



Percent Copper in Brass

AP* Chemistry Big Idea 1, Investigation 2

An Advanced Inquiry Lab

Introduction

The relative proportions of copper, zinc and iron in brass influence its properties and uses. How can the percent composition of brass be determined to verify these properties?

Concepts

- Spectroscopy
- Beer's law
- Concentration
- Absorbance
- Calibration curve
- Electron transitions

Background

Brass is a generic term for alloys of copper and zinc. In addition to these metals, brass may also contain small amounts of iron, lead, aluminum and tin. More than 300 different brass alloys are known, with uses ranging from decorative hardware to architectural construction, musical instruments, and electrical switches. The amount of copper in brass affects its color, hardness, ductility, mechanical strength, electrical conductivity, corrosion resistance, etc. Visible spectroscopy provides a simple tool for determining the percent copper in brass.

Spectroscopy involves the interaction of electromagnetic radiation and matter. The absorption of electromagnetic radiation results in different types of transitions in a substance, depending on the energy of the radiation. Low energy microwave radiation, for instance, is converted to energy of molecular rotation. Absorption of infrared radiation excites vibrational frequencies associated with covalent bonds in a molecule. Visible and ultraviolet light cause electron transitions between different electron energy levels in a substance. The energy of electromagnetic radiation is quantized, as are the energy levels associated with various transitions, whether rotational, vibrational or electronic. Furthermore, the energies of these transitions are characteristic of an atom, molecule or compound. As a result, the absorption spectra of substances generally consist of specific lines or bands that can be used as a type of fingerprint to identify a substance.

Transition metal ions have filled or partially filled d orbitals. The presence of water molecules or other ligands surrounding a transition metal ion in solution leads to energy differences among the d orbitals. Depending on the metal ion involved, the energy difference may correspond to different wavelengths and energies of visible light. This property of transition metal ions gives many their characteristic—and beautiful—colors.

The concentration of a colored transition metal ion solution can be determined by measuring the color intensity. A visible spectrophotometer is used to measure the absorption of visible light. In general, *absorbance* is proportional to concentration. The higher the concentration of a transition metal ion solution, the more intense its color will be, and the greater its absorbance. The linear relationship between absorbance (A) and concentration (c) is expressed in Beer's law, Equation 1, where b is the path length in cm and ϵ is a proportionality constant. If c is given in units of molarity ($M = \text{moles/L}$), then ϵ is known as the molar absorptivity coefficient, with units $M^{-1} \text{ cm}^{-1}$.

$$A = \epsilon bc \quad \text{Equation 1}$$

Beer's law can be used to determine the "unknown" concentration of a metal ion in solution if its absorbance is measured. The most accurate way to do this is by means of a standard graph called a *calibration curve*. Plotting absorbance versus concentration for a series of standard solutions, gives rise to a straight line that passes through the origin (see Equation 2).

$$y = mx + b, \text{ where } y = \text{absorbance}, x = \text{concentration}, \text{ and } b = 0 \quad \text{Equation 2}$$

Using a calibration curve for quantitative analysis evens out fluctuations due to random error and establishes the range of concentration values over which Beer's law is valid.

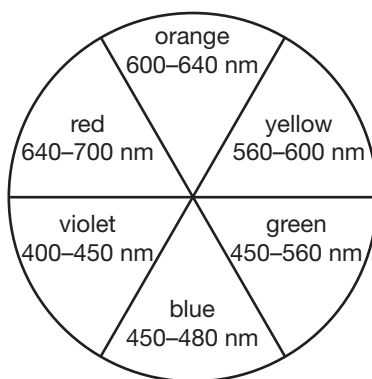
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Experimental Overview

The purpose of this advanced inquiry lab is to design a procedure to analyze the amount of copper in brass using visible spectroscopy. Brass can be dissolved by reacting it with concentrated nitric acid, which oxidizes the possible metal components of the alloy to their most common ions, Cu^{2+} , Zn^{2+} , and Fe^{3+} . The lab begins with an introductory activity to distinguish among these metal ions using visible spectroscopy. Students measure the absorbance of metal ion solutions at regular wavelength intervals from 400 to 700 nm and investigate the influence of the anion on the absorption spectra. The results provide a model for guided-inquiry design of an experiment to construct a calibration curve and determine the concentration of copper ions in a solution prepared by dissolving brass in nitric acid. Students must investigate the concentration range over which Beer's law is valid and identify the optimum wavelength for analysis.

