Inorganic Chemistry
Experiment 1
Synthesis of light sensitive potassium iron (III) oxalate

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I pledge my honor that I have abided by the Stevens Honor System.

Purpose

The purpose of this experiment is to illustrate the synthesis of iron oxalate, the “solvent exchange” method, and the stability of coordination complexes and the light sensitivity of iron oxalate.

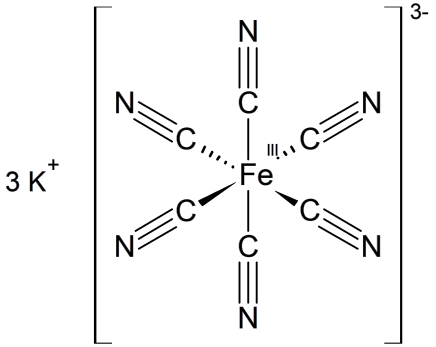
Drawing of structure of the main compound or balanced chemical equation if synthesis is performed

$$FeSO_4 + H_2C_2O_4 \rightarrow FeC_2O_4 + H_2SO_4$$

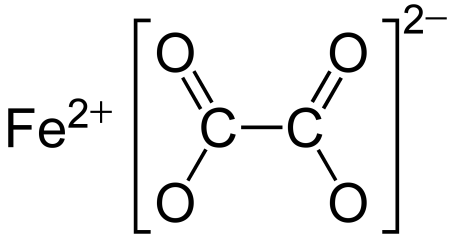
$$6\,FeC_2O_4 + 3\,H_2O_2 + 6\,K_2C_2O_4 \rightarrow 4\,K_3[Fe(C_2O_4)_3] + 2\,Fe(OH)_3$$

$$3\,H_2C_2O_4 + 2\,Fe(OH)_3 + 3\,K_2C_2O_4 \rightarrow 2\,K_3[Fe(C_2O_4)_3] + 6\,H_2O$$

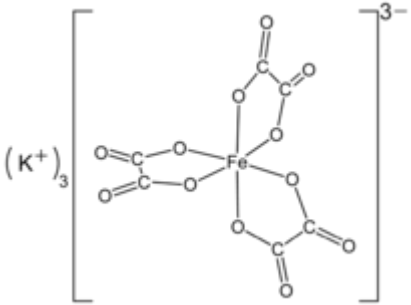
$$K_3[Fe(C_2O_4)_3]\ \text{(light green)} \xrightarrow{\text{light}} FeC_2O_4\ \text{(Yellow)} + K_2C_2O_4 + CO_2$$



Potassium Ferricyanide



Iron (II) Oxalate



Potassium Ferrioxalate

Reagents and Major Product

Name	M.W. (g/mol)	Density (g/cm^3)	Amount (mL / grams)	Moles	Hazards/Precautions	Role of Reagent
$FeSO_4 \cdot 7H_2O$ Ferrous Sulfate Heptahydrate	278.01	1.90	3.6 grams	0.013	Harmful if swallowed, causes skin and eye irritation. May cause respiratory tract irritation.	Reactant
H_2SO_4 Sulfuric Acid	98.08	1.83	Drops of 3 M		Very corrosive. Causes eye and skin burns. Also internal and respiratory burns. Handle in a fume hood and with gloves.	Reactant
$H_2C_2O_4 \cdot 2H_2O$ Oxalic Acid Dihydrate	126.07	1.65	1.7 grams	0.013	Causes burns, harmful of swallowed, inhaled, or absorbed through skin.	Reactant
$FeC_2O_4 \cdot 2H_2O$ Iron (II) Oxalate Dihydrate	179.89	2.28			Can cause skin and upper respiratory tract irritation.	Precipitate
$K_2C_2O_4 \cdot H_2O$ Potassium Oxalate Monohydrate	182.24	2.08	3.5 grams	0.019	Can cause skin, eye, and digestive tract irritation. Also possible burns with contact.	Reactant
H_2O_2 Hydrogen Peroxide	34.01	1.45	8 mL of 6%		A strong oxidizer and can be corrosive to the eyes, skin and respiratory system.	Reactant
$K_3Fe(CN)_6$ Potassium Ferricyanide	329.24	1.89			Harmful if swallowed, causes skin and eye irritation. May cause respiratory tract irritation.	Product

