

Experiment 7D

FV 10/24/05

YOU BET YOUR BRASS: ANALYSIS OF COPPER ALLOYS

MATERIALS: Spectronic-20 spectrophotometer, Genesys Scanning UV-Vis spectrometer, cuvettes, alloy sample, 7 M HNO₃, Cu turnings, mossy Zn, Sn pellets, Cu wire, 2 M NH₃, volumetric flasks: 100 mL (1), 25 mL (2); volumetric pipets: one each: 10 mL, 5 mL, 2 mL, 1 mL; 25 mL beaker; watch glass, 16 x 125 test tubes (6); plastic scintillation vials w/ caps (5), 10 mL graduated cylinder, centrifuge.

PURPOSE: The purpose of this experiment is to determine the mass percent of copper in an alloy sample (brass or bronze) using spectrophotometric analysis.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Properly calibrate and use a spectrophotometer.
2. Convert percent transmittance to absorbance, and vice versa.
3. Devise a sample preparation procedure yielding solutions (both the calibration and unknown solutions) that may be properly analyzed using spectrophotometry.
4. Construct a calibration curve relating absorbance and concentration for solutions of known concentrations.
5. Use a calibration curve to determine the concentration of an unknown solution.
6. Convert the molar concentration obtained via spectrophotometric analysis to a mass percent value for the original alloy sample.

PRELAB: Review Appendix I; complete the prelab exercises on p. E7D-6 and hand in to your instructor prior to the start of the lab period.

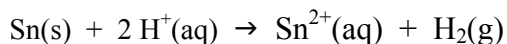
DISCUSSION:

Alloys. Alloys are uniform mixtures (*i.e.*, solutions) of two or more solid substances. For example, brass is a solid solution of primarily copper and zinc. Bulk samples of alloys often possess properties which are unique and distinct from those of the individual component elements. At the same time, the individual atoms of which the alloy is composed still retain properties similar to those they exhibit in their pure state. Thus, copper atoms in a brass sample have more or less the same atomic properties, such as ionization energy, as in a copper metal sample. Being mixtures, alloys can usually possess a wide range of composition, not just stoichiometric ratios of elements as would be typically found in molecular compounds. Some brasses also have small amounts of other types of metals, such as tin.

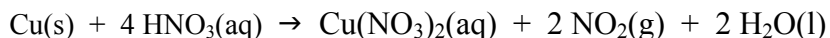
Brass with a high copper content is easy to form and bend and can be polished to a high luster. Naval brass is a particular mixture of copper and zinc, with a small amount of tin added, which is commonly used for hardware components, such as nuts, bolts, rivets, valve stems, and pump shafts. Bronze is also an alloy of copper, but the secondary metal in this case is tin. As a result, bronze is harder and less ductile, but more corrosion resistant (tin is less active than zinc). Bronze is used in fabrication of ship components that are in constant contact with seawater, such as propellers and seacocks.

Methods of chemical analysis. One type of chemical analysis involves determining the elemental composition of a sample, which is typically expressed in terms of the mass percent of each element in the sample. While methods for direct analysis of solid samples exist, they generally employ sophisticated and expensive instrumentation which may not be readily available. More commonly, a *known mass* of the substance to be analyzed is dissolved in a *known volume* of an appropriate liquid medium, and then the analysis is carried out on the resulting solution. In this case, the analysis yields the *concentration* of the component of interest (the *analyte*) in the solution, which is then used to calculate the mass of the analyte that was present in the original sample. Of course, in order to successfully apply any analytical method, care must be taken to ensure that components other than the analyte of interest do not interfere with the analysis.

