

## DETERMINATION OF THE WEIGHT PERCENT OXALATE WITH $\text{KMnO}_4$ :

### A PHOTOMETRIC REDOX TITRATION.

By Michael Collins, Viterbo University

The objective of this experiment is to determine the % sodium oxalate in your unknown by photometric titration with a solution of potassium permanganate. The first step is to determine the precise concentration of the  $\text{KMnO}_4$  solution, since it is impossible to obtain  $\text{KMnO}_4$  in a reproducibly pure state.

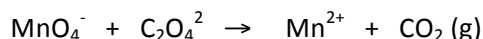
#### Equipment and reagents:

- MicroLab FS522 unit with built in FastSPEC spectrometer, power supply, USB cable, and large colorimeter vial
- PC with MicroLab photometric titration software installed
- Magnetic stirrer unit
- Stir bar to fit vial
- Autopipet to deliver ~10 uL aliquots
- Autopipet to deliver 1.00 uL aliquots
- Sodium oxalate
- Unknown oxalate mixture
- 0.01M  $\text{KMnO}_4$
- 0.01M  $\text{MnSO}_4$

#### Pre-Lab questions

Due at the beginning of lab: show your work!

1. Complete and balance the following redox reaction in acidic solution using the half reaction method:



[Answer:  $5 \text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$ ]

2. If 6 mL of 3M  $\text{H}_2\text{SO}_4$  solution were diluted to 250 mL, what would be the concentration of  $\text{H}_2\text{SO}_4$  in the final solution?

[Answer: 0.072M]

3. Suppose 0.125 grams of  $\text{Na}_2\text{C}_2\text{O}_4$  are dissolved to make 250.0 mL of solution. How many moles of  $\text{Na}_2\text{C}_2\text{O}_4$  are present in each 1.00 mL of this solution? [Answer: the solution is found to be 0.00373M; so #mol/mL =  $3.73 \times 10^{-6}$  mol or 3.73 micromoles ]

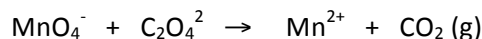
4. Suppose 1.00 mL of this solution is titrated with a  $\text{KMnO}_4$  solution in order to determine the concentration of the  $\text{KMnO}_4$ . The end point occurs after the addition of 145 uL. What is the molar concentration of the  $\text{KMnO}_4$  solution?

[Answer: 0.0103M]

5. Suppose 0.125 grams of an unknown mixture of  $\text{Na}_2\text{C}_2\text{O}_4$  and KCl (an inert additive) are dissolved in 250 mL of solution. If a 1.00 mL sample of this solution requires 93.0 uL of the same  $\text{KMnO}_4$  solution, what is the % sodium oxalate in the unknown? [Answer: 64.1%]

## I. Standardization of ~0.010 M KMnO<sub>4</sub>

Potassium permanganate is a relatively inexpensive, intensely colored compound commonly used in laboratories as a strong oxidizing agent. In this experiment a ~0.010 M KMnO<sub>4</sub> solution will be prepared for you by dissolving a weighed quantity of solid KMnO<sub>4</sub> in water. You will calculate the mole ratio of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> to MnO<sub>4</sub><sup>-</sup> in a titration reaction involving the oxidation of oxalate ion by permanganate ion, and determine the stoichiometry of the reaction by using the **balanced equation** for the reaction in acidic aqueous solution:



Sodium oxalate, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, the source of the oxalate ions in this titration, can be obtained in high purity as what is called *primary standard grade*. The actual molar concentration of the KMnO<sub>4</sub> solution must be analyzed from titration rather than by accurate weighing of the KMnO<sub>4</sub> because the KMnO<sub>4</sub> cannot be maintained in a state of high purity due to its reactivity. This kind of titration, in which the concentration of a solution of a material of unknown purity is determined by reacting it with a material of known purity is called a *standardization reaction*. Actually, for best results, the standardization and determination of unknowns should be done the same day, since the KMnO<sub>4</sub> slowly decomposes. In order to go from the titration data to the molarity, you need to use the balanced equation for the reaction. You will then use the "*standardized*" molarity of the KMnO<sub>4</sub> solution to determine the percent sodium oxalate in your unknown salt.