Procedure

Part 1: Preparation of $FeC_2O_4.2H_2O$

- **Solution A:** Weight 3.6g $FeSO_4.7H_2O$, add several drops of 3M H_2SO_4 (Why?) first and followed by water until $FeSO_4.7H_2O$ is totally dissolved;
- **Solution B:** Weight 1.7g $H_2C_2O_4.2H_2O$, add water until sample is totally dissolved. Remove any insolvable substance.
- Slowly mix solution A and solution B. Boil the solution for 4 mins with constant stirring. Get rid of the supernatant, and wash the $FeC_2O_4.2H_2O$ precipitation with hot water for several times to remove left SO_4^{2-} (how can you know SO_4^{2-} is completely removed).

- **Part 2: Preparation of $K_3[Fe(C_2O_4)_3]$**
- Weight 3.5g $K_2C_2O_4.H_2O$ and add 10 ml H_2O to dissolve the sample completely (heat may be needed).
- Add $K_2C_2O_4$ solution to prepared FeC_2O_4 crystals and then place the solution in 40 ^0C water bath. Slowly add 8 ml 6% H_2O_2(aq) with continue stirring. Solution will become turbidity when all H_2O_2 solution is added.
- Place one drop of reaction solution into a well on the assay plate, and then add another drop of $K_3[Fe(CN)_6]$. Development of blue color indicates the presence of Fe^{2+}. More H_2O_2 will be needed until all Fe^{2+} are converted into Fe^{3+}.
- Boil the solution with continuous stirring. Add 6 ml 0.5M $H_2C_2O_4$ into the solution. Keep adding $H_2C_2O_4$ until the solution is clear. Record added $H_2C_2O_4$ volume.

Procedure Cont.

