1. The following equations provide the relationships between the four variables in this table:

$$E = h\nu \qquad E = \frac{hc}{\lambda} \qquad \nu\lambda = c \qquad \bar{\nu} = \frac{1}{\lambda} \qquad E = hc\bar{\nu}$$

For the first row we find that for $\lambda = 4.50 \times 10^{-9}$ m

$$\nu = \frac{c}{\lambda} = \frac{3.00\times10^{8}\ \text{m/s}}{4.50\times10^{-9}\ \text{m}} = 6.67\times10^{16}\ \text{s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1\ \text{m}/100\ \text{cm}}{4.50\times10^{-9}\ \text{m}} = 2.22\times10^{6}\ \text{cm}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{Js})(3.00\times10^{8}\ \text{m/s})}{4.50\times10^{-9}\ \text{m}} = 4.42\times10^{-17}\ \text{J}$$

For the second row we find that for $\nu = 1.33 \times 10^{15}\ \text{s}^{-1}$

$$\lambda = \frac{c}{\nu} = \frac{3.00\times10^{8}\ \text{m/s}}{1.33\times10^{15}\ \text{s}^{-1}} = 2.26\times10^{-7}\ \text{m}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1\ \text{m}/100\ \text{cm}}{2.26\times10^{-7}\ \text{m}} = 4.42\times10^{4}\ \text{cm}^{-1}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{Js})(1.33 \times 10^{15}\ \text{s}^{-1}) = 8.81 \times 10^{-19}\ \text{J}$$

For the third row we find that for $\bar{\nu} = 3215\ \text{cm}^{-1}$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1\ \text{m}/100\ \text{cm}}{3215\ \text{cm}^{-1}} = 3.11\times10^{-6}\ \text{m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00\times10^{8}\ \text{m/s}}{3.11\times10^{-6}\ \text{m}} = 9.65\times10^{13}\ \text{s}^{-1}$$

$$E = hc\bar{\nu} = (6.626 \times 10^{-34}\ \text{Js})(3.00 \times 10^{8}\ \text{m/s})(3215\ \text{cm}^{-1})(100\ \text{cm/m}) = 6.39 \times 10^{-20}\ \text{J}$$

For the fourth row we find that for $E = 7.20 \times 10^{-19}$ J

$$\lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34}\ \text{Js})(3.00\times10^{8}\ \text{m/s})}{7.20\times10^{-19}\ \text{J}} = 2.76\times10^{-7}\ \text{m}$$

$$\nu = \frac{E}{h} = \frac{7.20 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}} = 1.09 \times 10^{15}\ \text{s}^{-1}$$

$$\bar{\nu} = \frac{E}{hc} = \frac{7.20 \times 10^{-19}\ \text{J} \times {}^{1\ \text{m}}\!/\!_{100\ \text{cm}}}{(6.626 \times 10^{-34}\ \text{Js})(3.00 \times 10^{8}\ \text{m/s})} = 3.62 \times 10^{4}\ \text{cm}^{-1}$$

2. The following equations provide the relationships between the five variables in this table:

$$A = \varepsilon b C \qquad\qquad A = -\log T$$

For the first row we find that

$$A = \varepsilon b C = (1120\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})(1.40 \times 10^{-4}\ \text{M}) = 0.157$$

$$T = 10^{-A} = 10^{-0.157} = 0.697 \text{ or } 69.7\%T$$

For the second row we find that

$$C = \frac{A}{\varepsilon b} = \frac{0.563}{(750\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})} = 7.51 \times 10^{-4}\ \text{M}$$

$$T = 10^{-A} = 10^{-0.563} = 0.274 \text{ or } 27.4\%T$$

For the third row we find that

$$b = \frac{A}{\varepsilon C} = \frac{0.225}{(440\ \text{cm}^{-1}\ \text{M}^{-1})(2.56 \times 10^{-4}\ \text{M})} = 2.00\ \text{cm}$$

$$T = 10^{-A} = 10^{-0.225} = 0.596 \text{ or } 59.6\%T$$

For the fourth row we find that

$$\varepsilon = \frac{A}{bC} = \frac{0.167}{(5.00\ \text{cm})(1.55 \times 10^{-3}\ \text{M})} = 21.5\ \text{cm}^{-1}\ \text{M}^{-1}$$

$$T = 10^{-A} = 10^{-0.167} = 0.681 \text{ or } 68.1\%T$$

For the fifth row we find that

$$A = -\log T = -\log(0.333) = 0.478$$

$$C = \frac{A}{\varepsilon b} = \frac{0.478}{(565\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})} = 8.46 \times 10^{-4}\ \text{M}$$

For the sixth row we find that

$$A = -\log T = -\log(0.212) = 0.674$$

$$b = \frac{A}{\varepsilon C} = \frac{0.674}{(1550\ \text{cm}^{-1}\ \text{M}^{-1})(4.35 \times 10^{-3}\ \text{M})} = 0.100\ \text{cm}$$

For the seventh row we find that

$$A = -\log T = -\log(0.813) = 0.0899$$

$$\varepsilon = \frac{A}{bC} = \frac{0.0899}{(10.00\ \text{cm})(1.20 \times 10^{-4}\ \text{M})} = 74.9\ \text{cm}^{-1}\ \text{M}^{-1}$$

3. To find the new %T we first calculate the absorbance for the original solution.

$$A = -\log T = -\log(0.350) = 0.456$$

Because $A = \varepsilon bC$, diluting the solution in half decreases the absorbance by half as well. The absorbance after diluting, therefore, is 0.228. The %T after diluting is

$$T = 10^{-A} = 10^{-0.228} = 0.592 \text{ or } 59.2\%T$$

4. To find the new %T we first calculate the absorbance for the original solution.

$$A = -\log T = -\log(0.850) = 0.0706$$

Because $A = \varepsilon bC$, increasing the pathlength by a factor of 10 increases the absorbance by a factor of 10. The absorbance when using the longer pathlength, therefore, is 0.706; thus

$$T = 10^{-A} = 10^{-0.706} = 0.197 \text{ or } 19.7\%T$$

6. Beer's law for a mixture of HA and A^-, at a wavelength where both species absorb, is

$$A = \varepsilon_{\text{HA}} b C_{\text{HA}} + \varepsilon_{\text{A}} b C_{\text{A}}$$

