Experiment 7F

QUANTITATIVE SPECTROSCOPY

MATERIALS: Spectronic 200 spectrometer; 50 mL beakers (3); 100 mL beaker (1); 25 mL volumetric flasks; 0.500 M $Cu(NO_3)_2$ solution, 0.100 M $Cu(NO_3)_2$ solution, 0.100 M $Ni(NO_3)_2$ solution, 0.100 M $Fe(NO_3)_2$ solution, Plexiglas sheets (4), cuvettes, plastic pipets, 18 x 150 mm test tubes (5), buret

PURPOSE: The purposes of this experiment are: (1) to observe the visible spectrum of copper(II) nitrate solutions and (2) to determine the quantitative aspects of spectroscopy, including the relationship between percent transmittance, absorbance, path length, concentration and molar absorptivity.

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

1. Obtain an absorbance spectrum for an aqueous solution.
2. Measure the percent transmittance of a solution at a given wavelength.
3. Determine how percent transmittance is effected by path length, concentration and wavelength.
4. Convert percent transmittance values to absorbance and determine how absorbance is effected by path length, concentration and wavelength.

DISCUSSION:

Purpose of this experiment. The two volumetric flasks in Figure 1 both contain the same compound, copper(II) nitrate, $Cu(NO_3)_2$, dissolved in water. In this experiment, we will try to understand why these solutions look so different.

I. **Color of Solution.** The concept of color is complex and involves not just the interaction of light with matter, but our perception of it by eye and brain. For example, when we look at the two solutions in Figure 1, we are seeing two things: (a) color and (b) intensity of color. The solutions are a different concentration, but they have the same chemical composition. Shouldn't they have the same color? However, the human eye perceives them as slightly different colors (royal blue to turquoise), in addition to the more concentrated solution being a "deeper" blue.

Figure 1: Solutions of copper(II) nitrate; the solution on the left is 1.0 M and the solution on the right is 0.10 M.

II. **The Spectrometer.** Like your eye, a spectrometer responds to light. Some major differences are that your eye takes in all light and has three color detectors (red, green and blue cones) then your brain synthesizes a color and shape response for every part of your field of view. *Many sources-multiple "samples"-three detectors*. The complexity of this process is amazing to behold. A spectrometer has a simpler task. The visible light source is split into its components using a diffraction grating. As the spectrometer scans across each wavelength of light, the light passes through and interacts with a (hopefully) homogenous sample, then the remaining light is observed using a detector. *One light source-one sample compound-one detector*.

III. **The Experiment.** We will use a spectrometer to determine exactly how the solutions, at different concentrations, are interacting with light. In Part A of the procedure, you'll examine the characteristics of the solution on the right. In Part D of the procedure, you'll examine if and how the solution on the left differs. In Part B of the procedure, you'll make several solutions of varying concentration and examine how they interact with light. In Part E, you'll look at two other compounds and see how they differ from the copper(II) nitrate.

IV.   **Intensity of Color.** Look more closely at the two flasks and you'll notice that for each solution, how dark the solution appears is different in the neck of the flask than it is in the bottom of the flask. Why is this so? What differs in this case is how much of the solution the light travels through. This is called the **path length** and Part C of the solution examines how varying path length varies the intensity of the solution.

V.   **Taking Observation to Mathematical Model:** Once you have made measurements as you changed wavelength of light, concentration of compound, path length of observation and compound observed, you will then summarize your findings into a mathematical relationship, called Beer's Law.

Light and Matter

Many substances and solutions absorb visible light, and thus some light is not there for us to see or detect with a spectrometer. Thus, what is <u>lost</u> in *light* tells us something about what is <u>there</u> in *matter*: **this is spectroscopy—we observe the sample by the light we are not observing**. The color and intensity that we do observe with our eyes are related to wavelengths of light and how much the incident light, I_o, is transmitted or reflected by the sample. Our spectrometer measures the light transmitted by our sample and we realize the wavelength of light absorbed is determined by the structure of the substance observed. So finding out how much light is missing from each incident (incoming) light wavelength tells us something about the amount and physical properties of the compound interacting with the light.

