# EXPERIMENT 6

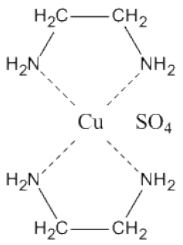
## *ANALYSIS OF COPPER IN BIS-ETHYLENEDIAMINE COPPER (II) SULFATE*

### Objectives:

The objective of this experiment is to analyze the amount of copper in bis-ethylenediamine copper (II) sulfate, Compound 2 synthesized in Experiment 4. The mass percent copper in the experimentally synthesized coordination complex will be determined through EDTA complexometric titration.

### Background:

Bis-ethylenediamine copper (II) sulfate, $Cu(H_2NCH_2CH_2NH_2)_2SO_4$, is a coordination complex synthesized in Experiment 4. It precipitates as an anhydrous compound, having no waters of hydration. In this experiment, the mass percent copper in Compound 2 will be evaluated through an analytical technique known as complexometric titration. Determining the percent copper in a compound aids in confirming the proposed molecular formula.

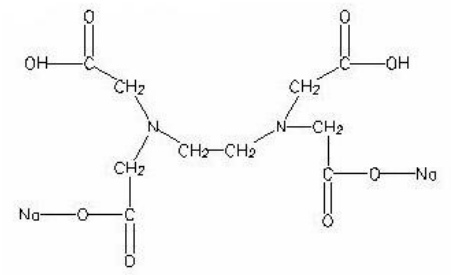



Compound 2
Bis-ethylenediamine copper (II) sulfate

A complexometric titration is similar to an acid-base titration in that the concentration of an analyte is determined. In the case of an acid-base titration, the analyte is an acid, the titrant is a base, and the indicator signals the end of the titration at the equivalence point when the sharp rise in pH causes a change in the color of the indicator. But in a **complexometric titration**, the analyte is a metal cation and its concentration is determined by creating a coordination complex with the titrant. The titrant acts as a ligand and binds to the metal cation, creating a coordination complex having a distinct color in solution. The endpoint is aided by an indicator that is also a ligand which when complexed to the free metal ion in solution having a different color. The endpoint of the titration is determined when the color of the solution changes from the color of the metal-indicator complex to that of the color of the metal-titrant complex.

The compound most commonly used as the titrant in a complexometric titration is ethylenediaminetetraacetic acid, more commonly referred to by its acronym, EDTA, because it can form stable complexes with many metal ions. Its structure, shown below, allows for a single molecule

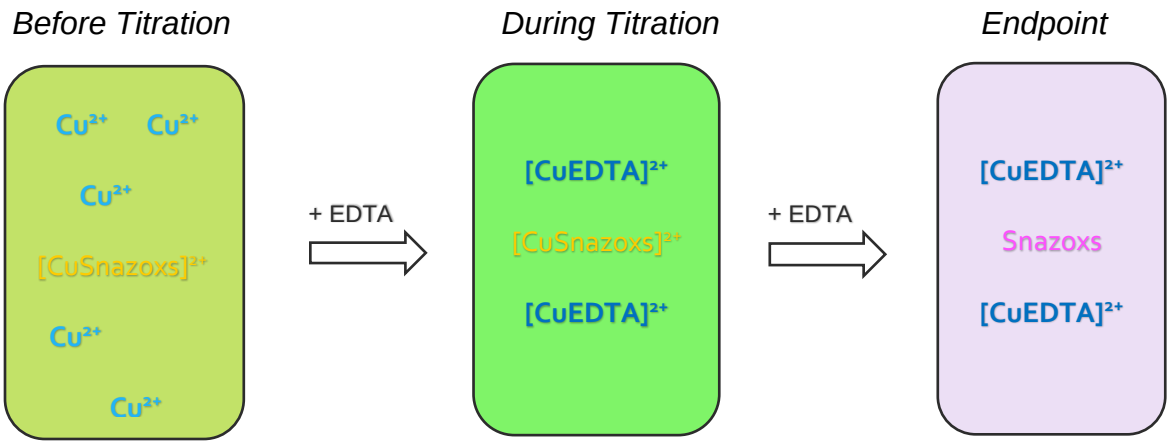
of EDTA to form multiple bonds with a single metal cation. It can thus be characterized as a **multidentate ligand**. Remember, the term **ligand** applies to an atom, ion or molecule that can bind to a metal ion through the sharing of a non-bonded pair of electrons. A multidentate ligand such as EDTA is also referred to as a **chelating agent**. The product of the reaction of a chelating agent and a metal ion is referred to as a **chelate**.



