S17-1. $(0.100 \text{ mol})\left(96\,485 \frac{\text{C}}{\text{mol}}\right) = I \cdot (3\,600 \text{ s}) \Rightarrow I = 2.680 \frac{\text{C}}{\text{s}} = 2.680 \text{ A}$

S17-2. (a) $E(\text{cathode}) = -0.828 - 0.059\,16 \log(0.033)^{1/2}(1.0) = -0.784_2$ V

$E(\text{anode}) = 1.078 - 0.059\,16 \log(0.010) = 1.196_3$ V

(Note that E(anode) is calculated for a reduction half-reaction.)

$E = E(\text{cathode}) - E(\text{anode}) = -1.981$ V

(b) Ohmic potential = $I{\cdot}R = (0.052 \text{ A})(4.3\ \Omega) = 0.22_4$ V

$E = E(\text{cathode}) - E(\text{anode}) - IR = -2.20_5$

(c) $E = E(\text{cathode}) - E(\text{anode}) - IR -$ overpotentials

$= -1.981 - 0.22_4 - 0.30 - 0.08 = -2.58_5$ V

(d) concentration polarization changes the electrode potentials:

$E(\text{cathode}) = -0.828 - 0.059\,16 \log(0.033)^{1/2}(2.0) = -0.802_0$

$E(\text{anode}) = 1.078 - 0.059\,16 \log(0.002\,0) = 1.237_7$

$E = \text{E}(\text{cathode}) - E(\text{anode}) - IR -$ overpotentials

$-0.802_0 - 1.237_7 - 0.22 - 0.30 - 0.08 = -2.64$ V

S17-3. (a) Let us assume that the left electrode is the anode:

cathode: $\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-$ $\quad E° = 1.360$ V

anode: $\frac{1}{2}Hg_2Cl_2(s) + e^- \rightleftharpoons Hg(l) + Cl^-$ $\quad E° = 0.268$ V

$$E(\text{cathode}) = 1.360 - 0.059\,16 \log \frac{[Cl^-]}{\sqrt{P_{Cl_2}}} = 1.360 - 0.059\,16 \log \frac{0.080}{\sqrt{0.10}} = 1.395 \text{ V}$$

$E(\text{anode}) = 0.241$ V (saturated calomel electrode.)

$E = E(\text{cathode}) - E(\text{anode}) = 1.395 - 0.241 = 1.154$ V

Since E is positive, we guessed the direction of the reaction correctly.

The net reaction is $\frac{1}{2}Cl_2(g) + Hg(l) + Cl^- = Cl^- + \frac{1}{2}Hg_2Cl_2(s)$

(b) $E_{\text{galvanic}} = E(\text{cathode}) - E(\text{anode}) - I{\cdot}R = 1.154 - (0.025 \text{ A})(2.12\ \Omega) = 1.101$ V

(c) $E_{\text{electrolysis}} = -[E(\text{cathode}) - E(\text{anode})] - I{\cdot}R = -1.154 - (0.025 \text{ A})(2.12\ \Omega) = -1.207$ V

(We wrote $-[E(\text{cathode}) - E(\text{anode})]$ because the cell is being run in reverse and the anode and cathode reactions are reversed from those of the galvanic cell.)

(d) $E(\text{cathode}) = 1.360 - 0.059\,16 \log \frac{0.040}{\sqrt{0.20}} = 1.422$ V

$E = E(\text{cathode}) - E(\text{anode}) = 1.422 - 0.241 = 1.181\text{ V}$

$E_{\text{electrolysis}} = -[E(\text{cathode}) - E(\text{anode})] - I{\cdot}R = -1.181 - (0.025\text{ A})(2.12\ \Omega) = -1.234\text{ V}$

(e) $E_{\text{electrolysis}} = -1.234 - 0.15 = -1.38\text{ V}$

S17-4. $\underset{Pb^{2+}}{\text{Pb(tartrate)}} + 2H_2O \rightarrow \underset{Pb^{4+}}{PbO_2(s)} + \text{tartrate}^{2-} + 4H^+ + 2e^-$ Oxidation occurs at the anode.

The mass of Pb (tartrate) (FM 355.3) giving 0.122 1 g of PbO_2 (FM = 239.2) is

$(355.3/239.2)(0.122\,1\text{ g}) = 0.181\,4\text{ g}.$ $\quad \%\text{ Pb} = \frac{0.181\,4}{0.531\,4} \times 100 = 34.13\%$

S17-5. (a) $Fe^{2+} + e^- \rightleftharpoons Fe(s) \qquad E^\circ = -0.44\text{ V}$

$E(\text{cathode}) = -0.44 - 0.059\,16 \log \frac{1}{1.0 \times 10^{-7}} = -0.85_4\text{ V}$

(b) $E(\text{cathode, vs Ag | AgCl}) = -0.85_4 - 0.197 = -1.05\text{ V}$

(c) Concentration polarization means that Fe^{2+} cannot diffuse to the cathode as fast as it is consumed. The concentration of Fe^{2+} at the electrode surface would be < 0.10 μM, so the potential would be more negative.

S17-6. When 99% of Hg(II) is reduced, the formal concentration will be 1.0×10^{-5} M, and the predominant form is $Hg(NH_3)_4^{2+}$.

$$\beta_4 = \frac{[Hg(NH_3)_4^{2+}]}{[Hg^{2+}][NH_3]^4} = \frac{(1.0 \times 10^{-5})}{[Hg^{2+}](1.0)^4} \Rightarrow [Hg^{2+}] = 5 \times 10^{-25}\text{ M}$$

$Hg^{2+} + 2e^- \rightleftharpoons Hg(l) \qquad E^\circ = 0.852$

$$E(\text{cathode}) = 0.852 - \frac{0.059\,16}{2} \log \frac{1}{5 \times 10^{-25}} = 0.133\text{ V}$$

S17-7. Relevant information :

$Fe^{2+} + 2e^- \rightleftharpoons Fe(s) \qquad E^\circ = -0.44\text{ V}$

$Co^{2+} + 2e^- \rightleftharpoons Co(s) \qquad E^\circ = -0.282\text{ V}$

$CoY^{2-}\ K_f = 2.0 \times 10^{16} \qquad FeY^{2-}\ K_f = 2.1 \times 10^{14} \qquad \alpha_{Y^{4-}} = 3.8 \times 10^{-9}$ at pH 4.0

When 99% of FeY^{2-} is removed, $[FeY^{2-}] = 1.0 \times 10^{-8}$ M.

$$[Fe^{2+}] = \frac{[FeY^{2-}]}{K_f\, \alpha_{Y^{4-}}\, [\text{EDTA}]} = \frac{1.0 \times 10^{-8}}{(2.1 \times 10^{14})(3.8 \times 10^{-9})(0.010)} = 1.3 \times 10^{-12}$$

The cathode potential required to reduce FeY^{2-} to this level is

$$E(\text{cathode}) = -0.44 - \frac{0.059\,16}{2} \log \frac{1}{1.3 \times 10^{-12}} = -0.79\text{ V}$$

Will this cathode potential reduce Co^{2+}?

$$\alpha_{Y^{4-}}\ K_f\,(\text{for } CoY^{2-}) = \frac{[CoY^{2-}]}{[Co^{2+}][EDTA]} \Rightarrow [Co^{2+}] = 1.3 \times 10^{-8}\ M$$

$$E(\text{cathode, } Co^{2+}) = -0.282 - \frac{0.059\,16}{2}\ \log \frac{1}{1.3 \times 10^{-8}} = -0.515\ V$$

Since E(cathode) < –0.515 V, CoY^{2-} will be reduced. The separation is not feasible.

S17-8. (a) $\text{mol } e^- = \frac{I \cdot t}{F} = \frac{(4.11 \times 10^{-3}\ C/s)(834\ s)}{96\,485\ C/mol} = 3.55 \times 10^{-5}\ mol$

(b) One mol e^- reacts with $\frac{1}{2}$ mol Br_2, which reacts with $\frac{1}{2}$ mol cyclohexene

$\Rightarrow 1.78 \times 10^{-5}$ mol cyclohexene.

