

# CHEM 334 Quantitative Analysis Laboratory

## *Determination of Multiple Analytes*

The determination of the concentration of an absorbing species can be made by the measurement of its absorption of radiation together with the use of the Beer-Lambert law. This method is most sensitive when it is performed at the so-called absorption maximum, that is, the wavelength of radiation where absorption by the species of interest is maximal. Additionally, this method is simple to apply when only one absorbing species is present. All that is required to accomplish the measurement is knowledge of the molar absorptivity of the species at the selected wavelength, as determined with a set of solutions of known concentrations of the species. The absorption of the species in solution with unknown concentration can then be measured and the concentration computed by application of the Beer-Lambert law:

$$A = \epsilon bc \quad (1)$$

where  $A$  is (dimensionless) absorbance,  $\epsilon$  is the molar absorptivity of the species in units of  $\text{M}^{-1} \text{cm}^{-1}$ ,  $b$  is the optical path length in centimeters and  $c$  is the concentration of the species in moles per liter (M). For the purposes of this document the path length,  $b$ , is taken as one cm.

At times, multiple absorbing species are present, each with its own absorption spectrum complicating the measurement. Simultaneous determination of the concentration of multiple species can be accomplished if the respective absorption maxima are well separated and there is no absorption at the absorption maximum of a particular species by any other species present. The absorption behavior of each species follows the Beer-Lambert law independently and measurement at multiple wavelengths suffices.

When significant overlap of the respective absorption spectra exists, the simultaneous determination of the concentrations of a mixture of several species is still possible but additional considerations are required. The multiple measurement wavelengths must still be selected for sensitivity but must also be selective in they must provide for differing sensitivity to the each of the multiple species. Both the molar absorptivities of each species must differ from each other and the size ranked order of those molar absorptivities must be unique at each measurement wavelength.

In this experiment, a sample containing more than one absorbing species will be analyzed. Nickel silver is an alloy of copper, nickel and zinc. Copper and nickel ions in aqueous solution form complex ions,  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$   $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  with different visible absorption spectra and the concentration of copper and nickel can be determined spectrophotometrically. Zinc has no visible absorption spectrum but in the case of this ternary alloy, the concentration of zinc can be found by difference from the copper and nickel content.

As the absorbance spectra of copper and nickel overlap significantly, absorbance measurements must be made at two different wavelengths to provide sufficient data to simultaneously determine the concentrations of both species. The wavelengths appropriate for copper and nickel in acidic aqueous solution are 806 and 710 nm, respectively.

The total absorbance at any particular wavelength is obtained by repeated application of the Beer-Lambert law and by the sum of the absorbances of the individual species:

$$A_{\text{total},806 \text{ nm}} = \epsilon_{\text{Cu}, 806 \text{ nm}}C_{\text{Cu}} + \epsilon_{\text{Ni}, 806 \text{ nm}}C_{\text{Ni}} \quad (2)$$

and

$$A_{\text{total},710 \text{ nm}} = \epsilon_{\text{Cu}, 710 \text{ nm}}C_{\text{Cu}} + \epsilon_{\text{Ni}, 710 \text{ nm}}C_{\text{Ni}} \quad (3)$$

By measurement of the total absorbance at two different wavelengths and with knowledge of the molar absorptivities of both species *at the two wavelengths*, equations (2) and (3) can be written with only two unknowns,  $c_{\text{Cu}}$  and  $c_{\text{Ni}}$ . The values of these two unknowns can be found by the solution of these simultaneous equations.

## Procedures

**Preparation of Standard Copper and Nickel Solutions:** Prepare 10 mL of solution of copper nitrate that is approximately 0.1 M but known accurately. Measure the absorbance of this solution at both wavelengths. Prepare a series of four solutions from this solution of various concentrations each with a volume of ten mL by serial dilution with a dilution factor of your own preference (inform this choice by the absorbance of the 0.1 M solution). Select an appropriate dilution factor based on the absorbance of the most concentrated solution and serious consideration of experimental limitations of the spectrophotometer and Beer's Law. Note that it is not necessary for each dilution to be the same even though it might be more convenient.

Similarly, prepare 10 mL of solution of nickel nitrate that is approximately 0.2 M but known accurately. Prepare a series of diluted solutions from this solution as described above.

**Preparation of Unknown Sample Solution:** Accurately weigh out approximately one gram of a metal sample. (What will you weigh it in?) Digest the sample in a 100-mL beaker (on a hot plate set to 200 °C) in the hood using 10 mL of concentrated (~16 M) nitric acid. (Verify that this is the appropriate amount of acid by calculation.) Add the acid slowly (~1 mL at a time) at first to prevent overflow of the beaker. When the sample has completely dissolved, gently heat the solution in the hood to remove the nitrogen dioxide (brown fumes) produced in the reaction. Let cool a bit in the hood to avoid noxious fumes. Bring the volume to 100.0 mL with water (in which flask?) on the bench.

**Measurement:** Record the absorbance of the known solutions and the unknown solution at wavelengths 806 and 710 nm. Blank with water. There will be eighteen absorbance measurements in total at both wavelengths ignoring blanks.

**Analysis:** The molar absorptivities for copper and for nickel at both 806 and 710 nm are determined by fitting a linear function to the corresponding sets of absorbance verses concentration measurements.

The concentrations for copper and nickel in solution are obtained by simultaneous solution of equations (2) and (3). The concentration of zinc in the original sample is obtained by difference.

## Results

Report the molar absorptivity for copper and for nickel at both 806 and 710 nm. Use a table. Include a suitable uncertainty analysis for these values. Report the mass concentration of copper, nickel and zinc of the unknown sample. Include a suitable uncertainty analysis for these values.

## Discussion

Discuss your experimental results. Explain the fundamental basis for the success of this method of simultaneously determining multiple analytes. Describe the conditions under which the accuracy of this method would suffer or the method itself would fail. Discuss the number of equations required for the simultaneous determination of an arbitrary number of analytes.

## References

- Harris, D.C., "Quantitative Chemical Analysis" (2007) seventh edition, Freeman & Co., NY, pp 402-407.
- Pandey, S.; McHale, M. E. R.; Coym, K. S.; Acree, W. E., Jr. *J. Chem. Educ.* **1998**, *75*, 878.
- MacQueen, J. T.; Knight, S. B.; Reilley, C. N. *J. Chem. Educ.* **1960**, *37*, 139.