Chapter 7

1. (a) The overall variance, which is the sum of the variance due to obtaining the sample and the variance due to the method

$$s_{overall}^2 = s_{sampling}^2 + s_{method}^2$$

is the variance in the results for the four replicate analyses of the sample, or 0.9144. The variance due to the method is the variance in the results for the four replicate analyses of the standard, or 0.0330. The variance due to sampling, therefore, is

$$s_{\text{sampling}}^2 = s_{\text{overall}}^2 - s_{\text{method}}^2 = 0.9144 - 0.0330 = 0.8814$$

(b) The percentage of the overall variance due to sampling is

$$\frac{s_{\text{sampling}}^2}{s_{\text{overall}}^2} \times 100 = \frac{0.8814}{0.9144} \times 100 = 96.4\%$$

(c) To decrease the variance due to sampling we need to increase the number of particles in each sample. We can accomplish this by taking a larger sample for analysis, by decreasing the average particle size through additional pulverizing of the sample, or both.

2. Our random number table is a list of five digit numbers. As our barrels are numbered 1–100, we will use an entry's last two digits to identify a barrel to sample, with *xyz*01 representing the first barrel and *xyz*00 representing the hundredth barrel. The twelfth entry in the random number table is 91791; thus our first sample is from Barrel 91. Continuing with every third entry in the random number table, the samples are drawn from barrels

91 54 85 38 49 62 77 66 95 52

3. The Nyquist sampling theorem states that we must collect at least two samples per period. To monitor a daily cycle we need to collect a sample at least once every 12 hr, although collecting a sample every 6-8 hr is better. To monitor a yearly cycle we need to collect a sample at least once every six months, although every 3-4 months is better.

4. A plot of pH as a function of time, which appears in Figure SM7.1, shows a periodic cycle with a period of approximately 8 hr. At a minimum, we should collect a sample every 4 hr, although collecting a sample very 2-3 hr is better.

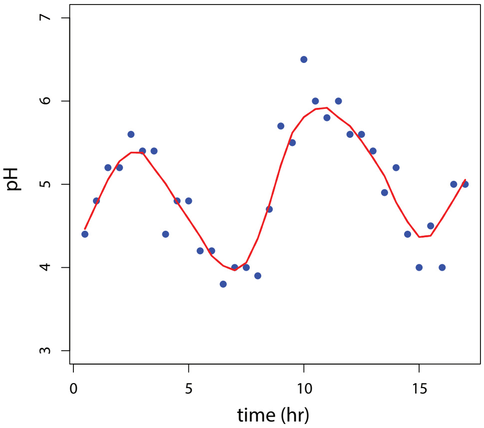

Figure SM7.1 The change in pH as a function of time for an industrial waste stream. The **blue** points are the data included with Problem 7.4 and the **red** line is a lowess fit, which uses a locally weighted polynomial linear regression to model the data; locally weighted means that the predicted value of *y* for each value of *x* is based on a subset of the data consisting of points adjacent to *x*.

5. (a) Several of the possible sampling plans are reasonable options; others are less reasonable. A random sampling plan, for example, is a poor choice because it does not take advantage of the expected periodic fluctuations in atmospheric ozone levels due to changes in traffic patterns. The best choice is systematic/judgmental. The systematic portion of the sampling plan allows us to acquire fewer samples by taking into account the daily fluctuations in traffic patterns. The

judgmental portion of the sampling plan allows us to focus sampling on key locations, such as busy intersections, and to use areas with low levels of traffic, such as city parks, to provide background readings.

(b) For this study we will collect grab samples as we are interested in the concentration of ozone at a specific location and at a specific time.

(c) If our interest is in an average daily concentration of ozone, then we are better served by collecting a single composite sample at each location as this decreases the number of individual samples that we need to analyze.

6. (a) A homogeneous population is uniform in time and space. A heterogeneous population is not uniform and shows some variation in time, in space, or in both time and space.

   (b) No. To show that a sample is homogeneous or heterogeneous, we must have information about the variability between samples, which requires that we analyze more than one sample.

7. Equation 7.4 provides a relationship between the relative sampling variance, $(s_{samp})^2_{rel}$, the probability, p, of obtaining a particular type of particle, and the number, n, of particles sampled.

$$n = \frac{1-p}{p} \times \frac{1}{(s_{samp})^2_{rel}}$$

Equation 7.5 is defined in terms of R^2, where R is the percent relative standard deviation

$$R^2 = (s_{samp})^2_{rel} \times (10^2)^2 = (s_{samp})^2_{rel} \times 10^4$$

Solving this equation for $(s_{samp})^2_{rel}$

$$(s_{samp})^2_{rel} = \frac{R^2}{10^4}$$

and substituting back into equation 7.4, and rearranging gives

$$nR^2 = \frac{1-p}{p} \times 10^4$$

The mass, m, of a single particle is the product of its density, d, and its volume, V, which, for a sphere is $\frac{4}{3}\pi r^3$ where r is the radius; thus, the mass of n particles is

$$m = \frac{4}{3} n d \pi r^3$$

Solving for n, substituting back, and rearranging gives

$$mR^2 = \frac{4}{3} d\pi r^3 \times \frac{1-p}{p} \times 10^4$$

For any given sample, each of the three terms on the right side of this equation is a constant, which leaves us with equation 7.5

$$mR^2 = K_s$$

where K_s is the sampling constant.

