

# Chapter 10

1. The following five equations provide the relationships between the four variables included in this problem

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

For the first row, given a wavelength of  $4.50 \times 10^{-9}$  m, we have

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{4.50 \times 10^{-9} \text{ m}} = 6.67 \times 10^{16} \text{ s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{4.50 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 2.22 \times 10^6 \text{ cm}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{4.50 \times 10^{-9} \text{ m}} = 4.42 \times 10^{-17} \text{ J}$$

For the second row, given a frequency of  $1.33 \times 10^{15} \text{ s}^{-1}$ , we have

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{1.33 \times 10^{15} \text{ s}^{-1}} = 2.26 \times 10^{-7} \text{ m}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.26 \times 10^{-7} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 4.42 \times 10^4 \text{ cm}^{-1}$$

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

For the third row, given a wavenumber of  $3215 \text{ cm}^{-1}$ , we have

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{3215 \text{ cm}^{-1}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 3.11 \times 10^{-6} \text{ m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{3.11 \times 10^{-6} \text{ m}} = 9.65 \times 10^{13} \text{ s}^{-1}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ Js})(9.65 \times 10^{13} \text{ s}^{-1}) = 6.39 \times 10^{-20} \text{ J}$$

For the fourth row, given an energy of  $7.20 \times 10^{-19} \text{ J}$ , we have

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{7.20 \times 10^{-19} \text{ J}} = 2.76 \times 10^{-7} \text{ m}$$

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

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.76 \times 10^{-7} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 3.62 \times 10^4 \text{ cm}^{-1}$$

2. The following two equations provide the relationships between the five variables included in this problem

$$A = \epsilon bC \quad A = -\log T$$

For the first row we find that

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

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

For the second row we find that

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

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

For the third row we find that

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

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

For the fourth row we find that

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

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

For the fifth row we find that

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

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

For the sixth row we find that

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

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

For the seventh row we find that

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

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

3. To find the new %*T*, we first calculate the solution's absorbance as it is a linear function of concentration; thus

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

Diluting 25.0 mL of solution to 50.0 mL cuts in half the analyte's concentration and, therefore, its absorbance; thus, the absorbance is 0.228 and the transmittance is

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

4. To find the new %*T*, we first calculate the solution's absorbance as it is a linear function of pathlength; thus

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

Increasing the pathlength by a factor of 10 increases the absorbance by a factor of 10 as well; thus, the absorbance is 0.706 and the transmittance is

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

5. To calculate the expected molar absorptivity,  $\epsilon$ , first we calculate the molar concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$

$$\frac{60.06 \text{ mg K}_2\text{Cr}_2\text{O}_7}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol K}_2\text{Cr}_2\text{O}_7}{294.18 \text{ g K}_2\text{Cr}_2\text{O}_7} = 2.042 \times 10^{-4} \text{ M K}_2\text{Cr}_2\text{O}_7$$

and then the expected molar absorptivity

$$\epsilon = \frac{A}{bC} = \frac{0.640}{(1.00 \text{ cm})(2.042 \times 10^{-4} \text{ M})} = 3134 \text{ M}^{-1} \text{ cm}^{-1}$$

6. For a mixture of  $\text{HA}$  and  $\text{A}^-$ , Beer's law requires that

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

where  $\epsilon_{\text{HA}}$  and  $C_{\text{HA}}$  are the molar absorptivity and the concentration of the analyte's weak acid form,  $\text{HA}$ , and  $\epsilon_{\text{A}}$  and  $C_{\text{A}}$  are the molar absorptivity and the concentration of its weak base form,  $\text{A}^-$ .

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

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

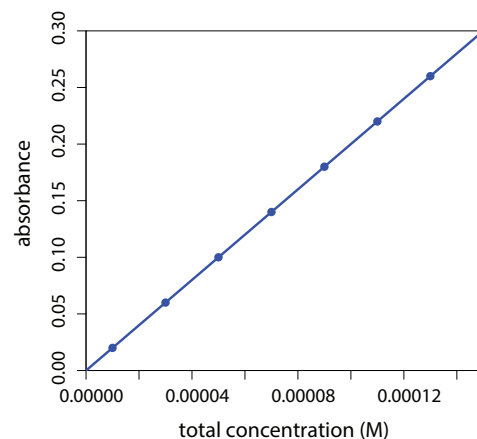
where  $C_{\text{total}} = C_{\text{HA}} + C_{\text{A}}$ ; thus, when  $C_{\text{total}}$  is  $1.0 \times 10^{-5}$ , the absorbance is

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

The remaining absorbance values are calculated in the same way and gathered here is this table

$C_{\text{total}}$ (M)	Absorbance
$1.0 \times 10^{-5}$	0.020
$3.0 \times 10^{-5}$	0.060
$5.0 \times 10^{-5}$	0.100
$7.0 \times 10^{-5}$	0.140
$9.0 \times 10^{-5}$	0.180
$11.0 \times 10^{-5}$	0.220
$13.0 \times 10^{-5}$	0.260

Figure SM10.1 shows the resulting calibration curve, which is linear and shows no deviations from ideal behavior.



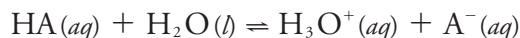
**Figure SM10.1** Beer's law calibration curve for the weak acid in Problem 6a where  $\epsilon_{\text{HA}} = \epsilon_{\text{A}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$ . The blue dots are the calculated absorbance values; the blue line is from a linear regression on the data.

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

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

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

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



for which the equilibrium constant is

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

Given  $C_{\text{total}}$ , we can solve this equation for  $x$ ; for example, when  $C_{\text{total}}$  is  $1.0 \times 10^{-5}$ ,  $x$  is  $7.32 \times 10^{-6}$ . The concentrations of HA and  $\text{A}^-$ , therefore, are

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

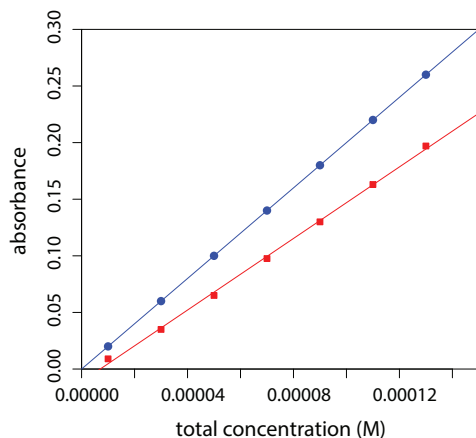
$$C_{\text{A}} = x = 7.32 \times 10^{-6} \text{ M}$$

and the absorbance is

$$A = (2000 \text{ M}^{-1})(2.68 \times 10^{-6} \text{ M}) + (500 \text{ M}^{-1})(7.32 \times 10^{-6} \text{ M}) = 0.009$$

The remaining absorbance values are calculated in the same way and gathered here is this table

$C_{\text{total}}$ (M)	$C_{\text{HA}}$ (M)	$C_{\text{A}}$ (M)	Absorbance
$1.0 \times 10^{-5}$	$2.68 \times 10^{-6}$	$7.32 \times 10^{-6}$	0.009
$3.0 \times 10^{-5}$	$1.35 \times 10^{-5}$	$1.65 \times 10^{-5}$	0.035
$5.0 \times 10^{-5}$	$2.68 \times 10^{-5}$	$2.32 \times 10^{-5}$	0.065
$7.0 \times 10^{-5}$	$4.17 \times 10^{-5}$	$2.83 \times 10^{-5}$	0.098
$9.0 \times 10^{-5}$	$5.64 \times 10^{-5}$	$3.36 \times 10^{-5}$	0.130
$11.0 \times 10^{-5}$	$7.20 \times 10^{-5}$	$3.80 \times 10^{-5}$	0.163
$13.0 \times 10^{-5}$	$8.80 \times 10^{-5}$	$4.20 \times 10^{-5}$	0.197



**Figure SM10.2** Beer's law calibration curves for the weak acid in Problem 6a and 6b: for the data in **blue**,  $\epsilon_{\text{HA}} = \epsilon_{\text{A}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$ , and for the data in **red**,  $\epsilon_{\text{HA}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{A}} = 500 \text{ M}^{-1} \text{ cm}^{-1}$ . For both sets of data, the symbols are the calculated absorbance values and the line is from a linear regression on the data.

Figure SM10.2 shows the resulting calibration curve, in **red**, along with the calibration curve from part (a), in **blue**, for comparison. Two features of the data for part (b) show evidence of a chemical limitation to Beer's law: first, the regression line's  $y$ -intercept deviates from its expected value of zero; and second, the fit of the individual data points to the regression line shows evidence of curvature, with the regression

line underestimating slightly the absorbance values for the largest and the smallest values of  $C_{\text{total}}$ . The source of this error is clear when we look more closely at how  $C_{\text{HA}}$  and  $C_{\text{A}}$  change as a function of  $C_{\text{total}}$ . For example, when  $C_{\text{total}}$  is  $1.0 \times 10^{-5}$ , 73% of the weak acid is present as  $\text{A}^-$ ; however, when  $C_{\text{total}}$  is  $9.0 \times 10^{-5}$ , only 37% of the weak acid is present as  $\text{A}^-$ . Because HA and  $\text{A}^-$  absorb to different extents, increasing  $C_{\text{total}}$  by a factor of  $9 \times$  does not increase the absorbance by a factor of  $9 \times$  (that is, from 0.009 to 0.081), because the relative contribution of the more strongly absorbing HA increases and the relative contribution of the more weakly absorbing  $\text{A}^-$  decreases.

