Chapter 13

1. To derive an appropriate equation we first note the following general relationship between the concentration of A at time t, $[A]_t$, the initial concentration of A, $[A]_0$, and the concentration of P at time t, $[P]_t$

$$[A]_t = [A]_0 - [P]_t$$

Substituting this relationship into equation 13.18 for times t_1 and t_2, gives the desired result

$$[A]_0 = \frac{[A]_{t1} - [A]_{t2}}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{([A]_0 - [P]_{t1}) - ([A]_0 - [P]_{t2})}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{[A]_0 - [P]_{t1} - [A]_0 + [P]_{t2}}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{[P]_{t2} - [P]_{t1}}{e^{-k't_1} - e^{-k't_2}}$$

2. For a one-point fixed time method, a pseudo-first order reaction obeys the equation

$$[A]_t = [A]_0 e^{-kt} = K[A]_0$$

where A is phenylacetate and K is equal to e^{-kt}. Using the standard, we find that K is

$$0.17 \text{ mM} = K(0.55 \text{ mM})$$

$$K = \frac{0.17 \text{ mM}}{0.55 \text{ mM}} = 0.309$$

Thus, for the sample, we have

$$[\text{phenylacetate}]_0 = \frac{0.23 \text{ mM}}{0.309} = 0.74 \text{ mM}$$

You can, of course, use the equation $[A]_t = [A]_0 e^{-kt}$ and the result for the standard to calculate the rate constant, k, and then use the same equation and the result for the sample to calculate the concentration of phenylacetate. The rate constant has a value of 0.0196 s^{-1}.

3. Because we are following the change in concentration for a product, the kinetics follow equation 13.15

$$[H_2O_2]_0 = \frac{[I_2]_t}{1 - e^{-k't}}$$

which we rearrange to solve for the product's concentration

$$[I_2]_t = [H_2O_2]_0(1 - e^{-k't})$$

From Beer's law, we know that the absorbance, A, is

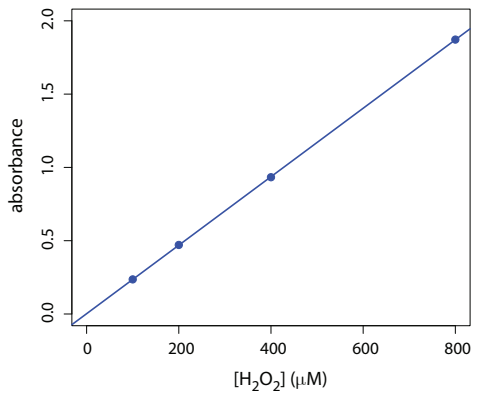

Figure SM13.1 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 3.

$$A_t = \varepsilon b[\mathrm{I_2}]_t$$

Substituting this equation back into the previous equation gives

$$A_t = (\varepsilon b)^{-1}[\mathrm{H_2O_2}]_0(1 - e^{-k't}) = K[\mathrm{H_2O_2}]_0$$

where K is equal to $(\varepsilon b)^{-1}(1 - e^{-k't})$. Using the data for the external standards gives the calibration curve shown in Figure SM13.1, the equation for which is

$$A_t = 0.002 + 2.336 \times 10^{-3}\,\mu\mathrm{M}^{-1}\,C_{\mathrm{H_2O_2}}$$

Substituting in the sample's absorbance of 0.669 gives the concentration of H_2O_2 as 286 μM.

4. For a two-point fixed-time method, we use equation 13.18

$$[\mathrm{H_2CrO_4}]_0 = \frac{[\mathrm{H_2CrO_4}]_{t_1} - [\mathrm{H_2CrO_4}]_{t_2}}{e^{-k't_1} - e^{-k't_2}}$$

From Beer's law, we know that

$$A_{t_1} = \varepsilon b[\mathrm{H_2CrO_4}]_{t_1} \qquad A_{t_2} = \varepsilon b[\mathrm{H_2CrO_4}]_{t_2}$$

Solving these two equations for the concentration of chromic acid at times t_1 and t_2, and substituting back gives

$$[\mathrm{H_2CrO_4}]_0 = \frac{\frac{A_{t_1}}{\varepsilon b} - \frac{A_{t_2}}{\varepsilon b}}{e^{-k't_1} - e^{-k't_2}} = \frac{(\varepsilon b)^{-1}(A_{t_1} - A_{t_2})}{e^{-k't_1} - e^{-k't_2}} = K(A_{t_1} - A_{t_2})$$