(a) When $\varepsilon_{\text{HA}} = \varepsilon_{\text{A}} = 2000\ \text{cm}^{-1}\ \text{M}^{-1}$ Beer's law becomes

$$A = (2000\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})(C_{\text{HA}} + C_{\text{A}}) = (2000\ \text{M}^{-1})C_{\text{tot}}$$

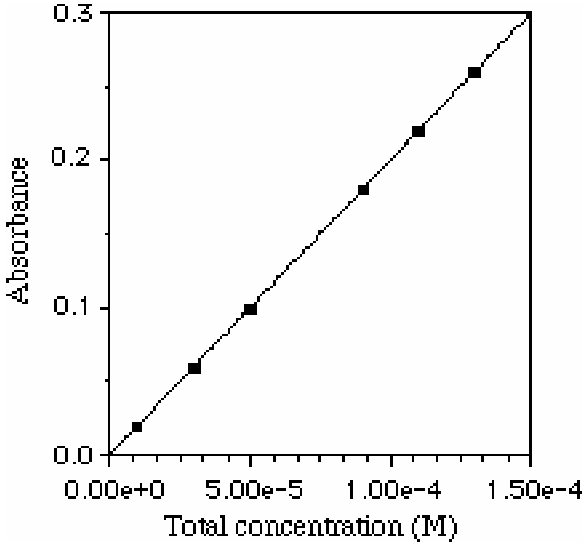
The absorbance when C_{tot} is 1.0×10^{-5}, therefore, is

$$A = (2000\ \text{M}^{-1})(1.0 \times 10^{-5}\ \text{M}) = 0.020$$

The remaining absorbances are calculated in the same way; thus

C_{tot} (M)	Absorbance	C_{tot} (M)	Absorbance
1.0×10^{-5}	0.020	9.0×10^{-5}	0.180
3.0×10^{-5}	0.060	11×10^{-5}	0.220
5.0×10^{-5}	0.100	13×10^{-5}	0.260

The resulting calibration curve of absorbance versus C_{tot}



is linear, showing no deviations due to chemical limitations.

(b) When $\varepsilon_{\text{HA}} = 2000\ \text{cm}^{-1}\ \text{M}^{-1}$ and $\varepsilon_{\text{A}} = 500\ \text{cm}^{-1}\ \text{M}^{-1}$, Beer's law is

$$A = (2000\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})C_{\text{HA}} + (500\ \text{cm}^{-1}\ \text{M}^{-1})(1.00\ \text{cm})C_{\text{A}}$$

$$A = (2000\ \text{M}^{-1})C_{\text{HA}} + (500\ \text{M}^{-1})C_{\text{A}}$$

To find C_{HA} and C_{A} we take advantage of the acid dissociation reaction for HA

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

for which the acid dissociation constant is

$$K_{\text{a}} = 2.0 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{C_{\text{tot}} - x}$$

where C_A =[A$^-$] = x and C_{HA} = [HA] = C_{tot} - x. Rearranging the expression for the acid dissociation constant gives a quadratic equation.

$$x^2 + (2.0\times 10^{-5})x - (2.0\times 10^{-5})C_{tot} = 0$$

Solving the quadratic equation using $C_{tot} = 1.0\times 10^{-5}$, for example, gives $x = 7.32\times 10^{-6}$. The concentrations of HA and A$^-$, therefore, are

$$C_{HA} = C_{tot} - x = 1.0\times 10^{-5} - 7.32\times 10^{-6} = 2.68\times 10^{-6}$$

$$C_A = 7.32\times 10^{-6}$$

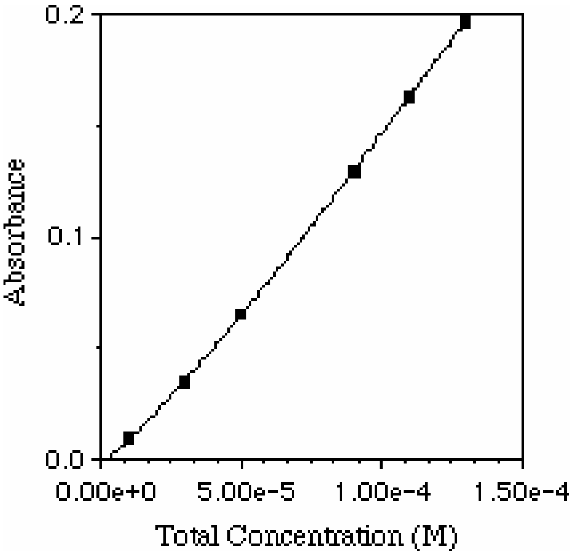
Substituting into the equation for Beer's law gives the absorbance as

$$A = (2000\ \mathrm{M}^{-1})(2.7\times 10^{-6}) + (500\ \mathrm{M}^{-1})(7.3\times 10^{-6}) = 0.009$$

The remaining absorbances are calculated in the same way; thus

C_{tot} (M)	C_{HA} (M)	C_A (M)	A
1.0 x 10^{-5}	2.68 x 10^{-6}	7.32 x 10^{-6}	0.009
3.0 x 10^{-5}	1.35 x 10^{-5}	1.65 x 10^{-5}	0.035
5.0 x 10^{-5}	2.68 x 10^{-5}	2.32 x 10^{-5}	0.065
9.0 x 10^{-5}	5.64 x 10^{-5}	3.36 x 10^{-5}	0.130
11 x 10^{-5}	7.20 x 10^{-5}	3.80 x 10^{-5}	0.163
13 x 10^{-5}	8.80 x 10^{-5}	4.20 x 10^{-5}	0.197

A calibration curve of absorbance versus C_{tot}



is curved, particularly for lower values of C_{tot}. Because the solution isn't buffered the relative proportions of HA and A^- depend on C_{tot}. For example, when C_{tot} is 1.0×10^{-5} M the concentration of A^- is almost 3 times as large as that for HA. When C_{tot} is 13×10^{-5} M, however, the concentration of HA is almost 2 times as large as that for A^-. The same is true in part (a), but because HA and A^- have the same molar absorptivity the effect is unimportant. In this case, where $\varepsilon_{\text{HA}} \neq \varepsilon_{\text{A}}$, doubling C_{tot} does not lead to a doubling of the absorbance.