8. (a) From equation 7.5, the expected percent relative standard deviation for sampling, R, of a homogeneous material is

$$R = \sqrt{\frac{K_s}{m}} = \sqrt{\frac{35\text{ g}}{1.0\text{ g}}} = 5.9\%$$

(b) To find the number of samples, n_{samp}, we use equation 7.7

$$n_{samp} = \frac{t^2 s_{samp}^2}{e^2}$$

where s_{samp} is equivalent to R, and e is the desired sampling error of 5%. We begin using $t(0.05,\infty)$ for an infinite number of degrees of freedom; thus

$$n_{samp} = \frac{(1.960)^2(5.9)^2}{(5.0)^2} = 5.3 \approx 5$$

This answer is not correct because we used $t(0.05,\infty)$ of 1.960 instead of the value for $5 - 1 = 4$ degrees of freedom. Using $t(0.05,4)$ of 2.776 and recalculating gives

$$n_{samp} = \frac{(2.776)^2(5.9)^2}{(5.0)^2} = 10.7 \approx 11$$

This answer is not correct because we used $t(0.05,4)$ of 2.776 instead of the value for $11 - 1 = 10$ degrees of freedom. Using $t(0.05,10)$ of 2.228 and recalculating gives

$$n_{samp} = \frac{(2.228)^2(5.9)^2}{(5.0)^2} = 6.9 \approx 7$$

This answer is not correct because we used $t(0.05,10)$ of 2.228 instead of the value for $7 - 1 = 6$ degrees of freedom. Using $t(0.05,6)$ of 2.447 and recalculating gives

$$n_{samp} = \frac{(2.447)^2(5.9)^2}{(5.0)^2} = 8.3 \approx 8$$

This answer is not correct because we used $t(0.05,6)$ of 2.447 instead of the value for $8 - 1 = 7$ degrees of freedom. Using $t(0.05,7)$ of 2.365 and recalculating gives

$$n_{samp} = \frac{(2.365)^2(5.9)^2}{(5.0)^2} = 7.8 \approx 8$$

This time there is agreement between the value of t and the degrees of freedom for n_{samp}; thus, we need to collect eight samples to achieve the desired maximum sample error of ±5%.

9. The mean and the standard deviation for the 12 samples are 0.264 %w/w K_2O and 0.0423 %w/w K_2O, respectively. The percent relative standard deviation, R, is

$$R = \frac{s}{\overline{X}} = \frac{0.0423}{0.264} \times 100 = 16.0$$

For a nominal mass of 0.10 g, this gives a sampling constant, K_s, of

$$K_s = mR^2 = (0.10 \text{ g})(16.0)^2 = 25.6 \text{ g}$$

To lower the relative standard deviation to 2%, we need to increase each sample's nominal mass to

$$m = \frac{K_s}{R^2} = \frac{25.6 \text{ g}}{2.0^2} = 6.4 \text{ g}$$

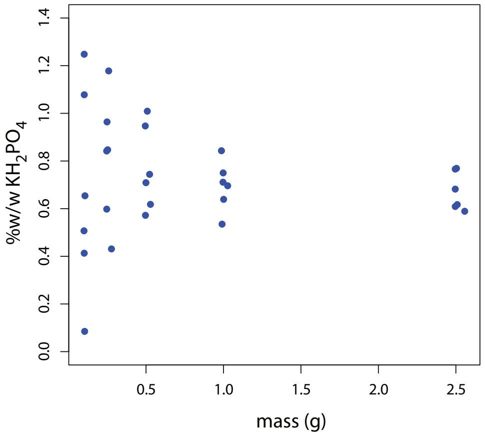

Figure SM7.2 The data for Problem 7.10 is shown here as a plot of %w/w K_2O as a function of the mass of sample taken. Note that the variability in the individual results decreases as the mass of sample taken increases.

10. (a) Figure SM7.2 shows the plot of %w/w K_2O as a function of the mass of sample taken. Although the gross sample presumably is homogeneous, the spread in results for individual samples collected at different nominal masses show that indeterminate errors in the sampling process have a greater affect on the variability in individual results for samples of smaller nominal mass.

(b) The following table organizes results by nominal mass; the experimental percent relative standard deviations, R_{exp}, are calculated using the mean and the standard deviation for each nominal mass, and the theoretical percent relative standard deviations, R_{theo}, are calculate using the mean for each nominal mass and the sampling constant.

nominal mass (g)	mean mass (g)	$C_{KH_2PO_4}$ (%w/w)	s (g)	R_{exp}	R_{theo}
0.10	0.1020	0.664	0.432	65.1	58.6
0.25	0.2548	0.810	0.265	32.7	37.1
0.50	0.5086	0.766	0.176	23.0	26.2
1.00	1.0002	0.696	0.104	14.9	18.7
2.50	2.5097	0.672	0.080	11.9	11.8

The results here are consistent with our observation from part (a) as the percent relative standard deviation, R_{exp}, is much larger for samples of smaller nominal mass.

