EXPERIMENT 5

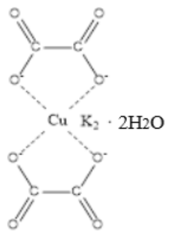
ANALYSIS OF POTASSIUM COPPER (II) OXALATE

Objectives:

The objective of this experiment is to analyze potassium copper (II) oxalate, Compound 1 synthesized in Experiment 4, for percent copper and to verify that the compound precipitates as a dihydrate. A drying study will be conducted to determine the numbers of waters of hydration associated with Compound 1. The mass percent copper in the experimentally synthesized coordination complex will be determined spectrophotometrically using Beer-Lambert Law.

Background:

In order to evaluate the structure of Compound 1 synthesized during Experiment 4 from the reaction of copper (II) sulfate pentahydrate and potassium oxalate monohydrate, associated waters of hydration must be known. Molar mass of the complex includes any water molecules bound to the complex, $K_2Cu(C_2O_4)_2 \cdot 2H_2O$, so the numbers of waters of hydration must be confirmed through drying studies.



Compound 1
Potassium copper (II) oxalate dihydrate

If a crystal precipitates as a **hydrate**, water molecules precipitate along with the crystals of the compound. These waters are incorporated within the crystal lattice of the precipitate and are known as **waters of hydration**. The chemical formula of hydrates are written with the notation "$\cdot XH_2O$", where X indicates the number of water molecules per compound unit. During a drying study, heating and cooling cycles are conducted and the mass of a sample is monitored to determine if water evaporates from the sample. The heating/cooling cycles continue until no change in mass is noted upon further drying. This process is known as **heat to constant mass**. In our experiment, constant mass is defined as a change in mass less than 0.003 g. The ratio of moles of waters evaporated to moles of dried compound reveals the number of waters of hydration, X.

When naming a hydrate, the name of the salt is written, followed by the number of water of hydration. Our starting reactant copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) has five water molecules for every molecule of copper sulfate and potassium oxalate monohydrate has one molecule of water for every molecule of potassium oxalate.

The following is a list of prefixes for naming hydrates:

mono-	1 water of hydration	penta-	5 waters of hydration
di-	2 waters of hydration	hexa-	6 waters of hydration
tri-	3 waters of hydration	hepta-	7 waters of hydration
tetra-	4 waters of hydration	octa-	8 waters of hydration

When the hydrates are dried, the water is evaporated leaving behind the **anhydrous compound**. Some anhydrous compounds have a strong tendency to absorb water vapor from the air, thus becoming hydrated compounds again. These anhydrous compounds find use as moisture reducing agents. You may have noticed that packets of such compounds are often found in bottles containing pills that would decompose if moisture were present. Such compounds are said to be **hygroscopic**. Some of these compounds absorb water to such a great extent that they actually dissolve in the water that they take up. When this is the case, the compounds are said to be **deliquescent**. Sodium hydroxide, NaOH, is an example of this type of compound. On the other hand, some hydrated compounds tend to spontaneously lose their waters of hydration when they are placed in a dry environment. These compounds are known as **efflorescent**. Knowing that spontaneous changes can occur in hydrates it is always best to keep lids of reagent bottles tightly closed when not in use.

In this experiment, the percent copper in potassium copper (II) oxalate will also be evaluated. Determining the percent copper aids in confirming the proposed molecular formula and provide further verification of the waters of hydration analysis. In this experiment, the percent of copper in potassium copper (II) oxalate will be determined through spectrophotometric analysis.

A spectrophotometer is used to measure the amount of light **transmitted** through a sample of matter. Light of a known wavelength is sent through the sample and the light coming through is measured by a detector. The quantity of light reaching the detector is compared to the quantity of light originating from the source, this is **transmittance**. A more meaningful quantity, **absorbance**, is calculated by taking the negative log of transmittance. A plot of absorbance versus wavelength, called a **spectrum**, shows the wavelengths of light that interact with the sample. The wavelength in which the compound has highest sensitivity is known as the wavelength of maximum absorbance or λ_{max}.

The spectrophotometer can be used to identify the concentration of a solution because the absorbance, A, of a solution at a given wavelength of light is directly proportional to the concentration, c, of a solution according to the **Beer-Lambert Law**.