(c) $1.78 \times 10^{-5}\ mol/3.00 \times 10^{-3}\ L = 5.92 \times 10^{-3}\ M$

S17-9. Step 1: $\text{Total Ti} = \frac{2.03\ \text{mg Ti}/47.88\ \text{mg/mmol}}{42.37\ \text{mg unknown}} = 1.00_0\,\frac{\mu\text{mol Ti}}{\text{mg unknown}}$

Step 2: $\text{Reducing equivalents of Ti} = \frac{9.27\ C/96\,485\ C/mol}{51.36\ \text{mg unknown}} = \frac{1.87\ \mu\text{mol}}{\text{mg unknown}}$

$$\text{Reducing equivalents per mol of Ti} = \frac{1.87\ \mu\text{mol/mg unknown}}{1.00\ \mu\text{mol Ti/mg unknown}} = 1.87\ \text{equivalents/mol Ti}$$

This represents the degree of reduction below Ti^{4+}.
The average oxidation state is $Ti^{+2.13}$ (= 0.87 $TiCl_2$ + 0.13 $TiCl_3$)

S17-10. If the reagent contains only $CoCl_2$ and H_2O, we can write

$$\text{grams of } CoCl_2 = \left(\frac{\text{grams of Co deposited}}{\text{atomic mass of Co}}\right)(\text{FM of } CoCl_2) = 0.218\,93\ g$$

$$\text{grams of } H_2O = 0.402\,49 - 0.218\,93 = 0.183\,56\ g$$

$$\frac{\text{moles of } H_2O}{\text{moles of Co}} = \frac{0.183\,56/\text{FM of } H_2O}{0.099\,37/\text{atomic mass of Co}} = 6.043$$

The reagent composition is close to $CoCl_2 \cdot 6H_2O$.

S17-11. The anode reaction is $Zn(s) \rightarrow Zn^{2+} + 2e^-$

5.0 g Zn = 7.65×10^{-2} mol Zn = 1.52×10^{-1} mol e^-

(0.152 mol e^-)(96 485 C/mol) = 1.48×10^4 C

The current following through the circuit is $I = E/R =$
1.02 V/2.8 W = 0.364 A = 0.364 C/s.

1.48×10^4 C/(0.364 C/s) = 4.06×10^4 s = 11.3 h

S17-12. 1.00 ppt corresponds to 30.0/1 000 = 0/030 0 mL of O_2/min = 5.00 x 10^{-4} mL of O_2/s. The moles of oxygen in this volume are

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ bar})(5.00 \times 10^{-7} \text{ L})}{(0.083\ 14 \text{ L bar atm K}^{-1} \text{ mol}^{-1})(293 \text{ K})} = 2.053 \times 10^{-8} \text{ mol}$$

For each mole of O_2, four moles of e^- flow through the circuit, so

$e^- = 8.210 \times 10^{-8}$ mol/s = 8.21×10^{-3} C/s = 8.21 mA.

An oxygen content of 1.00 ppm would give a current of 8.21 μA instead.

S17-13. The Zn^{2+} reacts first with PDTA freed by the reduction of $Hg(PDTA)^{2-}$ in the region BC.
Then additional Zn^{2+} goes on to liberate Hg^{2+} from $Hg(PDTA)^{2-}$.
This additional Hg^{2+} is reduced in the region DE.
The total Hg^{2+}, equivalent to the added Zn^{2+}, equals one-half the coulombs measured in regions BC and DE (because $2e^-$ react with 1 Hg^{2+}).
Coulombs = 3.89 + 14.47 = 18.36.
Moles of Hg^{2+} reduced = 0.5(18.36 C)/(96 485 C/mol) = 9.514×10^{-5} mol.
$[Zn^{2+}] = 9.514 \times 10^{-5}$ mol/2.00×10^{-3} L = 0.047 57 M.

S17-14. (a)

cathode:	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	$E° = 1.70$ V
anode:	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E° = 0.771$ V
net:	$Ce^{4+} + Fe^{2+} \rightleftharpoons Fe^{3+} + Ce^{3+}$	$E° = 1.70 - 0.771 = 0.93$ V

$$E_{\text{galvanic}} = E(\text{cathode}) - E(\text{anode}) - IR$$
$$= \left\{1.70 - 0.059\ 16 \log \frac{[0.050]}{[0.10]}\right\}$$
$$- \left\{0.771 - 0.059\ 16 \log \frac{[0.10]}{[0.10]}\right\} - (0.030\ 0 \text{ A})(3.50\ \Omega) = 0.84 \text{ V}$$

(b) $E_{\text{electrolysis}} = -[E(\text{cathode}) - E(\text{anode})] - IR = -1.06$ V

(c) $E_{\text{galvanic}} = E(\text{cathode}) - E(\text{anode}) - IR$

$$= \left\{1.70 - 0.059\ 16 \log \frac{[0.180]}{[0.070]}\right\}$$

$$- \left\{0.771 - 0.059\ 16 \log \frac{[0.050]}{[0.160]}\right\} - (0.100\ \text{A})\ (3.50\ \Omega)$$

$$= 1.67_6 - 0.801 - 0.350 = 0.52\ \text{V}$$

S17-15. In *controlled-potential* electrolysis, the potential of the working electrode is not allowed to vary. With two electrodes, the potential of the working electrode becomes more extreme as the concentration of reactant changes. Eventually the electrode potential reaches a range where other reactions can occur.

S17-16. Cathodic depolarizer

S17-17. (a) Since Mn is oxidized, it is the anode.

(b) $\dfrac{(2.60\ \text{C/s})(18.0 \times 60\ \text{s})}{96\ 485\ \text{C/mol}} = 0.029\ 10$ mol of e^- = 0.009 70 mol of M

(since one mole of M gives $3e^-$). 0.504 g/0.009 70 mol = 52.0 g/mol

(c) In the electrolysis 0.02910/2 = 0.014 55 mol of Mn^{2+} were produced.
$[Mn^{2+}]$ = 0.025 0 + 0.014 55 = 0.039 6 M.

S17-18. anode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ $\quad E° = 1.229$ V

cathode: $Zn(OH^-)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4OH^-$ $\quad E° = -1.199$ V

$E = E(\text{cathode}) - E(\text{anode}) - IR - \text{overpotential}$

$$= \left\{-1.199 - \frac{0.059\ 16}{2} \log \frac{[OH^-]^4}{[Zn(OH)_4{}^{2-}} \right\}$$

$$- \left\{1.229 - \frac{0.059\ 16}{2} \log \frac{1}{P_{O_2}{}^{1/2}[H^+]^2} \right\} - IR - \text{overpotential}$$

$$= \left\{-1.199 - \frac{0.059\ 16}{2} \log \frac{[0.10]^4}{[0.010]} \right\}$$

$$- \left\{1.229 - \frac{0.059\ 16}{2} \log \frac{1}{[0.20]^{1/2}[1.0 \times 10^{-13}]^2} \right\} - IR - \text{overpotential}$$

$$= -1.140 - 0.450 - (0.20\ \text{A})(0.35\ \Omega) - 0.519 = -2.179\ \text{V}$$

S17-19. Relevant information :

$CuY^{2-} + 2e^- = Cu(s) + Y^{4-}$ $\quad E° = -0.216$ V

$Co^{2+} + 2e^- = Co(s)$ $\quad E° = -0.282$ V

CoY^{2-} $\quad K_f = 2.0 \times 10^{16}$

$\alpha_{Y^{4-}} = 3.8 \times 10^{-9}$ at pH 4

When 99% of CuY^{2-} is reduced, $[CuY^{2-}] = 1.0 \times 10^{-8}$ M.

$$E(\text{cathode}) = -0.216 - \frac{0.059\ 16}{2} \log \frac{[Y^{4-}]}{[CuY^{2-}]}$$

But $[Y^{4-}] = \alpha_{Y^{4-}}[\text{EDTA}] = (3.8 \times 10^{-9})(0.010\ \text{M}) = 3.8 \times 10^{-11}$ M

$\Rightarrow E(\text{cathode}) = -0.144$ V

Will this cathode potential reduce Co^{2+}?

$$\alpha_{Y^{4-}} K_f (\text{for } CoY^{2-}) = \frac{[CoY^{2-}]}{[Co^{2+}][\text{EDTA}]} \Rightarrow [Co^{2+}] = 1.3 \times 10^{-8}\ \text{M}$$

$$E(\text{cathode}, Co^{2+}) = -0.282 - \frac{0.059\ 16}{2} \log \frac{1}{1.3 \times 10^{-8}} = -0.515\ \text{V}$$

The cobalt will not be reduced and the separation is feasible.

S17-20. (a) $n = \dfrac{PV}{RT} = \dfrac{(0.996\ \text{bar})(0.049\ 22\ \text{L})}{(0.083\ 14\ \text{L bar K}^{-1}\ \text{mol}^{-1})(303\ \text{K})} = 1.946$ mmol of H_2

(b) For every mole of H_2 produced, 2 moles of e^- are consumed and one mole of Cu is oxidized. Therefore, 1.946 mmol of Cu^{2+} are produced and the concentration of EDTA is 1.946 mmol/47.36 mL = 0.041 09 M.

(c) 1.946 mmol of H_2 comes from 2(1.946) = 3.892 mmol of e^-

$= (3.892 \times 10^{-3})(96\ 485) = 3.755 \times 10^2$ C

Time = 3.755×10^2 C/(0.021 96 C/s) = 1.710×10^4 s = 4.75 h.

