

REDOX TITRATIONS WITH IODINE

Introduction

The shelf life of pharmaceutical products must always be tested. Hydrogen peroxide used in disinfectants is slowly reduced to water; it also photodegrades. Vitamin C in vitamin tablets is inherently unstable, being slowly oxidized by air. The ability to accurately and reliably determine the concentration of the active ingredients in various formulations is an important one.

In this lab you will determine the content of hydrogen peroxide in a pharmaceutical disinfectant, as well as the concentration of ascorbic acid in Vitamin C supplemental tablets. Both analyses will involve the potentiometric titration of aqueous iodine with sodium thiosulfate using an automatic titrator. A platinum ring indicator electrode is used to follow the progress of the titration curve by potentiometry.

Background

Titration Involving Iodine

Iodine is a moderately weak oxidizing agent; it is reduced to form the iodide anion, as follows:



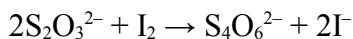
The above redox reaction is completely reversible, and so the iodide anion is a moderately weak reducing agent that will react with oxidizing analytes to produce iodine. Titrations involving iodine have evolved for the analysis of a number of oxidizing and reducing agents. In *iodimetric titrations*, the analyte (a reducing agent) reacts with iodine to produce iodide:



where A_{ox} and A_{red} are the oxidized and reduced forms, respectively, of the analyte. In *iodometric titrations*, the analyte (an oxidizing agent) reacts with an unmeasured excess of iodide to produce iodine:



The iodine produced in this reaction is stoichiometrically related to the amount of analyte originally present in the sample. The iodine may then be titrated to determine the analyte concentration in the sample. The nearly universal titrant for iodine is thiosulfate; they react quantitatively as follows:



So we see that reactions involving iodine can be used for the analysis of moderately strong reducing agents (by reacting with I_2 in iodimetry) or moderately strong oxidizing agents (through reaction with excess iodide in iodometry).

Solid iodine is not very soluble in water. As a result, iodine solutions are usually prepared by dissolving the solid in the presence of potassium iodide. Iodine reacts with iodide to produce the triiodide ion:



Due to this reaction, solid iodine is soluble in solutions of iodide salts. However, most of the dissolved iodine is actually present as triiodide, not as iodine. Thus, the reduction of iodine may be written as



Although the standard reduction potential of this reaction gives a more accurate indication of the oxidizing strength of iodine titrant solutions, it is usually $\text{I}_2(\text{aq})$ that is actually being reduced during the titration. Thermodynamically, of course, it makes no difference: the exact same titration curve would be calculated with either reaction.

Iodine/triiodide solutions are unstable for a variety of reasons. First of all, aqueous iodine exerts a significant vapor pressure. Also, under acidic conditions iodide is slowly air-oxidized to produce iodine. Finally, under alkaline conditions, iodine will disproportionate to produce iodide and iodate, as follows:



Thus, iodine solutions are generally most stable at neutral pH values. Iodine titrant solutions must be standardized fairly frequently against a standard sodium oxalate solution.

The disproportionation reaction of iodine is fully reversible, a fact that can be used to produce standard solutions of iodine. If a solution prepared by dissolving primary standard potassium iodate is mixed with a slight excess of iodide, and then acidified with sulfuric acid, a standard iodine solution is prepared by this “reverse disproportionation” reaction.

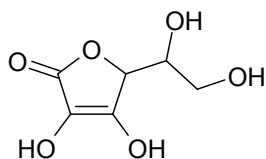


The solution that results can be used to standardize sodium thiosulfate titrant, or to generate a known quantity of iodine reagent *in situ*. Unfortunately, it is not stable enough for general use as a titrant (since, as mentioned previously, aqueous iodine is not so stable under acidic conditions).

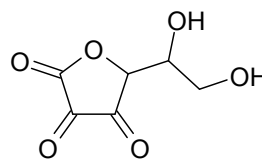
Analysis of Ascorbic Acid by Iodimetry

Ascorbic acid (vitamin C) is sometimes called an “anti-oxidant” (i.e., a reducing agent!) by pharmacists and food nutritionists. Iodine rapidly oxidizes ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$, to produce dehydroascorbic acid, $\text{C}_6\text{H}_6\text{O}_6$:





ascorbic acid
C₆H₈O₆

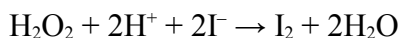


dehydroascorbic acid
C₆H₆O₆

Ascorbic acid is readily water-soluble, and direct iodimetric titration is a standard method for the analysis of vitamin C in a variety of citrus fruits and in vitamin tablets. In our experiment, we actually perform an iodimetric back-titration: we generate a measured excess of iodine in the sample solution and then titrate the unreacted iodine with sodium thiosulfate. This back titration is still an iodimetric titration, since it is based on the reaction of analyte with aqueous iodine; however, using a back titration allows us to use the same titrant (sodium thiosulfate) as we use in the iodometric analysis of hydrogen peroxide.

