.8526\times10^{-4}}{2.974\times10^{-5}\left(2.9486\times10^{-5}\right)^2} = 7.16 \times 10^9$$

14-22. $\varepsilon = 0.844/2.00 \times 10^{-4} = 4.22 \times 10^3$

$[\mathrm{NiB_2^{2+}}] = 0.316/4.22 \times 10^3 = 7.488 \times 10^{-5}$ M

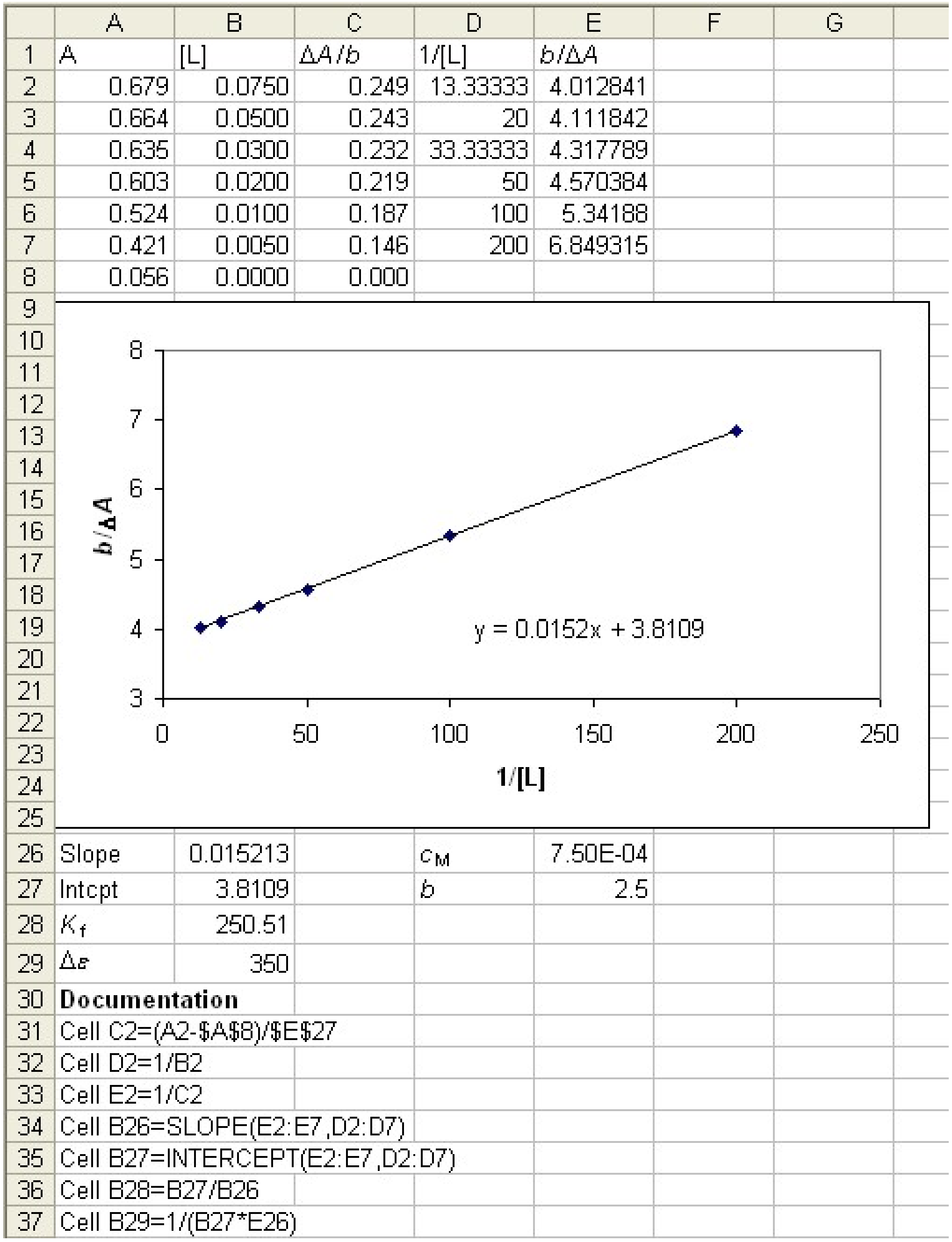
$[\mathrm{Ni^{2+}}] = 2.00 \times 10^{-4} - 7.488 \times 10^{-5} = 1.251 \times 10^{-4}$ M

$[\mathrm{B}] = 1.50 \times 10^{-3} - 2 \times 7.488 \times 10^{-5} = 1.35 \times 10^{-3}$ M

$$K_f = \frac{[\mathrm{NiB_2^{2+}}]}{[\mathrm{Ni^{2+}}][\mathrm{B}]^2} = \frac{7.488\times10^{-5}}{1.251\times10^{-4}\times\left(1.350\times10^{-3}\right)^2} = 3.28 \times 10^5$$

14-23.

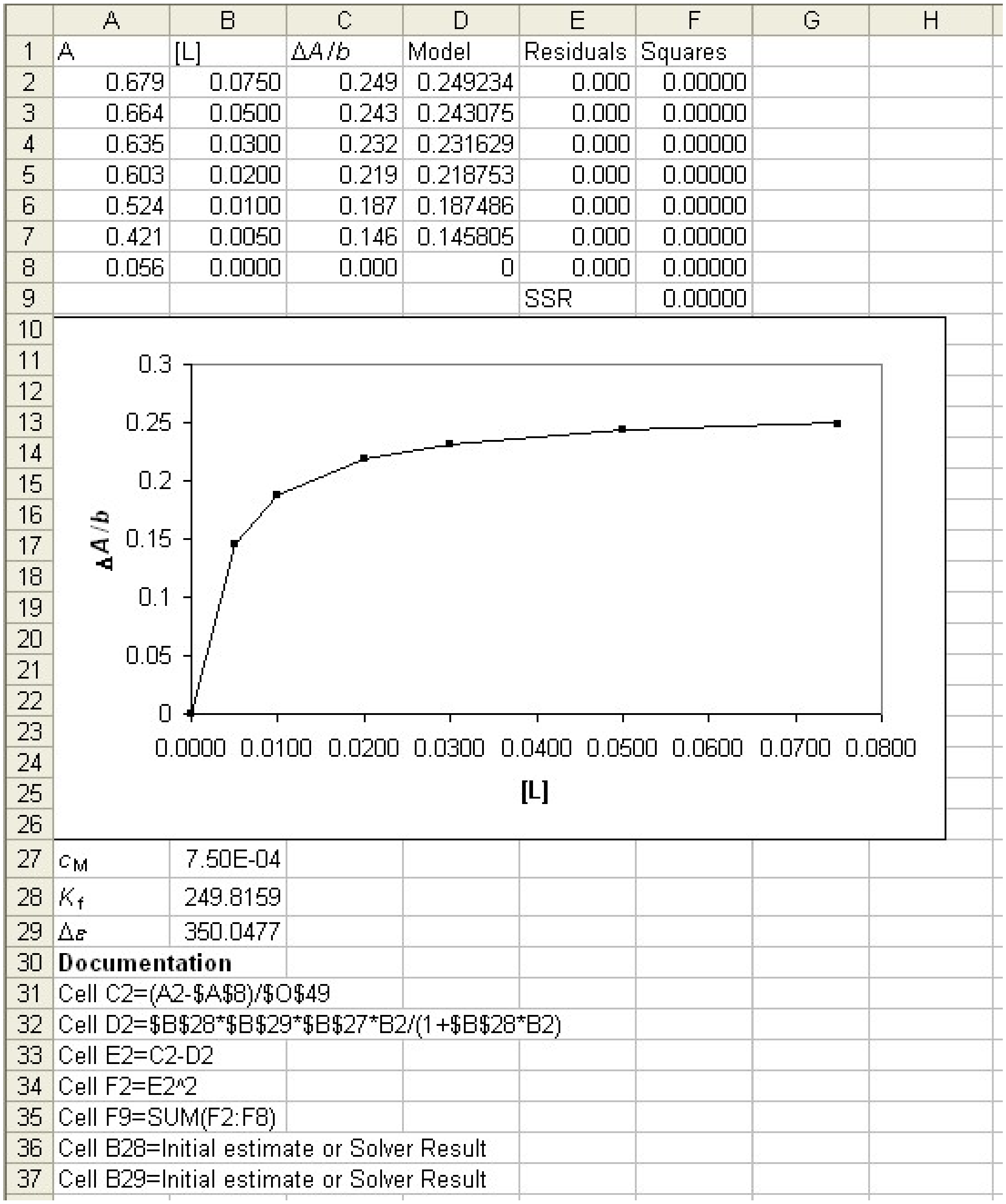
(a) The spreadsheet for the linearized Benesi-Hildebrand equation (Equation 14-11) is shown below. From this, the results are $K_f = 251$, and $\Delta\varepsilon = 350$ L mol^{-1} cm^{-1}.



	A	B	C	D	E	F	G
1	A	[L]	ΔA/b	1/[L]	b/ΔA		
2	0.679	0.0750	0.249	13.33333	4.012841		
3	0.664	0.0500	0.243	20	4.111842		
4	0.635	0.0300	0.232	33.33333	4.317789		
5	0.603	0.0200	0.219	50	4.570384		
6	0.524	0.0100	0.187	100	5.34188		
7	0.421	0.0050	0.146	200	6.849315		
8	0.056	0.0000	0.000				

	A	B	C	D	E	F	G
26	Slope	0.015213		c_M	7.50E-04		
27	Intcpt	3.8109		b	2.5		
28	K_f	250.51					
29	Δε	350					
30	**Documentation**						
31	Cell C2=(A2-$A$8)/$E$27						
32	Cell D2=1/B2						
33	Cell E2=1/C2						
34	Cell B26=SLOPE(E2:E7,D2:D7)						
35	Cell B27=INTERCEPT(E2:E7,D2:D7)						
36	Cell B28=B27/B26						
37	Cell B29=1/(B27*E26)						

(b). The final spreadsheet for the nonlinear regression (Equation 14-10) is shown below with the final Solver solution shown in the chart and in Cells B28 and B29. From this, the results are $K_f = 250$ and $\Delta\varepsilon = 350$ L mol^{-1} cm^{-1}.



	A	B	C	D	E	F	G	H
1	A	[L]	$\Delta A/b$	Model	Residuals	Squares		
2	0.679	0.0750	0.249	0.249234	0.000	0.00000		
3	0.664	0.0500	0.243	0.243075	0.000	0.00000		
4	0.635	0.0300	0.232	0.231629	0.000	0.00000		
5	0.603	0.0200	0.219	0.218753	0.000	0.00000		
6	0.524	0.0100	0.187	0.187486	0.000	0.00000		
7	0.421	0.0050	0.146	0.145805	0.000	0.00000		
8	0.056	0.0000	0.000	0	0.000	0.00000		
9					SSR	0.00000		
27	c_M	7.50E-04						
28	K_f	249.8159						
29	$\Delta\varepsilon$	350.0477						
30	**Documentation**							
31	Cell C2=(A2-$A$8)/$O$49							
32	Cell D2=$B$28*$B$29*$B$27*B2/(1+$B$28*B2)							
33	Cell E2=C2-D2							
34	Cell F2=E2^2							
35	Cell F9=SUM(F2:F8)							
36	Cell B28=Initial estimate or Solver Result							
37	Cell B29=Initial estimate or Solver Result							

CHAPTER 15

15-1. In a fluorescence emission spectrum, the excitation wavelength is held constant and the emission intensity is measured as a function of the emission wavelength. In an excitation spectrum, the emission is measured at one wavelength while the excitation wavelengths are scanned. The excitation spectrum closely resembles an absorption spectrum since the emission intensity is usually proportional to the absorbance of the molecule.

15-2. (a) *Fluorescence* is the process in which a molecule, excited by the absorption of radiation, emits a photon while undergoing a transition from an excited singlet electronic state to a lower state of the same spin multiplicity (e.g., a singlet → singlet transition).

(b) *Phosphorescence* is the process in which a molecule, excited by the absorption of radiation, emits a photon while undergoing a transition from an excited triplet state to a lower state of a different spin multiplicity (e.g., a triplet → singlet transition).

(c) *Resonance fluorescence* is observed when an excited species emits radiation of the same frequency at used to cause the excitation.

(d) A *singlet state* is one in which the spins of the electrons of an atom or molecule are all paired so there is no net spin angular momentum

(e) A *triplet state* is one in which the spins of the electrons of an atom or molecule are unpaired so that their spin angular moments add to give a net non-zero moment.

(f) *Vibrational relaxation* is the process by which a molecule loses its excess vibrational energy without emitting radiation.

(g) *Internal conversion* is the intermolecular process in which a molecule crosses to a lower electronic state with emitting radiation.

(h) *External conversion* is a radiationless process in which a molecule loses electronic energy while transferring that energy to the solvent or another solute.

(i) *Intersystem crossing* is the process in which a molecule in one spin state changes to another spin state with nearly the same total energy (e.g., singlet → triplet).

(j) *Predissociation* occurs when a molecule changes from a higher electronic state to an upper vibrational level of a lower electronic state in which the vibrational energy is great enough to rupture the bond.

(k) *Dissociation* occurs when radiation promotes a molecule directly to a state with sufficient vibrational energy for a bond to break.

(l) *Quantum yield* is the fraction of excited molecules undergoing the process of interest. For example, the quantum yield of fluorescence is the fraction of molecules which have absorbed radiation that fluoresce.

(m) *Chemiluminescence* is a process by which radiation is produced as a result of a chemical reaction.

15-3. For spectrofluorometry, the analytical signal F is proportional to the source intensity P_0 and the transducer sensitivity. In spectrophotometry, the absorbance A is proportional to the ratio of P_0 to P. Increasing P_0 or the transducer sensitivity to P_0 produces a corresponding increase in P or the sensitivity to P. Thus the ratio does not change. As a result, the sensitivity of fluorescence can be increased by increasing P_0 or transducer sensitivity, but the that of absorbance does not change.

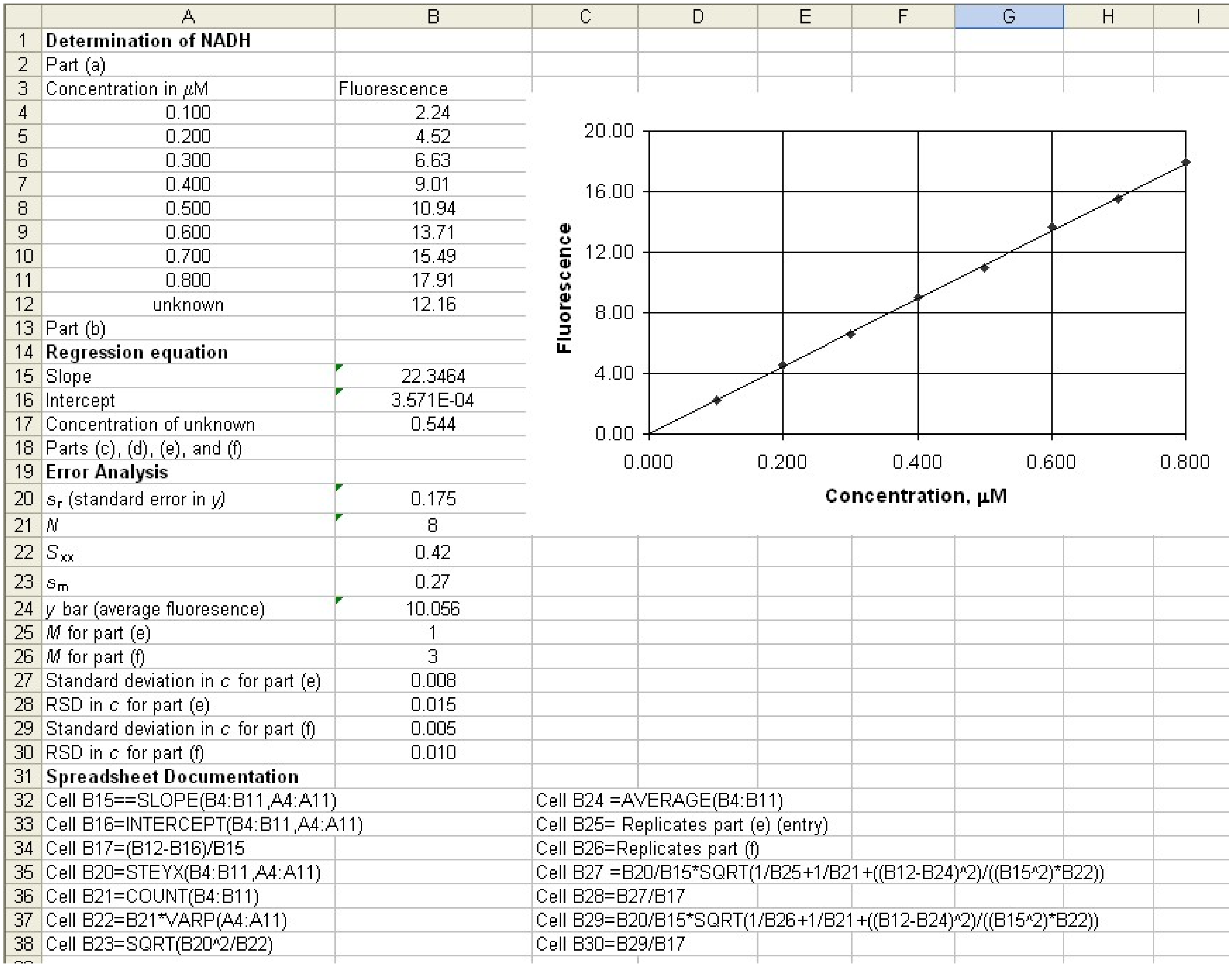
15-4. (a) Fluorescein because of its greater structural rigidity due to the bridging –O– groups.

(b) *o,o'*-Dihdroxyazobenzene because the –N=N– group provides rigidity that is absent in the –NH–NH– group.

15-5. Compounds that fluoresce have structures that slow the rate of nonradiative relaxation to the point where there is time for fluorescence to occur. Compounds that do not fluoresce have structures that permit rapid relaxation by nonradiative processes.

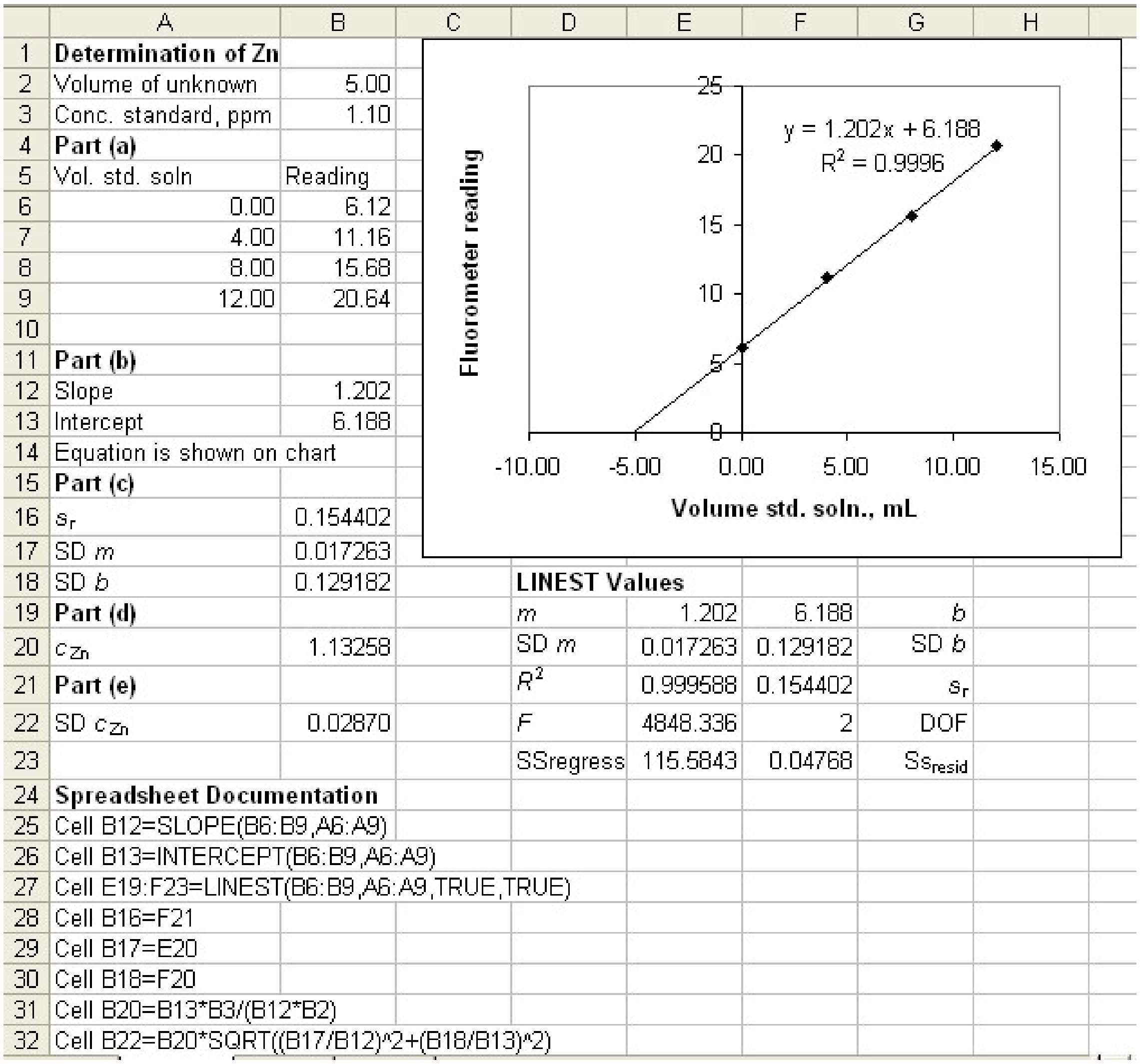
15-6. The triplet state has a long lifetime and is very susceptible to collisional deactivation. Thus, most phosphorescence measurements are made at low temperature in a rigid matrix or in solutions containing micelles or cyclodextrin molecules. Also, electronic methods must be used to discriminate phosphorescence from fluorescence. Not as many molecules give good phosphorescence signals as fluorescence signals. As a result, the experimental requirements to measure phosphorescence are more difficult than those to measure fluorescence and the applications are not as large.

15-7.



	A	B	C
1	**Determination of NADH**		
2	Part (a)		
3	Concentration in μM	Fluorescence	
4	0.100	2.24	
5	0.200	4.52	
6	0.300	6.63	
7	0.400	9.01	
8	0.500	10.94	
9	0.600	13.71	
10	0.700	15.49	
11	0.800	17.91	
12	unknown	12.16	
13	Part (b)		
14	**Regression equation**		
15	Slope	22.3464	
16	Intercept	3.571E-04	
17	Concentration of unknown	0.544	
18	Parts (c), (d), (e), and (f)		
19	**Error Analysis**		
20	s_r (standard error in *y*)	0.175	
21	*N*	8	
22	S_{xx}	0.42	
23	s_m	0.27	
24	*y* bar (average fluoresence)	10.056	
25	*M* for part (e)	1	
26	*M* for part (f)	3	
27	Standard deviation in *c* for part (e)	0.008	
28	RSD in *c* for part (e)	0.015	
29	Standard deviation in *c* for part (f)	0.005	
30	RSD in *c* for part (f)	0.010	
31	**Spreadsheet Documentation**		
32	Cell B15==SLOPE(B4:B11,A4:A11)		Cell B24 =AVERAGE(B4:B11)
33	Cell B16=INTERCEPT(B4:B11,A4:A11)		Cell B25= Replicates part (e) (entry)
34	Cell B17=(B12-B16)/B15		Cell B26=Replicates part (f)
35	Cell B20=STEYX(B4:B11,A4:A11)		Cell B27 =B20/B15*SQRT(1/B25+1/B21+((B12-B24)^2)/((B15^2)*B22))
36	Cell B21=COUNT(B4:B11)		Cell B28=B27/B17
37	Cell B22=B21*VARP(A4:A11)		Cell B29=B20/B15*SQRT(1/B26+1/B21+((B12-B24)^2)/((B15^2)*B22))
38	Cell B23=SQRT(B20^2/B22)		Cell B30=B29/B17

15-8.



	A	B	C	D	E	F	G	H
1	**Determination of Zn**							
2	Volume of unknown	5.00						
3	Conc. standard, ppm	1.10						
4	**Part (a)**							
5	Vol. std. soln	Reading						
6	0.00	6.12						
7	4.00	11.16						
8	8.00	15.68						
9	12.00	20.64						
10								
11	**Part (b)**							
12	Slope	1.202						
13	Intercept	6.188						
14	Equation is shown on chart							
15	**Part (c)**							
16	s_r	0.154402						
17	SD *m*	0.017263						
18	SD *b*	0.129182		**LINEST Values**				
19	**Part (d)**			*m*	1.202	6.188	*b*	
20	c_{Zn}	1.13258		SD *m*	0.017263	0.129182	SD *b*	
21	**Part (e)**			R^2	0.999588	0.154402	s_r	
22	SD c_{Zn}	0.02870		*F*	4848.336	2	DOF	
23				SSregress	115.5843	0.04768	Ss_{resid}	
24	**Spreadsheet Documentation**							
25	Cell B12=SLOPE(B6:B9,A6:A9)							
26	Cell B13=INTERCEPT(B6:B9,A6:A9)							
27	Cell E19:F23=LINEST(B6:B9,A6:A9,TRUE,TRUE)							
28	Cell B16=F21							
29	Cell B17=E20							
30	Cell B18=F20							
31	Cell B20=B13*B3/(B12*B2)							
32	Cell B22=B20*SQRT((B17/B12)^2+(B18/B13)^2)							

15-9. Q = quinine

$$\text{ppm Q in diluted sample} = 100\text{ ppm} \times \frac{245}{125} = 196$$

$$\text{mass Q} = \frac{196\text{ mg Q}}{10^3\text{ mL solution}} \times 100\text{ mL} \times \frac{500\text{ mL}}{20\text{ mL}} = 490\text{ mg Q}$$

15-10. $c_Q = \dfrac{A_1 c_s V_s}{(A_2 - A_1)V_Q} = \dfrac{(448)(50\text{ ppm})(10.0\text{ mL})}{(525-448)(20.0\text{ mL})} = 145.45\text{ ppm}$

$$145.45\text{ ppm} \times \frac{1\text{ mg quinine}}{1\times10^3\text{ g solution}} \times \frac{1\text{ g solution}}{1\text{ mL}} \times 1000\text{ mL} = 145.45\text{ mg quinine}$$

$$\frac{0.225\text{ g Q}}{4.236\text{ g tablet}} \times 100\% = 3.43\%$$

15-11. Assume that the luminescent intensity L is proportional to c_x, the concentration of iron in the original sample. Then,

$$L_1 = kc_x V_x / V_t$$

where V_x and V_t are the volume of sample and of the final solution, and k is a proportionality constant.

For the solution after addition of V_s mL of a standard of concentration c_s, the luminescence L_2 is

$$L_2 = kc_x V_x / V_t + kc_s V_s / V_t$$

Dividing the second equation by the first yields, after rearrangement,

$$c_x = \frac{L_1 c_s V_s}{(L_2 - L_1)V_x} = \frac{(14.3)(3.58 \times 10^{-5})(1.00)}{(33.3-14.3)(2.00)} = 1.35 \times 10^{-5}\text{ M}$$

15-12. Assume that the luminescence intensity L is proportional to the partial pressure of S_2^*.

We may then write

$$L = k[S_2^*] \qquad \text{and } K = \frac{[S_2^*][H_2O]^4}{[SO_2]^2[H_2]^4}$$

where the bracketed terms are all partial pressures and k and K are constants. The two equations can be combined to give after rearrangement

$$[\mathrm{SO_2}] = \frac{[\mathrm{H_2O}]^2}{[\mathrm{H_2}]^2}\sqrt{\frac{L}{kK}}$$

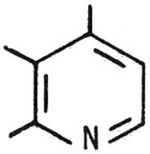
In a hydrogen-rich flame, the pressure of H_2O and H_2 should be more or less constant.

Thus,

$$[\mathrm{SO_2}] = k'\sqrt{L}$$

where $k' = \dfrac{1}{\sqrt{kK}}$

15-13. The fluorescent center is the rigid quinoline ring, which is rich in π electrons.



15-14. From Equation 15-7, we can write

$$F = 2.303\,\phi_{\mathrm{f}} K''\varepsilon bcP_0 = 2.303\,\frac{\tau}{\tau_0}K''\varepsilon bcP_0$$

Dividing both sides by the lifetime τ yields

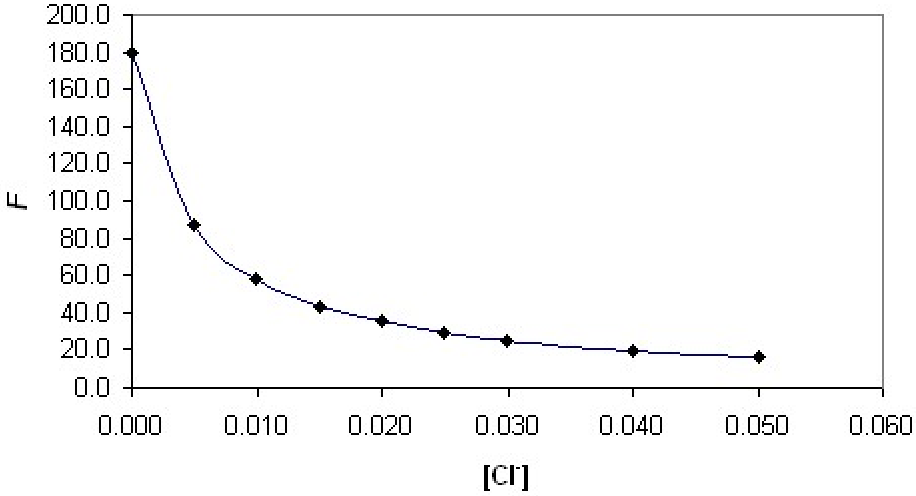
$$\frac{F}{\tau} = \frac{2.303K''\varepsilon bcP_0}{\tau_0}$$

Since K'', ε, b, τ_0 and P_0 are constants, we can write

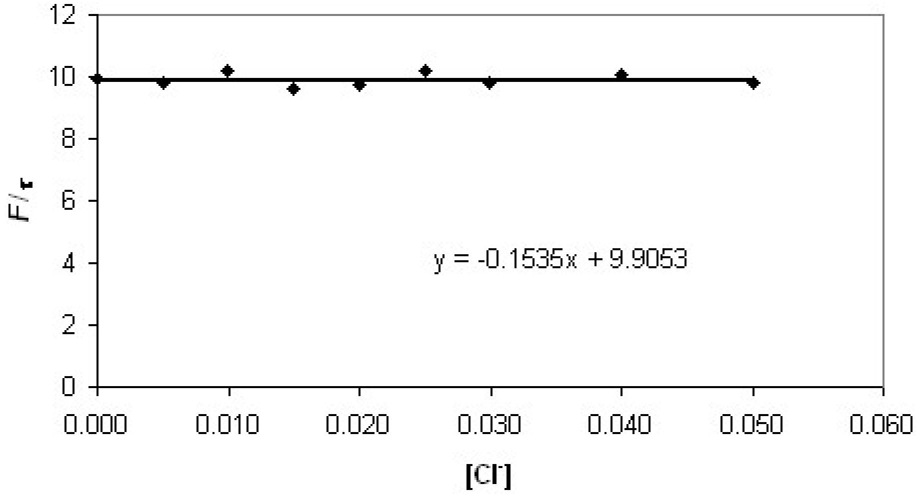
$$\frac{F}{\tau} = Kc$$

where K is a compilation of all the constants in the previous equation.

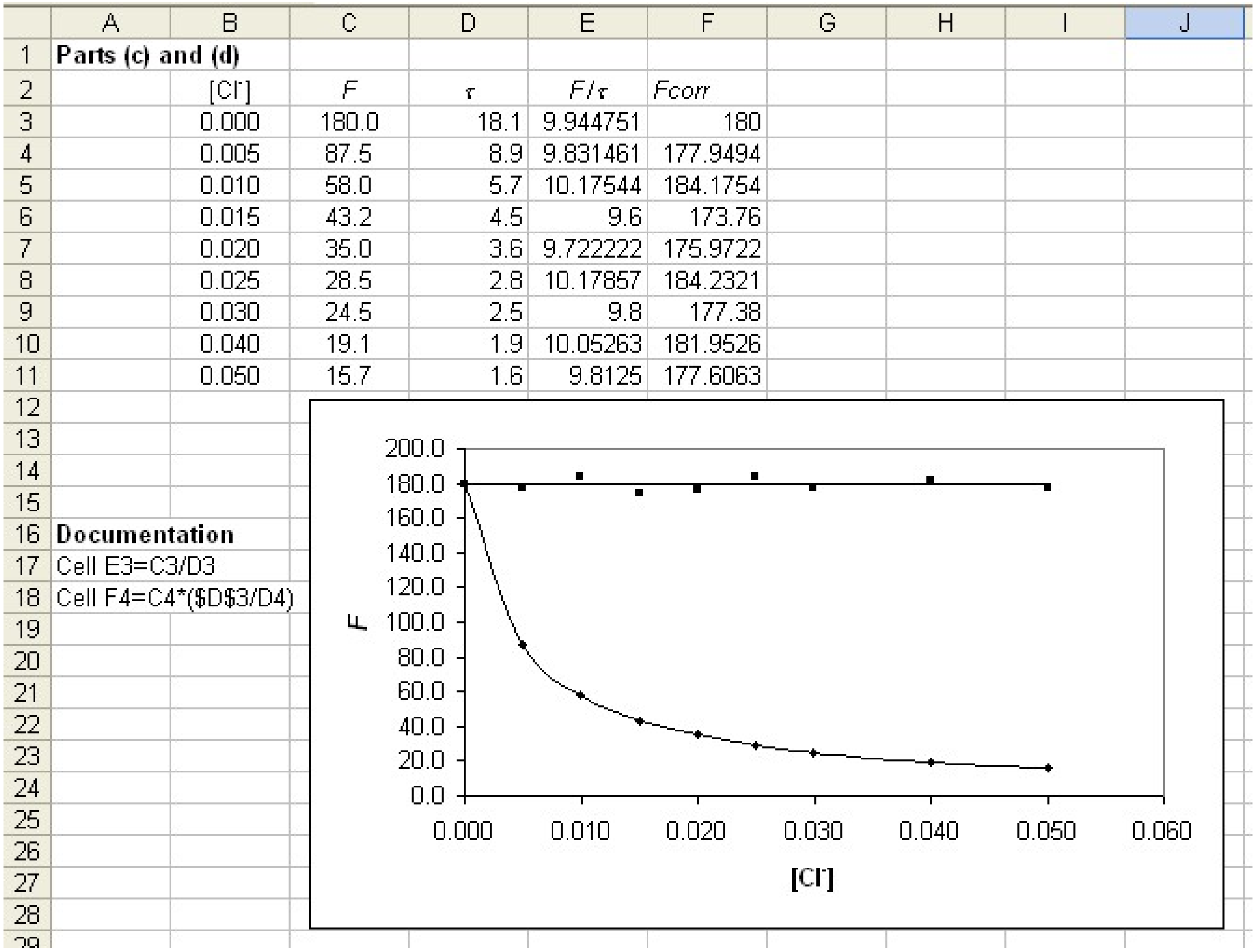
15-15. (a)



(b)



(c) The corrected fluorescence F_{corr} would be $F_{\text{corr}} = F\tau_0/\tau$, where F is the observed fluorescence, τ_0 is the lifetime for $[\text{Cl}^-] = 0.00$, and τ is the observed lifetime. The results are in the spreadsheet.



