Solutions to Selected Problems From Chapters 3 and 5

Chapter 3

3. (a) $k_A = \frac{S_A}{C_A} = \frac{23.3}{15\text{ ppm}} = 1.55\text{ ppm}^{-1} \approx 1.6\text{ ppm}^{-1}$

   (b) $k_I = \frac{S_I}{C_I} = \frac{13.7}{25\text{ ppm}} = 0.548\text{ ppm}^{-1} \approx 0.55\text{ ppm}^{-1}$

   (c) $K_{A,I} = \frac{k_I}{k_A} = \frac{0.548\text{ ppm}^{-1}}{1.55\text{ ppm}^{-1}} = 0.354 \approx 0.35$

   (d) Because $K_{A,I}$ is less than 1 ($k_A > k_I$), the method is more selective for the analyte.

   (e) To achieve an error of less than 1% requires that $K_{A,I}C_I < 0.01C_A$. Rearranging and solving shows us that the ratio C_I/C_A must be

$$\frac{C_I}{C_A} < \frac{0.01}{K_{A,I}} = \frac{0.01}{0.35} = 0.029$$

4. $S_{meas} = S_A + S_{reag} = kC_A + S_{reag}$

   $35.2 = (17.2\text{ ppm}^{-1})C_A + 0.06$

   $C_A = 2.01\text{ ppm}$

7. (a) In the following we will use GA to refer to glycolic acid and AA when referring to ascorbic acid. In the absence of ascorbic acid the signal is

$$S_1 = k_{GA}C_{GA}$$

   and in the presence of ascorbic acid the signal is

$$S_2 = k_{GA}(C_{GA} + K_{GA,AA}C_{AA})$$

   Knowing that the ratio S_2/S_1 is 1.44, we write

$$1.44 = \frac{k_{GA}(C_{GA} + K_{GA,AA}C_{AA})}{k_{GL}C_{GA}} = \frac{C_{GA} + K_{GA,AA}C_{AA}}{C_{GA}}$$

$$1.44 = \frac{1.0\times10^{-4}\ \text{M} + (K_{\text{GA,AA}})(1.0\times10^{-5}\ \text{M})}{1.0\times10^{-4}\ \text{M}}$$

$$K_{\text{GA,AA}} = K_{\text{A,I}} = 4.4$$

(b) The method is more selective for ascorbic acid because $K_{\text{GA,AA}}$ is greater than one.

(c) To avoid an error of more than 1.0% we require that $K_{\text{GA,AA}}C_{\text{AA}} < 0.01C_{\text{GA}}$; thus

$$C_{\text{GA}} > \frac{K_{\text{GA,AA}}C_{\text{AA}}}{0.01} = \frac{(4.4)(1.0\times10^{-5}\ \text{M})}{0.01} = 4.4\times10^{-3}\ \text{M}$$

Chapter 5

6. We begin by determining the value for k in the equation

$$S_{\text{meas}} = kC_{\text{A}} + S_{\text{reag}}$$

The average measured signal for the three samples is 0.1603; thus

$$0.1603 = k(10.0\ \text{ppm}) + 0.002$$

which gives k as 0.01583 ppm^{-1}. Substituting in the signal for the sample gives

$$0.118 = (0.01583\ \text{ppm}^{-1})C_{\text{A}} + 0.002$$

Solving for C_{A} gives the concentration of the analyte as 7.33 ppm.

7. This standard addition follows the format of equation 5.7 in which both the sample and standard addition are diluted to the same final volume; thus

$$\frac{0.235}{C_{\text{A}}\times\frac{10.00\ \text{mL}}{25.00\ \text{mL}}} = \frac{0.502}{C_{\text{A}}\times\frac{10.00\ \text{mL}}{25.00\ \text{mL}} + 1.00\ \text{ppm}\times\frac{10.00\ \text{mL}}{25.00\ \text{mL}}}$$

$$0.09400C_{\text{A}} + 0.09400\ \text{ppm} = 0.2008C_{\text{A}}$$

Solving for C_{A} gives the analyte's concentration in the diluted solution as 0.880 ppm. The concentration of analyte in the original sample, therefore, is

$$\frac{(0.880\ \text{mg/L})(0.250\ \text{L})\left(1\ \text{g}/1000\ \text{mg}\right)}{10.00\ \text{g}}\times100 = 2.20\times10^{-3}\%\ \text{w/w}$$

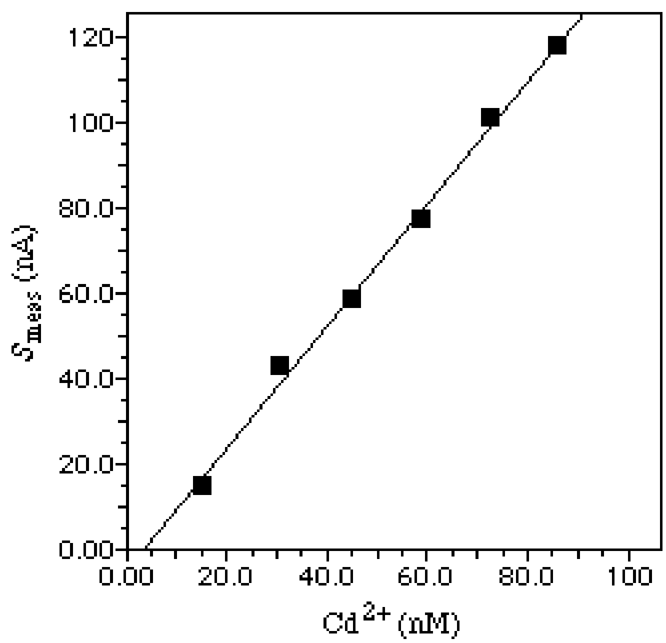
8. This standard addition follows the format of equation 5.9 in which the standard addition is made directly to the solution containing the analyte; thus

$$\frac{11.5}{C_A} = \frac{23.1}{C_A \times \frac{50.00 \text{ mL}}{50.00 \text{ mL} + 1.00 \text{ mL}} + 10.00 \text{ ppm} \times \frac{1.00 \text{ mL}}{50.00 \text{ mL} + 1.00 \text{ mL}}}$$

$$23.1C_A = 11.27C_A + 2.255 \text{ ppm}$$

Solving for C_A gives the concentration of the analyte as 0.191 ppm.

12. A regression analysis for the data at a pH of 3.7 provides the following results.



y-intercept: $b_0 = -5.02$
slope: $b_1 = 1.43$

Solving for the $[Cd^{2+}]$ using the standardization equation at a pH of 3.7 gives

$$\left[Cd^{2+}(\text{nM})\right] = \frac{S_{meas} + 5.02}{1.43} = \frac{66.3 + 5.02}{1.43} = 49.9 \text{ nM}$$