S17-21. Trichloroacetate is reduced at –0.90 V, consuming 224 C/(96 485 C/mol) = 2.322 mmol of e^-. This means that (1/2)(2.322) = 1.161 mmol of Cl_3CCO_2H (FM 163.386)

= 0.189 7 g of Cl_3CCO_2H were present.

The total quantity of Cl_2HCCO_2H (FM 128.943) is (1/2)[758 C/(96 485 C/mol)] = 3.928 mmol, of which 1.161 mmol came from reduction of Cl_3CCO_2H.

Cl_2HCCO_2H in original sample = 3.928 – 1.161 = 2.767 mmol = 0.356 8 g.

$$\text{wt \% trichloroacetic acid} = \frac{0.189\ 7}{0.721} \times 100 = 26.3\%$$

$$\text{wt \% dichloroacetic acid} = \frac{0.356\ 8}{0.721} \times 100 = 49.5\%$$

S17-22. (a) Because 1 ampere = 1 coulomb/s, we can say C = A·s:

coulombs = $(1.68 \times 10^{-3}$ s)(154.4 min)(60 s/min) = 15.5_6 C

moles of electrons = $(15.5_6$ C)/(96 485 C/mol) = $1.61_3 \times 10^{-4}$ mol

(b) One formula unit of polymer contains n pyrrole monomers and one anion.moles of polymer formula units $= \dfrac{13.5 \times 10^{-3}\text{ g}}{[n(65.075) + 325.49]\text{g/mol formula unit}}$

For every formula unit of polymer, $2n + 1$ electrons flow through the circuit.

The key stoichiometry relationship is:

$$\text{moles of polymer formula units} = \frac{\text{moles of electrons}}{2n+1}$$

$$\frac{13.5 \times 10^{-3}\text{ g}}{[n(65.075) + 325.49]\text{g/mol formula unit}} = \frac{1.613 \times 10^{-4}\text{ mol}}{2n+1} \quad \Rightarrow \quad n = 2.36$$

S17-23. Slope $= 11.91$ standard deviation $= 0.12$

intercept $= -0.012$ standard deviation $= 0.017$

$\sigma_y = 0.033 =$ standard deviation of current

The concentration of Al^{3+}, when $I_d = 0.904\ \mu A$, is found as follows :

$$I(\text{mA}) = m[Al^{3+}] + b$$

$$[Al^{3+}] = \frac{I-b}{m} = \frac{0.904 - (-0.012)}{11.91} = 0.076\,9\text{ mM}$$

Equation 5-14 gives an uncertainty of $\pm 0.002\,9$ mM

S17-24. $$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

$$\frac{x(\text{ppm})}{2.65\left(\frac{0.500}{3.50}\right) + x\left(\frac{3.00}{3.50}\right)} = \frac{152\text{ nA}}{206\text{ nA}} \quad \Rightarrow \quad x = 0.760\text{ ppm}$$

S17-25. Use the internal standard equation with X = DDT and S = chloroform.

From the standard mixture we find the response factor, F:

$$\frac{\text{signal}_X}{[X]} = F\left(\frac{\text{signal}_S}{[S]}\right) \Rightarrow \frac{1.00}{[1.00\text{ mM}]} = F\left(\frac{1.40}{[1.00\text{ mM}]}\right) \Rightarrow F = 0.714_3$$

For the unknown mixture, we can say

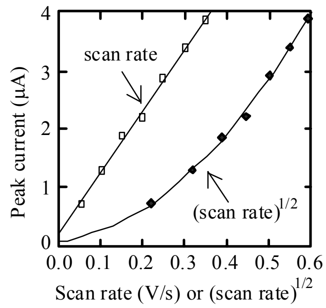
$$\text{signal}_X\text{,[X]}) = F\left(\frac{\text{signal}_S}{[S]}\right) \Rightarrow \frac{1.00}{[\text{DDT}]} = 0.714_3\left(\frac{0.86}{[0.500\text{ mM}]}\right) \Rightarrow [\text{DDT}] = 0.81\text{ mM}$$

S17-26. If the conditions were perfectly reproducible, the diffusion current for Tl^+ in experiment B would be $(1.21/1.15)(6.38) = 6.71\ \mu A$. The observed current in experiment B is only $6.11/6.71 = 91.1\%$ of the expected value. That is, in experiment B the response is only 91.1% as great as in experiment A. Therefore, the responses to Cd^{2+} and Zn^{2+} in experiment B are expected to be only 91.1% as great as they are in experiment A

$$[Cd^{2+}] = \frac{(4.76/6.48)}{0.911}(1.02) = 0.82\text{ mM}$$

$$[Zn^{2+}] = \frac{(8.54/6.93)}{0.911}(1.23) = 1.66 \text{ mM}$$

S17-27. The graph of current vs. scan rate gives a straight line with an intercept reasonably near zero. The analyte is confined to the electrode surface. Otherwise, the graph of current vs. $\sqrt{\text{scan rate}}$ would give the better straight line.



S17-28. (a) Slope = +0.049 V = 0.059(q–p) $\Rightarrow$ q–$p \approx$ +1. That is, the oxidized species has one more imidazole ligand than the reduced species. The chemistry is either $ML^+ + L + e^- \rightarrow ML_2$ or $M^+ + L + e^- \rightarrow ML$.

Intercept = 0.029V = $E_{1/2}^{\text{free}} - 0.059 \log (\beta_p^{ox} / \beta_q^{red})$.

Putting in $E_{1/2}^{\text{free}}$ = –0.18 V gives $\log (\beta_p^{ox} / \beta_q^{red}) = -3.5$.

(b) Since the slope is zero, the reaction is either $ML_2^+ + e^- \rightarrow ML_2$ or $ML^+ + e^- \rightarrow ML$.

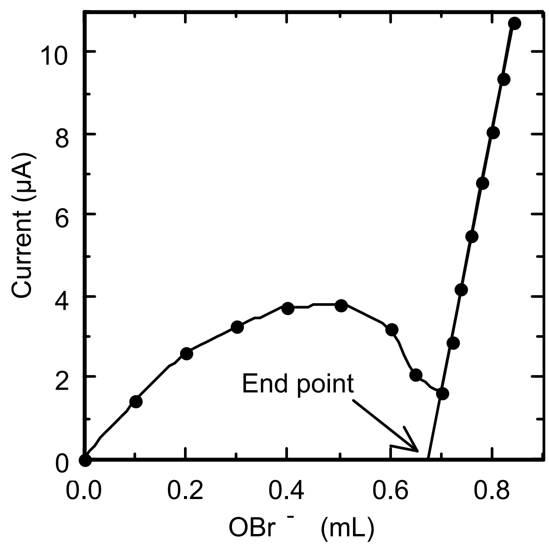
It cannot be $M^+ + e^- \rightarrow M$ because the product has one fewer ligand at lower free ligand concentration (–3.4 < log [L] < –2.1), and the product cannot have a negative number of ligands.

The reaction sequence in parts (a) and (b) has been interpreted as

(a) $ML^+ + L + e^- \rightarrow ML_2$ (b) $ML_2^+ + e^- \rightarrow ML_2$

S17-29. The end point (0.675 mL) in the figure below is where the linear current increase extrapolates back to zero. Two moles of NH_3 require 3 moles of OBr^-

$$[OBr^-] = (3/2)\frac{(30.0 \text{ mL})(4.43 \times 10^{-5} \text{ mmol/mL})}{0.675 \text{ mL}} = 2.95 \text{ mM}.$$



S17-30. 34.61 mL of methanol with 4.163 mg of H_2O/mL contains 144.08 mg H_2O = 7.997 8 mmol of H_2O.

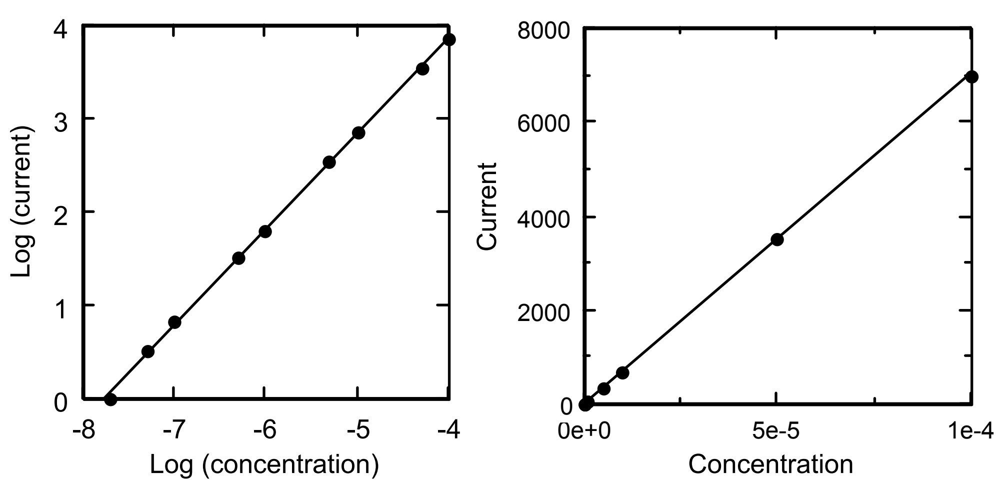
The titration of "dry" methanol tells us that 25.00 mL of methanol reacts with 3.18 mL of reagent.