(c) Buffering the standard solutions prevents the chemical limitation shown in part (b) by maintaining a fixed proportion between HA and A^-. The pH of a buffered solution is given by the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_{\text{a}} + \log\frac{[\text{A}^-]}{[\text{HA}]} = 4.70 + \log\frac{C_{\text{A}}}{C_{\text{HA}}}$$

where 4.70 is the pK_{a} for the weak acid. Substituting in a pH of 4.50 and $C_{\text{tot}} - C_{\text{HA}} = C_{\text{A}}$, and solving for C_{HA} gives

$$4.50 = 4.70 + \log\frac{C_{\text{tot}} - C_{\text{HA}}}{C_{\text{HA}}}$$

$$-0.2 = \log\frac{C_{\text{tot}} - C_{\text{HA}}}{C_{\text{HA}}}$$

$$0.631 = \frac{C_{\text{tot}} - C_{\text{HA}}}{C_{\text{HA}}}$$

$$C_{\text{HA}} = \frac{C_{\text{tot}}}{1.631}$$

For example, when C_{tot} is 1.0×10^{-5} M, we find that

$$C_{\text{HA}} = \frac{1.0\times 10^{-5}\text{ M}}{1.631} = 6.13\times 10^{-6}\text{ M}$$

$$C_{\text{A}} = 1.0\times 10^{-5}\text{ M} - 6.13\times 10^{-6}\text{ M} = 3.87\times 10^{-5}\text{ M}$$

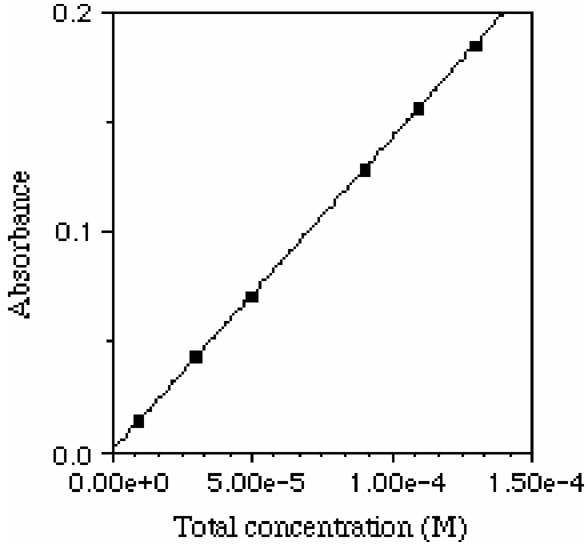
and the absorbance is

$$A = (2000\text{ cm}^{-1})(6.13\times 10^{-6}\text{ M}) + (500\text{ cm}^{-1})(3.87\times 10^{-6}\text{ M}) = 0.014$$

The remaining absorbances are calculated in the same way; thus

C_{tot} (M)	C_{HA} (M)	C_A (M)	A
1.0×10^{-5}	6.13×10^{-6}	3.87×10^{-6}	0.014
3.0×10^{-5}	1.84×10^{-5}	1.16×10^{-5}	0.043
5.0×10^{-5}	3.07×10^{-5}	1.93×10^{-5}	0.071
9.0×10^{-5}	5.52×10^{-5}	3.48×10^{-5}	0.128
11×10^{-5}	6.74×10^{-5}	4.26×10^{-5}	0.156
13×10^{-5}	7.97×10^{-5}	5.03×10^{-5}	0.185

As shown here



a calibration curve of absorbance versus C_{tot} obeys Beer's law.

7. (a) Beginning with

$$A = \log\frac{P_0' + P_0''}{P_T' + P_T''}$$

we expand the right side to get

$$A = \log(P_0' + P_0'') - \log(P_T' + P_T'')$$

We also know that for any wavelength the following equation holds

$$A = \log\frac{P_0}{P_T} = \varepsilon bC$$

Solving for P_T, which equals $P_0 10^{-ebC}$, and substituting back gives

$$A = \log(P_0' + P_0'') - \log(P_0' 10^{-\varepsilon' bC} + P_0'' 10^{-\varepsilon'' bC})$$

If $\varepsilon' = \varepsilon'' = \varepsilon$ then this equation becomes

$$A = \log(P_0' + P_0'') - \log(P_0' 10^{-\varepsilon bC} + P_0'' 10^{-\varepsilon bC})$$

$$A = \log(P_0' + P_0'') - \log\{(P_0' + P_0'')10^{-\varepsilon bC}\}$$

$$A = \log(P_0' + P_0'') - \log(P_0' + P_0'') - \log(10^{-\varepsilon bC})$$

$$A = - \log(10^{-\varepsilon bC}) = \varepsilon bC$$

(b) To calculate the absorbance we use the equation

$$A = \log(P_0' + P_0'') - \log(P_0' 10^{-e' bC} + P_0'' 10^{-e'' bC})$$

If $P_0' = P_0''$ then this equation simplifies to

$$A = \log(2) - \log(10^{-e' bC} + 10^{-e'' bC}) = 0.301 - \log(10^{-\varepsilon' bC} + 10^{-\varepsilon'' bC})$$

For a concentration of 1.0×10^{-4} M the absorbance when $\varepsilon' = \varepsilon'' = 1000 \text{ cm}^{-1} \text{ M}^{-1}$ is

$$A = 0.301 - \log\left(\begin{matrix} 10^{-(1000 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.0\times10^{-4} \text{M})} + \\ 10^{-(1000 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.0\times10^{-4} \text{ M})} \end{matrix}\right) = 0.100$$

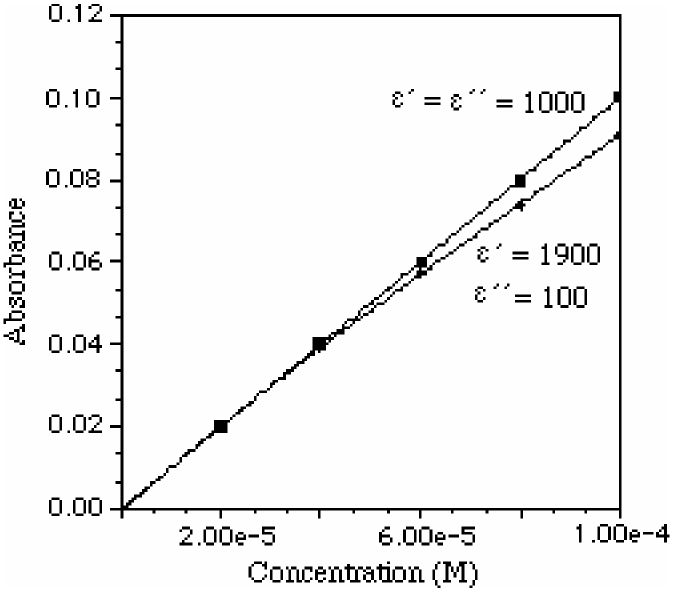
and, if $\varepsilon' = 1900$ and $\varepsilon'' = 100$ the absorbance is

$$A = 0.301 - \log\left(\begin{matrix} 10^{-(1900 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.0\times10^{-4} \text{M})} + \\ 10^{-(100 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.0\times10^{-4} \text{ M})} \end{matrix}\right) = 0.091$$

Results for several concentrations are summarized in the following table and calibration curves.