Pre-Lab Questions

1. Dissolving brass requires an oxidizing acid such as concentrated nitric acid. Nitrogen dioxide is produced as a by-product in this reaction. Write a balanced chemical equation for the reaction of copper metal with concentrated nitric acid to produce copper(II) nitrate, nitrogen dioxide, and water.
2. Nitrogen dioxide is a toxic, reddish-brown gas. What safety precautions are needed in this inquiry lab to protect against this hazard, as well as the hazards due to the use of concentrated acid?
3. Copper(II) ions appear blue in aqueous solution. This is the transmitted color. The wavelengths of light that are NOT absorbed give rise to the perceived or transmitted color of a substance. Based on the principle of complementary colors, which colors or wavelengths of light would you expect to be most strongly absorbed by Cu^{2+} ions?



4. Spectroscopy measurements may be made in either percent transmittance ($\% T$) or absorbance (A). Based on the mathematical relationship between absorbance and transmittance, $A = -\log T$, explain why calibration curves of absorbance versus concentration may deviate from a straight line when $A < 0.1$ and when $A > 1$.

Materials (for each lab group)

Solutions for the *Introductory Activity*

- Copper(II) nitrate solution, $\text{Cu}(\text{NO}_3)_2$, 0.1 M, 5 mL
- Copper(II) sulfate solution, CuSO_4 , 0.1 M, 5 mL
- Iron(III) nitrate solution, $\text{Fe}(\text{NO}_3)_3$, 0.1 M, 5 mL
- Iron(III) chloride solution, FeCl_3 , 0.1 M, 5 mL
- Zinc nitrate solution, $\text{Zn}(\text{NO}_3)_2$, 0.1 M, 5 mL
- Zinc sulfate solution, ZnSO_4 , 0.1 M, 5 mL
- Brass sample, 1–2 g
- Copper(II) nitrate stock solution, $\text{Cu}(\text{NO}_3)_2$, 0.40 M, 10 mL
- Nitric acid, concentrated, HNO_3 , 15.8 M, 5 mL
- Water, distilled or deionized

- Balance, 0.001-g precision
- Beaker, 50-mL, with watch glass
- Cuvets or test tubes, 13 × 100 mm, 7
- Graduated cylinder, 50-mL
- Pipet, serological, 10-mL
- Pipet bulb or pipet filler
- Spectrophotometer
- Stirring rod
- Test tube rack
- Volumetric flask, 100-mL
- Wash bottle
- Weighing dish

Safety Precautions

Concentrated nitric acid is severely corrosive, a strong oxidizer, and toxic by ingestion and inhalation. Reactions of nitric acid with metals generate nitrogen dioxide, a toxic, reddish-brown gas. Work with nitric acid only in a fume hood. Copper(II) sulfate, copper(II) nitrate, and zinc nitrate solutions are toxic and irritating to skin and body tissue. Iron(III) chloride and iron(III) nitrate solutions may be skin and body tissue irritants. Zinc sulfate is a mild body tissue irritant. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron or lab coat. Please follow all normal laboratory safety guidelines. Wash hands thoroughly with soap and water before leaving the laboratory.