As discussed in your text, the absorbance of a photon of light can occur when the photon energy matches an energy transition in the sample. For example, the proper energy photon causes an electron to move from a low energy orbital to a higher energy orbital. For atoms in the gas phase, absorbance is observed as missing narrow lines in the rainbow of the full spectrum of visible light—a line spectrum. The spectra of solid substances and solutions generally give spectra similar to that shown in Figure 2. Note that the y-axis is in absorbance, rather than transmittance, and is plotted against wavelength. This is often more convenient because absorbance should be related to the compound in solution, and the wavelength where the absorbance is highest (designated λ_{max}) should be a characteristic of that compound.
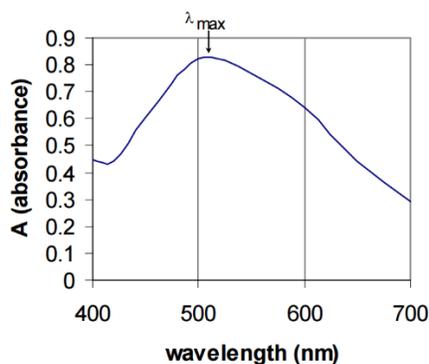

Figure 2: Absorbance spectrum of an aqueous solution. λ_{max} is the wavelength of maximum absorbance.

Light and Intensity

When light of a particular wavelength (λ) is absorbed by a sample, the intensity of light that initially strikes the sample (I_O) can be compared to the intensity of light that passes through the sample (I).
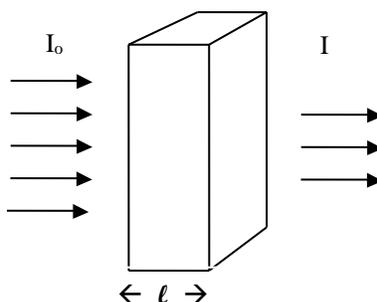

Figure 3: Incident light transmitted through a sample, path length ℓ.

The **transmittance** (T) is defined as the fraction of the light striking the sample that passes through the sample:

$$T = I/I_O \qquad \%T = (I/I_o) \times 100$$

Absorbance (A), how much light is absorbed, is related to transmittance <u>logarithmically</u>:

$$A = \log_{10}(1/T) = \log_{10}(I_O/I) = -\log(\%T/100) \qquad \textbf{Eqn. 1}$$

Thus, when no light is absorbed by a sample, $I = I_O$, $T = 1$, $\%T = 100$, and $A = 0$. Conversely, when all of the light that strikes a sample is absorbed by it, $I = 0$, $T = 0$, $\%T = 0$, and A is infinite.

Concentration. Matter is classified in many ways. When we have a pure substance, it can be either an element or a compound. Compounds can be ionic or molecular. Mixtures can be homogenous or heterogeneous.

A homogeneous mixture is a solution, and General Chemistry is especially interested in a solution consisting of a compound dissolved in water. In a process called solvation, water stays liquid and still changes nearest neighbors often, but now the neighbors include other things. When a molecular compound like ethanol (C_2H_5OH) dissolves, waters surround the individual ethanol molecules. When an ionic compound, such as copper(II) chloride ($CuCl_2$), dissolves, waters surround the individual cations (e.g. Cu^{2+}) and anions (e.g. Cl^-) are surrounded by water, thus the ions separate. The waters near the cation are oriented so that the oxygen atom is close to the cation. For anions, the opposite orientation is seen. For a more detailed discussion of this topic, consult the appropriate sections of your text (and see the figure below).
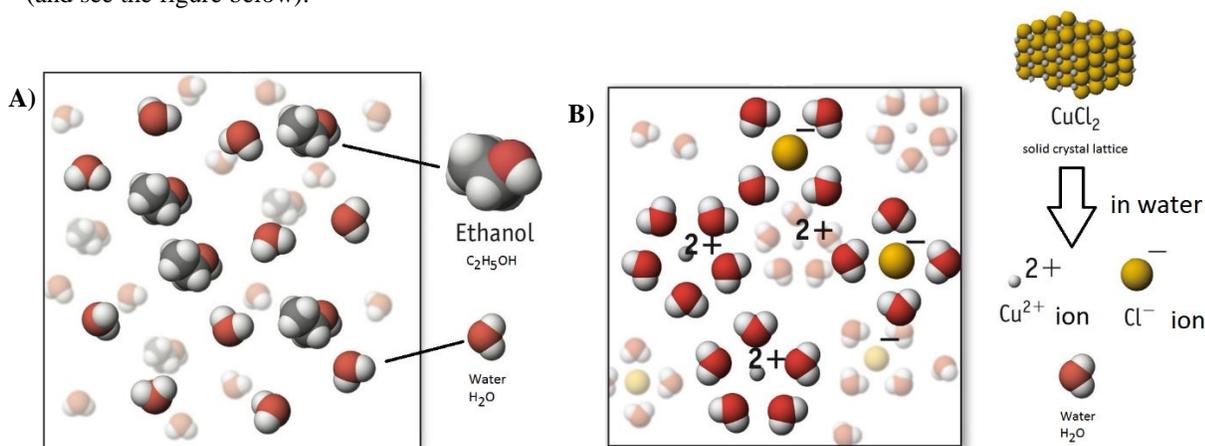
Figure 4: Solvation Process. A) Molecular: Ethanol in water, B) Ionic: $CuCl_2$ in water.