Therefore, 34.61 mL of methanol will react with (34.61/25.00)(3.18) = 4.40 mL of Karl Fischer reagent. The titer of the reagent is

$$\frac{7.997\,8 \text{ mmol } H_2O}{(25.00 - 4.40) \text{ mL reagent}} = 0.388\,24 \frac{\text{mmol } H_2O}{\text{mL reagent}}$$

Reagent needed to react with 1.000 g of salt in 25.00 mL of methanol = (38.12 – 3.18) = 34.94 mL. H_2O in 1.000 g of salt = (0.388 24)(34.94) = 13.565 mmol = 244.38 mg of H_2O = 24.44 wt % of the crystal.

S17-31.(a)



(b) $m = 7.002\ (\pm 0.005) \times 10^7$ $b = -1.5\ (\pm 1.9)$ $s_y = 5.0$

(c) $\text{Concentration} = \dfrac{\text{current - intercept}}{\text{slope}} = \dfrac{300\ (\pm 15) - [-1.5\ (\pm 1.9)]}{7.002\ (\pm 0.005) \times 10^7}$

$= \dfrac{301.5\ (\pm 15.1)}{7.002\ (\pm 0.005) \times 10^7} = 4.3_1\ (\pm 0.2_2) \times 10^{-6}\ \text{M}$

S17-32. Spreadsheet for weighted least squares

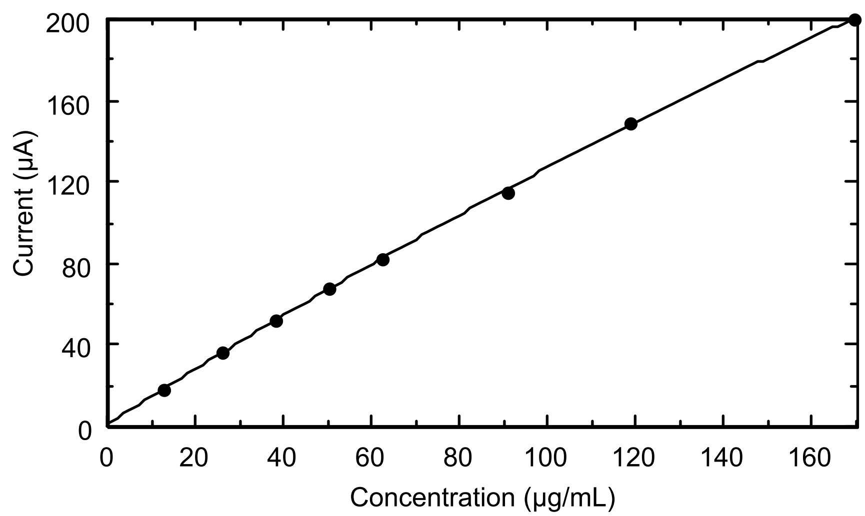
	A	B	C	D	E	F	G	H	I	J
1	n	x	y	std dev	weight (w)	w*x*y	w*x	w*y	w*x^2	w*d^2
2	1	1.00E-04	6995	112	8E-05	6E-05	8E-09	6E-01	8E-13	6E-02
3	2	5.00E-05	3510	74	2E-04	3E-05	9E-09	6E-01	5E-13	1E-01
4	3	1.00E-05	698	11	8E-03	6E-05	8E-08	6E+00	8E-13	2E-02
5	4	5.00E-06	345	18	3E-03	5E-06	2E-08	1E+00	8E-14	3E-02
6	5	1.00E-06	64.4	3.9	7E-02	4E-06	7E-08	4E+00	7E-14	2E+00
7	6	5.00E-07	32.4	1.8	3E-01	5E-06	2E-07	1E+01	8E-14	1E+00
8	7	1.00E-07	6.88	0.64	2E+00	2E-06	2E-07	2E+01	2E-14	2E-01
9	8	5.00E-08	3.17	0.32	1E+01	2E-06	5E-07	3E+01	2E-14	2E-02
10	9	2.00E-08	1.03	0.2	3E+01	5E-07	5E-07	3E+01	1E-14	8E-04
11	n=									
12	9									
13		1.667E-4	11656		4E+01	2E-04	2E-06	1E+02	2E-12	3E+00
14		|<--------------------------------Column sums (B-J)---------------------------------->|								
15	D=	sigma(y) =			Example: E13 = Sum(E2:E10)					
16	8.623E-11	6.93E-01								
17	m=	sigma(m)=		E2 = 1/D2^2		H2 = E2*C2				
18	6.967E+07	4.58E+05		F2 = E2*B2*C2		I2 = E2*B2*B2				
19	b=	sigma(b) =		G2 = E2*B2		J2 = E2*(C2-A18*B2-A20)^2				
20	-3.578E-01	1.15E-01								
21										
22	D = E13*I13-G13*G13				sigma(y) = Sqrt(J13/(A12-2))					
23	m = (E13*F13-G13*H13)/A16				sigma(m) = B16*Sqrt(E13/A16)					
24	b = (H13*I13-G13*F13)/A16				sigma(b) = B16*Sqrt(I13/A16)					

Unweighted parameters:
$m = 7.002\ (\pm 0.005) \times 10^7$
$b = -1.5\ (\pm 1.9)$
$s_y = 5.0$

Weighted parameters:
$m = 6.967\ (\pm 0.046) \times 10^7$
$b = -0.36\ (\pm 0.12)$
$s_y = 0.693$

S17-33. (a) $A = 0.97 \pm 0.95$ $B = 1.385 \pm 0.027$ $C = -0.001\,23 \pm 0.000\,14$ $s_y = 0.919$

(b)



(c) Current = A + B[α-tocopherol] + C[α-tocopherol]^2

$170 = 0.967 + 1.385\,[\alpha\text{-tocopherol}] - 0.001\,23\,[\alpha\text{-tocopherol}]^2$

$\Rightarrow$ [α-tocopherol] = 139.3 μg/mL

$171 = 0.967 + 1.385\,[\alpha\text{-tocopherol}] - 0.001\,23\,[\alpha\text{-tocopherol}]^2$

$\Rightarrow$ [α-tocopherol] = 140.2 μg/mL

$169 = 0.967 + 1.385\,[\alpha\text{-tocopherol}] - 0.001\,23\,[\alpha\text{-tocopherol}]^2$

$\Rightarrow$ [α-tocopherol] = 138.3 μg/mL

Answer: [α-tocopherol] = 139 ± 1 μg/mL

S17-34. To find the unknown concentration, we set up a proportionality:

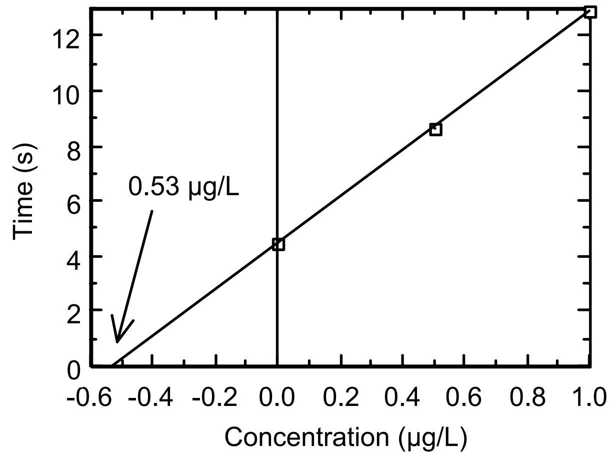
$$\frac{[Pb^{2+}]_{\text{unknown}}}{[Pb^{2+}]_{\text{unknown}} + [Pb^{2+}]_{\text{standard}}} = \frac{(\text{stripping time})_{\text{unknown}}}{(\text{stripping time})_{\text{unknown + standard}}}$$

$$\frac{[Pb^{2+}]_{\text{unknown}}}{[Pb^{2+}]_{\text{unknown}} + 0.5\ \mu\text{g/L}} = \frac{4.8\ \text{s}}{8.8\ \text{s}} \quad \Rightarrow\ [Pb^{2+}]_{\text{unknown}} = 0.6\ \mu\text{g/L} = 2.9 \times 10^{-9}\ \text{M}$$

S17-35. $$\frac{[Cu^{2+}]_{\text{unknown}}}{[Cu^{2+}]_{\text{unknown}} + [Cu^{2+}]_{\text{standard}}} = \frac{(\text{stripping time})_{\text{unknown}}}{(\text{stripping time})_{\text{unknown + standard}}}$$

$$\frac{[Cu^{2+}]_{\text{unknown}}}{[Cu^{2+}]_{\text{unknown}} + 0.5\ \mu\text{g/L}} = \frac{8.6\ \text{s}}{13.4\ \text{s}} \quad \Rightarrow [Cu^{2+}]_{\text{unknown}} = 0.90\ \mu\text{g/L} = 1.4 \times 10^{-8}\ \text{M}$$

S17-36.