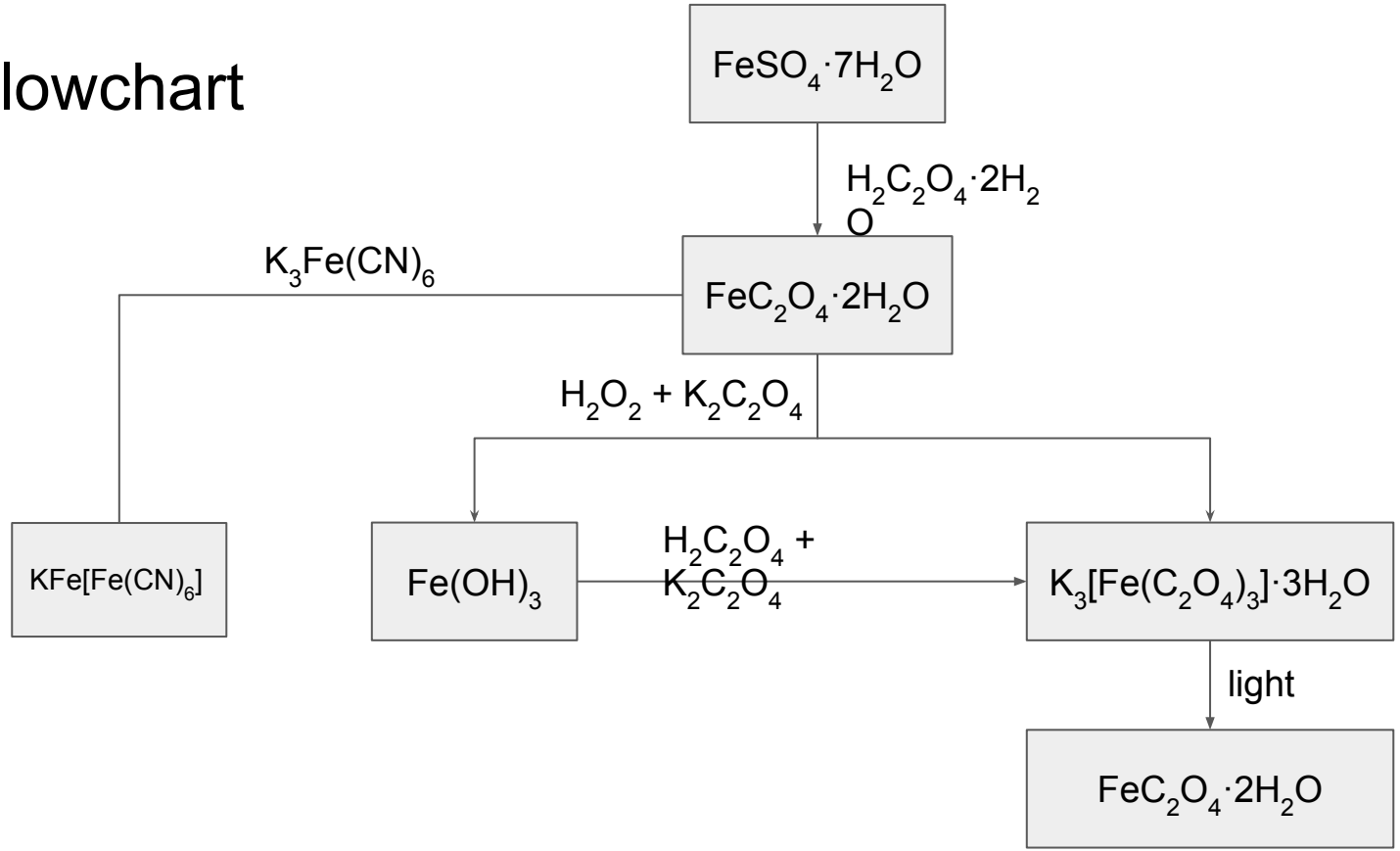
Part 3: Solvent-exchange precipitation

- Add 10 ml alcohol into the transparent $K_3[Fe(C_2O_4)_3]$ solution.
- Place one end of a cotton string into the solution and tie another end of the string to a glass rod placed cross the mouth of the beaker.
- Cover the beaker with a paper and leave it at a dark place overnight.
- Collect $K_3[Fe(C_2O_4)_3]$ crystals through filtration. Wash crystals with alcohol and dry the samples. Weight and calculate yield.

Part 4: Light sensitivity test

Prepare 0.5 ml $K_3[Fe(C_2O_4)_3]$ saturated solution.
Use the solution as the ink to write words or draw on the paper.
Expose the paper to light and observe the appearance of the words/drawings

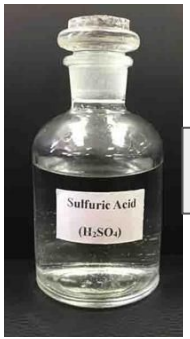
Flowchart


$FeSO_4 \cdot 7H_2O$
$H_2C_2O_4 \cdot 2H_2O$
$K_3Fe(CN)_6$
$FeC_2O_4 \cdot 2H_2O$
$H_2O_2 + K_2C_2O_4$
$KFe[Fe(CN)_6]$
$Fe(OH)_3$
$H_2C_2O_4 + K_2C_2O_4$
$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$
light
$FeC_2O_4 \cdot 2H_2O$

Stepwise Procedure

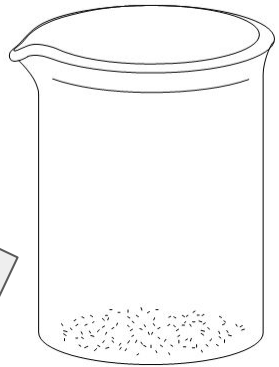
Preparation of $FeC_2O_4 \cdot H_2O$

1. Prepare solution A by weighing out 3.6 g $FeSO_4 \cdot 7H_2O$, adding several drops of 3M H_2SO_4, followed by water until $FeSO_4 \cdot 7H_2O$ is completely dissolved.