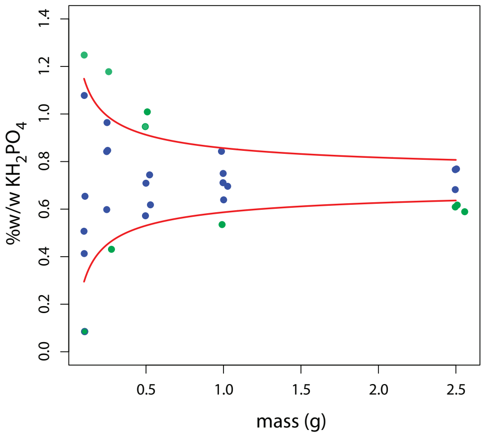

Figure SM7.3 The individual samples from Problem 7.10 are shown here as a series of **blue** and **green** points. The **red** curves show the range of expected results based on indeterminate sampling error defined here as $(\overline{X})_{global} \pm 1s$ where $(\overline{X})_{global}$ is the global mean of 0.722% w/w KH_2PO_4 for all 30 samples and s is the standard deviation for sampling based on a sampling constant of 350. The 20 **blue** points fall within this range and the 10 **green** points lie outside this range.

(c) The global mean, $(\overline{X})_{global}$, is 0.722%w/w KH_2PO_4. To calculate the theoretical standard deviation, s, for any mass, m, we use equation 7.5, where K_s is 350, and the definition of the percent relative standard deviation

$$R = \frac{s}{\overline{X}} \times 100$$

For example, taking m = 0.1000 g, we have

$$s = \sqrt{\frac{(350)(0.722)^2}{(0.1000)(10^4)}} = 0.427$$

Figure SM7.3 shows the same data as in Figure SM7.2 with two lines representing $(\overline{X})_{global} \pm 1s$ superimposed on the data. Of the 30 data points, 20 or 67% lie between the two curves. If the sampling error is normally distributed, we expect that approximately 68% of the samples will fall within $\pm 1s$ of the global mean. It appears, therefore, that the sample is homogeneous and that the variability between samples of different size is explained by indeterminate sampling error.

11. Answers to this problem, of course, will vary. Here is some data I collected using a 47.9 g bag of plain M&Ms, with each result reporting the number of red M&Ms in a sample of five M&Ms:

0	0	3	2	0	0	2	1	1	1
0	1	0	0	1	2	2	1	2	1

The mean and the standard deviation for this set of 20 results is 1.0 and 0.92, respectively, which correspond to percentages of 20% and of 18.4%, respectively.

After gathering this data, I counted the number of each color of M&Ms in the bag, obtaining the following results:

blue: 17 red: 9 yellow: 9
orange: 9 brown: 5 green: 6

for a total of 55 M&Ms. The percentage of red M&Ms in the bag is 16.4%, or a probability, p, of 0.164

Assuming binomial sampling statistics, if we draw five M&Ms from a population for which the probability of drawing a red M&M is 0.164, then we expect the average sample to contain

$$n_{red} = np_{red} = 5 \times 0.164 = 0.82$$

red M&Ms with a standard deviation of

$$s_{red} = \sqrt{np_{red}(1 - p_{red})} = \sqrt{5 \times 0.164 \times 0.836} = 0.83$$

red M&Ms, both of which are similar to the experimental values of 1.0 red M&Ms and 0.92 red M&Ms, respectively. Expressing these as percentages, the predicted mean and standard deviation are 16.4% and 16.6%, respectively, which compare favorably to the experimental values of 20% and 18.4%, respectively.

12. For all three scenarios, we use equation 7.8

$$e = t\sqrt{\frac{s_{samp}^2}{n_{samp}} + \frac{s_{meth}^2}{n_{samp}n_{rep}}}$$

where s_{samp}^2 is the sampling variance and s_{meth}^2 is variance in the analysis; thus, for (a) we have

$$e = 2.306\sqrt{\frac{0.050}{9} + \frac{0.0025}{9 \times 1}} = 0.176$$

and for (b) we have

Scenarios (a) and (b) each have a total of 9 analyses; thus, we use $t(0.05,8)$ as there are eight degrees of freedom. For scenario (c) there are 10 analyses and we use $t(0.05,9)$.

$$e = 2.306\sqrt{\frac{0.050}{1} + \frac{0.0025}{1 \times 9}} = 0.517$$

and for (c) we have

$$e = 2.260\sqrt{\frac{0.050}{5} + \frac{0.0025}{5 \times 2}} = 0.229$$

13. Because the error for scenario (b) exceeds the limit of 0.30, we need consider only scenario (a) and scenario (c). If the cost of obtaining a sample is \$1 and the cost of analyzing the sample is \$10, then scenario (a) is the more cost effective

scenario (a): cost = $9 \times \$1 + 9 \times \$10 = \$99$

scenario (c): cost = $5 \times \$1 + 10 \times \$10 = \$105$

If the cost of obtaining a sample is \$10 and the cost of analyzing the sample is \$1, then scenario (c) is the more cost effective

scenario (a): cost = $9 \times \$10 + 9 \times \$1 = \$99$

scenario (c): cost = $5 \times \$10 + 10 \times \$1 = \$60$

See Chapter 4F.4 to review the basic details for a paired *t*-test.