Using the data for the external standard, we find that

$$K = \frac{[\mathrm{H_2CrO_4}]_0}{(A_{t_1} - A_{t_2})} = \frac{5.1 \times 10^{-4}\,\mathrm{M}}{0.855 - 0.709} = 3.49 \times 10^{-3}\,\mathrm{M}$$

The concentration of chromic acid in the sample, therefore, is

$$[\mathrm{H_2CrO_4}]_0 = K(A_{t_1} - A_{t_2}) =$$
$$3.49 \times 10^{-3}\,\mathrm{M}(0.883 - 0.706) = 6.2 \times 10^{-4}\,\mathrm{M}$$

5. For a variable time kinetic method, there is an inverse relationship between the elapsed time, Δt, and the concentration of glucose. Figure SM13.2 shows the resulting calibration data and calibration curve, for which the equation is

$$(\Delta t)^{-1} = -6.30 \times 10^{-4}\,\mathrm{s}^{-1} + 1.50 \times 10^{-3}\,\mathrm{s}^{-1}\,\mathrm{ppm}^{-1}\,C_{\mathrm{glucose}}$$

where Δt for each standard is the average of the three measurements. Substituting in the sample's Δt of 34.6 s, or a $(\Delta t)^{-1}$ of 0.02890 s^{-1}, gives the concentration of glucose as 19.7 ppm for the sample. The relative error in the analysis is

$$\frac{19.7\ \mathrm{ppm} - 20.0\ \mathrm{ppm}}{20.0\ \mathrm{ppm}} \times 100 = -1.5\%\ \mathrm{error}$$

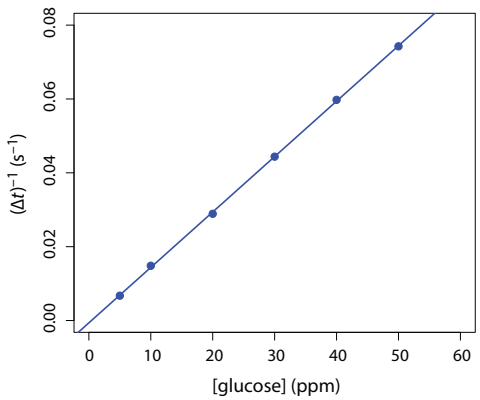

Figure SM13.2 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 5.

6. Substituting the sample's rate of 6.84×10^{-5} μmol $mL^{-1}s^{-1}$ into the calibration equation gives the volume as

$$V = \frac{6.84\times10^{-5}\,\mu mol^{-1}\,mL^{-1}s^{-1} - 2.7\times10^{-7}\,\mu mol^{-1}\,mL^{-1}s^{-1}}{3.485\times10^{-5}\,\mu mol^{-1}\,mL^{-2}s^{-1}}$$

$$V = 1.95\ mL$$

This is the volume of the standard enzyme that has the same amount of enzyme as is in the 10.00 mL sample; thus, the concentration of enzyme in the sample is approximately 5× more dilute than the concentration of enzyme in the standard.

7. For a first-order reaction, a plot of $\ln[A]_t$ versus time gives a straight line with a slope equal to $-k$ and a y-intercept equal to $\ln[A]_0$. Figure SM13.3 shows the data and the regression line, for which the equation is

$$\ln[A]_t = 0.4069 - (0.04862\ s^{-1})\,t$$

From the slope, we know that the reaction's rate constant is 0.0486 s^{-1}. Using the y-intercept, we know that $\ln[A]_0$ is 0.4069, which makes the initial concentration of A equal to 1.50 mM.

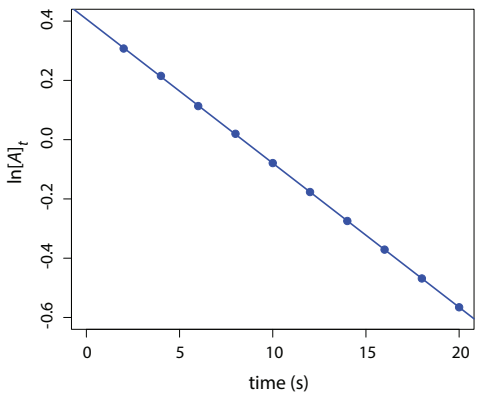

Figure SM13.3 Linearization of the data from Problem 6 for a reaction that is pseudo-first order in the analyte.