S17-37. $$\frac{[Cd^{2+}]_{unknown}}{[Cd^{2+}]_{unknown} + [Cd^{2+}]_{standard}} = \frac{(\text{stripping time})_{unknown}}{(\text{stripping time})_{unknown + standard}}$$

$$\frac{[Cd^{2+}]_{unknown}}{[Cd^{2+}]_{unknown} + 0.5\ \mu g/L} = \frac{1.0\ s}{3.7\ s} \Rightarrow [Cd^{2+}]_{unknown} = 0.19\ \mu g/L = 1.6 \times 10^{-9}\ M$$

S17-38. The equation of the straight line is time (s) = 8.00 $[Cu^{2+}]$ (μg/L) + 8.57

The *x*-intercept gives the concentration in the unknown = 1.07 μg/L

S17-39. The initial solution has a high concentration of Fe^{2+} and a low concentration of Fe^{3+}, so the current is low. As titrant is added, Fe^{2+} is converted to Fe^{3+} and the $Fe^{3+} | Fe^{2+}$ redox couple carries maximum current near the middle of the titration. As we approach the equivalence point, there is a high concentration of Fe^{3+} and little Fe^{2+}, so the current decreases (to near zero at the equivalence point). After the equivalence point, excess Ce^{4+} is added to the pot containing Ce^{3+} from the titration reaction. The current increases again as the $Ce^{4+} | Ce^{3+}$ couple reacts at the two electrodes.

S17-40. (a) The initial solution contains H_3AsO_3 and Br^-, neither of which can support a substantial current between two Pt electrodes. Only a small residual current is expected. As BrO_3^- is added, it is converted to Br_2 and then to Br^- by reaction with H_3AsO_3.

Since the $H_3AsO_4|H_3AsO_3$ does not conduct current, the current remains small.

After the equivalence point, when both Br_2 and Br^- are present, substantial current flows by virtue of oxidation of Br^- at one electrode and reduction of Br_2 at the other.. The expected titration curve is level near zero current until the end point, and then it increases steadily.

(b) Initially there is no easy mechanism for carrying current, so the voltage will be high. As I_2 is added, it is converted to I^- and H_3AsO_3 is oxidized to H_3AsO_4.
Since the $H_3AsO_3|H_3AsO_4$ couple does not carry current (as stated in part a), the voltage remains high. Only after the end point, when both I_2 and I^- are present, does the voltage drop to near zero. The titration curve is expected to look like the one in Demonstration 18-1.

S17-41. The standard curve is moderately linear with slope = 0.004 19 μA/ppb and intercept of 0.019 8.
The concentration of Ni^{2+} when 54.0 μL of 10.0 ppm solution is added to 5.00 mL is

$$\left(\frac{0.054\,0\text{ mL}}{5.054\,0\text{ mL}}\right)(10.0\text{ ppm}) = 0.107\text{ ppm} = 107\text{ ppb}$$

The expected current is $I = m[\mathrm{Ni}^{2+}] + b = (0.004\,19)(107) + 0.019\,8 = 0.468\ \mu\mathrm{A}$
A careful examination of the standard curve shows that a better fit might be obtained if the slope and intercept of just the first seven points are calculated. The curve appears to be starting to level off at the higher concentration in this experiment.

S17-42. Sample height (mm) = 26.8 – 2.4 = 24.4
Sample + 1 ppm Cu = 42.2 – 5.6 = 36.6
Sample + 2 ppm Cu = 57.8 – 8.7 = 49.1
The average response to added Cu is $\dfrac{(36.6-24.4) + (49.1-24.4)}{3} = 12.3\ \dfrac{\text{mm}}{\text{ppm Cu}}$
The initial sample must have contained $\dfrac{24.4}{12.3} = 1.98$ ppm Cu.

S17-43. A graph of $E_{1/2}$ versus log[OH^-] is shown below.
All but the lowest two points appear to lie on a line whose equation is

$$E_{1/2} = -0.080\,6\log[\mathrm{OH}^-] - 0.763$$

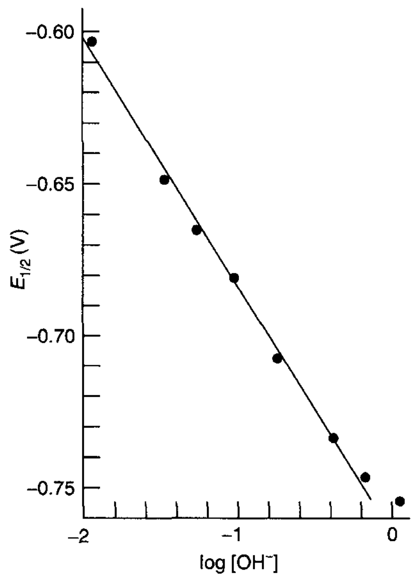
$E_{1/2}$ is related to $E_{1/2}$ for a free metal ion in a noncomplexing medium by the following equation.

$$E_{1/2} = E_{1/2}(\text{for free M}^{n+}) - \frac{0.059\,16}{n}\log\beta_p - \frac{0.059\,16p}{n}\log[\mathrm{L}^{-b}]$$

where β_p is the equilibrium constant for the reaction $M^{n+} + pL^{-b} = ML_p^{n-pb}$.

The slope of the graph is –0.059 16 p/n. Assuming that n = 2, we calculate p as follows:

$$p = \frac{(n)(\text{slope})}{-0.059\,16} = 2.72 \approx 3$$



The intercept is given by

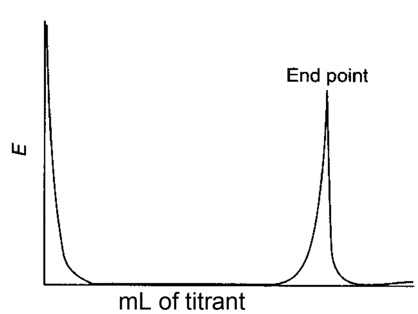
$$\text{intercept} = E_{1/2}(\text{for free Pb}^{2+}) - \frac{-0.059\,16}{n} \log \beta_3$$

$$-0.763 = -0.41 - \frac{-0.059\,16}{2} \log \beta_3 \Rightarrow \beta_3 = 9 \times 10^{11}$$

S17-44. Initially there is no redox couple to carry current, so the potential will be high. As Ce^{4+} is added, Fe^{2+} is converted to Fe^{3+}, the mixture of which can support current flow by the reactions

anode: $Fe^{2+} = Fe^{3+} + e^-$ cathode: $Fe^{3+} + e^- = Fe^{2+}$

The potential will therefore decrease. At the equivalence point, all of the Fe^{2+} and all of the Ce^{4+} are consumed, so the potential is very high. Beyond the equivalence point, the redox couple $Ce^{4+}|Ce^{3+}$ can support a current and the potential will be low again. The expected curve is shown below:



S17-45. See Figures 17-15 and 17-18.