14. The best way to evaluate these methods is to use a paired *t*-test. First, for each of the eight samples, we determine the mean for the microwave method, $(\overline{X})_{\text{MW}}$, and the mean for the standard method, $(\overline{X})_{\text{std}}$, and then the difference, *d*, between the means for each method; the results for all eight samples are tabulate below:

sample	$(\overline{X})_{\text{MW}}$	$(\overline{X})_{\text{std}}$	d
1	7.32	5.48	1.84
2	15.80	12.97	2.83
3	4.60	5.29	–0.69
4	9.04	6.77	2.27
5	7.16	6.00	1.16
6	6.80	5.84	0.96
7	9.90	14.30	–4.40
8	28.67	18.83	9.84

The mean difference for the eight samples, $\overline{d}$, is 1.73 and the standard deviation, s_d, is 3.99. For a paired *t*-test we use the following null hypothesis and alternative hypothesis

$$H_0\text{: } \overline{d} = 0 \qquad H_\text{A}\text{: } \overline{d} \neq 0$$

Calculating t_{exp}

$$t_{\text{exp}} = \frac{\overline{d}\sqrt{n}}{s_d} = \frac{(1.70)\sqrt{8}}{3.99} = 1.21$$

we find that it is less than the critical value of 2.365 for *t*(0.05,7); thus, there is no evidence to suggest that the difference between the methods is significant at $\alpha = 0.05$.

15. In anoxic sediments with relatively high concentrations of sulfide, S^{2-}, the speciation of Cu^{2+} is controlled by the formation of stable copper-sulfide phases, even at the very acidic pH levels obtained when using a strong acid, such as HNO_3, as a preservative. Adding H_2O_2 before adding HNO_3 oxidizes S^{2-} to SO_4^{2-}, which minimizes this problem.

16. (a) If the recovery for the interferent, R_I, is 1, then equation 7.19 for the error reduces to

$$E = R_A - 1 = 0.0630$$

and the apparent recovery for the analyte, R_A, is 1.063 or 106.3%.

(b) If the recovery for the analyte, R_A, is 1, then equation 7.19 for the error reduces to

$$E = \frac{K_{A,I}(C_I)_{\text{o}}}{(C_A)_{\text{o}}} \times R_I = \frac{(0.816)(1)}{5} \times R_I = 0.0630$$

and the apparent recovery for the interferent, R_I, is 0.386 or 38.6%.

17. (a) The recoveries for copper and for iron are

$$R_{\text{Co}} = \frac{275.9 \text{ mg}}{278.3 \text{ mg}} = 0.9914 \approx 0.991$$

$$R_{\text{Fe}} = \frac{3.6 \text{ mg}}{184.9 \text{ mg}} = 0.01947 \approx 0.019$$

(b) The separation factor, $S_{\text{Fe,Co}}$, in which iron is the interferent and cobalt is the analyte, is

$$S_{\text{Fe,Co}} = \frac{R_{\text{Fe}}}{R_{\text{Co}}} = \frac{0.01947}{0.9914} = 0.0196 \approx 0.020$$

(c) The selectivity of the method for the analyte, Co, relative to the interferent, Fe, is

$$K_{\text{Co,Fe}} = \frac{k_{\text{Fe}}}{k_{\text{Co}}} = \frac{0.699}{0.786} = 0.889$$

(d) If we make no attempt to separate the analyte and the interferent, then R_{Co} and R_{Fe} have values of 1; thus, the expected error in the analysis for Co is

$$E = (R_{\text{Co}} - 1) + \frac{K_{\text{Co,Fe}}(C_{\text{Fe}})_{\text{o}}}{(C_{\text{Co}})_{\text{o}}} \times R_{\text{Fe}} =$$

$$(1 - 1) + \frac{(0.889)(1)}{10.2} \times 1 = 0.0872$$

or an error of +8.72%.

(e) If we complete the separation, then the expected error in the analysis for Co is

$$E = (R_{\text{Co}} - 1) + \frac{K_{\text{Co,Fe}}(C_{\text{Fe}})_{\text{o}}}{(C_{\text{Co}})_{\text{o}}} \times R_{\text{Fe}} =$$

$$(0.991 - 1) + \frac{(0.889)(1)}{10.2} \times (0.019) = -0.0073$$

or an error of –0.73%.

(f) The error in this case is defined by

$$E = (R_{\text{Co}} - 1) + \frac{K_{\text{Co,Fe}}(C_{\text{Fe}})_{\text{o}}}{(C_{\text{Co}})_{\text{o}}} \times R_{\text{Fe}} =$$

$$(1 - 1) + \frac{(0.889)(1)}{10.2} \times R_{\text{Fe}} = 0.0005$$

Solving for R_{Fe} gives its value as 0.0057; thus, we cannot recover more than 0.57% of the Fe to achieve the desired error.

18. To determine the recoveries for Ca and for Mg, we begin with the following pair of equations

$$E = (R_{\text{Ca}} - 1) + \frac{(0.843)(0.5)}{1} \times R_{\text{Mg}} = -0.037$$

$$E = (R_{\text{Ca}} - 1) + \frac{(0.843)(2.0)}{1} \times R_{\text{Mg}} = +0.055$$

Subtracting the first equation from the second equation

$$1.2645 R_{\text{Mg}} = 0.092$$

and solving for R_{Mg} gives its value as 0.073; substituting back into either equation and solving for R_{Ca} gives its value as 0.932.

19. The relevant reactions are

$$\text{Al}^{3+}(aq) + \text{Y}^{4-}(aq) \rightleftharpoons \text{AlY}^{-}(aq)$$

$$\text{Al}^{3+}(aq) + 6\text{F}^{-}(aq) \rightleftharpoons \text{AlF}_6^{3-}(aq)$$

for which K_1 for AlY^- is 2.0×10^{16} and β_6 for AlF_6^{3-} is 6.3×10^{19}. Fluoride is an effective masking agent because it binds more strongly with Al^{3+} than does EDTA and, therefore, cannot be displaced by EDTA; thus, the reaction

$$\text{AlF}_6^{3-}(aq) + \text{Y}^{4-}(aq) \rightleftharpoons \text{AlY}^{-}(aq) + 6\text{F}^{-}(aq)$$

has an equilibrium constant of K_1/β_6, or 3.2×10^{-4}.