(c) One way to resolve the chemical limitation in part (b) is to buffer the solution, as the relative concentration of HA and  $\text{A}^-$  in a buffer is fixed. The pH of an HA/ $\text{A}^-$  buffer is given by the Henderson-Hasselbalch equation

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

Substituting in a pH of 4.50 and  $C_{\text{total}} - C_{\text{HA}}$  for  $C_{\text{A}}$

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

and solving for  $C_{\text{HA}}$  gives

$$-0.20 = \log \frac{C_{\text{total}} - C_{\text{HA}}}{C_{\text{HA}}}$$

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

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

Given  $C_{\text{total}}$ , we can calculate  $C_{\text{HA}}$ ,  $C_{\text{A}}$ , and the absorbance; for example, when  $C_{\text{total}}$  is  $1.0 \times 10^{-5}$ , we find

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

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

$$A = (2000 \text{ M}^{-1})(6.13 \times 10^{-6} \text{ M}) + (500 \text{ M}^{-1})(3.87 \times 10^{-6} \text{ M}) = 0.015$$

The remaining absorbance values are calculated in the same way and gathered here is this table

$C_{\text{total}}$ (M)	$C_{\text{HA}}$ (M)	$C_{\text{A}}$ (M)	Absorbance
$1.0 \times 10^{-5}$	$6.13 \times 10^{-6}$	$3.87 \times 10^{-6}$	0.015
$3.0 \times 10^{-5}$	$1.84 \times 10^{-5}$	$1.16 \times 10^{-5}$	0.043
$5.0 \times 10^{-5}$	$3.07 \times 10^{-5}$	$1.93 \times 10^{-5}$	0.071

Here is another way to understand the problem. When  $C_{\text{total}}$  is  $1.0 \times 10^{-5}$ , the average molar absorptivity is

$$\epsilon = \frac{0.009}{(1.00 \text{ cm}^{-1})(1.0 \times 10^{-5})}$$

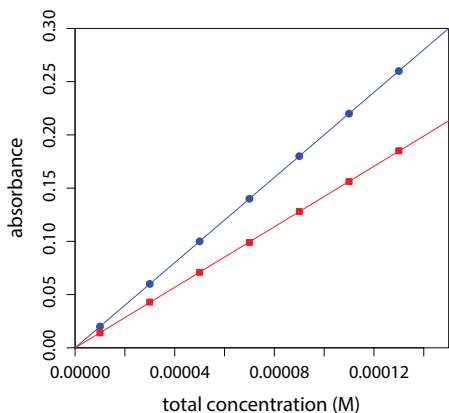
$$\epsilon = 900 \text{ M}^{-1} \text{ cm}^{-1}$$

When  $C_{\text{total}}$  is  $9.0 \times 10^{-5}$ , however, the average molar absorptivity is

$$\epsilon = \frac{0.130}{(1.00 \text{ cm}^{-1})(9.0 \times 10^{-5})}$$

$$\epsilon = 1440 \text{ M}^{-1} \text{ cm}^{-1}$$

See Chapter 6H to review buffers, in general, and the Henderson-Hasselbalch equation, more specifically.



**Figure SM10.3** Beer's law calibration curves for the weak acid in Problem 6a and 6c: for the data in **blue**,  $\epsilon_{\text{HA}} = \epsilon_{\text{A}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$ , and for the data in **red**,  $\epsilon_{\text{HA}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{A}} = 500 \text{ M}^{-1} \text{ cm}^{-1}$ , and the solutions are buffered to a pH of 4.50. For both sets of data, the symbols are the calculated absorbance values and the line is from a linear regression on the data.

$C_{\text{total}}$ (M)	$C_{\text{HA}}$ (M)	$C_{\text{A}}$ (M)	Absorbance
$7.0 \times 10^{-5}$	$4.29 \times 10^{-5}$	$2.71 \times 10^{-5}$	0.099
$9.0 \times 10^{-5}$	$5.52 \times 10^{-5}$	$3.48 \times 10^{-5}$	0.128
$11.0 \times 10^{-5}$	$6.74 \times 10^{-5}$	$4.26 \times 10^{-5}$	0.156
$13.0 \times 10^{-5}$	$7.97 \times 10^{-5}$	$5.03 \times 10^{-5}$	0.185

Figure SM10.3 shows the resulting calibration curve, in **red**, along with the calibration curve from part (a), in **blue**, for comparison. Although the absorbance for each standard is smaller than for the original data—because  $\epsilon_{\text{A}} = 500 \text{ M}^{-1} \text{ cm}^{-1}$  instead of  $2000 \text{ M}^{-1} \text{ cm}^{-1}$  as for the original data—there is no evidence of a chemical limitation to Beer's law: more specifically, the regression line's  $y$ -intercept does not deviate from its expected value of zero, and the fit of the individual data points to the regression line shows no evidence of curvature.

7. (a) Let's begin with the equation

$$A = -\log \frac{P'_{\text{T}} + P''_{\text{T}}}{P'_0 + P''_0}$$

and then expand the logarithmic function on the equation's right side

$$A = \log(P'_0 + P''_0) - \log(P'_{\text{T}} + P''_{\text{T}})$$

Next, we need to find a relationship between  $P_{\text{T}}$  and  $P_0$  (for any wavelength). To do this, we start with Beer's law

$$A = -\log \frac{P_{\text{T}}}{P_0} = \epsilon b C$$

and then solve for  $P_{\text{T}}$  in terms of  $P_0$

$$\log \frac{P_{\text{T}}}{P_0} = -\epsilon b C$$

$$\frac{P_{\text{T}}}{P_0} = 10^{-\epsilon b C}$$

$$P_{\text{T}} = P_0 \times 10^{-\epsilon b C}$$

Substituting this general relationship back into our wavelength-specific equation for absorbance, we obtain

$$A = \log(P'_0 + P''_0) - \log(P'_0 \times 10^{-\epsilon' b C} + P''_0 \times 10^{-\epsilon'' b C})$$

If  $\epsilon' = \epsilon'' = \epsilon$ , then this equation becomes

$$A = \log(P'_0 + P''_0) - \log(P'_0 \times 10^{-\epsilon b C} + P''_0 \times 10^{-\epsilon b C})$$

$$A = \log(P'_0 + P''_0) - \log\{(P'_0 + P''_0) \times 10^{-\epsilon b C}\}$$

$$A = \log(P'_0 + P''_0) - \log(P'_0 + P''_0) - \log(10^{-\epsilon b C})$$

$$A = -\log(10^{-\epsilon b C})$$

which we simplify to arrive at the simple form of Beer's law

$$A = \epsilon b C$$

(b) To calculate the absorbance, we begin with this equation from part (a)

$$A = \log(P'_0 + P''_0) - \log(P'_0 \times 10^{-\epsilon' b C} + P''_0 \times 10^{-\epsilon'' b C})$$

which, given that  $P'_0 = P''_0 = 1$ , we can simplify to

$$A = \log(2) - \log(10^{-\epsilon' b C} + 10^{-\epsilon'' b C})$$

$$A = 0.301 - \log(10^{-\epsilon' b C} + 10^{-\epsilon'' b C})$$

To see how the values of  $\epsilon'$  and  $\epsilon''$  affect the absorbance, we calculate the absorbance for different  $\epsilon$  concentrations of analyte; if the concentration is  $1 \times 10^{-4}$  M and the pathlength is 1.00 cm, then the absorbance is

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

when  $\epsilon' = \epsilon'' = 1000 \text{ M}^{-1} \text{ cm}^{-1}$  and is

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

when  $\epsilon' = 1900 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon'' = 100 \text{ M}^{-1} \text{ cm}^{-1}$ . Additional values for other concentrations are gathered here

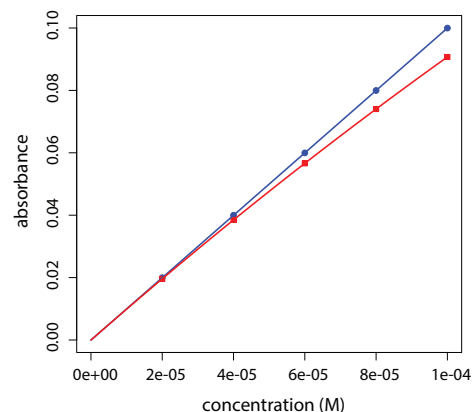
concentration (M)	absorbance when	absorbance when
	$\epsilon' = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon'' = 1000 \text{ M}^{-1} \text{ cm}^{-1}$	$\epsilon' = 1900 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon'' = 100 \text{ M}^{-1} \text{ cm}^{-1}$
$2.0 \times 10^{-5}$	0.020	0.020
$4.0 \times 10^{-5}$	0.040	0.039
$6.0 \times 10^{-5}$	0.060	0.057
$8.0 \times 10^{-5}$	0.080	0.074
$1.0 \times 10^{-4}$	0.100	0.091

with the resulting calibration curves shown in Figure SM10.4. Note that the relative difference between the two sets of data becomes increasingly larger at higher concentrations, suggesting that the calibration curve when  $\epsilon' = 1900 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon'' = 100 \text{ M}^{-1} \text{ cm}^{-1}$  is not a straight-line; this is even easier to see when extended to even greater concentrations, as seen in Figure SM10.5.