It is appropriate in determining how many individual molecules are present in a sample of pure molecular compounds to use the mass of the sample and the molar mass. For solutions, if we want to know how many molecules or ions are present, we use concentration instead. The most commonly used concentration unit is **molarity, M** which is defined as the number of moles of a specific compound (the solute) in 1.00 L of solution. Molarity is a very useful conversion factor that allows us to calculate the number of 1) moles of solute in the solution and 2) how many individual solute particles are present if we know the molarity of a solute and the volume of the solution.

$$M = \frac{moles\ of\ solute}{L\ of\ solution}$$

PROCEDURE:

Part A. Absorbance and Transmittance Spectra of Copper(II) Nitrate

1. Using a 50 mL beaker, obtain about 10 mL of **0.100 M** copper(II) nitrate solution. This solution will be used for parts A, B and D of the experiment, so keep this solution until the end of the experiment.

2. Turn on the Spectronic 200 spectrometer. Calibrate the instrument using the supplied instructions. Use distilled water as a blank. Set the instrument to scan the visible spectrum, from 400 nm to 900 nm in Absorption mode.

3. Rinse a plastic cuvette with deionized water; then rinse with the 0.100 M copper(II) nitrate solution, and finally fill the cuvette about 2/3 full with the copper(II) nitrate solution. Wipe any fingerprints off the cuvette with a light-duty wipe. Insert the cuvette in the spectrometer and scan the spectrum.   To find the wavelength(s) of maximum absorption, use your spectrum acquired to select a wavelength close to the maximum and then fine tune to the maximum using the wavelength knob. Record that wavelength and make a rough sketch of the absorbance spectrum in Part A of the Data Section.

4. Return to the SCAN menu and set the instrument to record in the %T mode. Scan your solution and sketch the Transmission spectrum in the Data Table.

5. Return to the Home menu and put the spectrometer in Spec 20D emulator mode. Set the wavelength to the maximum absorption value measured in step 3.   Record the absorbance of the solution at this wavelength.

Part B. Transmittance and Path length

1. Set the spectrometer to transmittance mode. If necessary, adjust the wavelength to the λ_{max} from Part A.

2. Obtain four polycarbonate sheets. Place all four into a cuvette, as shown in Figure 5, with the clear sides of the sheets facing the arrow on the cuvette.

3. Add 0.100 M copper(II) nitrate to the cuvette until it is 2/3 full. Look through the sample and make sure no air bubbles are present. Place the cuvette in the spectrometer and record the percent transmittance. Your value should be close to 75%. If it is very low, make sure you have inserted the sheets in the proper direction.

4. Remove one of the sheets and then add more copper(II) nitrate solution until the cuvette is 2/3 full. Record the percent transmittance.

5. Repeat step 4 twice, ending with a cuvette containing no sheets and 2/3 full of the copper(II) nitrate solution. Record percent transmittance for each step.

Figure 5.

Part C. Transmittance and Concentration

1. Obtain approximately 30 mL of **0.500 M Cu(NO₃)₂** solution in a 100 mL beaker. (Note the concentration.)

2. Rinse a buret and add approximately 20 mL of the 0.500 M copper(II) nitrate solution.

3. Dispense 1.00 mL of the copper(II) nitrate solution into a 25.00 mL volumetric flask. Dilute it to the mark with distilled water and mix. Record your initial and final buret readings. (It is <u>not</u> necessary to get exactly 1.00 mL since you can determine the actual volume delivered from your readings.)

4. Transfer this solution to a clean, dry test tube.

5. Repeat steps 3-4, using the volumes of copper(II) nitrate solution indicated in the table.

Solution	Target volume of 0.500 M $Cu(NO_3)_2$ (mL)
1	1.00
2	2.00
3	3.00
4	4.00
5	5.00

6. Rinse a clean cuvette with solution 1. Discard the rinse solution and then fill the cuvette to the line with solution 1. Measure the percent transmittance of this solution at the λ_{max} from Part A and record in the Part C table of the Data Section.