Several drops 3M

3.6 grams

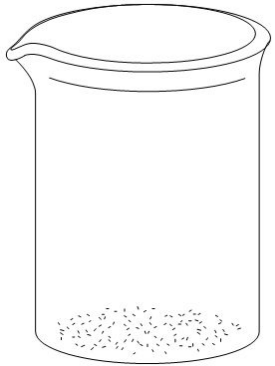


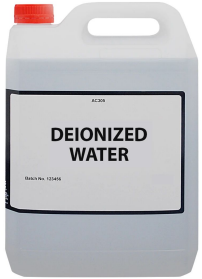
Dissolve with water

Preparation of $FeC_2O_4 \cdot H_2O$

2. Prepare solution B by weighing 1.7 grams $H_2C_2O_4 \cdot 2H_2O$, and adding water until sample is dissolved. Remove any insolubles from both solutions.

1.7 grams

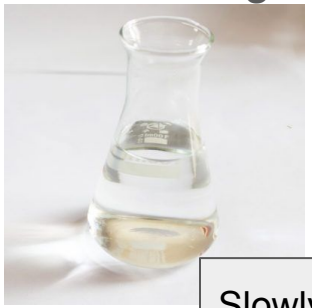




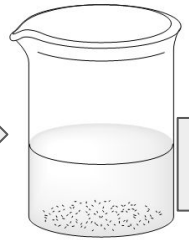
Enough to dissolve

Preparation of $FeC_2O_4 \cdot H_2O$

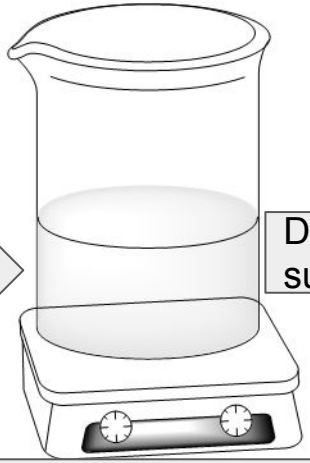
3. Slowly mix solution A and solution B. Boil the solution for 4 min with constant stirring. Decant supernatant, and wash FeC_2O_4 precipitation with hot water several times to get rid of leftover SO_4^{2-}



Slowly mix



Boil solution



100℃, 4 minutes
With constant stirring

Decant supernatant

Wash with hot water and decant several more times

2.Preparation of K3[Fe(C2O4)3]

•Weight 3.5g K2C2O4.H2O and add 10mlH2O to dissolve the sample completely (heat may be needed).

• Add K2C2O4 solution to prepared FeC2O4 crystals and then place the solution in 40 oC water bath.

Add 10mL H2O to dissolve completely

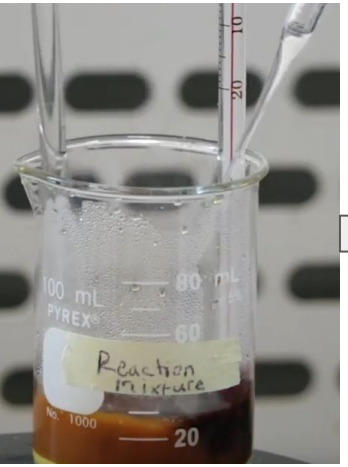
Weigh 3.5g K2C2O4.H2O

Add K2C2O4 solution to FeC2O4 and then place in water bath

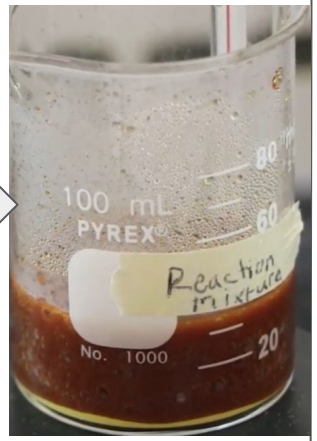
Water bath 40℃

•Slowly add 8 ml 6% H2O2 with continue stirring. Solution will become turbidity when all H2O2 solution is added.

• Place one drop of reaction solution into a well on the assay plate, and then add another drop of K3Fe(CN)6. Development of blue color indicates the presence of Fe 2+.