Concentration (M)	Absorbance for $\varepsilon' = \varepsilon'' = 1000 \text{ cm}^{-1} \text{ M}^{-1}$	Absorbance for $\varepsilon' = 1900 \text{ cm}^{-1} \text{ M}^{-1}$ and $\varepsilon'' = 100 \text{ cm}^{-1} \text{ M}^{-1}$
2.0×10^{-5}	0.020	0.020
4.0×10^{-5}	0.040	0.039

6.0×10^{-5}	0.060	0.057
8.0×10^{-5}	0.080	0.074
1.0×10^{-4}	0.100	0.091



Note that a straight-line is observed when ε′ and ε′′ are identical and that a deviation from Beer's law is found when the values for ε′ and ε′′ are not the same.

8. The equation relating P_0, P_T, and A is

$$A = -\log\frac{P_T}{P_0}$$

Letting $P_0 = 100$ and solving for P_T gives

$$P_T = 100 \times 10^{-A}$$

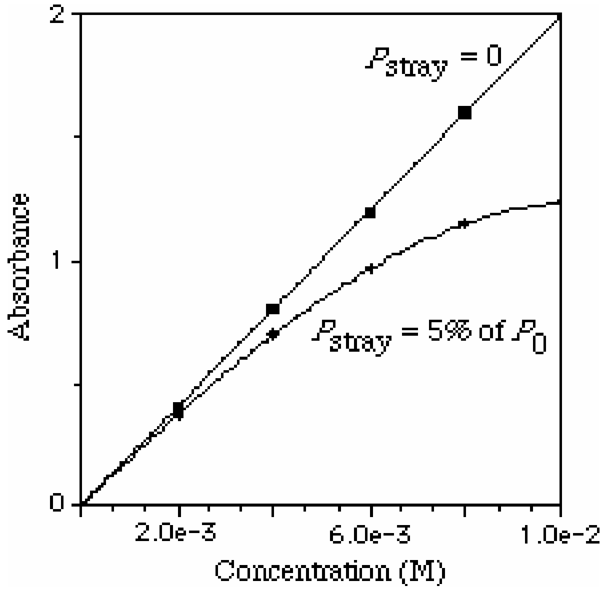
For example, when the absorbance is 0.40 (a concentration of 0.002 M), P_T is 39.8 in the absence of stray light ($P_{stray} = 0$). When stray light is present at 5% of P_0 ($P_{stray} = 5$), the absorbance is

$$A = \log\frac{P_0 + P_{stray}}{P_T + P_{stray}} = \log\frac{100 + 5}{39.8 + 5} = 0.37$$

Results for all samples are summarized in the following table and calibration curves.

Concentration (M)	Absorbance when $P_{stray} = 0$	Absorbance when $P_{stray} = 5$

0.000	0.00	0.00
0.002	0.40	0.37
0.004	0.80	0.70
0.006	1.20	0.97
0.008	1.60	1.15
0.010	2.00	1.24



Note that there is substantial curvature when P_{stray} is 5% of P_0.

11. Assuming a sample that is 50% w/w Fe we find that the concentration of iron in the prepared solution is

$$\frac{0.5 \text{ g sample} \times \dfrac{50 \text{ g Fe}}{100 \text{ g sample}} \times \dfrac{1000 \text{ mg}}{\text{g}}}{1 \text{ L}} = 250 \text{ ppm Fe}$$

Diluting a 5 mL portion of this solution in each of the available volumetric flasks gives solutions with the following concentrations of Fe

V_{flask}	ppm Fe	V_{flask}	ppm Fe
10	125	250	5
25	50	500	2.5
50	25	1000	1.25
100	12.5		

To avoid extrapolating the calibration curve beyond 20 ppm Fe (the highest concentration standard), using a 10-mL, 25-mL, or 50-mL volumetric flask is inadvisable. The best choice is the 100-mL volumetric flask because the concentration of Fe (12.5 ppm) falls near the middle of the calibration curve.

12. (a) A colored cola would contribute to the measured absorbance and interfere with the analysis. A suitable blank would be difficult to prepare without knowing the cola's composition.

(b) One approach would be to include a step in which either the PO_4^{3-} or the colored constituents is extracted from the cola sample.

(c) The presence of gas bubbles in the optical path distorts the pathlength through the sample leading to a determinate error.

(d) Dilute 2 mL of the ascorbic acid reducing solution to volume in a 5-mL volumetric flask.

(e) Substituting the sample's absorbance into the equation for the calibration curve gives the concentration of P_2O_5 as 0.813 ppm, as analyzed. The concentration of P, therefore, is

$$\frac{0.813 \text{ mg } P_2O_5}{\text{L}} \times \frac{61.95 \text{ mg P}}{141.94 \text{ mg } P_2O_5} = 0.355 \text{ ppm P}$$

Accounting for dilution, we find that the ppm P in the original sample is

$$0.355 \text{ ppm P} \times \frac{5.00 \text{ mL}}{0.250 \text{ mL}} \times \frac{50.00 \text{ mL}}{2.50 \text{ mL}} = 142 \text{ ppm P}$$

13. (a) The concentration of Cu^{2+} is found by making appropriate substitutions into Beer's law

$$0.338 = (95.2 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Cu}} \text{ or } C_{\text{Cu}} = 3.55 \times 10^{-3} \text{ M}$$

(b) For a binary mixture the following two equations must be solved simultaneously

$$0.453 = (2.11 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Co}} + (95.2 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Cu}}$$

$$0.107 = (15.8 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Co}} + (2.32 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Cu}}$$

