Experiment 18 - Absorption Spectroscopy and Beer's Law: Analysis of Cu^{2+}

Many substances absorb light. When light is absorbed, electrons in the ground state are excited to higher energy levels. Colored substances, including many transition metal ions, absorb light in the visible region of the electromagnetic spectrum. The color you see is often the opposite of the color absorbed. It is possible to measure the amount of light absorbed by a sample using an instrument called a spectrophotometer.

Spectrophotometers in general contain a light source, a diffraction grating that separates the light into different wavelengths, a sample holder, and a detector that detects the amount of light that passes through the sample. The percent transmittance of the sample is the percent of incident light that actually passes through the sample. The absorbance of the sample is defined as the negative log of the transmittance.

$$T = \frac{I^{\lambda}}{I_0^{\lambda}} \qquad \%T = \frac{I^{\lambda}}{I_0^{\lambda}} \times 100 \qquad A = -\log_{10} T$$

In the above equations, T represents the transmittance, I^{λ} represents the intensity of light transmitted through a sample at a specified wavelength, I_0^{λ} represents the intensity of the light transmitted with no sample in the spectrophotometer, $\%T$ represents the percent transmittance, and A represents the absorbance of the sample.

The absorbance of the sample is related to the molar concentration of the absorbing substance in the solution. The relationship is given by the following equation, which is also known as **Beer's Law**:

$$A = abc$$

Where A is the absorbance of the solution, a is a constant called the molar absorptivity (which has units of L cm^{-1} mol^{-1} and depends of the substance used), b is the path length of the light through the solution in centimeters (this corresponds to the width of the inside of the sample cell or cuvette), and c is the concentration of the absorbing substance in molarity (moles/liter). The absorbance A is unitless. The constant a is sometimes given the symbol ε.

If the type of substance and the path length are constant, then the absorbance is proportional to the concentration (in molarity) of the substance in the solution. The absorbance of several solutions of known concentration can be measured. If the results of absorbance vs. concentration are graphed, the result is a straight line. Each point on the line represents an ordered pair that gives the concentration that corresponds to a particular absorbance reading. An unknown solution can then be analyzed by measuring its absorbance. To determine the concentration of the unknown, one can merely locate the observed absorbance reading on the graph and see what concentration corresponds to this absorbance.

The wavelength of light that will be used in this experiment is 620 nm. This wavelength does not correspond to the wavelength of maximum absorbance for copper ions, but it gives conveniently-sized values of absorbance for the concentrations of Cu^{2+} that we will be using. (The absorbance readings are not so high that they are "off-scale.")

In this experiment, you will make a solution containing $Cu^{2+}_{(aq)}$. You must be careful to make your measurements quantitatively so that you know the molar concentration

of the copper ions as precisely as possible. You will then quantitatively make several dilutions of your copper solution. You will measure the absorbance of these solutions at 620 nm. Using this information, you will then prepare a graph of absorbance vs. concentration (this graph should be a straight line).

In the last part of the experiment, you will analyze an unknown. Your unknown will be an impure sample of the same copper compound that you used in the first part of the experiment. You will make a solution from this sample, measure the absorbance of the sample, and determine the concentration of Cu^{2+} from your Beer's Law graph. You will then calculate the percent purity of this impure sample.

$$\text{percent purity of X in a mixture} = \frac{\text{mass of X}}{\text{total mass of mixture}} \times 100$$

Safety Precautions:

- Wear your safety goggles.
- Treat the spectrophotometers and cuvettes carefully. They are very expensive!

Waste disposal:

- Solutions containing copper ions should go in the INORGANIC WASTE bottles (which have a blue label) in one of the fume hoods after the experiment.

Prelab Questions:

1. Calculate the mass of $CuSO_4 \bullet 5H_2O$ needed to make 100.0 mL of 0.35 M $CuSO_{4\ (aq)}$.
2. Why is it necessary to be so careful in making up the standard solution?
3. If 8.09 mL of 0.350 M $CuSO_4$ is mixed with 2.13 mL water, calculate the $[Cu^{2+}]$ in the resulting solution.

Procedure

Work in pairs or singly. (Do not work in groups of 3 or 4.)

Part 1 – Preparation of a Standard Copper Ion Solution

In this part of the experiment, you will prepare 100.0 mL of 0.35 M $CuSO_4$ solution using solid $CuSO_4 \bullet 5H_2O$ and a 100-mL volumetric flask. The solution does not have to be exactly 0.35 M, but it must be approximately 0.35 **and** it must be known to 4 significant figures. The procedure for doing this is as follows:

1. Get a 100.0-mL volumetric flask, a plastic weighing boat, a functional wash bottle containing deionized water, and a small plastic funnel that has a short neck.
2. Weigh the weighing boat on an **analytical** balance to 3 or 4 decimal places. (This will give you at least 4 significant figures for the mass measurement.)
3. Transfer the approximate amount of solid copper sulfate pentahydrate to the weighing boat. Record the mass of the weighing boat plus the solid.