8. Under these conditions—a concentration of acetylcholine that is significantly smaller than the constant, K_m—we can write the Michaelis-Menton equation as

$$R = \frac{k_2[E]_0[S]}{K_m}$$

where $[E]_0$ is the concentration of enzyme and $[S]$ is the concentration of the substrate acetylcholine; substituting in known values

$$12.33\times10^{-6}\ Ms^{-1} = \frac{(1.4\times10^{4}\,s^{-1})(6.61\times10^{-7}\,M)[S]}{9\times10^{-5}\,M}$$

and solving gives the concentration of acetylcholine as 1.2×10^{-7} M.

9. Under these conditions—a concentration of fumarate that is significantly greater than the constant, K_m—we can write the Michaelis-Menton equation as

$$R = k_2[E]_0$$

where $[E]_0$ is the concentration of enzyme. Using the rate and concentration of enzyme for the standard, the value of k_2 is

$$k_2 = \frac{R}{[E]_0} = \frac{2.00\ \mu M\ min^{-1}}{0.150\ \mu M} = 13.33\ min^{-1}$$

Using this value for k_2 and the rate for the sample, we find that the enzyme's concentration in the sample is

$$[E]_0 = \frac{R}{k_2} = \frac{1.15\ \mu M\ min^{-1}}{13.33\ min^{-1}} = 0.0863\ \mu M$$

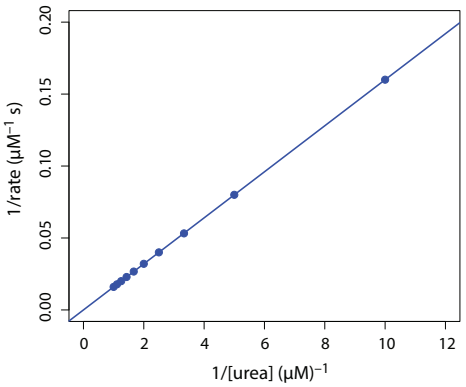

Figure SM13.4 Lineweaver-Burk plot of the data from Problem 10. The **blue** dots are the reciprocals of the concentration and rate data provided in the problem, and the **blue** line is the result of a regression analysis on the data.

10. Figure SM13.4 shows a Lineweaver-Burk plot of 1/rate as a function of 1/[urea], for which a regression analysis gives an equation of

$$\frac{1}{\text{rate}} = 2.464 \times 10^{-6}\,\mu\text{M}^{-1}\text{s} + \frac{(0.01600\text{ s})}{C_{\text{urea}}}$$

From the *y*-intercept we extract the value for the maximum rate; thus

$$V_{max} = \frac{1}{y\text{–intercept}} = \frac{1}{2.464 \times 10^{-6}\,\mu\text{M}^{-1}\text{s}} = 4.058 \times 10^{5}\,\mu\text{M s}^{-1}$$

or 0.406 M/s. From the slope, we determine the value for K_m, finding that it is

$$K_m = (slope) \times V_{max} = (0.01600\text{ s})\,(4.058 \times 10^{5}\,\mu\text{M s}^{-1}) = 6490\,\mu\text{M}$$

or 6.49×10^{-3} M. Finally, we know that $V_{max} = k_2[E]_0$, which we use to calculate the value for k_2

$$k_2 = \frac{4.058 \times 10^{5}\,\mu\text{M s}^{-1}}{5.0\,\mu\text{M}} = 8.1 \times 10^{4}\text{ s}^{-1}$$

11. If V_{max} remains constant, then the *y*-intercept of a Lineweaver-Burk plot is independent of the inhibitor's concentration. If the value of K_m increases and the value of V_{max} remains constant for higher concentrations of the inhibitor, then the slope of a Lineweaver-Burk plot, which is equal to K_m/V_{max}, must increase for higher concentrations of the inhibitor. Figure 13.14 shows that both are consistent with competitive inhibition.