Multiplying the second equation by 2.11/15.8 gives the two equations as

$$0.453 = (2.11 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Co}} + (95.2 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Cu}}$$

$$0.0143 = (2.11 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Co}} + (0.310 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})C_{\text{Cu}}$$

Subtracting the second equation from the first and solving for C_{Cu} gives

$$0.4387 = 94.89C_{\mathrm{Cu}} \text{ or } C_{\mathrm{Cu}} = 4.62\times 10^{-3}\ \mathrm{M}$$

The concentration of Co^{2+}, therefore, is

$$0.453 = (2.11\ \mathrm{cm^{-1}\ M^{-1}})(1.00\ \mathrm{cm})C_{\mathrm{Co}} + (95.2\ \mathrm{cm^{-1}\ M^{-1}})(1.00\ \mathrm{cm})(4.62\times 10^{-3}\ \mathrm{M})$$

$$C_{\mathrm{Co}} = 6.24\times 10^{-3}\ \mathrm{M}$$

(c) For a ternary mixture we must solve the following three simultaneous equations. In writing these equations note that the term εb has been multiplied out for simplicity.

$$0.423 = (2.11\ \mathrm{M^{-1}})C_{\mathrm{Co}} + (95.2\ \mathrm{M^{-1}})C_{\mathrm{Cu}} + (3.03\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

$$0.184 = (15.8\ \mathrm{M^{-1}})C_{\mathrm{Co}} + (2.32\ \mathrm{M^{-1}})C_{\mathrm{Cu}} + (1.79\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

$$0.291 = (3.11\ \mathrm{M^{-1}})C_{\mathrm{Co}} + (7.73\ \mathrm{M^{-1}})C_{\mathrm{Cu}} + (13.5\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

Multiplying the first equation by (15.8/2.11) and subtracting from the second equation gives

$$-2.9835 = (-710.55\ \mathrm{M^{-1}})C_{\mathrm{Cu}} - (20.899\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

Multiplying the third equation by (15.8/3.11) and subtracting from the second equation gives

$$-1.2944 = (-36.951\ \mathrm{M^{-1}})C_{\mathrm{Cu}} - (66.795\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

These two equations

$$-2.9835 = (-710.55\ \mathrm{M^{-1}})C_{\mathrm{Cu}} - (20.899\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

$$-1.2944 = (-36.951\ \mathrm{M^{-1}})C_{\mathrm{Cu}} - (66.795\ \mathrm{M^{-1}})C_{\mathrm{Ni}}$$

leave us with only two unknowns. Multiplying the second of these equations by (710.55/36.951) and subtracting from the first of these equations leaves us with

$$21.907 = (1263.54\ \mathrm{M^{-1}})C_{\mathrm{Ni}} \text{ or } C_{\mathrm{Ni}} = 1.734\times 10^{-2}\ \mathrm{M} \approx 1.73\times 10^{-2}\ \mathrm{M}$$

Substituting back we find the concentration of Cu to be

$$-1.2944 = (-36.951\ \mathrm{M^{-1}})C_{\mathrm{Cu}} - (66.795\ \mathrm{M^{-1}})(1.734\times 10^{-2}\ \mathrm{M})$$

$$C_{\mathrm{Cu}} = 3.685 \times 10^{-3}\ \mathrm{M} \approx 3.69 \times 10^{-3}\ \mathrm{M}$$

Substituting these concentrations back we find the concentration of Co to be

$$0.291 = (3.11\ \mathrm{M}^{-1})C_{\mathrm{Co}} + (7.73\ \mathrm{M}^{-1})(3.685 \times 10^{-3}\ \mathrm{M}) + (13.5\ \mathrm{M}^{-1})(1.734 \times 10^{-2}\ \mathrm{M})$$

$$C_{\mathrm{Co}} = 9.140 \times 10^{-3}\ \mathrm{M} \approx 9.14 \times 10^{-3}\ \mathrm{M}$$

14. For the standard we have

$$A = 0.424 = abC_{\mathrm{phenol}} = a(1.00\ \mathrm{cm})(4.00\ \mathrm{ppm})$$

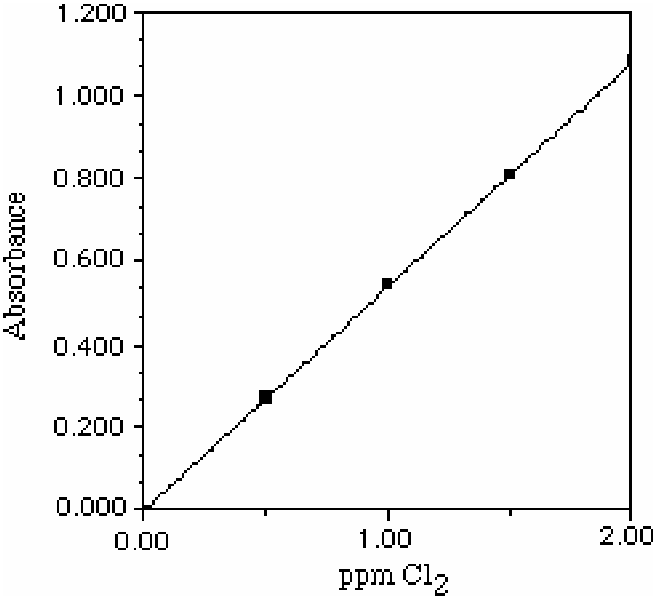
where a is the absorptivity. Solving for a gives its value as 0.106 $\mathrm{cm}^{-1}\ \mathrm{ppm}^{-1}$. Using the absorptivity we find that the concentration of phenol in the sample is

$$0.394 = (0.106\ \mathrm{cm}^{-1}\ \mathrm{ppm}^{-1})(1.00\ \mathrm{cm})C_{\mathrm{phenol}}$$

$$C_{\mathrm{phenol}} = 3.72\ \mathrm{ppm}$$

Because the sample was diluted in half (50 mL to 100 mL), the concentration of phenol in the sample is 7.44 ppm.