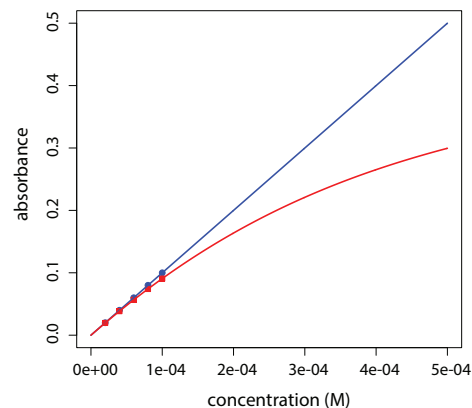
8. The equation that relates  $P_0$ ,  $P_T$ , and  $A$  to each other is

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

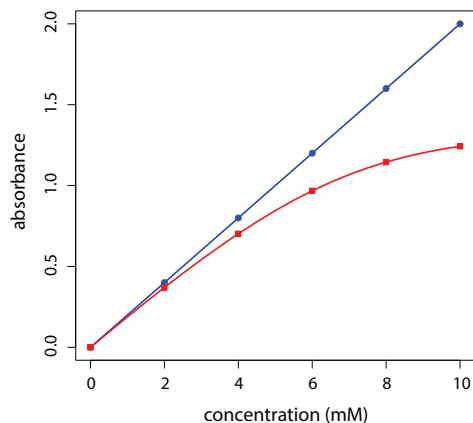
Letting  $P_0 = 100$  and solving for  $P_T$



**Figure SM10.4** Beer's law calibration curves when light is absorbed at two wavelengths: for the data in **blue**,  $\epsilon' = \epsilon'' = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ , and for the data in **red**,  $\epsilon' = 1900 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon'' = 100 \text{ M}^{-1} \text{ cm}^{-1}$ . Figure SM 10.5 shows the same data over a broader range of concentrations.



**Figure SM10.5** Beer's law calibration curves when light is absorbed at two wavelengths: for the data in **blue**,  $\epsilon' = \epsilon'' = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ , and for the data in **red**,  $\epsilon' = 1900 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon'' = 100 \text{ M}^{-1} \text{ cm}^{-1}$ . The individual data points are identical to those in Figure SM 10.4.



**Figure SM10.6** Beer's law calibration curves in the absence of stray light (blue), and in the presence of stray light (red) when  $P_{\text{stray}}$  is 5% of  $P_0$ .

$$P_T = 100 \times 10^{-4}$$

allows us to calculate  $P_T$  for any absorbance; thus, when the absorbance is 0.40,  $P_T$  is 39.8 in the absence of stray light ( $P_{\text{stray}} = 0$ ). When stray light is present at 5% of  $P_0$  (a  $P_{\text{stray}}$  of 5), the absorbance is

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

Results for all samples are summarized in the following table

concentration (mM)	absorbance ( $P_{\text{stray}} = 0$ )	$P_T$	absorbance ( $P_{\text{stray}} = 5$ )
0.0	0.00	100.	0.00
2.0	0.40	39.8	0.37
4.0	0.80	15.8	0.70
6.0	1.20	6.31	0.97
8.0	1.60	2.51	1.15
10.0	2.00	1.00	1.24

and the resulting calibration curves are shown in Figure SM10.6; note that there is substantial curvature when  $P_{\text{stray}}$  is 5% of  $P_0$ .

9. Yes. The new cuvette likely will have a slightly different pathlength and slightly different optical properties than did the original cuvette. The importance of the first difference is obvious because absorbance,  $A$ , is proportional to the cuvette's pathlength,  $b$ .

$$A = \epsilon b C$$

The importance of the second difference is less obvious; however, because absorbance,  $A$ , is related logarithmically to transmittance,  $T$ , and transmittance is inversely proportional to the amount of light that reaches the detector in the absence of analyte,  $P_0$

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

any difference between the optical properties of the two cuvettes introduces a source of determinate error.

10. This method for manganese relies on the direct oxidation of  $\text{Mn}^{2+}$ , which is colorless, to  $\text{MnO}_4^-$ , which is purple. The only critical requirement is that each sample and standard has sufficient time for the oxidation reaction to go to completion: as long as this is true, we can prepare the samples and standards at different times and do not need to reproduce the exact reaction conditions.

The method for glucose, on the other hand, relies on an indirect analysis in which glucose effects the partial reduction of  $\text{Fe}(\text{CN})_6^{3-}$ , which is yellow, to  $\text{Fe}(\text{CN})_6^{4-}$ , which is colorless. The extent of this



reaction depends on the reaction's kinetics, which means that maintaining a constant reaction time and reaction temperature for all samples and standards is critical.

11. (a) A blank should contain all reagents except the analyte; thus, the blank for this procedure should include 5 mL of thioglycolic acid, 2 mL of 20% w/v ammonium citrate, and 5 mL of 0.22 M  $\text{NH}_3$  diluted to 50 mL in a volumetric flask.

(b) No effect. By including ammonium citrate and thioglycolic acid in the blank, we account for the contribution of any trace impurity of iron.

(c) The choice to use a sample that contains approximately 0.1 g of  $\text{Fe}^{3+}$  ensures that the sample, as prepared, has a concentration of  $\text{Fe}^{3+}$  that falls within the range of concentrations of the external standards. To see that this is true, note that bringing 100 mg of  $\text{Fe}^{3+}$  to volume in a 1-L volumetric flask gives a solution that is 100 ppm  $\text{Fe}^{3+}$ . Diluting a 1-mL portion of this solution to 50 mL gives a final concentration of 2 ppm  $\text{Fe}^{3+}$ .

(d) Because we underestimate the 100-mL volumetric flask's true volume, the actual concentration of the 100-ppm  $\text{Fe}^{3+}$  standard is greater than 100 ppm. We use this standard to prepare all subsequent standards; thus, in turn, we underreport their concentrations. As we see in Figure SM10.7, if we use the resulting calibration curve, we will underreport the concentration of  $\text{Fe}^{3+}$  in our samples.

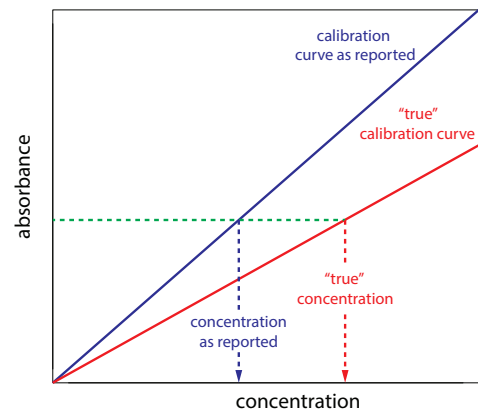
12. Let's assume our sample is 50% w/w Fe as this is in the middle of the expected range of concentrations. The concentration of iron in the 1-L volumetric flask, and thus the concentration of iron in the 5-mL volumetric pipet, is

$$\frac{0.5 \text{ g sample} \times \frac{50 \text{ g Fe}}{100 \text{ g sample}} \times \frac{1000 \text{ mg}}{\text{g}}}{1.0 \text{ L}} = 250 \text{ mg/L Fe}$$

We can dilute the 5-mL sample of this solution in one of many possible volumetric flasks, which give us a range of possible concentrations to consider; thus

volumetric flask	mg Fe/L	volumetric flask	mg Fe/L
10 mL	125	250 mL	5
25 mL	50	500 mL	2.5
50 mL	25	1000 mL	1.25
100 mL	12.5		

Our standard solutions of iron have concentrations that range from 5-20 mg/L. To avoid the need to extrapolate the calibration curve to a higher concentration of iron, which increases uncertainty, we do not



**Figure SM10.7** Illustration showing how underestimating the concentration of a standard results in underreporting the concentration of analyte in the sample: text and lines in blue are data and results as reported; text and lines in red show the “true” results; and the dashed green line shows the sample’s absorbance.

See Chapter 5D to review linear regression and the affect of an extrapolation on the uncertainty in a regression line’s slope and  $y$ -intercept.

want to use the 10-mL, 25-mL, or 50-mL volumetric flasks. The best option is the 100-mL volumetric flask as this ensures that the samples have concentrations of iron that fall near the center of the calibration curve where the uncertainty in the calibration curve is at its smallest.