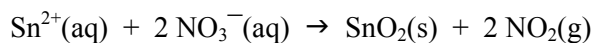
Solubilization of metal samples. In order to carry out solution analysis of solid samples, it is first necessary to render them in a soluble form. For metallic samples, this generally involves oxidation of constituent elements to their corresponding cations. Oxidation (corrosion) of metals is generally promoted by acidic conditions. The nature of the specific reaction that occurs depends upon both the chemical nature of the metal (specifically, its ease of oxidation or *activity*) and that of the acid employed. For some particularly active metals (e.g., Zn or Sn), H⁺ ions in acidic solution can act directly as the electron acceptor (or *oxidizing agent*), resulting in the formation of hydrogen gas:



Less active metals (e.g., Cu) may require the presence of a more potent oxidizing agent. For example, the nitrate (NO₃⁻) ions present in nitric acid are strong electron-acceptors owing to the high positive oxidation number of nitrogen:



Finally, it should be noted that not all metal cations are soluble in acidic aqueous solution. For example, Sn²⁺ ions initially formed by oxidation of metallic tin in nitric acid are soluble, but they slowly undergo further oxidation to tin(IV)oxide, a white powder:



The nature of metal ions in solution. While a full discussion of the chemistry of metal ions in aqueous solution is beyond the scope of this course, a few pertinent points that are essential to understanding the present lab procedure are presented here (for more details, consult Chapter 24 in your textbook). First, recall that the "molecular" formula for an ionic compound (e.g., ZnCl₂(aq)) commonly used in balanced chemical equations is a type of shorthand notation that may be expanded into the "ionic" form: Zn²⁺(aq) + 2 Cl⁻(aq). The latter representation emphasizes the fact that the anions and cations of the compound behave as independent particles in solution, and each has its own particular association with water molecules from the solvent, denoted by the suffix (aq). In the case of metal cations, this association may be strong enough to be regarded as a type of chemical bond, known as a *coordinate covalent bond*. The chemical species bonded to the metal ion (H₂O molecules in the present example) are known as *ligands*, and the resulting aggregates (typically containing from two to six ligands bonded to a single metal ion) are known as *coordination complexes*. Copper(II) and zinc(II) ions in aqueous solution are both known to bind four water ligands, yielding complexes which may be formulated as [Cu(H₂O)₄]²⁺ and [Zn(H₂O)₄]²⁺, respectively. Since these metal ions bind more strongly to ammonia molecules than they do to H₂O, addition of aqueous ammonia solution to Cu²⁺(aq) or Zn²⁺(aq) results in *ligand substitution* reactions:



In contrast, addition of the basic $NH_3(aq)$ solution to $Sn^{+4}(aq)$ does not result in the formation of a soluble ammonia complex, but instead produces only the insoluble hydroxide $Sn(OH)_4(s)$.

Aqueous solutions containing transition metal ions often, but not always, absorb visible light, resulting in colored solutions. For example, it is well-known that solutions containing $Cu^{2+}(aq)$ ions have a characteristic pale blue color. The specific wavelengths of light absorbed by such solution species, as well as the absorption intensity, depends upon many factors, chief among these being the nature of the ligands bound to the metal ion. In this experiment it will be necessary to transform a simple aqueous transition metal ion into its ammonia complex in order to enhance the absorption, making the techniques of spectrophotometry more appropriate for analysis.

Analysis of Colored Solutions. This experiment involves the analysis of solutions which absorb visible light. Instruments have been developed to assist in studying such solutions. Depending on availability and time constraints, your instructor may demonstrate the use of a sophisticated instrument known as a scanning UV-Visible spectrometer. A simpler, yet still extremely useful, instrument known as a spectrophotometer will be available for student use in this and other experiments. Please review [Appendix I](#) of the on-line Plebe Chemistry Laboratory Manual for more details about the theory and application of this type of analysis, known as spectrophotometry.

Calibration curves. One of the common challenges in science is to determine the value of some property for an unknown material. Here, you are presented with the challenge of determining the concentration of a specific metal complex in solution. Although there may be other methods available for determining the desired value, an often-used method involves establishing a calibration curve. This is done by constructing several similar materials, known as "standards", having known values of the property of interest. For the case of a colored solution, for example, Beer's Law predicts a linear dependence of absorbance on concentration. Thus, one might prepare several solutions of known analyte concentration, measure the absorbance of each, and make a graph of absorbance vs. concentration. The line which best fits these data is known as a calibration curve. Solutions of unknown analyte concentration can then be studied by measuring their absorbance. The calibration curve then enables the concentration of the absorbing species in the unknown solution to be determined.

