Protocol | Solution Preparation and Visible Spectroscopy

Introduction

Watch the conceptual introduction video Links to an external site.for this experiment.

Solutions are ubiquitous in chemistry. They provide a convenient medium for chemical reactions, enable safe and long-term chemical storage, and are generally easy to handle. They can also be studied systematically to reveal various properties of the solute. In this experiment, we will investigate a series of colored solutions, studying how their "brightness" depends on the concentration of the colored solute. We will then apply this relationship to determine the outcome of a chemical reaction. Specifically, we will measure the concentration of copper(II) ions in a solution produced via the oxidation of copper metal by nitric acid. Different pairs of students will measure the reaction at different time points, allowing the entire section to produce a graph of the time dependence of the reaction.

Visible Absorption Spectroscopy and the Beer-Lambert Law

Measurement of the color and "brightness" of a solution containing a colored solute can be accomplished through visible absorption spectroscopy. This technique is discussed in detail here. The absorbance *A* of the solution is measured as a function of the wavelength λ of light impinging on the sample. Absorbance is a logarithmic measure of the amount of light absorbed by the sample:

$$A(\lambda) = \log_{10} \frac{I_0}{I}$$

In this equation, I_0 and I are the intensity of the impinging light and transmitted light respectively. Even if the intensity of the impinging light is kept constant by the instrument, the intensity of transmitted light I depends on wavelength because the sample absorbs to different extents at different wavelengths. The graph that relates A to λ is called the visible absorption spectrum of the solute.

At any particular wavelength, there is a theoretical relation between the absorbance of the solute and its molarity. This relation is known as the Beer-Lambert law Links to an external site.. For a general solute M,

$$A(\lambda) = \epsilon(\lambda)[\mathrm{M}]\ell$$

The variable ℓ refers to the path length of light through the sample; in all our experiments it will be equal to 1.00 cm. Thus, ℓ can be omitted from the equation as long

as we keep in mind that the units of ε will be M^{-1} cm^{-1}. The proportionality constant ε is called the molar absorption coefficient Links to an external site.. This value reflects the extent to which the solute absorbs light at a given wavelength. Note that ε *does* vary as the wavelength of light is changed!

Because A and ε are directly proportional, absorption spectra are sometimes plotted with ε or $\log_{10} \varepsilon$ on the y-axis instead of A. Spectra plotted this way do not depend on the concentration of M. Thus, they provide a concentration-independent measure of how strongly the solute absorbs light over the range of wavelengths plotted on the x-axis. Large values of ε correspond to wavelengths at which the sample absorbs strongly.

We often are not concerned with the entire absorption spectrum, but only the wavelength where the solute absorbs most strongly. This wavelength, which is associated with the maximum value of ε (ε_{max}) is known as the wavelength of maximum absorption λ_{max}. Absorbance at λ_{max} provides maximum sensitivity when using A to measure concentration [M] because ε is as large as it can possibly be at this wavelength. A small change in concentration thus produces a relatively large change in absorbance at λ_{max}.

We will measure absorbance at λ_{max} over a series of known concentrations of copper(II) ion to determine ε_{max} by linear regression. See the detailed discussion of visible absorption spectroscopy for more details on the Beer-Lambert law and this analytical method. A video tutorial for measuring visible absorption spectra using LabQuest 2 and the SpectroVis spectrophotometer is here Links to an external site..

Chemical Systems Under Study

Copper metal is oxidized by nitric acid to form a solution of aqueous copper(II) nitrate according to the balanced chemical equation below. Orange-red nitrogen dioxide gas is given off and water is also produced.

$$Cu(s) + 4\ HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

Nitric acid is colorless but aqueous copper(II) ions are blue, so a color change will be observed as this reaction proceeds. Measurement of the visible absorption spectrum, combined with knowledge of the relationship between maximum absorbance and concentration ($[Cu^{2+}]$) for copper(II), will thus allow us to determine the concentration of copper(II) in the reaction mixture.

Before we can measure the reaction, we must determine how absorbance and $[Cu^{2+}]$ are related. (In other words, we must determine the form of the Beer-Lambert law for copper(II).) In Part A, we will first prepare standard solutions of copper(II) nitrate starting from a stock solution with a concentration of 1.00 mol/L. Systematic dilution of the stock solution will produce solutions with concentrations of 0.10 M, 0.080 M, 0.060 M, 0.040 M, and 0.020 M. We will also prepare a deionized water "blank" with a copper(II) concentration of 0.00 M. The absorbance of each solution at λ_{max} will be measured and we will construct a graph of absorbance as a function of molarity of copper(II). The equation reflecting the line of best fit for this data (*including the y-intercept as an error*

term!) will be used to measure the molarity of copper(II) in Part B of the experiment. By periodically sampling a reaction that produces copper(II), we will prepare a graph of the molarity of copper(II) over time and chart this concentration as the reaction proceeds.