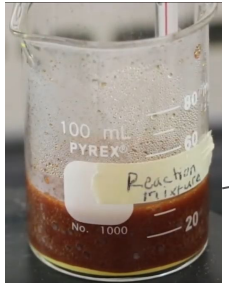


Add 8 mL 6% H2O2

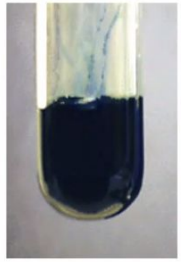


Yields turbid solution

One drop of K3Fe(CN)6

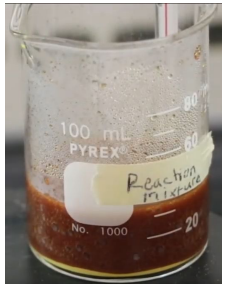


One drop of reaction solution



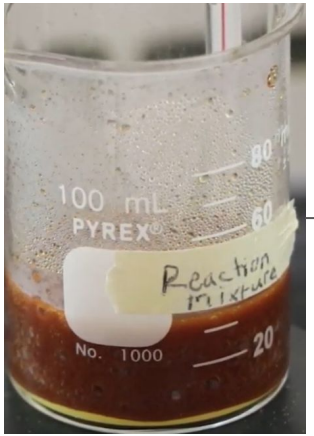
If blue appears, there is Fe2+ present and **KFe[Fe(CN)6]** has formed

If no color change, no Fe2+ present

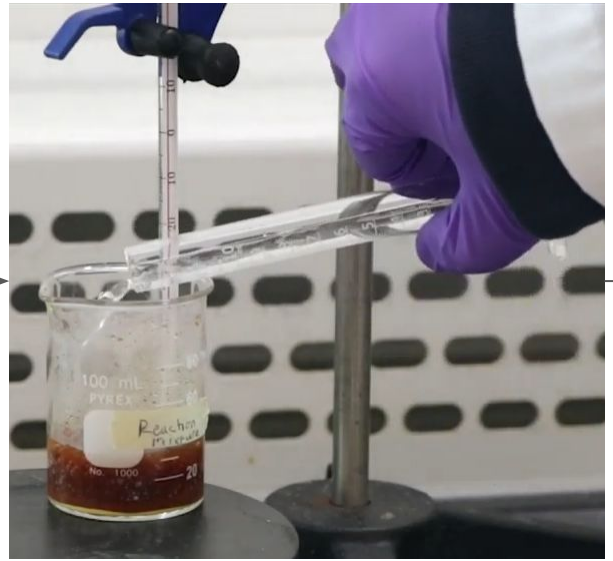


• More H2O2 will be needed until all Fe 2+are converted into Fe 3+. Boil the solution with continuous stirring.

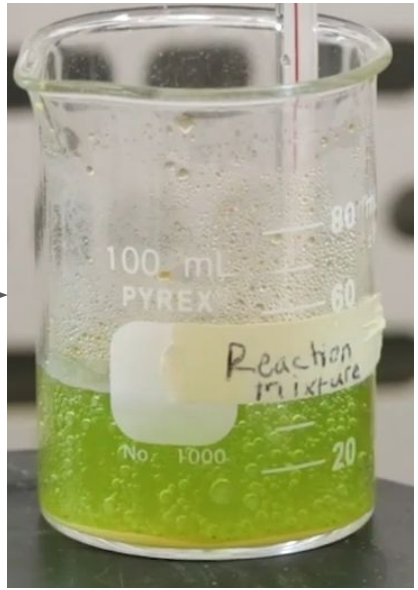
• Add 6 ml 0.5M H2C2O4 into the solution. Keep adding H2C2O4 until the solution is clear. Record added H2C2O4 volume.