	A	B	C	D	E	F
1	**Parts (c) and (d)**					
2		$[Cl^-]$	*F*	τ	F/τ	*Fcorr*
3		0.000	180.0	18.1	9.944751	180
4		0.005	87.5	8.9	9.831461	177.9494
5		0.010	58.0	5.7	10.17544	184.1754
6		0.015	43.2	4.5	9.6	173.76
7		0.020	35.0	3.6	9.722222	175.9722
8		0.025	28.5	2.8	10.17857	184.2321
9		0.030	24.5	2.5	9.8	177.38
10		0.040	19.1	1.9	10.05263	181.9526
11		0.050	15.7	1.6	9.8125	177.6063

16 **Documentation**
17 Cell E3=C3/D3
18 Cell F4=C4*($D$3/D4)

CHAPTER 16

16-1. (a) $\nu = 3.00\times10^{10}\ \text{cm s}^{-1} \times 2170\ \text{cm}^{-1} = 6.51\times10^{13}\ \text{s}^{-1}$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{(Equation 16-14)}$$

$$k = (2\pi\nu)^2\mu = (2\pi\nu)^2\frac{m_1m_2}{m_1+m_2} \qquad \text{(Equation 16-9)}$$

$$m_1 = \frac{12\times10^{-3}\ \text{(kg C/mol C)}}{6.02\times10^{23}\ \text{(atom C/mol C)}} = 1.99\times10^{-26}\ \text{kg C/atom C}$$

$$m_2 = \frac{16\times10^{-3}\ \text{(kg O/mol O)}}{6.02\times10^{23}\ \text{(atom O/mol O)}} = 2.66\times10^{-26}\ \text{kg O/atom O}$$

$$k = (2\pi\nu\ \text{s}^{-1})^2\times\frac{1.99\times10^{-26}\ \text{kg}\times2.66\times10^{-26}\ \text{kg}}{1.99\times10^{-26}\ \text{kg} + 2.66\times10^{-26}\ \text{kg}}$$

$$= (2\pi\times6.51\times10^{13}\ \text{s}^{-1})^2\times1.14\times10^{-26}\ \text{kg} = 1.91\times10^3\ \text{kg/s}^2$$

Multiplying the right side of this equation by m/m gives

$$k = 1.90\times10^3\ \frac{\text{kg m}}{\text{s}^2\ \text{m}} = 1.90\times10^3\ \text{N/m}$$

(b) Here $m_1 = 2.326\times10^{-26}$ kg and $\mu = 1.24\times10^{-26}$ kg

$$\nu = \frac{1}{2\pi}\sqrt{\frac{1.91\times10^3}{1.24\times10^{-26}}} = 6.25\times10^{13}\ \text{s}^{-1}$$

$$\bar{\nu} = 6.25\times10^{13}\ \text{s}^{-1}/3.00\times10^{10}\ \text{cm s}^{-1} = 2083\ \text{cm}^{-1}$$

16-2. (a) We will use Equation 16-15 to obtain k

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$$m_1 = \frac{1.00\times10^{-3}\text{ kg /mol H}}{6.02\times10^{23}\text{ atom H/molH}} = 1.66\times10^{-27}\text{ kg}$$

$$m_2 = \frac{35.5\times10^{-3}\text{ kg /mol Cl}}{6.02\times10^{23}\text{ atom Cl/mol Cl}} = 5.90\times10^{-26}\text{ kg}$$

$$\mu = \frac{1.66\times10^{-27}\text{ kg}\times5.90\times10^{-26}\text{ kg}}{1.66\times10^{-27}\text{ kg} + 5.90\times10^{-26}\text{ kg}} = 1.62\times10^{-27}\text{ kg}$$

Rearranging Equation 16-15 and substituting yields

$$k = (2\bar{\nu}\pi c)^2\mu = (2\pi\times2890\text{ cm}^{-1}\times\ 3.00\times10^{10}\text{ cm s}^{-1})^2\times1.62\times10^{-27}\text{ kg}$$

$$= 4.81\times10^2\text{ kg s}^{-2} = 4.81\times10^2\text{ N/m}$$

(b) The force constant in HCl and DCl should be the same and

$$m_1 = \frac{2.00\times10^{-3}}{6.02\times10^{23}} = 3.32\times10^{-27}\text{ kg}$$

$$\mu = \frac{3.32\times10^{-27}\text{ kg}\times5.90\times10^{-26}\text{ kg}}{3.32\times10^{-27}\text{ kg} + 5.90\times10^{-26}\text{ kg}} = 3.14\times10^{-27}\text{ kg}$$

$$\bar{\nu} = \frac{1}{2\pi\times3.00\times10^{10}\text{ cm/s}}\sqrt{\frac{4.81\times10^2\text{ kg s}^{-2}}{3.14\times10^{-27}\text{ kg}}} = 2075\text{ cm}^{-1}$$

16-3. $$m_1 = \frac{1.00\times10^{-3}\text{ kg /mol H}}{6.02\times10^{23}\text{ atom H/molH}} = 1.66\times10^{-27}\text{ kg}$$

$$m_2 = \frac{12\times10^{-3}\text{ (kg /mol C)}}{6.02\times10^{23}\text{ (atom C/mol C)}} = 1.99\times10^{-26}\text{ kg /atom C}$$

$$\mu = \frac{1.66\times10^{-27}\text{ kg}\times1.99\times10^{-26}\text{ kg}}{1.66\times10^{-27}\text{ kg} + 1.99\times10^{-26}\text{ kg}} = 1.53\times10^{-27}\text{ kg}$$

Substituting into Equation 16-15, yields

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3\times10^{-12}\ \text{s cm}^{-1}\sqrt{\frac{5.0\times10^{2}\ \text{kg s}^{-2}}{1.53\times10^{-27}\ \text{kg}}} = 3.0\times10^{3}\ \text{cm}^{-1}$$

From the correlation charts, the range for C—H bond is 2850 to 3300 cm^{-1}.

16-4. $\bar{\nu} = 1/(1.4\times10^{-4}\ \text{cm}) = 7.1\times10^{3}\ \text{cm}^{-1}$

The first overtone occurs at 2 × $\bar{\nu}$ or 14.2 × 10^3 cm^{-1} or 1.4 × 10^4 cm^{-1}.

$$\lambda = \frac{1}{14.2\times10^{3}\ \text{cm}^{-1}} = 7.0\times10^{-5}\ \text{cm} = 0.70\ \mu\text{m}$$

16-5. Proceeding as in Solution 16-4, we find $2\bar{\nu}$ = 1.3 × 10^4 cm^{-1} and λ = 0.75 μm.

16-6. Sulfur dioxide is a nonlinear triatomic molecule that has (3 × 3) –6 = 3 vibrational modes including a symmetric and an asymmetric stretching vibration and a scissoring vibration. All these result in absorption bands.

16-7. Bonds will be inactive if no change in dipole moment accompanies the vibration.

(a) Inactive (b) Active (c) Active (d) Active (e) Inactive (f) Active (g) Inactive

16-8. The advantages of FTIR instruments over dispersive spectrometers include (1) superior signal-to-noise ratios, (2) speed, (3) higher resolution, (4) highly accurate and reproducible frequency axis, and (5) freedom from stray radiation effects.

16-9. We employ Equation 7-????.

$$\Delta\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1 = \frac{1}{\delta}$$

(a) $$\delta = \frac{1}{\Delta\bar{\nu}} = \frac{1}{0.05\ \text{cm}^{-1}} = 20\ \text{cm}$$

and the length of mirror movement = 50 cm/s = 25 cm

(b) In the same way, length = 1.25 cm

(c) Length = 0.125 cm

16-10. We write Equation 8-1 In the form

$$\frac{N_1}{N_0} = \exp\left(-\frac{E_j}{kT}\right)$$

Here we assume that the degeneracies of the upper and lower states are equal so that $g_1 = g_0$.

(a) $E_j = h\nu = hc\overline{\nu}$

$= 6.626 \times 10^{-34}$ J s × 3.00×10^{10} cm s^{-1} × 2885 cm^{-1} = 5.73×10^{-20} J.

$$\frac{N_1}{N_0} = \exp\left(\frac{-5.73\times10^{-20}\ \text{J}}{1.38\times10^{-23}\ \text{J K}^{-1}\times298\ \text{K}}\right) = 8.9\times10^{-7}$$

(b) We assume that the energy differences between the $\nu = 0$ and $\nu = 1$ states is the same as that between the $\nu = 1$ and $\nu = 2$ states. Thus the energy difference between the $\nu = 0$ and $\nu = 2$ states is $2 \times 5.73 \times 10^{-20}$ J = 11.46×10^{-20} J, and

$$\frac{N_2}{N_0} = \exp\left(\frac{-11.46\times10^{-20}\ \text{J}}{1.38\times10^{-23}\ \text{J K}^{-1}\times298\ \text{K}}\right) = 7.9\times10^{-13}$$

16-11. They are inexpensive, rugged, nearly maintenance-free, and easy to use.

16-12. The white light interferometer is eliminated in some modern instruments because the IR interferogram also has its maximum at zero retardation. This eliminates the need for a white light interferogram.

16-13. The signal-to-noise ratio (S/N) for the co-addition process increases in proportion to the square root of the number of individual interferograms that have been added (Equation 5-

11). Thus a 4-fold increase in *S*/*N* requires a 16-fold increase in the number of interferograms that must be collected and added or 16 × 16 = 256 interferograms.

16-14. According to Equation 7-24.

$$f = \frac{2\nu_{\mathrm{M}}\nu}{c}$$

(a) $$f = \frac{2\times 1.00\text{ cm s}^{-1}\times 4.8\times 10^{13}\text{ s}^{-1}}{3.00\times 10^{10}\text{ cm s}^{-1}} = 3.2\times 10^{3}\text{ s}^{-1} = 3.20\text{ kHz}$$

(b) 3.27 kHz

(c) 3.33 kHz

CHAPTER 17

17-1. (a) The wavenumber of the absorption band is (1/5.86 μm) $\times 10^4$ cm/μm = 1706 cm^{-1}.

An examination ot Table 17-3 and Figure 17-6 suggests that this band arises from the C=O group in the compound.

(b) Examination of Figure 17-1 reveals that any of the chlorinated solvents as well as cyclohexane could be used. The last is probably preferable from a cost and toxicity standpoing.

(c) If we assume that the detection limit is reached when the signal is three times the standard deviation of the blank, the smallest detectable signal will be 3 × 0.001 = 0.003. Beer's law can be written

$$A = abc$$

$$0.080 = ab \times 4.00 \text{ mg/mL}$$

$$0.003 = ab \times c_{\text{min}}$$

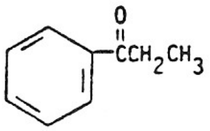
Dividing the second equation by the first allows calculation of the detection limit, c_{min}.

$$c_{\text{min}} = \frac{0.003}{0.800} \times 4.00 \text{ mg/mL} = 0.015 \text{ mg/mL}$$

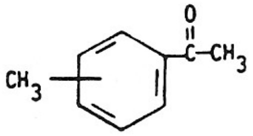
17-2. The broad band at ≈ 3400 cm^{-1} is typical of alcohols. Vinyl alcohol with a formula C_3H_6O is suggested

$CH_2{=}CH{-}CH_2{-}OH$

17-3. The strong band at 1700 cm^{-1} suggests a carbonyl group. The lack of a band at 2800 cm^{-1} favors it being a ketone. The empirical formula plus the pattern of four bands in the 1600 to 1450 cm^{-1} range is strong evidence for an aromatic structure. The band at 1250 cm^{-1} suggests an aromatic ketone. The possible structures are



and



(In fact the spectrum is for *o*-methyl acetophenone).

17-4. The strong absorption at about 1710 cm^{-1} suggests the presence of a carbonyl group while the bands just below 2800 cm^{-1} indicate that the compound contains an alkane or alkene group. The broad band at about 3500 cm^{-1} is probably an OH stretching vibration. Thus, the compound appears to be a carboxylic acid. We find, however, no low molecular weight carboxylic acid with a boiling point as low as 50°C. At table of boiling points of aldehydes, on the other hand, reveals that acrolein (CH_2=CH–CHO) has a boiling point of 52°C. It also has a sharp odor. The data are all compatible with this compound providing we assume the OH bond is a consequence of water in the sample.

17-5. The sharp band at 2250 cm^{-1} is characteristic of a nitrile or alkyne group. No evidence is found in the 1600-1450 cm^{-1} range for an aromatic structure. Thus, the bands at about 3000 cm^{-1} are probably due to aliphatic hydrogens. The pair of absorptions between 1425 and 1475 cm^{-1} is compatible with one or more alkane groups. No evidence for amine or amide groups is seen. It therefore seems likely that the compound is an alkyl nitrile. Propanenitrile ($CH_3CH_2C{\equiv}N$) boils at 97°C and seems to be a probable candidate.

17-6. For near-infrared measurements, instrumentation similar to UV-visible spectrophotometers is often used. Cell path lengths are often longer than in the midinfrared, and detectors are more sensitive. While bands are broad and overlapping in the near-infrared, chemometric software is used for multivariate calibration.

17-7. Absorption of the IR beam by the sample excites various vibrational modes. Nonradiative decay can transfer heat to the surface of the sample and result in the generation of an acoustic wave in the gas inside the chamber. A very sensitive microphone then detects the acoustic wave. The technique is most useful for solids and turbid liquids.

17-8. Reflection and absorption by cell walls and inexact cancellation of solvent absorption can result in attenuation of the beam even in regions where the analyte does not absorb. This results in transmittances in these regions less than 100%.

17-9. We use Equation 17-2

$$b = \frac{\Delta N}{2(\bar{\nu}_1 - \bar{\nu}_2)}$$

$$\bar{\nu}_1 = \frac{1}{\lambda_1} = \frac{1}{6.0\ \mu\text{m} \times 10^{-4}\ \text{cm}/\mu\text{m}} = 1667\ \text{cm}^{-1}$$

$$\bar{\nu}_2 = \frac{1}{\lambda_2} = \frac{1}{12.2\ \mu\text{m} \times 10^{-4}\ \text{cm}/\mu\text{m}} = 820\ \text{cm}^{-1}$$

$$b = \frac{15}{2(1667 - 820)\ \text{cm}^{-1}} = 8.9 \times 10^{-3}\ \text{cm}$$

17-10.

$$b = \frac{11.5}{(1580 - 1050)\ \text{cm}^{-1}} = 0.022\ \text{cm}$$

17-11. Between 2700 cm^{-1} and 2000 cm^{-1}, there are 11 minima. Thus

$$b = \frac{11}{2(700)\ \text{cm}^{-1}} = 7.9 \times 10^{-3}\ \text{cm}$$

CHAPTER 18

18-1. A virtual state is an unquantized electronic energy statethat lies between the ground state of the molecule and an excited electronic state.

18-2. Anti-Stokes scattering involves promotion of an electron in the first vibrational state of the ground electronic state to a virtual level that is greater in energy than the virtual level resulting from the promotion of an electron from the lowest vibrational level of the ground state (see Figure 18-1). The number of molecules in the first vibrational level of the ground state increases as the temperature increases. Thus, the ratio of anti-Stokes to Stokes intensity increases with increasing temperature.

18-3. Let $\bar{\nu}_{\text{st}}$ and λ_{st} be the wavenumber (cm^{-1}) and wavelength (nm) of the Stokes line and let $\bar{\nu}_{\text{as}}$ and λ_{as} be the wavenumber (cm^{-1}) and wavelength (nm) of the anti-Stokes line and let $\bar{\nu}_{\text{ex}}$ and λ_{ex} be the excitation wavenumber (cm^{-1}) and wavelength (nm)

$$\bar{\nu}_{\text{st}} = \bar{\nu}_{\text{ex}} - \Delta\bar{\nu} \qquad \text{and} \qquad \bar{\nu}_{\text{as}} = \bar{\nu}_{\text{ex}} + \Delta\bar{\nu}$$

$$\bar{\nu}_{\text{st}} = \frac{1}{\lambda_{\text{ex}}}\times 10^{7}\,\text{nm/cm} - \Delta\bar{\nu} \qquad \text{and} \qquad \bar{\nu}_{\text{as}} = \frac{10^{7}}{\lambda_{\text{ex}}} + \Delta\bar{\nu}$$

$$\lambda_{\text{st}} = \frac{10^{7}}{\bar{\nu}_{\text{st}}} = \frac{10^{7}}{10^{7}/\lambda_{\text{ex}} - \Delta\bar{\nu}} = \frac{10^{7}\lambda_{\text{ex}}}{10^{7} - \Delta\bar{\nu}\lambda_{\text{ex}}} = \frac{\lambda_{\text{ex}}}{1 - 10^{-7}\Delta\bar{\nu}\lambda_{\text{ex}}}$$

Similarly, $\lambda_{\text{as}} = \dfrac{\lambda_{\text{ex}}}{1 + 10^{-7}\Delta\bar{\nu}\lambda_{\text{ex}}}$

For $\lambda_{\text{ex}} = 632.8$ and $\Delta\bar{\nu} = 218$

$$\lambda_{\text{st}} = \frac{632.8}{1 - 218 \times 632.8 \times 10^{-7}} = 641.7 \text{ nm}$$

$$\lambda_{\text{as}} = \frac{632.8}{1 + 218 \times 632.8 \times 10^{-7}} = 624.2 \text{ nm}$$

For

	(a) λ_{ex} = 632.8 nm		(b) λ_{ex} = 488.0 nm	
$\Delta\bar{\nu}$, cm^{-1}	λ_{st}	λ_{as}	λ_{st}	λ_{as}
218	641.7	624.2	493.2	482.9
314	645.6	620.5	495.6	480.6
459	651.7	614.9	499.2	477.3
762	664.9	603.7	506.8	470.5
790	666.1	620.7	507.6	469.9

18-4. (a) The intensity of Raman lines varies directly as the fourth power of the excitation frequency. Thus,

$$I = K' \times \nu^4 = K/\lambda^4$$

For the argon ion laser

$$I_{\text{Ar}} = K/\lambda_{\text{Ar}}^4$$

For the He-Ne laser

$$I_{\text{HeNe}} = K/\lambda_{\text{HeNe}}^4$$

$$\frac{I_{\text{Ar}}}{I_{\text{HeNe}}} = \frac{K/(488.0 \text{ nm})^4}{K/(632.8 \text{ nm})^4} = \left(\frac{632.8}{488.0}\right)^4 = 2.83$$

(b) The recorded intensity ratio would differ from that calculated in (a) because the detector efficiency is wavelength dependent.

18-5. $\dfrac{N_1}{N_0} = e^{-E_j/kT}$ (Equation 8-1)

The intensity ratio of the Stokes to the anti-Stokes line (I_{as}/I_{st}) will be equl to the ratio of the number of species in the ground vibrational state species N_0 to the number in the first excited vibrational state, N_1.

(a) $\nu = \bar{\nu}c = 218\ \text{cm}^{-1} \times 3 \times 10^{10}\ \text{cm/s} = 6.54 \times 10^{12}\ \text{s}^{-1}$

$E_j = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 6.54 \times 10^{12}\ \text{s}^{-1} = 4.33 \times 10^{-21}\ \text{J}$

At 20°C = 393 K,

$$\frac{I_{as}}{I_{st}} = \frac{N_1}{N_0} = \exp\left(-\frac{4.33 \times 10^{-21}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 293\ \text{K}}\right) = 0.342$$

At 40°C = 313 K,

$$\frac{I_{as}}{I_{st}} = 0.367$$

(b) At $\Delta\bar{\nu} = 459\ \text{cm}^{-1}$, $E_j = 9.12 \times 10^{-21}$ J

At 20°C, $I_{as}/I_{st} = 0.105$

At 40°C, $I_{as}/I_{st} = 0.121$

(c) At $\Delta\bar{\nu} = 459\ \text{cm}^{-1}$, $E_j = 1.57 \times 10^{-20}$ J

At 20°C, $I_{as}/I_{st} = 0.0206$

At 40°C, $I_{as}/I_{st} = 0.0264$

18-6. (a) One reason for selecting a He-Ne laser would be that the analyte or some other component in the sample absorbs at the wavelengths available from the Ar^+ source, but not at 632.8 nm. A second reasons is that the energy of the He-Ne source is much less than that of most lines of the Ar^+ source, making the He-Ne laser the preferred source if the compound being studied undergoes photochemical decomposition or if the sample has background fluorescence excited by the Ar^+ laser.

(b) A diode laser can be operated at relatively high power without causing photodecomposition. Fluorescence is minimized or eliminated with a near-infrared source.

(c) Ultraviolet emitting sources are usually avoided because they can cause photodecomposition of many samples and are energetic enough to excite fluorescence.

18-7. (a) $p = \frac{I_\perp}{I_\parallel} = \frac{0.46}{0.60} = 0.77$

(b) $\frac{I_\perp}{I_\parallel} = \frac{0.1}{8.4} = 0.012$ polarized

(c) $\frac{I_\perp}{I_\parallel} = \frac{0.6}{7.9} = 0.076$ polarized

(d) $\frac{I_\perp}{I_\parallel} = \frac{3.2}{4.2} = 0.76$

18-8. The FT-Raman spectrometer uses an infrared source (usually a Nd/YAG laser) which virtually eliminates fluorescence and photodecomposition. The FT-Raman instrument provides superior frequency precision which allows spectral subtractions and high resolution measurements. However, the detectors used with FT-Raman instruments (photoconductive devices such as InGaAs and Ge) are not as sensitive as detectors used in the visible and near-IR (photomultipliers and CCDs). Water also absorbs in the 1000 nm region which can cause difficulties with aqueous samples. Because a large aperture interferometer is used, extensive filtering to eliminate the laser line and Rayleigh scattering is a necessity with FT-Raman instruments.

CHAPTER 19

19-1. In a continuous wave NMR experiment, the intensity of the absorption signal is monitored as the frequency of the source or the field strength of the magnet is scanned. In a Fourier Transform NMR experiment, the analyte is subjected to periodic pulses of radio-frequency radiation. After each pulse, the decay of the emitted signal is monitored as a function of time. This free induction decay signal is then converted to a frequency domain signal by a Fourier Transformation.

19-2. On of the advantages of Fourier Transform NMR is much greater sensitivity, which results in marked improvements in signal-to-noise ratios. This makes possible recording proton spectra on microgram quantities of sample and carbon-13 spectra on samples that contain the isotope in natural abundance concentrations. Another advante is a significant reduction in time required to record spectra. The frequency reproducibility is also greater as is the resolution. The main disadvantage of Fourier Transform NMR instruments is their cost.

19-3. First, if the line width is constant, resolution improves with field strength. Second, sensitivity improves with field strength according to Equation 19-8. Third, as the $\Delta\nu/J$ ratio increases, spectral interpretation becomes easier.

19-4. By varying the magnetic field strength. Spin-spin splitting is independent of the magnetic field strength, whereas chemical shifts increase with increases in field strength.

19-5. (a) Magnetic anisotropy is a property of a molecule having magnetic properties that vary with molecular orientation.

(b) The screening constant σ is a measure of the degree to which circulation of electrons around the nucleus reduce (or sometimes increase) the magnetic field felt by the nucleus. It is defined by the equation

$$\sigma = \frac{B_{\mathrm{appl}} - B_0}{B_0}$$

where B_{appl} is the external field and B_0 is the field felt by the nucleus.

(c) The chemical shift parameter measures the shift in parts per million of the peak for a given nucleus from that of a reference (usually TMS). It is defined by Equations 19-18 and 19-19

$$\delta = \left(\frac{\nu_{\mathrm{r}} - \nu_{\mathrm{s}}}{\nu_{\mathrm{r}}} \right) \times 10^6$$

where ν_{r} and ν_{s} are the resonance frequencies of the reference and sample, respectively.

(d) Continuous wave NMR measurements are performed by measuring the amplitude of the NMR signal as the radio frequency of the source is varied or the field strength of the magnet is scanned.

(e) The Larmor frequency ν_0 is the frequency of precession of a nucleus in an external field. It is given by

$$\nu_0 = \gamma B_0/2\pi$$

where γ is the magnetogyric ratio for the nucleus and B_0 is the magnetic field at the nucleus.

(f) The coupling constant is the spacing in frequency units between the peaks produced by spin-spin splitting.

(g) First-order NMR spectra are those in which the chemical shift between interacting groups $\Delta\nu$ is large with respect to their coupling constant ($\Delta\nu/J > 10$).

19-6. The number of magnetic energy states is given by $2I + 1$, where I is the spin quantum number. Thus, the number of energy states is $2(5/2) + 1 = 6$, and the magnetic quantum number of each is +5/2, +3/2 , +1/2, –1/2, –3/2, and –5/2.

19-7. $\nu_0 = \gamma B_0/2\pi$

(a) For ^{1}H, $\gamma = 2.68 \times 10^8$ T^{-1}s^{-1} (Table 19-1) and

$$\nu_0 = \frac{2.68 \times 10^8\ \text{T}^{-1}\text{s}^{-1} \times 7.05\ \text{T}}{2\pi} = 3.007 \times 10^8\ \text{Hz} = 300.7\ \text{MHz or } 301\ \text{MHz}$$

(b) For ^{13}C, $\gamma = 6.73 \times 10^7$ T^{-1}s^{-1} and $\nu_0 = 75.5$ MHz

(c) For ^{19}F, $\gamma = 2.52 \times 10^8$ T^{-1}s^{-1} and $\nu_0 = 283$ MHz

(d) For ^{31} P, $\gamma = 1.08 \times 10^8$ T^{-1}s^{-1} and $\nu_0 = 121$ MHz

19-8. $\nu_0 = \gamma B_0/2\pi$

(a) At 1.41 T, $\nu_0 = \dfrac{2.68 \times 10^8\ \text{T}^{-1}\text{s}^{-1} \times 1.41\ \text{T}}{2\pi} = 60.1 \times 10^6$ Hz or 60 MHz

(b) At 4.69 T, $\nu_0 = \dfrac{2.68 \times 10^8\ \text{T}^{-1}\text{s}^{-1} \times 4.69\ \text{T}}{2\pi} = 200 \times 10^6$ Hz or 200 MHz

(c) At 7.05 T, $\nu_0 = 301$ MHz (see answer to Problem 19-7)

(d) At 11.7 T, $\nu_0 = 499$ MHz

(e) At 18.8 T, $\nu_0 = 802$ MHz

(f) At 21.2 T, $\nu_0 = 904$ MHz

19-9. The frequency difference is directly proportional to the magnetic field strength (see Equations 19-14 and 19-15).

(a) At 4.69 T, $\Delta\nu$ = 90 Hz × 4.69/1.41 = 299 Hz

(b) At 7.05 T, $\Delta\nu$ = = 90 Hz × 7.05/1.41 = 450 Hz

(c) At 18.8 T, $\Delta\nu$ = 90 Hz × 18.8/1.41 = 1200 Hz

Since δ is independent of field strength B_0, a 90 Hz shift at 60 MHz is a δ value of

$$\delta = \left(\frac{90\text{ Hz}}{60 \times 10^6\text{ Hz}}\right)\times 10^6 = 1.5$$

This will be the same at the other magnetic field values.

19-10. Because of the natural abundance of ^{13}C, it is highly improbable that two ^{13}C atoms will be adjacent to one another in ordinary organic compounds. Hence, ^{13}C spin-spin splitting is not observed.

19-11. Here, we employ Equation 19-7 and write

$$\frac{N_j}{N_0} = \exp\left(\frac{-\gamma h B_0}{2\pi kT}\right) = \exp\left(-\frac{6.73\times 10^7\text{ T}^{-1}\text{s}^{-1}\times 6.626\times 10^{-34}\text{ J s}\times 7.05\text{ T}}{2\pi\times 1.38\times 10^{-23}\text{ J K}^{-1}\times 298\text{ K}}\right)$$

$$= \exp(-1.217 \times 10^{-5)} = 0.9999878$$

19-12. Longitudinal, or spin-lattice, relaxation arises from the complex magnetic fields that are generated by the rotational and vibrational motions of the host of other nuclei making up a sample. At least some of these generated magnetic fields must correspond in frequency and phase with that of the analyte nucleus and can thus convert it from the higher to the lower spin state. Transverse, or spin-spin, relaxation, in contrast is brought about by interaction between neighboring nuclei having identical precession rates but different magnetic quantum states. Here, the nucleus in the lower spin state is excited while the excited nucleus relaxes. Not net change in the spin state population occurs, but the average lifetime of a particular excited nucleus is shortened.

19-13. The radio-frequency excitation pulse in FT NMR causes the sample magnetization vector to tip away from the direction of the external magnetic field. When the pulse terminates, the same magnetic moment rotates around the external field axis at the Larmor frequency. This motion constitutes a radio-frequency signal that decays to zero as the excited nuclei relax. This decreasing signal is the free induction decay (FID) signal.

19-14. A rotating frame of reference consists of a set of mutually perpendicular coordinates (usually labeled x', y' and z') in which the x' and y' coordinates rotate at a constant rate around the z' coordinate.

19-15. Writing Equation 19-4 for the two nuclei gives

$$\Delta E(^{13}\mathrm{C}) = \gamma_{\mathrm{C}} hB_0/2\pi = 6.73 \times 10^7\ hB_0/2\pi$$

$$\Delta E(^{1}\mathrm{H}) = \gamma_{\mathrm{H}} hB_0/2\pi = 2.68 \times 10^8\ hB_0/2\pi$$

Dividing the first equation by the second gives

$$\frac{\Delta E(^{13}\mathrm{C})}{\Delta E(^{1}\mathrm{H})} = 0.251$$

19-16. (a) $\gamma_{\mathrm{F}} = 2.5181 \times 10^8\ \mathrm{T^{-1}s^{-1}}$

$$\nu_0 = \gamma_{\mathrm{F}}\mathrm{B}_0/2\pi = 2.5181 \times 10^8\ \mathrm{T^{-1}s^{-1}} \times 7.05\ \mathrm{T}/(2\pi) = 283\ \mathrm{MHz}$$

(b) $\gamma_{\mathrm{P}} = 1.0841 \times 10^8\ \mathrm{T^{-1}s^{-1}}$

$$\nu_0 = 1.0841 \times 10^8\ \mathrm{T^{-1}s^{-1}} \times 7.05\ \mathrm{T}/(2\pi) = 122\ \mathrm{MHz}$$

19-17. $$\frac{N_j}{N_0} = \exp(-\Delta E / kT)$$

For the proton in a 500 MHz instrument

$$\nu_0 = \frac{\gamma_{\mathrm{H}} B_0}{2\pi} \qquad \text{and} \qquad B_0 = \frac{2\pi\nu_0}{\gamma_{\mathrm{H}}}$$

For ^{13}C

$$\Delta E = \frac{\gamma_{\mathrm{C}} h B_0}{2\pi} = \frac{\gamma_{\mathrm{C}} h}{2\pi} \times \frac{2\pi\nu_0}{\gamma_{\mathrm{H}}} = \frac{\gamma_{\mathrm{C}}}{\gamma_{\mathrm{H}}} \times h\nu_0$$

and $\dfrac{N_j}{N_0} = \exp\left(-\dfrac{\gamma_{\mathrm{C}}}{\gamma_{\mathrm{H}}} \times \dfrac{h\nu_0}{kT}\right) = \exp\left(-\dfrac{6.73\times10^{7}\times6.626\times10^{-34}\ \mathrm{J\,s}\ 500\ \times\ 10^{6}\ \mathrm{Hz}}{2.68\times10^{8}\times1.38\times10^{-23}\,\mathrm{J\,K^{-1}}\times300\ \mathrm{K}}\right)$

$= \exp(-2.0096 \times 10^{-5}) = 0.99998$

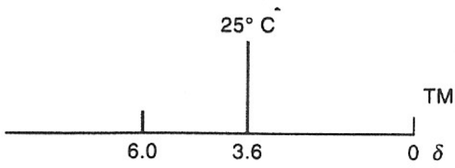
19-18. For ^{1}H, $\nu_0 = \gamma_{\mathrm{H}} B_0/2\pi = 2.68 \times 10^{8}\ \mathrm{T^{-1}s^{-1}} \times 4.69/2\pi = 200$ MHz

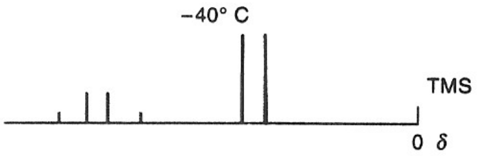
For ^{31}P, $\nu_0 = \gamma_{\mathrm{P}} B_0/2\pi = 1.08 \times 10^{8}\ \mathrm{T^{-1}s^{-1}} \times 4.69/2\pi = 80$ MHz

The lower frequency at which ^{31}P resonates means that the energy gap for this nucleus is smaller than that of the proton. Therefore, the net magnetization vector for ^{31}P will be smaller and the signal per atom for ^{31}P will be lower even though isotopic abundances are approximately the same. This means that the ^{1}H signal will be much more intense than that due to ^{31}P.

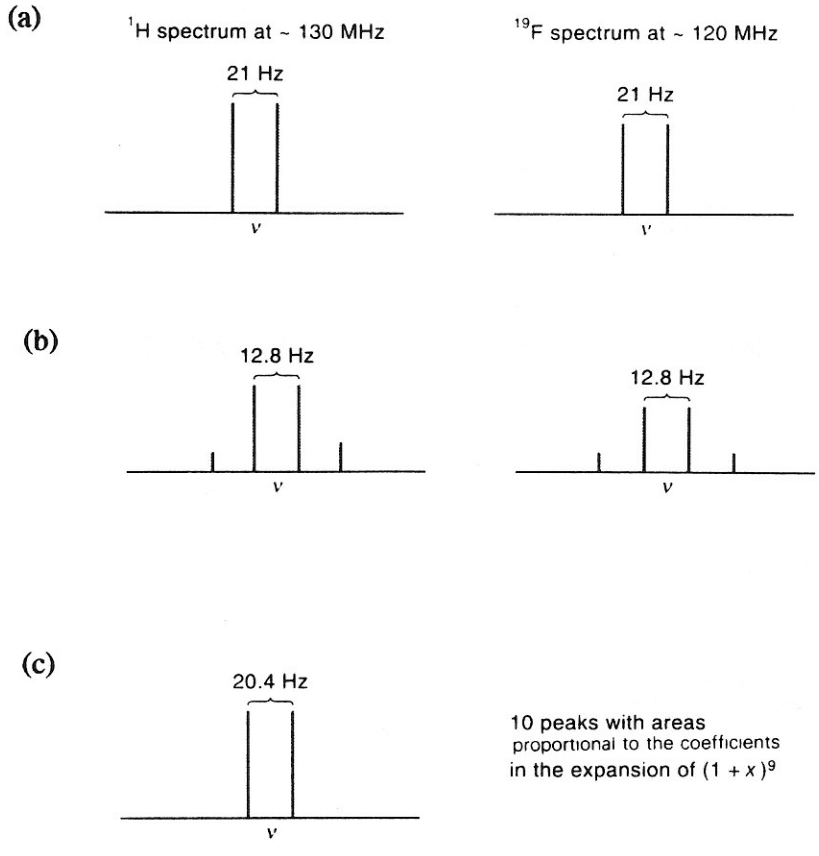
Weak spin-spin coupling means the ^{1}H signal will be split into a doublet while the ^{31}P signal will be given as the coefficients of the expansion of $(1 + x)^9$.

19-19. According to entries 21 and 23 in Figure 19-17, the chemical shifts in methanol should be ~3.6 ppm and ~6.0 ppm for the methyl and hydroxyl protons, respectively. In reality both of these are considerably different than their empirical values, but the order is correct and will thus be used.



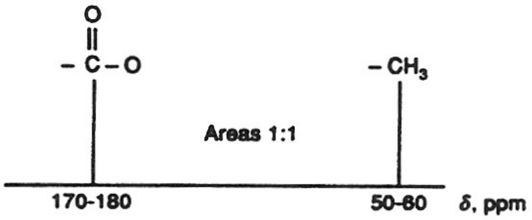


19-20.

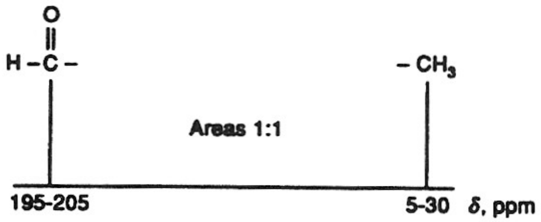


19-21. The data in Figure 19-29 are used for assigning chemical shifts.

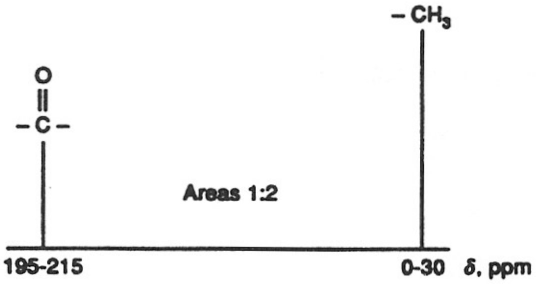
(a)



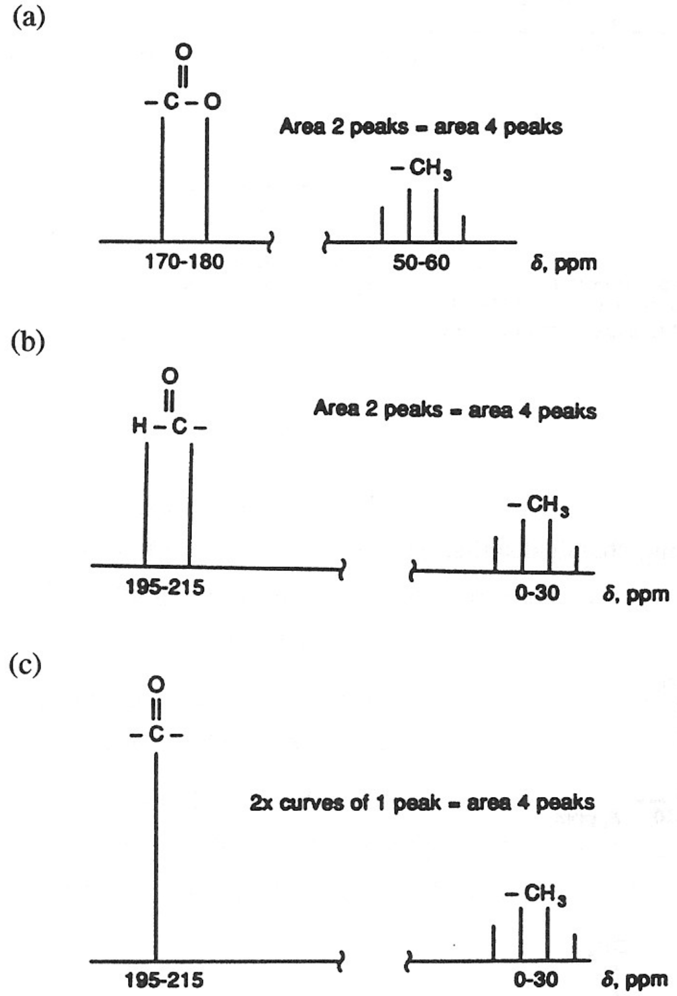
(b)



(c)



19-22. We assume in the figures below that ^1H only couples to the ^{13}C to which it is bonded.



19-23. A field frequency lock system is used in NMR instruments in order to overcome the effect of magnetic field fluctuations. In this device, a reference nucleus is continuously irradiated, and its output signal is continuously monitored at its resonance maximum. Changes in the intensity of this signal control a feedback circuit, the output of which is fed into coils to correct for drift in the magnetic field. The drift correction is applicable to signals for all types of nuclei because the ratio of field strength to resonance frequency is constant and independent of the type of nuclei.

19-24. Shim coils are pairs of wire loops through which carefully controlled currents are passed. These produce small magnetic fields that compensate for inhomogeneities in the primary magnetic field.

19-25. Liquid samples in NMR are spun along their longitudinal axis to overcome the effects of small field inhomogeneities. In this way, nuclei experience an averaged environment that produces less band broadening.

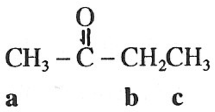
19-26. CH_3CH_2COOH

From Table 19-2 and Figure 19-17, we deduce that the carboxylic acid proton should produce a single peak at $\delta = 11$ to 12. The methylene proton should produce four peaks (area ratio = 1:3:3:1) centered about $\delta = 2.2$, and the methyl proton three peaks (area ratio 1:2:1) at about $\delta = 1.1$.

19-27. (a) Acetone-$(CH_3)_2C{=}O$ Because all the protons are identical there should be a single peak at about $\delta = 1.6$.

(b) acetaldehyde-CH_3CHO The single proton should produce four peaks (area ratio 1:3:3:1) at $\delta = 9.7$ to 9.8; the methyl protons should yield a doublet at $\delta = 2.2$.

(c) methyl ethyl ketone-

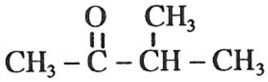


$$\underset{a}{CH_3} - \overset{O}{\overset{\|}{C}} - \underset{b}{CH_2}\underset{c}{CH_3}$$

The protons on carbon atom **a** will yield a singlet at $\delta = 2.1$. The protons on atom **b** should yield a quartet (1:3:3:1) at about $\delta = 2.4$, while the proton on atom **c** will give triplet peaks (1:2:1) at $\delta = 1.1$.