13. (a) If the cola is colored, then it will contribute to the measured absorbance and interfere with the analysis. Because the ingredients for commercial colas are proprietary, it is not possible to prepare a blank that corrects for this absorbance.

(b) One approach is to include a step in the procedure in which we either extract the analyte,  $\text{PO}_4^{3-}$ , from the sample, or extract from the sample those constituents responsible for the color.

(c) The presence of gas bubbles in the optical path shortens the path-length through the sample, which introduces a systematic error; bubbles also scatter light, which introduces additional random error into the analysis.

(d) A suitable blank will consist of 2 mL of the ascorbic acid reducing solution diluted 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  $\text{P}_2\text{O}_5$  as 0.8125 ppm. The concentration of P in the sample as analyzed is

$$\frac{0.8125 \text{ mg P}_2\text{O}_5}{\text{L}} \times \frac{61.95 \text{ g P}}{141.94 \text{ g P}_2\text{O}_5} = 0.3546 \text{ mg P/L}$$

or 0.3546 ppm P. The concentration of P in the original sample is

$$0.3546 \text{ ppm P} \times \frac{5.00 \text{ mL}}{250 \mu\text{L}} \times \frac{1000 \mu\text{L}}{\text{mL}} \times \frac{50.00 \text{ mL}}{2.50 \text{ mL}} = 142 \text{ mg P/L}$$

14. (a) Using Beer's law for copper at a wavelength of 732.0 nm

$$A = 0.338 = \epsilon b C = (95.2 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}}$$

we find that the concentration of  $\text{Cu}^{2+}$  is  $3.55 \times 10^{-3} \text{ M}$ .

(b) For a binary mixture of copper and cobalt, we must solve the following pair of simultaneous equations derived from Beer's law

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

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

Multiplying through the second equation by 2.11/15.8 and then subtracting the second equation from the first equation gives

$$0.4387 = (94.89 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}}$$

for which we find that the concentration of  $\text{Cu}^{2+}$  is  $4.62 \times 10^{-3}$  M. Substituting this concentration back into either of the first two equations gives the concentration of  $\text{Co}^{2+}$  as  $6.24 \times 10^{-3}$  M.

(c) For a ternary mixture of copper, cobalt, and nickel we must solve the following three simultaneous equations derived from Beer's law

$$\begin{aligned} 0.423 &= (2.11 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Co}} \\ &\quad + (95.2 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}} \\ &\quad + (3.03 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}} \\ 0.184 &= (15.8 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Co}} \\ &\quad + (2.32 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}} \\ &\quad + (1.79 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}} \\ 0.291 &= (3.11 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Co}} \\ &\quad + (7.73 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}} \\ &\quad + (13.5 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}} \end{aligned}$$

Multiplying through the first equation by 15.8/2.11 and then subtracting the first equation from the second equation gives

$$\begin{aligned} -2.9835 &= -(710.55 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}} \\ &\quad - (20.899 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}} \end{aligned}$$

Multiplying through the third equation by 15.8/3.11 and then subtracting the second equation from the third equation gives

$$\begin{aligned} -1.2944 &= -(36.951 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Cu}} \\ &\quad - (66.795 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}} \end{aligned}$$

With two equations and two unknowns, we solve these equations using the same general approach; thus, multiplying through the second of these equations by 710.55/36.951 and subtracting from the first equation leaves us with

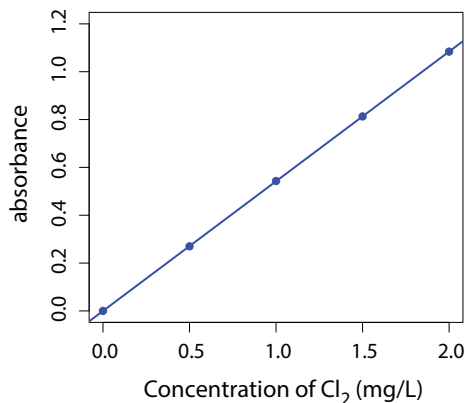
$$21.907 = (1263.54 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{Ni}}$$

for which the concentration of  $\text{Ni}^{2+}$  is  $1.73 \times 10^{-2}$  M. Substituting back gives the concentration of  $\text{Cu}^{2+}$  as  $3.69 \times 10^{-3}$  M and the concentration of  $\text{Co}^{2+}$  as  $9.14 \times 10^{-3}$  M.

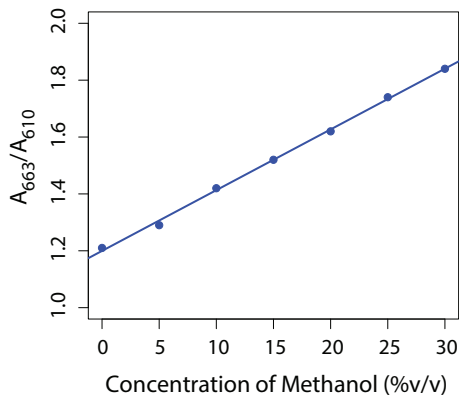
15. For the standard solution of phenol we have

$$A = 0.424 = abC = a(1.00 \text{ cm})(4.00 \text{ ppm})$$

where  $a$  is phenol's absorptivity (which we use here in place of the molar absorptivity,  $\epsilon$ , because concentration is expressed in ppm instead of M). Solving for  $a$  gives its value as  $0.106 \text{ ppm}^{-1} \text{ cm}^{-1}$ . Using this value of  $a$ , we find that the concentration of phenol in the sample as analyzed is



**Figure SM10.8** Calibration data and calibration curve for Problem 17. The **blue** dots give the absorbance values for the blank and for the standards, and the **blue** regression line is the best fit to the data.



**Figure SM10.9** Calibration data and calibration curve for Problem 18. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

$$C_{\text{phenol}} = \frac{A}{ab} = \frac{0.394}{(0.106 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} = 3.72 \text{ ppm}$$

Because we diluted the original sample by a factor of  $2\times$ , the concentration of phenol in the original sample is 7.44 ppm.

16. Substituting the absorbance into the equation for the calibration curve gives the concentration of  $\text{Fe}^{2+}$  as  $1.16 \times 10^{-5} \text{ M}$ , or

$$\frac{1.16 \times 10^{-5} \text{ mol Fe}^{2+}}{\text{L}} \times \frac{55.845 \text{ g Fe}^{2+}}{\text{mol Fe}^{2+}} \times \frac{1000 \text{ mg}}{\text{g}} = 0.648 \text{ mg Fe}^{2+}/\text{L}$$

17. Figure SM10.8 shows the calibration curve for the four standards and the blank, the calibration equation for which is

$$A = -2.0 \times 10^{-4} + (0.5422 \text{ mg}^{-1} \text{ L}) \times C_{\text{Cl}_2}$$

Substituting the sample's absorbance into the calibration equation gives the concentration of  $\text{Cl}_2$  as 0.209 mg  $\text{Cl}_2/\text{L}$ .

18. Figure SM10.9 shows the calibration curve for the seven standards, the calibration equation for which is

$$\frac{A_{663}}{A_{610}} = 1.200 + (2.136 \times 10^{-2} \%v/v^{-1}) C_{\text{methanol}}$$

For the sample, we have  $A_{663}/A_{610} = 1.07/0.75 = 1.427$ , which, when substituted back into the calibration equation gives the concentration of methanol in the sample as 10.6% v/v.

19. The spectrophotometric determination of serum barbiturates uses the absorbance at a pH of 10 as a means of correcting the absorbance at a pH of 13 for contributions from the sample's matrix; thus, the corrected absorbance for any standard or sample is

$$A_{\text{barb}} = A_{\text{pH}13} - \frac{V_{\text{samp}} + V_{\text{NH}_4\text{Cl}}}{V_{\text{samp}}} \times A_{\text{pH}10}$$

Using the data for the standard, we find a corrected absorbance of

$$A_{\text{barb}} = 0.295 - \frac{3.00 \text{ mL} + 0.50 \text{ mL}}{3.00 \text{ mL}} \times 0.002 = 0.293$$

Substituting this absorbance into Beer's law

$$0.293 = a(1.00 \text{ cm})(3.0 \text{ mg}/100 \text{ mL})$$

gives an absorptivity,  $a$ , of  $9.77 \text{ mL cm}^{-1} \text{ mg}^{-1}$  for barbital. The corrected absorbance for the sample is

$$A_{\text{barb}} = 0.115 - \frac{3.00 \text{ mL} + 0.50 \text{ mL}}{3.00 \text{ mL}} \times 0.023 = 0.0882$$

which gives the concentration of barbital as

$$C_{\text{barb}} = \frac{A_{\text{barb}}}{ab} = \frac{0.0882}{(9.77 \text{ mL cm}^{-1} \text{ mg}^{-1})(1.00 \text{ cm})} = 9.0 \times 10^{-3} \text{ mg/mL}$$

or 0.90 mg/100 mL.

