Chapter 3

1. In a total analysis technique the signal is proportional to the absolute amount of analyte, in grams or in moles, in the original sample. If we double the amount of sample, then the signal also doubles. For this reason, an accurate analysis requires that we recover all analyte present in the original sample, which is accomplished here in two key ways: (a) the beaker in which the digestion is carried out is rinsed several times and the rinsings are passed through the filter paper, and (b) the filter paper itself is rinsed several times. The volume of solvent used in the digestion and the volumes used to rinse the beaker and the filter paper are not critical because they do not affect the mass or moles of analyte in the filtrate.

   In a concentration technique the signal is proportional to the relative amount, or concentration of analyte, which means our treatment of the sample must not change the analyte's concentration or it must allow us to do so in a precise way. Having completed the digestion, we need to ensure that the concentration of analyte in the beaker and the concentration of analyte in the filtrate are the same, which is accomplished here by not washing the beaker or the filter paper, which would dilute the analyte's concentration, and by taking a precisely measured volume of the filtrate to the next step in the procedure. Because we know precisely the original volume of sample (25.00 mL) and the volume of filtrate taken (5.00 mL), we can work back from the concentration of analyte in the filtrate to the absolute amount of analyte in the original sample.

2. (a) Here we must assume that a part per billion is expressed as a mass per unit volume, which, in this case, is best expressed as ng/mL; thus

$$\frac{10\text{ ng}}{\text{mL}} \times 0.5\text{ mL} = 5\text{ ng}$$

   (b) A concentration of 10% w/v is equivalent to 10 g of analyte per 100 mL of sample or 10^8 ng/mL. Because the final concentration is 10 ng/mL, we must dilute the sample by a factor of 10^7, which we can accomplish, for example, by diluting 0.1 μL of sample to a final volume of 1 L.

   (c) A concentration of 10% w/w is equivalent to 10 g of analyte per 100 g of sample. To prepare the solution we need to take

$$1000\text{ mL} \times \frac{10\text{ ng analyte}}{\text{mL}} \times \frac{1\text{ g analyte}}{10^9\text{ ng analyte}} \times \frac{100\text{ g sample}}{10\text{ g analyte}} = 1 \times 10^{-4}\text{ g sample}$$

   or 0.1 mg of sample.

(d) This method is not particularly suited for a major analyte because we must dissolve a very small amount of sample (0.1 μL or 0.1 mg) in a large volume of solution (1000 mL), which is difficult to do with precision and with accuracy. We might consider a serial dilution from an initial solution that is more concentrated; however, multiple dilutions increase the opportunity for introducing error.

3. (a) The analyte's sensitivity, k_A, is

$$k_A = \frac{S_A}{C_A} = \frac{23.3}{15\text{ ppm}} = 1.55\text{ ppm}^{-1} \approx 1.6\text{ ppm}^{-1}$$

(b) The interferent's sensitivity, k_I, is

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

(c) The selectivity coefficient, $K_{A,I}$, is

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

(d) Because k_A is greater than k_I, which makes $K_{A,I}$ less than one, we know that the method is more selective for the analyte than for the interferent.

(e) To achieve an error of less than 1% we know that

$$K_{A,I} \times C_I < 0.01 \times C_A$$

Rearranging for the ratio C_I/C_A and solving gives

$$\frac{C_I}{C_A} < \frac{0.01}{K_{A,I}} = \frac{0.01}{0.354} = 0.028 \approx 0.03$$

Thus, the interferent can be present with a concentration that is no more than 3% of the analyte's concentration.

4. We know that $S_{total} = S_A + S_{reag} = k_A C_A + S_{reag}$. Making appropriate substitutions

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

and solving for C_A gives the analyte's concentration as 2.01 ppm.

5. A relative error of –2.0% means that

$$K_{\text{Ca,Zn}} \times C_{\text{Zn}} = -0.020 \times C_{\text{Ca}}$$

We know that the concentrations of Ca and Zn are in a 50:1 ratio, so it is convenient to assign a concentration of 50 to Ca and a concentration of 1 to Zn; making appropriate substitutions

$$K_{Ca,Zn} \times 1 = -0.02 \times 50$$

and solving for $K_{\text{Ca,Zn}}$ gives its value as –1.0. Note that an absolute value for $K_{\text{Ca,Zn}}$ of one implies the method is equally sensitive to the analyte, Ca, and the interferent, Zn, and that the negative sign for

$K_{Ca,Zn}$ implies the interferent, Zn, decreases the signal. A sample for which $C_{Ca} = C_{Zn}$ will have $S_{samp} = 0$!