19-28. (a) Ethyl nitrite-$CH_3CH_2NO_2$ The methylene protons should yield a quartet (area ratio 1:3:3:1) centered about $\delta = 4.4$; the methyl protons should give a triplet (ratio 1:2:1) centered about $\delta = 1.6$.

(b) Acetic acid-CH_3COOH The carboxylic acid proton should produce a single peak at $\delta = 11$ to 12, while the three methyl protons should also give a singlet at $\delta = 2.2$.

(c) methyl-*i*-propyl ketone 

$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

The methyl group adjacent to the carbonyl will give a singlet at $\delta = 2.1$. The other six methyl protons will yield a doublet (1:1), while the single proton should yield seven peaks centered at $\delta = 2.6$.

19-29. (a) Cyclohexane-C_6H_{12} All the protons are equivalent. Thus, the compound will yield a singlet at $\delta = 1.2$ to 1.4.

(b) Diethyl ether-$CH_3CH_2OCH_2CH_3$ The two methylene protons should give rise to a quartet at about $\delta = 3.4$. The methyl protons should produce a triplet at $\delta = 1.2$.

(c) 1,2-dimethoxyethane-$CH_3OCH_2CH_2OCH_3$ The protons on the two methyl groups should yield a singlet at $\delta = 3.2$. The protons on the other two carbon atoms will also yield a single peak at $\delta = 3.4$. The ratio of peak areas should be 6:4.

19-30. (a) Toluene-$C_6H_5CH_3$ The five aromatic ring protons will produce a single peak at $\delta = 6.5$ to 8. The three methyl protons will produce a triplet at $\delta = 2.2$.

(b) Ethyl benzene-$C_6H_5CH_2CH_3$ The five aromatic ring protons will produce a single peak at $\delta = 6.5$ to 8. The two methylene protons will yield a quartet centered at $\delta = 2.6$. The methyl proton will give a triplet at $\delta = 1.1$.

(c) *i*-butane-$(CH_3)_3CH$ The nine methyl protons should appear as a doublet at $\delta = 0.9$. The single proton will appear as ten peaks centered at about $\delta = 1.5$.

19-31. The triplet patterns at $\delta = 1.6$ to 1.7 suggest a methyl group with a brominated methylene group in the α position. The quartet at $\delta = 3.4$ would then arise from the protons on the methylene group. The compound is ethyl bromide-CH_3CH_2Br.

19-32. The empirical formula and the peak at $\delta = 11$ suggests a carboxylic acid. The triplet at $\delta = 1.1$ would appear to be a methyl group adjacent to a methylene group. The upfield triplet at $\delta = 4.2$ is compatible with a —CHBr— group. Thus the compound is

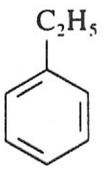
$\mathrm{CH_3CH_2}\overset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}\mathrm{HCOOH}$

19-33. The strong singlet suggests a methyl group adjacent to a carbonyl group. The absence of a peak at $\delta > 9.7$ eliminates the possibility of an aldehyde group and suggests the compound is a ketone. The four peaks at $\delta = 2.5$ would appear to be from a methylene group adjacent to a methyl group as well as a carbonyl group (ketone). Thus, the compound appears to be methyl ethyl ketone.

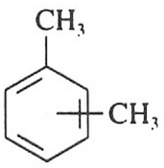
19-34. The strong singlet at $\delta = 2.1$ and the empirical formula suggests a methyl group adjacent to a —COOR group. The triplet and quartet structure is compatible with an ethylene group. Thus, the compound appears to be ethyl acetate.

19-35. The peaks at $\delta = 7$ to 7.5 suggest an aromatic ring as does the empirical formula. If this is true, the compounds must be isomers having the formula $C_6H_5C_2H_5$ and would be either

(a)

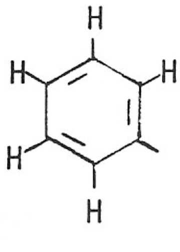


(b)



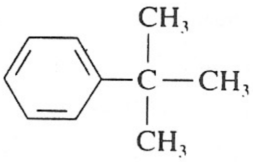
The triplet and quartet splitting in Figure 19-43a is compatible with the ethylene group in ethyl benzene (a). Thus the spectrum in Figure 19-43b must be for one of the dimethylbenzene isomers (b).

19-36. A notable feature of the NMR spectrum in Figure 19-44 is the broad peak at $\delta = 7.2$ corresponding to five protons; a monosubstituted aromatic ring is suggested. The other signal is a sharp single at $\delta = 1.3$ with an area of nine protons. The chemical shigt of this singlet indicates a saturated methyl group. The methyl groups cannot be attached to any electron withdrawing substituents or it would be shifted further downfield. Since the integrated area corresponds to nine protons, it seems likely that the compound contains three equivalent methyl groups. We now know that this unknown contains the following pieces.

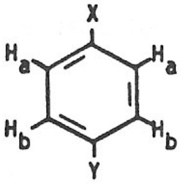


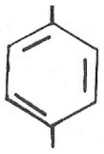
CH_3 CH_3 CH_3

When these are combined with the addition of one carbon, we get *t*-butyl benzene



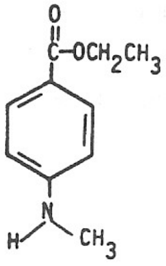
19-37. The set of signals between $\delta = 6.5$ and 8.0 immediately suggests an aromatic ring. It is clear that the ring must be disubstituted and the splitting pattern is indicative of para substitution. A para substituted ring gives this characteristic pattern because the two types of protons, H_a and H_b are together to give two doublets. This compound must also contain an ethyl group which causes the triplet at $\delta = 1.3$ and the quartet at $\delta = 4.0$ The chemical shift of this quartet is considerably further downfield than expected for a saturated ethyl group. This shift suggests that the ethyl group must be bonded to a strongly electronegative atom such as an oxygen. The singlet at $\delta = 2.1$ is probably a methyl group on an electronegative atom. The broad singlet at $\delta = 9.5$ is most likely due to a proton on an oxygen or nitrogen. The foregoing analysis yields the following parts:



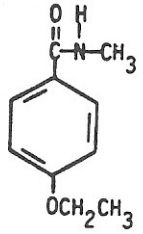


$$+ \quad OCH_2CH_3 \quad + \quad X-H \quad + \quad X-CH_3 \quad = \quad C_9H_{13}O$$

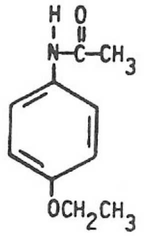
The empirical formula is $C_{10}H_{13}NO_2$ so we still need to account for $C_1O_1N_1$. A carbonyl group would account for the C and the O. When these pieces are assembled, several possible structures emerge:



(I)



(II)



(III)

However, the problem states that the unknown is a common painkiller, which indicates that phenacetin (structure III) is the correct answer. In the absence of this information, all three structures given are equally correct interpretations of the NMR spectrum.

19-38. A monochromatic source that is pulsed for τ seconds can be shown to be made up of a band of frequencies having a range of $1/\tau$ Hz (see Figure 6-????). If a 100 MHz instrument is used, the entire carbon-13 spectrum would require a frequency bandwidth Δf of

$$100 \times 10^6 \text{ Hz} \times \frac{200 \text{ Hz}}{10^6 \text{ Hz}} = 2 \times 10^4 \text{ Hz}$$

$$\Delta f = 1/(4\tau) \quad \text{or} \quad \tau = 1/(4\,\Delta f)$$

$$\tau = 1/(4 \times 2 \times 10^4 \text{ s}^{-1}) = 1.25 \times 10^{-5} \text{ s} \quad (12.5\ \mu\text{s})$$

13-39. Folded spectral lines are obtained when the sine or cosine waves making up the signal are sampled less than twice each cycle for Fourier transformation. The consequence of folding is the appearance of spurious bands at lower frequencies.

19-40. The nuclear Overhauser effect involves the enhancement of carbon-13 peak areas brought about by broad-band proton decoupling. The effect arises from direct magnetic coupling between decoupled protons and neighboring carbon-13 nuclei. This interaction results in an increase in the population of the lower-energy state carbon-13 nuclei. An enhancement of the carbon-13 signal by as much as a factor of three results.

19-41. One cause of band broadening in solids is dipolar interactions between carbon-13 and proton nuclei. In liquids, these interactions are averaged to zero by the rapid and random motion of molecules. In solids, dipolar interactions between the two types of nuclei result in splittings of peaks, which vary depending on the angle between C—H bonds and the external field. In solids a large number of orientations of the bonds exist, and hence a large number of splittings can occur producing a broad absorption band made up of closely spaced peaks. This type of broadening can be avoided by irradiating the sample with high-power level proton frequencies. This procedure, called dipolar decoupling, is similar to spin decoupling except that much higher power levels are used.

A second cause of band broadening in solids is chemical shift anisotropy, which is discussed in Section 19B-2. The broadening here results from changes in the chemical shift with orientation of the molecule or part of the molecule with respect to the external magnetic field. This type of broadening in solids is eliminated by magic angle spinning in which the sample is spun at greater than 2 kHz at an angle of 57.4 deg with respect to the direction of the applied magnetic field.

CHAPTER 20

20-1. With gaseious ionization sources, the sample is first volatilized (by heating if necessary) and then transmitted to the ionization area for ionization. In a desorption source, a probe is used and ionization takes place directly from the condensed phase. The advantage of desorption ionization is that it can be applied to high molecular weight and thermally unstable samples. The advantage of gaseous ionization sources are their simplicity and speed (no need to use probe and wait for probed area to be pumped out).

20-2. The most fragementation and thus the most complex spectra are encountered with electron impact ionization. Field ionization produces the simplest spectra. Chemical and electron impact ionization result in higher sensitivities than does field ionization.

20-3. Both field ionization and field desoprtion ionization are performed at anodes containing numerous sharp tips so that very high electrical fields are realized. In field ionization, the sample is volatilized before ionization, whereas field desorption takes place an an anode that has been coated with the sample. The latter requires the use of a sample probe.

20-4. (a) The total kinetic energy acquired by an electron moving between the filament and the target will be eV, where e is the charge on the electron and V is the potential difference. Because *SS* is approximately half way between the filament and the target, the total difference in potential must be 140 V, if the electron is to have 70 eV of energy at *SS*.

(b) An ion formed at point *P* will almost certainly collide with a solid part of the exit slit as a reulst of the repeller-accelerating plate voltage.

20-5. (a) For CH_4^+, $m/z = 16$ and

$$16 = \frac{B^2 r^2 e}{2V} = kB^2 = k \times (0.126\ \text{T})^2 \qquad \text{(Equation 20-9)}$$

Similarly for *m*/*z* = 250

$$250 = kB^2$$

Dividing the second equation by the first yields

$$\frac{250}{16} = \frac{B^2}{(0.126\ \text{T})^2}$$

$$B = 0.498\ \text{T}$$

Thus, to scan the range of *m*/*z* from 16 to 250, the field strength would be scanned from 0.126 to 0.498 T.

(b) Here, Equation 20-9 takes the form

$$16 = \frac{B^2 r^2 e}{2V} = \frac{k'}{V} = \frac{k'}{3.00 \times 10^3}$$

At *m*/*z* = 250

$$250 = k'/V$$

Dividing the first equation by the second gives

$$\frac{16}{250} = \frac{k'/3.00 \times 10^3}{k'/V} = \frac{\text{V}}{3.00 \times 10^3}$$

or

$$V = 16 \times 3.00 \times 10^3/250 = 192\ \text{V}$$

Thus, scan from 3000 to 192 V.

20-6. Here,

$$m = 7500\ \frac{\text{g}}{\text{mol}} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{ions}} \times \frac{1\ \text{kg}}{10^3\ \text{g}} = 1.246 \times 10^{-23}\ \frac{\text{kg}}{\text{ion}}$$

Substituting into Equation 20-9 gives, after rearranging,

$$V = \frac{(0.240\ \text{Vs/m}^2)^2(0.127\ \text{m})^2\ \times\ 1.60\ \times\ 10^{-19}\ \text{C/ion}}{2\ \times\ 1.246\ \times\ 10^{-23}\ \text{kg/ion}} = 5.96\ \frac{(\text{Vs})^2\text{C}}{\text{m}^2\text{kg}} = 5.97\ \text{V}$$

20-7. After acceleration the velocity *v* can be calculated with the aid of Equation 20-4. Thus,

$$\text{zeV} = ½\, mv^2$$

where *m* for cyclohexane ($\mathcal{M} = 84$) is given by

$$m = 84.0\ \frac{\text{g C}_6\text{H}_{12}^+}{\text{mol}} \times \frac{1\ \text{mol}}{6.02\ \times\ 10^{23}\ \text{ions}} \times \frac{1\ \text{kg}}{10^3\ \text{g}} = 1.395\ \times\ 10^{-25}\ \frac{\text{kg}}{\text{ion}}$$

$$v = \sqrt{\frac{2zeV}{m}} = \sqrt{\frac{2\ \times\ 1.60\ \times\ 10^{-19}\ \text{C/ion}\ \times\ 5.00\ (\text{Vs})^2\text{C/(m}^2\text{kg)}}{1.395\ \times 10^{-25}\ \text{kg/ion}}} = 3.39\ \times\ 10^3\ \text{m/s}$$

$$\text{time} = \frac{15.0\ \text{cm}\ \times\ 10^{-2}\ \text{m/cm}}{3.39\ \times\ 10^3\ \text{m/s}} = 4.43\ \times\ 10^{-5}\ \text{s} = 44.3\ \mu\text{s}$$

20-8. The presence of a negative dc voltage in the *yz* plane causes positive ions to move toward the rods where they are annihilated. In the presence of an added ac voltage, this movement is inhibited during the positive half of the cycle with the lighter ions being more affected than the heavier ions. Thus the *yz* plane acts as a low-pass filter removing heavier ions (see Figure 11-????).

20-9. The resolution of a single focusing mass spectrometer is limited by the initial kinetic energy spread of the sample molecules. This spread is minimized in a double focusing instrument by accelerating the sample through an electrostatic analyzer, which limits the range of kinetic energies of ions being introduced into the magnetic sector analyzer. Signicantly narrower peaks are the result.

20-10. A quadrupole ion trap is similar to a linear quadrupole filter except it as a spherical 3-dimensional configuration. By a combination of fields, ions are temporarily stored within the trap. They are then released sequentially by increasing the radio frequency voltage applied to the ring electrode. The ejected ions then strike a detector. A plot of detector signal vs. the radio frequency voltage, related to the m/z value, is the mass spectrum. In an FT ICR instrument, ions are trapped in a cell by an electric trapping voltage and a magnetic field. Each ion assumes a circular motion in a plane perpendicular to the direction of the field. The cyclotron frequency depends on the inverse of the m/z value. In modern instruments a radio frequency pulse that increases linearly in frequency is employed. A time domain image current is generated after termination of the pulse. Fourier transformation of the time decay signal yields the mass spectrum.

20-11. Resolution = $m/\Delta m$

(a) $m = (28.0187 + 28.0061)/2 = 28.012$

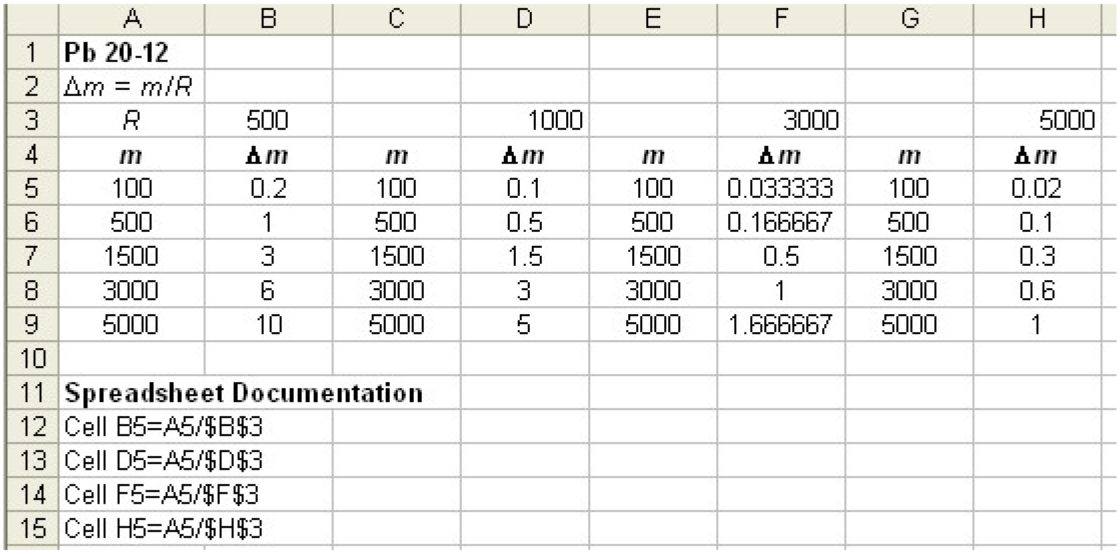
$m/\Delta m = 28.012/(28.0187 - 28.0061 = 2.22 \times 10^3$

(b) $m/\Delta m = 28.013/(28.0313 - 27.9949) = 770$

(c) $m/\Delta m = 85.0647/(85.0653 - 85.0641) = 7.09 \times 10^4$

(d) $m/\Delta m = 286.158/(286.1930 - 286.1240) = 4.15 \times 10^3$

20-12.



	A	B	C	D	E	F	G	H
1	**Pb 20-12**							
2	$\Delta m = m/R$							
3	R	500		1000		3000		5000
4	m	Δm	m	Δm	m	Δm	m	Δm
5	100	0.2	100	0.1	100	0.033333	100	0.02
6	500	1	500	0.5	500	0.166667	500	0.1
7	1500	3	1500	1.5	1500	0.5	1500	0.3
8	3000	6	3000	3	3000	1	3000	0.6
9	5000	10	5000	5	5000	1.666667	5000	1
10								
11	**Spreadsheet Documentation**							
12	Cell B5=A5/$B$3							
13	Cell D5=A5/$D$3							
14	Cell F5=A5/$F$3							
15	Cell H5=A5/$H$3							

20-13. (a) In Table 20-3, we find that for every 100 ^{79}Br atoms there are 98 ^{81}Br atoms.

Because the compound in question has two atoms of bromine

$$(M + 2)^+/M^+ = 2 \times 98/100 = 1.96$$

and

$$(M + 4)^+/M^+ = (98/100)^2 = 0.96$$

(b) Table 20-3 reveals that for every 100 ^{35}Cl atoms there are 32.5 ^{37}Cl atoms. Thus,

$$(M + 2)^+/M^+ = (1 \times 98/100) + (1 \times 32.5/100) = 1.30$$

$$(M + 4)^+/M^+ = (1 \times 98/100) \times (1 \times 32.5/100) = 0.32$$

(c) $$(M + 2)^+/M^+ = 2 \times 32.5/100 = 0.65$$

$$(M + 4)^+/M^+ = (0.325/100)^2 = 0.106$$

20-14. (a) Because all conditions except accelerating voltage are constant, Equation 20-9 can be abbreviated to $(m/z)_s = K/V_s$ and $(m/z)_u = K/V_u$

where the subscripts s and u designate standard and unknown respectively. Dividing one of these equations by the other gives the desired relationship.

$$\frac{(m/z)_\mathrm{s}}{(m/z)_\mathrm{u}} = \frac{K/V\mathrm{s}}{K/V_u} = \frac{V_\mathrm{u}}{V_s}$$

(b) $$\frac{69.00}{(m/z)_\mathrm{u}} = 0.965035$$

$(m/\mathrm{z})_\mathrm{u} = 71.50$

(c) The approximately half-integral *m*/*z* value suggests that the ion being studied in part (b) was doubly charged. This conclusion is in agreement with the fact that the molecular mass of the unknown is 143. The second conclusion is that the unknown must contain an odd number of nitrogen atoms.

20-15. The difference in mass between ^{12}C and ^{13}C is 1.00335. Therefore, making the assumption that $(\mathrm{P} + 1)^+$ is due only to ^{13}C means

mass $(\mathrm{P} + 1)^+ =$ mass $\mathrm{P}^+ + 1.00335$

In Problem 20-14, we derived the following relationship

$$\frac{(m/z)_\mathrm{s}}{(m/z)_\mathrm{u}} = \frac{V_\mathrm{u}}{V_s}$$

Taking into accound the fact that only singly charged ions were specified, and rewriting this equation with V_1 representing the standard and V_2 the unknown, we find

$$\frac{m(\mathrm{P}^+)}{m(\mathrm{P}+1)^+} = \frac{m(\mathrm{P}^+)}{m(\mathrm{P}^+)+1.00335} = \frac{V_2}{V_1}$$

(b) Substituting the voltage ratio into the last equation allows $m(\mathrm{P}^+)$ to be calculated

$$\frac{m(\mathrm{P}^+)}{m(\mathrm{P}^+)+1.00335} = \frac{V_2}{V_1} = 0.987753$$

$m(P^+) = 80.92$

20-16. In tandem in space instruments, two independent mass analyzers are used in two different regions in space. This is a rather straight-forward way to do tandem ms and some conventional mass spectrometers can be converted to tandem instruments. The advantages are that it is relatively easy to take all the different types of spectra (product ion, precursor ion, neutral loss, multidimensional. The disadvantages are that the efficiency can be very low and thus the sensitivity can be low. Tandem in time instruments form the ions in a certain spatial region and then at a later time expel the unwanted ions and leave the selected ions to be dissociated and mass analyzed in the same spatial region. The efficiency can be fairly high and the process can be repeated many times. It is, however, only straight forward to take product ion spectra. Both approaches require quite expensive instrumentation.

20-17. $m/z = 131$ due to ${}^{35}Cl_3CCH_2^+$

$m/z = 133$ due to ${}^{37}Cl{}^{35}Cl_2CCH_2^+$

$m/z = 135$ due to ${}^{37}Cl_2{}^{35}ClCCH_2^+$

$m/z = 117$ due to ${}^{35}Cl_3C^+$

$m/z = 119$ due to ${}^{37}Cl{}^{35}Cl_2C^+$

$m/z = 121$ due to ${}^{37}Cl_2{}^{35}ClC^+$

20-18. $m/z = 84$ due to ${}^{35}Cl_2C^+$

$m/z = 85$ due to ${}^{35}Cl_2{}^{13}CH_2^+$

$m/z = 86$ due to ${}^{37}Cl{}^{35}Cl{}^{12}CH_2^+$

$m/z = 87$ due to ${}^{37}Cl{}^{35}Cl{}^{13}CH_2^+$

$m/z = 88$ due to ${}^{37}Cl_2{}^{12}CH_2^+$

CHAPTER 21

21-1. An M electron is ejected by X-radiation or by a beam of electrons. An N electron then descends to the M orbital while ejected a second N electron as an Auger electron.

21-2. Auger and XPS peaks can be distinguished by comparing spectra obtained with two different sources (such as an Al and Mg tube). Auger peaks are unaffected by the change in sources whereas XPS peaks are displaced by the change.

21-3. The XPS binding energy is the minimum energy required to remove an inner electron from its orbital to a region where it no longer feels the nuclear charge. The absorption edge results from this same transition. Thus, in principle it is possible to observe chemical shifts by either type of measurement.

21-4. (a) $E_b = h\nu - E_k - w$ (Equation 21-2)

To obtain $h\nu$ in eV,

$$h\nu = \frac{hc}{\lambda} = \frac{6.6256 \times 10^{-34}\ \text{Js} \times 2.9979 \times 10^{8}\ \text{m/s}}{0.98900\ \text{nm} \times 10^{-9}\ \text{m/nm}} \times 6.2418 \times 10^{18}\ \frac{\text{eV}}{\text{J}}$$

$= 1253.6$ eV

$E_b = 1253.6 - 1073.5 - 14.7 = 165.4$ eV

(b) From Figure 21-6, E_b for SO_3^{2-} = 165.4 eV. Thus, SO_3^{2-} seems likely.

(c) As in part (a),

$$\frac{hc}{\lambda} = \frac{6.6256 \times 10^{-34}\ \text{Js} \times 2.9979 \times 10^{8}\ \text{m/s}}{0.83393\ \text{nm} \times 10^{-9}\ \text{m/nm}} \times 6.2418 \times 10^{18}\ \frac{\text{eV}}{\text{J}}$$

$= 1486.7$ eV

$E_k = 1486.7 - 165.4 - 14.7 = 1306.6$ eV

(d) The kinetic energy of an Auger electron is independent of source energy. Thus,

$E_k = 1073.5$ eV

21-5. (a) $E_b = h\nu - E_k - w = h\nu - 1052.6\ \ 27.8$ (Equation 21-2)

$$\frac{hc}{\lambda} = \frac{6.6256 \times 10^{-34}\ \text{Js} \times 2.9979 \times 10^{8}\ \text{m/s}}{0.83393\ \text{nm} \times 10^{-9}\ \text{m/nm}} \times 6.2418 \times 10^{18}\ \frac{\text{eV}}{\text{J}}$$

$= 1486.7$ eV

$E_b = 1486.7 - 1052.6 - 27.8 = 406.3$ eV

(b) $E_k = h\nu - 406.3 - 27.8$

$$h\nu = \frac{hc}{\lambda} = \frac{6.6256 \times 10^{-34}\ \text{Js} \times 2.9979 \times 10^{8}\ \text{m/s}}{0.98900\ \text{nm} \times 10^{-9}\ \text{m/nm}} \times 6.2418 \times 10^{18}\ \frac{\text{eV}}{\text{J}}$$

$= 1253.6$ eV

$E_k = 1253.6 - 406.3 - 27.8 = 819.5$ eV

(c) By obtaining the peak with sources of differing energy, such as the Al and Mg X-ray tubes. Auger peaks do not change with the two sources, whereas XPS peaks do.

(d) From Table 21-2, the N(1*s*) peak for nitrate (NO_3^-)is shifted by +8.0 eV against the reference while that for nitrite (NO_2^-) is shifted 5.1 eV. Thus the binding energy for NO_2^- should be

$E_b = 406.3 - (8.0 - 5.1) = 403.4$ eV

21-6. With EELS, low energy electrons are incident on a surface, and the scattered electrons are detected and analyzed. Energy losses can occur due to vibrational excitation of molecules on the surface. With infrared absorption spectrometry, IR radiation is sent through a the sample and the transmitted IR radiation is measured. With Raman spectrometry, radiation in the visible region is sent through a sample, and the scattered radiation in the visible region is measured. The shifts away from the Rayleigh scattered line correspond to vibrational modes. EELS has the advantage that it is surface sensitive and can provide information on molecules adsorbed or bound to the surface. Conventional IR and Raman spectrometry measure vibrational modes within a bulk sample, although ATR and SERS can provide surface information. The major limitations of EELS are its relatively low resolution compared to IR and Raman and the expense of instrumentation.

21-7. In both ion scattering spectroscopy and Rutherford backscattering spectroscopy, ions are scattered from a surface and the backscattered ions detected. In ISS, low energy ions (0.5 to 5 keV) form the primary beam, whereas in RBS, high energy ions (MeV) from an accelerator are used. The experimental arrangements for both techniques are similar to that shown in Figure 21-13 for RBS. With ISS, a low-energy electron impact source substitutes for the high-energy source shown. With ISS, information comes from the top-most layer of the sample, whereas with RBS, information can arise from as much as 100 nm into the sample. It is difficult to obtain quantitative information with ISS, wherease with RBS, quantitative analysis is readily obtained.

21-8. In static SIMS, conditions are arranged so that sputtering from the surface is slow compared to the time-scale of the experiment. Hence, the surface composition is little changed during the experiment. In dynamic SIMS, conditions are arranged so that the surface is sputtered away during the experiment providing information as a function of depth below the surface. Imaging SIMS, or scanning SIMS, scans over the surface while obtaining secondary ion information. A spatial image of surface composition is generated.

21-9. Surface photon techniques have the major advantage that the surface been examined does not have to be in an ultra high vacuum environment and can be in contact with liquids. Thus, the environment in the surface photon techniques can be more like that found in actual use (catalyst, sensor, biological material, etc.) The major disadvantage is that surface composition can be altered by adsorption of gases or by attraction of molecules to the surface.

21-10. A buried interface is an interface found not at the surface, but below the surface in layered structures. Most surface characterization methods probe only the surface or a few nanometers into the surface. However, semiconductors, sensors, and many other materials contain interfaces that are buried below the surface and important to characterize. Another example is the interface between two immisicible liquids. Sum-frequency generation (and second harmonic) can provide access to buried interfaces.

21.11. Sources of signals in SEM can be backscattered electrons, secondary electrons, and X-ray photons. In elastic scattering of electrons, the electrons interact with a solid in such a way that their direction is altered, but no energy is lost in the process. In inelastic scattering, part of the energy of the incoming electron is lost during the scattering process.

21-12. The two types of scanning probe microscopes are the scanning tunneling microscope (STM) and the atomic force microscope (AFM).

(a) In the STM, the surface being studied is scanned with a sharp metallic tip whose position above the surface is controlled by a tunneling current between the tip and surface. In the AFM, the surface is scanned by a fine stylus mounted on a force-sensitive cantilever whose vertical position is sensed optically with a laser beam. In contrast to the STM, the sensor comes in contact with the sample surface in an AFM.

(b). The advantage of the STM is that the tip never makes contace with the sample surface and hence never disturbs or damages the surface. The primary advantage of the AFM is that it does not require that the sample be a conductor of electricity.

(c). The main disadvantage of the STM is that it requires that the surface be an electrical conductor. The chief disadvantage of the AFM is that stylus tip comes in physical contact with the surface which may alter its characteristics. Non-contact AFM and tapping mode AFM help to minimize alterations and damage of the surface.

21-13. $I_t = Ve^{-Cd}$ (Equation 21-9)

First we can calculate the constant C from the two tunneling currents.

$$\frac{(I_t)_2}{(I_t)_1} = \frac{e^{-Cd_2}}{e^{-Cd_1}}$$

$$C = \frac{\ln(I_t)_2 - \ln(I_t)_1}{d_1 - d_2}$$

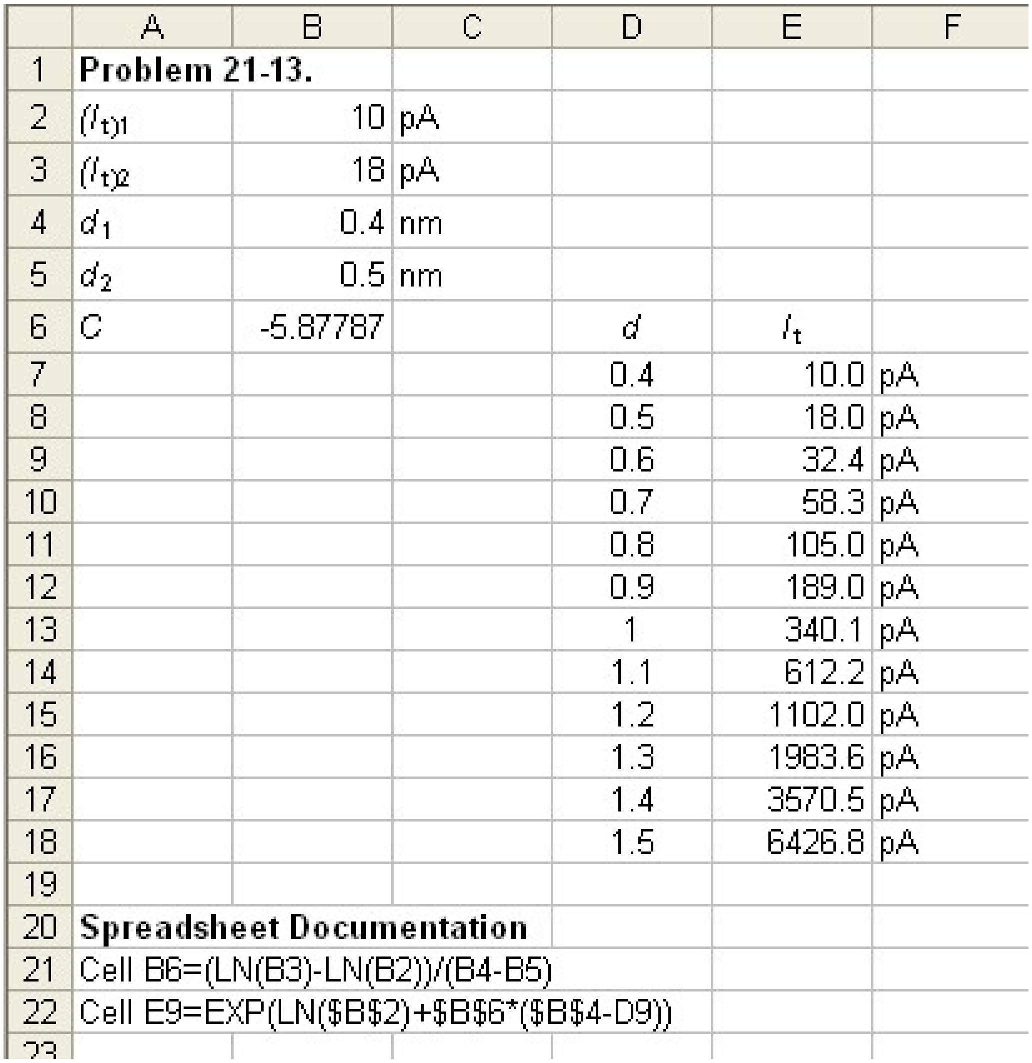
Knowing C, and one of the tunneling currents we can calculate the other currents, I_x from

$$\ln(I_t)_x = \ln(I_t)_1 + C(d_1 - d_3)$$

Or

$$(I_t)_x = \exp[\ln(I_t)_1 + C(d_1 - d_3)]$$

The results are given in the spreadsheet.



	A	B	C	D	E	F
1	**Problem 21-13.**					
2	$(I_t)_1$	10	pA			
3	$(I_t)_2$	18	pA			
4	d_1	0.4	nm			
5	d_2	0.5	nm			
6	C	-5.87787		d	I_t	
7				0.4	10.0	pA
8				0.5	18.0	pA
9				0.6	32.4	pA
10				0.7	58.3	pA
11				0.8	105.0	pA
12				0.9	189.0	pA
13				1	340.1	pA
14				1.1	612.2	pA
15				1.2	1102.0	pA
16				1.3	1983.6	pA
17				1.4	3570.5	pA
18				1.5	6426.8	pA
19						
20	**Spreadsheet Documentation**					
21	Cell B6=(LN(B3)-LN(B2))/(B4-B5)					
22	Cell E9=EXP(LN($B$2)+$B$6*($B$4-D9))					
23						

CHAPTER 22

22-1. (a)

$$E = 0.799 - \frac{0.0592}{1}\log\frac{1}{[\mathrm{Ag}^+]} = 0.799 - 0.0592\log\frac{1}{0.0261}$$

$E = 0.799 - 0.094 = 0.705$ V

(b)

$$E = 0.771 - 0.0592\log\frac{0.100}{6.72\times10^{-4}} = 0.771 - 0.129 = 0.642\text{ V}$$

(c)

$E = 0.073 - 0.0592 \log 0.05 = 0.141$ V

22-2. (a)

$$E = 0.000 - \frac{0.0592}{2}\log\frac{p_{\mathrm{H}_2}}{[\mathrm{H}^+]^2} = -\frac{0.0592}{2}\log\frac{0.987}{(1.76)^2} = 0.015\text{ V}$$

(b)

$$E = 1.178 - \frac{0.0592}{5}\log\frac{\left(2\times10^{-4}\right)^{1/2}}{(0.194)(3.5\times10^{-3})^6} = 0.826\text{ V}$$

(c)

$$E = 0.446 - \frac{0.0592}{2}\log 0.0520 = 0.446 + 0.038 = 0.484\text{ V}$$

22-3. (a) $2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons \mathrm{H}_2$ $E^0 = 0.000$ V

(1) $E = 0.000 - (0.0592/2)\log[1/(0.020)^2] = -0.101$ V

(2) ionic strength $\mu = ½[0.02 \times 1^2 + 0.03 \times 1^2 + 0.05 \times 1^2] = 0.050$

From Table a2-1, $\gamma_{\mathrm{H}^+} = 0.86$ and $a_{\mathrm{H}^+} = 0.86 \times 0.02 = 0.0172$

$E = 0.000 - (0.0592/2)\log[1.00/(0.0172)^2] = -0.104$ V

(b) $\mathrm{Fe}^{3+} + \mathrm{e}^- \rightleftharpoons \mathrm{Fe}^{2+}$ $E^0 = 0.771$ V

(1) $E = 0.771 - 0.0592 \log (0.0111/0.0111) = 0.771$ V

(2) $\mu = ½[0.0111 \times 2^2 + 0.0111 \times 3^2 + 2 \times 0.0111 \times 1^2 + 3 \times 0.0111 \times 1^2]$

$= 0.100$

From Table a2-1,

$\gamma_{\mathrm{Fe}^{2+}} = 0.40$ and $a_{\mathrm{Fe}^{2+}} = 0.40 \times 0.0111 = 0.00444$

$\gamma_{\mathrm{Fe}^{3+}} = 0.18$ and $a_{\mathrm{Fe}^{3+}} = 0.18 \times 0.0111 = 0.00200$

$E = 0.771 - 0.0592 \log[0.00444/0.00200] = 0.750$ V

22-4. (a) $\mathrm{Sn}^{4+} + 2e^- \rightleftharpoons \mathrm{Sn}^{2+}$ $E^0 = 0.154$ V

(1) $E = 0.154 - (0.0592/2) \log[3.00 \times 10^{-5}/6.00 \times 10^{-5}] = 0.163$ V

(2) $\mu = ½[3.00 \times 10^{-5} \times 2^2 + 6.00 \times 10^{-5} \times 4^2 + 6.00 \times 10^{-5} \times 1^2 + 24 \times 10^{-5} \times 1^2]$

$= 6.9 \times 10^{-4}$

From Equation a2-3,

$$-\log \gamma_{\mathrm{Sn}^{2+}} = \frac{0.509(2)^2\sqrt{6.9\times10^{-4}}}{1+3.28\times0.6\sqrt{6.9\times10^{-4}}} = 0.05085$$

$\gamma_{\mathrm{Sn}^{2+}} = 0.890$ and $a_{\mathrm{Sn}^{2+}} = 0.890 \times 3.00 \times 10^{-5} = 2.67 \times 10^{-5}$

$$-\log \gamma_{\mathrm{Sn}^{4+}} = \frac{0.509(4)^2\sqrt{6.9\times10^{-4}}}{1+3.28\times1.1\sqrt{6.9\times10^{-4}}} = 0.195$$

$\gamma_{\mathrm{Sn}^{4+}} = 0.638$ and $a_{\mathrm{Sn}^{4+}} = 0.638 \times 6.00 \times 10^{-5} = 3.83 \times 10^{-5}$

$E = 0.154 - (0.0592/2) \log[(2.67 \times 10^{-5})/(3.83 \times 10^{-5})] = 0.159$ V

(b) (1) As in Solution 22-4a, $E = 0.163$ V

(2) Here the contribution of the tin species to μ is neglible and $\mu = 0.0800$

$$-\log \gamma_{\mathrm{Sn}^{2+}} = \frac{0.509(2)^2\sqrt{0.080}}{1+3.28\times 0.6\sqrt{0.080}} = 0.3699$$

$\gamma_{\mathrm{Sn}^{2+}} = 0.427$ and $a_{\mathrm{Sn}^{2+}} = 0.427 \times 3.00 \times 10^{-5} = 1.28 \times 10^{-5}$

$$-\log \gamma_{\mathrm{Sn}^{4+}} = \frac{0.509(4)^2\sqrt{0.080}}{1+3.28\times 1.1\sqrt{0.080}} = 1.140$$

$\gamma_{\mathrm{Sn}^{4+}} = 0.072$ and $a_{\mathrm{Sn}^{4+}} = 0.072 \times 6.00 \times 10^{-5} = 4.35 \times 10^{-6}$

$E = 0.154 - (0.0592/2) \log[(1.28 \times 10^{-5})/(4.35 \times 10^{-6})] = 0.140$ V

22-5. (a) $E = -0.151 - 0.0592 \log(0.0150) = -0.043$ V

(b) $$E = -0.31 - 0.0592 \log\frac{(0.0040)^2}{0.0600} = -0.10 \text{ V}$$

(c) mmol Br^- = 25.0 × 0.0500 = 1.25

mmol Ag^+ = 20.0 × 0.100 = 2.00

excess Ag^+ = 2.00 – 1.25 = 0.75 mmol in a total volume of 45.0 mL

$[\mathrm{Ag}^+] = 0.75/45.0 = 0.0167$ M

$$E = 0.799 - 0.0592 \log\frac{1}{0.0167} = 0.694 \text{ V}$$

(d) mmol Br^- = 20.0 × 0.100 = 2.00

mmol Ag^+ = 25.0 × 0.0500 = 1.25

excess Br^- = 2.00 – 1.25 = 0.75 mmol in a total volume of 45.0 mL

$[\mathrm{Br}^-] = 0.75/45.0 = 0.0167$ M

$E = 0.073 - 0.0592 \log(0.0167) = 0.178$ V

22-6. (a) $$E = 1.33 - \frac{0.0592}{6}\log\left[\frac{(2.00\times 10^{-2})^2}{(4.00\times 10^{-3})(0.100)^{14}}\right] = 1.20 \text{ V}$$

(b) $$E = 0.334 - \frac{0.0592}{2}\log\frac{0.100}{0.200\times(0.600)^4} = 0.307\text{ V}$$

22-7. (a) $$E_{\text{right}} = -0.126 - \frac{0.0592}{2}\log\frac{1}{5.6\times10^{-2}} = -0.159\text{ V}$$

$$E_{\text{left}} = -0.408 - 0.0592\log\frac{2\times10^{-3}}{1\times10^{-4}} = -0.485$$

E_{cell} = –0.159 – (–0.485) = 0.326 V

The cell is spontaneous as written oxidation on the left, reduction on the right

(b) On the right we have $VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$

$$E_{\text{right}} = 0.359 - 0.0592\log\frac{3.00\times10^{-2}}{(2.00\times10^{-3})(1.00\times10^{-2})^2} = 0.053\text{ V}$$

$$E_{\text{left}} = 0.788 - \frac{0.0592}{2}\log\frac{1}{2\times10^{-2}} = 0.738\text{ V}$$

E_{cell} = 0.053 – 0.738 = –0.685 V

The cell is not spontaneous in the direction considered (oxidation on the left, eduction on the right), but is spontaneous in the opposite direction

(c) $$E_{\text{right}} = 0.154 - \frac{0.0592}{2}\log\frac{5.50\times10^{-2}}{(3.50\times10^{-4})} = 0.089\text{ V}$$

$$E_{\text{right}} = 0.771 - 0.0592\log\frac{3.00\times10^{-5}}{(4.00\times10^{-2})} = 0.956\text{ V}$$

E_{cell} = 0.089 – 0.956 = –0.867 V

The cell is not spontaneous in the direction considered, but instead is spontaneous n the opposite direction (reduction on the left, oxidation on the right).