12. For competitive inhibition, the initial concentration of enzyme is divided between free enzyme, *E*, enzyme complexed with the substrate, *ES*, and enzyme complexed with the inhibitor, *EI*; thus, a mass balance on the enzyme requires that

$$[E]_0 = [E] + [ES] + [EI]$$

If we assume that k_2 is much smaller than k_{-1}, then we can simplify the equation for K_m to

$$K_m = \frac{k_{-1} + k_2}{k_1} \approx \frac{k_{-1}}{k_1} = K_{ES} = \frac{[E]\,[S]}{[ES]}$$

where K_{ES} is the equilibrium dissociation constant for the enzyme-substrate complex. We also can write the equilibrium dissociation constant for the enzyme-inhibitor complex, which is

$$K_{EI} = \frac{[E]\,[I]}{[EI]}$$

Solving K_m and K_{EI} for the concentrations of *E* and of *EI*, respectively

$$[E] = \frac{K_m[ES]}{[S]} \qquad [EI] = \frac{[E][I]}{K_{EI}}$$

and substituting back into the mass balance equation gives

$$[E]_0 = \frac{K_m[ES]}{[S]} + [ES] + \frac{[E][I]}{K_{EI}}$$

$$[E]_0 = \frac{K_m[ES]}{[S]} + [ES] + \frac{K_m[ES][I]}{[S]K_{EI}}$$

Factoring out $[ES]$ from the right side of the equation

$$[E]_0 = [ES]\left\{\frac{K_m}{[S]} + 1 + \frac{K_m[I]}{[S]K_{EI}}\right\}$$

and then solving for $[ES]$ gives

$$[ES] = \frac{[E]_0}{\left\{\frac{K_m}{[S]} + 1 + \frac{K_m[I]}{[S]K_{EI}}\right\}}$$

Finally, the rate of the reaction, d$[P]$/dt, is equal to $k_2[ES]$, or

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E]_0}{\left\{\frac{K_m}{[S]} + 1 + \frac{K_m[I]}{[S]K_{EI}}\right\}}$$

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{\left\{K_m + [S] + \frac{K_m[I]}{K_{EI}}\right\}}$$

$$\frac{d[P]}{dt} = \frac{V_{\max}[S]}{K_m\left(1 + \frac{[I]}{K_{EI}}\right) + [S]}$$

13. For first-order kinetics, we know that

$$\ln\frac{[A]_t}{[A]_0} = -k_A t \qquad \ln\frac{[B]_t}{[B]_0} = -k_B t$$

To obtain 0.001 for $[A]_t/[A]_0$ and 0.999 for $[B]_t/[B]_0$, the ratio of the rate constants must be

$$\frac{\ln\frac{[A]_t}{[A]_0}}{\ln\frac{[B]_t}{[B]_0}} = \frac{-k_A t}{-k_B t}$$

$$\frac{\ln(0.001)}{\ln(0.999)} = \frac{k_A}{k_B} = 6900$$

14. Figure SM13.5 shows a plot of the data, where we place $\ln[C]_t$ on the y-axis as the kinetics are first-order. Early in the reaction, the plot is curved because both A and B are reacting. Because A reacts faster than B, eventually the reaction mixture consists of B only, and the plot becomes linear. A linear regression analysis of the data from $t =$ 36 min to $t = 71$ min gives a regression equation of

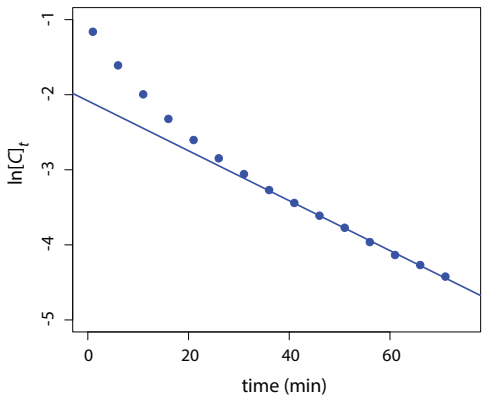

Figure SM13.5 Plot of the data for Problem 14. The **blue** dots are the original data and the **blue** line is a regression analysis restricted data from $t = 36$ min to $t = 71$ min when the reaction of A is complete.