Solution	$[Cu^{2+}]$ (mol/L)	Total Volume (mL)
1	0.000	10.00
2	0.020	10.00
3	0.040	10.00
4	0.060	10.00
5	0.080	10.00
6	0.10	50.00

Safety and Materials

The following reagents will be available:

- Copper(II) nitrate ($Cu(NO_3)_2$) solution, 1.00 MLinks to an external site.
- Copper metalLinks to an external site.
- Nitric acid (HNO_3) solution, 6.0 MLinks to an external site.

Consult the linked safety data sheets for important information related to handling and emergency procedures for these reagents.

Relevant Experimental Techniques

- Dilution and Solution Preparation
- Pipetting Liquids
- Recording Absorbance Spectra

Research Question

What is the average rate of reaction of copper with nitric acid?

Procedures

A. Measuring the Beer-Lambert Law for Aqueous Copper(II) Solutions

1. Prepare a table in your lab notebook that includes columns for solution number, [Cu^{2+}] (mol/L), and absorbance. List solutions 1 – 6 in the first column. In the second column, list the molarity of Cu^{2+} in each solution.
2. *Prepare a spectrophotometer or colorimeter.* Connect a SpectroVis spectrophotometer to a laptop by USB with the LoggerLite software opened. (Alternative: Use LabQuest 2 data acquisition device). Blank the spectrometer using a cuvette containing deionized water by clicking "Experiment" → "Calibrate" → "Spectrometer 1". (On a LabQuest, tap *Sensors* → *Calibrate*.) If only a colorimeter is available, set it to measure at 635 nm.
3. *Obtain the stock copper(II) nitrate solution.* In the hood, transfer about 10 mL of **1.00 M copper(II) nitrate solution** to a 50 mL beaker. The exact amount is not critical but do minimize the amount of stock you use.
4. *Dilute the stock solution to prepare a large quantity of solution 6.* Use the stock **1.00 M copper(II) nitrate solution** to prepare 50.00 mL of solution 6 (0.10 M) using a volumetric flask.
5. *Prepare solutions with accuracy and precision.* Use solution 6 as a stock to prepare solutions 1-5. Use a 5 mL serological pipet to transfer the stock solution and a 10 mL graduated cylinder to contain the diluted solutions.
6. First, determine the volumes of solution 6 required in each solution to prepare 10.0 mL of diluted solution at the target concentrations (from the table above).
7. Example: To prepare solution 2, transfer the required volume of solution 6 into the graduated cylinder and add **deionized water** *with extreme care* to the 10.0 mL mark, using a Pasteur pipet to add water dropwise until the meniscus sits right on the 10.0 mL line. If you overshoot this mark, repeat the dilution. Transfer the diluted solution into a clean, dry, and labeled test tube. Stir the solution briefly with the empty Pasteur pipet and discard the pipet.
8. Rinse out the graduated cylinder with deionized water and repeat the previous step to prepare other solutions, transferring into a different labeled test tube.
9. *Observe the sequence of solutions.* After all the solutions have been prepared, arrange them from least to most concentrated and record your observations.
10. *Measure the absorption spectrum of the most concentrated solution (spectrophotometer only).* Transfer a small amount of the most concentrated solution to a clean and dry cuvette. Click "Collect" to measure the full spectrum of absorbance for the sample. Click "Scale" to make it fit the window better. (If using LabQuest, set it to record in Full Spectrum mode, place the cuvette in the spectrophotometer, and press Play (▶). Stop recording after a few seconds, tap on the top of the absorbance peak.) Record the wavelength of maximum absorbance (λ_{max}).
11. Change the experiment mode. In LoggerLite, select "Wave" at the top and click "Absorbance vs Concentration" and enter the λ_{max} value. (LabQuest: on the first tab of the display, tap on the gray Mode box and set the LabQuest to record absorbance at λ_{max} by changing the mode to Time Based. Ensure that "Abs @ [your λ_{max} value]" is displayed in the red box. *Leave the spectrophotometer connected to the LabQuest for the duration of the experiment.*

12. *Measure absorbances at λ_{max} for solutions.* Measure the absorbance at λ_{max} for each solution. Transfer a small amount of solution into a clean and dry cuvette, place the cuvette in the spectrophotometer, and record the absorbance reading once it settles. In the LoggerLite software, click "Collect" and "Keep" for each sample. You can enter the molarity value for each point. This will generate a plot in the software as you add each solution absorbance and concentration. (for LabQuest or colorimeter, simply read the value on the screen and write it down)