Boil the solution with constant stirring



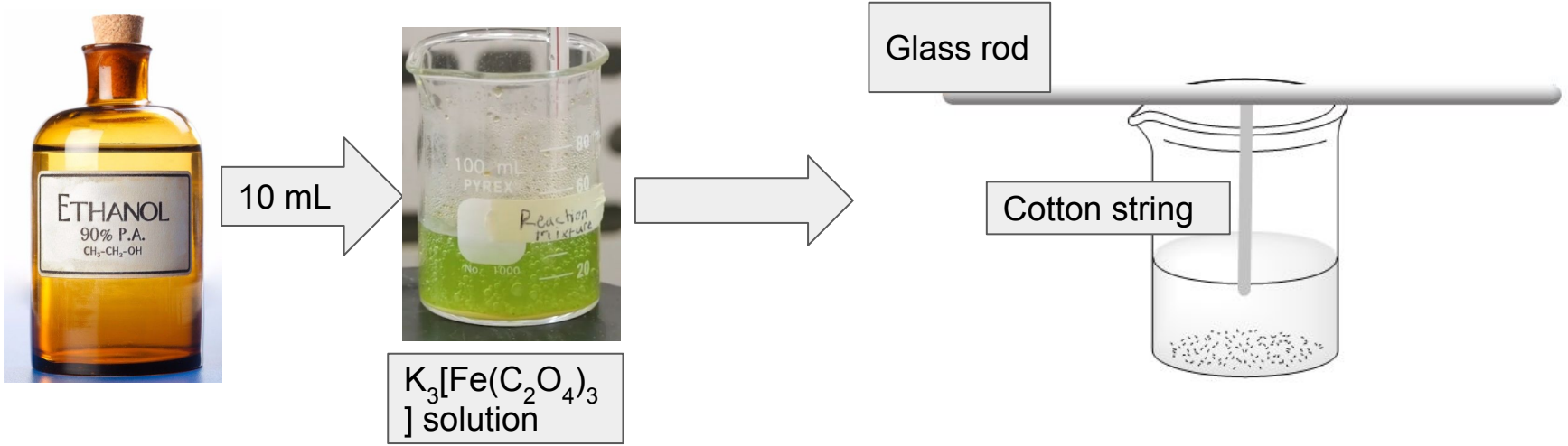
Add 6mL 0.5M oxalic acid



Add until solution is clear, and record added volume

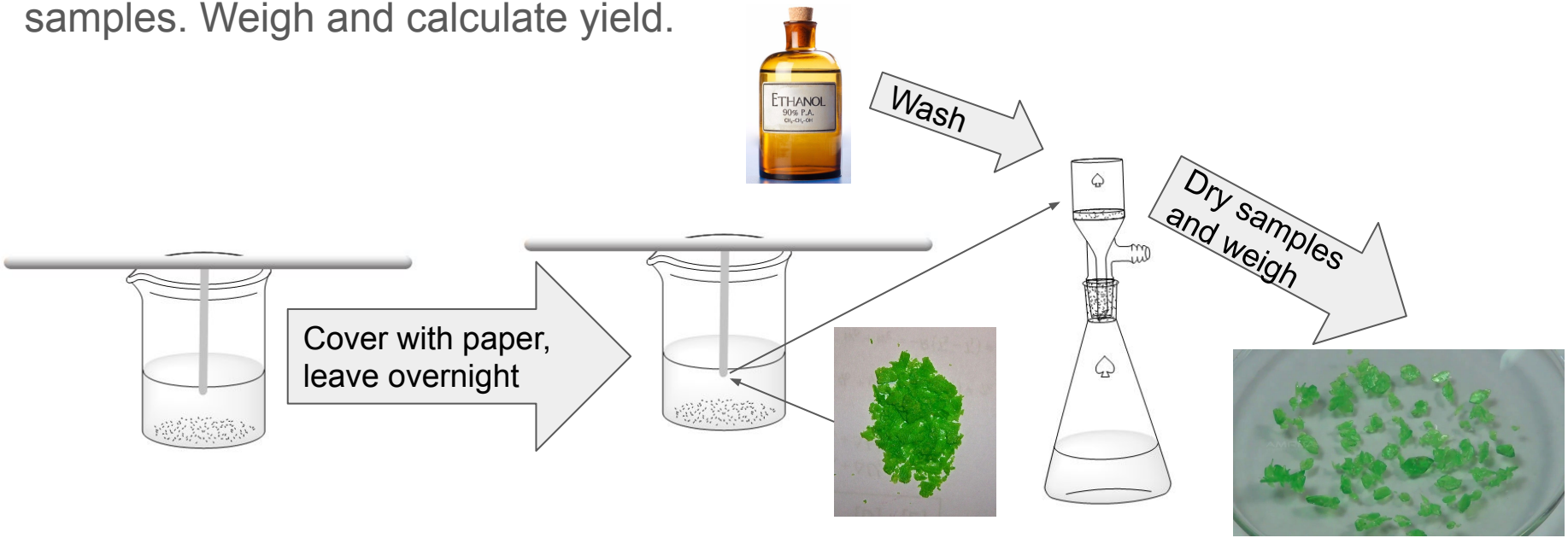
Solvent-exchange precipitation

1. Add 10 mL ethanol to the transparent $K_3[Fe(C_2O_4)_3]$ solution. Place one end of a cotton string into the solution and tie another end of the string to a glass rod placed across the mouth of the beaker.



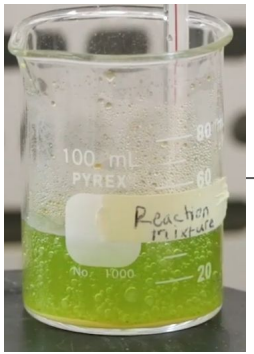
Solvent-exchange precipitation

Cover the beaker with paper and leave it in a dark place overnight. Collect $K_3[Fe(C_2O_4)_3]$ crystals through filtration. Wash crystals with alcohol and dry samples. Weigh and calculate yield.

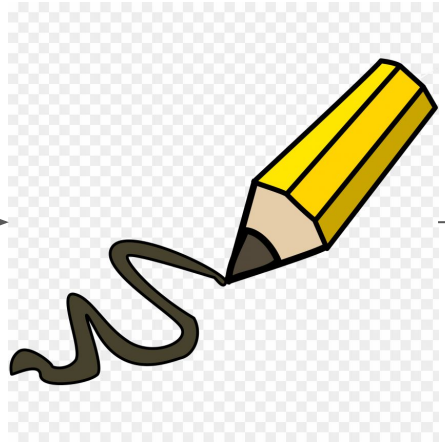


Part 4: Light Sensitivity Test

Prepare 0.5 ml $K_3[Fe(C_2O_4)_3]$ saturated solution. Use the solution as the ink to write words or draw on the paper. Expose the paper to light and observe the appearance of the words/drawings



0.5 ml $K_3[Fe(C_2O_4)_3]$ saturated solution



Use solution as ink to write on paper

Expose paper to light and observe change

Observe color change

Conclusion

The synthesis of iron oxalate was demonstrated using the “solvent exchange” method”. Also, the stability of coordination complexes and light sensitivity of iron oxalate were illustrated. The FeC_2O_4 crystals were created using ferrous sulfate, sulfuric acid, and oxalic acid. The resulting precipitate was FeC_2O_4 crystals. Sulfuric acid had to be added to prevent hydrolysis of the Fe^{2+} ions and to prevent the Fe^{2+} ions from being oxidized to Fe^{3+} ions. $K_3[Fe(C_2O_4)]$ was prepared by adding potassium oxalate to the FeC_2O_4 crystals and then heating them. For the solvent-exchange method, a cotton string was used with the solution because the complex binds more easily to the cotton string.

Post Lab Questions

Why a cotton string is needed in $K_3[Fe(C_2O_4)_3]$ crystallization? What may happen if you do not do it like that?

The complex binds more easily to the cotton string, allowing for better accumulation, which will make it easier to weigh it at the end to determine percent yield.

Do you have any methods to erase the developed words/drawings on the paper in the light sensitive experiments?

Adding a strong acid or a strong base to the solution would react with it and change the composition of the solution and therefore alter its pH. This would erase the words/drawings.