S17-46. $\dfrac{[X]_i}{[S]_f + [X]_f} = \dfrac{I_X}{I_{S+X}}$

$$\frac{[X]_i}{\left(\frac{1.00}{101.0}\right)(0.050\,0) + \left(\frac{100.0}{101.0}\right)[X]_i} = \frac{10.0}{14.0} \Rightarrow [X]_i = 1.21 \text{ mM}$$

S17-47. The least squares parameters for a graph of I_d vs $[Cu^{2+}]$ are

slope $= m = 6.616$ standard deviation $= 0.018$

intercept $= b = -0.086$ standard deviation $= 0.062$

$\sigma_y = 0.142$

An unknown giving a current of 15.6 μA has a concentration of

$$[Cu^{2+}] = \frac{(I_d - b)}{m} = \frac{15.6 - (-0.086)}{6.616} = 2.371 \text{ mM}$$

and an uncertainty calculated with Equation 5-14:

uncertainty = ±0.023 $\Rightarrow$ $[Cu^{2+}] = 2.37\ (\pm 0.02)$ mM

S17-48. The relative heights of the signals for acetone are $\dfrac{\text{signal for unknown}}{\text{signal for unknown + standard}} = 0.259$

$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

$$\frac{x\ (\text{wt\%})}{0.001\,00 + x} = 0.259 \Rightarrow x = 0.000\,35 \text{ wt\%}$$

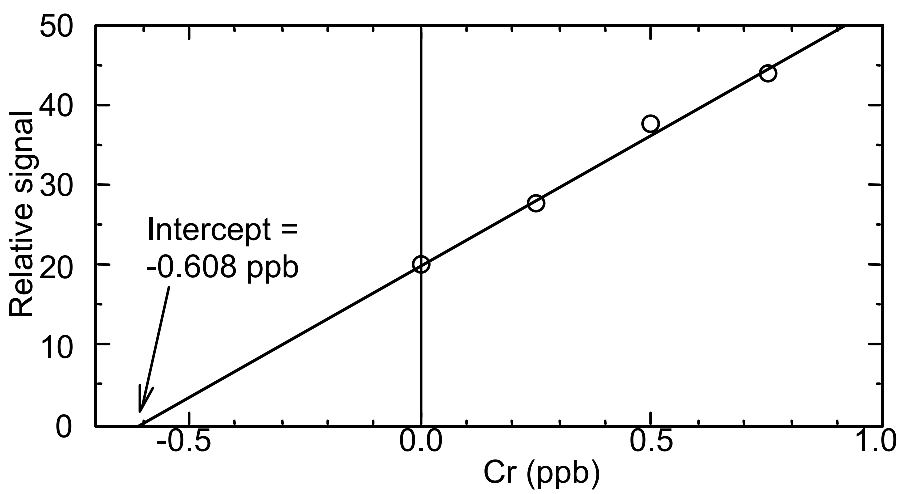
S17-49. At room temperature the interconversion between axial and equatorial conformations is much faster than the reduction, and one peak is seen (near –2.5 V). At low temperature, interconversion slows down and we observe one reduction wave for each molecule. It turns out that the –2.5 V signal is from the axial molecule and the –3.1 V signal is from the equatorial molecule. At –80˚ the relative heights of the waves are close to the relative equilibrium concentrations, because interconversion is much slower than reduction. At –60˚, some of the axial species (–3.1 V) is converted to the equatorial species (–2.5 V) at a rate similar to the rate of reduction of the equatorial species. If the voltage scan rate is increased, less interconversion occurs and the –3.1 V signal grows relative to the –2.5 V signal.

S17-50. Addition of 2-methylimidazole makes it easier to reduce PFe^+ (–0.18 V shifts to –0.14 V) and harder to reduce PFe (–1.02 V shifts to –1.11 V). Therefore, Fe^{2+} is stabilized the most.

S17-51. The high overpotential for reduction of H^+ at a mercury surface allows thermo-dynamically less favorable reductions to occur without competitive reduction of H^+. However, Hg is too easily oxidized to be used for anodic reactions.

S17-52. (a) You need to decide how to treat the baseline. I drew a horizontal line at the position of the gentle maximum in the baseline near –0.9 V and measured peak heights above this baseline for the Cr peak near –1.23 V. Here are my results, which should be considered as relative numbers.

Curve	measured peak height	corrected peak height
Baseline (a)	0.3	+0
Unknown (b)	20.3	20.0
Unknown + 0.25 ppb Cr	27.8	27.5
Unknown + 0.50 ppb Cr	37.8	37.5
Unknown + 0.75 ppb Cr	44.3	44.0



Multiplying the x-intercept by 2.00×10^5 tells us that the soil contains 122 ppm of Cr(VI).

(b) A least-squares spreadsheet gives the following parameters:

Equation of line: $y = 32.80x + 19.95$; $s_y = 1.0124$; $\bar{y} = 32.25$; $\bar{x} = 0.375$

Putting these numbers into Equation 5-17 (with $n = 4$ points) gives standard deviation of unknown concentration = 0.056. Multiplying 0.608 ±0.056 ppb by 2.00×10^5 gives [Cr(VI)] in soil = 122 ±11 ppm.

CHAPTER 18: SUPPLEMENTARY SOLUTIONS
FUNDAMENTALS OF SPECTROPHOTOMETRY

S18-1. Using $\nu = c/\lambda$, $\tilde{\nu} = 1/\lambda$, and $E = h\nu$, we find

	250 nm	10 μm
ν(hz)	1.20×10^{15}	3.00×10^{13}
$\tilde{\nu}$ (cm^{-1})	4.00×10^{4}	1 000
J/photon	7.95×10^{-19}	1.99×10^{-20}
KJ/mol	479	12.0

S18-2. (a) $\dfrac{15.0 \times 10^{-3}\, g}{(384.63\ \text{g/mol})(5 \times 10^{-3}\ \text{L})} = 7.80 \times 10^{-3}$ M (b) One tenth dilution $\Rightarrow$ 7.80×10^{-4} M

(c) $\varepsilon = A/bc = 0.634/[(0.500\ \text{cm})(7.80 \times 10^{-4}\ \text{M})] = 1.63 \times 10^{3}\ \text{M}^{-1}\ \text{cm}^{-1}$

S18-3. Original concentration $= \dfrac{(0.267\ \text{g})/(337.69\ \text{g/mol})}{(0.100\,0\ \text{L})} = 7.91 \times 10^{-3}$ M

Diluted concentration $= \left(\dfrac{2.000}{100.0}\right)(7.91 \times 10^{-3}\ \text{M}) = 1.58 \times 10^{-4}$ M

$$\varepsilon = \frac{A}{bc} = \frac{0.728}{(1.58 \times 10^{-4}\ \text{M})(2.00\ \text{cm})} = 2.30 \times 10^{3}\ \text{M}^{-1}\ \text{cm}^{-1}$$

S18-4. $A = -\log T = 0.085\,1$ for $T = 82.2\%$ and 0.295 for $T = 50.7\%$.
Ratio $= 0.085\,1/0.295 = 0.288$.

S18-5. (a) $\varepsilon = \dfrac{A}{cb} = \dfrac{0.494 - 0.053}{(3.73 \times 10^{-5}\ \text{M})(1.000\ \text{cm})} = 1.18_2 \times 10^{-4}\ \text{M}^{-1}\ \text{cm}^{-1}$

(b) $c = \dfrac{A}{\varepsilon b} = \dfrac{0.777 - 0.053}{(1.182 \times 10^{4}\ \text{M}^{-1}\text{cm}^{-1})(1.000\ \text{cm})} = 6.12_5 \times 10^{-5}$ M

Original concentration was $\dfrac{250.0}{5.00}$ times as great $=$ 3.06 mM

S18-6. (a) The concentration of phosphorus in solution A is 1.196×10^{-3} M .
When 0.140 mL of A is diluted to 5.00 mL, [P] = 3.349×10^{-5} M .
$\varepsilon = A/bc = (0.829 - 0.017)/[(1.00\ \text{cm})(3.349 \times 10^{-5}\ \text{M})] = 2.42_5 \times 10^{4}\ \text{M}^{-1}\ \text{cm}^{-1}$.

(b) [P] in analyte $= \dfrac{A}{\varepsilon b} = \dfrac{(0.836 - 0.038)}{(2.425 \times 10^{4}\ \text{M}^{-1}\text{cm}^{-1})(1.00\ \text{cm})} = 3.291 \times 10^{-5}$ M

[P] in 1.00 mL of undiluted analyte $= \left(\dfrac{5.00}{0.300}\right)(3.291 \times 10^{-5}\ \text{M}) = 5.48_5 \times 10^{-4}$ M .

1.00 mL contains 5.485×10^{-7} mol P = 1.699×10^{-5} g = 1.26% phosphorus.

S18-7. If self absorption is negligible, Equation F reduces to $I = k'P_0(1 - 10^{-\varepsilon_{ex}b_2c})$.

At low concentration, this expression reduces to $I = k'P_0(\mathrm{e}_{ex}b_2c \ln 10)$ (using the first term of a power series expansion). As the concentration increases, the second expression becomes greater than the first expression. When the first expression is 5% below the second, we can say

$$k'P_0(1 - 10^{-\varepsilon_{ex}b_2c}) = 0.95\,k'P_0(\mathrm{e}_{ex}b_2c \ln 10) \text{ or } 1 - 10^{-A} = 0.95\,A \ln 10$$

By trial and error, this equation can be solved to find that when $A = 0.045$, $1 - 10^{-A} = 0.95\,A \ln 10$. (Alternatively, you could make a graph of $1 - 10^{-A}$ versus A and $0.95\,A \ln 10$ versus A. The solution is the intersection of the two curves.)

S18-8. Move the cell diagonally toward the upper right hand side, so that only the lower left corner is illuminated. Then $b_1 = 0$ and b_3 is minimized.

S18-9.