4. Place the funnel into the neck of the volumetric flask. Transfer the solid to the volumetric flask by rinsing it into the funnel using a jet of water from the wash bottle. Make sure not to lose any of the solid sample. The precision of your experiment depends on this: all of the solid that was weighed in the weighing boat must get into the volumetric flask. This is very important.
5. When all of the solid has been rinsed out of the weighing boat, rinse the inside of the funnel thoroughly into the volumetric flask. The purpose of this is to make sure that all traces of the solid get into the flask and thus into your solution. Set the funnel aside.
6. Rinse down the inner walls of the stem of the volumetric flask, so that all of the solid is below the level of the mark.
7. Add more water so that the flask is about 3/4 full. Use parafilm to close the top of the flask. Hold the parafilm in place and mix well for several minutes to dissolve the solid.
8. Remove the parafilm and add more deionized water up to the point at which the neck of the flask starts, rinsing down the inner walls of the neck of the flask as you go. Swirl the flask gently.
9. Add deionized water **using a dropper** so that the level of the solution is just at the marking on the neck of the flask. (The bottom of the meniscus should be right on the line.) If you accidentally put in too much water and the volume is over the line on the flask, you must start over. (You will not know the volume to 4 significant figures!)
10. Use parafilm to seal the flask. Hold the parafilm in place and mix by swirling and inverting for several minutes.
11. Calculate the actual concentration of the copper sulfate solution in units of molarity. The volume of the flask is 100.0 mL. Since you prepared this solution very carefully and since you know its concentration to 4 significant figures, this is known as your "standard solution."

Part 2 - Preparation of Diluted Solutions

In this part of the experiment, you will prepare several dilutions of the standard Cu^{2+} solution. You must prepare them quantitatively so that you can determine their concentrations to 3 significant figures. You will be using graduated pipets to make these dilutions. The instructor will demonstrate the proper procedure for using pipets. Make sure to examine the markings on the pipets before using them so that you know how to read the volume correctly. It will be less confusing if you select two pipets that have identical graduations.

1. Obtain 4 medium-sized test tubes from your locker. They must be dry. Label them as tubes 2, 3, 4, and 5. (Solution 1 will be your standard copper solution.)
2. Obtain two 10-mL graduated pipets and one pipet bulb. Label one pipet "Cu^{2+}" and the other pipet "water".
3. Obtain 3 beakers. A large one can be labeled "waste". Rinse a small, clean, **dry** beaker with a small amount of your copper standard solution, pour the rinse solution into the waste beaker, and then put approximately half of the copper standard solution into this beaker. Rinse a different clean beaker with deionized water and then fill it with deionized water.
4. Rinse the pipet labeled "water" three times with deionized water from the beaker. Each time, dump the rinse into the "waste" beaker. Be very careful to never get water or any other solution into the pipet bulb. *You will only use this pipet for water.*

5. Rinse the pipet labeled "Cu^{2+}" three times with small amounts of the standard copper solution. Dump the rinses into the waste beaker. *You will only use this pipet for the copper standard solution.*
6. Now you are ready to make dilutions. You will need the approximate amounts listed in the following table. Each time you use the graduated pipet, you will need to record the actual volume used to 3 significant figures (2 decimal places). For example, test tube 2 should contain approximately 8 mL of Cu^{2+} solution and 2 mL of water, for a total volume of about 10 mL. However, you must record the actual volumes used so that you can calculate the precise concentration of this solution later. You could use, for example, 8.13 mL of copper solution and 2.08 mL of water. This would give a total volume of 10.21 mL. Again, the important thing is to know the actual amounts used. Therefore, you **do not** need to spend lots of time getting volumes of exactly 8.00 mL and 2.00 mL.

Test tube #	# mL Std. Cu	# mL water
2	8	2
3	6	4
4	4	6
5	2	8

Record the actual volume of each solution used to make each mixture in your lab notebook.

7. Get 4 separate small pieces of parafilm. Close the top of each of these test tubes securely with parafilm and mix each one well (by shaking).

Part 3 – Absorbance Measurements for a Standard Curve

Follow the directions for proper use of the spectrophotometer (see the appendix). Let the instrument warm up for 15 minutes prior to using it. Make sure it is set to the appropriate wavelength (620 nm), using the appropriate filter. You will use the same cuvette for all measurements. All of the absorbance measurements should be done on the same day, using the same equipment, so that it is consistent.