22.8. (a) E_{right} = –0.151 – 0.0592 log 0.100 = –0.092 V

$$E_{\text{left}} = 0.320 - \frac{0.0592}{3}\log\frac{1}{(0.0400)(0.200)^2} = 0.265\text{ V}$$

$E_{\text{cell}} = -0.092 - 0.265 = -0.357$ V   Not spontaneous as written

(b) $$E_{\text{right}} = 0.36 - 0.0592\log\frac{4.50\times10^{-2}}{(7.00\times10^{-2})} = 0.37\text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\frac{1}{(7.50\times10^{-4})} = -0.855$$

$E_{\text{cell}} = 0.37 - (-0.86) = 1.23$ V Spontaneous as written (oxidation on left)

(c) $E_{\text{right}} = 0.222 - 0.592\log(7.50\times10^{-4}) = 0.407$ V

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\frac{0.200}{(7.50\times10^{-4})^2} = -0.164\text{ V}$$

$E_{\text{cell}} = 0.407 - (-0.164) = 0.571$ V Spontaneous as written (oxidation on left)

22-9. $Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$ $E^0 = -0.250$ V

$Ni(CN)_4^{2-} + 2e^- \rightleftharpoons Ni(s) + 4CN^-$ $E^0 = ?$

$$E_{Ni^{2+}/Ni} = -0.250 - \frac{0.0592}{2}\log\frac{1}{[Ni^{2+}]}$$

$$K_f = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$$

$$E = -0.250 - \frac{0.0592}{2}\log\frac{K_f[CN^-]^4}{[Ni(CN)_4^{2-}]}$$

For the 2nd reaction,

$$E = E^0 - \frac{0.0592}{2}\log\frac{[CN^-]^4}{[Ni(CN)_4^{2-}]}$$

When $[CN^-]^4/[Ni(CN)_4^{2-}] = 1.00$, $E = E^0 = -0.250 - \frac{0.0592}{2}\log K_f$

$$E^0 = -0.250 - \frac{0.0592}{2}\log 1\times 10^{22} = –0.90 \text{ V}$$

22-10. $Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$ $E^0 = –0.126$ V

$$E_{Pb^{2+}/Pb} = -0.126 - \frac{0.0592}{2}\log\frac{1}{[Pb^{2+}]}$$

$PbI_2(s) + 2e^- \rightleftharpoons Pb(s) + 2I^-$ $E^0 = ?$

$$E_{PbI_2/Pb} = E^0 - \frac{0.0592}{2}\log[I^-]^2$$

$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$

$$E_{Pb^{2+}/Pb} = -0.126 - \frac{0.0592}{2}\log\frac{[I^-]^2}{K_{sp}}$$

When $[I^-] = 1.00$, $E = E^0$

$$E^0 = -0.126 - \frac{0.0592}{2}\log\frac{(1.00)^2}{7.1\times 10^{-9}} = –0.367 \text{ V}$$

22-11. Proceeding as in Solution 22-10, we obtain,

$E^0 = –0.037$ V

22-12. Proceeding as in Solution 22-9, we find

$E^0 = –1.92$ V

22-13. $$E = -0.336 - 0.0592\log\frac{1}{[Tl^+]} = -0.336 - 0.0592\log\frac{[Cl^-]}{K_{sp}}$$

When $[Cl^-] = 1.00$, $E = E^0_{TlCl} = –0.557$ V

$–0.557 = –0.336 – 0.0592 \log(1.00/K_{sp})$

$K_{sp} = 1.85 \times 10^{-4}$

22-14. Proceeding as in Solution 22-13, we obtain

$K_{sp} = 1.0 \times 10^{-15}$

22-15. $E_{\text{right}} = 0.073 - 0.0592 \log (0.0850) = 0.136$ V

$$E_{\text{left}} = -0.256 - 0.0592 \log \frac{0.448}{3.7\times10^{-5}} = -0.498 \text{ V}$$

$E_{\text{right}} - E_{\text{left}} = 0.136 - (-0.498) = 0.634$ V

$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} - IR = 0.634 - 0.075 \times 4.87 = 0.268$ V

22-16. $$E_{\text{right}} = 0.337 - 0.0592 \log \frac{1}{2.50\times10^{-2}} = 0.242 \text{ V}$$

$$E_{\text{left}} = 1.00 - 0.0592 \log \frac{3.42\times10^{-2}}{2.67\times10^{-4}\times(4.81\times10^{-3})^2} = 0.601 \text{ V}$$

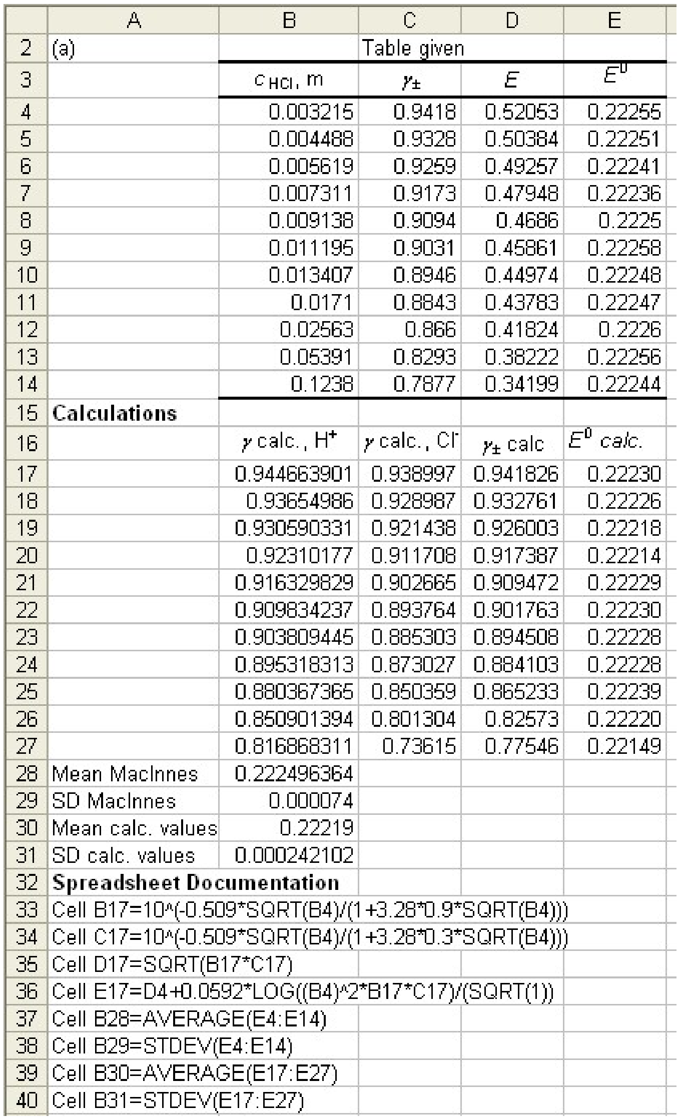
$E_{\text{right}} - E_{\text{left}} = 0.242 - 0.601 = -0.359$ V

$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} - IR = -0.359 - 0.0750 \times 3.81 = -0.644$ V

22-17. Proceeding as in Solution 22-16, we obtain,

$E_{\text{cell}} = 0.24$ V

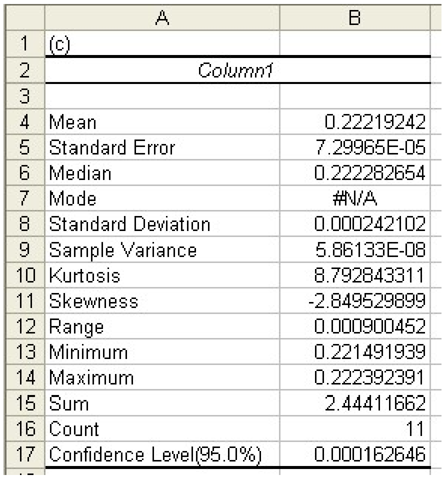
22-18. (a) The spreadsheet follows.



	A	B	C	D	E
2	(a)		Table given		
3		c_{HCl}, m	$\gamma_\pm$	E	E^0
4		0.003215	0.9418	0.52053	0.22255
5		0.004488	0.9328	0.50384	0.22251
6		0.005619	0.9259	0.49257	0.22241
7		0.007311	0.9173	0.47948	0.22236
8		0.009138	0.9094	0.4686	0.2225
9		0.011195	0.9031	0.45861	0.22258
10		0.013407	0.8946	0.44974	0.22248
11		0.0171	0.8843	0.43783	0.22247
12		0.02563	0.866	0.41824	0.2226
13		0.05391	0.8293	0.38222	0.22256
14		0.1238	0.7877	0.34199	0.22244
15	**Calculations**				
16		γ calc., H^+	γ calc., Cl^-	$\gamma_\pm$ calc	E^0 *calc.*
17		0.944663901	0.938997	0.941826	0.22230
18		0.93654986	0.928987	0.932761	0.22226
19		0.930590331	0.921438	0.926003	0.22218
20		0.92310177	0.911708	0.917387	0.22214
21		0.916329829	0.902665	0.909472	0.22229
22		0.909834237	0.893764	0.901763	0.22230
23		0.903809445	0.885303	0.894508	0.22228
24		0.895318313	0.873027	0.884103	0.22228
25		0.880367365	0.850359	0.865233	0.22239
26		0.850901394	0.801304	0.82573	0.22220
27		0.816868311	0.73615	0.77546	0.22149
28	Mean MacInnes	0.222496364			
29	SD MacInnes	0.000074			
30	Mean calc. values	0.22219			
31	SD calc. values	0.000242102			
32	**Spreadsheet Documentation**				
33	Cell B17=10^(-0.509*SQRT(B4)/(1+3.28*0.9*SQRT(B4)))				
34	Cell C17=10^(-0.509*SQRT(B4)/(1+3.28*0.3*SQRT(B4)))				
35	Cell D17=SQRT(B17*C17)				
36	Cell E17=D4+0.0592*LOG((B4)^2*B17*C17)/(SQRT(1))				
37	Cell B28=AVERAGE(E4:E14)				
38	Cell B29=STDEV(E4:E14)				
39	Cell B30=AVERAGE(E17:E27)				
40	Cell B31=STDEV(E17:E27)				

(b) The values of $\gamma_\pm$ compare quite well to those of MacInnes at the lower ionic strengths. At the higher ionic strengths there is a small deviation with the calculated values being a little lower than MacInnes's values. A look at MacInnes's book reveals that he used experimental values of $\gamma_\pm$ when possible and used the Debye-Hückel equation to interpolate between experimental values. This probably accounts for the differences seen. Likewise the E^0 values show small differences which may be attributed to the differences in γ values.

(c) The desriptive statistics are shown in the spreadsheet that follows.



	A	B
1	(c)	
2	*Column1*	
3		
4	Mean	0.22219242
5	Standard Error	7.29965E-05
6	Median	0.222282654
7	Mode	#N/A
8	Standard Deviation	0.000242102
9	Sample Variance	5.86133E-08
10	Kurtosis	8.792843311
11	Skewness	-2.849529899
12	Range	0.000900452
13	Minimum	0.221491939
14	Maximum	0.222392391
15	Sum	2.44411662
16	Count	11
17	Confidence Level(95.0%)	0.000162646

(d) The mean value using our calculations is 0.2222 ± 0.0002 V. The mean of MacInnes values is 0.22250 ± 0.00007 V. These results are very close. Also, the 95% CI for our results is

95% CI = 0.2222 ± 0.0002. Hence, we can be 95% certain that the mean lies within the interval 0.2220 to 0.2224 if the only uncertainties are random. We can also conclude that MacInnes's results are very precise and of extremely high quality.

CHAPTER 23

23-1. If an indicator exhibits nernstian behavior, it follows the Nernst equation with its potential changing by 0.059/*n* V per ten-fold change in concentration.

23-2. The alkaline errors in pH measurements with a glass electrode arise from the exchange of singly charged ions, such as sodium or potassium ions, in the surface of the glass membrane with the protons from the water. The potential then responds to the alkali metal activity as well as to the hydrogen ion activity.

23-3. Temperature Coefficients for Reference Electrodes, V/°C

0.1 M calomel	3.5 M calomel	Sat'd calomel	3.5 M Ag/AgCl	Sat'd Ag/AgCl
-9×10^{-5}	-4.0×10^{-4}	-6.8×10^{-4}	-7.5×10^{-4}	1.0×10^{-3}

23-4. Hydration of the surface of the glass takes place in which singly charged metal ions in the glass are exchanged with protons of the water.

23-5. An electrode of the first kind is a metal that responds directly to the activity of its metal ion. An electrode of the second kind is a metal electrode whose potential depends on the activity of an anion that forms a precipitate with the electrode metal ion.

23-6. A gas-sensing probe functions by permitting the gas to penetrate a hydrophobic membrane and altering the composition of liquid on the inner side of the membrane. The changes are registered by an indicator/reference electrode pair in contact with the inner solution. Thus, there is no direct contact between the electrodes and the test solution as there is with membrane electrodes. In a membrane electrode the observed potential is a type of boundary potential that develops across the membrane that separates the analyte solution from a reference solution.

23-7. (a) The asymmetry potential in a membrane arises from differences in the composition or structure of the inner and outer surfaces. These differences may arise from contamination of one of the surfaces, wear and abrasion and/or strains set up during manufacturing.

(b) The boundary potential for a membrane electrode is a potential that develops when the membrane separates two solutions that have different concentrations of a cation or an anion that the membrane binds selectively.

(c) The junction potential in a glass/reference electrode system develops at the interface between the saturated KCl solution in the salt bridge and the sample solution. It is caused by charge separation created by the differences in the rates at which ions migrate across the interface.

(d) The membrane in a solid-state electrode for F^- is crystalline LaF_3, which when immersed in aqueous solution, dissociates according to the equation

$$\mathrm{LaF_3}(s) \rightleftarrows \mathrm{La^{3+}} + 3\mathrm{F^-}$$

Thus, the boundary potential develops across this membrane when it separates two solutions of F^- ion concentration.

23-8. Uncertainties include (1) the acid error in highly acidic solutions, (2) the alkaline error in strongly basic solutions, (3) the error that arises when the ionic strength of the calibration standards differs from that of the analyte solution, (4) uncertainties in the pH of the standard buffers, (5) nonreproducible junction potentials with solutions of low ionic strength and (6) dehydration of the working surface.

23-9. An ionophores is a neutral, lipophilic compound that form complexes with analyte ions. When incorporated into a membrane, the target ions are carried across the solution-membrane boundary by the formation of the complex. The separation of charge across the solution-membrane barrier produces a nernstian response toward the analyte.

23-10. Potentiometric titrations are widely applicable and do not require an indicator. They are inherently more accurate than titrations with an indicator. They can also be used for titrations of colored or turbid solutions. A disadvantage is that they often require more time than a visual titration. The equipment needed is more expensive than that for a visual titration.

23-11. The *operational definition of pH* is based on the direct calibration of the pH meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions. For example, if immerses one glass/reference electrode pair in a standard buffer, we would write the relationship below

$$\mathrm{pH_S} = \frac{E_\mathrm{S} - K}{0.0592}$$

where E_S is the cell potential when the electrodes are immersed in the buffer. Similarly, if the cell potential is E_U when the electrodes are immersed in a solution of unknown pH, we would write

$$\mathrm{pH_U} = \frac{E_\mathrm{U} - K}{0.0592}$$

Subtracting the two relationships, we find

$$\mathrm{pH_U} = \mathrm{pH_S} = \frac{E_\mathrm{U} - E_\mathrm{S}}{0.0592}$$

The last relationship has been adopted throughout the world as the *operational definition of pH*. This definition ensures that pH measurements can be easily duplicated at various times and in various laboratories.

23-12. Microfabricated ion-selective electrodes are of small size and require only small volumes of solution. They are small enough and rugged enough to be used in portable instruments for field use. For example, clinical bedside instruments for Na^+, K^+, Ca^{2+}, pH, and several others, have used microfabriacted electrodes.

23-13. (a) $$E_{\text{right}} = 0.771 - 0.0592 \log \frac{0.0150}{0.0250} = 0.784\text{ V}$$

$$E_{\text{left}} = E_{SCE} = 0.244\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.784 - 0.244 = 0.540\text{ V}$$

(b) $$E_{\text{right}} = -0.763 - \frac{0.0592}{2} \log \frac{1}{0.00228} = -0.841\text{ V}$$

$$E_{\text{left}} = E_{SCE} = 0.244\text{ V}$$

$$E_{\text{cell}} = -0.841 - 0.244 = -1.085\text{ V}$$

(c) $$E_{\text{right}} = -0.369 - 0.0592 \log \frac{0.0450}{0.0250} = -0.384\text{ V}$$

$$E_{\text{left}} = E_{\text{Ag/AgCl}} = 0.199\text{ V}$$

$$E_{\text{cell}} = -0.384 - 0.199 = -0.583\text{ V}$$

(d) $$E_{\text{right}} = 0.536 - \frac{0.0592}{2} \log \frac{(0.00433)^3}{0.00667} = 0.681\text{ V}$$

$$E_{\text{left}} = 0.199\text{ V}$$

$$E_{\text{cell}} = 0.482\text{ V}$$

23-14. (a) $Cu^+ + e^- \rightleftharpoons Cu(s)$ $E^0 = 0.521\text{ V}$

$$E = 0.521 - 0.0592 \log \frac{1}{[Cu^+]} = 0.521 - 0.0592 \log \frac{[Br^-]}{K_{sp}}$$

When $[Br^-] = 1.00$, $E = E^0_{\text{CuBr}}$

$$E^0_{\mathrm{CuBr}} = 0.521 - 0.0592\log\frac{1.00}{5.2\times10^{-9}} = 0.031\text{ V}$$

(b) SCE||CuBr(*sat'd*), Br^-(x M)|Cu

(c) $E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} = 0.031 - 0.0592\log[\mathrm{Br}^-] - E_{\mathrm{SCE}}$

$= 0.031 + 0.0592\text{ pBr} - 0.244$

pBr = $(E_{\mathrm{cell}} - 0.031 + 0.244)/0.0592 = (E_{\mathrm{cell}} + 0.213)/0.0592$

(d) pBr = (–0.095 + 0.213)/0.0592 = 1.99

23-15. (a) $Ag_3AsO_4(s) \rightleftharpoons 3Ag^+ + AsO_4^{3-}$ $K_{sp} = [Ag^+]^3[AsO_4^{3-}] = 1.2\times10^{-22}$

$Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^0 = 0.799$ V

$$E = 0.799 - 0.0592\log\frac{1}{[\mathrm{Ag}^+]} = 0.799 - \frac{0.0592}{3}\log\frac{[\mathrm{AsO_4}^{3-}]}{K_{\mathrm{sp}}}$$

When $[AsO_4^{3-}] = 1.00$, $E = E^0_{\mathrm{Ag_3AsO_4}}$

$$E^0_{\mathrm{Ag_3AsO_4}} = 0.799 - \frac{0.0592}{3}\log\frac{1.00}{1.2\times10^{-22}} = 0.366\text{ V}$$

(b) SCE||Ag_3AsO_4(*sat'd*), AsO_4^{3-}(x M)|Ag

(c) $$E_{\mathrm{cell}} = 0.366 - \frac{0.0592}{3}\log[\mathrm{AsO_4}^{3-}] - E_{\mathrm{SCE}}$$

$$= 0.366 + \frac{0.0592}{3}\mathrm{pAsO_4} - 0.244 = 0.122 + \frac{0.0592}{3}\mathrm{pAsO_4}$$

$$\mathrm{pAsO_4} = \frac{(E_{\mathrm{cell}} - 0.122)\times3}{0.0592}$$

(d) $$\mathrm{pAsO_4} = \frac{(0.247 - 0.122)\times3}{0.0592} = 6.33$$

23-16. $Ag_2CrO_4 + 2e^- \rightleftharpoons 2Ag(s) + CrO_4^{2-}$ $\qquad E^0 = 0.446$ V

$$E_{\text{cell}} = E_{\text{SCE}} - \left(0.446 - \frac{0.0592}{2}\log[CrO_4^{2-}]\right)$$

$$-0.386 = 0.244 - 0.446 + \frac{0.0592}{2}\log[CrO_4^{2-}] = -0.202 - \frac{0.0592}{2}\text{pCrO}_4$$

$$\text{pCrO}_4 = \frac{(-0.202 + 0.386)\times 2}{0.0592} = 6.22$$

23-17. $Hg_2SO_4(s) + 2e^- \rightleftharpoons 2Hg(s) + SO_4^{2-}$ $\qquad E^0 = 0.615$ V

By a derivation similar to that in Solution 23-16, we find

$$\text{pSO}_4 = \frac{(0.537 - 0.371)\times 2}{0.0592} = 5.61$$

23-18. $K_f = \dfrac{[Hg(OAc)_2]}{[Hg^{2+}][OAc^-]^2} = 2.7 \times 10^8$

$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$ $\qquad E^0 = 0.854$ V

$$E = 0.854 - \frac{0.0592}{2}\log\frac{1}{[Hg^{2+}]} = 0.854 - \frac{0.0592}{2}\log\frac{K_f[OAc^-]^2}{[Hg(OAc)_2]}$$

When $[OAc^-]$ and $[Hg(OAc)_2] = 1.00$, $E = E^0_{Hg(OAc)_2}$

$$E^0_{Hg(OAc)_2} = 0.854 - \frac{0.0592}{2}\log 2.7\times 10^8 = 0.604 \text{ V}$$

23-19. $CuY^{2-} + 2e^- \rightleftharpoons Cu(s) + Y^{4-}$ $\qquad E^0 = 0.13$ V $\qquad K_f = \dfrac{[CuY^{2-}]}{[Cu^{2+}][Y^{4-}]}$

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $\qquad E^0 = 0.337$ V

$$E = E^0 - \frac{0.0592}{2}\log\frac{1}{[\mathrm{Cu}^{2+}]} = 0.337 - \frac{0.0592}{2}\log\frac{K_\mathrm{f}[\mathrm{Y}^{4-}]}{[\mathrm{CuY}^{2-}]}$$

When $[\mathrm{Y}^{4-}] = [\mathrm{CuY}^{2-}] = 1.00$, $E = E^0_{\mathrm{CuY}^{2-}}$

$$0.13 = 0.337 - \frac{0.0592}{2}\log K_\mathrm{f}$$

$$\log K_\mathrm{f} = \frac{(0.337 - 0.13)\times 2}{0.0592} = 6.993$$

$K_\mathrm{f} = 9.8 \times 10^6$

23-20. (a) $\mathrm{pH_U} = \mathrm{pH_S} - \dfrac{(E_\mathrm{U} - E_\mathrm{S})}{0.0592}$ Equation 23-32

$$\mathrm{pH_U} = 4.006 - \frac{-0.2806 + 0.2094}{0.0592} = 5.21$$

$a_{\mathrm{H}^+} = 6.18 \times 10^{-6}$

(b) $\mathrm{pH_U} = 4.006 - (-0.2132 + 0.2094)/0.0592 = 4.07$

$a_{\mathrm{H}^+} = 8.51 \times 10^{-5}$

(c) $\mathrm{pH} = -\dfrac{(E_\mathrm{cell} - K)}{0.0592}$ Equation 23-26

$$\mathrm{pH} = 4.006 = \frac{0.2094 + K}{0.0592}$$

$K = 0.0592 \times 4.006 - 0.2094 = 0.0278$

If $K = 0.0278 + 0.001 = 0.0288$

For (a) $\mathrm{pH_U} = -\dfrac{(-0.2806 - 0.0288)}{0.0592} = 5.23$

If $K = 0.0278 - 0.001 = 0.0268$, $\mathrm{pH_U} = 5.19$

For (b), the pH would range between 4.09 and 4.05

23-21. pCu = –log[Cu^{2+}] = 2.488

$$2.488 = -\frac{E_{\text{cell}} - K}{0.0592/2} = -\frac{0.124 - K}{0.0592/2}$$

$K = 2.488 \times (0.0592/2) + 0.124 = 0.1976$

$$\text{pCu} = -\frac{0.086 - 0.1976}{0.0592/2} = 3.77$$

23-22 $Cd^{2+} + 2e^{-} \rightleftharpoons Cd(s)$ $E^{0} = -0.403$ V

$CdX_2(s) + 2e^{-} \rightleftharpoons Cd(s) + 2X^{-}$

$$E_{\text{cell}} = -0.403 - \frac{0.0592}{2}\log\frac{1}{[Cd^{2+}]} - 0.244 = -0.647 - \frac{0.0592}{2}\log\frac{[X^{-}]^2}{K_{\text{sp}}}$$

$$-1.007 = -0.647 + \frac{0.0592}{2}\log\frac{K_{\text{sp}}}{(0.02)^2}$$

$$= -0.647 - \frac{0.0592}{2}\log(0.02)^2 + \frac{0.0592}{2}\log K_{\text{sp}}$$

$$\log K_{\text{sp}} = \frac{[0.647 - 1.007 + 0.0592\log(0.02)] \times 2}{0.0592} = -15.56$$

$K_{\text{sp}} = 2.75 \times 10^{-16}$

23-23. $$-0.492 = 0.000 - \frac{0.0592}{2}\log\frac{1.00}{[H^{+}]^2} - 0.199$$

$$-0.293 = -\frac{0.0592}{2}\log\frac{1.00}{[H^{+}]^2} = 0.0592\log[H^{+}]$$

pH = – log [H^{+}] = 0.293/0.0592 = 4.95

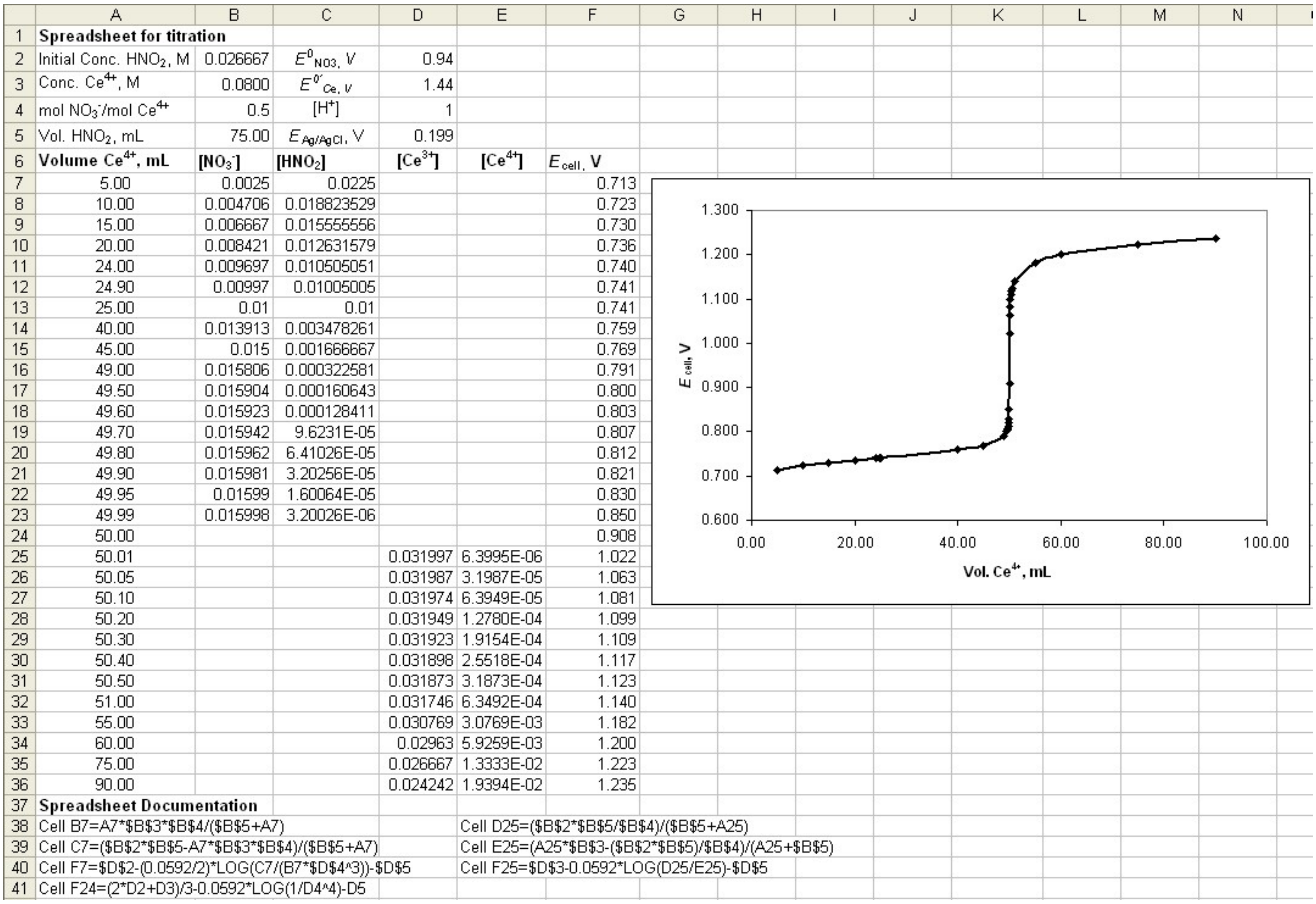
[H^{+}] = 1.1238×10^{-5}

$$K_a = \frac{(1.1238 \times 10^{-5})(0.300)}{(0.200} = 1.69 \times 10^{-5}$$

23-24 $Ce^{4+} + HNO_2 + H_2O \rightleftharpoons 2Ce^{3+} + NO_3^- + 3\,H^+$

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E^0 = 1.44$ V

$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$ $E^0 = 0.94$ V



	A	B	C	D	E	F
1	**Spreadsheet for titration**					
2	Initial Conc. HNO_2, M	0.026667	E^0_{NO3}, V	0.94		
3	Conc. Ce^{4+}, M	0.0800	$E^{0'}_{Ce}$, V	1.44		
4	mol NO_3^-/mol Ce^{4+}	0.5	$[H^+]$	1		
5	Vol. HNO_2, mL	75.00	$E_{Ag/AgCl}$, V	0.199		
6	**Volume Ce^{4+}, mL**	**$[NO_3^-]$**	**$[HNO_2]$**	**$[Ce^{3+}]$**	**$[Ce^{4+}]$**	**E_{cell}, V**
7	5.00	0.0025	0.0225			0.713
8	10.00	0.004706	0.018823529			0.723
9	15.00	0.006667	0.015555556			0.730
10	20.00	0.008421	0.012631579			0.736
11	24.00	0.009697	0.010505051			0.740
12	24.90	0.00997	0.01005005			0.741
13	25.00	0.01	0.01			0.741
14	40.00	0.013913	0.003478261			0.759
15	45.00	0.015	0.001666667			0.769
16	49.00	0.015806	0.000322581			0.791
17	49.50	0.015904	0.000160643			0.800
18	49.60	0.015923	0.000128411			0.803
19	49.70	0.015942	9.6231E-05			0.807
20	49.80	0.015962	6.41026E-05			0.812
21	49.90	0.015981	3.20256E-05			0.821
22	49.95	0.01599	1.60064E-05			0.830
23	49.99	0.015998	3.20026E-06			0.850
24	50.00					0.908
25	50.01			0.031997	6.3995E-06	1.022
26	50.05			0.031987	3.1987E-05	1.063
27	50.10			0.031974	6.3949E-05	1.081
28	50.20			0.031949	1.2780E-04	1.099
29	50.30			0.031923	1.9154E-04	1.109
30	50.40			0.031898	2.5518E-04	1.117
31	50.50			0.031873	3.1873E-04	1.123
32	51.00			0.031746	6.3492E-04	1.140
33	55.00			0.030769	3.0769E-03	1.182
34	60.00			0.02963	5.9259E-03	1.200
35	75.00			0.026667	1.3333E-02	1.223
36	90.00			0.024242	1.9394E-02	1.235
37	**Spreadsheet Documentation**					
38	Cell B7=A7*$B$3*$B$4/($B$5+A7)				Cell D25=($B$2*$B$5/$B$4)/($B$5+A25)	
39	Cell C7=($B$2*$B$5-A7*$B$3*$B$4)/($B$5+A7)				Cell E25=(A25*$B$3-($B$2*$B$5)/$B$4)/(A25+$B$5)	
40	Cell F7=$D$2-(0.0592/2)*LOG(C7/(B7*$D$4^3))-$D$5				Cell F25=$D$3-0.0592*LOG(D25/E25)-$D$5	
41	Cell F24=(2*D2+D3)/3-0.0592*LOG(1/D4^4)-D5					

23-25. (a) pMg = – log 3.32 × 10^{-3} = 2479

$$2.479 = -\frac{0.2897 - K}{0.0592/2}$$

$$0.07338 = -0.2897 + K$$

$$K = 0.3631$$

$$\text{pMg} = -\frac{0.2041 - 0.3631}{0.0592/2} = 5.372$$

$$a_{\text{Mg}^{2+}} = 4.25 \times 10^{-6}$$

(b) When $K = 0.3651$, pMg = 5.439 and $a_{\text{Mg}^{2+}} = 3.64 \times 10^{-6}$

When $K = 0.3611$, pMg = 5.304 and $a_{\text{Mg}^{2+}} = 4.97 \times 10^{-6}$

(c) error for $K = 0.3651 = 3.64 \times 10^{-6} - 4.25 \times 10^{-6} = -0.99 \times 10^{-6} = 9.9 \times 10^{-7}$

error for $K = 0.3611 = 4.96 \times 10^{-6} - 4.25 \times 10^{-6} = 7.1 \times 10^{-7}$

$$\text{relative error (1)} = \frac{-9.9 \times 10^{-7} \times 100\%}{4.25 \times 10^{-6}} = -23.3\%$$

$$\text{relative error (2)} = \frac{7.1 \times 10^{-7} \times 100\%}{4.25 \times 10^{-6}} = 16.7\%$$

23-26. We can write Equation 23-30 as

$$E_{\text{cell}} = K + 0.0592\ \text{pA} = K - 0.0592 \log[\text{F}^-]$$

Let c_x be the concentration of the diluted sample and c_s be the concentration of the added standard. If –0.1823 V is the potential of the system containing the diluted sample only, we may write,

$$-0.1823 = K - 0.0592 \log c_x$$

The concentration c_1 after the addition of standard is

$$c_1 = \frac{25.0c_x + 5.00c_\text{s}}{30.0} = 0.833c_x + 0.1667c_\text{s}$$

and the potential –0.2446 V after the addition is given by

$$-0.2446 = K - 0.0592 \log (0.833c_x + 0.1667c_\text{s})$$

Subtracting this equation from the first potential expression gives

$$0.0623 = -0.0592 \log \frac{c_x}{(0.833c_x + 0.1667c_\text{s})}$$

$$\frac{c_x}{(0.833c_x + 0.1667c_\text{s})} = 0.0887$$

Since concentrations appear in both numerator and denominator, we can substitute for molar concentrations, the concentration in terms of mgF$^-$/mL and write

$$c_x = 0.0887 \times 0.833c_x + 0.0887 \times 0.1667c_\text{s} = 0.0739c_x + 0.0887 \times 0.1667 \times 0.00107 \text{ mg F}^-/\text{mL}$$

$$c_x = 1.71 \times 10^{-5} \text{ mg F}^-/\text{mL}$$

$$\%\text{F}^- = \frac{1.71 \times 10^{-5} \text{ mg F}^-/\text{mL} \times 100 \text{ mL} \times 10^{-3} \text{ g/mg}}{0.400 \text{ g sample}} \times 100\% = 4.28 \times 10^{-4}\%$$

CHAPTER 24

24-1. (a) $2Pb^{2+} + 2H_2O \rightleftharpoons Pb(s) + O_2 + 4H^+$

$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$ $E^0 = –0.126V$

$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^0 = 1.229\text{ V}$

$$E_{\text{right}} = -0.126 - \frac{0.0592}{2}\log\frac{1}{0.100} = –0.1556\text{ V}$$

$$E_{\text{left}} = 1.299 - \frac{0.0592}{4}\log\frac{1}{0.800\times(0.200)^4} = 1.1862\text{ V}$$

$$E_{\text{cell}} = –0.1566 – 1.1862 = –1.342\text{ V}$$

(b) $0.250 \times 0.950 = 0.238\text{ V}$

24-2. (a) To lower M_1 to $2.00 \times 10^{–4}$.

$$E_1 = E^0_{M_1} - \frac{0.0592}{2}\log\frac{1}{2\times10^{-4}} = E^0_{M_1} - 0.109\text{ V}$$

M_2 begins to deposit when

$$E_2 = E^0_{M_2} - 0.0592\log\frac{1}{0.100} = E^0_{M_2} - 0.0592$$

When $E_2 = E_1$, the concentration of M_1 will be reduced to $2.00 \times 10^{–4}$ and M_2will not have begun to deposit. That is,

$$E^0_{M_2} - 0.0592 = E^0_{M_1} - 0.109\text{ V}$$

$$E^0_{M_2} - E^0_{M_1} = \Delta E^0 = -0.109 - (-0.0592) = –0.050\text{ V}$$

	Charge on M_2	Charge on M_1	$\Delta E^0 = E^0_{M_2} - E^0_{M_1}$, V
(a)	1	2	–0.109 + 0.0592 = –0.050
(b)	2	2	–0.109 + 0.0296 = –0.079
(c)	3	1	–0.219 + 0.020 = –0.199
(d)	2	1	–0.219 + 0.0296 = –0.189
(e)	2	3	–0.073 + 0.0296 = –0.043

24-3. $Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^0 = 0.799$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $E^0 = 0.337$ V

$BiO^+ + 2H^+ + 3e^- \rightleftharpoons Bi(s) + H_2O$ $E^0 = = 0.320$ V

(a) First, we calculate the potentials vs. Ag-AgCl needed to reduce the concentrations to 10^{-6} M. For Ag^+,

$$E_{cell} = 0.799 - 0.0592 \log \frac{1}{1.00 \times 10^{-6}} - 0.199 = 0.444 - 0.199 = 0.245 \text{ V}$$

For Cu^{2+}

$$E_{cell} = 0.337 - \frac{0.0592}{2} \log \frac{1}{1.0 \times 10^{-6}} - 0.199 = -0.040 \text{ V}$$

For BiO^+

$$E_{cell} = 0.320 - \frac{0.0592}{3} \log \frac{1}{1.0 \times 10^{-6} \times (0.5)^2} - 0.199 = -0.009 \text{ V}$$

Bi(*s*) begins to deposit when

$$E_{cell} = 0.320 - \frac{0.0592}{3} \log \frac{1}{0.0550 \times (0.5)^2} - 0.199 = 0.084 \text{ V}$$

Cu(*s*) begins to deposit when

$$E_{cell} = 0.337 - \frac{0.0592}{2} \log \frac{1}{0.125} - 0.199 = 0.111 \text{ V}$$

(b) Silver could be separated from BiO^+ and Cu^{2+} by keeping the cell potential greater than 0.111 V. Cu^{2+} and BiO^+ cannot be separated by controlled-potential electrolysis.

