A. INTRODUCTION

In this experiment you will synthesize the iron coordination compound, potassium trioxalatoferrate (III), K$_3$[Fe(C$_2$O$_4$)$_3$]. In the subsequent experiment, you will analyze this salt for iron (III) and oxalate ion content in order to assess its purity.

The interesting portion of the compound is the complex ion, [Fe(C$_2$O$_4$)$_3$]$^{3-}$, which has an octahedral geometry in which two oxygens from each oxalate ion occupy adjacent corners of an octahedron, with the Fe$^{3+}$ at the center.

\[
\begin{align*}
\text{Trioxalatoferrate (III) Ion} \\
\end{align*}
\]

The synthesis of the salt will be carried out in several steps. In the first, Fe$^{2+}$ ion in a solution of ammonium iron (II) sulfate, Fe(NH$_4$)$_2$(SO$_4$)$_2$, reacts with oxalic acid to form iron (II) oxalate, FeC$_2$O$_4$.

\[
\text{Fe}^{2+}{}_{(aq)} + \text{H}_2\text{C}_2\text{O}_4{}_{(aq)} + 2\text{H}_2\text{O}{}_{(l)} \rightarrow \text{FeC}_2\text{O}_4{}_{(s)} + 2 \text{H}_3\text{O}^+{}_{(aq)}
\]

The iron (II) oxalate, FeC$_2$O$_4$, precipitate is separated from the solution and then oxidized to iron (III) oxalate, Fe$_2$(C$_2$O$_4$)$_3$, using hydrogen peroxide as the oxidizing agent and potassium oxalate as the source of oxalate ions. The net ionic equation for the reaction is:

\[
2 \text{FeC}_2\text{O}_4{}_{(s)} + \text{H}_2\text{O}_2{}_{(aq)} + 2 \text{H}_3\text{O}^+{}_{(aq)} + \text{C}_2\text{O}_4{}^2-{}_{(aq)} \rightarrow \text{Fe}_2(\text{C}_2\text{O}_4)_{3(s)} + 4 \text{H}_2\text{O}{}_{(l)}
\]

After removing excess hydrogen peroxide by heating, the iron (III) oxalate is converted to trioxalatoferrate (III) ion by treatment with oxalic acid according to the net ionic equation:

\[
\text{Fe}_2(\text{C}_2\text{O}_4)_{3(s)} + 3 \text{H}_2\text{C}_2\text{O}_4{}_{(aq)} + 6 \text{H}_2\text{O}{}_{(l)} \rightarrow 2 [\text{Fe}(\text{C}_2\text{O}_4)_{3}]^{3-}{}_{(aq)} + 6 \text{H}_3\text{O}^+{}_{(aq)}
\]
Since the salt produced, K₃[Fe(C₂O₄)₃], is soluble in water, it will not precipitate from an aqueous solution. (The potassium ions of the salt are spectator ions in reaction 3.) However, when ethanol (a miscible liquid) is added to the solution the resulting solvent system of water-ethanol is less polar than water. This reduction in the polarity of the solvent system, coupled with cooling of the mixture and allowing it to stand overnight, causes the salt to precipitate.

\[ 3 \text{K}^+_{(aq)} + [\text{Fe(C}_2\text{O}_4\text{)}_3]^{3-}_{(aq)} \rightarrow \text{K}_3[\text{Fe(C}_2\text{O}_4\text{)}_3]_{(s)} \]

**B. Equations:**

**C. Materials:**

*Use a table format*

**D. Safety:**

**Oxalic acid:** Poisonous. May be fatal if swallowed. Corrosive. Causes severe irritation and burns to skin, eyes, and respiratory tract. Harmful if inhaled or absorbed through skin. May cause kidney damage.

**3% Hydrogen peroxide:** May be harmful if swallowed. Causes eye irritation.

**Ethanol** is Flammable

**Acetone:** Extremely flammable liquid and vapor. Vapor may cause flash fire. Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract

**E. Disposal:**

Dispose of all mixtures into the specially labeled waste container:

“Waste Solns of: MnO₄⁻, Mn²⁺, Fe³⁺, C₂O₄²⁻, and H₂SO₄”

**F. PROCEDURE**

**1. FORMATION OF IRON (II) OXALATE FROM AMMONIUM IRON (II) SULFATE AND OXALIC ACID**

Weigh out approximately 7.5 g of solid ammonium iron (II) sulfate, Fe(NH₄)₂(SO₄)₂, into a 250 mL beaker. Record the mass of the sample in your lab notebook. Add 20 mL of warm deionized water and 8 drops of 3 M H₂SO₄ solution and stir to dissolve the solid. To the resulting solution add 35 mL of 1.0 M H₂C₂O₄ solution, and heat to boiling over a Bunsen burner, stirring continuously. The solid formed is iron (II) oxalate, FeC₂O₄. Allow the solid FeC₂O₄ to settle and then decant off the supernatant solution. Dispose of the supernatant by pouring it into the waste container provided.