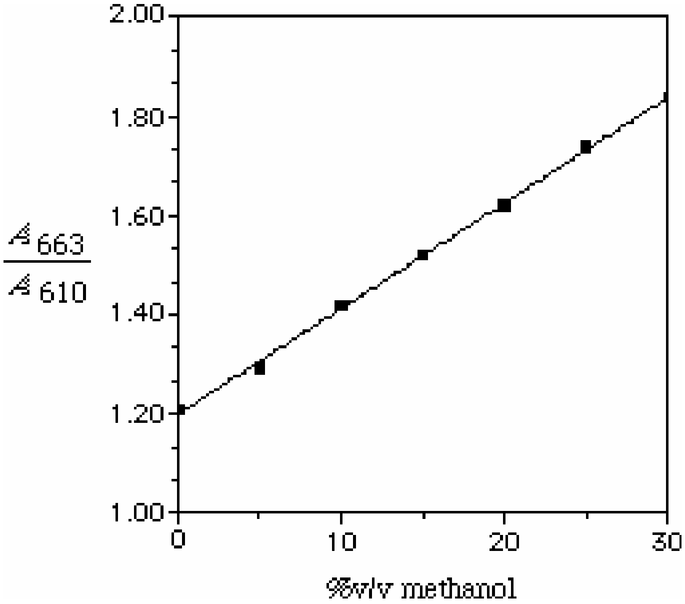
16. The calibration curve and linear regression calibration equation are shown here.



$$A = -2.0 \times 10^{-4} + (0.5422)(\mathrm{ppm\ Cl_2})$$

Substituting the sample's absorbance gives the concentration of Cl_2 in the sample as 0.209 ppm.

17. The calibration curve and linear regression calibration equation are shown here.



$$\frac{A_{663}}{A_{610}} = 1.200 + (2.136 \times 10^{-2})C_{\text{methanol}}$$

Substituting the sample's absorbance gives C_{methanol} as 10.6% v/v.

19. The concentration of aspirin in the prepared sample is determined using Beer's law and the absorbance at 277 nm

$$0.600 = (0.00683 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{aspirin}} \text{ or } C_{\text{aspirin}} = 87.98 \text{ ppm}$$

To find the mg of aspirin in the analgesic tablet we account for the sample preparation; thus

$$87.98 \text{ ppm} \times \frac{100.0 \text{ mL}}{20.00 \text{ mL}} \times 0.5000 \text{ L} = 220 \text{ mg aspirin}$$

To find the concentrations of caffeine, C_{caf}, and phenacetin, C_{phen}, we solve the following pair of simultaneous equations

$$0.466 = (0.0131 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{caf}} + (0.0702 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{phen}}$$

$$0.164 = (0.0485 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{caf}} + (0.0159 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{phen}}$$

Multiplying the second equation by (0.0131/0.0485) and subtracting from the first equation gives

$$0.4217 = 0.06591 \times C_{\text{phen}}$$

$$C_{\text{phen}} = 6.398 \text{ ppm} \approx 6.40 \text{ ppm phenacetin}$$

Substituting this concentration back into the equation for the absorbance at 250 nm gives

$$0.466 = (0.0131 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})C_{\text{caf}} + (0.0702 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})(6.40 \text{ ppm})$$

$$C_{\text{caf}} = 1.287 \text{ ppm} \approx 1.29 \text{ ppm caffeine}$$

The mg of phenacetin and caffeine in the tablets are

$$6.40 \text{ ppm} \times \frac{200.0 \text{ mL}}{2.00 \text{ mL}} \times 0.2500 \text{ L} = 160 \text{ mg phenacetin}$$

$$1.29 \text{ ppm} \times \frac{200.0 \text{ mL}}{2.00 \text{ mL}} \times 0.2500 \text{ L} = 32 \text{ mg caffeine}$$

20. The concentration of SO_2 in the standard solution is

$$C_{SO_2} = 15.00 \text{ ppm} \times \frac{1.00 \text{ mL}}{25.00 \text{ mL}} = 0.600 \text{ ppm } SO_2$$

Substituting this concentration into Beer's law gives the absorptivity of SO_2 as

$$0.181 = a(1.00 \text{ cm})(0.600 \text{ ppm } SO_2)$$

$$+6 = 0.302 \text{ cm}^{-1} \text{ ppm}^{-1}$$

Now we can solve for the ppm SO_2 in the sample

$$0.485 = (0.302 \text{ cm}^{-1} \text{ ppm}^{-1})(1.00 \text{ cm})(\text{ppm } SO_2)$$

$$\text{ppm } SO_2 = 1.61 \text{ ppm}$$

This, of course, is the concentration of SO_2 in the solution. To find the ppm SO_2 in the air we must determine the micrograms of SO_2 in the air sample and the grams of air collected; thus

$$\frac{1.61\text{ mg SO}_2}{\text{L}}\times\frac{1000\ \mu\text{g}}{\text{mg}}\times 0.02500\text{ L} = 40.2\ \mu\text{g SO}_2$$

$$\frac{1.6\text{ L air}}{\text{min}}\times 75\text{ min}\times\frac{1.18\text{ g air}}{\text{L}} = 142\text{ L}$$

$$\frac{40.2\ \mu\text{g SO}_2}{142\text{ L}} = 0.28\text{ ppm SO}_2$$

32. (a) The sample's absorbance is

$$A = (1.0\times 10^{4}\text{ cm}^{-1}\text{ M}^{-1})(1.00\text{ cm})(2.0\times 10^{-4}) = 2.0$$

Converting the absorbance to transmittance gives T = 0.01. Substituting into the equation for the relative uncertainty in concentration, we find that

$$\frac{s_\text{C}}{C} = \frac{0.434 s_\text{T}}{T\log T} = \frac{(0.434)(\pm 0.002)}{(0.01)\log(0.01)} = \pm 0.043\text{ or }4\%$$

(b) Because the blank is 1.0×10^{-4} M in analyte the apparent concentration of analyte in the sample is

$$2.0\times 10^{-4}\text{ M} - 1.0\times 10^{-4}\text{ M} = 1.0\times 10^{-4}\text{ M}$$