C(M)	I (multiples of $k'P_o$)	C	I
10^{-7}	0.000 070 4	10^{-4}	0.055 8
10^{-6}	0.000 703	10^{-3}	0.069 9
10^{-5}	0.006 88	10^{-2}	2.54×10^{-9}

S18-10. Spreadsheet for florescence intensity with self quenching

	A	B	C
1	E(excitation) =	Concentration	Relative Intensity
2	2120	0.0000001	1.95E-04
3	E(emission) =	0.000001	1.95E-03
4	810	0.00001	1.89E-02
5	b1 =	0.0001	1.40E-01
6	0.3	0.001	7.81E-02
7	b2 =	0.01	3.89E-11
8	0.4		
9	b3 =		
10	0.5		

S18-11. In the simplest case, the colorimetric reagent in the glass particles reacts completely with analyte in the water. For a given volume of water, the quantity of analyte is proportional to the concentration of analyte. The amount of colorimetric reagent reacting with analyte is proportional to the length of column that has changed color. Even if only a fraction of colorimetric reagent reacts with analyte, the length of column that changes color is still directly proportional to the quantity of analyte in the water.

S18-12. At the intersection of the two lines, $y = m_1x + b_1 = m_2x + b_2$. $x = \dfrac{b_2 - b_1}{m_1 - m_2} =$

$$\frac{82\ (\pm 2) - 6.8\ (\pm 0.7)}{1.08\ (\pm 0.02) - 0.12\ (\pm 0.02)} = \frac{75.2(\pm 2.82\%)}{0.96(\pm 2.95\%)} = 78.33\ (\pm 4.08\%) = 78\ (\pm 3)\ \mu\mathrm{L}$$

CHAPTER 19: SUPPLEMENTARY SOLUTIONS
APPLICATIONS OF SPECTROPHOTOMETRY

S19-1. Setting b = 0.100 cm, we find

$$[X] = \frac{\begin{vmatrix} 0.282 & 387 \\ 0.303 & 642 \end{vmatrix}}{\begin{vmatrix} 1\,640 & 387 \\ 399 & 642 \end{vmatrix}} = \frac{(0.282)(642) - (387)(0.303)}{(1\,640)(642) - (387)(399)} = 7.10 \times 10^{-5}\ \text{M}$$

$$[Y] = \frac{\begin{vmatrix} 1\,640 & 0.282 \\ 399 & 0.303 \end{vmatrix}}{\begin{vmatrix} 1\,640 & 387 \\ 399 & 642 \end{vmatrix}} = 4.28 \times 10^{-4}\ \text{M}$$

S19-2.

	A	B	C	D	E	F	G	H
1	Solving Simultaneous Linear Equations with Excel Matrix Operations							
2								
3	Wavelength		Coefficient Matrix		Absorbance		Concentrations	
4		X	Y	Z	of unknown		in mixture	
5	246	12200	3210	290	0.846		6.4667E-05	< - [X]
6	298	4140	6550	990	0.400		1.4179E-05	< - [Y]
7	360	3000	2780	8080	0.555		3.9799E-05	< - [Z]
8			K		A		C	
9								
10	1. Highlight block of blank cells required for solution (G5:G7)							
11	2. Type the formula "= MMULT(MINVERSE(B5:D7),E5:E7)"							
12	3. Press CONTROL+SHIFT+ENTER on a PC or COMMAND+RETURN on a Mac							
13	4. The answer appears in cells G5:G7							

S19-3. We can use the spreadsheet from the previous problem if we divide the absorbances by 2 to change from a 2.000-cm cell to a 1.000-cm cell.
Putting in absorbances of 0.333, 0.249 and 0.180 gives
[X] = 2.086×10^{-5} M, [Y] = 2.387×10^{-5}, and [Z] = 6.317×10^{-6} M.

S19-4. A graph of ΔA/[X] versus ΔA is a scattered straight line with a slope of –1.401 5 and an intercept of 5.943 2.

K = –slope = 1.40. $\quad \Delta\varepsilon = \dfrac{\text{intercept}}{KP_0} = \dfrac{5.943\,2}{1.40 \times 0.001\,00} = 4\,240\ \text{M}^{-1}\ \text{cm}^{-1}$

[X] (M)	ΔA	ΔA/[X]	[X] (M)	ΔA	ΔA/[X]
0	0	—	0.050 9	0.280	5.501
0.005 09	0.030	5.894	0.065 0	0.350	5.385
0.008 52	0.050	5.869	0.077 9	0.420	5.392
0.017 3	0.100	5.780	0.093 2	0.490	5.25
0.029 5	0.170	5.763	0.106 2	0.550	5.179
0.038 7	0.220	5.685			

S19-5. For Zn^{2+}, the maximum absorbance occurs at a mole fraction of metal of 0.33, indicating formation of a 2:1 ligand:metal complex.

For Ga^{3+}, the maximum absorbance at a mole fraction of 0.25, indicates formation of a 3:1 ligand:metal complex.

S19-6. 340 nm: $E = h\nu = h\frac{c}{\lambda} = (6.626\,1 \times 10^{-34}\text{ J·s})\ \frac{2.997\,9 \times 10^{8}\text{ m/s}}{340 \times 10^{-9}\text{ m}} = 5.84 \times 10^{-19}\text{ J}$

To convert to J/mol, multiply by Avogadro's number:

5.84×10^{-19} J/molecule $\times$ 6.022×10^{23} molecules/mol = 352 kJ/mol.

613 nm: $E = (6.626\,1 \times 10^{-34}\text{ J·s})\ \frac{2.997\,9 \times 10^{8}\text{ m/s}}{613 \times 10^{-9}\text{ m}} = 3.24 \times 10^{-19}\text{ J} = 195\ \frac{\text{kJ}}{\text{mol}}$

The difference between the irradiation energy and the fluorescence energy is 352 – 195 = 157 kJ/mol.

S19-7. (a) The equation for intensity can be solved for K, giving $K = \dfrac{[S]\,(1-I_s/I_{s+x})}{I_s/I_{s+x} - [S]/([S]+[X])}$

Putting in $I_s/I_{s+x} = 58.7/74.5$, [S] = 250 μM and [X] = 200 μM gives K = 228 μM.

(b) Solving the intensity equation for [X] gives $[X] = \dfrac{K[S]}{(I_s/I_{s+x})(K+[S]) - [S]} - [S]$

Using the values $I_s/I_{s+x} = 63.5/74.6$, [S] = 250 + 200 = 450 μM and K = 228 μM gives [X] = 357 μM.

S19-8. (a) (b) spreadsheet reproduced

S19-9.

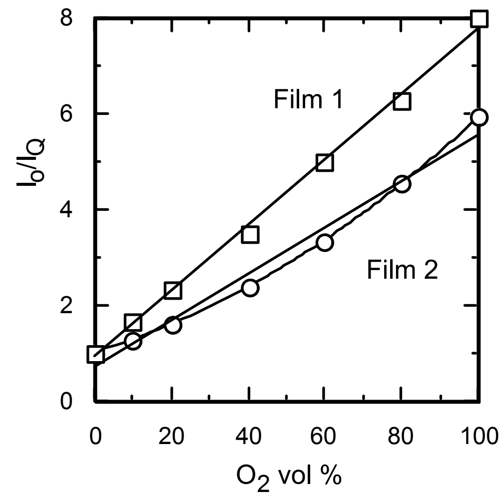
	A	B	C	D	E
1	Cramer's rule spreadsheet				
2				Constant	Solution
3	Coefficient matrix (3x3)			vector	vector
4	4800	11100	18900	0.412	1.219E-05
5	7350	11200	11800	0.350	9.295E-06
6	36400	13900	4450	0.632	1.324E-05
7					
8	Denominator = determinant of coefficient matrix				
9	-1.91768E+12				
10					
11	A9=A4*B5*C6+A5*B6*C4+B4*C5*A6-C4*B5*A6-B4*A5*C6-C5*B6*A4				
12	E14=(D4*B5*C6+D5*B6*C4+B4*C5*D6-C4*B5*D6				
13			-B4*D5*C6-C5*B6*D4)/A9		
14	E15=(A4*D5*C6+A5*D6*C4+D4*C5*A6-C4*D5*A6				
15			-D4*A5*C6-C5*D6*A4)/A9		
16	E16=(A4*B5*D6+A5*B6*D4+B4*D5*A6-D4*B5*A6				
17			-B4*A5*D6-D5*B6*A4)/A9		

S19-10 (a) The absorption spectrum shows that the absorbance of fluorescein decreases with increasing pH at a wavelength of 442 nm. Since the chromophore absorbs less light, the emission intensity will also decrease as pH increases. At an excitation wavelength of 488 nm, the situation is reversed: Absorbance increases with increasing pH, and so does emission intensity.