7. Repeat step 6 with solutions 2-5, recording their percent transmittances.

Part D. Absorbance and Wavelength

1. Set the Spectronic 200 to SCAN mode. Rinse a plastic cuvette with deionized water; then rinse with the 0.100 M copper(II) nitrate solution, and finally fill it about 2/3 full with the copper(II) nitrate solution. Insert the cuvette in the spectrometer and scan the spectrum. As in Part A.3, use the wavelength knob to find the wavelength(s) of maximum absorption.

2. Record the absorbance at the maximum wavelength in the table.

3. Adjust the wavelength to 675 nm. Record the absorbance at this wavelength.

4. Adjust the wavelength to 500 nm. Record the absorbance at this wavelength.

Part E. Absorbance Spectra of other Metal Cations

1. Obtain approximately 5 mL of 0.100 M $Ni(NO_3)_2$ solution in a 50 mL beaker. Rinse a plastic cuvette with deionized water; then rinse with the 0.100 M nickel(II) nitrate solution, and finally fill it about 2/3 full with the nickel(II) nitrate solution. Insert the cuvette in the spectrometer and scan the absorbance spectrum. Use the wavelength knob to find the wavelength(s) of maximum absorption. Record that wavelength and make a rough sketch the absorbance spectrum in the Data Table.

2. Record the absorbance at the maximum wavelength in the table.

3. Obtain approximately 5 mL of 0.100 M $Fe(NO_3)_3$ solution in a 50 mL beaker. Rinse a plastic cuvette with deionized water; then rinse with the 0.100 M iron(III) nitrate solution, and finally fill it about 2/3 full with the iron(III) nitrate solution. Insert the cuvette in the spectrometer and scan the absorbance spectrum. Use the wavelength knob to find the wavelength(s) of maximum absorption. Record that wavelength and make a rough sketch the absorbance spectrum in the Data Table.

4. Record the absorbance at the maximum wavelength in the table.

Clean-Up: Dispose of all metal ion solutions in the appropriate waste container. Rinse all glassware and cuvettes with distilled water and turn off the spectrometer.

Name _____   Section _____

Partner _____   Date _____

DATA SECTION
Experiment 7F
Part A. Absorbance and Transmittance Spectra of Copper(II) Nitrate

Wavelength of Maximum Absorbance, λ_{max} (nm)	Absorption Spectrum Sketch	Transmission Spectrum Sketch	Absorbance at λ_{max}
	Abs wavelength	%T wavelength	

Part B. Transmittance and Path Length

Width of sheet: _____0.20 cm_____

Number of sheets	Path length (cm)	percent transmittance
4		
3		
2		
1		
0	1.00 cm	

Part C. Transmittance and Concentration

Solution	Initial Buret Volume (mL)	Final Buret Volume (mL)	Volume added (mL)	percent transmittance
1				
2				
3				
4				
5				

Part D. Absorbance and Wavelength

Wavelength (nm)	Absorbance

Part E. Absorbance Spectra of other Metal Cations

Solution	Observed Color of solution	Wavelength of Maximum Absorbance, λ_{max} (nm)	Absorption Spectrum Sketch	Absorbance at λ_{max}
$Ni(NO_3)_2$			Abs · wavelength	
$Fe(NO_3)_3$			Abs · wavelength	

DATA TREATMENT AND ANALYSIS
Experiment 7F

Part B. Transmittance and Path length

(B.1) Using Excel, enter your data for this section. Your column headings should be Number of Sheets, Path length and %T. Each sheet is 0.20 cm thick and the cuvette is 1.00 cm in width.

(B.2) Insert a graph of percent transmittance vs. path length. Properly format your graph with appropriate titles and axes labels. Add a linear trendline and R^2 value.

(B.3) Add a column and calculate the Absorbance of each run, using Eqn. 1 from page 7F-3. Insert a graph of Absorbance vs. path length. Properly format your graph with appropriate titles and axes labels. Add a linear trendline and R^2 value.

(B.4) Which graph was most linear? (Circle one)

      % Transmittance vs. path length   **Absorbance vs. path length**

      How do you know this? _____

(B.5) When a linear relationship is found, we can express that relationship as the equation of the line, substituting the appropriate symbols from the values measured in the experiment. In this experiment, you chose values for path length, l, for your independent variable, shown on the x-axis. What value is on the y-axis in the linear graph? _____
Complete the expression below.

$$\underline{\hspace{2cm}} = (slope) \cdot l \ + \ y\text{-}intercept$$

$$y \quad = \quad m \cdot x \ + \ b$$

(B.6) What are the units for the slope of the line? _____

Part C. Transmittance and Concentration

(C.1) Using Excel, enter your data for this section. Add a column and calculate the concentration in molarity of each solution. In the procedure, you carried out a dilution: making less concentrated solutions from a more concentrated solution. To calculate the concentration, the equation $M_1V_1 = M_2V_2$ should be used. M_1 is the concentration of the solution in the buret; the more concentrated solution. V_1 is the amount added from the buret. V_2 is the volume of the volumetric flask or final solution. You are calculating M_2, the concentration of the dilute solution. Thus your equation is: $M_{buret}V_{buret} = M_{solution}V_{solution}$.