1. Rinse out a cuvette with deionized water and fill it with deionized water. This will be your "blank" solution. Wipe off the outside of the cuvette with a kimwipe, and place it in the spectrophotometer. Close the sample cover. Follow the steps to "zero" the spectrophotometer. Water does not absorb light in the visible region of the electromagnetic spectrum, so it should measure zero absorbance. You will adjust the instrument so that it actually does read zero absorbance with the water in the sample chamber.
2. Dump out the water from the cuvette, then rinse it thoroughly three times with small portions of the standard copper solution that you made in part one. Each time, discard the rinse solution into a waste beaker. The purpose of this step is to make sure that you don't dilute the concentration of the solution you made with any drops of water still adhering to the inside of the cuvette. This way, you can be sure that the solution you are measuring the absorbance of is still the same concentration as the solution you made. To summarize the steps: rinse the cuvette three times with the first solution, fill it with the solution, wipe off the outside of the cuvette with a kimwipe, and then measure the absorbance of this solution.
3. Dump the first solution into the waste beaker, then rinse the cuvette three times with the next solution to be tested, and measure its absorbance.

4. Repeat this procedure for each solution to be tested.

Part 4- Analysis of an Unknown

1. Obtain an unknown vial and record the unknown number.
2. Weigh the unknown vial with the unknown solid in it, and record the mass. Transfer all of the solid to a 250.0-mL volumetric flask. Weigh the empty vial and record its mass. Make 250.0 mL of solution from this sample, using the same general procedure you used when making the standard solution in Part 1.
3. Measure the absorbance of this solution. (Don't forget to zero it with a blank and rinse the cuvette three times with the solution to be used in it. For best results, use the same cuvette that you used in part 3.)
4. If the absorbance is too high, make a dilution (it is very important to keep track of the exact amounts used so that you can calculate the concentration). In order to use the graph that you made, the absorbance of your sample must fall within the area that contains the plotted points in your graph. (This means that the absorbance reading you use should be within the range of the absorbance readings of your standard solution and dilutions. It should be higher that the lowest absorbance and lower than the highest absorbance you found in Part 3.) After making the dilution, measure the absorbance of the new solution.
5. Using the graph, determine the concentration of copper ions in the solution. The unknown consists of solid $CuSO_4 \bullet 5H_2O$ and an inert impurity. Calculate the mass of copper (II) sulfate pentaydrate present in the unknown sample. From this result and the total mass of the sample, calculate the percent purity of the unknown.

Procedural note for two 1.5-hour lab periods:

Make all solutions and dilutions, including the unknown solutions, on day one. Save these, stoppered and labeled, in your locker.

Take all absorbance measurements on day 2.

Calculations

1. Calculate the concentration (in M) of the standard copper solution you made in Part 1.
2. Calculate the concentration of copper ions for each of the dilutions you made in Part 2.
3. Make a graph of absorbance at 620 nm vs. concentration of copper (II) ions in units of molarity. You will have 5 points, plus the origin (0,0). Since the absorbance of a solution containing no copper ions should be zero, (0,0) is one of the points to plot. Follow the graphing guidelines. Draw the best straight line among the points.
4. Using the straight line on the graph you made, determine the concentration of copper ions in your unknown solution from its absorbance at 620 nm. (Estimate the value from the graph.)
5. From the concentration of your unknown and the volume of the solution, determine the number of moles of copper present in the unknown sample. Don't forget to take into account any dilutions you made.
6. Determine the mass of $CuSO_4 \bullet 5H_2O$ present in your unknown sample. Calculate the percent purity of the sample.

$$\text{percent purity} = \frac{\text{mass of compound present}}{\text{mass of entire sample}} \times 100$$

7. Include the unknown number in the "Summary of Results" sections.

Questions

1. When preparing the standard solution in Part 1, why can't we just put the solid in the flask, fill it with water up to the mark, and then mix?
2. Why is it necessary to rinse the pipets with the solution to be used in them before using the pipets?
3. Why is it necessary to rinse out the cuvette with the solution to be used in it before making our measurements?
4. Why must we use the same cuvette for all measurements?
5. What is the purpose of "zeroing" the spectrophotometer using a "blank" solution (water)?
6. What assumptions are we making in the calculations and analysis for this lab?
7. 6.019 g of an unknown copper compound was dissolved in 100.0 mL solution. The absorbance of this solution was 0.477 at 620 nm. Use your Beer's law graph to determine the concentration of copper ions in this solution. Then determine the mass percent copper in the copper compound.