### Experimental Procedure:

1. Weigh to the nearest mg between 0.12 and 0.13 g of pure Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> into a clean and dry 250 ml volumetric flask and add 60 ml of distilled water to dissolve. Add 12 ml of benchtop 3M (6N) sulfuric acid to the flask and dilute to volume with DI water. Mix thoroughly. [**Note:** The sulfuric acid is needed to maintain an acidic solution. In neutral or alkaline solution, the product of the reaction is not Mn<sup>2+</sup>, but MnO<sub>2</sub>(s), which changes the stoichiometry. Also note that the balanced equation shows that lots of H<sup>+</sup> ions are consumed in the reaction, so a large excess of acid is needed.]
2. Obtain a flask or vial with approximately 5 mL of *ca.* 0.01 M KMnO<sub>4</sub>. At this point you can begin setting up the PC and the MicroLab FS522.
3. Place the MicroLab unit securely on a magnetic stirrer, connect the MicroLab unit to a PC, and open the photometric titration experiment.
4. Obtain a large spectrometer vial. Add a small stir bar and 15 mL of DI water. Place the vial into the FastSpec and begin stirring at a moderate speed. Add about 10-15 drops of benchtop H<sub>2</sub>SO<sub>4</sub> to the vial as it is stirred.
5. Next, add 50  $\mu$ L of 0.01M Mn(II)SO<sub>4</sub> solution to the spectrometer vial. [**Note:** The Mn(II) serves as a catalyst in the reaction between permanganate and oxalate. This small aliquot of Mn(II) greatly speeds the initial reaction.]
6. Run the software and obtain a blank spectrum.
7. Use an autopipet to transfer 1.00 mL of the standard Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution that you have prepared. Let it mix for a few seconds and record an initial spectrum, entering "0" for the volume of KMnO<sub>4</sub> added at the prompt.
8. Begin the titration: use a small autopipet to add 10  $\mu$ L of the KMnO<sub>4</sub> solution to the vial. Wait until the pink MnO<sub>4</sub><sup>-</sup> color completely disappears before you record a spectrum. Enter the volume added at the prompt. [**Note:** You should not expect to see much change in the spectrum until after the end point since the color comes from unreacted KMnO<sub>4</sub>.]

9. Continue the titration: add replicate 10 uL portions to the vial, recording the spectrum and RUNNING TOTAL VOLUME ADDED after each addition, just as you would if you were reading from a buret, being careful to wait until the solution has reacted before getting a spectrum. Once you start to see a spectrum from the  $\text{KMnO}_4$ , determine the best wavelength to view the photometric titration curve as it continues to develop.

10. Repeat until the appearance of a spectrum due to the slight excess of  $\text{MnO}_4^-$ . Add at least four more 10 uL portions beyond the first appearance of the  $\text{MnO}_4^-$  spectrum. You will in all probability not be able to hit the end point exactly this way, so you will need points both before and after the end point to obtain linear regressions on the two regions of the photometric titration to obtain a precise end point.

11. End the experiment, and SAVE YOUR DATA. EXPORT TO EXCEL or other spreadsheet program for graphing as needed. Turn off the stirrer and clean out the vial (**NOT DOWN THE DRAIN! Dispose of the contents of the vial as instructed**). Be sure that the stir bar is not discarded.

12. Repeat this procedure with two more 1.00 mL samples of  $\text{Na}_2\text{C}_2\text{O}_4$  titrated in a similar manner. Use your titration data to prepare suitable plots and find the molarity of the permanganate solution from each run and the average of the three runs. You will need to use the **balanced equation** describing this reaction.