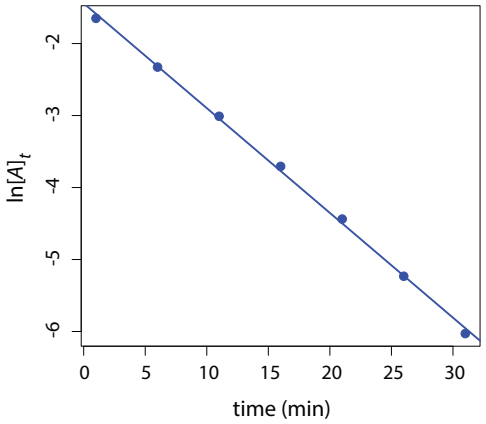

Figure SM13.6 Plot of the data for Problem 14 after we remove the contribution from *B*. The **blue** dots are the recalculated data and the **blue** line is a regression analysis restricted data from $t = 1$ min to $t = 31$ min when the reaction of *A* is complete.

$$\ln [C]_t \approx \ln [B]_t = -2.082 - (3.325 \times 10^{-2}\ \text{min}^{-1})\, t$$

The *y*-intercept of –2.082 is equivalent to $\ln[B]_0$; thus,

$$[B]_0 = e^{-2.082} = 0.125\ \text{mM}$$

The slope of the regression line in Figure SM13.5 gives the rate constant k_B, which is approximately 0.0332 min^{-1}. To find values for $[A]_0$ and for k_A, we must correct $[C]_t$ for the contribution of *B*. This is easy to do because we know that

$$[C]_t = [A]_t + [B]_t$$

and that

$$[B]_t = [B]_0 e^{-k_B t}$$

which means that

$$[A]_t = [C]_t - [B]_0 e^{-k_B t}$$

For example, at time $t = 1$, the concentration of *B* is 0.1209 mM and the concentration of *A* is 0.313 mM – 0.1209 mM = 0.1921 mM. Figure SM13.6 shows a plot of $\ln[A]_t$ versus time from $t = 1$ min to $t = 31$ min. A regression analysis of the data gives the following equation

$$\ln [A]_t = -1.442 - (0.1455\ \text{min}^{-1})\, t$$

from which the slope gives the value of k_A as 0.146 min^{-1} and the *y*-intercept of –1.442 yields the initial concentration of *A*

$$[A]_0 = e^{-1.442} = 0.236\ \text{mM}$$

15. For radioactive decay, we know that $t_{1/2} = 0.693/\lambda$. Using the first entry in Table 13.1 as an example, we find that

$$\lambda_{^3\text{H}} = \frac{0.693}{12.5\ \text{yr}} = 5.54 \times 10^{-2}\ \text{yr}^{-2}$$

The decay constants for the isotopes in Table 13.1 are provided here

isotope	half-life	decay constant
^{3}H	12.5 yr	5.54×10^{-1} yr^{-2}
^{14}C	5730 yr	1.21×10^{-4} yr^{-1}
^{32}P	14.3 d	4.85×10^{-2} d^{-1}
^{35}S	87.1 d	7.96×10^{-3} d^{-1}
^{45}Ca	152 d	4.56×10^{-3} d^{-1}
^{55}Fe	2.91 yr	2.38×10^{-1} yr^{-1}
^{60}Co	5.3 yr	1.31×10^{-1} yr^{-1}
^{131}I	8 d	8.66×10^{-2} d^{-1}

16. Combining equation 13.33 and equation 13.37 allows us to calculate the number of atoms of ^{60}Co in a sample given the sample's activity, A, and the half-life for ^{60}Co

$$N = \frac{At_{1/2}}{0.693}$$

$$N = \frac{\frac{2.1 \times 10^7 \text{ atoms}}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}} \times \frac{24 \text{ h}}{\text{d}} \times \frac{365 \text{ d}}{\text{yr}} \times 5.3 \text{ yr}}{0.693}$$

$$N = 5.06 \times 10^{15} \text{ atoms } ^{60}C$$

The concentration of ^{60}Co, therefore, is

$$\frac{5.06 \times 10^{15} \text{ atoms } ^{60}Co}{(6.022 \times 10^{23} \text{atoms/mol})\,(0.00500 \text{ L})} = 1.7 \times 10^{-6} \text{M}$$