From Appendix 12, we have $\log K_1 = 6.11$, $\log K_2 = 5.01$, $\log K_3 = 3.88$, $\log K_4 = 3.00$, $\log K_5 = 1.4$, and $\log K_6 = 0.4$ for the complexes between Al^{3+} and F^-. Adding together these six values gives $\log \beta_6$ as 19.8 and β_6 as 6.3×10^{19}.

20. Cyanide, CN^-, is a weak base, which means at more acidic pH levels it converts to its conjugate weak acid form, HCN. For example, consider the equilibria in a solution of Ag(CN)_2^-

$$\text{Ag(CN)}_2^-(aq) \rightleftharpoons \text{Ag}^+(aq) + 2\text{CN}^-(aq)$$

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

Adding acid pushes the second reaction to the right, decreasing the concentration of CN^-; in turn, the decrease in the concentration of CN^- pushes the first reaction to the right, decreasing the extent of complexation.

21. There are several approaches that we can use; here is one. First, make the solution strongly basic by adding NaOH, precipitating tin as SnO_2, copper as $Cu(OH)_2$, and lead as $Pb(OH)_2$, leaving zinc in solution as $Zn(OH)_4^{2-}$. After isolating the precipitates by filtration, dissolve the $Cu(OH)_2$ and the $Pb(OH)_2$ using a solution of HNO_3, leaving behind solid SnO_2. Next, we make the solution of Cu^{2+} and of Pb^{2+} basic using a NH_4^+/NH_3 buffer, precipitating the lead as $Pb(OH)_2$ and leaving the copper behind as $Cu(NH_3)_6^{2+}$.

22. For n identical extractions, the amount of solute remaining in the aqueous phase after the last extraction, $(Q_{aq})_n$ is given by equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n$$

where V_{aq} is the volume of aqueous phase, V_{org} is the volume of organic extracting phase, and D is the distribution ratio. The extraction efficiency is $1 - (Q_{aq})_n$; thus, for (a) we have

$$(Q_{aq})_1 = \left(\frac{50.0}{(7.5)(50.0) + 50.0}\right)^1 = 0.118$$

or an extraction efficiency of 0.882 or 88.2%; for (b) we have

$$(Q_{aq})_2 = \left(\frac{50.0}{(7.5)(25.0) + 50.0}\right)^2 = 0.0443$$

or an extraction efficiency of 0.956 or 95.6%; for (c) we have

$$(Q_{aq})_4 = \left(\frac{50.0}{(7.5)(12.5) + 50.0}\right)^4 = 0.0146$$

or an extraction efficiency of 0.985 or 98.5%; for (d) we have

$$(Q_{aq})_5 = \left(\frac{50.0}{(7.5)(10.0) + 50.0}\right)^5 = 0.0102$$

or an extraction efficiency of 0.990 or 99.0%. As expected, we see a greater extraction efficiency when we divide the organic extracting phase into smaller portions and carry out more extractions.

23. To extract 99.9% of the solute we need an extraction efficiency of 0.999; in turn, this requires that $(Q_{aq})_n = 0.001$. Beginning with equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n$$

we solve for V_{org} by taking the n^{th} root of each side of the equation

$$\sqrt[n]{(Q_{aq})_n} = \frac{V_{aq}}{DV_{org} + V_{aq}}$$

multiplying through by $DV_{org} + V_{aq}$

$$DV_{org}\sqrt[n]{(Q_{aq})_n} + V_{aq}\sqrt[n]{(Q_{aq})_n} = V_{aq}$$

and then gathering terms

$$V_{org} = \frac{V_{aq} - V_{aq}\sqrt[n]{(Q_{aq})_n}}{D\sqrt[n]{(Q_{aq})_n}}$$

For (a) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times 0.001}{7.5 \times 0.001} = 6600 \text{ mL/extraction}$$

or a total volume of 6600 mL for one extraction; for (b) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt{0.001}}{7.5 \times \sqrt{0.001}} = 204 \text{ mL/extraction}$$

or a total volume of 408 mL for two extractions; for (c) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt[4]{0.001}}{7.5 \times \sqrt[4]{0.001}} = 30.8 \text{ mL/extraction}$$

or a total volume of 123.2 mL for four extractions; and for (d) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt[5]{0.001}}{7.5 \times \sqrt[5]{0.001}} = 19.9 \text{ mL/extraction}$$

or a total volume of 79.5 mL for five extractions. As expected, we use less total solvent when we use multiple extractions.