Wash the precipitate by adding about 30mL of deionized water, warming for five (5) minutes while stirring, allowing the precipitate to settle, and then decanting the supernatant solution. Again, dispose of the supernatant by pouring it into the waste container provided.

**2. FORMATION OF IRON (III) OXALATE BY TREATING IRON (II) OXALATE WITH HYDROGEN PEROXIDE AND POTASSIUM OXALATE**

To the FeC₂O₄ precipitate add 15mL of saturated K₂C₂O₄ solution and heat to about 40°C. Slowly add 30mL of 3-5% H₂O₂ solution to the mixture, stirring continuously and keeping the temperature of the mixture near 40°C.
3. **Formation of trioxalatoferrate (III) ion by treating iron (III) oxalate with oxalic acid**

After the H$_2$O$_2$ addition, heat the mixture to just boiling (40 ºC), and keep it at boiling while adding 12 mL of 1.0 M H$_2$C$_2$O$_4$ solution – the first 10 mL all at once and the last 2 mL drop-by-drop.

At this point, the solution should be clear. If the mixture is very turbid, you’ll need to begin the synthesis again.

4. **Precipitation of potassium trioxalatoferrate (III)** *

Allow the solution to cool partially (still warm but not hot) and then add 8 mL of 95% ethanol.

**NOTE:** If the ethanol is added while the solution is still hot, most of the ethanol will evaporate.

Optional: Tie a short piece of cotton thread to a wooden splint and suspend the thread in the solution. Cover the beaker with a cover glass and allow it to stand in your locker until the next laboratory period.

Note: Potassium trioxalatoferrate (III) decomposes slowly in light, therefore, extended periods of exposure to light should be avoided as much as possible.

5. **Isolation of potassium trioxalatoferrate (III)**

Obtain a Buchner funnel, filtering flask, and filtration trap from the side of the room. Place a piece of filter paper in the funnel. Obtain 5mL of 50% ethanol. Attach the filtration apparatus to the filtration trap and then attach the filtering trap to the vacuum line. Swirl the crystal mixture and then pour it into the funnel. Wash the crystals first with 5mL of 50% ethanol and then with a few mL of acetone. If there are crystals left in the beaker, rinse them out into the funnel with the 5mL of ethanol.

Use tape to attach a piece of filter paper to your watch glass. Scrape your crystals onto the dry filter papers and allow the crystals to dry under the sun lamp or in the hood until the ethanol and acetone odors are gone. It may take the crystals 20 minutes or more to dry.

6. **Weighing of potassium trioxalatoferrate (III) crystals**

Weigh a clean, dry test tube with a cork in it. When dry, transfer your crystals to the test tube, cork it, and weigh. Record a description of your crystals in your Lab Book.

**F. Observations and Data**

(Approximately ¼ - ½ page)

Record all weights, observations, and a description of your product (green crystal)

**G. Calculations**

1. **Theoretical yield of potassium trioxalatoferrate (III)**

Calculate the theoretical yield of K$_3$[Fe(C$_2$O$_4$)$_3$] using the recorded starting mass of ammonium iron (II) sulfate, Fe(NH$_4$)$_2$(SO$_4$)$_2$. The ammonium iron (II) sulfate you used was the hexahydrate – Fe(NH$_4$)$_2$(SO$_4$)$_2$· 6 H$_2$O – which has a molar mass of 392.14 g/mole. The product is also a hydrate - K$_3$[Fe(C$_2$O$_4$)$_3$] · 3 H$_2$O – and has a molar mass of 491.24 g/mole.
2. **Percent yield of potassium trioxalatoferrate (III)**
Calculate the percent yield of potassium trioxalatoferrate (III) using the theoretical yield calculated above, and the experimental (actual) yield.

H. **QUESTIONS**

1. In Step 1 of the Procedure you treated your sample of Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O with 1.0 M H$_2$C$_2$O$_4$.

   The volume of 1.0 M H$_2$C$_2$O$_4$ solution that you actually added to your sample was 35 mL. This volume is quite a bit larger than the volume your sample required. What was the purpose of adding H$_2$C$_2$O$_4$ solution in large excess? (Hint: Think about equilibria effects!)

2. Why was 95% ethanol added in Step 4 of the Procedure?

I. **SUMMARY**

   *(Approximately ¾-1 page)*