

MAKING FERRIC OXALATE – A SOLUTION

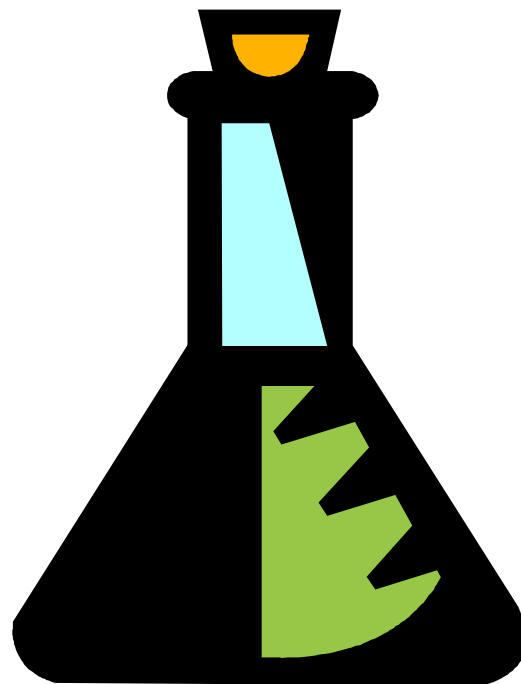
Here is a recommended procedure for making ferric oxalate.

List of chemicals needed for making ferric oxalate.

- 1) Ferrous Ammonium Sulfate (Ammonium Iron II Sulfate)
- 2) Hydrogen Peroxide 30-50% (H_2O_2)
- 3) Oxalic Acid (Dihydrate)
- 4) Potassium Ferricyanide

List of Lab ware needed for making ferric oxalate.

- 1) 500-100,l Flask
- 2) high quality scale measure up to min. 200g
- 3) 50ml Buret
- 4) Fume Mask
- 5) Eye protection
- 6) Strong pair of rubber gloves



It has been my experience that the final volume of 28% ferric oxalate made equals twice that of the amount in grams of the ferrous ammonium sulfate used. Using this as a guide, adjust the amounts below to produce the desired amounts.

- 1) Weigh out 200 grams of Ferrous Ammonium Sulfate. With constant stirring, add it to 500ml of rather warm distilled water – 125 °F to 150 °F. I use a 1000ml flask to mix the solution in with an electric stirrer. After the ferrous ammonium sulfate (FAS) has completely dissolved, add to it 65g of Oxalic Acid. You will see a yellow precipitate form. Continue to carefully stir the solution for 5 minutes.
- 2) Allow the solution to sit for at least an hour. You will notice that the yellow precipitate has settled to the bottom of the mixing vessel. Carefully pour off the clear liquid. This is a strong acid and should be handled with care.
- 3) Add distilled water to the precipitate and allow it to settle again. You will repeat this step several times. I try to continue rinsing the precipitate until the rinse water has a pH of 3.0 or higher.
- 4) Weigh out 55g Oxalic Acid and add it to 125ml water @ 125°F to 150°F. After the Acid has dissolved completely, add the solution to the yellow precipitate and stir for several minutes.
- 5) Using a buret, carefully add the H_2O_2 to the precipitate and oxalic acid solution. This will be a very violent reaction which creates much heat. You will add approximately 80ml to reach final reaction. **DO NOT ADD IT QUICKLY.** It should be added a ½ ml at a time with constant stirring. To prevent the solution from becoming extremely hot, I use a cool water bath for this step.
- 6) As the reaction reaches its conclusion, the addition of H_2O_2 will produce little effervescence. If the solution has been kept relatively cool, about 80F during the addition of the H_2O_2 it will appear a greenish brown color.
- 7) You should begin testing for the presence for Ferrous ions left in solution. To do this, mix a small very dilute solution of Potassium Ferricyanide. Place a small sample of this solution into a 50ml beaker or other small vessel. Add a drop or two of the ferric oxalate solution to it. A brown precipitate should form when you do this. If a blue precipitate forms there are still ferrous ions in solution.
- 8) To eliminate the ferrous ions, add small amounts of oxalic acid to the solution; a ½ gram amount at a time. Allow some time for this to get into solution and retest for ions with the potassium ferricyanide and a few drops of your ferric solution. There will be a color shift as you r get closer to eliminating the ferrous ions; the solution will get greener with less of a yellow brown quality.

- 9) You can add a few drops of H_2O_2 to the solution until a slight effervescence returns. It is believed in some circles that the addition of the H_2O_2 at the stage will convert excess oxalic acid to CO_2 .
- 10) If you do not have a positive test for ferrous ion, it is time to let the solution set for a while (This may be several hours or overnight) and then test the Sp. Gr. Of your ferric. It will need to be cooled to 60F to use the chart on page???
- 11) If you plan to use the ferric oxalate for the other iron processes such as Kallitype you may want to make further alteration to this formula.

The above method was basically from method 2 of 3 in Dick Steven's book on making kallitypes. I have had Vincente Vizcay Castro review this method for making ferric oxalates. Here are his comments. He has provided the platinum printing community a procedure for making ferric oxalate powder. Here is what he had to say about the three methods in.

Eric:

Examining closely: "The three best ways to make Ferric oxalate" de Dick (pages 40 to 57 / "Making Kallitypes")

Method 1:

Use:

1: Ferric ammonium sulfate and ammonia to obtain "ferric hydroxide" : The obtained gelatinous ferric hydroxide (a hydrated form of $Fe_2O_3 \cdot x H_2O$) have a great power to retain anions and water.

Product not well defined (purity and composition?)

2: "Ferric hydroxide (with water and anions)" and oxalic acid to obtain ferric oxalate

As consequence of ill defined "ferric hydroxide" the product (a solution of $Fe_2(C_2O_3)_3$ and $H_2C_2O_4$ in water) is also ill defined.

Method 2: (the best of three)

Use:

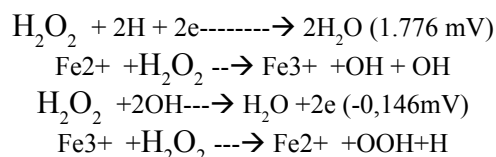
1: (Steps 1 to 5)

Ferrous ammonium sulfate and oxalic to obtain ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) Product well defined and very pure if you are careful with selections of reactants, washing and drying the precipitate.

2: (Steps 6 to end)

The purpose of these steps is to oxidize the ferrous ion to ferric and obtain ferric oxalate. This oxidation process has been very well studied (Fenton's reactions). It is very complex and implicates, above all, in this case many variables. Elements to take into account: The H_2O_2 can act as an oxidizer or reducing depending (pH depending)

1. If pH is increased (local or general) (>6) appears $Fe(OH)_3$



2. The H_2O_2 oxidizes $\text{C}_2\text{O}_4^{2-}$
3. the H_2O_2 liberates oxygen.
4. The $\text{Fe}(\text{OH})_3$ catalytically decomposes the H_2O_2 to oxygen
5. etc, etc
6. As consequence of above the product (a solution of $\text{Fe}_2(\text{C}_2\text{O}_3)_3$ and $\text{H}_2\text{C}_2\text{O}_4$ in water) is also ill defined.

Method 3: (similar to 2)

The oxidizing agent is potassium permanganate (this method introduces an additional anions)