Beer-Lambert Law : $A = \varepsilon bc$

A = absorbance
ε = molar absorptivity, liter/(mole cm) (a characteristic of the analyte)
b = path length, cm (distance through which the light travels through the substance)
c = concentration, mole/liter

In practice if different solutions containing the same analyte are analyzed using the same spectrophotometer, the molar absorptivity of the substance and path length of the experimental set-up will be the same. If a standard solution, a solution having known concentration of the analyte, is analyzed then the concentration of an unknown solution of the same analyte can be directly determined by measuring the absorbance of that solution. One can see the relationship by writing Beer-Lambert Law for both the solution and solving for the concentration of the unknown solution:

Equation 1 $A_{standard} = \varepsilon_{analyte}\, b_{setup}\, c_{standard}$ then $\frac{A_{standard}}{c_{standard}} = \varepsilon_{analyte}\, b_{setup}$

Equation 2 $A_{unknown} = \varepsilon_{analyte}\, b_{setup}\, c_{unknown}$ then $\frac{A_{unknown}}{c_{unknown}} = \varepsilon_{analyte}\, b_{setup}$

Setting Equations 1 and 2 equal to each other allows for the concentration of the unknown solution to be determined:

$$c_{unknown} = A_{unknown}\left(\frac{c_{standard}}{A_{standard}}\right)$$

In this experiment, two solutions of copper (II) tetraethylenepentamine, $[CuTEPA]^{2+}$, will be prepare by reacting the tetraethylenepentamine (TEPA) ligand with Cu^{2+} from a copper (II) chloride standard solution and Cu^{2+} from Compound 1. Absorbance of both solutions will be measured at λ_{max} to determine the concentration of copper (II) tetraethylenepentamine in the solution prepared from Compound 1. This concentration will then be related to the mass percent copper in the Compound 1.

Tasks to be completed:

1. A <1 g sample of Compound 1, potassium copper (II) oxalate, is prepared for a drying study to determine the numbers of waters of hydration.
2. A standard solution of $[CuTEPA]^{2+}$ is prepared in a volumetric flask using a copper (II) chloride standard solution.
3. A sample of Compound 1 is dissolved in water and reacted with TEPA to form the $[CuTEPA]^{2+}$ unknown solution. This solution is transferred to a volumetric flask to dilute to 100 mL total volume.
4. The absorbance values for both $[CuTEPA]^{2+}$ complex ion solutions are collected at lambda max using a spectrophotometer.

Experimental Procedure: To be run independently.

I. Analysis of Waters of Hydration in Compound 1, Potassium copper (II) oxalate

1. Place your initials on a 100 mL beaker so that it can be identified from others.
2. Wipe the outside of the beaker with a paper towel then measure and record the mass of the clean, dry beaker on the appropriate Data sheet. *Do not touch the beakers after the initial mass has been determined. Handle using a paper towel.*
3. Place between 0.8-0.9 gram of your sample of potassium copper (II) oxalate (Compound 1) into the 100 mL beaker. Measure and record the total mass of the beaker containing Compound 1 on the appropriate Data sheet.
4. Place the beaker in the baking dish beside the 150 ^{o}C oven and cover with the clean-dry watch glass.
5. The sample will be heated for 40 minutes. **During this time you will be working on the spectrophotometric portion of the experiment.**
6. When the sample is removed from the oven the beaker will be immediately covered with a watch glass to prevent the dried sample from picking up water from the atmosphere.
7. Cool the beaker at room temperature for approximately 10 minutes or until the sample is at room temperature. Measure and record the mass of the dried sample and beaker on the Data sheet.
8. Evaluate for constant mass. The difference in mass before and after heating should not change by more than 0.003 g. If this condition has been met the sample no longer requires heating.
9. If the difference in mass is greater than 0.003 g, repeat the heating, cooling and massing process with 20 minute heating intervals until a constant mass is achieved.

II. Analysis of Cu^{2+} in Potassium copper (II) oxalate by spectrophotometry

a. Prepare a $[CuTEPA]^{2+}$ standard solution from a $CuCl_2{\cdot}2H_2O$, solution

1. Use a clean dry 50 ml beaker to obtain approximately 25 mL of the copper(II) chloride dihydrate stock solution. Be certain to record the concentration of the solution.
2. Prepare a pipet by rinsing with a small portion of the $CuCl_2{\cdot}2H_2O$ solution. Discard rinse in a <u>waste beaker</u>. Pipet 10.00 mL of the stock solution into a 100 mL volumetric flask.
3. Using a graduated cylinder, add 4 mL of 2% tetraethylenepentamine to the volumetric flask. Swirl the flask to allow the metal and ligand to react then dilute to the mark with deionized water. Invert the flask to mix well.
4. Transfer the standard solution to a clean, dry Erlenmeyer flask. Thoroughly wash and rinse the volumetric flask and cap so that it can be used to make the next solution. Use soap and water and rinse four to five times with deionized water.
5. The compound should be allowed to react for at least 10 minutes before analysis.