17. Using the data for the standard, we know that

$$k = \frac{(A_0)_s}{w_s} = \frac{3540 \text{ cpm}}{1.000 \text{ g} \times \frac{0.0593 \text{ g Ni}}{\text{g}}} = 5.97 \times 10^4 \text{cpm/g Ni}$$

For the sample, therefore, we have

$$w_x = \frac{(A_0)_x}{k} = \frac{1020 \text{ cpm}}{5.97 \times 10^4 \text{cpm/g Ni}} = 0.1709 \text{ g Ni}$$

Finally, the concentration of Ni in the sample is

$$\frac{0.1709 \text{ g Ni}}{0.500 \text{ g sample}} \times 100 = 34.2\% \text{w/w Ni}$$

18. Using equation 13.42, we find that mass of vitamin B_{12} in the sample as analyzed is

$$w = \frac{572 \text{ cpm}}{361 \text{ cpm}} \times 18.6 \text{ mg} - 0.500 \text{ mg} = 28.97 \text{ mg}$$

This represents half of the original sample; thus, there are 57.94 mg of vitamin B_{12} in the 10 tablets, or 5.79 mg/tablet.

19. For radioactive decay, we know that

$$\ln \frac{A_t}{A_0} = -\lambda t = -\frac{0.693}{t_{1/2}} \times t$$

Substituting in $t_{1/2}$ from Table 13.1 and letting $t = 30\,000$ yr, gives

$$\ln \frac{A_t}{A_0} = -\frac{0.693}{5730 \text{ yr}} \times 30000 \text{ yr} = -3.628$$

$$\frac{A_t}{A_0} = e^{-3.628} = 0.0266$$

The percentage of ^{14}C remaining, therefore, is 2.66%.

20. Because we assume that ^{40}Ar was not was present in the original sample, we know that the initial moles of ^{40}K is the sum of the moles of ^{40}Ar and of ^{40}K present when the sample is analyzed; thus

$$(n_{^{40}K})_0 = (4.63 \times 10^6 \text{ mol } ^{40}K)_t + (2.09 \times 10^6 \text{ mol } ^{40}Ar)_t = 6.72 \times 10^6 \text{ mol}$$

Using the equation for first-order radioactive decay, we find that

$$\ln \frac{(n_{^{40}K})_t}{(n_{^{40}K})_0} = -kt = -\frac{0.693}{t_{1/2}} \times t$$

$$\ln \frac{4.63 \times 10^{-6} \text{ mol}}{6.72 \times 10^{-6} \text{ mol}} = -0.3725 = -\frac{0.693}{1.3 \times 10^9 \text{ yr}} \times t$$

$$t = \frac{(0.3725)(1.3 \times 10^9 \text{ yr})}{0.693} = 7.0 \times 10^8 \text{ yr}$$

21. The relationship between the percent relative standard deviation and the number of counts is

$$(\sigma_A)_{\text{rel}} = \frac{1}{\sqrt{M}} \times 100$$

where M is the number of counts. To obtain a percent relative standard deviation of 1%, therefore, requires

$$1.0 = \frac{1}{\sqrt{M}} \times 100$$

$$M = \left(\frac{100}{1.0}\right)^2 = 10000 \text{ counts}$$

To obtain 10 000 counts, we need a sample that contains

$$10000 \text{ counts} \times \frac{1.00 \text{ g C}}{12 \text{ cpm}} \times \frac{1}{60 \text{ min}} = 13.9 \text{ g C}$$

To obtain a 1% relative standard deviation when counting the radioactive decay from a 0.50 g sample of C, we must count for

$$10000 \text{ counts} \times \frac{1.00 \text{ g C}}{12 \text{ cpm}} \times \frac{1}{0.50 \text{ g C}} = 1333 \text{ min} \approx 1300 \text{ min}$$

22. Sensitivity in a flow-injection analysis is directly proportional to the height of an analyte's peak in the fiagram, which, in turn, is proportional to the analyte's concentration. As the analyte moves from the point of injection to the point of detection, it undergoes continuous dispersion, as shown in Figure 13.19. Because dispersion reduces the analyte's concentration at the center of its flow profile, anything that limits dispersion will increase peak height and improve sensitivity. Increasing the flow rate or decreasing the length and diameter of the manifold allows less time for dispersion, which improves sensitivity. Injecting a larger volume of sample means it will take more time for the analyte's concentration to decrease at the center of its flow profile,