24-4. We calculate the potentials at which the silver salts first form

For I^-, $E_{cell} = 0.244 - (-0.151 - 0.0592 \log 0.0250) = 0.300$ V

For Br^-, $E_{cell} = 0.244 - (0.073 - 0.0592 \log 0.0250) = 0.076$ V

For Cl^-, $E_{cell} = 0.244 - (0.222 - 0.0592 \log 0.0250) = -0.073$ V

(a) AgI forms first at a potential of 0.0300 V (galvanic cell).

(b) When $[I^-] \leq 10^{-5}$ M

$E_{cell} = 0.244 - (-0.151 - 0.0592 \log 10^{-5}) = 0.099$ V

AgBr does not form until $E_{cell} = 0.076$ V so the separation is feasible if the E_{cell} does is kept above 0.076 V.

(c) I^- could be separated from Cl^- by maintaining the cell potential above –0.073 V.

(d) For $[Br^-] \leq 10^{-5}$ M

$E_{cell} = 0.244 - (0.073 - 0.0592 \log 10^{-5}) = -0.125$ V

But AgCl forms at a cell potential of –0.073 V, so separation is not feasible.

24-5. (a) $$E_{cell} = 0.854 - \frac{0.0592}{2}\log\frac{1}{10^{-6}} - 0.244 = 0.432 \text{ V}$$

(b) $$K_f = 1.8 \times 10^7 = \frac{[Hg(SCN)_2]}{[Hg^{2+}][SCN^-]^2} = \frac{[Hg(SCN)_2]}{[Hg^{2+}](0.150)^2}$$

$[Hg(SCN)_2] + [Hg^{2+}] = 10^{-6}$

Because of the large amount of SCN^-, we can safely assume that $[Hg^{2+}] << [Hg(SCN)_2]$

Substituting into the expression for K_f, we find

$$1.8 \times 10^7 = \frac{1.00\times10^{-6}}{[\text{Hg}^{2+}]\times(0.150)^2}$$

$[\text{Hg}^{2+}] = 2.47 \times 10^{-12}$

$$E_{\text{cell}} = 0.854 - \frac{0.0592}{2}\log\frac{1}{2.47\times10^{-12}} - 0.244 = 0.266 \text{ V}$$

(c) With a large [Br^-], we can assume $[\text{Hg}^{2+}] + [\text{HgBr}_4^{2-}] \approx [\text{HgBr}_4^{2-}] = 1.00 \times 10^{-6}$

$$E_{\text{cell}} = 0.223 - \frac{0.0592}{2}\log\frac{(0.150)^4}{1.00\times10^{-6}} - 0.244 = -0.101 \text{ V}$$

24-6. (a) $\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}(s)$

To deposit 0.270 g of Co(*s*) would require the following charge

$$Q = 0.270 \text{ g} \times \frac{1 \text{ mol Co}}{58.93 \text{ g}} \times \frac{2 \text{ mol e}^-}{\text{mol Co}} \times \frac{1 \text{ F}}{\text{mol e}^-} \times \frac{96485 \text{ C}}{\text{F}} = 8.841 \times 10^2 \text{ C}$$

$Q = It$ so $t = Q/I$

$t = 8.841 \times 10^2$ C/0.750 C/s = 1178.8 s or 19.6 min

(b) $3\,\text{Co}^{2+} + 4\,\text{H}_2\text{O} \rightleftharpoons \text{Co}_3\text{O}_4(s) + 8\text{H}^+ + 2\text{e}^-$ 3 mol Co^{2+} consumed per 2 mol e^-

$$Q = 0.270 \text{ g} \times \frac{1 \text{ mol Co}}{58.93 \text{ g}} \times \frac{2 \text{ mol e}^-}{3 \text{ mol Co}} \times \frac{1 \text{ F}}{\text{mol e}^-} \times \frac{96485 \text{ C}}{\text{F}} = 2.947 \times 10^2 \text{ C}$$

$t = 2.947 \times 10^2$ C/0.750 C/s = 392.95 s or 6.55 min

24-7. (a) $$Q = 0.300 \text{ g} \times \frac{1 \text{ mol Tl}}{204.37 \text{ g}} \times \frac{3 \text{ mol e}^-}{\text{mol Tl}} \times \frac{1 \text{ F}}{\text{mol e}^-} \times \frac{96485 \text{ C}}{\text{F}} = 4.249 \times 10^2 \text{ C}$$

$t = Q/I = 4.249 \times 10^2$ C/0.905 C/s = 469.5 s or 7.83 min

(b) $2\text{Tl}^+ + 3\,\text{H}_2\text{O} \rightleftharpoons \text{Tl}_2\text{O}_3(s) + 6\text{H}^+ + 4\,\text{e}^-$ 2 mol Tl^+ consumed per 4 mol e^-

$$Q = 0.300\ \text{g} \times \frac{1\ \text{mol Tl}}{204.37\ \text{g}} \times \frac{4\ \text{mol e}^-}{2\ \text{mol Tl}} \times \frac{1\ \text{F}}{\text{mol e}^-} \times \frac{96485\ \text{C}}{\text{F}} = 283.27\ \text{C}$$

t = 283.27 C/0.905 C/s = 313.00 s or 5.22 min

(c) Proceeding as in part (a), with the only difference being 1 mol e^-/mol Tl

Q = 141.63 C

t = 156.5 s or 2.61 min

24-8. Sample 1 at – 1.0V $11.63\ \text{C} \times \frac{1\ \text{mol e}^-}{96485\ \text{C}} \times \frac{2\ \text{mol CCl}_4}{2\ \text{mol e}^-} = 1.25 \times 10^{-4}\text{mol CCl}_4$

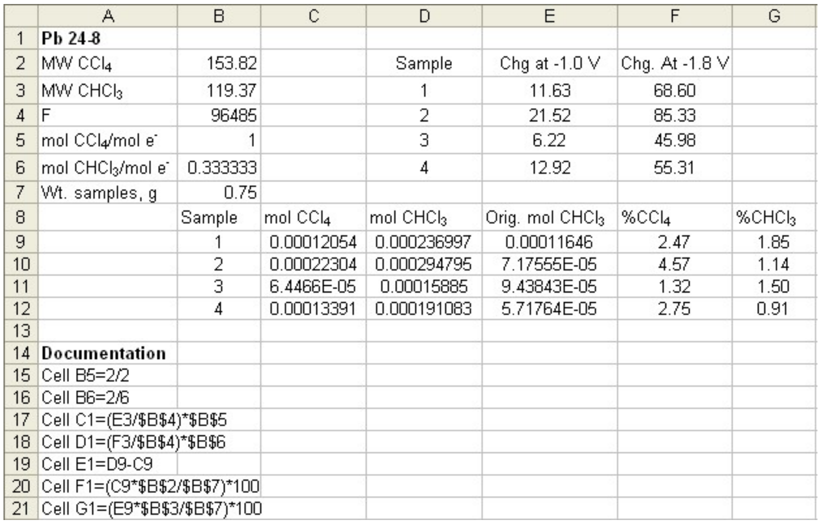
at –1.80 V $68.60\ \text{C} \times \frac{1\ \text{mol e}^-}{96485\ \text{C}} \times \frac{2\ \text{mol CHCl}_3}{6\ \text{mol e}^-} = 2.370 \times 10^{-4}\ \text{mol CHCl}_3$

original no. mol $CHCl_3 = 2.370 \times 10^{-4} - 1.205 \times 10^{-4} = 1.165 \times 10^{-4}$

$$\frac{1.205 \times 10^{-4}\ \text{mol CCl}_4 \times 153.82\ \text{g CCl}_4/\text{mol CCl}_4}{0.750\ \text{g sample}} \times 100\% = 2.47\%\ \text{CCl}_4$$

$$\frac{1.165 \times 10^{-4}\ \text{mol CHCl}_3 \times 119.37\ \text{g CHCl}_3/\text{mol CHCl}_3}{0.750\ \text{g sample}} \times 100\% = 1.85\%\ \text{CHCl}_3$$

In a similar manner, we can calculate the other percentages as shown in the spreadsheet.



	A	B	C	D	E	F	G
1	**Pb 24-8**						
2	MW CCl_4	153.82		Sample	Chg at -1.0 V	Chg. At -1.8 V	
3	MW $CHCl_3$	119.37		1	11.63	68.60	
4	F	96485		2	21.52	85.33	
5	mol CCl_4/mol e^-	1		3	6.22	45.98	
6	mol $CHCl_3$/mol e^-	0.333333		4	12.92	55.31	
7	Wt. samples, g	0.75					
8		Sample	mol CCl_4	mol $CHCl_3$	Orig. mol $CHCl_3$	%CCl_4	%$CHCl_3$
9		1	0.00012054	0.000236997	0.00011646	2.47	1.85
10		2	0.00022304	0.000294795	7.17555E-05	4.57	1.14
11		3	6.4466E-05	0.00015885	9.43843E-05	1.32	1.50
12		4	0.00013391	0.000191083	5.71764E-05	2.75	0.91
13							
14	**Documentation**						
15	Cell B5=2/2						
16	Cell B6=2/6						
17	Cell C1=(E3/$B$4)*$B$5						
18	Cell D1=(F3/$B$4)*$B$6						
19	Cell E1=D9-C9						
20	Cell F1=(C9*$B$2/$B$7)*100						
21	Cell G1=(E9*$B$3/$B$7)*100						

24-9. 1 mol As_2O_3 = 2 mol $HAsO_3^{2-}$ = 2 mol I_2 = 4 mol e^-

$$Q = 0.1276 \text{ C/s} \times (11 \text{ min} \times 60 \text{ s/min} + 54 \text{ s}) = 91.106 \text{ C}$$

$$\text{Mass } As_2O_3 = \frac{91.106 \text{ C}}{96485 \text{ C/mol e}^-} \times \frac{1 \text{ mol } As_2O_3}{4 \text{ mol e}^-} \times \frac{197.8 \text{ g } As_2O_3}{\text{mol}} = 0.04669$$

$$\%As_2O_3 = \frac{0.04669 \text{ g}}{6.39} \times 100 = 0.731$$

24-10. The equivalent mass of an acid is that mass that contains one mole of titratable H^+.

$$0.0441 \text{ C/s} \times 266 \text{ s} \times \frac{1 \text{ F}}{96485 \text{ C}} \times \frac{1 \text{ equiv HA}}{\text{F}} = 1.216 \times 10^{-4} \text{ equiv HA}$$

$$\text{equiv mass} = \frac{0.0809 \text{ g HA}}{1.216 \times 10^{-4} \text{ equiv HA}} = 665 \text{ g/equiv}$$

24-11. 1 mol $C_6H_5NH_2$ = 3 mol Br_2 = 6 mol e^-

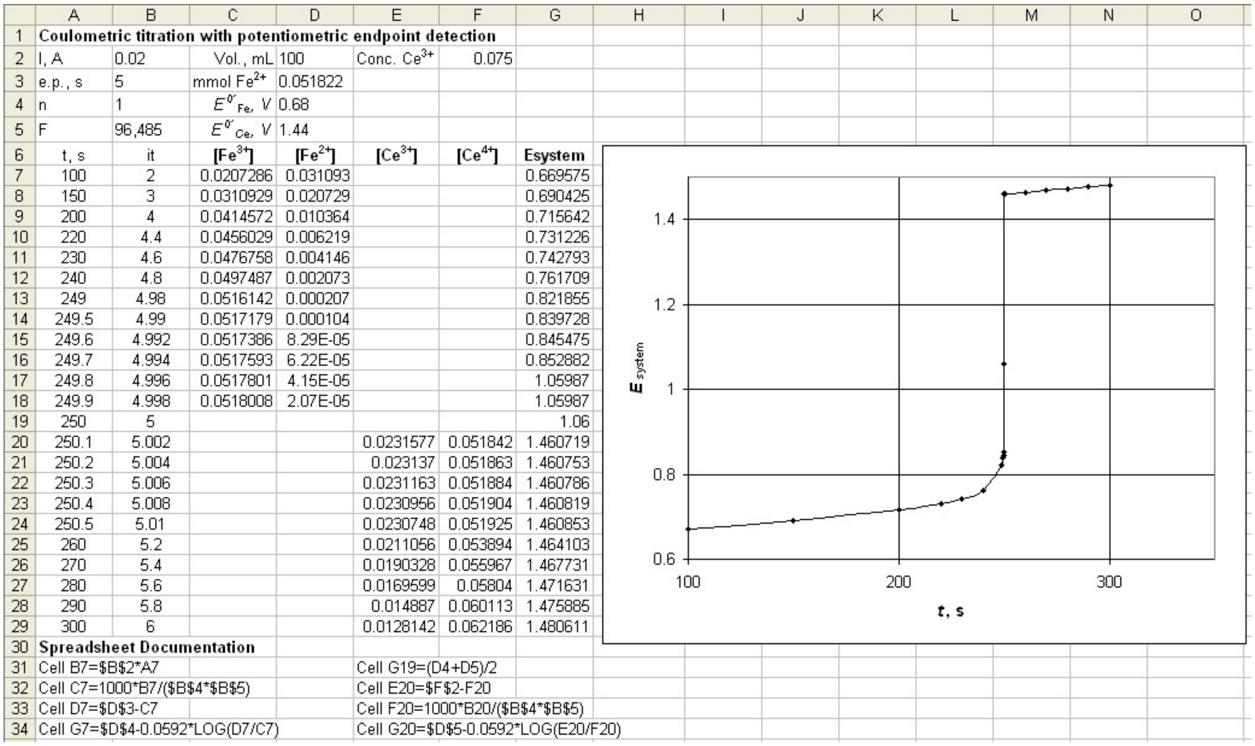
$$Q = (3.76 - 0.27) \text{ min} \times 60 \text{ s/min} \times 1.00 \times 10^{-3} \text{ C/s} = 0.2094 \text{ C}$$

$$\text{mol } C_6H_5NH_2 = 0.2094 \text{ C} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol } C_6H_5NH_2}{6 \text{ mol e}^-} = 3.617 \times 10^{-7}$$

$$\text{mass } C_6H_5NH_2 = 3.617 \times 10^{-7} \text{ mol } C_6H_5NH_2 \times \frac{93.128 \text{ g}}{\text{mol } C_6H_5NH_2} \times 10^6 \text{ µg/g}$$

$$= 33.7 \text{ µg}$$

24-12. The spreadsheet is attached.



	A	B	C	D	E	F	G
1	**Coulometric titration with potentiometric endpoint detection**						
2	I, A	0.02	Vol., mL	100	Conc. Ce^{3+}	0.075	
3	e.p., s	5	mmol Fe^{2+}	0.051822			
4	n	1	$E^{0'}_{Fe}$, V	0.68			
5	F	96,485	$E^{0'}_{Ce}$, V	1.44			
6	t, s	it	**$[Fe^{3+}]$**	**$[Fe^{2+}]$**	**$[Ce^{3+}]$**	**$[Ce^{4+}]$**	**Esystem**
7	100	2	0.0207286	0.031093			0.669575
8	150	3	0.0310929	0.020729			0.690425
9	200	4	0.0414572	0.010364			0.715642
10	220	4.4	0.0456029	0.006219			0.731226
11	230	4.6	0.0476758	0.004146			0.742793
12	240	4.8	0.0497487	0.002073			0.761709
13	249	4.98	0.0516142	0.000207			0.821855
14	249.5	4.99	0.0517179	0.000104			0.839728
15	249.6	4.992	0.0517386	8.29E-05			0.845475
16	249.7	4.994	0.0517593	6.22E-05			0.852882
17	249.8	4.996	0.0517801	4.15E-05			1.05987
18	249.9	4.998	0.0518008	2.07E-05			1.05987
19	250	5					1.06
20	250.1	5.002			0.0231577	0.051842	1.460719
21	250.2	5.004			0.023137	0.051863	1.460753
22	250.3	5.006			0.0231163	0.051884	1.460786
23	250.4	5.008			0.0230956	0.051904	1.460819
24	250.5	5.01			0.0230748	0.051925	1.460853
25	260	5.2			0.0211056	0.053894	1.464103
26	270	5.4			0.0190328	0.055967	1.467731
27	280	5.6			0.0169599	0.05804	1.471631
28	290	5.8			0.014887	0.060113	1.475885
29	300	6			0.0128142	0.062186	1.480611
30	**Spreadsheet Documentation**						
31	Cell B7=$B$2*A7				Cell G19=(D4+D5)/2		
32	Cell C7=1000*B7/($B$4*$B$5)				Cell E20=$F$2-F20		
33	Cell D7=$D$3-C7				Cell F20=1000*B20/($B$4*$B$5)		
34	Cell G7=$D$4-0.0592*LOG(D7/C7)				Cell G20=$D$5-0.0592*LOG(E20/F20)		

CHAPTER 25

25-1. (a) In voltammetry, we measure the current in a cell as the applied electrode potential is varied in a systematic fashion. In amperometry, we measure the current in a cell at a fixed value of electrode potential.

(b) In linear scan voltammetry, the current in a cell is measured as the applied potential is varied at a constant rate. In pulse voltammetry, an excitation signal is used that consists of a series of pulses that increase in size as a function of time.

(c) As shown in Figures 25-29 and 25-31, differential pulse voltammetry and square-wave voltammetry differ in the pulse sequence used.

(d) Figure 25-21 compares the rotating disk electrode and the ring-disk electrode. The RDE usually constains a single disk. A ring-disk electrode contains a second ring-shaped electrode that is electrically isolated from the center disk. After an electroactive species is generated at the disk, it is then swept passed the ring where it undergoes a second electrochemical reaction.

(e) The faradaic impedance models the frequency-dependent mass- and electron-transfer processes that occur in the cell. The entire array of charged species and dipoles at the electrode-solution interface is the electrical double layer. The interface behaves like a capacitor when the potential across it is changed.

(f) In voltammetry, a limiting current is a constant current that is independent of applied potential. Its magnitude is limited by the rate at which a reactant is brought to the electrode surface by diffusion, migration , or convection. A diffusion current is the limiting current when mass transport is by diffusion and migration and convection have been eliminated.

(g) Turbulent flow is a type of liquid flow that has no regular pattern. Laminar flow is a type of liquid flow in which layers of liquid slide by one another in a direction that is parallel to a solid surface.

(h) The difference between the half-wave potential $E_{1/2}$ and the standard potential E^0 for a reversible reaction is shown by Equation 25-12

$$E_{1/2} = E_{\mathrm{A}}^0 - \frac{0.0592}{n}\log\frac{k_{\mathrm{A}}}{k_{\mathrm{P}}} - E_{\mathrm{ref}}$$

If the mass transfer coefficients k_{A} and k_{P} are nearly the same, $E_{1/2} \approx E_{\mathrm{A}}^0 - E_{\mathrm{ref}}$. Hence, $E_{1/2}$ is often very nearly equal to E^0 versus the reference electrode.

(i) In normal stripping methods, the analyte is deposited on a mecury drop or in a film by electrolysis. In adsorptive stripping methods, the analyte is deposited by physical adsorption. The deposited analyte is determined by stripping in the same way by the two methods.

24-2. (a) A voltammogram is a plot of current as a function of the potential applied to a working electrode in an electrochemical cell.

(b) Hydrodynamic voltammetry is a type of voltammetry in which the analyte solution is vigorously stirred or caused to flow by an electrode thus causing the reactant to be brought to the electrode surface by convection as well as diffusion.

(c) The Nernst diffusion layer is the thin layer of stagnant solution that is immediately adjacent to the surface of an electrode.

(d) A mecury film electrode is formed by depositing a thin film of mercury on a small solid metal or graphite surface.

(e) The half-wave potential is the potential on a voltammetric wave at which the current is one-half of the limiting current.

(f) A voltammetric sensor is an device containing a molecular recognition element (enzyme, antibody, complexing agent, etc.) with which the analyte reacts selectively and the product is detected by voltammetry.

24-3. A high supporting electrolyte concentration is used to minimize the effects of migration to the electrode surface and to reduce the cell resistance which decreases the *IR* drop.

24-4. The reference electrode is placed near the working electrode to minimize the *IR* drop that can distort voltammograms.

24-5. Most organic electrode processes involve hydrogen ions. Unless buffered solutions are used, marked pH changes can occur at the electrode surface as the reaction proceeds.

24-6. Stripping methods are more sensitive than other voltammetric procedures because the analyte can be removed from a relatively large volume of solution and concentrated in a small volume. After concentration, the potential is reversed and all the analyte that has been deposited can be rapidly oxidized or reduced, producing a large current.

24-7. The purpose of the electrodeposition step in stripping analysis is to concentrate the analyte in the thin film of mercury on the surface of the working electrode.

24-8. The advantages of a mercury film electrode compared with platinum or carbon electrodes include (1) the high hydrogen overvoltage on mercury, (2) the ability to detect metal ions that are reduced at cathodic potentials, (3) the ability to be used in stripping methods, and (4) the ease of preparation by electrodeposition. The disadvantages include (1) the poor anodic potential range, (2) the relatively large residual currents, and (3) the toxicity of mercury.

24-9. A plot of E_{appl} versus $\log\dfrac{i}{i_l - i}$ should yield a straight line having a slope of $\dfrac{-0.0592}{n}$.

Thus, n is readily obtained from the slope.

24-10. For the reduction of quinine (Q) to hydroquinone (H_2Q), Equation 25-3 takes the form

$$E_{\text{appl}} = E^{\circ}_{\text{Q}} - \frac{0.0592}{n}\log\left(\frac{c^{\circ}_{\text{H}_2\text{Q}}}{c^{\circ}_{\text{Q}}\left(c^{\circ}_{\text{H}^+}\right)^2}\right) - E_{\text{ref}}$$

where $c^{0}_{\text{H}^+}$ is the concentration of H^+ at the electrode surface. Substituting Equations 25-7 and 25-10 into this equation gives

$$E_{\text{appl}} = E^{\circ}_{\text{Q}} - \frac{0.0592}{n}\log\left(\frac{k_{\text{Q}}}{k_{\text{H}_2\text{Q}}\left(c^{\circ}_{\text{H}^+}\right)^2}\right) - \frac{0.0592}{n}\log\left(\frac{i}{i_l - i}\right) - E_{\text{ref}}$$

When $i = i_l/2$, E_{appl} is the half-wave potential. With the added assumption that $k_{\text{Q}} \approx k_{\text{H}_2\text{Q}}$, the foregoing equation becomes

$$E_{1/2} = E^{\circ}_{\text{Q}} - E_{\text{ref}} - \frac{0.0592}{n}\log\left(\frac{1}{\left(c^{\circ}_{\text{H}^+}\right)^n}\right) \qquad (1)$$

$$= 0.599 - 0.244 - 0.0592\text{pH}$$

$$= 0.355 - 0.0592\text{pH}$$

(a) At pH 7.00,

$$E_{1/2} = 0.355 - 0.0592 \times 7.00 = -0.059 \text{ V}$$

(b) At pH 5.00

$$E_{1/2} = 0.355 - 0.0592 \times 5.00 = +\,0.059 \text{ V}$$

25-11. Equation 25-17 gives the relationship between peak current, diffusion coefficients and scan rate.

$$i_\mathrm{p} = 2.686\times 10^5 n^{3/2} AcD^{1/2} v^{1/2}$$

If we take the ratio of peak current for experiment 2 $(i_\mathrm{p})_2$ to that for experiment 1, $(i_\mathrm{p})_1$ and eliminate the common terms (e.g., 2.686×10^5, $n^{3/2}$, A) we find

$$\frac{(i_\mathrm{p})_2}{(i_\mathrm{p})_1} = \frac{4.38\ \mathrm{mM} \times 0.72 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}}{0.167\ \mathrm{mM} \times 0.98 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}} \times \frac{(v_2)^{1/2}}{(v_1)^{1/2}} = 19.269 \times \frac{(v_2)^{1/2}}{(v_1)^{1/2}}$$

If the peak currents are to be equal,

$$\frac{(v_2)^{1/2}}{(v_1)^{1/2}} = \frac{1}{19.269} = 0.0519$$

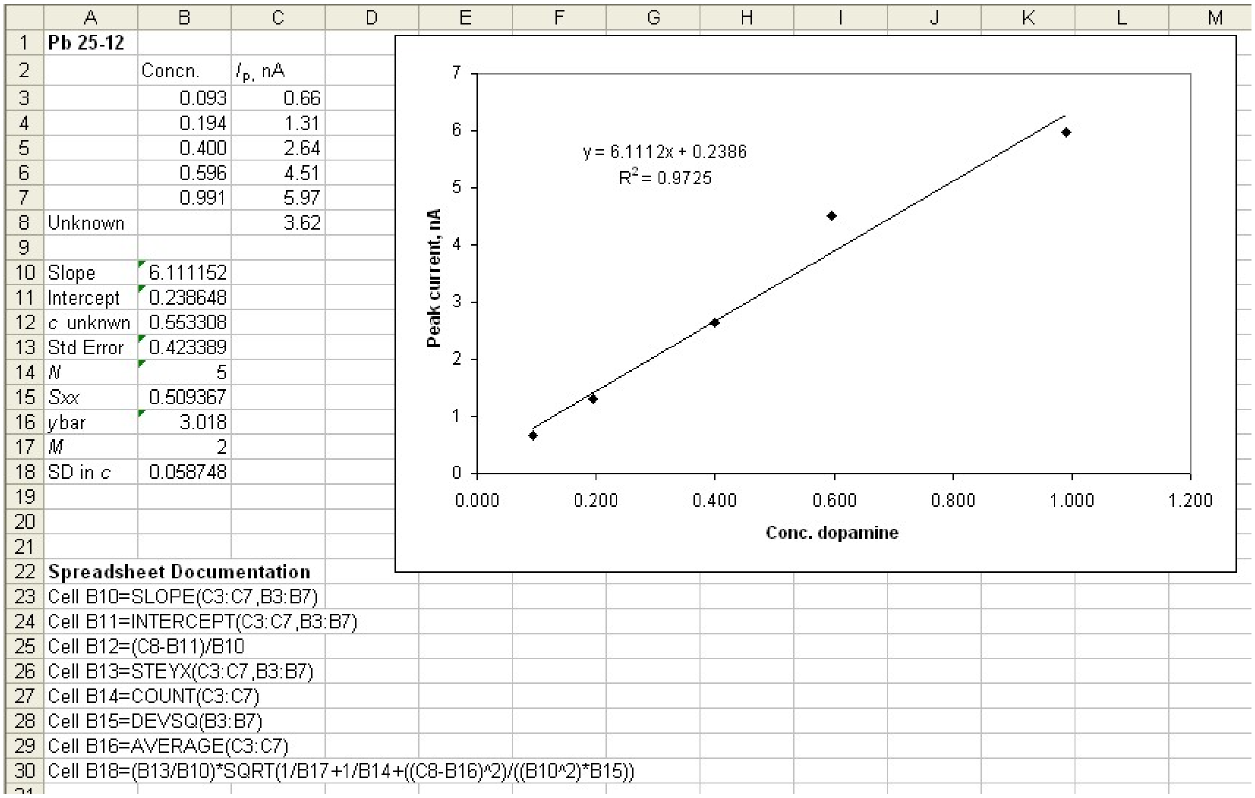
$$v_2 = (0.0519)^2 \times v_1 = 2.693 \times 10^{-3} \times 2.5\ \mathrm{V/s} = 6.7 \times 10^{-3}\ \mathrm{V/s}\ \text{or}\ 6.7\ \mathrm{mV/s}$$

25-12. (a) See attached spreadsheet

(b) As shown in the spreadsheet, the unknown concentration is 0.553 mM (553 μM)

(c) The standard deviation is 0.06 so the unknown should be reported as 0.55 mM.

$$95\%\ \mathrm{CI} = 0.550 \pm \frac{4.30 \times 0.06}{\sqrt{2}} = 0.550 \pm 0.18$$



	A	B	C
1	**Pb 25-12**		
2		Concn.	I_p, nA
3		0.093	0.66
4		0.194	1.31
5		0.400	2.64
6		0.596	4.51
7		0.991	5.97
8	Unknown		3.62
9			
10	Slope	6.111152	
11	Intercept	0.238648	
12	*c* unknwn	0.553308	
13	Std Error	0.423389	
14	*N*	5	
15	*Sxx*	0.509367	
16	*y*bar	3.018	
17	*M*	2	
18	SD in *c*	0.058748	
19			
20			
21			
22	**Spreadsheet Documentation**		
23	Cell B10=SLOPE(C3:C7,B3:B7)		
24	Cell B11=INTERCEPT(C3:C7,B3:B7)		
25	Cell B12=(C8-B11)/B10		
26	Cell B13=STEYX(C3:C7,B3:B7)		
27	Cell B14=COUNT(C3:C7)		
28	Cell B15=DEVSQ(B3:B7)		
29	Cell B16=AVERAGE(C3:C7)		
30	Cell B18=(B13/B10)*SQRT(1/B17+1/B14+((C8-B16)^2)/((B10^2)*B15))		

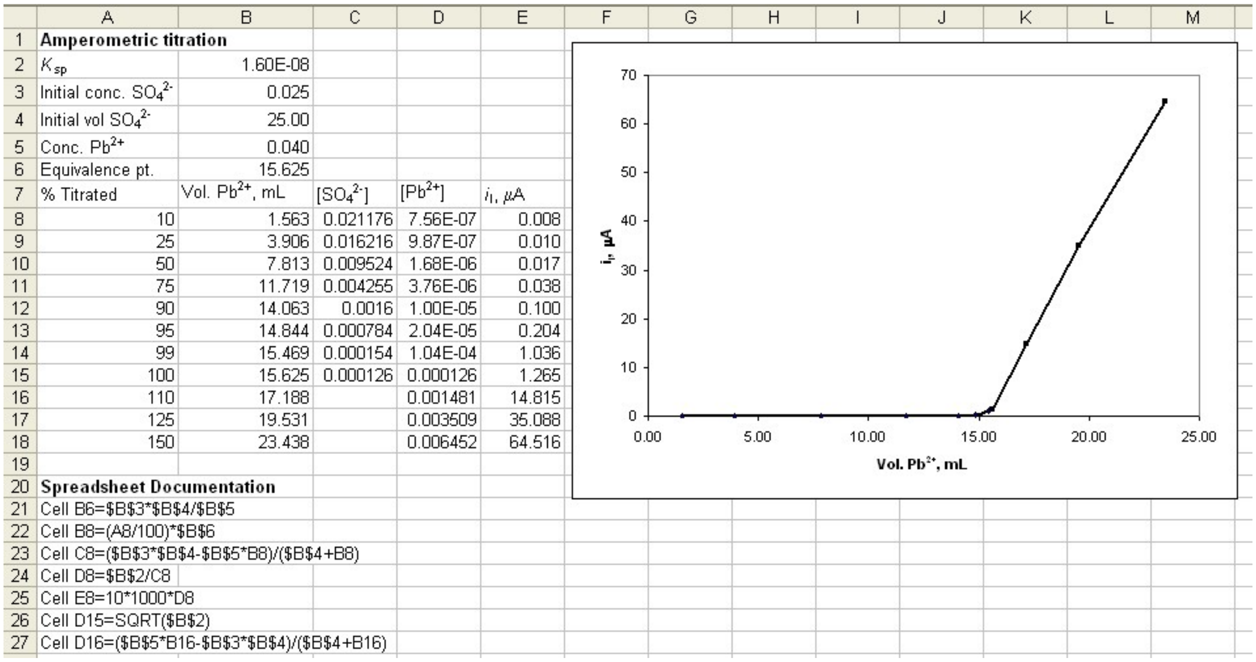
25-13. $i_1 = kc_u$ where $i_1 = 1.78$ µA and c_u is the concentration of the unknown

$$i_2 = \frac{k\left(25.00c_u + 5.00 \times 2.25 \times 10^{-3}\right)}{25.00 + 5.00} = 4.48\ \mu\text{A}$$

From the first equation, $k = i_1/c_u$. Substituting this into the second equation and solving for c_u gives

$$c_u = 2.23 \times 10^{-4}\ \text{M}$$

25-14. See the attached spreadsheet



	A	B	C	D	E
1	**Amperometric titration**				
2	K_{sp}	1.60E-08			
3	Initial conc. SO_4^{2-}	0.025			
4	Initial vol SO_4^{2-}	25.00			
5	Conc. Pb^{2+}	0.040			
6	Equivalence pt.	15.625			
7	% Titrated	Vol. Pb^{2+}, mL	$[SO_4^{2-}]$	$[Pb^{2+}]$	i_l, µA
8	10	1.563	0.021176	7.56E-07	0.008
9	25	3.906	0.016216	9.87E-07	0.010
10	50	7.813	0.009524	1.68E-06	0.017
11	75	11.719	0.004255	3.76E-06	0.038
12	90	14.063	0.0016	1.00E-05	0.100
13	95	14.844	0.000784	2.04E-05	0.204
14	99	15.469	0.000154	1.04E-04	1.036
15	100	15.625	0.000126	0.000126	1.265
16	110	17.188		0.001481	14.815
17	125	19.531		0.003509	35.088
18	150	23.438		0.006452	64.516
19					
20	**Spreadsheet Documentation**				
21	Cell B6=$B$3*$B$4/$B$5				
22	Cell B8=(A8/100)*$B$6				
23	Cell C8=($B$3*$B$4-$B$5*B8)/($B$4+B8)				
24	Cell D8=$B$2/C8				
25	Cell E8=10*1000*D8				
26	Cell D15=SQRT($B$2)				
27	Cell D16=($B$5*B16-$B$3*$B$4)/($B$4+B16)				

25-15. (a) surface area = $4\pi \times r^2 = 4\ \pi \times (3.17\ \text{nm} \times 10^{-7}\ \text{cm/nm})^2 = 1.26 \times 10^{-12}\ \text{cm}^2$

(b) Equation 25-21 can be used to obtain the concentration gradient and Equation 25-22 can be used to find the current. See attached spreadsheet

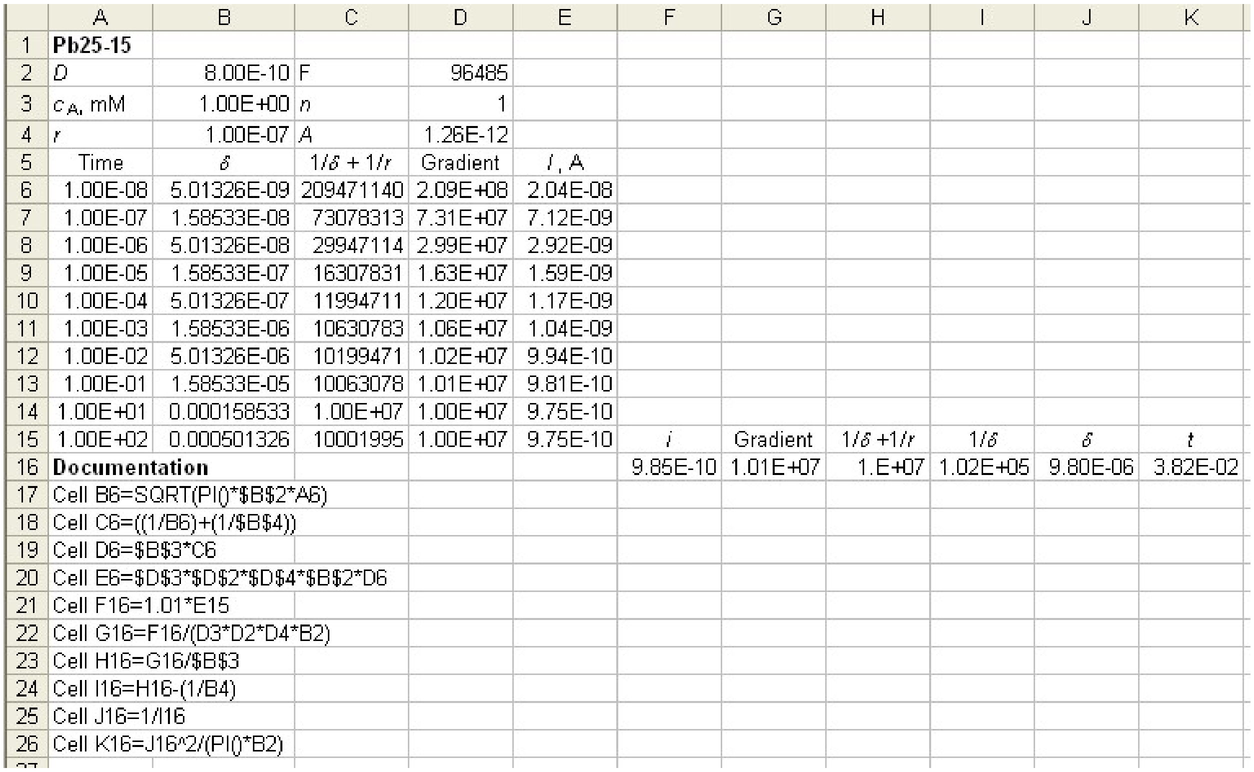
(c) 3.84 µA as shown in the spreadsheet.