(b) For excitation at 488 nm, the ratio of emission intensities I_{540}/I_{610} is small at low pH and large at high pH. The calibration graph shows that this ratio is sensitive to pH in the range pH 6 to pH 8 and could be used to measure pH in this interval.

S19-11 (a)

vol % O_2	Film 1 response (V)	Film 2 response (V)	Film 1 I_o/I_Q	Film 2 I_o/I_Q
0	7.60	8.42	1.000	1.000
10	4.61	6.63	1.647	1.269
20	3.33	5.30	2.280	1.588
40	2.18	3.57	3.487	2.356
60	1.52	2.54	5.000	3.313
80	1.22	1.87	6.241	4.511
100	0.95	1.43	7.981	5.889



(b) If the sensor obeyed the Stern-Volmer equation, each set of data would give a straight line with a *y*-intercept of 1.

(c) Film 1 gives a reasonable straight line but film 2 does not. The dashed line for film 2 is the least-squares straight line fit to the data. The dashed line, which fits the data well, is a quadratic polynomial. In film 2, there are probably multiple environments for Ru(II) with different quenching characteristics.

SPECTROPHOTOMETERS

S20-1. (a) The critical angle, θ_c, is such that $(n_1/n_2)\sin\theta_c = 1$. For $n_1 = 2.7$ and $n_2 = 2.0$, $\theta_c = 48°$. That is θ must be $\geq 48°$ for total internal reflection.

(b) $$\frac{\text{power out}}{\text{power in}} = 10^{-\ell(\text{dB/m})/10} = 10^{-(0.50\text{ m})(0.0120\text{ dB/m})/10} = 0.9986$$

S20-2. $n_1 \sin\theta_1 = n_2 \sin\theta_2$, where $n_1 = 1.46$ and $n_2 = 1.63$

(a) If $\theta_1 = 30°$, $\theta_2 = 26.6°$ (b) If $\theta_1 = 0°$, $\theta_2 = 0°$ (no refraction)

S20-3. (a) For incident light: $n_{\text{air}} \sin\theta = n_{\text{prism}} \sin\alpha \Rightarrow \sin\theta = \dfrac{n_{\text{prism}} \sin\alpha}{n_{\text{air}}}$

For exiting light: $n_{\text{prism}} \sin\alpha = n_{\text{air}} \sin\theta \Rightarrow \sin\theta = \dfrac{n_{\text{prism}} \sin\alpha}{n_{\text{air}}}$

Therefore, entrance and exit angles are the same.

(b) $\alpha = 30°$ if light is parallel to the prism base.

Therefore, $\sin\theta = \dfrac{(1.500)\sin 30°}{1.000} \Rightarrow \theta = 48.59°$

S20-4. Since exitance is proportional to T^4, $\dfrac{\text{exitance at 900 K}}{\text{exitance at 300 K}} = \left(\dfrac{900}{300}\right)^4 = 81$

$$\text{Exitance at 900 K} = \left(5.6698 \times 10^{-8}\,\frac{\text{W}}{\text{m}^2\text{K}^4}\right)(900\text{ K})^4 = 3.72 \times 10^4\,\frac{\text{W}}{\text{m}^2}$$

S20-5. (a) The mass of a 1-cm length of the cylinder is: (volume) (density)

$= \pi r^2(\text{length})(7.89\text{ g/cm}^3) = \pi(0.32\text{ cm})^2(1\text{ cm})(7.86\text{ g/cm}^3) = 2.5_3\text{ g}$

The surface area of the 1-cm length of cylinder is

$\pi(\text{diameter})(\text{length}) = \pi(0.64\text{ cm})(1\text{ cm}) = 2.0_1\text{ cm}^2$

$$\text{Exitance from iron} = \left(5.6698 \times 10^{-8}\,\frac{\text{W}}{\text{m}^2\text{K}^4}\right)(1373\text{ K})^4 = 2.01 \times 10^5\,\frac{\text{W}}{\text{m}^2}$$

$$\text{Exitance from surroundings into iron} = \left(5.6698 \times 10^{-8}\,\frac{\text{W}}{\text{m}^2\text{K}^4}\right)(300\text{ K})^4 = 459\,\frac{\text{W}}{\text{m}^2}$$

$$\text{Net energy loss from iron} = (2.01 \times 10^5 - 459\,\frac{\text{W}}{\text{m}^2}) = 2.01 \times 10^5\,\frac{\text{W}}{\text{m}^2}$$

$$= 20._1\,\frac{\text{W}}{\text{cm}^2} = 20._1\,\frac{\text{J}}{\text{s·cm}^2}$$

$$\text{Energy loss rate (J/s)} = \left[\text{exitance}\left(\frac{\text{J}}{\text{s·cm}^2}\right)\right]\,[\text{surface area (cm}^2)]$$

$$= \left(20._1\ \frac{\text{J}}{\text{s·cm}^2}\right)(2.0_1\ \text{cm}^2) = 40._4\ \text{J/s}$$

$$\text{Heat capacity of 1-cm length is [mass(g)]}\left[\text{heat capacity}\left(\frac{\text{J}}{\text{g K}}\right)\right] = (2.5_3\ \text{g})\left(0.606\ \frac{\text{J}}{\text{g·K}}\right)$$

$$= 1.5_3\ \text{J/K}$$

$$\text{Cooling rate} = \frac{\text{energy loss rate}}{\text{heat capacity}} = \frac{40._4\ \text{J/s}}{1.5_3\ \text{J/K}} = 26\ \text{K/s}$$

(b) The ratio of surface area/volume is 10 times greater so the cooling rate is also 10 times greater = 260˚C/s.

S20-6. (a) $n\lambda = d(\sin\theta - \sin\phi)$ $\quad 1 \cdot 400 \times 10^{-9}\ \text{m} = d(\sin 20^\circ - \sin 10^\circ) \Rightarrow d = 2.38 \times 10^{-6}\ \text{m}$

Lines/cm $= 1/(2.38 \times 10^{-4}\ \text{cm}) = 4.21 \times 10^3$ lines/cm

(b) $\lambda = 1/(1\,000\ \text{cm}^{-1}) = 10^{-3}\ \text{cm} \Rightarrow d = 5.94 \times 10^{-3}\ \text{cm} \Rightarrow 168$ lines/cm

S20-7. (a) $\text{Resolution} = \dfrac{\lambda}{\Delta\lambda} = \dfrac{443.531}{0.072} = 6.2 \times 10^3$

For $\lambda = 443.495$ nm, $\tilde{\nu} = 1/\lambda = 2.254\,82 \times 10^6\ \text{m}^{-1} = 2.254\,82 \times 10^4\ \text{cm}^{-1}$.

For $\lambda = 443.567$ nm, $\tilde{\nu} = 2.254\,45 \times 10^4\ \text{cm}^{-1}$ Difference = $3.7\ \text{cm}^{-1}$.

For $\lambda = 443.495$ nm, $\nu = c/\lambda = 6.759\,77 \times 10^{14}$ Hz.

For $\lambda = 443.567$ nm, $\nu = 6.758\,67 \times 10^{14}$ Hz Difference = 1.10×10^{11} Hz.

(b) $\Delta\lambda = \dfrac{\lambda}{10^4} = \dfrac{443.495}{10^4} = 0.04$ nm

(c) $\text{Resolution} = nN = (2)(6.00\ \text{cm} \times 2\,120\ \text{cm}^{-1}) = 2.54 \times 10^4$

(d) 200 lines/mm = 5 μm/line $= d\dfrac{\Delta\phi}{\Delta\lambda} = \dfrac{2}{d\cos\phi} = \dfrac{1}{(5\ \mu\text{m})\cos 10^\circ}$

$$= 0.406\ \frac{\text{radians}}{\mu\text{m}} = 23.3°/\mu\text{m}$$

For $\Delta\lambda = 0.072$ nm, $\Delta\phi = (23.3°/\mu\text{m})(7.2 \times 10^{-5}\ \mu\text{m}) = 1.7 \times 10^{-3}$ degrees

For 20th order diffraction, the dispersion will be 10 times greater, or 0.017°.

S20-8. True transmittance = $10^{-1.26} = 0.055$. With 0.4% stray light, the apparent transmittance is

$\dfrac{P + S}{P_0 + S} = \dfrac{0.055 + 0.004}{1 + 0.004} = 0.058_8$ The apparent absorbance is $-\log 0.058_8 = 1.23$.

S20-9. (a) $\Delta = \pm 4$ cm (b) Resolution $\approx 1/\Delta = 0.25\ \text{cm}^{-1}$

(c) $\delta = 1/(2\Delta\nu) = 1/(2 \cdot 4\,000\ \text{cm}^{-1}) = 1.25\ \mu\text{m}$

S20-10. To increase the ratio from 3/1 to 9/1 (a factor of 9/3 = 3) requires $3^2 = 9$ scans.

S20-11.