20. The concentration of aspirin,  $C_{\text{asp}}$ , is determined using the absorbance at 277 nm where it is the only analyte that absorbs; thus

$$0.600 = (0.00682 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{\text{asp}}$$

which gives  $C_{\text{asp}}$  as 87.98 ppm in the sample as analyzed. To find the amount of aspirin in the analgesic tablet, we account for the sample preparation

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

To find the concentrations of caffeine,  $C_{\text{caf}}$ , and of phenacetin,  $C_{\text{phen}}$ , we must solve the following pair of simultaneous equations for the absorbance at 250 nm and at 275 nm where they are the only analytes that absorb

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

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

Multiplying through the second equation by 0.0131/0.0485 and then subtracting the second equation from the first equation gives

$$0.4217 = (0.06591 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}^{-1}) C_{\text{phen}}$$

for which we find that the concentration of phenacetin is 6.40 ppm. Substituting this concentration back into either of the first two equations gives the concentration of caffeine as 1.29 ppm. These are their respective concentrations as analyzed; the amount of each in the analgesic tablet is

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

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

21. The concentration of  $\text{SO}_2$  in the standard as analyzed is

$$15.00 \text{ ppm SO}_2 \times \frac{1.00 \text{ mL}}{25.00 \text{ mL}} = 0.600 \text{ ppm SO}_2$$

Substituting this concentration into Beer's law

$$0.181 = a(1.00 \text{ cm})(0.600 \text{ ppm SO}_2)$$

we find that the absorptivity,  $a$ , of  $\text{SO}_2$  is  $0.302 \text{ ppm}^{-1} \text{ cm}^{-1}$ . Next, we calculate the concentration of  $\text{SO}_2$  in the sample as analyzed, finding that it is

$$C_{\text{SO}_2} = \frac{A}{bC} = \frac{0.485}{(1.00 \text{ cm})(0.302 \text{ ppm}^{-1} \text{ cm}^{-1})} = 1.61 \text{ ppm SO}_2$$

This is, of course, the concentration of  $\text{SO}_2$  in solution; to find its concentration in the sample of air, we determine the micrograms of  $\text{SO}_2$  in the sample

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

the mass of the air collected

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

and the concentration

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

22. To find the amount of carbon monoxide in a sample, we first calculate the partial pressure of CO using the equation for the calibration curve, and then calculate the %CO relative to the total pressure; for example, the partial pressure of CO in the first sample is

$$P_{\text{CO}} = \frac{0.1146 + 1.1 \times 10^{-4}}{9.9 \times 10^{-4} \text{ torr}^{-1}} = 116 \text{ torr}$$

which makes the %CO in the sample

$$\frac{116 \text{ torr}}{595 \text{ torr}} \times 100 = 19.5\%$$

The results for all five samples are gathered here

absorbance	$P_{\text{CO}}$ (torr)	$P_{\text{total}}$ (torr)	%CO
0.1146	116	595	19.5
0.0642	65.0	354	18.4
0.0591	59.8	332	18.0
0.0412	41.7	233	17.9
0.0254	25.8	143	18.0

The mean and the standard deviation for the five samples are 18.4% CO and 0.666 %CO, respectively, which gives us a 95% confidence interval of

$$\mu = \bar{X} \pm \frac{ts}{\sqrt{n}} = 18.4 \pm \frac{(2.776)(0.666)}{\sqrt{5}} = 18.4 \pm 0.8\% \text{ CO}$$

23. For this internal standardization, the calibration curve plots the analyte's absorbance relative to the internal standard's absorbance ( $A_{1494}/A_{2064}$ ) on the  $y$ -axis versus the mass of polystyrene on the  $x$ -axis. Figure SM10.10 shows the resulting calibration data and calibration curve for which the calibration equation is

$$\frac{A_{1494 \text{ cm}^{-1}}}{A_{2064 \text{ cm}^{-1}}} = 6.97 \times 10^{-3} + (1.456 \text{ g}^{-1}) m_{\text{polystyrene}}$$

To determine the concentration of polystyrene in a sample, we first use the sample's absorbance at  $1494 \text{ cm}^{-1}$  and at  $2064 \text{ cm}^{-1}$  to calculate the mass of polystyrene in the sample, and then calculate the %w/w polystyrene relative to the sample's mass; thus, for the first replicate we have

$$m_{\text{polystyrene}} = \frac{0.2729}{0.3582} - 6.97 \times 10^{-3}}{1.456 \text{ g}^{-1}} = 0.5185 \text{ g}$$

$$\frac{0.5185 \text{ g polystyrene}}{0.8006 \text{ g sample}} \times 100 = 64.76\% \text{ w/w polystyrene}$$

The results for all three replicates are 64.76%, 62.50%, and 65.00% with a mean of 64.09% and a standard deviation of 1.38%. To determine if there is evidence of a determinate error, we use a  $t$ -test of the following null and alternative hypotheses

$$H_0: \bar{X} = \mu \quad H_A: \bar{X} \neq \mu$$

The test statistic is

$$t_{\text{exp}} = \frac{|\mu - \bar{X}| \sqrt{n}}{s} = \frac{|67 - 64.09| \sqrt{3}}{1.38} = 3.65$$

which is smaller than the critical value for  $t(0.05, 2)$  of 4.303; thus, we do not have evidence of a determinate error at  $\alpha = 0.05$ .

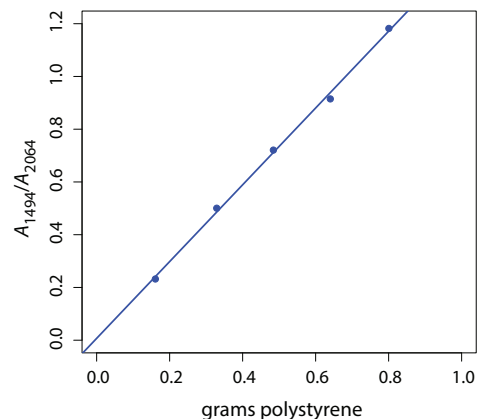
24. The optimum wavelengths are those where the ratio of  $\epsilon_{\text{Cu}}/\epsilon_{\text{Ba}}$  has its maximum and its minimum value. As we see in Figure SM10.11, the optimum wavelengths are at approximately 613 nm and at 658 nm.
25. (a) Figure SM10.12 shows a plot that displays  $A_{\text{mix}}/A_{\text{Ti}}$  on the  $y$ -axis and  $A_{\text{V}}/A_{\text{Ti}}$  on the  $x$ -axis. A linear regression analysis of the calibration data gives a calibration equation of

$$\frac{A_{\text{mix}}}{A_{\text{Ti}}} = 0.4993 + 0.6069 \times \frac{A_{\text{V}}}{A_{\text{Ti}}}$$

with the  $y$ -intercept equivalent to  $(C_{\text{Ti}})_{\text{sample}}/(C_{\text{Ti}})_{\text{standard}}$  and with the slope equivalent to  $(C_{\text{V}})_{\text{sample}}/(C_{\text{V}})_{\text{standard}}$ ; thus

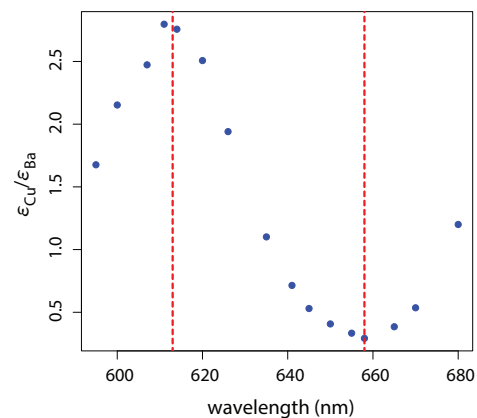
$$(C_{\text{Ti}})_{\text{sample}} = 63.1 \text{ ppm} \times 0.4993 = 31.5 \text{ ppm Ti(IV)}$$

$$(C_{\text{V}})_{\text{sample}} = 96.4 \text{ ppm} \times 0.6069 = 58.5 \text{ ppm V(V)}$$

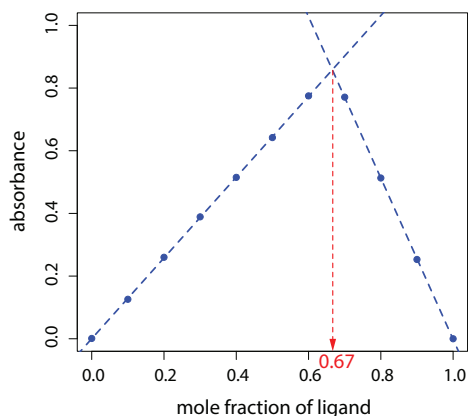


**Figure SM10.10** Internal standards calibration curve for the data in Problem 23. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.