6. In the absence of ascorbic acid the signal is

$$S_1 = k_{GL} \times C_{GL} = k_{GL} \times (10.0 \text{ ppb})$$

where GL represents glutathione. In the presence of ascorbic acid, AA, the signal is

$$S_2 = k_{GL}(C_{GL} + K_{GL,AA} \times C_{AA}) = k_{GL}(10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb})$$

We know that the signal in the presence of ascorbic acid, S_1, is 5.43× the signal in the absence of ascorbic acid, S_2; thus

$$\frac{S_2}{S_1} = 5.43 = \frac{k_{GL}(10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb})}{k_{GL} \times (10.0 \text{ ppb})}$$

$$5.43 = \frac{10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb}}{10.0 \text{ ppb}}$$

$$54.3 \text{ ppb} = 10.0 \text{ ppb} + K_{GL,AA} \times (1.5 \text{ ppb})$$

Solving for $K_{GL,AA}$ gives its value as 3.0×10^1. When the interferent is methionine, which we abbreviate as ME, we have

$$\frac{S_2}{S_1} = 0.906 = \frac{k_{GL}(10.0 \text{ ppb} + K_{GL,ME} \times 3.5 \times 10^2 \text{ ppb})}{k_{GL} \times (10.0 \text{ ppb})}$$

$$\frac{S_2}{S_1} = 0.906 = \frac{10.0 \text{ ppb} + K_{GL,ME} \times 3.5 \times 10^2 \text{ ppb}}{10.0 \text{ ppb}}$$

$$9.06 \text{ ppb} = 10.0 \text{ ppb} + K_{GL,ME} \times (3.50 \times 10^2 \text{ ppb})$$

which gives $K_{GL,ME}$ as –0.0027. There are two important differences between these two interferents. First, although the method is more sensitive for that analyte glutathione than it is for the interferent methionine (the absolute value for $K_{GL,ME}$ is less than one), it is more sensitive for the interferent ascorbic acid than it is for the analyte glutathione ($K_{GL,AA}$ is greater than one). Second, the positive value for $K_{GL,AA}$ indicates that ascorbic acid increases the total signal and the negative value for $K_{GL,ME}$ indicates that methionine decreases the total signal.

7. (a) In the absence of ascorbic acid the signal is

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

where GA represents glycolic acid, and in the presence of ascorbic acid, AA, the signal is

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

We know that the signal in the presence of ascorbic acid, S_1, is 1.44× the signal in the absence of ascorbic acid, S_2; thus

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

$$1.44 = \frac{(1 \times 10^{-4}\ \text{M}) + K_{GA,AA} \times (1 \times 10^{-5}\ \text{M})}{1 \times 10^{-4}\ \text{M}}$$

Solving for $K_{GA,AA}$ gives its value as 4.4.

(b) The method is more selective for the interferent, ascorbic acid, than it is for the analyte, glycolic acid, because $K_{GA,AA}$ is greater than one.

(c) To avoid an error of more than 1%, we require that

$$K_{GA,AA} \times C_{AA} < 0.01 \times C_{GA}$$

which requires that

$$C_{GA} > \frac{K_{GA,AA} \times C_{AA}}{0.01} = \frac{4.4 \times (1.0 \times 10^{-5}\ \text{M})}{0.01} = 4.4 \times 10^{-3}\ \text{M}$$

8. (a) To determine the sensitivity for the analyte, we begin with the equation $S_{samp} = k_A C_A$ and solve for k_A; thus

$$k_A = \frac{S_{samp}}{C_A} = \frac{7.45 \times 10^{-5}\ \text{A}}{1.12 \times 10^{-6}\ \text{M}} = 66.5\ \text{A/M}$$

(b) In the presence of an interferent, the signal is

$$S_{samp} = k_A(C_A + K_{A,I} \times C_I)$$

Rearranging to solve for $K_{A,I}$ and making appropriate substitutions

$$K_{A,I} = \frac{S_{samp} - k_A C_A}{k_A C_I} = \frac{4.04 \times 10^{-5}\ A - (66.5\ A/M) \times (1.12 \times 10^{-6}\ M)}{(66.5\ A/M) \times (6.5 \times 10^{-5}\ M)}$$

gives -7.9×10^{-3} as the value for $K_{A,I}$.

