Experiment 7F

WBH 10-2/2022 FV

QUANTITATIVE SPECTROSCOPY

MATERIALS: Spec200 spectrometer; 50 mL beaker (1); 25 mL volumetric flask with cap (1); 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; Plexiglass sheets (4); Cuvettes (2); Plastic transfer pipets; 18 x 150 mm test tubes (5); Test tube rack; Buret clamp; Ring stand; 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 depends upon path length, concentration and wavelength.
4. Convert percent transmittance values to absorbance and determine how absorbance depends upon 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 conduct a series of experiments using a spectrometer to understand why these solutions look so different.

I. **Color of Solution.** The concept of color is complex, involving not only the interaction of light with matter, but also our perception of it by the eye and brain. For example, when we look at the two solutions in Figure 1, are seeing two things: (a) color and (b) intensity of color. Although the solutions have different concentrations, both have the same chemical composition, so we might expect them to have the same color. In fact, 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 Eye vs. the Spectrometer.** A spectrometer is an instrument for measuring color and intensity of light. Both the eye and the spectrometer respond to light, but that is where the comparison ends. In the vision process, light from the entire visual field enters the eye, where it is sensed by the retina using three color detectors (red, green and blue cones); this information is then transmitted to the brain, which 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. In contrast, a spectrometer has a far simpler task. In this case, a beam of visible light is split into its component wavelengths using a diffraction grating. As the spectrometer scans across each wavelength of light, the light passes through and interacts with a (theoretically) homogenous sample, and the light that emerges from the sample 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 more dilute solution on the right. In **Part D** of the procedure, you'll examine if and how the more concentrated 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 use the spectrometer to observe two other compounds and see how they differ from the copper (II) nitrate.

IV. **Intensity of Color.** Look 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 experiment examines how varying path length varies the intensity of the solution.

V. **From Observation to Mathematical Model:** Once you have completed the measurements in **Part A – Part D**, using wavelength of light, concentration of compound, and path length, you will then summarize the relationships between these variables in the form of a fundamental mathematical relationship known as 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. What is lost as *light* passes through matter tells us something about what is there in the *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 is 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 substance(s) interacting with the light.

As discussed in Chapter 3 of the Gilbert text, the energy of light is transmitted in discrete "packets" known as photons, and absorption of a photon of light by a sample can occur when the photon energy matches an energy transition in the sample. For example, light is absorbed by an atom or molecule whenever its photons have the proper energy to move an electron from a low energy orbital to a higher energy orbital. For atoms in the gas phase, absorbance is observed as missing (dark) narrow lines in the rainbow of the full spectrum of transmitted visible light—a line spectrum. The spectra of solid substances and solutions are typically presented as shown in Figure 2. Note that in this spectrum, the y-axis values are given as absorbance, rather than transmittance, and are plotted against wavelength. The wavelength at which the absorbance is highest (designated λ_{max}) is an important characteristic of the substance being studied and is also helps to determine the color we perceive when we look at the sample.

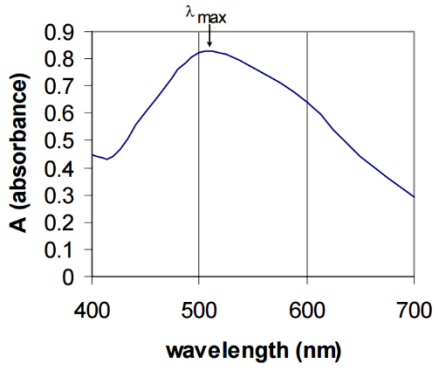


Figure 2: Absorbance spectrum of an aqueous solution. λ_{max} is the wavelength of maximum absorbance.

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):

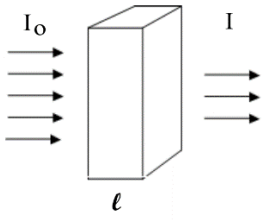


Figure 3: Incident light transmitted through a sample, path length ℓ.

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), which expresses the amount of light absorbed, is related to transmittance logarithmically:

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

Thus, when *none* of the light that strikes a sample is absorbed by it, $I = I_o$, $T = 1$, $\%T = 100$, and $A = 0$. Conversely, when *all* of the light striking a sample is absorbed, $I = 0$, $T = 0$, $\%T = 0$, and A is infinite. It is important to note that transmittance and absorbance are both dimensionless quantities (they have **no units**).

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 solution is simply a homogeneous mixture, and in this course we will be specifically interested in solutions formed by dissolving pure substances in water. In pure water, individual H_2O molecules interact only with other neighboring H_2O molecules, but in a solution, the water ("solvent") molecules also interact with the dissolved substance (known as the "solute") through a process known as *solvation*. When a molecular compound like ethanol (C_2H_5OH) dissolves, H_2O molecules surround the individual ethanol molecules. When an ionic compound, such as copper (II) chloride ($CuCl_2$), dissolves, individual cations (e.g. Cu^{2+}) and anions (e.g. Cl^-) separate and are likewise surrounded by water molecules. For a more detailed discussion of this topic, consult the appropriate sections of your text (and see the figure below).