(d) Taking as our criterion that the current is 1.01 × the steady state value, we find the time required is 0.0382 s as shown in the spreadsheet.

(e) & (f) The 3-µm electrode is much larger and requires more than 10 s to reach steady state. The Ir electrode radius is

$$r = \sqrt{\frac{A}{4\pi}} = \sqrt{\frac{0.785\ \text{mm}^2\ \times 10^{-6}\ \text{m}^2/\text{mm}^2}{4\pi}} = 2.5 \times 10^{-4}\ \text{m}.$$

Its much larger and does not reach steady state in the foreseeable future.



	A	B	C	D	E	F	G	H	I	J	K
1	**Pb25-15**										
2	D	8.00E-10	F	96485							
3	c_A, mM	1.00E+00	n	1							
4	r	1.00E-07	A	1.26E-12							
5	Time	δ	$1/\delta + 1/r$	Gradient	I, A						
6	1.00E-08	5.01326E-09	209471140	2.09E+08	2.04E-08						
7	1.00E-07	1.58533E-08	73078313	7.31E+07	7.12E-09						
8	1.00E-06	5.01326E-08	29947114	2.99E+07	2.92E-09						
9	1.00E-05	1.58533E-07	16307831	1.63E+07	1.59E-09						
10	1.00E-04	5.01326E-07	11994711	1.20E+07	1.17E-09						
11	1.00E-03	1.58533E-06	10630783	1.06E+07	1.04E-09						
12	1.00E-02	5.01326E-06	10199471	1.02E+07	9.94E-10						
13	1.00E-01	1.58533E-05	10063078	1.01E+07	9.81E-10						
14	1.00E+01	0.000158533	1.00E+07	1.00E+07	9.75E-10						
15	1.00E+02	0.000501326	10001995	1.00E+07	9.75E-10	i	Gradient	$1/\delta + 1/r$	$1/\delta$	δ	t
16	**Documentation**					9.85E-10	1.01E+07	1.E+07	1.02E+05	9.80E-06	3.82E-02
17	Cell B6=SQRT(PI()*$B$2*A6)										
18	Cell C6=((1/B6)+(1/$B$4))										
19	Cell D6=$B$3*C6										
20	Cell E6=$D$3*$D$2*$D$4*$B$2*D6										
21	Cell F16=1.01*E15										
22	Cell G16=F16/(D3*D2*D4*B2)										
23	Cell H16=G16/$B$3										
24	Cell I16=H16-(1/B4)										
25	Cell J16=1/I16										
26	Cell K16=J16^2/(PI()*B2)										

25-16. (a) The advantages include reaching steady-state currents rapidly, having very small charging currents which enables rapid potential scanning, having small *IR* drops, being able to respond to very small volumes and in flowing streams, and having large signal-to-noise ratios.

(b) The currents become very small as the electrode size decreases. Problems can also arise if the electrode dimensions become comparable to the double-layer thickness or to molecular dimensions. In some cases for nanoelectrodes, new theories and experimental approaches may be necessary.

CHAPTER 26

26-1. (a) *Elution* is a process in which species are washed through a chromatographic column by the flow or addition of fresh solvent.

(b) The *mobile phase* in chromatography is the one the moves over or through an immobilized phase that is fixed in place in a column or on the surface of a flat plate.

(c) The *stationary phase* in a chromatographic column is a solid or liquid that is fixed in place. The mobile phase then passes over or through the stationary phase.

(d) The *distribution constant* K in chromatography is the ratio of the concentration (strictly acitivity) of the analyte in the stationary phase to its concentration (activity) in the mobile phase when equilibrium exists between the two phases.

(e) The *retention time* for an analyte is the time interval between its injection onto a column and the appearance of its peak at the other end of the column.

(f) The *retention factor* k is defined by the quation

$$k = K_A V_S / V_M$$

where K_A is the distribution constant for species A and V_S and V_M are the volumes of the stationary and mobile phases respectively.

(g) The *selectivity factor* α of a column toward species A and B is given by $\alpha = K_B/K_A$, where K_B is the distribution constant of the more strongly held species and K_A is the distribution constant for the less strongly held species.

(h) The *plate height* H of a chromatographic column is defined by the relationship

$$H = \sigma^2/\mathrm{L}$$

where σ^2 is the variance obtained from the Gaussian shaped chromatographic peak and L is the length of the column in cm.

(i) *Longitudinal diffusion* is a source of band broadening in a column in which a solute diffuses from the concentrated center of the band to the more dilute regions on either side.

(j) *Eddy diffusion* is a phenomenon in which molecules of an analyte reach the end of a column at different times as a result of traveling through the column by pathways that differ in length.

(k) The *resolution* R_s of a column toward two species A and B is given by the equation

$$R_s = 2\Delta Z/(W_A + W_B)$$

where ΔZ is the distance (in units of time) between the peaks for the two species and W_A and W_B are the widths (also in units of time) of the peaks at their bases.

(l) The *eluent* in chromatography is the fresh mobile phase that carries the analyte through the column.

26-2. The *general elution problem* arises whenever chromatograms are obtained on samples that contain species with widely different distribution constants. When conditions are such that good separations of the more stongly retained species are realized, lack of resolution among the weakly held species is observed. Conversely when conditions are chosend that give satisfactory separations of the weakly retained compounds, severe band broadening and long retention times are encountered for the strongly bound species. The general elution problem is often solved in liquid chromatography by gradient elution and in gas chromatography by temperature programming.

26-3 The variables that lead to *zone broadening* include (1) large particle diameters for stationary phases; (2) large column diamters; (3) high temperatures (important only in GC); (4) for liquid stationary phases, thick layers of the immobilized liquid; and (5) very high or very low flow rates.

26-4. In gas-liquid chromatography, the mobile phases is a gas, whereas in liquid-liquid chromatography, it is a liquid.

26-5. In liquid-liquid chromatography, the stationary phase is a liquid which is immobilized by adsorption or chemical bonding to a solid surface. The equilibria that cause separation are distribution equilibria between two immiscible liquid phases. In liquid-solid chromatography, the stationary phase is a solid surface and the equilibria involved are adsorption equilibria.

26-6. Variables that affect the selectivity factor α include the composition of the mobile phase, the column temperature, the composition of the stationary phase, and chemical interactions between the stationary phase and one of the solutes being separated.

26-7. In GC, the retention factor is varied by changing the column temperature as is done in temperature programming. In LC, variations is achieved by altering the composition of the solvent as in gradient elution.

26-8. The number of plates in a column can be determined by measuring the retention time t_R and the width of a peak at its base W. The number of plates N is then $N = 16(t_R/W)^2$.

26-9. Decreasing the peak widths will increase resolution as will increasing the peak separation. Increasing separation can be done by lengthening the column to increase the number of plates or increasing the selectivity.

26-10. Longitudinal diffusion is much more important in GC that in LC. Longitudinal diffusion is a large contribution to H at low flow rates. The initial decreases in H in plots of plate height vs. flow rate are thus largely the result of longitudinal diffusion.. Because gaseous diffusion coefficients are orders of magnitude larger than liquid values, the phenomenon becomes noticeable at higher flow rates in GC than in LC. The minimum is sometimes not observed at all in LC.

26-11. *Gradient elution* is a method of performing liquid chromatography in which the composition of the mobile phase is change continuously or in steps in order to optimize separations.

26-12. Zone separation is influenced by (1) packing that produce distribution coefficients that differ significantly; (2) increases in the column length; (3) variations in mobile phase composition (LC); (4) optimizing column temperature (GC); (5) changes in the pH of the mobile phase (LC); (6) incorporation of a species in the stationary phase that selectively complexes certain analytes (LC).

26-13. Slow sample introduction leads to band broadening.

26-14. $N = 16(t_R/W)^2$ (Equation 26-21)

(a) For A, $N = 16 \times (5.4/0.41)^2 = 2775.49$ or 2775

For B, $N = 16 \times (13.3/1.07)^2 = 2472.04$ or 2472

For C, $N = 16 \times (14.1/1.16)^2 = 2363.97$ or 2364

For D, $N = 16 \times (21.6/1.72)^2 = 2523.31$ or 2523

(b) $\bar{N} = (2775.49 + 2472.04 + 2363.97 + 2523.31)/4 = 2533.70$ or 2500

$s = 174$ or 200

(c) $H = L/N$ (Equation 26-16 rearranged)

$H = 24.7 \text{ cm}/ 2534 \text{ plates} = 9.749 \times 10^{-3} \text{ cm} = 0.0097 \text{ cm}$

26-15. (a) $k = (t_R - t_M)/t_M$ (Equation 26-12)

For A, $k_A = (5.4 - 3.1)/3.1 = 0.74$

For B, $k_B = (13.3 - 3.1)/3.1 = 3.3$

For C, $k_C = (14.1 - 3.1)/3.1 = 3.5$

For D, $k_D = (21.6 - 3.1)/3.1 = 6.0$

(b) Rearranging Equation 26-9, yields

$K = k(V_M/V_S)$

Substituting the equation in part (a) and the numerical data for V_M and V_S gives

$K = [(t_R - t_M)/t_M] \times 1.37/0.164 = [(t_R - t_M)/t_M] \times 8.35$

$K_A = (5.4 - 3.1)/3.1 \times 8.35 = 6.2$

$K_B = (13.3 - 3.1)/3.1 \times 8.35 = 27$

$K_C = (14.1 - 3.1)/3.1 \times 8.35 = 30$

$K_D = (21.6 - 3.1)/3.1 \times 8.35 = 50$

26-16. (a) $$R_s = \frac{2\left[(t_R)_C - (t_R)_B\right]}{W_B + W_C}$$ (Equation 26-25)

$R_s = 2(14.1 - 13.3)/(1.07 + 1.16) = 0.72$

(b) $$\alpha_{C,B} = \frac{(t_R)_C - t_M}{(t_R)_B - t_M}$$ (Equation 26-15)

$$\alpha_{C,B} = \frac{14.1 - 3.1}{13.3 - 3.1} = 1.08$$

(c) Proceeding as in Example 26-1d, we write

$$\frac{(R_s)_1}{(R_s)_2} = \frac{\sqrt{N_1}}{\sqrt{N_2}} = \frac{0.717}{1.5} = \frac{\sqrt{2534}}{\sqrt{N_2}}$$

$N_2 = 2534 \times (1.5)^2/(0.717)^2 = 11090$ plates.

$L = HN$

From solution 26-14c, $H = 9.749 \times 10^{-3}$ cm/plate

$L = 9.749 \times 10^{-3} \times 11090 = 108$ cm

(d) Proceeding as in Example 26-1e

$$\frac{(t_R)_1}{(t_R)_2} = \frac{(R_s)_1^2}{(R_s)_2^2} = \frac{14.1}{(t_R)_2} = \frac{(0.717)^2}{(1.5)^2}$$

$(t_R)_2 = 14.1 \times (1.5)^2/(0.717)^2 = 61.7$ or 62 min.

26-17. (a)

$$R_s = \frac{2\left[(t_R)_C - (t_R)_B\right]}{W_B + W_C} \qquad \text{(Equation 26-25)}$$

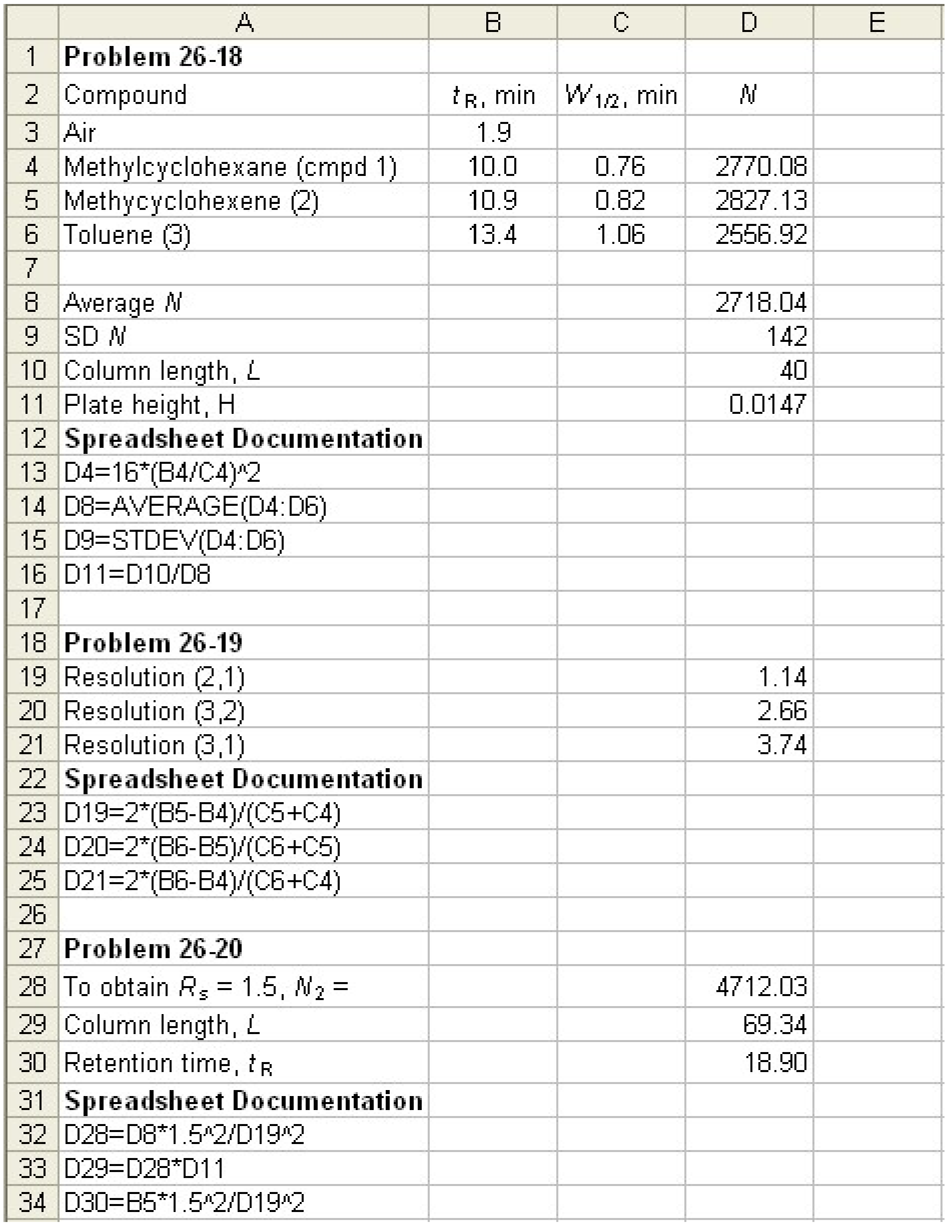
$R_s = 2(21.6 - 14.1)/(1.72 + 1.16) = 5.2$

(b) Proceeding as in Example 26-1d, we write

$$N_1 = N_2 \frac{(R_s)_1^2}{(R_s)_2^2} = 2534 \times \frac{(1.5)^2}{(5.21)^2} = 210 \text{ plates}$$

$L = HN = 9.749 \times 10^{-3}$ cm/plate × 210 plates = 2.0 cm

26-18 through 26-20.



	A	B	C	D	E
1	**Problem 26-18**				
2	Compound	t_R, min	$W_{1/2}$, min	N	
3	Air	1.9			
4	Methylcyclohexane (cmpd 1)	10.0	0.76	2770.08	
5	Methycyclohexene (2)	10.9	0.82	2827.13	
6	Toluene (3)	13.4	1.06	2556.92	
7					
8	Average N			2718.04	
9	SD N			142	
10	Column length, L			40	
11	Plate height, H			0.0147	
12	**Spreadsheet Documentation**				
13	D4=16*(B4/C4)^2				
14	D8=AVERAGE(D4:D6)				
15	D9=STDEV(D4:D6)				
16	D11=D10/D8				
17					
18	**Problem 26-19**				
19	Resolution (2,1)			1.14	
20	Resolution (3,2)			2.66	
21	Resolution (3,1)			3.74	
22	**Spreadsheet Documentation**				
23	D19=2*(B5-B4)/(C5+C4)				
24	D20=2*(B6-B5)/(C6+C5)				
25	D21=2*(B6-B4)/(C6+C4)				
26					
27	**Problem 26-20**				
28	To obtain R_s = 1.5, N_2 =			4712.03	
29	Column length, L			69.34	
30	Retention time, t_R			18.90	
31	**Spreadsheet Documentation**				
32	D28=D8*1.5^2/D19^2				
33	D29=D28*D11				
34	D30=B5*1.5^2/D19^2				

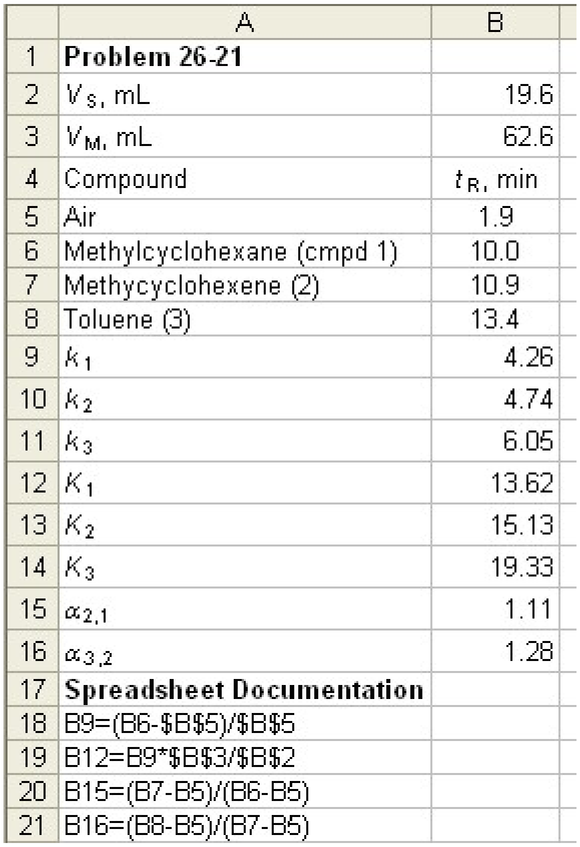
26-18. Rounding results appropriately,

(a) $\overline{N} = 2.7 \times 10^3$; (b) $s = 100$; (c) $H = 0.015$

26-19. (a) $R_s = 1.1$; (b) $R_s = 2.7$; (c) $R_s = 3.7$

26-20. (a) $N = 4.7 \times 10^3$; (b) $L = 69$ cm; (c) $t_R = 19$ min

26-21.



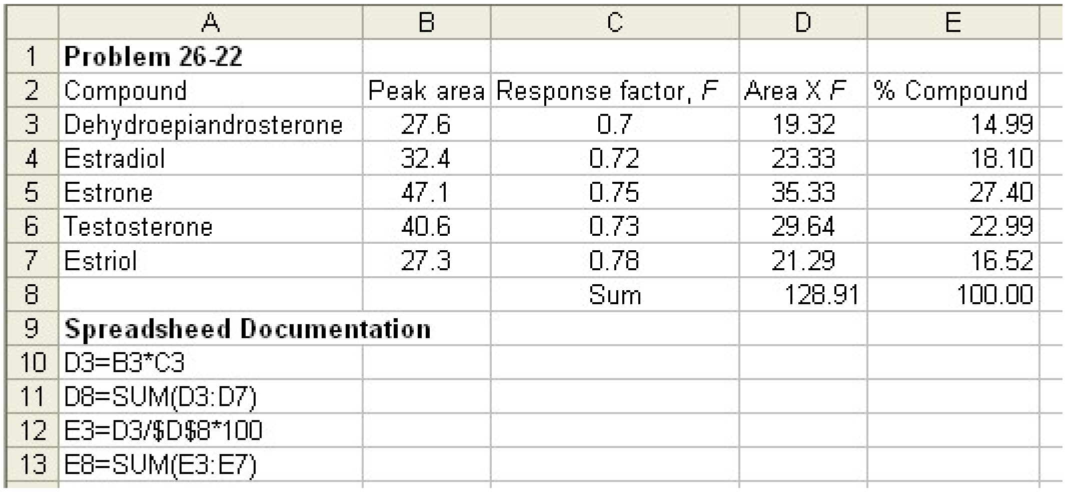
	A	B
1	**Problem 26-21**	
2	V_S, mL	19.6
3	V_M, mL	62.6
4	Compound	t_R, min
5	Air	1.9
6	Methylcyclohexane (cmpd 1)	10.0
7	Methycyclohexene (2)	10.9
8	Toluene (3)	13.4
9	k_1	4.26
10	k_2	4.74
11	k_3	6.05
12	K_1	13.62
13	K_2	15.13
14	K_3	19.33
15	$\alpha_{2,1}$	1.11
16	$\alpha_{3,2}$	1.28
17	**Spreadsheet Documentation**	
18	B9=(B6-$B$5)/$B$5	
19	B12=B9*$B$3/$B$2	
20	B15=(B7-B5)/(B6-B5)	
21	B16=(B8-B5)/(B7-B5)	

Hence (a) $k_1 = 4.3$; $k_2 = 4.7$; $k_3 = 6.1$

(b) $K_1 = 14$; $K_2 = 15$; $K_3 = 19$

(c) $\alpha_{2,1} = 1.11$; $\alpha_{3,2} = 1.28$

26-22.



	A	B	C	D	E
1	**Problem 26-22**				
2	Compound	Peak area	Response factor, *F*	Area X *F*	% Compound
3	Dehydroepiandrosterone	27.6	0.7	19.32	14.99
4	Estradiol	32.4	0.72	23.33	18.10
5	Estrone	47.1	0.75	35.33	27.40
6	Testosterone	40.6	0.73	29.64	22.99
7	Estriol	27.3	0.78	21.29	16.52
8			Sum	128.91	100.00
9	**Spreadsheed Documentation**				
10	D3=B3*C3				
11	D8=SUM(D3:D7)				
12	E3=D3/$D$8*100				
13	E8=SUM(E3:E7)				

CHAPTER 27

27-1. In *gas-liquid chromatography*, the stationary phase is a liquid that is immobilized on a solid. Retention of sample constituents involves equilibria between a gaseous and a liquid phase. In *gas-solid chromatography*, the stationary phase is a solid surface that retains analytes by physical adsorption. Here separations involve adsorption/desorption equilibria.

27-2. In a soap bubble meter, a soap film is formed in a gas buret through which the effluent from a GC column is flowing. The flow rate is then determined from the time required for the film to travel between two of the graduations in the buret.

27-3. *Temperature programming* involves increasing the temperature of a GC column as a function of time. This technique is particularly useful for samples that contain constituents whose boiling points differ significantly. Low boilin point constituents are separated initially at temperatures that provide good resolution. As the separation proceeds, the column temperature is increased so that the higher boilin constituents come off the column with good resolution and at reasonable lengths of time.

27-4. (a) Retention volume V_R is defined by the equation

$$V_R = t_R F$$

where t_R is the retention time and F is the volumetric flow rate.

(b) The corrected retention volume V_R^0 is the retention volume after correctionto the average pressure within the column. It is given by

$$V_R^0 = j t_R F$$

where j is the pressure correction factor given by Equation 27-5.

(c) The specific retention volume V_g is defined tye the equation

$$V_g = \frac{V_R^0 - V_M^0}{m_S} \times \frac{273}{T_C}$$

where V_M is the retention volume of an unretained species, m_S is the mass of the stationary phase, and T_C is the column temperature in kelvins.

27-5. A concentration-sensitive detector responds to the concentration of the analyte in the mobile phase, whereas a mass-sensitive detector responds to the number of analyte molecules or ions that come in contact with the detector. Peak areas for a concentration-sensitive detector increase as the flow rate decreases because the analyte is in contact with the detector for a longer period. Peak areas for a mass-sensitive detector are not greatly affected by flow rate. Using CS for concentration sensitive and MS for mass sensitive, we find for each of the detectors listed: (a) *thermal conductivity* (CS), (b) *atomic emission* (MS), (c) *thermionic* (MS), (d) *electron capture* (CS), (e) *flame photometric* (MS), (f) flame ionization (MS).

27-6. (a) The *thermal conductivity detector* is based on the decrease in thermal conductivity of the helium or hydrogen carrier gas brought about by the presence of analyte molecules.

(b) The *atomic emission detector* is based on the intensity of atomic emission lines generated from certain of the elements contained in analyte molecules. Atomization of the analyte and excitation of atomic emission is brought about by passing the eluent through an energetic microwave field.

(c) The *thermionic detector* is based on the ion currents produced when the mobile phase is combusted in a hydrogen flame and then passed overa heated rubidium silicate bead. It is used primarily for analytes that contain phosphorus or nitrogen.

(d) The *electron capture detector* is based on the attenuation by analyte molecules of a standing ion current generated in the effluent by ionization of mobile phase molecules with a β emitter. Electronegative functional groups are particularly effective at capturing electrons and reducing the ion current.

(e) The *flame photometric detector* is based on the radiation emitted by sulfur and phosphorus containing molecules when the eluent is passed into a low-temperature hydrogen/air flame.

(f) The *flame ionization detector* is based on ionization of the analyte in a small air/hydrogen flame. The ions and electrons produced are collected by a pair of biased electrodes giving rise to a current.

27-7. (a) Advantages, thermal conductivity: general applicability, large linear range, simplicity, nondestructive. Disadvatage: low sensitivity.

(b) Advantages, atomic emission: selectivity, large linear range, high sensitivity, general applicability. Disadvantages: destructive, high equipment costs.

(c) Advantages, thermionic: high sensitivity for compounds containing N and P, good linear range. Disadvantages: destructive, not applicable for many analytes.

(d) Advantages, electron capture: high sensitivity, selectivity toward analytes with electronegative functional groups, nondestructive. Disadvantages: nonlinear response under some circumstances, limited response range.

(e) Advantages, flame photometric: selectivity toward S and P containing analytes, good sensitivity. Disadvantages: destructive, limited applicability.

(f) Advantages, flame ionization: general applicability, large linear range, good sensitivity, low noise, low sensitivity toward most carrier gases and water, simplicity, ease of use. Disadvantage: destructive

27-8. A *total ion chromatogram* is obtained by summing the ion abundances in each mass spectrum and plotting versus time. A *mass chromatogram* is obtained by monitoring one *m/z* value during the chromatography experiment and plotting the ion abundance versus time.

27-9. The combination of GC with MS allows the identification of species eluting from the chromatographic column. The total ion chromatogram gives information similar to a conventional GC chromatogram. By monitoring selected ions, information about specific species can be obtained. By scanning the mass spectrum during the chromatography experiment, species eluting at various times can be identified. Gas chromatography coupled with tandem mass spectrometry allows even more specific identifications to be made.

27-10. *Hyphenated methods* couple GC with a different instrumental technique such as mass spectrometry, FTIR, NMR spectroscopy, or electrochemical methods. The effluent from the GC column is either continuously monitored by the second technique or collected and measured.

27-11. The packing material most often used is diatomaceous earth particles having diameters ranging from 250 to 170 μm or 170 to 149 μm.

27-12. (a) A PLOT column is a porous layer open tubular column, which is also called a support coated open tubular (SCOT) column. The inner surface of a PLOT column is lined with a thin film of a support material, such as a diatomaceous earth. This type of column holds several times a much stationary phase as does a wall-coated column.

(b) A WCOT column is simply a capillary tube fashioned from fused silica, stainless steel, aluminum, copper, plastic, or glass. Its inner walls are coated with a thin layer of the mobile phase.

(c) The SCOT column is described in part (a) of this question.

27-13. Megabore columns are open tubular columns that have a greater inside diameter (530 μm) than typical open tubular columns, which range in diameter from 150 to 320 μm.

27-14. Fused silica columns have greater physical strength and flexibility than glass open tubular columns and are less reactive toward analytes than either glass or metal columns.

27-15. Desirable properties of a stationary phase for GC include: low volatility, thermal stability, chemical inertness, and solvent characteristics that provide suitale k and α values for the analytes to be separated.

27-16. Film thickness influences the rate at which analytes are carried through the column, with the rate increasing as the thickness is decreased. Less band broadening is encountered with thin films.

27-17. Liquid stationary phases are generally bonded and/or cross-linked in order to provide thermal stability and a more permanent stationary phase that will not leach off the column. Bonding involves attaching a monomolecular layer of the stationary phase to the packing surface by means of chemical bonds. Cross linking involves treating the stationary phase while it is in the column with a chemical reagent that creates cross links between the molecules making up the stationary phase.

27-18. (a) Band broadening arises from very high or very low flow rates, large particles making up the packing, thick layers of stationary phase, low temperature and slow injection rates.

(b) Band separation is enhanced by maintaining conditions so that k lies in the range of 1 to 10, using small particles for packing, limiting the amount of stationary phase so that particle coatings are thin, and injecting the sample rapidly.

27-19. The retention index for an analyte is a measure of the rate at which it is carried through a column compared with the rate of movement of two normal alkanes, one that moves faster than the analyte and the other thatmoves more slowly. To obtain the retention index of an analyte on a given column, the log of the adjusted retention times for the two alkanes and the analyte are determined. The retention index for butane is always 400 and for pentane 500. The retention index for the analyte is then derived by interpolation between the two logarithmic retention indexes of the alkane (see solution to Problem 27-21).

27-20. The distribution coefficient for a polar compound will be larger on the carbowax 20M column than on the nonpolar SE-30 column.

27-21.

Sample	Adjusted Retention Time $t'_R = t_R - t_M$	Retention Index, I
n-Pentane	1.59	500
n-Hexane	3.66	600
1-Hexene	2.58	

For 1-hexene,

$$I = 500 + \frac{(\log 2.58 - \log 1.59)}{(\log 3.66 - \log 1.59)} \times 100 = 558$$

27-22. From Handbook of Chemistry and Physics, $P_{\mathrm{H_2O}}$ = 18.88 torr at 21.2°C.

Substituting into Equation 27-3, $T_C = 102.0 + 273 = 375$ K, $F_m = 25.3$ mL/min, $T = 273 + 21.2 = 294.2$ K, $P = 748$ torr gives

$$F = F_m \times \frac{T_C}{T} \times \frac{\left(P - P_{\mathrm{H_2O}}\right)}{P} = 24.3 \times \frac{375}{294.2} \times \frac{(748 - 18.88)}{748} = 30.2 \text{ mL/min}$$

(b) $V_M^0 = jt_M F$ and $P_i = 748$ torr + 26.1 psi × 5.17 torr/psi = 883 torr

$$j = \frac{3[(883/748)^2 - 1]}{2[(883/748)^3 - 1]} = 0.915 \qquad \text{(Equation 27-5)}$$

$t_M = 18.0$ s/60s/min = 0.3 min

$V_M^0 = jt_M F = 0.915 \times 0.3 \text{ min} \times 30.2 \text{ mL/min} = 8.3$ mL

$(V_R^0)_1 = 0.915 \times 1.98 \text{ min} \times 30.2 \text{ mL/min} = 54.7$ mL

$(V_R^0)_2 = 0.915 \times 4.16 \times 30.2 = 115.0$ mL

$(V_R^0)_3 = 0.915 \times 7.93 \times 30.2 = 219.1$ mL

(c) Substituting into Equation 27-6 gives

$$(V_g)_1 = \frac{54.7 - 8.3}{1.40} \times \frac{273}{375} = (54.7 - 8.3) \times 0.520 = 24.1 \text{ mL/g stationary phase}$$

$(V_g)_2 = (115.0 - 8.3) \times 0.520 = 55.5$ mL/g

$(V_g)_3 = (219.1 - 8.3) \times 0.520 = 109.6$ mL/g

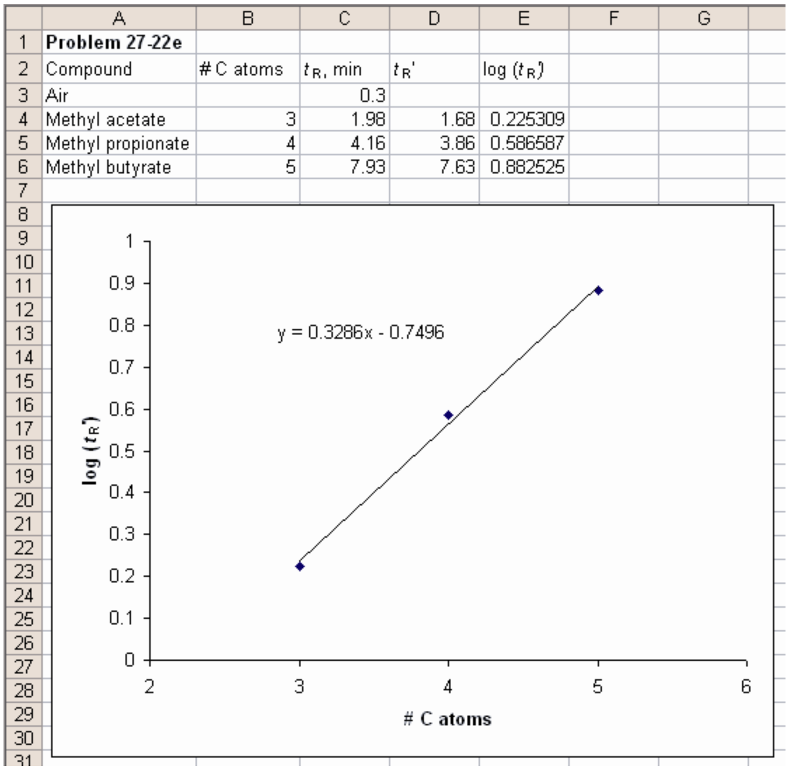
(d) We rearrange Equation 27-7 to give $K = V_g \rho_S T_C/273$

$K_1 = 24.1 \text{ mL/g} \times 1.02 \text{ g/mL} \times 375/273 = 24.1 \times 1.40 = 33.8$

$K_2 = 55.5 \times 1.40 = 77.8$

$K_3 = 109.6 \times 1.40 = 154$

(e) The spreadsheet follows:



	A	B	C	D	E	F	G
1	**Problem 27-22e**						
2	Compound	# C atoms	t_R, min	t_R'	log (t_R)		
3	Air		0.3				
4	Methyl acetate	3	1.98	1.68	0.225309		
5	Methyl propionate	4	4.16	3.86	0.586587		
6	Methyl butyrate	5	7.93	7.63	0.882525		
7							

The equation for the line is

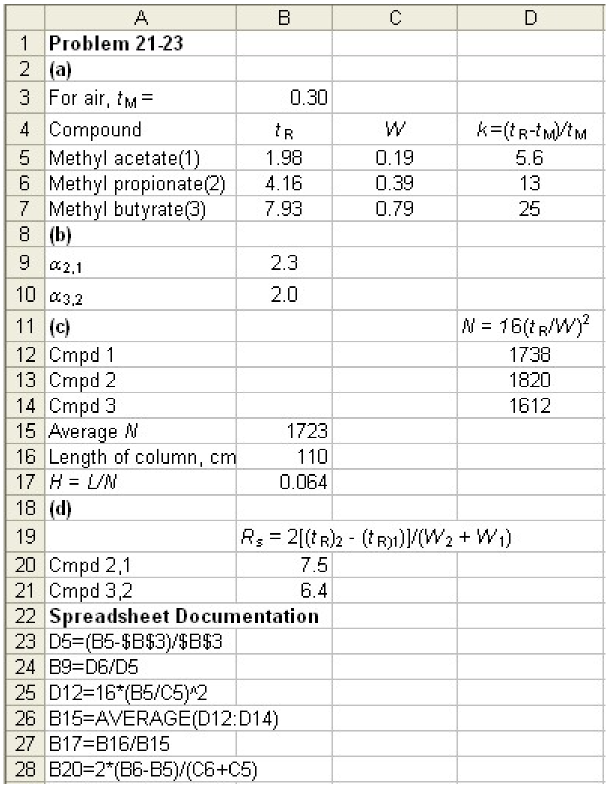
$$\log\ t'_{\mathrm{R}} = m \times (\#\ \text{C atoms}) + b = 0.3286 \times (\#\ \text{C atoms}) - 0.7496$$

For 7 C atoms, $\log\ t'_{\mathrm{R}} = 0.3286 \times 7 - 0.7496 = 1.55$

$t'_{\mathrm{R}} = 35.53$ and $t_{\mathrm{R}} = 35.53 + 0.30 = 35.83$ min

$V^0_{\mathrm{R}} = jt_{\mathrm{R}}F = 0.915 \times 35.83 \times 30.2 = 990$ mL

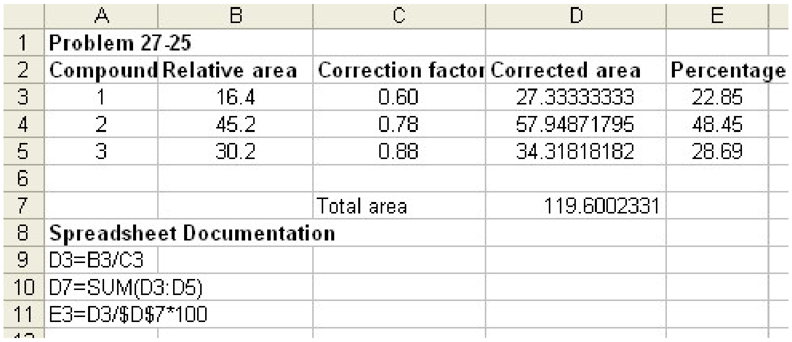
27-23. Using Equations 26-12 for *k*, 26-24 for α, 26-21 for *N*, 26-16 for *H* and 26-25 for R_s, we can construct the following spreadsheet.