B. Reaction of Copper Metal with Nitric Acid

1. Prepare a table in your lab notebook that includes columns for time (min) and absorbance. List 0.00 min, 1.0 min, 2.0 min, 3.0 min, 4.0 min, 5.0 min, and 10.0 min in the first column.
2. Empty all your cuvettes into a waste beaker, rinse them out using deionized water in a wash bottle, and dry them using Kimwipes. You will need “all cuvettes on deck” for this part of the experiment. Ensure that you have at least five clean and dry cuvettes available.
3. Label a clean and dry 50 mL beaker with your partner’s and your initials.
4. *Obtain a measurement of absorbance at 0.00 min.* In the hood, very carefully transfer about 25 mL of **6.0 M nitric acid solution** into the beaker. The exact amount is not critical.
5. Return the beaker to your bench, transfer a small amount of the nitric acid into a clean and dry cuvette, and measure its absorbance at λ_{max}. The value should be nearly zero and may well be negative (this is fine; consider why!).
6. Transfer the nitric acid back into the beaker and immediately rinse out the cuvette in the sink to remove residual nitric acid.
7. *Prepare and begin the reaction.* Obtain a small piece of copper metal and return it to your bench. Using a phone timer or one of the timers available in your lab room, prepare a stopwatch that will start when the reaction begins.
8. Add the copper metal to the solution, ensuring that it is fully submerged. Start your stopwatch!
9. *Remove a portion of the reaction mixture at each time point.* At 60 seconds (1.0 minute), transfer a portion of the reaction solution into a clean and dry cuvette supplied by your partner. Ensure that the reaction mixture remains in the hood when you transfer.
10. Repeat the previous step using another cuvette at 2.0 minutes. Repeat at 3.0, 4.0, 5.0, and 10.0 minutes. At the end of the reaction, you should have six cuvettes containing the reaction mixture “frozen” at the six time points in the table in your notebook.
11. *Record the absorbance at λ_{max} for each reaction mixture.* Place each cuvette in the spectrophotometer and record its absorbance at λ_{max}. Record the results in

your notebook. Make sure to record an absorbance value for the 10-minute mark as well.

12. Using tweezers or crucible tongs, extract remaining copper metal from the reaction mixture. Rinse it with water, dry it, and return it to the "Used Copper" container in the hood.
13. Discard the reaction mixture and the contents of any waste beakers and cuvettes in the waste bottle in the hood. Use a wash bottle with deionized water to rinse out the beakers and cuvettes.
14. Unplug the spectrometer from the laptop (or LabQuest) and return the spectrometer to the data devices box.
15. ***Concept Check!*** Draw two boxes of equal size in your notebook. Label one "1.00 min" and the other "5.00 min." Depict the copper(II) ions in solution in each box at each time point, using simple labeled circles to represent the ions. Pay close attention to the numbers of ions in each box. Indicate which box has the greater concentration of copper(II) ions.

Group Argumentation

Merge data with the other students at your lab bench. Decide whether to average measured absorbances for each time point or use two lines and get an average rate at the end. Together conduct an analysis that approximates the rate (molarity per minute) of copper ion formation. Discuss and determine a conclusion that answers the research question based on your findings. Support the conclusion with evidence from the experiment and background information that helped to lead you to this conclusion. The argument your group develops should be recorded in your lab notebook before leaving class.

Post-lab Calculations and Data Workup | Spreadsheet

Part A. Using the data workup spreadsheet as a template, prepare a graph with absorbance at λ_{max} on the *y*-axis and concentration of copper(II) in mol/L on the *x*-axis (Table 1, Figure 1). Add a line of best fit with equation and R^2 to the graph. Ensure that your graph meets the specifications outlined here, which will apply for *all graphs* of CHEM 1211K and 1212K data. The equation of the line of best fit on this graph is the Beer-Lambert relation for aqueous copper(II).

$$A = \epsilon \ell [\mathrm{Cu}^{2+}] + \delta$$

Note that δ is an error term that absolutely *should* be included in all your calculations related to Part B of the experiment, as it captures systematic error in the measurement of absorbance and/or concentration.

Part B. Tabulate the time dependence of absorbance at λ_{max} for the reaction of copper metal with 6.0 M nitric acid, applying your best-fit equation from Part A to determine $[Cu^{2+}]$ at each time point (Table 2). Prepare a graph of the time dependence of $[Cu^{2+}]$ (Figure 2). *Do not* add a line of best fit to this graph as the data is not expected to be linear (stay tuned for more on that in CHEM 1212K).