b. Prepare a $[CuTEPA]^{2+}$ solution from Compound 1

1. Mass 0.10 to 0.12 g sample Compound 1, potassium copper (II) oxalate, in a clean, dry weigh dish and record the actual mass. Using a glass funnel and wash bottle, rinse all of Compound 1 into a clean volumetric flask. Add approximately 20 mL additional deionized water to the volumetric flask and swirl until all of Compound 1 is dissolved.
2. Using a graduated cylinder, add 8 mL of 2% tetraethylenepentamine to the volumetric flask. Swirl the flask to allow the metal and ligand to react then dilute to the mark with deionized water. Invert the flask to mix well.
3. The compound should be allowed to react for at least 10 minutes before analysis.

c. Analyze the $[CuTEPA]^{2+}$ solutions using the spectrophotometer.

1. Use the USB cable to connect a Vernier Spectro-Vis Spectrophotometer to the computer. Start Logger Pro software on the computer.
2. Blank the spectrophotometer using deionized water.
    a. Prepare a blank by filling an empty cuvet ¾ full with deionized water. Verify that the cuvet is free of fingerprints, scratches, and air bubbles. Dry the outside of the cuvet.
    b. Open the Experiment menu and select Calibrate → (Spectrometer). The following message appears in the Calibrate dialog box: “Waiting … seconds for the device to warm up.” After 90 seconds, the message changes to: “Warmup complete.”
    c. Place the blank in the cuvet holder of the spectrophotometer. If using a cuvet with frosted sides, align the cuvet so that the clear sides are in line with the light source of the spectrophotometer. Click “Finish Calibration”, and then click OK .
3. Configure the software to measure solution absorbance at the wavelength of maximum absorbance.
    a. Using the same cuvet prepare a sample of the prepared Standard solution and place it in the spectrophotometer. Be certain to rinse the cuvet with the $[CuTEPA]^{2+}$ standard solution to be certain the solution is not diluted with any water remaining in the cuvet. REMEMBER TO COLLECT RINSE IN A WASTE BEAKER. Select ▶ Collect to obtain an absorption spectrum of the standard solution. After the spectrum appears select ■ Stop .
    b. **Leaving the sample in the spectrophotometer** , select the Configure Spectrometer Data Collection icon, 📊, on the toolbar. Select the Abs vs Concentration collection mode.
    c. Note the wavelength of maximum absorbance as identified by the program. Record this value on the appropriate Data sheet. Click OK to proceed. Select “No” in the dialog box that appears concerning the storing of the latest run.
    d. The absorbance of the standard solution at the selected wavelength should now appear in the bottom left corner of the screen. Record the absorbance of the standard at this wavelength.

4. Measure the absorbance of the $[CuTEPA]^{2+}$ solution prepared from Compound 1.
    a. Using the same cuvet, analyze the $[CuTEPA]^{2+}$ solution prepared from Compound 1. Empty the cuvet into a waste beaker then rinse with deionized water followed by several rinses with the new solution to be analyzed.
    b. Dry the outside of the cuvet then place the cuvet into the spectrophotometer and read the absorbance of the solution at λ_{max} from the bottom corner of the screen. Record the absorbance on the Data sheet.

Waste Handling and Clean Up:

- ➢ Discard all liquid waste in marked waste containers available in the fume hood.
- ➢ Discard the remainder of Compound 1 and the filter paper in the appropriate solid waste container.
- ➢ Rinse used pipets with deionized water by drawing deionized water into the pipet several times. Set aside for Instructor to inspect.
- ➢ Disconnect the cords from the SpectroVis spectrophotometer and computer and leave at the work station.
- ➢ Discard the cuvet in the trash.
- ➢ Wipe down benchtop areas, including sink area, with a damp sponge.

Data Analysis:

I. Analysis of Waters of Hydration in Potassium copper (II) oxalate, Compound 1

a. Drying study

1. Calculate the initial mass of the sample before heating.

$$Initial\ Mass\ beaker\ and\ sample, g - Mass\ empty\ beaker, g = Initial\ mass\ of\ the\ sample, g$$

2. Calculate mass of the sample after each drying cycle.

$$Mass\ beaker\ and\ sample, g - Mass\ empty\ beaker, g = Mass\ of\ anhydrous\ sample, g$$

