

### Take-Home Assignment 3 Answer Key

1. The following molar absorptivities are known for the cobalt and nickel complexes of 8-quinolinol in an acetone solution that is 1 M in HCl:  $\epsilon_{\text{Co}, 365 \text{ nm}} = 3529$ ;  $\epsilon_{\text{Ni}, 365 \text{ nm}} = 3228$ ;  $\epsilon_{\text{Co}, 700 \text{ nm}} = 428.9$ ;  $\epsilon_{\text{Ni}, 700 \text{ nm}} = 0$  [all values are with units of  $\text{M}^{-1} \text{ cm}^{-1}$ ; data from Mukhedkar, A. J.; Deshpande, N. V., *Anal. Chem.*, **1963**, 35, 47-48]. Calculate the concentrations of cobalt and nickel in a solution for the which the absorbance at 365 nm is 0.721 and the absorbance at 700 nm is 0.067. Assume that the sample cell is 1.00 cm.

$$0.067 = (428.9)[\text{Co}]$$

$$[\text{Co}] = 1.56 \times 10^{-4} \text{ M}$$

$$0.721 = (3529)(1.56 \times 10^{-4}) + (3228)[\text{Ni}]$$

$$[\text{Ni}] = 5.28 \times 10^{-5} \text{ M}$$

2. Suppose you are to prepare a set of calibration standards for the spectrophotometric analysis of acetone at a wavelength of 211 nm using a 1.00 cm cell. The molar absorptivity for acetone at this wavelength is 562. To maintain an acceptable precision for the analysis you wish to keep the %T for your standards between 15% and 85%. What is the most concentrated and the least concentrated standard that you would want to prepare for this analysis?

$$A = -\log T$$

$$A = -\log(0.15) = 0.824$$

$$0.824 = (562)[\text{analyte}]$$

$$[\text{analyte}] = 1.47 \times 10^{-3} \text{ M is most concentrated}$$

$$A = -\log(0.85) = 0.070$$

$$0.070 = (562)[\text{analyte}]$$

$$[\text{analyte}] = 1.26 \times 10^{-4} \text{ M is least concentrated}$$

3. The amount of calcium in tissue samples can be determined spectrophotometrically. In a typical analysis, a 10.0 gram sample of tissue was homogenized in a calcium-free buffer solution. The homogenate was diluted to 50.0 mL, and centrifuged to remove cellular debris. A 10.0 mL portion of the clear supernatant fluid was mixed with 10.0 mL of trichloroacetic acid, precipitating any proteins and filtered. The clear filtrate was then analyzed spectrophotometrically giving an absorbance of 0.505. A

calibration curve prepared using external standards showed the following relationship between absorbance and the concentration of  $\text{Ca}^{2+}$

$$\text{abs} = 0.070 + 1.885 \times [\text{Ca}^{2+} \text{ (mM)}]$$

Report the concentration of  $\text{Ca}^{2+}$  in the original tissue sample as mmoles/gram.

The concentration in the sample as analyzed is

$$0.505 = 0.070 + 1.885[\text{Ca}^{2+}]$$

$$[\text{Ca}^{2+}] = 0.231 \text{ mM}$$

This sample was prepared by diluting 10 mL of a stock sample to 20 mL; thus, the concentration of the stock sample is twice as large, or 0.461 mM. To find the mmoles of  $\text{Ca}^{2+}$  in the tissue sample we must account for the total volume in which it was originally prepared; thus

$$0.461 \text{ mM} \times 0.0500 \text{ L} = 0.02305 \text{ mmoles Ca}^{2+}$$

This calcium was in the 10.0 g sample, so the concentration in the sample is

$$0.02305 \text{ mmoles}/10.0 \text{ g} = 2.31 \times 10^{-3} \text{ mmol/g}$$

4. The amount of boron in plant material can be determined spectrophotometrically after complexing with Azomethine H to form a highly-colored complex. In a typical procedure a 7.94 g sample was treated to destroy organic material and the residue transferred to a 250-mL volumetric flask, diluting to volume with 0.35 M  $\text{H}_2\text{SO}_4$ . A 50.00 mL aliquot was transferred to a 100-mL volumetric flask along with 20.00 mL of an Azomethine H solution. After diluting to volume the solution was allowed to stand for two hours to allow the color to develop. The resulting absorbance at 430 nm in a 1-cm cell was 0.364. A second 50.00 mL aliquot was treated in an identical manner except that a 4.00 mL aliquot of a 3.00 ppm boron standard was added before diluting to 100 mL. The absorbance of this solution was 0.688. What is the % w/w B in the plant sample?

This is a one-point standard addition. There are several ways to solve this problem, one of which is outlined here:

$$\frac{0.364}{C(50/100)} = \frac{0.688}{C(50/100) + (3.00)(4/100)}$$

where C is the concentration of B in the prepared sample. Solving gives this concentration as 0.270  $\mu\text{g/mL}$ . The plant sample has been placed into a total volume of 250 mL; thus, the amount of B in the plant is

$$0.270 \mu\text{g/mL} \times 250 \text{ mL} = 67.5 \mu\text{g B}$$

The concentration of B in the plant sample, therefore, is

$$\{67.5 \times 10^{-6} \text{ g} / 7.94 \text{ g}\} \times 100 = 8.5 \times 10^{-4} \% \text{w/w}$$