The absorbance, transmittance, relative uncertainty, therefore, are

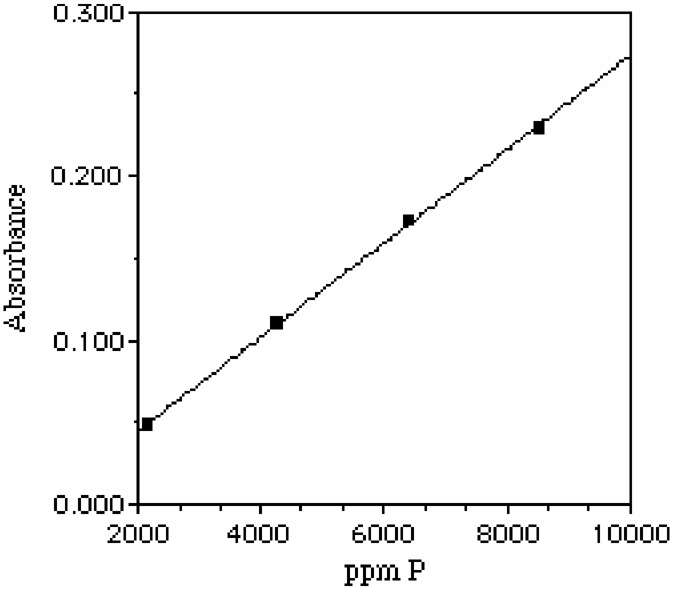
$$A = (1.0\times 10^{4}\text{ cm}^{-1}\text{ M}^{-1})(1.00\text{ cm})(1.0\times 10^{-4}) = 1.0$$

$$1.0 = -\log T$$

$$T = 0.1$$

$$\frac{s_\text{C}}{C} = \frac{0.434 s_\text{T}}{T\log T} = \frac{(0.434)(\pm 0.002)}{(0.1)\log(0.1)} = \pm 0.009\text{ or }0.9\%$$

33. The calibration curve and its equation are shown here.



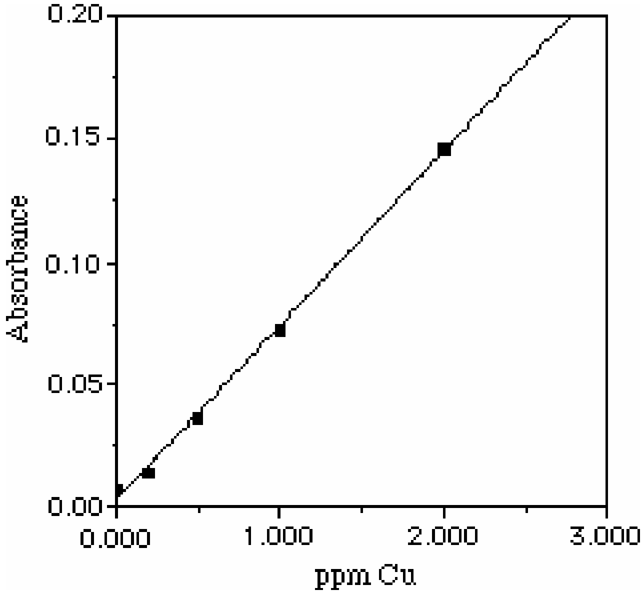
$$A = -1.186\times 10^{-2} + (2.854\times 10^{-5}\ \text{ppm}^{-1})(\text{ppm P})$$

Substituting the absorbance for the sample gives the concentration of P as 5146 ppm; thus

$$\frac{5146\ \text{mg P}}{\text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times 0.1000\ \text{L} \times \frac{141.97\ \text{g Na}_2\text{HPO}_4}{30.974\ \text{g P}} = 2.359\ \text{g Na}_2\text{HPO}_4$$

$$\frac{2.359\ \text{g Na}_2\text{HPO}_4}{2.469\ \text{g sample}} \times 100 = 95.5\%\ \text{pure}$$

34. (a) *A* calibration curve for Cu is shown here.



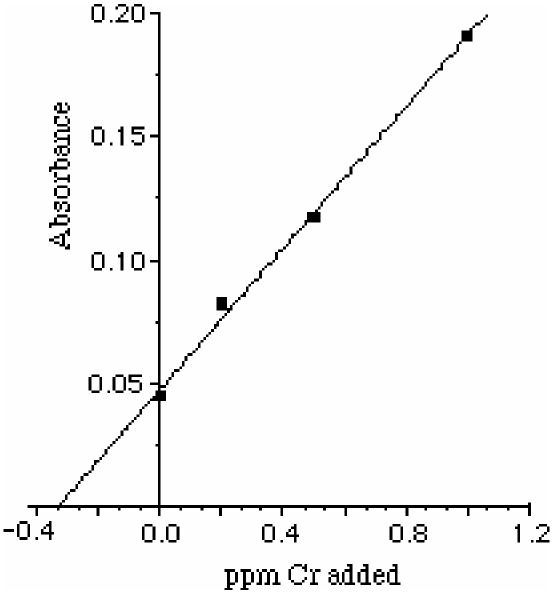
Linear regression gives an equation for the calibration curve of

$$A = 2.429 \times 10^{-3} + (7.104 \times 10^{-2}\ \text{ppm}^{-1})(\text{ppm Cu})$$

Substituting the absorbance for the sample gives the concentration of Cu as 0.346 ppm. Accounting for the sample's preparation gives the concentration of Cu in the original sample as

$$0.346\ \text{ppm Cu} \times \frac{500.0\ \text{mL}}{200.0\ \text{mL}} = 0.865\ \text{ppm Cu}$$

(b) After correcting for the blank's absorbance, we obtain the standard additions calibration curve shown here.



Linear regression gives the equation for the calibration curve as

$$A = 4.750 \times 10^{-2} + (0.1435\ \text{ppm}^{-1})(\text{ppm Cr added})$$

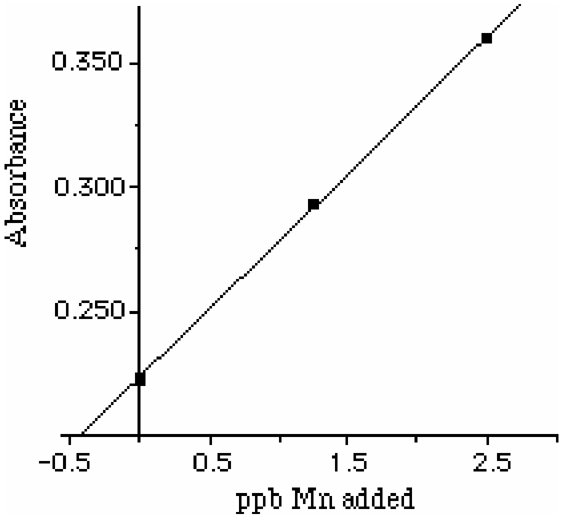
Setting the absorbance to zero and solving gives

$$\text{ppm Cr added} = -0.331\ \text{ppm}$$

The concentration of Cr in the sample as analyzed, therefore, is 0.331 ppm. After accounting for the sample's preparation, we find that the concentration of Cr in the original sample is

$$0.331\ \text{ppm Cu} \times \frac{50.00\ \text{mL}}{200.0\ \text{mL}} = 0.0828\ \text{ppm Cr}$$

35. The concentration of added Mn^{2+} for the three standard additions is 0.00 ppb, 1.25 ppb, and 2.50 ppb. The resulting calibration curve is shown on the next page.