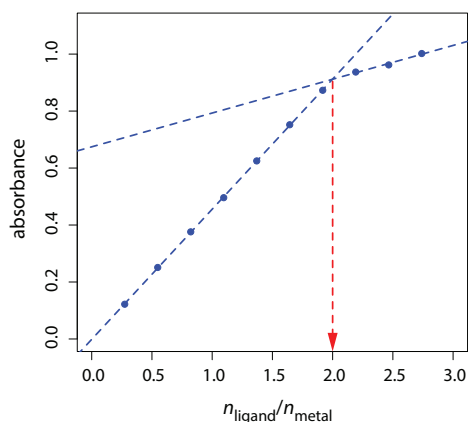
To review the  $t$ -test, see Chapter 4F.



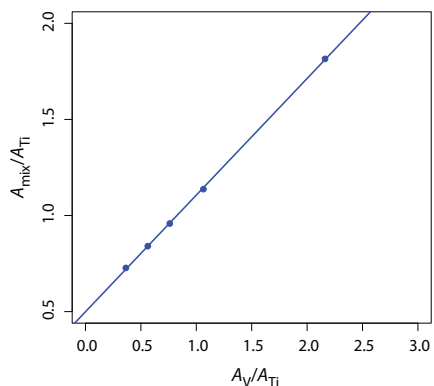
**Figure SM10.11** Plot showing the relative absorptivity of copper and barium. The points in blue are the data from Problem 24; the dashed red lines show the wavelengths where the difference in their relative absorptivities are at their greatest.



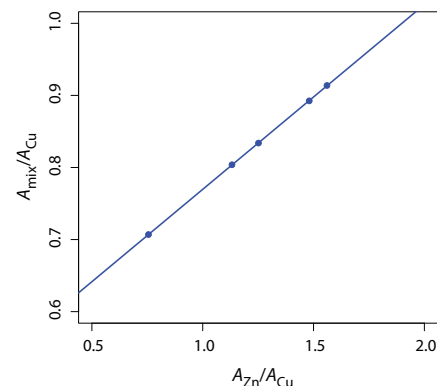
**Figure SM10.14** Continuous variations plot for the data (blue dots) in Problem 26. The intersection of the data's left branch and its right branch, as shown by the dashed blue lines and the dashed red line, gives the mole fraction of ligand in the complex.



**Figure SM10.15** Mole-ratio plot for the data (blue dots) in Problem 27. The intersection of the data's left branch and its right branch, as shown by the dashed blue lines and the dashed red line, gives the ratio of ligand-to-metal in the complex.



**Figure SM10.12** Calibration data and calibration curve for Problem 25a. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.



**Figure SM10.13** Calibration data and calibration curve for Problem 25b. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.

(b) To correct the absorbance values for the contribution of PAR, we subtract its absorbance at each wavelength from the absorbance of each standard and from the absorbance of the mixture; for example, at a wavelength of 480 nm, the corrected absorbance values are 0.487 for  $\text{Cu}^{2+}$ , 0.760 for  $\text{Zn}^{2+}$ , and 0.445 for the mixture. Figure SM10.13 shows a plot that displays  $A_{\text{mix}}/A_{\text{Cu}}$  on the  $y$ -axis and  $A_{\text{Zn}}/A_{\text{Cu}}$  on the  $x$ -axis. A linear regression analysis of the calibration data gives a calibration equation of

$$\frac{A_{\text{mix}}}{A_{\text{Cu}}} = 0.5134 + 0.2563 \times \frac{A_{\text{Zn}}}{A_{\text{Cu}}}$$

with the  $y$ -intercept equivalent to  $(C_{\text{Cu}})_{\text{sample}}/(C_{\text{Cu}})_{\text{standard}}$  and with the slope equivalent to  $(C_{\text{Zn}})_{\text{sample}}/(C_{\text{Zn}})_{\text{standard}}$ ; thus

$$(C_{\text{Cu}})_{\text{sample}} = 1.00 \text{ ppm} \times 0.5134 = 0.51 \text{ ppm Cu}^{2+}$$

$$(C_{\text{Zn}})_{\text{sample}} = 1.00 \text{ ppm} \times 0.2563 = 0.26 \text{ ppm Zn}^{2+}$$

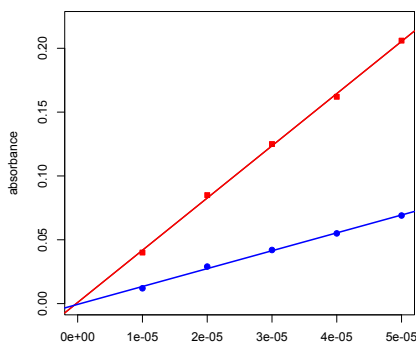
26. Figure SM10.14 shows the continuous variations plot for the data, in which the  $x$ -axis is defined by the mole fraction of ligand in each sample. The intersection of the plot's left branch and its right branch is at  $X_{\text{L}} = 0.67$ ; thus, the metal-ligand complex's stoichiometry is

$$\frac{n_{\text{ligand}}}{n_{\text{metal}}} = \frac{X_{\text{L}}}{1 - X_{\text{L}}} = \frac{0.67}{0.33} = 2$$

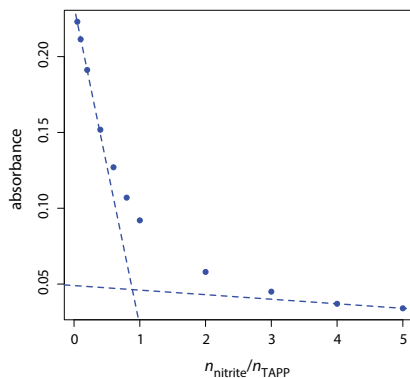
and the complex is  $\text{ML}_2$ .

27. Figure SM10.15 shows the mole-ratio plot for the data, in which the  $x$ -axis is defined by the ratio of ligand-to-metal in each sample. The intersection of the two linear branches is at a mole ratio of 2; thus, the metal-ligand complex's stoichiometry is  $\text{ML}_2$ .





**Figure SM10.16** Slope-ratio plot for the data (blue dots) in Problem 28. The red data points and line are for the metal, and the blue data points and line are for the ligand.



**Figure SM10.17** Mole-ratio plot for the data (blue dots) in Problem 28. The intersection of the data's left branch and its right branch, as shown by the two dashed blue lines, gives the ratio of ligand-to-metal in the complex.

28. Figure SM10.16 shows the slope-ratio plot for the data, in which the  $x$ -axis is the concentration of metal or the concentration of ligand. The slope for the metal's data is  $1400 \text{ M}^{-1}$  and the slope for the ligand's data is  $4090 \text{ M}^{-1}$ ; thus,

$$\frac{n_{\text{metal}}}{n_{\text{ligand}}} = \frac{\text{slope for metal}}{\text{slope for ligand}} = \frac{4090 \text{ M}^{-1}}{1400 \text{ M}^{-1}} = 2.92 \approx 3$$

The metal-ligand complex's stoichiometry, therefore, is  $\text{ML}_3$ .

29. As shown in Figure SM10.17, the data are best treated using a mole-ratio plot of absorbance versus the ratio of moles  $\text{NO}_2^-$ -to-moles TAPP. The intersection of the two line segments suggests that the stoichiometry is 1:1.
30. The relationship between the three absorbance values, the solution's pH, and the indicator's  $\text{p}K_a$  is

$$\text{p}K_a = \text{pH} - \log \frac{A - A_{\text{HIIn}}}{A_{\text{In}} - A}$$

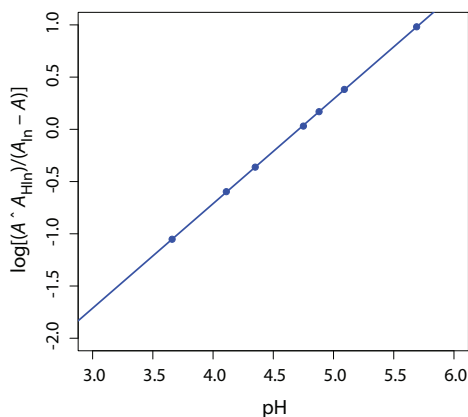
Substituting known values gives the indicator's  $\text{p}K_a$  as

$$\text{p}K_a = 4.17 - \log \frac{0.439 - 0.673}{0.118 - 0.439} = 4.31$$

31. Looking at the table, we note that the absorbance is the same for solutions with pH levels of 1.53 and 2.20, which tells us that  $A_{\text{HIIn}}$  is 0.010. We also note that the absorbance is the same for solutions with pH levels of 7.20 and 7.78, which tells us that  $A_{\text{In}}$  is 0.317. Using these values, we calculate

$$\log \frac{A - A_{\text{HIIn}}}{A_{\text{In}} - A}$$

We have sufficient information here to place some limits on the indicator's  $\text{p}K_a$ . A ladder diagram for any weak acid suggests that we will find its weak acid form, HA, as the only significant species when  $\text{pH} < \text{p}K_a - 1$ , and that we will find its weak base form,  $\text{A}^-$ , as the only significant species when  $\text{pH} > \text{p}K_a + 1$ ; thus, we expect that the indicator's  $\text{p}K_a$  is greater than 3.20 and less than 6.20.