3. Determine if the heating is complete, if the sample has reached constant mass.
    a. Calculate the change in mass after each heating cycle.
        - $Mass\ of\ sample\ after\ 1st\ heating - Initial\ mass\ of\ sample$
        - $Mass\ of\ sample\ after\ 2nd\ heating - Mass\ of\ sample\ after\ 1st\ heating$
        - $Mass\ sample\ after\ 3rd\ heating - Mass\ of\ sample\ after\ 2nd\ heating$
        - $Mass\ sample\ after\ 4th\ heating - Mass\ of\ sample\ after\ 3rd\ heating$
    b. If the change in mass between heating cycles is less than 0.003 g the sample is at constant mass and the heating is complete. It is not necessary to complete all four heating cycles.

b. Determine the Number of Waters of Hydration in Compound 1

1. Using the Periodic Table on the inside cover of the lab manual, calculate the molar mass of the anhydrous compound. The anhydrous formula for Compound 1 is $K_2Cu(C_2O_4)_2$.

2. Enter the final mass of the anhydrous (dried) sample, the smallest Mass of Sample value from the table in Part I on page 5-10

3. Convert the mass of anhydrous compound (the dried sample) to moles of anhydrous compound using the calculated molar mass.

$$\frac{Mass\ anhydrous\ sample, g}{Molar\ mass\ of\ Anhydrous\ Compound\ 1,\ g/mol} = Moles\ anhydrous\ sample$$

4. Determine the mass of the water lost by the sample through evaporation during heating.

$$Initial\ mass\ beaker +\ sample, g - Smallest\ mass\ beaker +\ dried\ sample, g\ =\ Mass\ of\ water\ lost, g$$

5. Convert the mass of the waters of hydration lost by evaporation to moles of water lost using the molar mass of water (18.02 g/mol).

$$\frac{Mass\ water\ lost\ , g}{Molar\ mass\ water, g/mol} = Moles\ water\ lost\ by\ evaporation$$

6. Determine the ratio of moles of waters lost by evaporation to moles of anhydrous compound. Round to a whole number. This represents the number of waters of hydration in Compound 1, the coefficient X in $K_2Cu(C_2O_4)_2{\cdot}XH_2O$.

$$\frac{Moles\ water\ lost\ by\ evaporation}{Moles\ \ of\ anhydrous\ sample} =\ Number\ of\ Waters\ of\ Hydration$$

NOTE: If the ratio is <0.5, round to 0 waters of hydration- the product crystallized without any waters of hydration. The formula of the complex will be that of the anhydrous compound.

II. Analysis of Cu^{2+} in Potassium copper (II) oxalate by Spectrophotometry

a. Determine the concentration of the $[Cu(TEPA)]^{2+}$ Standard solution

1. Calculate the mass of copper (II) chloride dihydrate, $CuCl_2{\cdot}2H_2O$, present in the <u>pipetted</u> volume of solution.

$$(volume\ of\ CuCl_2{\cdot}2H_2O, L)\left(concentration\ of CuCl_2{\cdot}2H_2O\ \frac{g}{L}\right) = mass\ CuCl_2{\cdot}2H_2O, g$$

2. Calculate the moles of copper present in the mass of copper (II) chloride dihydrate. Molar mass of copper (II) chloride dihydrate is 170.48 g/mol.

$$\left(\frac{Mass\ of\ CuCl_2{\cdot}2H_2O, g}{molar\ mass\ of\ CuCl_2{\cdot}2H_2O\ g/mole}\right)\left(\frac{1\ mole\ Cu}{1\ mole\ CuCl_2{\cdot}2H_2O}\right) = moles\ of\ Cu$$

3. Determine the moles of the copper complex $[Cu(TEPA)]^{2+}$ formed using the reaction stoichiometry.

$$(moles\ of\ Cu)\left(\frac{1\ mole\ [\mathrm{Cu(TEPA)}]^{2+}}{1\ mole\ Cu}\right) = moles\ of\ [\mathrm{Cu(TEPA)}]^{2+}$$

4. Determine the molarity of the standard solution in the 100.00 mL (or 0.10000 L) volumetric flask from the moles of solute and volume of solution.

$$\left(\frac{moles\ of\ [\mathrm{Cu(TEPA)}]^{2+}}{volume\ of\ solution\ prepared,\ L}\right) = concentration\ of\ [\mathrm{Cu(TEPA)}]^{2+}\ Standard\ solution, M$$

b. Determine the mass percent copper in Compound 1, Potassium copper(II) oxalate

1. Using the Beer-Lambert Law determine the molarity of the $[Cu(TEPA)]^{2+}$ solution prepared using Compound 1 by relating its absorbance to the absorbance and concentration of the $[Cu(TEPA)]^{2+}$ Standard solution.

$$A_{[\mathrm{Cu(TEPA)}]^{2+} from\ Compound\ 1}\left(\frac{c_{[\mathrm{Cu(TEPA)}]^{2+}\ Standard\ Solution}}{A_{[\mathrm{Cu(TEPA)}]^{2+}\ Standard\ Solution}}\right) = c_{\ [\mathrm{Cu(TEPA)}]^{2+} from\ Compound\ 1},\frac{mol}{L}$$

Calculate the moles of copper present in the $[Cu(TEPA)]^{2+}$ solution prepared using Compound 1.