EDTA-disodium salt, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$
Molar mass 372.24 g/mole

In this procedure, EDTA is used to analyze for the presence of copper cation in bis-ethylenediamine copper(II) sulfate, Compound 2. The disodium EDTA salt is easier to dissolve in water and thus is used as the titrant. To perform the titration, the copper cation ($Cu^{2+}$) in Compound 2 is released into solution using a strong acid and then reacted through titration with EDTA to form the blue $[CuEDTA]^{2+}$ complex ion. As noted in the formula, EDTA and copper (II) cation reacts in a 1:1 ratio.

The indicator in a complexometric titration is used to identify the endpoint of the titration by changing color once all the $Cu^{2+}$ from Compound 2 has been reacted with the titrant EDTA. A small quantity of the indicator Snazoxs is added to the light blue copper cation containing solution and immediately forms a yellow coordination complex $[CuSnazoxs]^{2+}$. Excess copper cation in solution has a characteristic blue color and the solution before titration begins will appear green. As EDTA is added to the titration solution, the EDTA first reacts with the free copper cation in solution and then displaces the Snazoxs in the $[CuSnazxos]^{2+}$ complex eliminating the yellow compound responsible for the solution's green color. The displaced Snazoxs has a pink color in solution and the $[CuEDTA]^{2+}$ complex is blue so the solution color changes from green to violet. <u>The endpoint is specifically identified by the absence of the green or yellow</u>. The diagram below outlines the chemical species in solution and the corresponding solution color during titration.




During the titration, the formation of the $[CuEDTA]^{2+}$ complex results in the release of hydrogen ions from EDTA which causes a decrease in the pH of the titration solution. A change in pH would affect the titration and needs to be prevented. The pH of the solution is controlled with the addition of a **buffer**. A buffer is a solution that resists pH changes when a strong acid or base is added. An acetic acid/sodium acetate buffer is used to maintain the pH of the titration solution near 5.

As with any titration to determine moles of a solute, multiple trials will be completed. For each trial the mass percent copper will be determined then the results averaged. Because high accuracy is desired, completing multiple trial of the titrations allow the experimenter to analyze precision of the titration and to evaluate for outliers to determine if one trial needs to be repeated or perhaps excluded from the average.

## Tasks to be completed:

1. Dissolve disodium EDTA in a 250 mL volumetric flask to be used as the titrant for the titration.
2. A sample of bis-ethylenediamine copper (II) sulfate is dissolved in water and treated with acid to release $Cu^{2+}$ into solution. The solution is diluted to 100.00 ml in a volumetric flask in preparation for titration.
3. Three 10.00 ml **aliquots**, or exact portions, of the copper solution are prepared for titration by adjusting the pH, adding buffer to maintain the pH, and adding an indicator. Finally, the solution is titrated with the EDTA.

## Experimental Procedure: To be run individually.

## I. Prepare Standard EDTA Titrant

1. Accurately mass between 0.58 and 0.60 g of $Na_2H_2EDTA \cdot 2H_2O$. Record the actual mass. Transfer the compound to a 250 mL volumetric flask and fill to about 3/4 full with deionized water.
2. Note: At this point, for efficiency, it is recommended that the volumetric flask be set aside while the copper compound solution is prepared. The EDTA has limited solubility and this extra time will allow the EDTA to complete dissolve before final dilution.
3. When the EDTA is completely dissolved, dilute to the mark with deionized water, adding the last bit of water with a dropper.
4. Invert the flask several times to mix.
5. Prepare and fill a 50 mL buret with this solution.