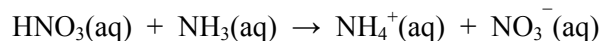
PROCEDURE: Work with a partner

1. Using test tubes, observe the reactions of small samples of Cu, Zn and Sn with 7M HNO_3 . Using a disposable Pasteur pipet, withdraw a small amount of the solution resulting from each reaction and add each sample dropwise into a separate test tube containing several mL of 2M NH_3 solution. Record your observations.
2. Absorption spectra at all visible wavelengths for several separate solutions will be provided, including 0.010 M Cu^{2+} , 0.010 M Zn^{2+} , 0.010 M Sn^{2+} , and solutions of the complexes resulting from reaction of these ions with excess 2 M NH_3 solution. The spectra will be helpful for determining procedures later. Take note of any special instructions for future use, especially with respect to the procedure for diluting a solution.
3. Observe your instructor's demonstration of the Spectronic 20 spectrophotometer, including how to prepare it for use. Take note of any special instructions for future use.

4. Devise and implement a procedure for determining the mass percent of copper in an alloy sample assigned by your instructor. Use no more than 0.1 g of the unknown alloy sample in your procedure. Samples can be assumed to contain only copper, zinc and possibly some tin. Consider the following when making your plans:
 - a. Reactions of metals with acids observed in step 1: How will you dissolve your sample? Note: in order to ensure complete reaction, use ~ twice the amount of acid dictated by stoichiometry.
 - b. The absorption spectra of the solutions: What is the optimum wavelength for the analysis? What potential interferences might there be from other components in your alloy sample, and how will you deal with them?
 - c. Limitations on the validity of the Beer-Lambert Law and the reliability of absorbance measurements (see Appendix I); what concentration ranges of either the $\text{Cu}^{2+}(\text{aq})$ or the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ solutions have absorbances appropriate for analysis using the Beer-Lambert Law? How can the standards and alloy sample be prepared to fall within the appropriate concentration range using the glassware provided?
 - d. Utility of a calibration curve relating concentration and absorbance (see Appendix I): How will you prepare a set of standard solutions with known copper concentration as part of the calibration process?
 - e. Any safety considerations, *e.g.*, need for proper ventilation for certain reactions, waste disposal, etc.

QUESTIONS FOR CONSIDERATION:

1. What is the % by mass of Cu in your alloy sample? Based upon your observations while dissolving the unknown sample and preparation of the analysis solution, do you think your unknown alloy would be best described as brass or bronze? Explain your answer.
2. Why was it important to review the absorption spectra for the Cu, Zn and Sn ion solutions in determining the procedure for this experiment?
3. Why is it not appropriate to simply use more concentrated Cu^{2+} solutions in order to bring the absorbances into a more reliable range?
4. In the preparation of your standard copper solution, added ammonia neutralizes the excess acid via the following equation:



Using your data from the preparation of the standard solution, calculate the volume of added ammonia that was consumed in neutralizing the excess acid. What fraction of the total amount of added ammonia was this?

5. Using your calibration curve and the data below, calculate the mass percent of copper in an alloy sample prepared by reacting with nitric acid, transferring completely to a 50-mL volumetric flask, filling with 2 M ammonia to the mark, then pipeting 10.00 mL of this solution into another 50-mL volumetric flask and filling with 2M ammonia to the mark.

Mass of empty weighing dish:	5.3244 g
Mass of dish plus brass sample:	5.5589 g
%T of the solution taken from the last 50-mL volumetric flask:	35.8%

6. Describe how the observed color of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ solution is consistent with its visible absorption spectrum.
7. From your calibration curve, determine the value for ϵ at the wavelength selected for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ species at room temperature. In this consistent with the value obtained from the visible absorption spectrum provided for the same species? Using the absorption spectrum, estimate the value of ϵ at 650 nm for the Cu^{2+} species at room temperature.