24. To extract 99% of the solute we need an extraction efficiency of 0.99; in turn, this requires that $(Q_{aq})_n = 0.01$. Beginning with equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n$$

we solve for D by taking the n^{th} root of each side of the equation

$$\sqrt[n]{(Q_{aq})_n} = \frac{V_{aq}}{DV_{org} + V_{aq}}$$

multiplying through by $DV_{org} + V_{aq}$

$$DV_{org}\sqrt[n]{(Q_{aq})_n} + V_{aq}\sqrt[n]{(Q_{aq})_n} = V_{aq}$$

and then gathering terms

$$D = \frac{V_{aq} - V_{aq}\sqrt[n]{(Q_{aq})_n}}{V_{org}\sqrt[n]{(Q_{aq})_n}}$$

For (a) we need a D of

$$D = \frac{50.0 - 50.0 \times 0.01}{50.0 \times 0.01} = 99.0$$

and for (b) we need a D of

$$D = \frac{50.0 - 50.0 \times \sqrt{0.01}}{25.0 \times \sqrt{0.01}} = 18.0$$

25. From equation 7.27, an extraction efficiency of 99.9%, requires that

$$Q_{aq} = 0.001 = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{D \times 50.0 + 50.0}$$

for a single extraction of 50.0 mL of sample using 50.0 mL of organic solvent. Solving gives the minimum value of D as 999. Because the analyte is a weak acid, the distribution ratio's value depends on the pH of the aqueous phase, with more acidic pH levels favoring a larger value for D. From equation 7.31, we know that

$$D = \frac{K_{\mathrm{D}}[\mathrm{H_3O}^+_{aq}]}{[\mathrm{H_3O}^+_{aq}] + K_{\mathrm{a}}}$$

$$999 = \frac{(1200)[\mathrm{H_3O}^+_{aq}]}{[\mathrm{H_3O}^+_{aq}] + (1.00 \times 10^{-5})}$$

$$999[\mathrm{H_3O}^+_{aq}] + 9.99 \times 10^{-3} = 1200[\mathrm{H_3O}^+_{aq}]$$

$$9.99 \times 10^{-3} = 201[\mathrm{H_3O}^+_{aq}]$$

gives $[\mathrm{H_3O}^+_{aq}]$ as 4.97×10^{-5}, or a maximum pH of 4.30.

26. For a pH of 7.00 ($[\mathrm{H_3O}^+_{aq}] = 1.00 \times 10^{-7}$), the distribution ratio, D, is

$$D = \frac{K_{\mathrm{D}}[\mathrm{H_3O}^+_{aq}]}{[\mathrm{H_3O}^+_{aq}] + K_{\mathrm{a}}} = \frac{(1200) \times (1.00 \times 10^{-7})}{(1.00 \times 10^{-7}) + (1.00 \times 10^{-5})} = 11.9$$

To find the number of extractions, we make appropriate substitutions into equation 7.27 and solve for n

$$0.001 = \left(\frac{50.0}{11.9 \times 50.0 + 50.0}\right)^n$$

$$\log(0.001) = n\log(0.0775)$$

$$-3.00 = -1.11n$$

finding that n is 2.7; thus, we need to complete at least three extractions to achieve an extraction efficiency of 99.9%.

27. From equation 7.27, an extraction efficiency of 99.9%, requires that

$$(Q_{aq})_2 = 0.001 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^2 = \left(\frac{50.0}{D \times 25.0 + 50.0}\right)^2$$

for two extractions of 50.0 mL of sample using 25.0 mL of organic solvent per extraction. Taking the square root of both sides

$$0.03162 = \frac{50.0}{D \times 25.0 + 50.0}$$

and solving for D gives its minimum value of as 61.3. Because the analyte is a weak base, the distribution ratio's value depends on the pH of the aqueous phase, with more basic pH levels favoring a larger value for D. From Practice Exercise 7.9, we know that

$$D = \frac{K_\text{D}[\text{OH}^-_{aq}]}{[\text{OH}^-_{aq}] + K_\text{b}}$$

$$61.3 = \frac{(5.00 \times 10^2)[\text{OH}^-_{aq}]}{[\text{OH}^-_{aq}] + (1.0 \times 10^{-3})}$$

$$61.3[\text{OH}^-_{aq}] + 0.0613 = (5.00 \times 10^2)[\text{OH}^-_{aq}]$$

$$0.0613 = 438.7[\text{OH}^-_{aq}]$$

gives $[\text{OH}^-_{aq}]$ as 1.40×10^{-4}, or a minimum pH of 10.15.

28. (a) To calculate the extraction efficiencies for HA and HB, we first find their respective distribution ratios at a pH of 7.00

$$D_\text{HA} = \frac{K_\text{D,HA}[\text{H}_3\text{O}^+_{aq}]}{[\text{H}_3\text{O}^+_{aq}] + K_\text{a,HA}} = \frac{(5.00 \times 10^2)(1.0 \times 10^{-7})}{1.0 \times 10^{-7} + 1.0 \times 10^{-3}} = 0.0500$$

$$D_\text{HB} = \frac{K_\text{D,HB}[\text{H}_3\text{O}^+_{aq}]}{[\text{H}_3\text{O}^+_{aq}] + K_\text{a,HB}} = \frac{(5.00 \times 10^2)(1.0 \times 10^{-7})}{1.0 \times 10^{-7} + 1.0 \times 10^{-7}} = 250$$

and then calculate the fraction of HA and HB that remain in the aqueous phase when the extraction is complete

$$Q_{aq,\text{HA}} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{0.0500 \times 50.0 + 50.0} = 0.952$$

$$Q_{aq,\text{HB}} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{250 \times 50.0 + 50.0} = 0.00398$$

Thus, the extraction efficiency for HA is 0.048 or 4.8% and for HB is 0.996 or 99.6%

(b) The aqueous phase is enriched in the analyte, HA, with 95.2% of HA remaining unextracted.