Introductory Activity

Visible Spectra of Transition Metal Ions

1. Read the entire procedure before beginning the activity.
2. Each group will be given 2–3 transition metal salt solutions to analyze. The possible solutions are $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 ; FeCl_3 and $\text{Fe}(\text{NO}_3)_3$; and $\text{Zn}(\text{NO}_3)_2$ and ZnSO_4 . All solutions are 0.1 Molar.
3. Follow the procedure for colorimetric measurements of the solutions as directed by the instructor. Generally, spectrophotometers are used as follows: Turn the instrument on and allow it to warm up for 15–20 minutes. Set the wavelength to the desired value. Handle cuvetts at the top so no fingerprints are in the light path. Polish cuvetts with a lens tissue. Place a cuvette that is about 2/3 full of distilled or deionized water into the sample holder and set the percent transmittance to 100% with the appropriate control. Fill a cuvette about 2/3 full of a test solution, place it in the spectrophotometer and record both wavelength and the absorbance.
4. Measure the absorbance of the first metal salt solution to be tested at 400 nm.
5. Increase the wavelength to 420 nm and reset the 100% T using the blank (distilled or deionized water). Replace the metal salt solution in the instrument and measure the absorbance.
6. Repeat step 5 every 20 nm to 700 nm.
7. Repeat steps 4–6 for each metal salt solution you have been assigned.
8. Plot the visible spectrum (absorbance versus wavelength) from 400 to 700 nm for each salt solution.
9. Report all spectra to the class for analysis in the guided-inquiry investigation.

Guided-Inquiry Design and Procedure

Part A. Calibration Curve for Cu^{2+} Solutions

Compare the visible spectra for the metal salt solutions studied by the class. Form a working group with other students and discuss the following questions.

1. For each salt solution, determine the species (cation and/or anion) that is responsible for the absorbance spectrum. Explain your reasoning.
2. Do Zn^{2+} ions absorb visible light? Discuss the answer in terms of (a) the color and appearance of Zn^{2+} aqueous solutions and (b) the electronic structure of Zn^{2+} ions. *Hint:* See the *Background* section for information on the electronic transitions of transition metal ions.

Consider the information provided in Questions 3–5 together. Recall that absorbance measurements are most accurate in the range 0.1 to 1.0.

3. Identify a suitable wavelength for analysis of Cu^{2+} ions in aqueous solution. The radiant intensity of light is highest in the middle of the visible range, and falls off dramatically at long wavelengths (700 nm).
4. If Cu^{2+} ions and Fe^{3+} ions are both suspected of being present in the solution, will Fe^{3+} ions interfere with the analysis of Cu^{2+} at the wavelength selected? Why or why not? Revise your answer to Question 3, if needed.

5. In order to accommodate the range of possible $[\text{Cu}^{2+}]$ concentrations that may be obtained by dissolving brass, it's recommended that the calibration curve extend from approximately 0.05 M to 0.4 M. Estimate the absorbance of standard solutions containing 0.05 M, 0.1 M, 0.2 M, and 0.4 M copper(II) nitrate at the selected wavelength. Revise your answer to Question 3, if needed.
6. Calculate the volumes of 0.4 M $\text{Cu}(\text{NO}_3)_2$ stock solution and water required to prepare 8.0 mL of each standard solution for your calibration curve.
7. Write detailed, step-by-step procedures for preparing the standard solutions and obtaining the calibration curve data. Include the glassware (e.g., pipets) and laboratory techniques needed to ensure precision and accuracy in transferring liquids, as well as the procedure for spectroscopic measurements.
8. Carry out the experiment, record the data, and graph the results. Analyze the best-fit straight line for the data and determine the slope of the Beer's law curve.

Part B. Percent Copper in Brass

Concentrated nitric acid is severely corrosive and the reaction of nitric acid with brass generates a toxic gas. The following procedure is provided to ensure laboratory safety.

1. Add two (2) brass shot pieces (about 1 g) to a small tared weighing dish and determine the mass to ± 0.001 g. Place the shot samples in a small beaker.
2. Concentrated nitric acid is required to dissolve the brass shot. You will need a slight excess of acid to completely dissolve the shot. Since the reaction generates the toxic gas nitrogen dioxide, $\text{NO}_2(\text{g})$, a fume hood is required for this step in the procedure. Place your beaker in the fume hood and have your instructor dispense 6 mL of 15.8 M nitric acid into your beaker. Cover the beaker with a watch glass.
3. Place the beaker on a hot plate dialed to a low setting (1–2). The shot should be completely dissolved within 10–20 minutes. Once the brass has dissolved, carefully remove the beaker from the hot plate and let it cool.
4. With the beaker still in the hood, use a graduated cylinder to carefully add 30 mL of deionized water to the beaker and stir the solution with a glass rod. The beaker can now be removed from the hood.
5. Using a stirring rod, quantitatively transfer the solution in the beaker to a 100-mL volumetric flask. Use a wash bottle to rinse the beaker with a small portion of deionized water. Transfer the rinse water to the flask. Repeat this washing two more times. Fill the flask to the mark with deionized water. Cap and mix well.
6. Analyze the absorbance of the brass solution and calculate the percent copper in the original brass sample.
7. Dispose of all solutions as directed by your instructor.