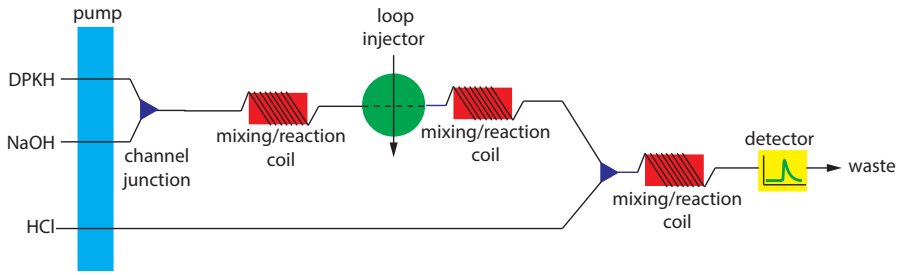

Figure SM13.7 One possible FIA manifold for the analysis described in Problem 24.

which also improves sensitivity. Finally, injecting the analyte into a channel results in its dilution and a loss of sensitivity. If we merge this channel with another channel, then we dilute further the analyte; whenever possible, we want to dilute the analyte just once, when we inject it into the manifold.

23. Depending on your measurements, your answers may vary slightly from those given here: the travel time, t_a, is 14.1 s; the residence time, T, is 15.8 s; the baseline-to-baseline time, Δt, is 15.2 s; the return time, T', is 13.5 s; and the difference between the residence time and the travel time, t', is 1.7 s. The peak height is 0.762 absorbance units; thus, the sensitivity is

$$k = \frac{A}{C} = \frac{0.762}{100.0 \text{ ppm}} = 7.62 \times 10^{-3} \text{ ppm}^{-1}$$

We can make injections at a rate of one per unit return time, which for this system is 1 every 13.5 s; thus, in one hour we can analyze

$$1 \text{ hr} \times \frac{3600 \text{ s}}{\text{hr}} \times \frac{1 \text{ sample}}{13.5 \text{ s}} = 267 \approx 260 \text{ to } 270 \text{ samples/hr}$$

24. Figure SM13.7 shows one possible manifold. Separate reagent channels of DPKH and NaOH are merged together and mixed, and the sample injected into their combined channel. After allowing sufficient time for the reaction to occur, the carrier stream is merged with a reagent channel that contains HCl, the concentration of which is sufficient to neutralize the NaOH and to make the carrier stream acidic.

25. Figure SM13.8 shows the calibration data and the calibration curve, the equation for which is

$$A = 2.28 \times 10^{-3} + (1.146 \times 10^{-2} \text{ ppm}^{-1})\, C_{\text{ppm}}$$

Substituting in the sample's absorbance of 0.317 gives the concentration of Cl^- as 27.46 ppm in the sample as analyzed, which means the concentration of Cl^- in the original sample of seawater is

$$24.76 \text{ ppm } Cl^- \times \frac{500.0 \text{ mL}}{1.00 \text{ mL}} = 13700 \text{ ppm } Cl^-$$

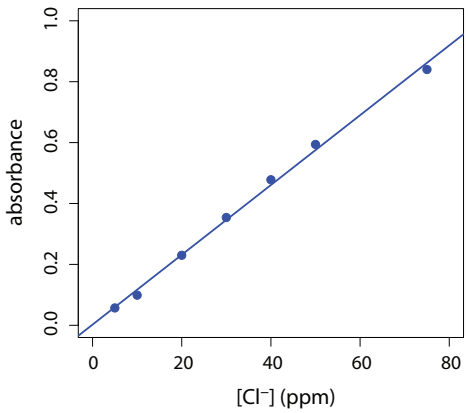

Figure SM13.8 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 25.