## 2. Determination of the Percent Oxalate in your Unknown Salt

The percent oxalate in an unknown sample will be determined by titration a solution containing a known mass of sample with the standardized 0.01XX M  $\text{KMnO}_4$ . The mass and percent of  $\text{C}_2\text{O}_4^{2-}$  in the sample can be determined by measuring the volume, V, of standard  $\text{KMnO}_4$  needed to completely oxidize the  $\text{C}_2\text{O}_4^{2-}$  in your sample. The reaction describing this redox reaction is the same as that used in the standardization of the  $\text{KMnO}_4$ .

### Experimental Procedure:

Weigh a *ca.* 0.12-0.15 g sample of your unknown to the nearest 0.001 g and transfer it to a 250 mL volumetric flask. Dissolve the sample with about 60 ml of distilled water. Add 12 ml of 3M sulfuric acid, dilute to the mark with DI water, and mix thoroughly by inverting the volumetric flask at least 20 times. NOTE: if your sample contains dissolved iron, you should also add 1 mL of 85% phosphoric acid to keep the Fe(III) in solution during the titration.

Repeat the procedure that you used for the standardization titration, starting with the blank, and substituting your unknown solution for the solution of primary standard  $\text{Na}_2\text{C}_2\text{O}_4$ . Depending on the makeup of your unknown, it may require more or less of the  $\text{KMnO}_4$  solution than was needed for the standardization steps.

Do at least duplicate runs on your unknown, triplicate if time permits.

Discard your titrated solutions in the waste as before.

Clean the vial and other glassware with 6 M HCl if they appear to have any yellow or brown stains. Follow this by thoroughly rinsing with distilled water. Be sure to turn in the carbon copy of your lab notebook page(s) with today's work before you leave the lab.

### **Standardization Calculations:**

1. Use the mass of standard  $\text{Na}_2\text{C}_2\text{O}_4$  to calculate the moles of  $\text{Na}_2\text{C}_2\text{O}_4$  that you weighed into the volumetric flask.

2. Calculate the moles of  $\text{Na}_2\text{C}_2\text{O}_4$  you transferred in 1.00 mL of the sodium oxalate solution.

3. Use the balanced equation to calculate the number of moles of permanganate ion needed to react with your moles of  $\text{Na}_2\text{C}_2\text{O}_4$ .
4. Determine the end point volume. This is best done by creating the titration curve (absorbance vs. volume  $\text{KMnO}_4$  solution) at the optimum wavelength in a spreadsheet or in the MicroLab Photometric Titration software. Obtain the regression line (first order) for the points prior to the endpoint. Obtain the regression line for the points beyond the endpoint. Use the two equations for the lines to determine the (x,y) point of intersection (this is first year algebra stuff). This is the endpoint. Convert the endpoint volume from microliters to liters.
5. Take the ratio of moles of  $\text{MnO}_4^-$  to the end point volume (liters) to get the #mol/L in the  $\text{KMnO}_4$  solution.
6. Repeat this for each standardization titration and take the average. Expect the results to agree within about 3%.
7. **Report individual concentrations and the average.**

#### **Unknown Calculations:**

These calculations kind of work in the reverse of the standardization titrations, since now you know the composition of the  $\text{KMnO}_4$  but do not know the composition of the unknown sodium oxalate.

1. Determine the end point volume for each of your unknown runs. Convert these from microliters to liters.
2. For each unknown run, use your average value of the molarity of  $\text{KMnO}_4$  solution to calculate the number of moles of  $\text{MnO}_4^-$  to get to the end point volume.
3. For each unknown run, use the balanced equation to determine the number of moles of  $\text{C}_2\text{O}_4^{2-}$  this would require.
4. For each unknown run, convert moles of oxalate to mass of sodium oxalate in the titration run.
5. For each unknown run, convert the mass of sodium oxalate in the titration sample to the mass of sodium oxalate in the entire 100 mL of unknown oxalate solution.
6. For each unknown run, determine the % sodium oxalate by taking 100 times the ratio of mass of sodium oxalate in your complete sample to the mass of the sample.
7. Repeat for each run and take the average.
8. **Report the individual results and the average.**