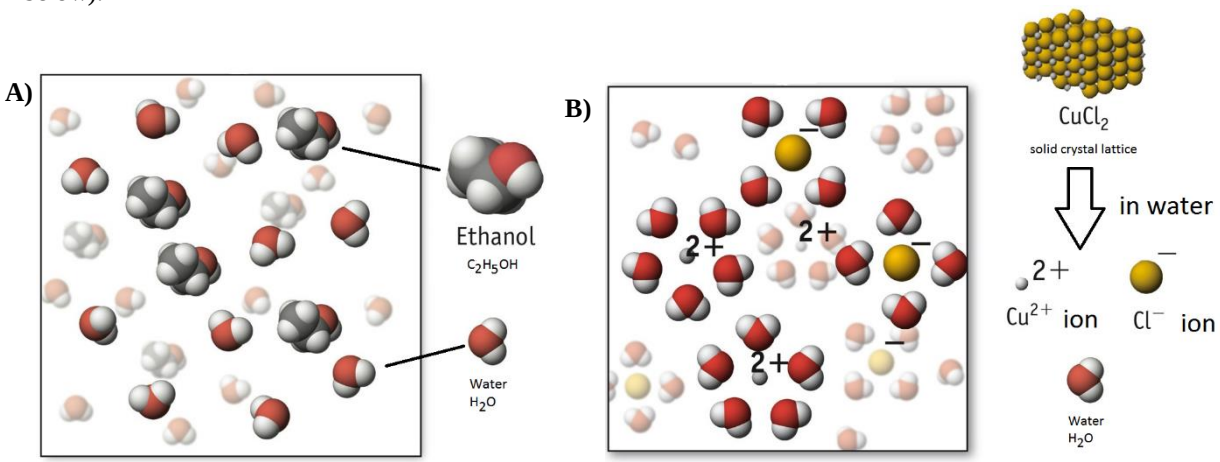


Figure 4: Solvation Process. A) Molecular: Ethanol in water, B) Ionic: $CuCl_2$ in water.

When calculating the number of individual molecules present in a sample of a pure molecular compound, we use the mass of the sample and the molar mass. For solutions, if we want to know how many molecules or ions are present in a sample, we must use sample volume and 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:

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

Molarity is a very useful conversion factor that allows us to calculate either (1) the number of moles of solute, or (2) the number of individual solute particles (molecules or ions) that are present in a sample of a solution, provided that we know the volume of the sample.

PROCEDURE:

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

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 lab tissue and insert it in the spectrometer. **Note: when inserting the cuvette, always ensure that the optically clear faces, indicated by the triangular "arrow" molded into the cuvette, are aligned with the light path, which is oriented laterally across the sample compartment**.

4. 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.

5. 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.

6. 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 4. Record the absorbance of the solution at this wavelength.

Part B. Effect of 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. Example of polycarbonate sheet placement in cuvette.

Note: It is acceptable to move on to Part D for data collection before beginning Part C.

Part C. Effect of Concentration

1. Obtain approximately 30 mL of **0.500 M** copper (II) nitrate solution in a 50 mL beaker. (Note the concentration and color.)

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 not 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 a few mL of 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. Effect of Wavelength

1. Set the Spec200 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 absorbance.

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 nickel (II) nitrate 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 iron (III) nitrate 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.

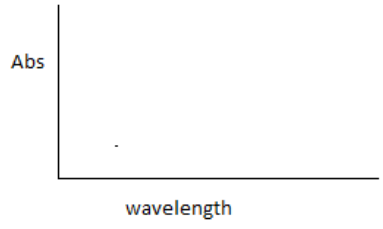
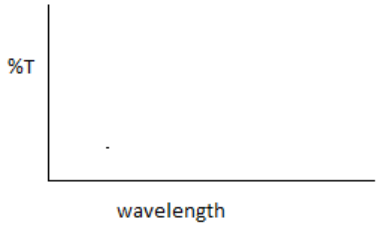
Clean-Up: Dispose of all metal ion solutions in the appropriate waste container. Rinse all glassware and cuvettes with distilled water and turn off the spectrometer.

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}
			

Part B. Effect of Path Length

Note: thickness of each sheet = 0.20 cm

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

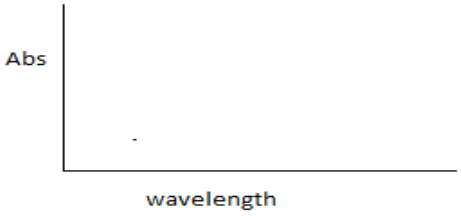
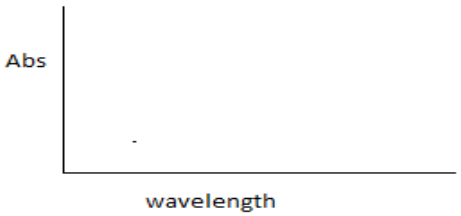
Part C. Effect of Concentration

Solution	Initial Buret Vol (mL)	Final Buret Vol (mL)	Volume added (mL)	% Transmittance
1				
2				
3				
4				
5				

Part D. Effect of 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}
$Ni(NO_3)_2$				
$Fe(NO_3)_3$				

DATA TREATMENT AND ANALYSIS
Experiment 7F

Part B. Effect of 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 using 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:

_____ = (slope) · *l* + *y-intercept*

$y = m \cdot x + b$

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

Part C. Effect of 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 final volume of the diluted solution (in this case, the volume of the volumetric flask). 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 using 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:

_____ = (slope) · *c* + *y-intercept*

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

(C.7) For both **parts B** and **D**, 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:

_____ = [(slope) · *c* · *l*] + *y-intercept*

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

_____ = (slope) · *c* · *l* = *(constant)* · *c* · *l*

In **part D** 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.

ε = _____ (be sure to include units)

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

Part D. Effect of 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.

(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 XXXX						

Part B. Effect of 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. Effect of Concentration						
Cu Stock Conc (M) =	0.500					

Solution	**Initial Buret Vol (mL)**	**Final Buret Vol (mL)**	**Vol Added (mL)**	**% Transmittance**	**Conc (M)**	**Absorbance**
1						
2						
3						
4						
5						