## II. Analysis of $Cu^{2+}$ in Bis-ethylenediamine Copper (II) Sulfate by EDTA Titration

1. Obtain about 30 mL of the Standard pH = 4.00 buffer solution to a 50 mL beaker. Standardize a pH meter using the calibration instructions located near the meter. After calibration, rinse the electrode and store in a 400 mL beaker of deionized water. NOTE: The pH meter should be centrally located between two students. The meter will be shared but titrations will be run individually. Calibration is only necessary once per lab period.
2. Rinse a buret with the prepared EDTA standard solution, emptying the waste into a beaker. Fill the buret near the 0.00 mL marking.
3. Accurately mass between 0.70 and 0.75 g of bis-ethylenediamine copper(II) sulfate. Record this mass on the appropriate Data sheet. Completely transfer all the massed compound to a 100 mL volumetric flask by rinsing the contents of the weigh dish into the flask using deionized water in a wash bottle.
4. Add 1 mL of **concentrated $HNO_3$** directly from the reagent buret, see caution. Swirl the flask, the solution will turn blue once $Cu^{2+}$ is no longer coordinated to the ethylenediamine ligand.
5. Dilute the solution up to the mark with deionized water, adding the last little bit with a medicine dropper. Mix thoroughly by inversion of the stoppered flask. Transfer to a 250 mL Erlenmeyer flask.
6. Using the copper solution in the Erlenmeyer flask, properly prepare a 10.00 mL pipet by rinsing with a small quantity of solution. Rinse solution MUST be collected in a waste beaker!

**CAUTION when handling concentrated (16M) nitric acid, $HNO_3$!** Avoid contact with skin. If contact with skin occurs, wash with large amounts of water and notify the instructor. Immediately clean up any spills by neutralizing with sodium hydrogen carbonate, $NaHCO_3$. **DO NOT** apply $NaHCO_3$, to skin!

7. Pipet a 10.00 mL aliquot of the copper solution into a clean 250 mL beaker and add about 75 mL of deionized water. Add a magnetic stir bar to the beaker and place on a magnetic stir plate. Bring the stir plate over to the pH meter and adjust stirring to avoid splashing. Properly position the pH electrode in the beaker so that the sensing bulb is fully submerged, having no contact with the stir bar to avoid damage. Use the procedure outlined below to adjust the pH of the aliquot to a pH between 4.8 to 5.0.

    a. **If the pH is less than 4**; add 1.0 M NaOH dropwise until the pH is close to 4; then use 0.10 M NaOH until the pH is close to 5.
    b. **If the pH is greater than 5.2**, adjust it down with 0.10 M $HNO_3$, one drop at a time until the pH of the solution is between 4.8 and 5.0.
    c. **If the pH is greater than 8.0**, notify your instructor to help recover the solution.

8. Once the pH is adjusted, raise the pH electrode and rinse electrode with deionized water, having the rinse going into the beaker of copper solution. Store the electrode in a beaker of clean deionized water. Do not allow the pH electrode to dry.

9. Add 2 mL of acetic acid/sodium acetate buffer to maintain the pH of the solution throughout the titration. Add 10 drops of Snazoxs indicator to the aliquot of copper solution and titrate with the EDTA to the endpoint, the absence of any green color.

10. Titrate three additional 10 mL aliquots of the copper solution for a total of four trials by repeating steps 7-9.

## Waste Handling and Clean Up:

- Discard all liquid and solid waste in the appropriate waste container.
- Discard the remainder of Compound 2 in the appropriate solid waste container.
- Rinse used pipets, burets and plastic funnels/caps with deionized water. Set aside for Instructor to inspect.
- Return buret clamp to the bin under the sink. Unplug the stir motor and leave at the work station.
- Verify that pH electrodes are completely immersed in provided storage solution, the meter is in stand-by mode, and operating instructions are nearby. If storage solution is low, notify the instructor.
- Wipe down benchtop areas, including sink area, with a damp sponge.