Note: the solution was prepared in a 100.00 mL volumetric flask.

$$(0.10000\ , L)\left(c_{\ [\mathrm{Cu(TEPA)}]^{2+} from\ Compound\ 1},\frac{mol}{L}\right)\left(\frac{1\ mole\ Cu\ in\ Compound\ 1}{1\ mole\ [\mathrm{Cu(TEPA)}]^{2+}}\right)$$

$$= moles\ of\ Cu\ in\ Compound\ 1$$

2. Determine the mass percent copper in the Compound 1 from the moles of copper in the sample.

$$\frac{(moles\ of\ \ Cu\ in\ Compound\ 1)\left(molar\ mass\ Cu, \frac{g}{mole}\right)}{mass\ of\ Compound\ 1\ sample, g}\ x\ 100\% = mass\ \%\ copper$$

c. Determine percent error in mass percent copper in potassium copper (II) oxalate

1. The theoretical value for copper in the potassium copper(II) oxalate can be found by dividing the molar mass of copper by the molar mass of the complex then multiplying by 100%.

$$\frac{molar\ mass\ Cu, g/mol}{molar\ mass\ Compound\ 1, g/mol}\ x\ 100\% =\ Theoretical\ mass\ \%\ copper$$

2. Determine the percent error by comparing the average experimental mass percent copper to the theoretical value calculated from the formula of potassium copper (II) oxalate.

$$\left|\frac{experimental\ value - theoretical\ value}{theoretical\ value}\right|\ x\ 100\ \% = Percent\ error$$

Data Sheet

Date: ______________ Name:____

124L section ___________ Instructor_______________________________________

I. Analysis of Waters of Hydration in Potassium copper (II) oxalate

	Mass of empty beaker (g)	Mass of beaker + sample (g)	Mass of sample (g)	Has sample reached constant mass and heating complete? Yes/No Calculate change in mass after each heating. (show work)
Initial				N/A
After 1st heating				
After 2nd heating				
After 3rd heating (if needed)				
After 4th heating (if needed)				

Data Sheet, cont.

II. Analysis of Cu^{2+} in Potassium copper (II) oxalate by spectrophotometry

Concentration of standard $CuCl_2 \cdot 2H_2O$ solution ______________

Mass of Compound 1 sample use to prepare 100.00 mL of solution ____________

Wavelength of maximum absorbance for $[CuTEPA]^{2+}$ standard solution (λ_{max}) ___________

Absorbance of $[CuTEPA]^{2+}$ standard solution at λ_{max} ____________

Absorbance of $[CuTEPA]^{2+}$ solution prepared from Compound 1 at λ_{max} ___________

Report Sheet

Date: ______________ Name:____

124L section ___________ Instructor_____________________________________

I. Analysis of Waters of Hydration in Potassium copper (II) oxalate Compound 1.

Anhydrous formula of Compound 1 ______________________________________

Show all work in the table.

Molar Mass of anhydrous Compound 1	
Final mass of anhydrous (dried) sample	
Moles of anhydrous (dried) sample	
Mass of waters lost through evaporation during heating	
Moles of water lost through evaporation	
Mole ratio to determine number of waters of hydration	

Report Sheet, cont.

II. Analysis of Cu^{2+} in Potassium copper (II) oxalate by Spectrophotometry

a. Determine the concentration of the Standard solution. Show work.

Mass $CuCl_2 \cdot 2H_2O$ in 10.00 mL solution	
Moles copper in 10.00 mL sample	
Moles of $[CuTEPA]^{2+}$	
Molarity of $[CuTEPA]^{2+}$ Standard solution	

Report Sheet

Name: ______________________________________

Date: _____________

Section #/Instructor_____________________________

b. Determine the mass percent copper in Compound 1. Show work.

Molarity of $[CuTEPA]^{2+}$ solution prepared with Compound 1	
Moles copper present in 100.00 mL $[CuTEPA]^{2+}$ solution prepared with Compound 1	
Mass percent copper in Compound 1	

Report Sheet, cont.

c. Determine percent error in mass percent copper in potassium copper (II) oxalate, show work.

Theoretical mass percent copper in Compound 1	
Percent error analysis	