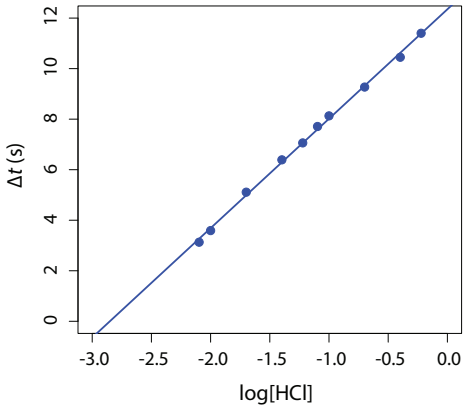

Figure SM13.9 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 26.

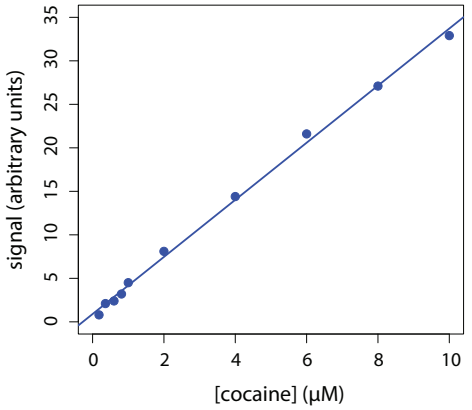

Figure SM13.10 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 28.

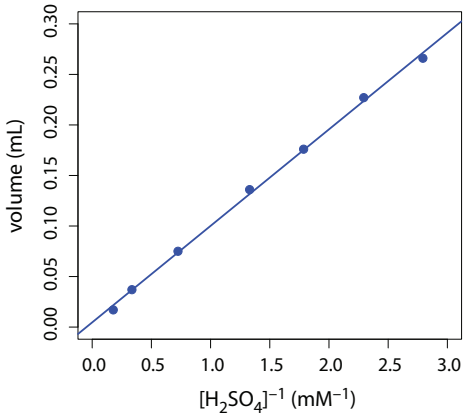

Figure SM13.11 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 29.

26. Figure SM13.9 shows the calibration data and the calibration curve, which for an FIA titration is a plot of Δt as a function of log[HCl]. The equation for this calibration curve is

$$\Delta t = 12.349\text{ s} + (4.331\text{ s}) \times \log[\text{HCl}]$$

The average Δt for the five trials is 7.364 s. Substituting this back into the calibration equation gives

$$\log[\text{HCl}] = \frac{7.364\text{ s} - 12.349\text{ s}}{4.331\text{ s}} = -1.151$$

$$[\text{HCl}] = 10^{-1.151} = 0.0706\text{ M}$$

27. Using the data for the single external standard, we know that

$$k = \frac{S}{C_{\text{glucose}}} = \frac{7.13\text{ nA}}{6.93\text{ mM}} = 1.029\text{ nA mM}^{-1}$$

Using this value for k, the concentration of glucose in the sample is

$$C_{\text{glucose}} = \frac{11.50\text{ nM}}{1.029\text{ nA mM}^{-1}} = 11.2\text{ mM}$$

28. (a) The mean and the standard deviation for the 12 replicate samples are 23.97 and 0.605, respectively. The relative standard deviation, therefore, is

$$\frac{0.605}{23.97} \times 100 = 2.52\%$$

(b) Figure SM13.10 shows the calibration data and the calibration curve, for which the equation is

$$S = 0.8979 + 3.281 C_{\text{cocaine}}$$

Substituting the sample's signal of 21.4 into the calibration equation gives the concentration of cocaine as 6.249 μM as analyzed. The concentration of cocaine in the original sample, therefore, is

$$\frac{\left\{\dfrac{6.249 \times 10^{-6}\text{ mol}}{\text{L}} \times \dfrac{25.00\text{ mL}}{0.125\text{ mL}} \times 0.02500\text{ L} \times \dfrac{303.36\text{ g}}{\text{mol}} \times \dfrac{1000\text{ mg}}{\text{g}}\right\}}{10.0\text{ mg}} \times 100 = 94.8\%\text{w/w}$$

29. Figure SM13.11 shows the calibration data and the calibration curve, for which the equation is

$$V = 4.632 \times 10^{-3}\text{ mL} + \frac{9.550 \times 10^{-2}\text{ mM mL}}{C_{H_2SO_4}}$$

Substituting in a volume of 0.157 mL for the sample, gives the concentration of H_2SO_4 as 0.627 mM.