(c) The method is more selective for the analyte, hypoxanthine, than for the interferent, ascorbic acid, because the absolute value of $K_{A,I}$ is less than one.

(d) To avoid an error of 1.0% requires that $K_{A,I} \times C_I < -0.01 \times C_A$, where we use a relative error of –0.010 because the interferent decreases the signal (note that $K_{A,I}$ is negative). Rearranging and making appropriate substitutions gives

$$C_I < \frac{-0.010 C_A}{K_{A,I}} = \frac{-0.010 \times (1.12 \times 10^{-6}\ \text{M})}{-7.9 \times 10^{-3}}$$

or a concentration of ascorbic acid less than 1.4×10^{-6} M.

9. Answers will vary with the selected procedure, but what follows is an example of a typical response.

Surfactants are compounds that decrease the surface tension between normally immiscble compounds, allowing them to mix together. Common examples of surfactants, which have many practical applications, include detergents and emulsifiers. Many surfactants consist of a long non-polar hydrocarbon chain of 10–20 carbon atoms with a polar functional group on one end that either carries a charge (anionic or cationic) or is neutral. Although surfactants themselves generally are not a health hazard, their presence in the environment may help solubilize other, more harmful compounds. One method for determining the concentration of anionic surfactants in water is the Methylene Blue Method for Methylene-Blue-Active Substances (MBAS), which is Method 5540 C in *Standard Methods for the Examination of Water and Wastewater*.

Not all anionic surfactants react with MB, which is why the procedure's name includes the qualifying statement "methylene-blue-active substances. (MBAS)" The most important class of MBAS surfactants are linear alkylbenzene sulfonates (LAS) with the general formula $R–C_6H_4SO_3^-$ where R is an linear alkyl chain of 10–14 carbons.

This method relies on the reaction of methylene blue (MB), which is a cationic dye, with anionic surfactants to form a neutral complex. The aqueous sample is made slightly basic, a strongly acidic solution of MB is added, and the resulting complex extracted into chloroform. When the extraction is complete, the chloroform layer is isolated and then washed with an acidic solution of water to remove interferents. The intensity of the complex's color in chloroform is proportional to the concentration of anionic surfactants in the original sample.

See Chapter 7 for more details on solvent extractions.

The absorbance of the surfactant-MB complex is measured in a spectrophotometer using a cell with a 1-cm pathlength at a wavelength of 652 nm. A blank consisting of chloroform is used to calibrate the spectrophotometer.

See Chapter 10 for more details about absorption spectrophotometry.

Although a sample will contain a variety of different anionic surfactants, the method is standardized using a single, standard reference material of linear alkylbenzene sulfonates (LAS). A stock standard solution is prepared that is 1.00 g LAS/L, which is used to prepare a working standard solution that is 10.0 μg LAS/mL. At least five calibration standards are prepared from the working standard with concentrations of LAS in the range of 0.10 μg/mL to 2.0 μg/L.

See Chapter 5 for more details about methods of standardization, including calibration curves.

The method is sensitive to a variety of interferents. If cationic surfactants are present, they will compete with methylene blue for the anionic surfactants, decreasing the reported concentration of MBAS; when present, their concentration is minimized by first passing the sample through a cation-exchange column. Some organic anions, such as chloride ions and organic sulfates, form complexes with methylene blue that also extract into chloroform, increasing the reported concentration of MBAS; these interferences are minimized by the acidic wash that follows the extraction step.

See Chapter 12 for more details about ion-exchange.

The volume of sample taken for the analysis is based on the expected MBAS concentration as follows: 400 mL if the expected concentra-

tion is between 0.025–0.080 mg/L; 250 mL if the expected concentration is between 0.08–0.40 mg/L; and 100 mL if the expected concentration is between 0.4–2.0 mg/L. If the expected concentration is greater than 2 mg/L, a sample that contains between 40–200 μg is diluted to 100 mL with distilled water.