AP Chemistry Review Questions

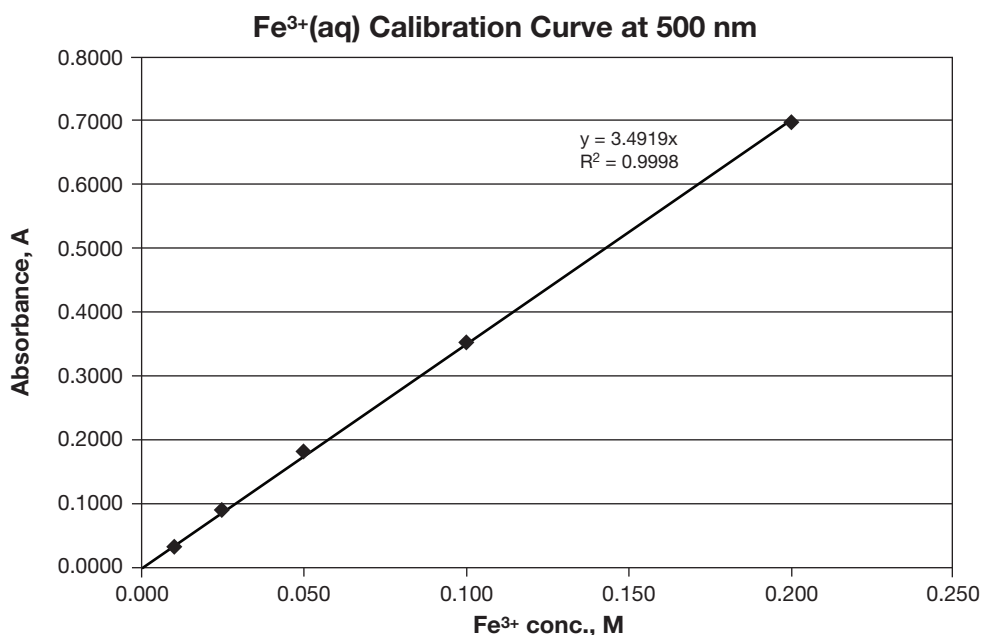
Integrating Content, Inquiry and Reasoning

1. Quality control samples were taken of a batch of nickel–iron alloy produced by Ionic Steel, Inc. in the furnace at their Springfield plant. The alloy must contain 43% nickel, $\pm 0.5\%$, with the remaining percent iron.

A 1.200-g sample was dissolved in hydrochloric acid and diluted to 100 mL in a volumetric flask. The Beer's law plot for the absorbance of $\text{Fe}(\text{NO}_3)_3(\text{aq})$ versus its concentration is listed below.

| $\text{Fe}^{3+}(\text{aq})$ Conc., M | Absorbance, A |
|---|------------------|
| 0.200 | 0.6954 |
| 0.100 | 0.3530 |
| 0.050 | 0.1790 |
| 0.025 | 0.0883 |
| 0.010 | 0.0318 |
| Sample | 0.3730 |

Slope = 3.4919



Calculate the percent iron contained in the alloy sample. Based on your results, is the batch of 43% nickel–iron alloy acceptable?

2. The characteristic flame test colors of metal ions are due to atomic emission spectra. Discuss the relationship between the absorption and emission of light and the factors responsible for flame test colors. Include quantization of electron energy levels and Planck's law in your answer.
3. The wavelength of the characteristic, bright yellow-orange flame test color of sodium is 590 nm. Calculate the average energy (ΔE) associated with this atomic emission line.