(C.2) Insert a graph of percent transmittance vs. concentration. Properly format your graph with appropriate titles and axes labels. Add a linear trendline and R^2 value.

(C.3) Add a column and calculate the Absorbance of each run. Insert a graph of Absorbance vs. concentration. Properly format your graph with appropriate titles and axes labels. Add a linear trend line and R^2.

(C.4) Which graph was most linear? (Circle one)

      % Transmittance vs. concentration   **Absorbance vs. concentration**

      How do you know this? _____

(C.5) When a linear relationship is found, we can express that relationship as the equation of the line, substituting the appropriate symbols from the values measured in the experiment. In this experiment, you chose values for concentration, c, for your independent variable, shown on the x-axis. What value is on the y-axis in the linear graph? _____ Complete the expression below.

$$\underline{\hspace{2cm}} = (slope) \cdot c \ + \ y\text{-}intercept$$

(C.6) What are the units for the slope of the line? _____

(C.7) For both parts B and C, the linear relationship should have had the same variable, %T or A, on the y-axis. In cases like these, we say that quantity is proportional to both path length and concentration and can write another equation, showing that,

$$\underline{\hspace{2cm}} = [(slope) \cdot c \cdot l \ ] + y\text{-}intercept$$

In an ideal case, the y-intercept for this experiment should be zero and the equation simplifies to

$$\underline{\hspace{2cm}} = (slope) \cdot c \cdot l \ = (constant) \cdot c \cdot l$$

In part C of the experiment, the path length (l) was 1.00 cm. From your linear graph for part C, determine the value for the constant, which is called the molar absorptivity and has the symbol, ε.

$$\varepsilon = \underline{\hspace{3cm}} \qquad \text{(be sure to include units)}$$

This relationship is known as Beer's Law: $\qquad A \ = \ \varepsilon \ \cdot c \cdot l$

Part D. Absorbance and Wavelength

(D.1) Were all the absorbance values the same for the copper(II) nitrate solution at different wavelengths?

(D.2) If we were to collect absorbance vs. concentration data for each wavelength, similar to Part C, the relationship would be linear but the slope of the line would change. This tells us that the constant in our equation from C.7 depends on the wavelength, so wavelength must always be specified. This constant is called the **molar absorptivity** and has the symbol ε.

What is the value for molar absorptivity for copper(II) nitrate at your λ_{max}? Be sure to include the appropriate units.

What is the value for molar absorptivity for copper(II) nitrate at 500 nm? Be sure to include the appropriate units.

Part E. Absorbance Spectra of other Metal Cations.   **Alpha** _____

(E.1) What species (atoms, ions or molecules) are present in the copper(II) nitrate solution from Part A?

(E.2) What species are present in the 0.10 M nickel(II) nitrate solution?

(E.3) What species are present in the 0.10 M iron(III) nitrate solution?

(E.4) What species are responsible for the distinctive colors of the three solutions?

(E.5) By comparing the three absorbance spectra of these ions, could you use spectroscopy to determine which ions are present in a mixture containing at least two of the ions? Explain your answer.

Name _____   Date _____

Expt. 7F Pre-lab
Quantitative Spectroscopy

You will be using Excel to analyze your data in Expt. 7F. To prepare for this, your pre-lab is to create an initial spreadsheet for the Expt. 7F data.

From a **blank** Excel spreadsheet, create a spreadsheet similar to the example below. Note how the data tables are properly formatted and easy to read. Print your spreadsheet on **one page** to submit as your pre-lab for this experiment. This must be done prior to the start of lab.

Save your spreadsheet onto your laptop to be used in lab. Bring your laptop to lab.

Expt. 7F
Name
Date
Section 8141

Part B. Transmittance and Path Length

sheet width (cm) =   0.20   cuvette width (cm) =   1.00

Number of sheets	Path length (cm)	% Transmittance	Absorbance
4			
3			
2			
1			
0	1.00		

Part C. Transmittance and Concentration

Cu Stock Conc (M) =   0.500

Solution	Initial Buret Volume (mL)	Final Buret Volume (mL)	Volume Added (mL)	% Transmittance	Concentration (M)	Absorbance
1						
2						
3						
4						
5						