	A	B	C	D
1	**Problem 21-23**			
2	**(a)**			
3	For air, t_M =	0.30		
4	Compound	t_R	W	$k=(t_R-t_M)/t_M$
5	Methyl acetate(1)	1.98	0.19	5.6
6	Methyl propionate(2)	4.16	0.39	13
7	Methyl butyrate(3)	7.93	0.79	25
8	**(b)**			
9	$\alpha_{2,1}$	2.3		
10	$\alpha_{3,2}$	2.0		
11	**(c)**			$N = 16(t_R/W)^2$
12	Cmpd 1			1738
13	Cmpd 2			1820
14	Cmpd 3			1612
15	Average *N*	1723		
16	Length of column, cm	110		
17	*H* = *L*/*N*	0.064		
18	**(d)**			
19		$R_s = 2[(t_R)_2 - (t_{R)1})]/(W_2 + W_1)$		
20	Cmpd 2,1	7.5		
21	Cmpd 3,2	6.4		
22	**Spreadsheet Documentation**			
23	D5=(B5-$B$3)/$B$3			
24	B9=D6/D5			
25	D12=16*(B5/C5)^2			
26	B15=AVERAGE(D12:D14)			
27	B17=B16/B15			
28	B20=2*(B6-B5)/(C6+C5)			

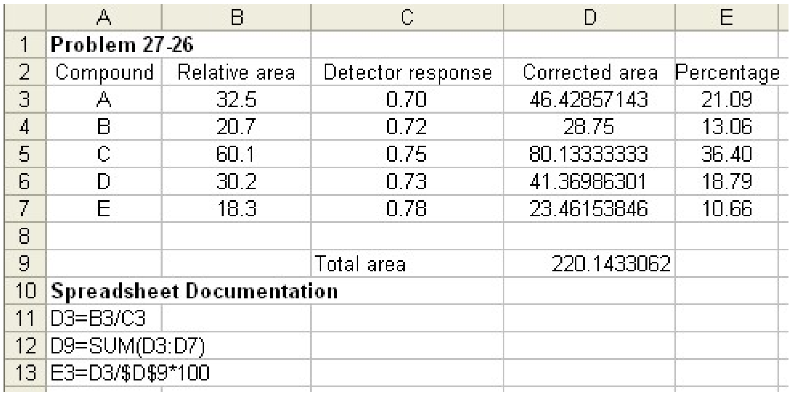
27-24. Since the three compounds are relatively polar, they would be less compatible with a nonpolar solvent such as a silicone oil than with didecylphthalate. Since less time would be spent in the stationary phase for the silicone oil, t_R would be smaller.

27-25.



	A	B	C	D	E
1	**Problem 27-25**				
2	**Compound**	**Relative area**	**Correction factor**	**Corrected area**	**Percentage**
3	1	16.4	0.60	27.33333333	22.85
4	2	45.2	0.78	57.94871795	48.45
5	3	30.2	0.88	34.31818182	28.69
6					
7			Total area	119.6002331	
8	**Spreadsheet Documentation**				
9	D3=B3/C3				
10	D7=SUM(D3:D5)				
11	E3=D3/$D$7*100				

27-26



	A	B	C	D	E
1	**Problem 27-26**				
2	Compound	Relative area	Detector response	Corrected area	Percentage
3	A	32.5	0.70	46.42857143	21.09
4	B	20.7	0.72	28.75	13.06
5	C	60.1	0.75	80.13333333	36.40
6	D	30.2	0.73	41.36986301	18.79
7	E	18.3	0.78	23.46153846	10.66
8					
9			Total area	220.1433062	
10	**Spreadsheet Documentation**				
11	D3=B3/C3				
12	D9=SUM(D3:D7)				
13	E3=D3/$D$9*100				

27-27. (a) Increasing V_S/V_M leads to an increase in the film thickness d_f. This increases causes a marked increase in $C_S u$ (Table 26-3) and thus an increase in H.

(b) Reducing the rate of sample injection will lead to band broadening because all the molecules do not start to traverse the column at the same instant. Reduced efficiency and an increase in H results.

(c) Increasing the injection port temperature will tend to decrease H because the same evaporation rate will increase. Thus, the sample will be put on the column in a narrow band with less initial zone spreading.

(d) Increasing the flow rate may cause either increases or decreases in H depending on the flow rate as can be seen in Figure 26-8b.

(e) Reducing particle size increases the surface area and thus decreases film thickness d_f in the $C_S u$ term in Equations 26-23 and 26-24. A decrease in particle size also makes the $C_M u$ term smaller. Both effects lead to a smaller plate height (Table 26-3).

(f) Decreasing temperature will decrease the diffusion rates D_M and D_S. In Table 26-3, it can be seen that the B/u term becomes smaller and the $C_S u$ and $C_M u$ terms become larger with decreasing diffusion coefficients. This can lead to an increase in H if the $C_S u$ and $C_M u$ terms dominate or a decrease in H if the B/u term dominates. In most cases, H increases as the temperature decreases.

27-28. Gas-solid chromatography is used primarily for separating low molecular mass gaseous species such as carbon dioxide, carbon monoxide and oxides of nitrogen.

27-29. Gas-solid chromatography has limited application because active or polar compounds are retained more or less permanently on the stationary phase. In addition, severe tailing is often observed due to the nonlinear characteristics of the physical adsorption process.

CHAPTER 28

28-1. (a) Species that are somewhat volatile and thermally stable.

(b) Nonpolar low to moderate molecular mass organics and particularly isomeric organic species.

(c) Molecular species that are nonvolatile or thermally unstable.

(d) Most low to moderate molecular mass organic compounds that are nonvolatile or thermally unstable.

(e) Substances that are ionic or that can be derivatized to form ions.

(f) High molecular mass compounds that are soluble in nonpolar solvents.

(g) Low molecular mass nonpolar gases.

(h) High molecular mass hydrophilic compounds.

(i) Small organic and inorganic ions.

28-2. Three methods for improving resolution include:

(1) Adjustment of k_A and k_B by employing a multicomponent mobile phase and varying the raiot of the solvents to find an optimal mixture.

(2) Variation in the chemical composition of the solvent system in such a way as to make α larger.

(3) Employing a different packing in which α is greater.

28-3. In partition chromatography, k is conveniently varied by using a two (or more) component solvent system and varying the ratio of the solvents.

28-4. (a) In gas chromatography, α is generally varied by varying the column packing.

(b) in LC, both column packing and chemical composition of the mobile phase can be varied to yield better α values.

28-5. In adsorption chromatography on an alumina packing, it is generally best to increase the polarity of the mobile phase as the elution proceeds. Thus the rato of acetone to hexane should be increased as the elution proceeds.

28-6. The linear response range of a detector is the range of analyte concentration or mass over which the detector responds linearly. It is the same as the dynamic range defined in Section 1E-2.

28-7. (a) In an *isocratic elution*, the solvent composition is held constant throughout the elution.

(b) In a *gradient elution*, two or more solvents are used and the composition of the mobile phase is changed continuously or in steps as the separation proceeds.

(c) In a *stop-flow* injection, the flow of solvent is stopped, a fitting at the head of the column is removed, and the sample is injected directly onto the head of the column. The fitting is then replaced and pumping is resumed.

(d) A *reversed-phase packing* is a nonpolar packing that is used in partition chromatography with a relatively polar mobile phase.

(e) In a *normal-phase packing*, the stationary phase is polar and the mobile phase is relatively nonpolar.

(f) In *ion-pair chromatography* a large organic counter-ion is added to the mobile phase as an ion-pairing reagent. Separation is achieved either through partitioning of the neutral ion-pair or as a result of electrostatic interactions between the ions in solution and charges on the stationary phase resulting from adsorption of the organic counter-ion.

(g) In *ion chromatography*, the stationary phase is an ion-exchange resin, and detection is ordinarily accomplished by a conductivity detector.

(h) A *bulk property detector* responds to some property of the mobile phase (such as thermal or electrical conductivity) that is altered by the presence of analytes.

(i) A *solute property detector* responds to some property of analytes, such as absorption or fluorescence.

(j) *Sparging* is a process for removing dissolved gases from a solution by sweeping the liquid with a stream of fine bubbles of an inert gas of low solubility.

28-8. A *guard column* is a short column through which the mobile phase flows before it reaces the injection region and the analytical column in HPLC instruments. The composition of the guard column is similar to that of the analytical column except that the particles are generally larger to minimize pressure drop. The purpose of the guard column is to remove particulate matter and contaminants from the mobile phase and to saturate the mobile phase with the stationary phase so that losses of that phase from the analytical column are minimized.

28-9. Normal-phase partition chromatography and adsorption chromatographyare similar in the respect that the stationary phases in both are polar, whereas the mobile phases are relatively nonpolar.

28-10. (a) diethyl ether, benzene, *n*-hexane

(b) acetamide, acetone, dichloroethane

28-11. (a) ethyl acetate, dimethylamine, acetic acid

(b) hexane, propylene, benzene, dichlorobenzene

28-12. In *adsorption chromatography,* separations are based on adsorption equilibria between the components of the sample and a solid surface. In *partition chromatography*, separations are based on distribution equilibria between two immiscible liquids.

28-13. In *size-exclusion chromatography* separations are based upon the size, and to some extent the shape, of molecules with little interactions between the stationary phase and the sample components occurring. In *ion-exchange chromatography,* in contrast, separations are based upon ion-exchange reactions between the stationary phase and the components of the sample in the mobile phase.

28-14. Nonvolatile and thermally unstable compounds can be separated by HPLC by not GC.

28-15. *Pneumatic pumps* are simple, inexpensive and pulse free. They consist of a collapsible solvent container housed in a vessel that can be pressurized by a compressed gas. This pump has limited capacity and pressure output and is not adaptable to gradient elution. The pumping rate depends on solvent viscosity. *Screw-driven syringe pumps* consist of a large syringe in which the piston is moved by a motor-driven screw. They are pulse free and the rate of delivery is easily varied. They suffer from lack of capacity and are inconvenient when solvents must be changed. *Reciprocating pumps* are versatile and widely used. They consist of a small cylindrical chamber that is filled and then emptied by the back-and-forth motion of a piston. Advantages include small internal volume, high output pressures, adaptability to gradient elution, and constant flow rates that are independent of viscosity and back pressure. The pulsed output must be damped.

28-16. In *suppressor-column ion chromatography* the chromatographic column is followed by a suppressor column whose purpose is to convert the ions used for elution to molecular species that are largely nonionic and thus do not interfere with conductometric detection of the analyte species. In *single-column ion chromatography*, low capacity ion exchangers are used so that the concentrations of ions in the eluting solution can be kept low. Detection then is based on the small differences in conductivity caused by the presence of eluted sample components.

28-17. A gas-phase sample is needed for mass spectrometry. The output of the LC column is a solute dissolved in a solvent, whereas the output of the GC column is a gas and thus directly compatible. As a first step in LC/MS, the solvent must be vaporized. When vaporized, however, the LC solvent produces a gas volume that is 10-1000 times greater than the carrier gas in GC. Hence, most of the solvent must also be removed.

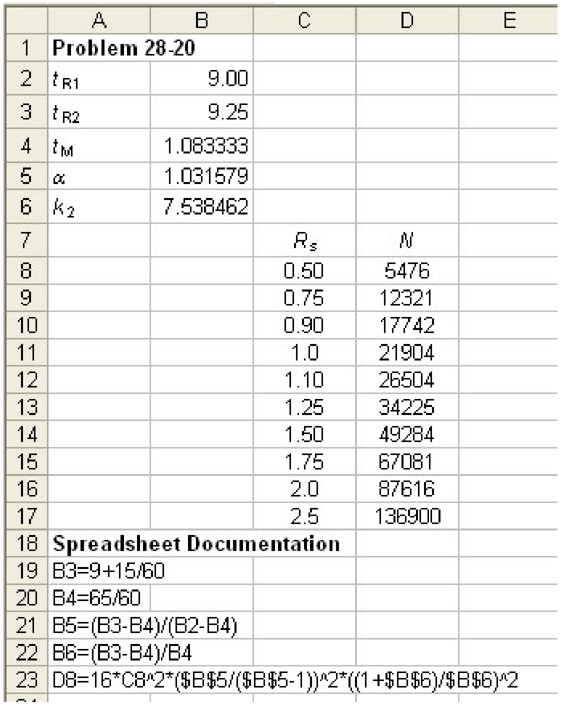
28-18. Comparison of Table 28-1 with Table 27-1 suggests that the GC detectors that are suitable for HPLC are the mass spectrometer, FTIR and possibly photoionization. Many of the GC detectors are unsuitable for HPLC because they require the eluting analyte components to be in the gas-phase.

28-19. A number of factors that influence separation are clearly temperature dependent including distribution constants and diffusion rates. In addition, temperature changes can influence selectivity if components A and B are influenced differently by changes in temperature. Because resolution depends on all these factors, resolution will also be temperature dependent

(a) For a reversed phase chromatographic separation of a steroid mixture, selectivity and, as a consequence, separation could be influenced by temperature dependent changes in distribution coefficients.

(b) For an adsorption chromatographic separation of a mixture of isomers, selectivity and, as a consequence, separation could be influenced by temperature dependent changes in distribution coefficients.

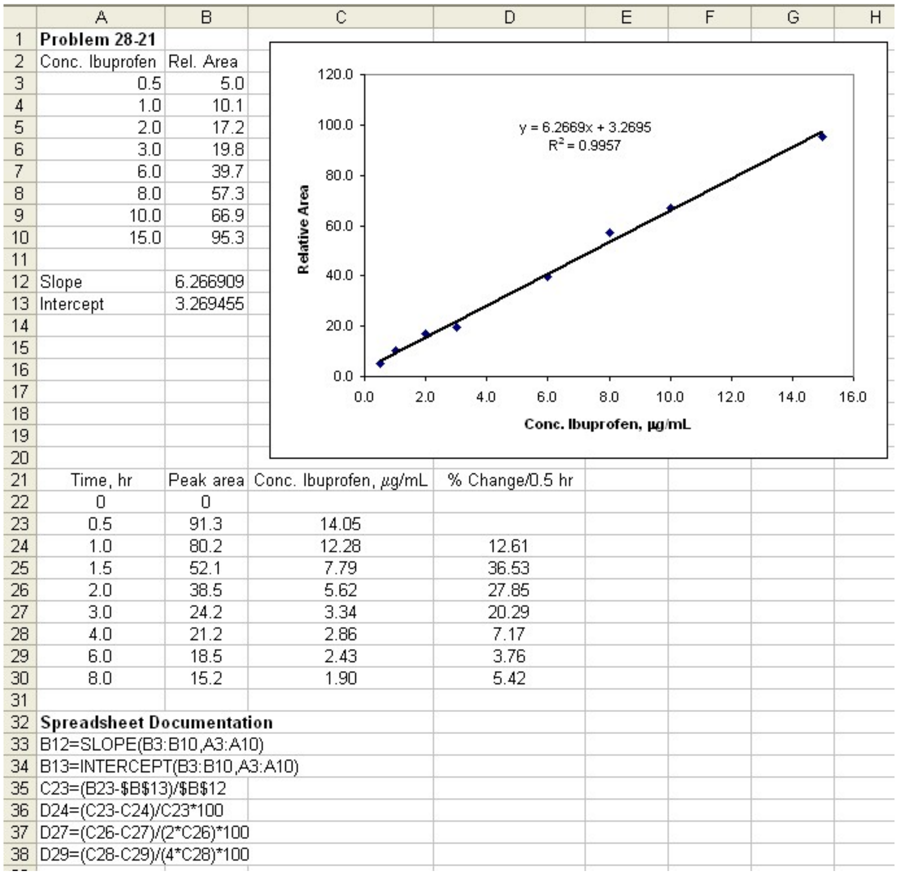
28-20.



	A	B	C	D	E
1	**Problem 28-20**				
2	t_{R1}	9.00			
3	t_{R2}	9.25			
4	t_M	1.083333			
5	α	1.031579			
6	k_2	7.538462			
7			R_s	N	
8			0.50	5476	
9			0.75	12321	
10			0.90	17742	
11			1.0	21904	
12			1.10	26504	
13			1.25	34225	
14			1.50	49284	
15			1.75	67081	
16			2.0	87616	
17			2.5	136900	
18	**Spreadsheet Documentation**				
19	B3=9+15/60				
20	B4=65/60				
21	B5=(B3-B4)/(B2-B4)				
22	B6=(B3-B4)/B4				
23	D8=16*C8^2*($B$5/($B$5-1))^2*((1+$B$6)/$B$6)^2				

If the second peak were twice as broad as the first, R_s and N would be smaller.

28-21.



	A	B	C	D
1	**Problem 28-21**			
2	Conc. Ibuprofen	Rel. Area		
3	0.5	5.0		
4	1.0	10.1		
5	2.0	17.2		
6	3.0	19.8		
7	6.0	39.7		
8	8.0	57.3		
9	10.0	66.9		
10	15.0	95.3		
11				
12	Slope	6.266909		
13	Intercept	3.269455		
14				
15				
16				
17				
18				
19				
20				
21	Time, hr	Peak area	Conc. Ibuprofen, μg/mL	% Change/0.5 hr
22	0	0		
23	0.5	91.3	14.05	
24	1.0	80.2	12.28	12.61
25	1.5	52.1	7.79	36.53
26	2.0	38.5	5.62	27.85
27	3.0	24.2	3.34	20.29
28	4.0	21.2	2.86	7.17
29	6.0	18.5	2.43	3.76
30	8.0	15.2	1.90	5.42
31				
32	**Spreadsheet Documentation**			
33	B12=SLOPE(B3:B10,A3:A10)			
34	B13=INTERCEPT(B3:B10,A3:A10)			
35	C23=(B23-$B$13)/$B$12			
36	D24=(C23-C24)/C23*100			
37	D27=(C26-C27)/(2*C26)*100			
38	D29=(C28-C29)/(4*C28)*100			

From the spreadsheet the largest percentage loss occurs between 1.0 and 1.5 hrs.

28-22. For a normal-phase packing, Equation 28-3 applies. That is

$$\frac{k_2}{k_1} = 10^{(P_1' - P_2')/2}$$

where P_1' and P_2' are the polarity indexes of chloroform and *n*-hexane respectively.

(a) $k_1 = (29.1 - 1.05)/1.05 = 26.7$ (Equation 26-12)

(b) $P'_{AB} = 0.50 \times 4.1 + 0.50 \times 0.1 = 2.10$ (Equation 28-2)

Substituting into the equation for k_2/k_1 gives

$$\frac{10}{26.7} = 10^{(2.1\,-\,P_2')/2}$$

Taking the logarithm of both sides of this equation gives

$$\log\frac{10}{26.7} = -0.427 = (2.1 - P_2')/2$$

$$P_2' = 2 \times 0.427 + 2.1 = 2.95$$

Substituting P_2' for P'_{AB} in Equation 28-2 gives

$$2.95 = \phi_A \times 4.1 + \phi_B \times 0.1$$

where $\phi_A + \phi_B = 1.00$

$$2.95 = 4.1\phi_A + 0.1(1.00 - \phi_A)$$

$$\phi_A = (2.95 - 0.1)/4.0 = 0.712$$

Thus the mixture should be 71% $CHCl_3$ and 29% *n*-hexane.

CHAPTER 29

29-1. (a) The *critical temperature* of a substance is the temperature above which it cannot exist as a liquid phase regardless of pressure. The critical pressure of a substance is the vapor pressure of that substance when it is at its critical temperature.

(b) A *supercritical fluid* is a substance that is maintained above its critical temperature so that it cannot be liquefied regardless of pressure.

29-2. The properties of a supercritical fluid that are of particular importance in chromatography are its density, its viscosity, and the rates at which solutes diffuse in it. The magnitude of each of these properties lies intermediate between a typical gas and a typical liquid.

29-3. (a) Instruments for HPLC and SFC are similar except that a column thermostat and a restrictor device are required for SFC but not for HPLC.

(b) SFC instruments are more complex than GC instruments in that they require a high-pressure pump, a solvent manifold system, a mobile-phase treatment system, a back-pressure regulator, and often a pulse-dampener system.

29-4. Pressure increases cause the density of a supercritical fluid to increase which causes the *k* value for analytes to change. Generally increases in pressure reduce the elution times of solutes.

29-5. Supercritical CO_2 has a number of advantages over the liquid phases used in HPLC including: low cost, nontoxicity, ready availability, lack of odor, and its relatively high critical temperature and low critical pressure.

29-6. SFC is ordinarily faster than HPLC and exhibits less band spreading than is encountered in GC. In contrast to GC, SFC separations can be carried out at relatively low temperatures making the technique applicable to thermally unstable and nonvolatile species. Unlike HPLC, but like GC, flame ionization detectors can be used, which makes the method applicable to more analytes.

29-7. (a) Initially, an increase in flow rate will shorten the elution time to a minimum value, after which the elution time will increase nearly linearly with flow rate (see Figure 29-3).

(b) Pressure increases usually result in reduced elution times.

(c) Temperature increases result in reduced elution times.

29-8. (a) Off-line extractions are simpler. The analytes are collected by dipping the restrictor into a few mL of solvent and allowing the gaseous fluid to escape or by using an adsorbent like silica. On-line extractions involve transferring the effluent from the restrictor directly to a chromatographic system such as a GC. Sample handling between the extraction and measurement is eliminated in an on-line extraction.

(b) In a dynamic extraction, the sample is continually supplied with fresh supercritical fluid. In a static extraction, the extraction cell is pressurized under static conditions and the cell contents are later transferred by flow of fluid from the pump.

29-9. SFE is generally faster than liquid-liquid extractions. The solvent strength can be varied by changes in pressure and temperature. The recovery of analytes in simpler with SFE because the many supercritical fluids are gases at ambient temperature. Also, supercritical fluids are inexpensive, inert, and nontoxic in contrast to most solvents used in liquid-liquid extractions.

29-10. Analytes can be recovered by adsorbing them on silica or another adsorbent or by allowing the supercritical fluid to escape as a gas while the restrictor is immersed in a solvent.

CHAPTER 30

30-1. Electroosmotic flow occurs when a mobile phase in a capillary tube is subjected to a high potential difference between one end of the tube and the other. For a silica tube, the flow is generally away from the positive electrode towards the negative. The flow occurs because of the attraction of positively charge species toward the negative silica surface. This layer of positive charge is mobile and is attracted toward the negative electrode carrying with it the mobile phase molecules.

30-2. Electroosmotic flow can be suppressed by reducing the charge on the interior of the capillary by chemical treatment of the surface.

30-3. In solution, amino acids exist as zwitterions that bear both a positive and a negative charge. At low pH values, the net effective charge is positive because of the interaction of hydrogen ions with the amine groups of the amino acid. At high pH values, the net charge is negative due to the dissociation of the carboxylic acid groups. Thus, at low pH values, the amino acid molecules will be strongly attracted to the negative electrode while in basic solution the opposite will be the case.

30-4. Under the influence of an electric field, mobile ions in solution in a capillary are attracted or repelled by the negative potential of one of the electrodes. The rate of movement toward or away from the negative electrode is dependent on the net charge on the analyte and the size and shape of the analyte molecules. These properties vary from analyte to analyte. Thus, the rate at which molecules migrate under the influence of the electric field vary, and the time it takes them to traverse the column varies, making separation possible.

30-5. (a) $N = \dfrac{\mu_e V}{2D} = \dfrac{(4.31\times10^{-4})(5000)}{2(9.8\times10^{-6})} = 1.1\times10^5$

(b) $N = (4.31\times10^{-4})(10{,}000)/[2(9.8\times10^{-6}) = 2.2\times10^5$

(c) $N = (4.31\times10^{-4})(30{,}000)/[2(9.8\times10^{-6}) = 6.6\times10^5$

30-6. The electrophoretic mobility is given by

$$v = \frac{\mu_e V}{L} = \frac{4.31\times10^{-4}\,\text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1}\times10\times10^3\ \text{V}}{50\ \text{cm}} = 0.0862\ \text{cm s}^{-1}$$

The electroosmotic flow rate is given as 0.85 mm s^{-1} = 0.085 cm s^{-1}

Thus, the total flow rate = 0.0862 + 0.085 = 0.1712 cm s^{-1}, and

t = [(40.0 cm) / 0.1712 cm s^{-1})] × (1 min / 60 s) = 3.9 min

30-7. In *micellar electrokinetic capillary chromatography* surfactants are added to the operating buffer in amounts that exceed the critical micelle concentration. The components of a sample added to this system distribute themselves between the aqueous phase and the hydrocarbon phase in the interior of the micelles according to their distribution coefficients, similar to partition chromatography. The negatively charged micelles do exhibit electrophoretic flow but at a much slower rate than the buffer. Thus, MECC is a true chromatography, where CZE separates sample components simply on the basis of ion mobility in a homogeneous buffer solution.

30-8. The major advantages of MECC include higher column efficiencies and the ease with which pseudostationary phase can be altered.

30-9. The order of elution should be B^+ followed by A^{2+} followed by C^{3+}.

30-10. The elution order in sedimentation FFF is determined by particle size and mass.

30-11. FFF methods are particularly well suited to high molecular weight materials such as polymers, large particles and colloids. In addition, no packing material or stationary phase is needed for separation to occur avoiding undesirable interactions between the packing material and the sample constituents. Finally, the geometry and flow profiles in FFF are well characterized allowing fairly exact theoretical predictions of retention and plate height to be made.

CHAPTER 31

31-1. (a) In TGA, the mass of a sample is measured as a function of temperature.

(b) In DTA, the difference in temperature between the sample and an inert reference is measured as a function of temperature.

(c) In DSC, the difference in heat needed to keep the sample and reference at the same temperature is measured versus temperature. During an endothermic transition, energy must be supplied to the sample, and during an exothermic transition, energy is added to the reference.

(d) In scanning thermal microscopy, a thermally sensitive probe is scanned across the surface of a sample. The electrical power needed to keep the probe temperature constant is measured during the scan. When the probe hits a region of high thermal conductivity, it cools off, and more power is needed to keep it at a constant temperature. When it touches a region of low thermal conductivity, less power is required.

31-2. wt CaC_2O_4 + wt BaC_2O_4 = 0.5713 g

wt $CaCO_3$ + wt $BaCO_3$ = 0.4673 g

$$\text{wt CaC}_2\text{O}_4 = \frac{\text{wt Ca} \times \text{gfw CaC}_2\text{O}_4}{\text{gfw Ca}} = \frac{\text{wt Ca} \times 128.1}{40.08} = 3.196 \times \text{wt Ca}$$

Similarly,

$$\text{wt BaC}_2\text{O}_4 = \text{wt Ba} \times \frac{225.4}{137.3} = 1.642 \times \text{wt Ba}$$

$$\text{wt CaCO}_3 = \text{wt Ca} \times \frac{100.00}{40.08} = 2.497 \times \text{wt Ca}$$

$$\text{wt BaCO}_3 = \text{wt Ba} \times \frac{197.4}{137.3} = 1.436 \times \text{wt Ba}$$

$3.196 \times \text{wt Ca} + 1.642 \times \text{wt Ba} = 0.5713$ g

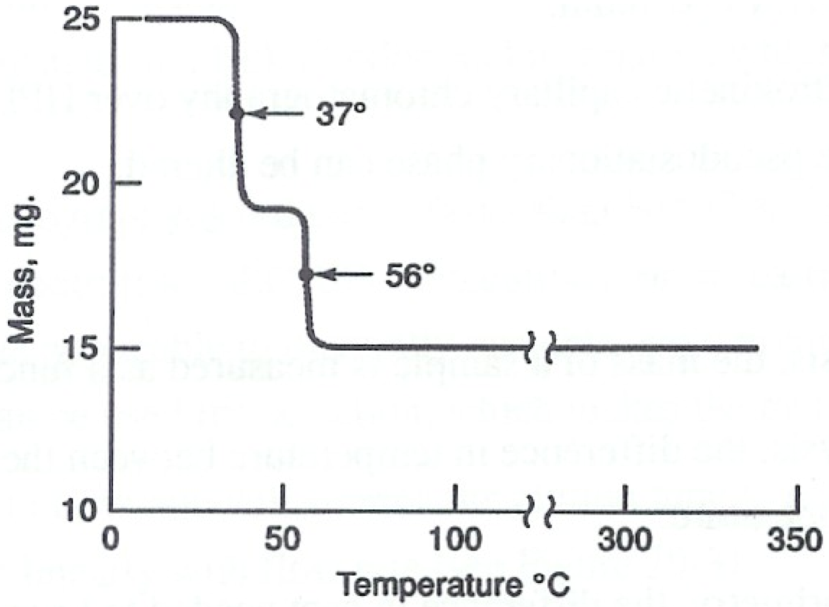
$2.497 \times \text{wt Ca} + 1.438 \times \text{wt Ba} = 0.4673$ g

wt Ca = 1.09 g wt Ba = 0.135g

%Ca = 0.109 × 100/0.6025 = 18.1

% Ba = 0.135 × 100/0.6025 = 22.4

31-3. If 25.0 mg of $FeCl_3{\cdot}6H_2O$ decomposes, 19.2 mg of $FeCl_3{\cdot}5H_2O$ will be the first reaction product, and further heating will produce 15.0 mg of anhydrous $FeCl_3$. There is no change in mass associated with the melting of $FeCl_3$. See the following sketch.



31-4. The melting point of benzoic acid is not very pressure dependent. The boiling point, however, increases as the pressure increases.

31-5. The organic matter in most oil shale is a complex bituminous material called Kerogen that can be converted into recoverable oil. High quality oil shales typically contain 10% to 15% organic matter. A thermogravimetric analysis in an inert atmosphere would provide an indication of the volatile mass fraction in the sample, and a TGA run in an oxygen atmosphere could be used to evaluate the combustible mass fraction. A DSC experiment run in an inert atmosphere would provide information about the temperature requirements for volatilizing the organic matter, and a DSC run in an oxygen atmosphere would provide information about the total energy content of the sample. (NOTE: Crushing and grinding shale without significantly changing the composition of the sample would be a very challenging part of any such experiment as would obtaining a representative sample of an oil shale deposit.

31-6. The thermocouple is seldom immersed directly in the sample because, first the precision of the experiment is highly dependent on the reproducible placement of the thermocouple, and second, the thermocouple my react with the sample or catalyzis seldom immersed directly in the sample because, first the precision of the experiment is highly dependent on the reproducible placement of the thermocouple, and second, the thermocouple my react with the sample or catalyze reactions of the sample.

31.7.

Physical Change	**Thermal Behavior**
Melting/Crystallization	Endo/Exo
Vaporization	Endo
Sublimation	Endo
Adsorption/Desorption	Exo/Endo

31-8.

Chemical Change	**Thermal Behavior**
Dehydration	Endo
Decomposition	Endo/Exo
Oxidation	Exo

31-9. DSC is of more widespread utility than TGA because many important thermal transitions (melting, crystallization, glass transition, etc.) are not accompanied by a change in mass.

31-10. The glass-like state of a sample has one heat capacity, and the rubber-like state of the same sample has a different heat capacity. Because the heat capacities for the two states differ, there is a shift in the baseline at the glass transition, but, in an ideal sample, no exothermic or endothermic peak is observed.

31-11. Power-compensated DSC uses two small individual heaters and temperature sensors (Figure 31-11), and the power required to keep the sample and reference at the same temperature is the analytical parameter. Heat flux DSC uses a single oven with sample and reference temperature sensors (See Figure 31-12); the difference in the temperature of the sample and the reference is proportional to the differential heat flow and serves as the analytical parameter.