## Data Analysis:

### I. Concentration of EDTA standard solution

Determine the molarity of the EDTA solution prepared by calculating the moles of the EDTA used from the mass used and dividing by the 0.25000L of solution prepared.

$$molarity\ of\ EDTA = \frac{(Mass\ EDTA\ disodium\ dihydrate)\left(\frac{1}{molar\ mass\ EDTA\ disodium\ dihydrate\ {}^{g}/_{mole}}\right)}{volume\ of\ solution\ prepared, L}$$

## II. Analysis of $Cu^{2+}$ in Bis-ethylenediamine Copper (II) Sulfate by EDTA Titration

### a. Determine the mass percent copper in the bis-ethylenediamine copper(II) sulfate

1. Calculate the number of moles of EDTA at the endpoint of the titration from the volume of EDTA needed to reach the endpoint and the molarity of the solution.

$$\left(molarity\ EDTA, \frac{mol}{L}\right)(volume\ EDTA, L) = moles\ of\ EDTA\ in\ titration$$

2. Relate the moles of EDTA to the moles of copper cation in the 10.00 mL aliquot using the mole ratio of 1 mole copper cation per 1 mole EDTA.

$$(moles\ of\ EDTA)\left(\frac{1\ mole\ copper\ cation}{1\ mole\ EDTA}\right) = \ moles\ of\ copper\ cation\ in\ aliquot$$

3. Relate the moles of copper cation in a 10.00 mL aliquot to the moles of copper in the compound sample used to prepare the entire 100.00 mL of solution.

$$(100.00\ ml\ solution)\left(\frac{moles\ of\ copper\ cation}{10.00\ ml}\right) = moles\ of\ copper\ in\ sample$$

4. Determine the mass percent copper in the compound from the moles of copper in the complex sample. Find the molar mass of copper in the Periodic table in the front cover of the manual.

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

### b. Determine percent error in mass percent copper in bis-ethylendiamine copper (II) sulfate

The theoretical value for copper in the bis-ethylenediamine copper(II) sulfate can be found by dividing the molar mass of copper by the molar mass of the complex then multiplying by 100%.

$$\frac{molar\ mass\ Cu, g/mol}{molar\ mass\ Compound\ 2, g/mol}\ x\ 100\% = Theoretical\ mass\ \%\ copper$$

Determine the percent error by comparing the average experimental mass percent copper to the theoretical value calculated from the formula of bis-ethylenediamine copper (II) sulfate.

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

***Data Sheet***

Date _____ Name:_____

124L section _____ Instructor_____

Mass of EDTA used to prepare 250.00 mL of titrant _____

Mass of Compound 2 sample use to prepare 100.00 mL of solution _____

Titration of 10.00 mL aliquots of the copper (II) solution

| | Trial 1 | Trial 2 | Trial 3 | Trial 4 |
|---|---|---|---|---|
| Initial buret reading, mL | | | | |
| Final buret reading, mL | | | | |
| Volume of EDTA needed to reach endpoint, mL | | | | |

***Report Sheet***

Date _____ Name:_____

124L section _____ Instructor_____

## I. Concentration of the EDTA Standard Solution

Determine the molarity of the EDTA titrant. Show all work.

## II. Analysis of $Cu^{2+}$ in Bis-ethylenediamine Copper (II) Sulfate by EDTA Titration

a. Determine the mass percent copper in the bis-ethylenediamine copper(II) sulfate. Show all work.

| | Trial 1 | Trial 2 | Trial 3 | Trial 4 |
|---|---|---|---|---|
| Moles EDTA at endpoint | | | | |
| Moles copper in 10.00 mL aliquot | | | | |
| Moles copper in the entire 100.00 mL sample | | | | |
| Mass % copper in Complex 2 | | | | |
| Average Mass % copper | | | | |

***Report Sheet***

Date _____ Name:_____

124L section _____ Instructor_____

b. Determine percent error in mass percent copper in bis-ethylendiamine copper (II) sulfate. Show all work.

| | |
|---|---|
| Theoretical mass percent copper in Compound 2 | |
| Percent error analysis | |