(c) The recovery for HA in the aqueous phase, R_HA, is 0.952 or 95.2%; for HB, R_HB is 0.00398 or 0.398%.

(d) The separation factor, $S_\text{HB,HA}$, is

$$S_\text{HB,HA} = \frac{R_\text{HB}}{R_\text{HA}} = \frac{0.00398}{0.952} = 4.18 \times 10^{-3}$$

(e) The error is

$$E = (R_\text{HA} - 1) + \frac{K_\text{HA,HB}(C_\text{HB})_\text{o}}{(C_\text{HA})_\text{o}} \times R_\text{HB}$$

$$E = (0.952 - 1) + \frac{0.500 \times 10}{1} \times 0.00398 = -0.0281$$

or an error of –2.81%.

29. (a) Decreasing the concentration of I^- pushes the equilibrium reaction between I_2 and I_3^- to the left, which increases the concentration of I_2*(aq)*; in turn, this pushes the equilibrium reaction between I_2*(aq)* and I_2*(org)* toward the organic phase, increasing the extraction efficiency.

    (b) We start by writing equations for K_D and for K_f for the two equilibrium reactions; these are

$$K_D = \frac{[I_2]_{org}}{[I_2]_{aq}} \qquad K_f = \frac{[I_3^-]_{aq}}{[I_2]_{aq}[I^-]_{aq}}$$

    and the distribution ratio for the extraction

$$D = \frac{[I_2]_{org}}{[I_2]_{aq} + [I_3^-]_{aq}}$$

    Solving K_f for $[I_3^-]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[I_2]_{org}}{[I_2]_{aq} + K_f[I_2]_{aq}[I^-]_{aq}}$$

    factoring our $[I_2]$*(aq)* in the denominator

$$D = \frac{[I_2]_{org}}{[I_2]_{aq}\{1 + K_f[I^-]_{aq}\}}$$

    and simplifying by replacing $[I_2]_{org}/[I_2]_{aq}$ with K_D leaves us with the desired final equation

$$D = \frac{K_D}{1 + K_f[I^-]_{aq}}$$

30. (a) We start by writing equations for K_D and for β_2 for the two equilibrium reactions; these are

$$K_D = \frac{[ML_2]_{org}}{[ML_2]_{aq}} \qquad \beta_2 = \frac{[ML_2]_{aq}}{[M^{2+}]_{aq}[L^-]_{aq}^2}$$

    and the distribution ratio for the extraction

$$D = \frac{[ML_2]_{org}}{[ML_2]_{aq} + [M^{2+}]_{aq}}$$

    Solving β_2 for $[M^{2+}]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[ML_2]_{org}}{[ML_2]_{aq} + \dfrac{[ML_2]_{aq}}{\beta_2[L^-]_{aq}^2}}$$

    factoring out $[ML_2]_{aq}$ in the denominator

$$D = \frac{[\mathrm{ML}_2]_{org}}{[\mathrm{ML}_2]_{aq}\left\{1 + \frac{1}{\beta_2[L^-]^2_{aq}}\right\}}$$

and simplifying by replacing $[\mathrm{ML}_2]_{org}/[\mathrm{ML}_2]_{aq}$ with K_D leaves us with the desired final equation

$$D = \frac{K_\mathrm{D}}{1 + \frac{1}{\beta_2[L^-]^2_{aq}}} = \frac{K_\mathrm{D}\beta_2[L^-]^2_{aq}}{1 + \beta_2[L^-]^2_{aq}}$$

(b) Because the initial concentration of L^- (0.12 M) is much greater than the initial concentration of M^{2+} (0.15 mM), we can assume that $[\mathrm{L}^-]_{aq}$ is 0.12 M. Substituting known values into the equation for D from part (a) gives the distribution ratio as

$$D = \frac{K_\mathrm{D}\beta_2[L^-]^2_{aq}}{1 + \beta_2[L^-]^2_{aq}} = \frac{(10.3)(560)(0.12)^2}{1 + (560)(0.12)^2} = 9.16$$

the fraction remaining in the aqueous phase as

$$Q_{aq} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{9.16 \times 25.0 + 50.0} = 0.179$$

and an extraction efficiency of 0.821 or 82.1%.

31. We start by writing equations for $K_{\mathrm{D,c}}$, $K_{\mathrm{D,L}}$, K_a, and β_n for the four equilibrium reactions; these are

$$K_{\mathrm{D,c}} = \frac{[\mathrm{ML}_n]_{org}}{[\mathrm{ML}_n]_{aq}} \qquad K_{\mathrm{D,HL}} = \frac{[\mathrm{HL}]_{org}}{[\mathrm{HL}]_{aq}}$$

$$\beta_n = \frac{[\mathrm{ML}_n]_{aq}}{[\mathrm{M}^{n+}]_{aq}[\mathrm{L}^-]^n_{aq}} \qquad K_\mathrm{a} = \frac{[\mathrm{H_3O^+}]_{aq}[\mathrm{L}^-]_{aq}}{[\mathrm{HL}]_{aq}}$$

and the distribution ratio for the extraction

$$D = \frac{[\mathrm{ML}_n]_{org}}{[\mathrm{ML}_n]_{aq} + [\mathrm{M}^{n+}]_{aq}}$$