CHAPTER 32

32-1. (a) α or ${}^{4}_{2}\mathrm{He}$ (d) ${}^{160}_{62}\mathrm{Sm}$

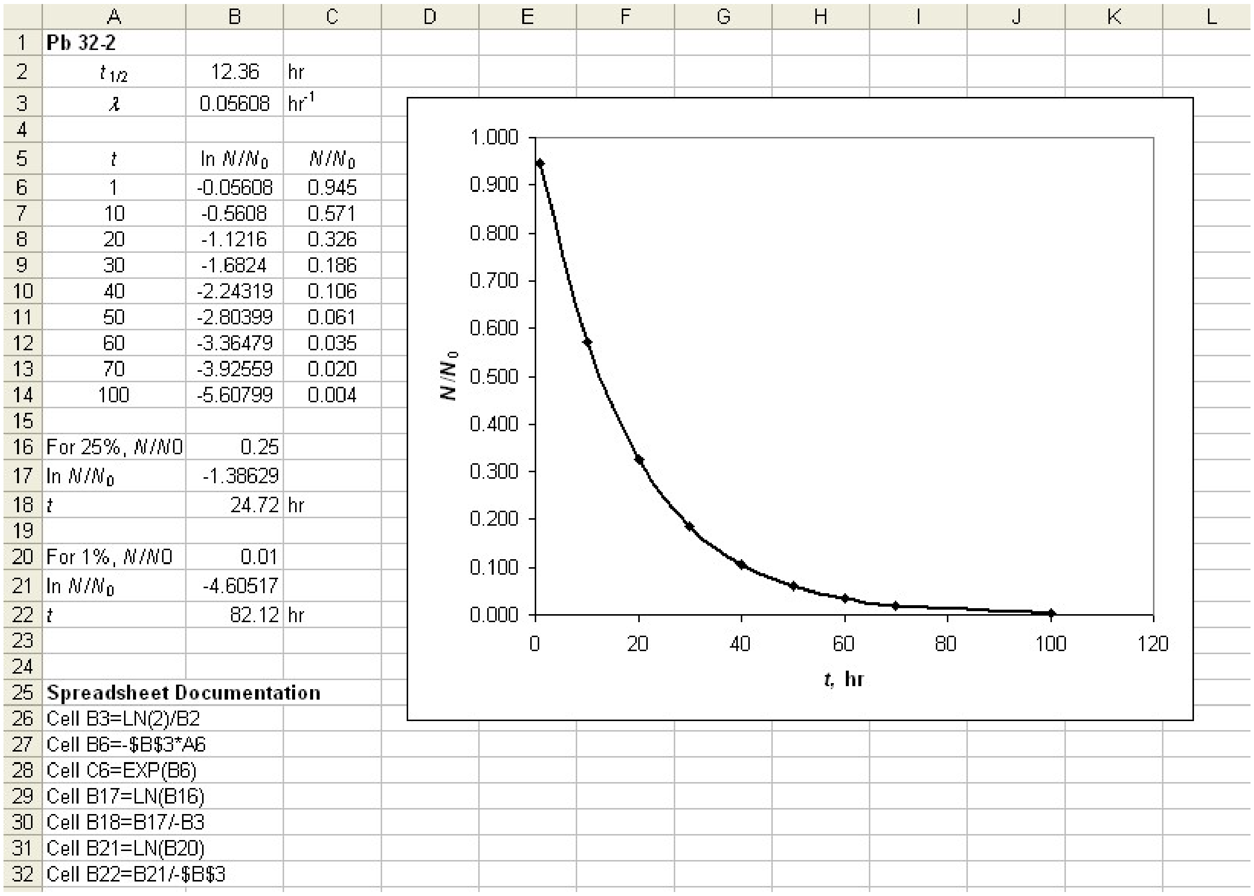
(b) β^{+} (e) n

(c) β^{-} (f) e^{-} (K capture)

32-2. Here, in the spreadsheet below, we use Equations 32-5

$$t_{1/2} = \ln 2/\lambda$$

and 32-3 $\ln (N/N_0) = -\lambda t$

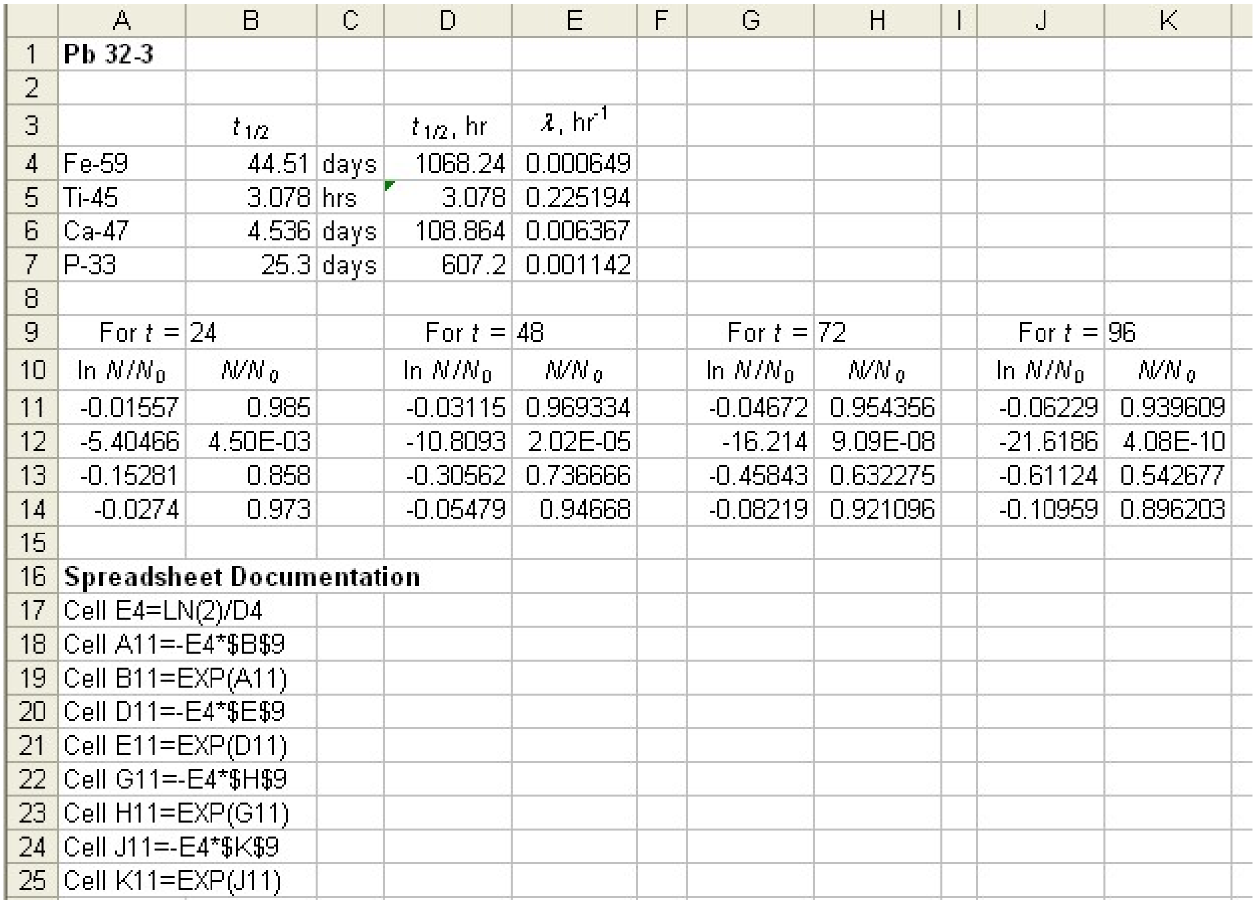


	A	B	C
1	**Pb 32-2**		
2	$t_{1/2}$	12.36	hr
3	λ	0.05608	hr^{-1}
4			
5	t	$\ln N/N_0$	N/N_0
6	1	-0.05608	0.945
7	10	-0.5608	0.571
8	20	-1.1216	0.326
9	30	-1.6824	0.186
10	40	-2.24319	0.106
11	50	-2.80399	0.061
12	60	-3.36479	0.035
13	70	-3.92559	0.020
14	100	-5.60799	0.004
15			
16	For 25%, $N/N0$	0.25	
17	$\ln N/N_0$	-1.38629	
18	t	24.72	hr
19			
20	For 1%, $N/N0$	0.01	
21	$\ln N/N_0$	-4.60517	
22	t	82.12	hr
23			
24			
25	**Spreadsheet Documentation**		
26	Cell B3=LN(2)/B2		
27	Cell B6=-\$B\$3*A6		
28	Cell C6=EXP(B6)		
29	Cell B17=LN(B16)		
30	Cell B18=B17/-B3		
31	Cell B21=LN(B20)		
32	Cell B22=B21/-\$B\$3		

32-3. Here, in the spreadsheet below, we use Equations 32-5

$$t_{1/2} = \ln 2/\lambda$$

and 32-3 $\ln (N/N_0) = -\lambda t$



	A	B	C	D	E	F	G	H	I	J	K
1	**Pb 32-3**										
2											
3		$t_{1/2}$		$t_{1/2}$, hr	λ, hr^{-1}						
4	Fe-59	44.51	days	1068.24	0.000649						
5	Ti-45	3.078	hrs	3.078	0.225194						
6	Ca-47	4.536	days	108.864	0.006367						
7	P-33	25.3	days	607.2	0.001142						
8											
9	For t =	24		For t =	48		For t =	72		For t =	96
10	ln N/N_0	N/N_0		ln N/N_0	N/N_0		ln N/N_0	N/N_0		ln N/N_0	N/N_0
11	-0.01557	0.985		-0.03115	0.969334		-0.04672	0.954356		-0.06229	0.939609
12	-5.40466	4.50E-03		-10.8093	2.02E-05		-16.214	9.09E-08		-21.6186	4.08E-10
13	-0.15281	0.858		-0.30562	0.736666		-0.45843	0.632275		-0.61124	0.542677
14	-0.0274	0.973		-0.05479	0.94668		-0.08219	0.921096		-0.10959	0.896203
15											
16	**Spreadsheet Documentation**										
17	Cell E4=LN(2)/D4										
18	Cell A11=-E4*$B$9										
19	Cell B11=EXP(A11)										
20	Cell D11=-E4*$E$9										
21	Cell E11=EXP(D11)										
22	Cell G11=-E4*$H$9										
23	Cell H11=EXP(G11)										
24	Cell J11=-E4*$K$9										
25	Cell K11=EXP(J11)										

32-4. $t_{1/2} = \ln 2/\lambda$ $\lambda = \ln 2/ t_{1/2} = 0.693/21.5 = 3.223 \times 10^{-2}\ \text{h}^{-1}$

$\ln(N/N_0) = \ln(0.0100/1.00) = -4.605 = -\lambda t = 3.223 \times 10^{-2}\ t$

$t = 4.605/3.223 \times 10^{-2} = 143$ h or 5.95 days.

32-5. $\sigma_M = \sqrt{M}$ and $\sigma_M/M = 1/\sqrt{M}$ (Equations 32-10 and 32-11)

(a) $\sigma_M = \sqrt{100} = 10.0$ counts and $\sigma_M/M = 1/\sqrt{100} = 0.100$ or 10.0%

(b) $\sigma_M = \sqrt{750} = 27.4$ counts and $\sigma_M/M = 1/\sqrt{750} = 0.0365$ or 3.65%

(c) $\sigma_M = \sqrt{7000} = 83.7$ counts and $\sigma_M/M = 1/\sqrt{7000} = 0.0120$ or 1.20%

(d) $\sigma_M = \sqrt{2.00 \times 10^4} = 141$ counts and $\sigma_M/M = 1/\sqrt{2.00 \times 10^4} = 0.0071$ or 0.71%

32-6. $\sigma_M = \sqrt{800} = 28.3$ counts and $\sigma_M/M = 1/\sqrt{800} = 0.0354$ or 3.54%

From Table a1-3, we find $z = 1.64$ (90%), 1.96 (95%), and 2.58 (99%)

(a) 90% CI = 800 ± 1.64 × 28.3 counts = 800 ± 64 counts (absolute uncertainty)

90% CI = 800 ± 1.64 × 3.54% = 800 ± 5.8% (relative uncertainty)

(b) 95% CI = 800 ± 1.96 × 28.3 counts = 800 ± 55 counts

95% CI = 800 ± 1.96 × 3.54% = 800 ± 6.9%

(c) 99% CI = 800 ± 2.58 × 28.3 counts = 800 ± 73 counts

99% CI = 800 ± 2.58 × 3.54% = 800 ± 9.1%

32-7. (a) $R_c = R_x - R_b = 450$ cpm – 7 cpm = 443 cpm

(b) $$\sigma_{R_c} = \sqrt{\frac{R_x}{t_x} + \frac{R_b}{t_b}} \qquad \text{(Equation 32-16)}$$

$$= \sqrt{\frac{450}{15} + \frac{7}{2}} = 5.79 \text{ cpm}$$

(c) 95% CI for $R_c = R_c \pm z\sigma_{R_c}$ = 443 cpm ± 1.96 × 5.79 cpm = 443 ± 11 cpm

32-8. $$\sigma_{R_c} = \sqrt{\frac{R_x}{t_x} + \frac{R_b}{t_b}} \qquad \text{(Equation 32-16)}$$

(a) $$\sigma_{R_c} / R_c = 0.05 = \frac{\sqrt{\dfrac{R_x}{t_x} + \dfrac{R_b}{t_b}}}{R_x - R_b}$$

$$0.05 = \frac{\sqrt{\frac{70}{t_x}+\frac{9}{3}}}{70-9}$$

$$(0.05 \times 63\ \text{cpm})^2 = \frac{70\ \text{cpm}}{t_x} + 3\ \text{cpm}^2$$

$$t_x = \frac{70}{9.9225-3} = 10.11\ \text{min}$$

$M = t_x \times R_x = 10.11 \times 70 = 708$ counts

(b) $$0.05 = \frac{\sqrt{\frac{400}{t_x}+\frac{9}{3}}}{400-9}$$

$$382\ \text{cpm}^2 = \frac{400\ \text{cpm}}{t_x} + 3\ \text{cpm}^2$$

$t_{\text{x}} = 0.948$ min

$M = t_x \times R_x = 0.948 \times 400$ cpm = 379 counts

32-9. Equation 32-4 can be used to calculate the decay constant λ

$$2230\ \text{cpm} = 3250\ \text{cpm}\ e^{-\lambda(10.0\ \text{h})}$$

$$\ln\left(\frac{2230}{3250}\right) = -\lambda(10.00\ \text{hr})$$

$$\lambda = 0.0377\ \text{h}^{-1}$$

Equation 32-5 can then be used to calculate the half-life

$$t_{1/2} = \ln 2/\lambda = 0.693/0.0377\ \text{h}^{-1} = 18.4\ \text{h}$$

32-10. Equation 32-5 can be used to calculate the decay constants

$$\lambda(^{38}\text{Cl}) = \frac{\ln 2}{87.2\ \text{min} \times 1\ \text{h}/60\ \text{min}} = 0.4769\ \text{h}^{-1}$$

$$\lambda(^{35}\text{S}) = \frac{\ln 2}{37.5\text{ days} \times 24\text{ h/day}} = 7.70 \times 10^{-4}\text{ h}^{-1}$$

Equation 32-8 can be written in terms of activity rather than counting rates

$$A = A_0\exp(-\lambda t)$$

$$A(^{38}\text{Cl}) = A_0(^{38}\text{Cl})\exp(-0.4769t)$$

$$A(^{35}\text{S}) = A_0(^{35}\text{S})\exp(-7.70 \times 10^{-4}t)$$

or $$0.001 = \frac{A(^{38}\text{Cl})}{A(^{35}\text{S})} = \frac{A_0(^{38}\text{Cl})\exp(-0.4769t)}{A_0(^{35}\text{S})\exp(-7.70 \times 10^{-4}t)}$$

But, the starting activities are equal, so $A_0(^{38}\text{Cl}) = A_0(^{35}\text{S})$

So,

$$0.001 = \exp(-0.4769t + 7.70 \times 10^{-4}t)$$

Taking the natural logarithm of both sides of this equation gives

$$-6.908 = -0.4769t + 7.70 \times 10^{-4}t$$

$$t = 14.5\text{ h}$$

32-11. $$\frac{\sigma_R}{R} = \frac{\sigma_M / t}{M / t} = \frac{\sigma_M}{M}$$

Using Equation 32-10 to replace σ_M gives

$$\frac{\sigma_R}{R} = \frac{\sigma_M}{M} = \frac{\sqrt{M}}{M} = M^{-1/2}$$

32-12. If the activity of the tracer is large, the mass of the added tracer, m_t can be kept small and the second term will be negligible relative to the first term. We may then write

$$m_x = \frac{R_t}{R_m}m_m - m_t \approx \frac{R_t}{R_m}m_m$$

32-13. We will use Equation 32-23 with R_m being the activity of the sample containing the tracer and R_t being the activity of the tracer itself. We will modify this equation by letting m_m, m_x, and m_t be the volumes of the sample, the unknown, and the tracer respectively.

R_m = 15.8 cps

$1\ \text{C}_\text{i} = 3.70 \times 10^{10}\ \text{Bq} = 3.70 \times 10^{10}\ \text{cps}$

$$R_t = 0.120\ \frac{\cancel{\mu\text{C}}_\text{i}}{\cancel{\text{mL}}} \times 2.00\ \cancel{\text{mL}} \times 3.70 \times 10^{10}\ \frac{\text{cps}}{\cancel{\text{C}}_\text{i}} \times 10^{-6}\ \frac{\cancel{\text{C}}_\text{i}}{\cancel{\mu\text{C}}_\text{i}} = 8880\ \text{cps}$$

$$\text{blood volume} = m_x = \frac{R_t}{R_m} m_m - m_t \qquad \text{(Equation 3-23)}$$

$$= \frac{8880\ \text{cps}}{15.8\ \text{cps}} \times 1.00\ \text{mL} - 2.00\ \text{mL} = 560\ \text{mL}$$

32-14. $A_0 = 5.42 \times 10^3\ \text{cpm mg}^{-1} \times 0.981\ \text{mg} = 5317\ \text{cpm}$

Substituting into Equation 32-23

$$m_x = \text{mg penicillin} = \frac{5317\ \text{cpm}}{343\ \text{cpm}} \times 0.406\ \text{mg} - 0.981\ \text{mg} = 5.31\ \text{mg}$$

32-15. We first convert the activity to specific activities in terms of Cl^-.

For NaCl,

$$R_t = \frac{4.0 \times 10^4\ \text{cps/mg NaCl}}{35.45\ \text{mg Cl}^-/58.44\ \text{mg NaCl}} = 6.59 \times 10^4\ \text{cps/mg Cl}^-$$

$$R_m = \frac{35\ \text{cps}}{400\ \text{mg AgCl} \times 35.45\ \text{mg Cl}^-/143.32\ \text{mg AgCl}} = 0.354\ \text{cps/mg Cl}^-$$

In order to correct R_m for the time delay, we use Equation 32-5 to obtain λ.

$\lambda = \ln(2)/37.3\ \text{min} = 1.858 \times 10^{-2}\ \text{min}^{-1}$

Equation 32-8 is rearranged to give the counting rate before any decay. Thus,

$R_m = 0.354 \exp(0.01858 \text{ min}^{-1} \times 148 \text{ min}) = 5.54 \text{ cps}$

Substituting into Equation 32-23, gives

$$m_x = \frac{6.59 \times 10^4 \text{ cps/mg Cl}^-}{5.54 \text{ cps}} \times 3.0 \text{ mg Cl}^- - 3.0 \text{ mg Cl}^-$$

$$= 3.6 \times 10^4 \text{ mg Cl}^- \text{ or } 36 \text{ g Cl}^-$$

32-16. (a) Because ^{14}C has a long half life,

$$m_x = \frac{1000 \text{ cpm/mg}}{20 \text{ cpm/mg}} \times 11.5 \text{ mg} - 3.0 \text{ mg} = 572 \text{ mg}$$

$$\% \text{ threonine} = \frac{572 \times 10^{-3} \text{ g}}{10.0 \text{ g}} \times 100\% = 5.7\%$$

(b) Proceeding as in Problem 32-17 to obtain a corrected count

$\lambda = \ln(2)/20.5 \text{ min} = 0.0338 \text{ min}^{-1}$

$$R_M = 20 \frac{\text{cpm}}{\text{mg}} \times \exp(0.0338 \text{ min}^{-1} \times 32 \text{ min}) = 58.99 \text{ cpm/mg}$$

Then proceeding as in part (a), we obtain

$$m_x = \frac{1000}{58.99} \times 11.5 - 3.0 = 191.9 \text{ mg}$$

$$\% \text{ threonine} = \frac{191.9 \times 10^{-3} \text{ g}}{10.0 \text{ g}} \times 100\% = 1.9\%$$

32-17. $A_0 = 223 \text{ cpm/mg} \times 1.34 \text{ mg} = 298.8 \text{ cpm}$

$$m_x = \frac{298.8 \text{ cpm}}{654/60.0 \text{ cpm}} \times 0.112 \text{ mg} - 1.34 \text{ mg} = 1.73 \text{ mg}$$

$$\text{ppm analyte} = \frac{1.73 \text{ mg analyte}}{500 \times 10^3 \text{ mg sample}} \times 10^6 = 3.46$$

32-18. The kinetic energy KE of thermal neutrons is given by

$$\text{KE} = \frac{3}{2}kT$$

where k is Boltzmann's constant. Thus, assuming $T = 298$ K,

$$\text{KE} = \frac{3}{2}\left(1.39 \times 10^{-23}\ \text{J K}^{-1} \times 298\ \text{K} \times 6.24 \times 10^{18}\ \text{eV J}^{-1}\right)$$

$$= 0.039\ \text{eV} \approx 0.04\ \text{eV}$$

32-19. (a) We use Equation 32-17

$$A = N\phi\sigma S$$

If we assume a unit detection coefficient,

$$S = 1 - \exp(-0.693t/t_{1/2})$$

$$= 1 - \exp(-0.693 \times 1.00\ \text{h}/2.50\ \text{h}) = 0.242$$

$A = 10$ cpm × 1 min/60 s $= 0.167\ \text{s}^{-1}$, $\phi = 1.8 \times 10^{12}\ \text{cm}^{-2}\ \text{s}^{-1}$, $\sigma = 13.3 \times 10^{-24}\ \text{cm}^2$

$$N = \frac{0.167\ \text{s}^{-1}}{\left(1.8 \times 10^{12}\ \text{cm}^{-2}\text{s}^{-1}\right)\left(13.3 \times 10^{-24}\ \text{cm}^2\right)(0.236)} = 3.0 \times 10^{10}\ \text{atoms}$$

$$3.0 \times 10^{10}\ \text{atoms} \times \left(\frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{atoms}}\right)\left(\frac{55\ \text{g Mn}}{\text{mol}}\right) = 2.7 \times 10^{-12}\ \text{g or } 2.7 \times 10^{-6}\ \mu\text{g}$$

(b) The calculated value assumes unit detection coefficient. In reality detection coefficients are on the order of 10% to 15% which means that the calculated values are too low by about an order of magnitude. This accounts for most of the difference between the value in Figure 32-8 and the value calculated here.

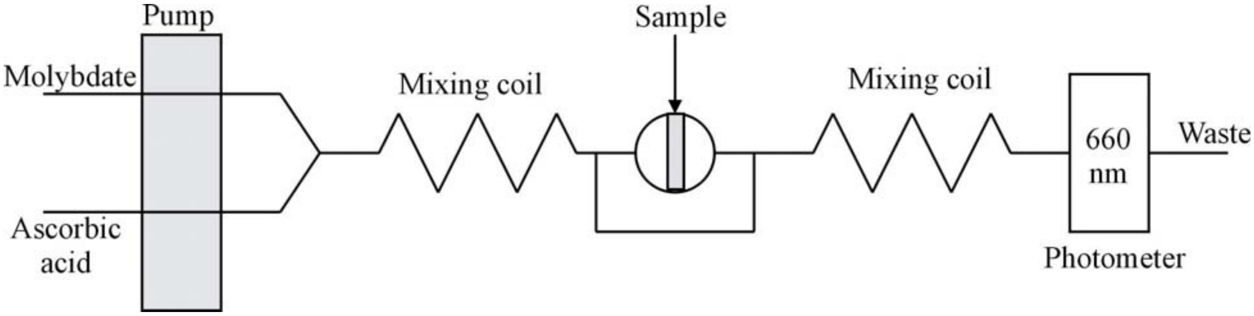
CHAPTER 33

33-1. (a) Aquire paint sample
Sample Preparation: grind and mix.
Dissolve Sample: heat with aqueous oxidizing acid followed by dilution with water.
Change Chemical form: not required.
Eliminate Interferences: not required.
Measure Property: introduce solution into ICP
Calculation of Results: compare lead spectrum to that of standard.
Estimate Reliability: make rough estimate of amount and confidence level.

(b) Aquire multivitam tablets
Sample Preparation: count out, grind, and homogenize several tablets. Weigh out replicate samples into small containers.
Sample Dissolution: heat samples in concentrated HCl.
Eliminate Interferences: filter insoluble residue from solution. Dilute to volume and introduce aliquots into suitable container.
Change Chemical Form: adjust pH and add measured volume of KSCN solution.
Measure property: determine absorbance with spectrophotometer.
Calculation of Results: prepare calibration curve with iron standards. Determine unknown iron concentration from least squares analysis.
Estimation of Reliability: calculate standard deviation of iron results and estimate 95% confidence interval.

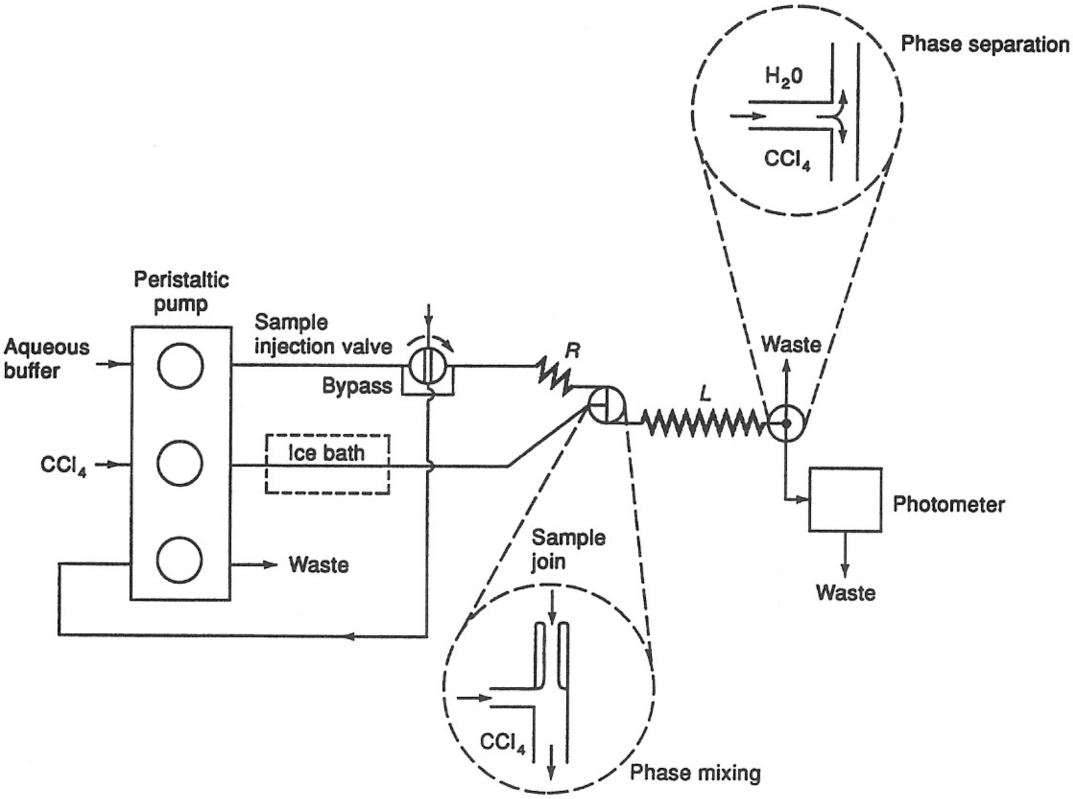
(c) Aquire blood sample
Sample Preparation: not required.
Sample Dissolution: not required.
Change Chemical Form: not required.
Eliminate Interferences: not required.
Measure Property: apply droplet of blood to immobilized enzyme test strip. Obtain glucose results with glucose meter.
Calculation of Results: automatically obtained with meter.
Estimation of Reliability: consult manufacturer's data sheet or obtain replicate results.

33-2. The flow injection manifold for determining phosphate in an aqueous sample is shown below



The molybdate and ascorbic acid are first mixed and then the phosphate sample is injected. After mixing in the second coil, the absorbance at 660 nm is measured.

33-3. In the apparatus that follows, the sample is injected into a buffered solvent and



transported to a mxing area where it is mixed with CCl_4. The apparatus is similar to that of Figure 33-9.

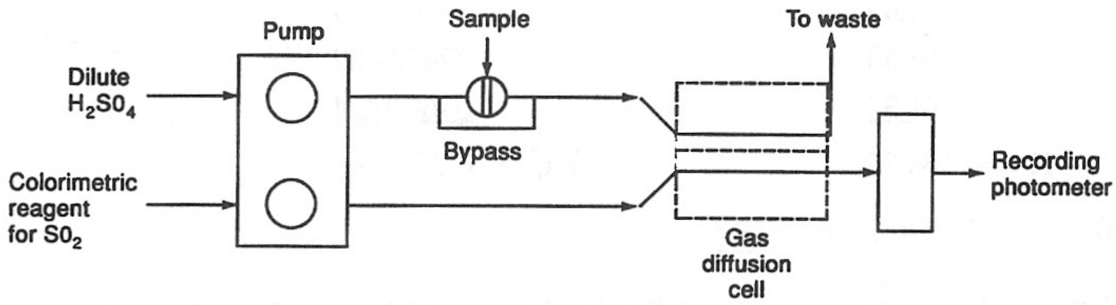
33-4. Continuous flow systems have the advantages of relatively simple equipment and easy automation. Mixing occurs as a result of dispersion due to the flow, and various diffusion processes. A continuous flow analyzer has few moving parts and is easier to construct and maintain than a discrete analyzer. However, because of the continuous pumping, continuous flow systems can use large amounts of reagent leading to extra expense and waste management problems. Also, cross contamination between samples can be a problem. A manual determination must often be changed in order to adapt it to a continuous flow procedure.

Discrete analyzers carry out reactions in discrete containers. Cross contamination is eliminated and sample identity is preserved. Reagent waste can be less than with continuous flow systems. Discrete analyzers more closely mimic the steps that occur in a manual version of the same determination. A major disadvantage is that they are mechanically complex with more moving parts that have limited lifetimes. In some cases volumes of reagents used are larger than with a well-designed continuous flow procedure.

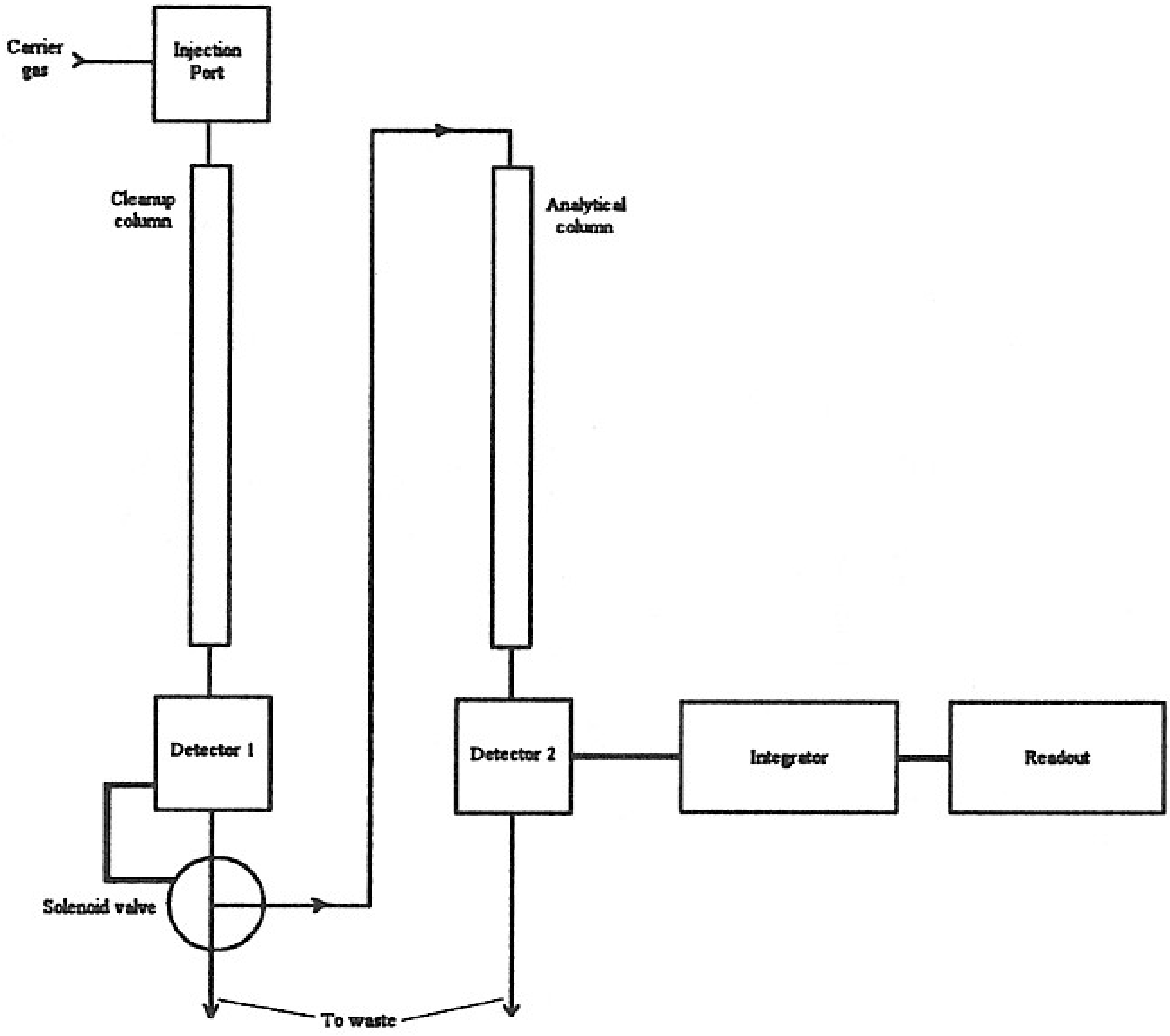
33-5. Sequential injection analyzers can overcome some of the reagent waste problems that can limit normal flow injection procedures. The manifolds are simpler than with traditional FIA, and it is easier to change from one procedure to another because only the reagents and flow program need to be changed. Sequential injection is advantageous for some separation and pre-concentration procedures and can be used with a variety of detectors.

33-6. One of the Agilent lab-on-a chip products is the “Bioanalyzer” for the analysis of DNA, RNA, proteins, and cells. The microfluidics are used to minimize sample and reagent consumption as well as exposure of laboratory workers to potential health hazards. The instrument is compact and easily sits on a laboratory workbench. Automation leads to improved accuracy and precision. The microfluidics are used for on-chip electrophoresis, for flow cytometry, for protein analysis, and for DNA fragmentation. The advantages are low sample and reagent volumes, compact instrument footprint, and minimal health hazards to workers.

33-7. The FIA system below is for the determination of sulfite. The sample is injected into a stream of dilute H_2SO_4, which converts sulfite to SO_2. The membrane in this case is porous and transmits part of the SO_2 into the stream containing the colorimetric reagent.



33-8. The sample is injected, and the solvent separates from the analytes on the relatively short general purpose cleanup column. As soon as the solvent passes through detector 1, the detector generates an electrical signal that switches the solenoid valve from waste to the analytical column where the two analytes are separated. The analyte peaks are then recorded by detector 2, integrated, and displayed as shown in the accompanying diagram.


Carrier gas
Injection Port
Cleanup column
Analytical column
Detector 1
Detector 2
Integrator
Readout
Solenoid valve
To waste

CHAPTER 34

34-1. The particle size distribution is a plot of the number of particles having a particular size (diameter, volume, surface area) versus that quantity. The cumulative distribution represents the fraction of particles bigger than or smaller than a particular size plotted against the size.

34-2. The problem is that a single quantity, such as diameter, radius, volume, etc., cannot adequately describe a three dimensional particle unless it is spherical.

34-3. Usually diameter (or radius), volume, or surface area.

34-4. Generally, we assume the particles are spherical and proceed as we would with spherical particles, or the values are converted to those of an equivalent sphere.

34-5. With particles that are not perfect spheres, even the same technique can give different results depending on what quantity is used to describe the size. Different instruments often measure different quantities or make assumptions related to the theoretical models. Also, other quantities may be needed like refractive index, viscosity, density, etc. These quantities may not be known accurately for the system under study.

34-6. Mie scattering is scattering from finite objects with diameters larger than the wavelength of the incident light. Mie scattering shows an intensity distribution that varies with scattering angle because of constructive and destructive interference between the rays emitted from one part of the particle and those emitted from another. Mie scattering shows predominately forward scattering.

34-7. An Airy pattern is a diffraction pattern that is a function of $x = 2\pi rs/\lambda f$. It shows a maximum at $x = 0$ and small maxima to either side. The Airy pattern is broader for particles of smaller size and narrower for larger particles. The extrema shift to higher values of x as the particle size decreases.

34-8. The cumulative undersize distribution shows the fraction of particles having diameters less than or equal to a particular diameter as a function of diameter.

34-9. In laser diffraction, the pattern resulting from scattering of the incident laser beam is analyzed using Mie theory or Franhofer diffraction theory. The intensity distribution of the scattered light is used to obtain the particle size from the theoretical model. In dynamic light scattering, the time fluctuations of the Doppler broadened Rayleigh scattered light are analyzed by correlation techniques to obtain translational diffusion coefficients. These are then converted to particle diameters via a model such as the relationship.

34-10. We use the Stokes-Einstein relationship to obtain the hydrodynamic diameter, d_h. Note that 1 cp = 10^{-3} Pa s

$$d_\mathrm{h} = \frac{kT}{3\pi\eta D_\mathrm{T}} = \frac{1.38066\times10^{-23}\ \cancel{\mathrm{J}}\ \cancel{\mathrm{K}}^{-1}\times293.15\ \cancel{\mathrm{K}}\times1\ \mathrm{m}^3\,\cancel{\mathrm{Pa}}/\cancel{\mathrm{J}}}{3\times\pi\times1.002\times10^{-3}\ \cancel{\mathrm{Pa}}\ \cancel{\mathrm{s}}\times3.75\times10^{-7}\ \cancel{\mathrm{cm}^2}\,\cancel{\mathrm{s}}\times10^{-4}\ \mathrm{m}^2/\cancel{\mathrm{cm}^2}}$$

$$= 1.14\times10^{-8}\ \mathrm{m} = 11.4\ \mathrm{nm}$$

34-11.

$$D_\mathrm{T} = \frac{kT}{3\pi\eta d_\mathrm{h}} = \frac{1.38066\times10^{-23}\ \cancel{\mathrm{J}}\ \cancel{\mathrm{K}}^{-1}\times293.15\ \cancel{\mathrm{K}}\times1\ \mathrm{m}^3\,\cancel{\mathrm{Pa}}/\cancel{\mathrm{J}}}{3\times\pi\times1.002\times10^{-3}\ \cancel{\mathrm{Pa}}\ \mathrm{s}\times35\times10^{-6}\ \mathrm{m}}$$

$$= 1.22\times10^{-14}\ \mathrm{m^2s^{-1}}\times10^{4}\ \mathrm{cm^2/m^2} = 1.22\times10^{-10}\ \mathrm{cm^2s^{-1}}$$

34-12. Here we note 1 G = 6.6720×10^{-11} N $\mathrm{m^2/kg^2}$, and 1 cp = 10^{-3} N s $\mathrm{m^{-2}}$

$$u = \frac{\left(d - d_{\mathrm{F}}\right)g}{18\eta}D^2$$

$$= \frac{(1.05\ -\ 0.998)\ \mathrm{g\ cm^{-3}} \times 10^{-3}\ \mathrm{kg/g} \times (100\ \mathrm{cm/m})^3 \times 6.6720\times10^{-11}\ \mathrm{N\ m^2/kg}}{18\times1.002\times10^{-3}\ \mathrm{N\ s\ m^{-2}}} \times (10.0\times10^{-6}\ \mathrm{m})^2$$

$$= 1.92\times10^{-12}\ \mathrm{m\ s^{-1}} \times 100\ \mathrm{cm/m} = 1.92\times10^{-10}\ \mathrm{cm\ s^{-1}}$$

To fall 10 mm would require $t = h/u = 10\ \mathrm{mm}/(1.92 \times 10^{-10}\ \mathrm{cm/s} \times 10\ \mathrm{mm/cm}) = 5.2 \times 10^9\ \mathrm{s}$

34-13.

$$u = \frac{\left(d - d_{\mathrm{F}}\right)\omega^2 r_a D^2}{18\eta}$$

$$= \frac{(1.05\ -\ 0.998)\ \mathrm{g\ cm^{-3}} \times\ (1.0\times10^4\ \mathrm{rev/min}\ \times\ 2\ \times \pi\ \mathrm{rad\ rev^{-1}}/60\ \mathrm{s\ min^{-1}})^2 \times 8.0\ \mathrm{cm} \times (10.0\times10^{-4}\ \mathrm{cm})^2}{18\times1.002\times10^{-3}\ \mathrm{kg\ m^{-1}s^{-1}} \times 1000\ \mathrm{g/kg} \times 0.01\ \mathrm{m\ cm^{-1}}}$$

$$= 2.53\times\ 10^{-4}\ \mathrm{cm\ s^{-1}}$$

$t = \ln(r_a/r_0)r_a/u = \ln(80/70) \times 8.0\ \mathrm{cm}/\ 2.53 \times 10^{-2}\ \mathrm{cm\ s^{-1}} = 4.22 \times 10^3\ \mathrm{s}$ or 70.4 min

The centrifugal acceleration is

$\omega^2 r_a = (10{,}000\ \mathrm{rev/min} \times 2 \times \pi\ \mathrm{rev^{-1}}/60\ \mathrm{s/min})^2 \times 8.0\ \mathrm{cm} = 8.77 \times 10^6\ \mathrm{cm\ s^{-2}} = 8.77 \times 10^4\ \mathrm{m\ s^{-2}}$

Near the earth's surface, g is approximately 9.8 m $\mathrm{s^{-2}}$. Hence a 10000 rpm centrifuge produces an acceleration that is $8.77 \times 10^4/9.8 = 8952$ G or approximately 9000 G.

34-14. $u = \ln(r_a/r_0)r_a/t = \ln(80/70) \times 8.0\ \mathrm{cm}/2.9\ \mathrm{s} = 0.368\ \mathrm{cm\ s^{-1}}$

$$D_{\text{Stokes}} = \sqrt{\frac{18\eta\ln\left(r_a/r_0\right)r_a}{\omega^2 r_a t\left(d - d_F\right)}} = \sqrt{\frac{18\eta u}{\omega^2 r_a\left(d - d_F\right)}}$$

$$= \sqrt{\frac{18\times1.002\ \times10^{-2}\ \mathrm{g\ cm^{-1}\ s^{-1}} \times 0.368\ \mathrm{cm\ s^{-1}}}{9000\times9.8\ \mathrm{m\ s^{-2}} \times 100\ \mathrm{cm/m}\ (1.05\ -\ 0.998)\ \mathrm{g\ cm^{-3}}}} = 145\ \mathrm{nm\ or}\ 0.145\ \mu\mathrm{m}$$