**Figure SM10.18** Plot of the data from Problem 31. The blue dots are the individual values from the table and the blue line is the result of a linear regression of this data.

for the pH levels where both  $\text{HIn}$  and  $\text{In}^-$  are present, gathering together the results in the following table and in Figure SM10.18.

pH	$\log\left(\frac{A - A_{\text{HIn}}}{A_{\text{In}} - A}\right)$
3.66	-1.052
4.11	-0.597
4.35	-0.362
4.75	0.031
4.88	0.169
5.09	0.382
5.69	0.982

A regression analysis of the data in Figure SM10.18 gives a slope of  $-4.716$ , or a  $\text{p}K_a$  for the indicator of  $4.72$ .

32. (a) First, we need to convert the limits for the analyte's % $T$  to limits for its absorbance; thus

$$A = -\log T = -\log(0.15) = 0.82$$

$$A = -\log T = -\log(0.85) = 0.071$$

Next, we convert these limits for the analyte's absorbance to limits for its concentration; thus

$$C = \frac{A}{\epsilon b} = \frac{0.82}{(1138 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} = 7.2 \times 10^{-4} \text{ M}$$

$$C = \frac{A}{\epsilon b} = \frac{0.071}{(1138 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} = 6.2 \times 10^{-5} \text{ M}$$

or between  $6.2 \times 10^{-5} \text{ M}$  and  $7.2 \times 10^{-4} \text{ M}$ .

(b) A sample that is  $10 \mu\text{M}$  in analyte has a concentration that is  $1.0 \times 10^{-5} \text{ M}$ , which is less than our lower limit. To increase the absorbance we can try concentrating the analyte or we can use a sample cell that has a longer pathlength. A sample that is  $0.1 \text{ mM}$  in analyte has a concentration of  $1.0 \times 10^{-4} \text{ M}$ ; as this falls within our limits, we can analyze the sample as is. A sample that is  $1.0 \text{ mM}$  in analyte has a concentration of  $1.0 \times 10^{-3} \text{ M}$ , which is more than our upper limit. To decrease the absorbance, we can dilute the sample or we can use a sample cell that has a shorter pathlength.

33. (a) The sample's absorbance is

$$A = \epsilon b C =$$

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

or a transmittance,  $T$ , of  $10^{-A} = 10^{-2.0} = 0.01$ . From Table 10.8, we know that the relative uncertainty in concentration is

$$\frac{s_C}{C} = \frac{0.434s_T}{T \log T} = \frac{(0.434)(\pm 0.002)}{(0.01)\log(0.01)} = \pm 0.043$$

or 4%.

(b) If we use a blank that is  $1.0 \times 10^{-4}$  M in analyte, then the analyte's apparent concentration is  $2.0 \times 10^{-4}$  M  $- 1.0 \times 10^{-4}$  M, or  $1.0 \times 10^{-4}$  M. In this case the sample's absorbance is

$$A = \epsilon b C =$$

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

or a transmittance,  $T$ , of  $10^{-A} = 10^{-1.0} = 0.1$ . From Table 10.8, we know that the relative uncertainty in concentration is

$$\frac{s_C}{C} = \frac{0.434s_T}{T \log T} = \frac{(0.434)(\pm 0.002)}{(0.1)\log(0.1)} = \pm 0.00868$$

or 0.9%.

34. Figure SM10.19 shows the calibration data and the calibration curve, the equation for which is

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

Substituting the sample's absorbance into the calibration equation and solving for  $C_P$  gives

$$C_P = \frac{0.135 + 1.186 \times 10^{-2}}{2.854 \times 10^{-5} \text{ ppm}^{-1}} = 5146 \text{ ppm P}$$

Converting the concentration of P in the sample into an equivalent mass of  $\text{Na}_2\text{HPO}_4$

$$\frac{5146 \text{ mg P}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times 0.1000 \text{ L} \times \frac{141.96 \text{ g Na}_2\text{HPO}_4}{30.974 \text{ g P}} = 2.359 \text{ g Na}_2\text{HPO}_4$$

The sample's purity, therefore, is

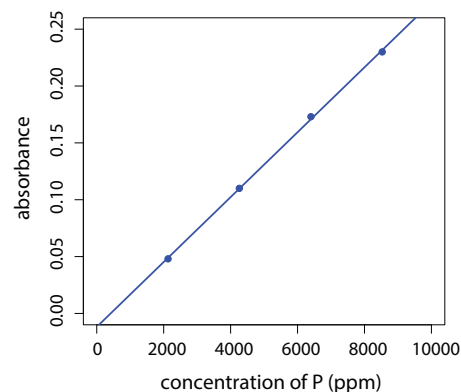
$$\frac{2.359 \text{ g Na}_2\text{HPO}_4}{2.469 \text{ g sample}} \times 100 = 95.5\% \text{ pure}$$

35. (a) Figure SM10.20 shows the calibration data and the calibration curve for the analysis of copper, for which the calibration curve's equation is

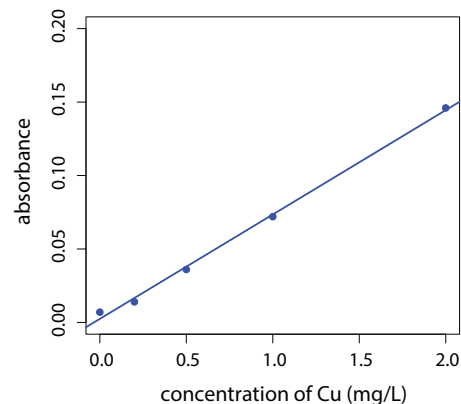
$$A = 2.429 \times 10^{-3} + (7.104 \times 10^{-2} \text{ mg}^{-1} \text{ L}) \times C_{\text{Cu}}$$

Substituting the sample's absorbance into the calibration equation and solving for  $C_{\text{Cu}}$  gives

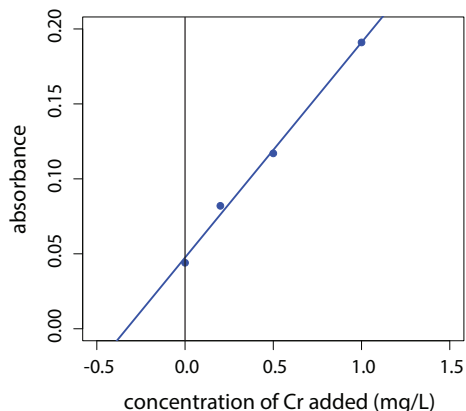
$$C_{\text{Cu}} = \frac{0.027 - 2.429 \times 10^{-3}}{7.104 \times 10^{-2} \text{ mg}^{-1} \text{ L}} = 0.346 \text{ mg Cu/L}$$



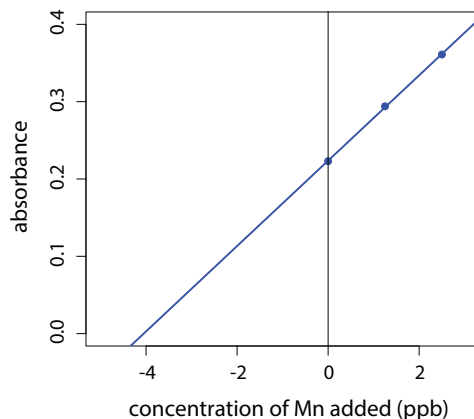
**Figure SM10.19** Calibration data and calibration curve for Problem 34. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.



**Figure SM10.20** Calibration data and calibration curve for Problem 35a. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.



**Figure SM10.21** Calibration data and calibration curve for Problem 35b. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.



**Figure SM10.22** Calibration data and calibration curve for Problem 36. The blue dots give the absorbance values for the standards, and the blue regression line is the best fit to the data.