Solving β_n for $[\mathrm{M}^{n+}]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[\mathrm{ML}_n]_{org}}{[\mathrm{ML}_n]_{aq} + \frac{[\mathrm{ML}_n]_{aq}}{\beta_n[\mathrm{L}^-]^n_{aq}}}$$

and factoring out $[\mathrm{ML}_n]_{aq}$ in the denominator gives

$$D = \frac{[\mathrm{ML}_n]_{org}}{[\mathrm{ML}_n]_{aq}\left\{1 + \frac{1}{\beta_n[L^-]^n_{aq}}\right\}} = \frac{K_{\mathrm{D,c}}}{1 + \frac{1}{\beta_n[L^-]^n_{aq}}} = \frac{K_{\mathrm{D,c}}\beta_n[L^-]^n_{aq}}{1 + \beta_n[L^-]^n_{aq}}$$

Next we solve K_a for $[\mathrm{L}^-]_{aq}$ and substitute into the equation for the distribution ratio, giving

$$D = \frac{K_{\mathrm{D,c}}\beta_n\left(\frac{K_{\mathrm{a}}[HL]_{\mathrm{aq}}}{[\mathrm{H_3O^+}]_{\mathrm{aq}}}\right)^n}{1+\beta_n\left(\frac{K_{\mathrm{a}}[HL]_{\mathrm{aq}}}{[\mathrm{H_3O^+}]_{\mathrm{aq}}}\right)^n} = \frac{K_{\mathrm{D,c}}(K_{\mathrm{a}})^n\beta_n[HL]^n_{aq}}{[\mathrm{H_3O^+}]^n_{aq}+\beta_n(K_{\mathrm{a}})^n[HL]^n_{aq}}$$

Next, we solve $K_{\mathrm{D,L}}$ for $[\mathrm{HL}]_{aq}$ and substitute into the equation for the distribution ratio

$$D = \frac{K_{\mathrm{D,c}}(K_{\mathrm{a}})^n\beta_n\left(\frac{[\mathrm{HL}]_{org}}{K_{\mathrm{D,HL}}}\right)^n}{[\mathrm{H_3O^+}]^n_{aq}+\beta_n(K_{\mathrm{a}})^n\left(\frac{[\mathrm{HL}]_{org}}{K_{\mathrm{D,HL}}}\right)^n}$$

$$D = \frac{K_{\mathrm{D,c}}(K_{\mathrm{a}})^n\beta_n[\mathrm{HL}]^n_{org}}{(K_{D,HL})^n[\mathrm{H_3O^+}]^n_{aq}+\beta_n(K_{\mathrm{a}})^n[\mathrm{HL}]^n_{org}}$$

Finally, because the solubility of HL in the aqueous phase is so poor, we make the following assumption for a mass balance on HL

$$C_{\mathrm{HL}} = [\mathrm{HL}]_{org} + [\mathrm{HL}]_{aq} \approx [\mathrm{HL}]_{org}$$

and substitute back into the equation for the distribution ratio to yield equation 7.32.

$$D = \frac{\beta_n K_{\mathrm{D,c}}(K_a)^n(C_{HL})^n}{(K_{D,HL})^n[\mathrm{H_3O^+}]^n_{aq}+\beta_n(K_a)^n(C_{HL})^n}$$

32. We begin by calculating the distribution ration using equation 7.32

$$D = \frac{(5\times10^{22})(7\times10^{4})(3\times10^{-5})^2(4.0\times10^{-4})^2}{(1.1\times10^{4})^2(1)^2+(5\times10^{22})(3\times10^{-5})^2(4.0\times10^{-4})^2}$$
$$D = 3930$$

and then calculate the fraction of $\mathrm{Cu^{2+}}$ remaining in the aqueous phase

$$Q_{aq} = \frac{V_{aq}}{DV_{org}+V_{aq}} = \frac{100}{3930\times10.0+100.0} = 0.00254$$

finding that the extraction efficiency is 0.997 or 99.7%.

33. (a) One approach is to start by adjusting the pH of the aqueous phase to 1.0 and extract the $\mathrm{Hg^{2+}}$. We can then raise the pH to 4.0 and extract the $\mathrm{Pb^{2+}}$. Finally, we can raise the pH to 9.0 (or 10.0) and extract the $\mathrm{Zn^{2+}}$.

(b) After three extractions, the fraction of $\mathrm{Hg^{2+}}$ that remains in the aqueous phase is

$$(Q_{aq})_3 = \left(\frac{V_{aq}}{DV_{org}+V_{aq}}\right)^3 = \left(\frac{50.0}{3.3\times50.0+50.0}\right)^3 = 0.0126$$

or 1.26%; the extraction efficiency is 98.7%

(c) The minimum volume of solvent needed to extract 99.5% of the $\mathrm{Pb^{2+}}$ in the aqueous phase is

$$Q_{aq} = 0.005 = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{9999V_{org} + 50.0}$$

$$49.995V_{org} + 0.25 = 50.0$$

$$V_{org} = 0.995 \text{ mL}$$

or a minimum volume of 1 mL of the organic solvent.

(d) The number of extractions needed to remove 99.5% of the Zn^{2+} is

$$(Q_{aq})_n = 0.005 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n = \left(\frac{50.0}{2.57 \times 25.0 + 50.0}\right)^n$$

$$\log(0.005) = n\log(0.4376)$$

$$-2.301 = -0.3589n$$

$$n = 6.41$$

or a minimum of 7 extractions.