Linear regression gives the equation for the calibration curve as

$$A = 0.224 + (0.0552 \text{ ppb}^{-1})(\text{ppb Mn added})$$

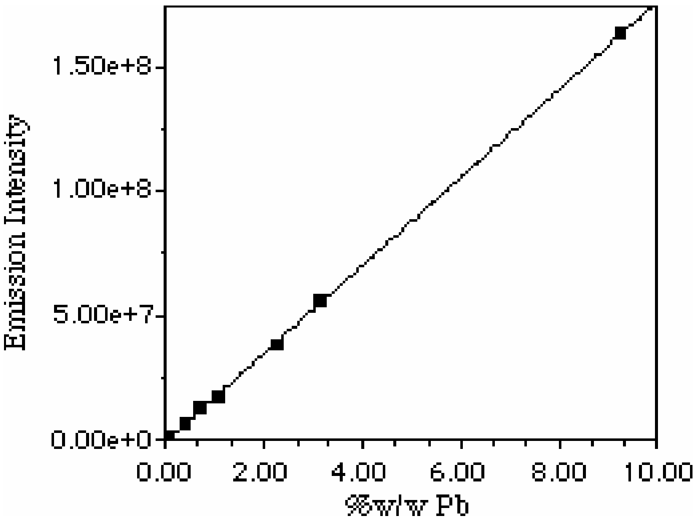
Setting the absorbance to zero and solving gives

$$\text{ppm Mn added} = -4.06 \text{ ppb}$$

The concentration of Mn^{2+} in the sample as analyzed, therefore, is 4.06 ppb. Accounting for the sample's preparation, we find that the concentration of Mn^{2+} in sea water is

$$\frac{4.06 \text{ ppb Mn}^{2+} \times \dfrac{5.0\ \mu\text{L}}{2.5\ \mu\text{L}} \times \dfrac{100.0 \text{ mL}}{1.000 \text{ mL}} \times 0.05000 \text{ L}}{1 \text{ L}} = 40.6 \text{ ppb Mn}^{2+}$$

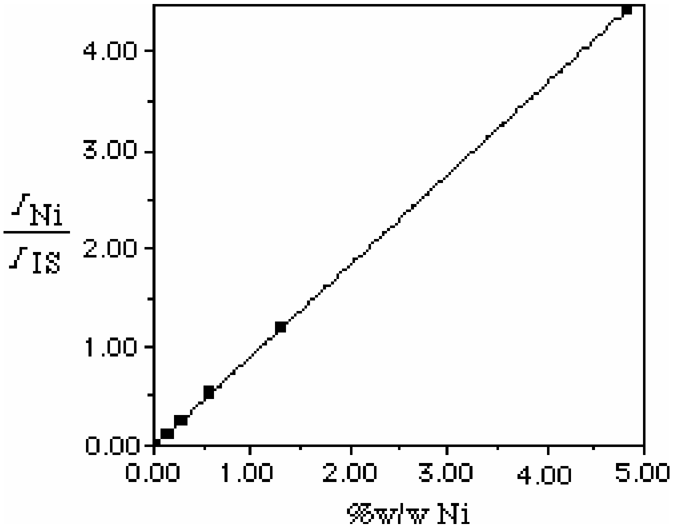
37. For Pb the calibration curve and equation are



$$I = -1.028 \times 10^5 + (1.773 \times 10^7)(\%\text{w/w Pb})$$

Substituting the sample's emission intensity gives the concentration of Pb as 0.011% w/w.

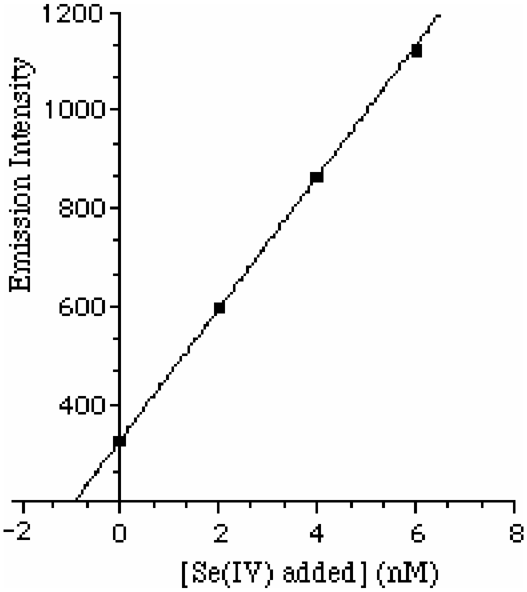
(b) For Ni the internal standards calibration curve and equation are



$$\frac{I_{\text{Ni}}}{I_{\text{IS}}} = -5.926 \times 10^{-3} + (0.9231)(\%w/w\ \text{Ni})$$

Substituting the sample's emission intensity, we find that the concentration of Ni is 7.61×10^{-3} %w/w.

42. The calibration curve and equation for this standard addition are



$$I = 326.5 + 133.25[\text{Se(IV) added}]$$

Setting the absorbance to zero and solving gives

$$[\text{Se(IV) added}] = -2.45 \text{ nM}$$

The concentration of Se(IV) in the sample as analyzed, therefore, is 2.45 nM.

43. Substituting the sample's emission intensity into the calibration curve's equation gives

$$44.70 = -4.66 + (9907.63)C_A$$

$$C_A = 4.98 \times 10^{-3} \text{ g fibrinogen/L}$$

Accounting for the sample's preparation gives the concentration of fibrinogen in the plasma as

$$(4.98 \times 10^{-3}\ \text{g/L}) \times \frac{250.0\ \text{mL}}{1.000\ \text{mL}} \times \frac{10.00\ \text{mL}}{9.00\ \text{mL plasma}} = 1.38\ \text{g fibrinogen/L}$$