Accounting for the sample's preparation gives the concentration of copper in the original sample as

$$\frac{0.346 \text{ mg Cu}}{\text{L}} \times \frac{500.0 \text{ mL}}{200.0 \text{ mL}} = 0.865 \text{ mg Cu/L}$$

(b) Figure SM10.21 shows the calibration data and the calibration curve for the analysis of chromium, for which the calibration curve's equation is

$$A = 4.750 \times 10^{-2} + (0.1435 \text{ mg}^{-1} \text{ L}) \times C_{\text{Cr}}$$

For a standard addition, the concentration of chromium is the absolute value of the  $x$ -intercept; thus, setting the absorbance to zero and solving

$$\frac{0 - 4.750 \times 10^{-2}}{0.1435 \text{ mg}^{-1} \text{ L}} = -0.331 \text{ mg Cr/L}$$

gives  $C_{\text{Cr}}$  as 0.331 mg/L for the sample as analyzed. Accounting for the sample's preparation gives the concentration of chromium in the original sample as

$$\frac{0.331 \text{ mg Cr}}{\text{L}} \times \frac{50.0 \text{ mL}}{200.0 \text{ mL}} = 0.0828 \text{ mg Cr/L}$$

36. The concentration of  $\text{Mn}^{2+}$  added to the sample in the three standard additions are 0.00, 1.25, and 2.50 ppb, respectively. Figure SM10.22 shows the calibration data and the calibration curve, for which the calibration equation is

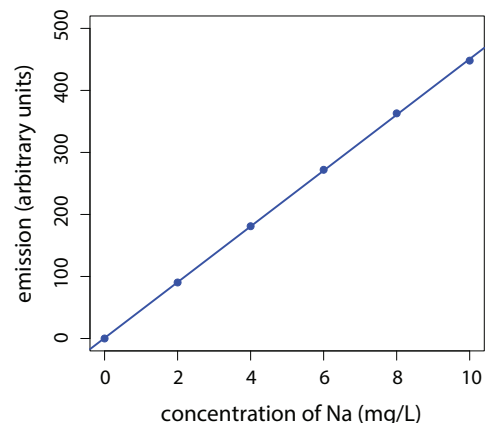
$$A = 0.224 + (0.0552 \text{ ppb}^{-1}) C_{\text{Mn}}$$

For a standard addition, the concentration of chromium is the absolute value of the  $x$ -intercept; thus, setting the absorbance to zero and solving

$$\frac{0 - 0.224}{0.0552 \text{ ppb}^{-1}} = -4.06 \text{ ppb Mn}$$

gives  $C_{\text{Mn}}$  as 4.06 ppb for the sample as analyzed. Accounting for the sample's preparation gives the concentration of  $\text{Mn}^{2+}$  in the original sample as

$$\left( \frac{4.06 \text{ ppb Mn}^{2+} \times \frac{5.0 \mu\text{L}}{2.5 \mu\text{L}} \times \frac{100.0 \text{ mL}}{1.000 \text{ mL}} \times 0.05000 \text{ L}}{1.00 \text{ L seawater}} \right) = 40.6 \text{ ppb Mn}^{2+}$$



**Figure SM10.23** Calibration data and calibration curve for Problem 37. The **blue** dots give the emission values for the standards, and the **blue** regression line is the best fit to the data.

37. Figure SM10.23 shows the calibration data and the calibration curve for the analysis of sodium, for which the calibration curve's equation is

$$I = 0.7810 + (44.99 \text{ mg}^{-1} \text{ L}) \times C_{\text{Na}}$$

Substituting the sample's emission into the calibration equation and solving for  $C_{\text{Na}}$  gives

$$C_{\text{Na}} = \frac{238 - 0.7810}{44.99 \text{ mg}^{-1} \text{ L}} = 5.273 \text{ mg Na/L}$$

Accounting for the sample's preparation gives the concentration of sodium in the original sample as

$$\frac{\frac{5.273 \text{ mg Na}}{\text{L}} \times 0.0500 \text{ mL} \times \frac{1000 \mu\text{g}}{\text{mg}}}{4.0264 \text{ g sample}} = 65.5 \mu\text{g Na/g sample}$$

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

$$\frac{5.72 + 0.03}{1.594 \text{ mg}^{-1} \text{ L}} = 3.607 \text{ mg Fe}^{3+} / \text{L}$$

Accounting for the sample's preparation gives the concentration of iron in the original sample as

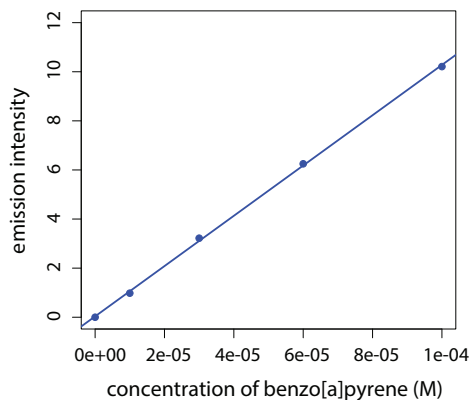
$$\frac{\frac{3.607 \text{ mg Fe}^{3+}}{\text{L}} \times 0.05000 \text{ L} \times \frac{1000 \mu\text{g}}{\text{mg}}}{0.5113 \text{ g sample}} = 353 \mu\text{g Fe}^{3+} / \text{g sample}$$

39. For a single external standard, we have

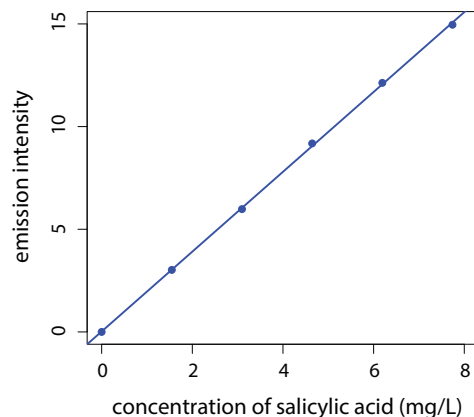
$$I = k[1,3\text{-dihydroxynaphthalene}]$$

$$4.85 = k(5.00 \times 10^{-5} \text{ M})$$

$$k = 9.70 \times 10^4$$



**Figure SM10.24** Calibration data and calibration curve for Problem 40. The blue dots give the emission values for the standards, and the blue regression line is the best fit to the data.



**Figure SM10.25** Calibration data and calibration curve for Problem 41. The blue dots give the emission values for the standards, and the blue regression line is the best fit to the data.

The concentration of 1,3-dihydroxynaphthalene in the sample, therefore, is

$$[1,3\text{-dihydroxynaphthalene}] = \frac{I}{k} = \frac{3.74}{9.70 \times 10^4 \text{ M}^{-1}} = 3.86 \times 10^{-5} \text{ M}$$

40. Figure SM10.24 shows the calibration data and the calibration curve for the analysis of benzo[a]pyrene, for which the calibration curve's equation is

$$I = 3.503 \times 10^{-2} + (1.024 \times 10^5 \text{ M}^{-1}) \times C_{\text{benzo[a]pyrene}}$$

Substituting the sample's emission into the calibration equation and solving for  $C_{\text{benzo[a]pyrene}}$  gives

$$C_{\text{benzo[a]pyrene}} = \frac{4.97 - 3.503 \times 10^{-2}}{1.024 \times 10^5 \text{ M}^{-1}} = 4.82 \times 10^{-5} \text{ M}$$

41. The stock solution of salicylic acid, SA, has a concentration of 77.4 mg/L, which makes the concentration of SA in the standards 0.00, 1.55, 3.87, 4.64, 6.19, and 7.74 mg/L. Figure SM10.25 shows the calibration data and the calibration curve for the analysis of SA, for which the calibration curve's equation is

$$I = 1.847 \times 10^{-2} + (1.945 \text{ mg}^{-1} \text{ L}) \times C_{\text{SA}}$$

Substituting the sample's emission into the calibration equation and solving for  $C_{\text{SA}}$  gives

$$C_{\text{SA}} = \frac{8.69 - 1.847 \times 10^{-2}}{1.945 \text{ mg}^{-1} \text{ L}} = 4.458 \text{ mg/L}$$

Accounting for the sample's preparation gives the concentration of acetylsalicylic acid, ASA, in the original sample as

$$\left( \frac{4.458 \text{ mg SA}}{\text{L}} \times \frac{180.16 \text{ g ASA}}{122.12 \text{ g SA}} \times \frac{100.0 \text{ mL}}{10.0 \text{ mL}} \times 1.000 \text{ L} \times \frac{1.000 \text{ g}}{1000 \text{ mg}} \right) \times 100 = 64.9\% \text{ w/w ASA}$$

42. Figure SM10.26 shows the calibration data and the calibration curve, for which the calibration equation is

$$I = 326.5 + (133.25 \text{ nM}^{-1}) C_{\text{Se(IV)}}$$

For a standard addition, the concentration of Se(IV) is the absolute value of the  $x$ -intercept; thus,

$$\frac{0 - 326.5}{133.25 \text{ nM}^{-1}} = -2.45 \text{ nM Se(IV)}$$

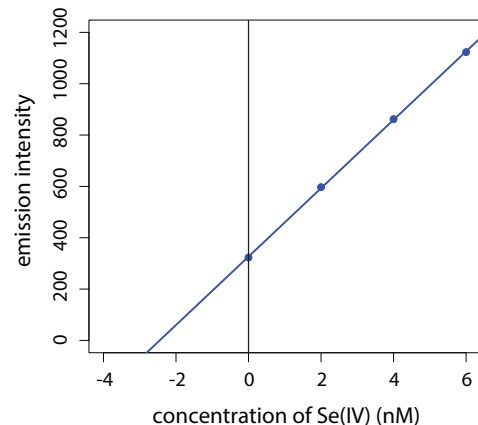
gives  $C_{\text{Se(IV)}}$  as 2.45 nM.

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

$$C = \frac{44.70 + 4.66}{9907.63 \text{ g}^{-1}\text{L}} = 4.98 \times 10^{-3} \text{ g/L}$$

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

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



**Figure SM10.26** Calibration data and calibration curve for Problem 42. The blue dots give the emission values for the standards, and the blue regression line is the best fit to the data.