Analysis of Hydrogen Peroxide by Iodometry

Solutions of hydrogen peroxide are widely sold as disinfectants. Since hydrogen peroxide is an oxidizing agent, it will react with iodide in a redox reaction:



The reaction is not instantaneous, but it is fast enough to form the basis of a practical analysis by iodometric titration. The sample is added to an acidic solution containing an unmeasured excess of iodide. After the reaction is complete, the iodine produced by the above reaction is titrated with sodium thiosulfate.

References

- Harris chapter 16, especially section 16-7.
- GH Jeffery, J Bassett, J Mendham, RD Denney, "Vogel's Textbook of Quantitative Chemical Analysis," 5th ed, 1989, Wiley, NY.
- DN Bailey, *J Chem Ed*, 1974, **51**, 488-489.

TITRATIONS WITH IODINE: *PROCEDURE*

Materials

- 1M H₂SO₄
- solid potassium iodide
- a standard solution (approx 0.01M; see label for exact concentration) of potassium bi-iodate, KH(IO₃)₂
- 0.1M sodium thiosulfate, Na₂S₂O₃, as titrant
- Mettler-Toledo DL58 titrator, using a platinum indicator electrode to follow the titration reaction
- mortar and pestle

Standardization Procedure

Use the following procedure to standardize the sodium thiosulfate titrant. The standard potassium bi-iodate solution is acidified in the presence of excess iodide to produce a standard solution of iodine.

1. Add approximately 30 mL of deionized water to three clean sample cups
2. Add approximately 5 mL of 1M H₂SO₄ to each cup.
3. Add approximately 0.4g of KI into one sample cup and swirl until dissolved.
4. Accurately pipette 5.00 mL of standard bi-iodate solution into the sample cup. The formation of iodine should be apparent. Titrate immediately with thiosulfate. You will use method #301b; ask the instructor or a TA to show you how to use the titrator.
5. Repeat steps 3-4 for at least two other sample cups.

Analysis of Hydrogen Peroxide

This procedure describes the analysis of hydrogen peroxide by iodometric titration. An unmeasured excess of iodide is mixed with the sample under acidic conditions. The iodine produced by the oxidation of iodide by the analyte is titrated with thiosulfate. The reaction between iodide and analyte needs about 15 minutes to be complete.

1. Add approximately 40 mL of 1M H₂SO₄ to at least 3 sample cups (do more than 3 if you feel industrious).
2. Add approximately 0.6g of KI to each sample cup and swirl to dissolve
3. Accurately pipette 0.40 mL of sample solution into each cup, swirl well, and **cover with a watch glass**. Make sure the reactants are well mixed, because they can form two distinct layers, slowing the reaction. Allow 15 minutes and then titrate each solution with thiosulfate.

Analysis of Ascorbic Acid in Vitamin C Tablets

The following procedure describes the analysis of vitamin C by iodimetric back titration. A measured excess of iodine is generated *in situ* by the acidification of standard bi-iodate in the presence of excess iodide. The unreacted excess is determined by thiosulfate titration.

In this procedure, you will grind vitamin C tablets before weighing and dissolving the sample. This action greatly hastens the oxidation of ascorbic acid. In addition, the back-titration should be performed as soon as possible due to the instability of iodine in acidic solutions. Thus, each analysis should be performed in its entirety before proceeding to the next sample.

1. Add approximately 30 mL of deionized water and 5 mL of 1M H₂SO₄ to a sample cup.
2. Add approximately 0.7g of KI to the cup and swirl to dissolve.
3. Randomly sample a single vitamin C tablet, weigh it **accurately** in a weighing boat, and grind it using the mortar and pestle. Once ground, use weighing paper to rapidly **but accurately** weigh 0.09-0.10g of the powder. Pour the sample into the solution and swirl. Note that the binder in the tablet will not dissolve in water. Be sure that all of the powder ends up in the solution.
4. Accurately pipette 10.00 mL of standard bi-iodate into the solution, swirl briefly and titrate immediately with thiosulfate.
5. Clean the mortar and pestle and the spatula thoroughly and repeat steps 1-4 for at least two more samples, using two new tablets.

TITRATIONS WITH IODINE: *DATA SHEET*

Along with the raw data and results (below), please submit your calculations. Be careful with the stoichiometry! And don't forget to account for the effect of the uncertainty in the thiosulfate concentration (from the standardization) on the confidence intervals. See the Argentometric Determination of Chloride experiment for more details.

How do your results compare with the nominal values of 3% hydrogen peroxide (by weight) and 500 mg/tablet for ascorbic acid?

Raw Data

Concentration of standard $\text{KH}(\text{IO}_3)_2(\text{aq})$: _____ M

	Standardization	H_2O_2 analysis	Vitamin C analysis		
	endpt vol, mL	endpt vol, mL	tablet mass, g	sample mass, g	endpt vol, mL
sample 1					
sample 2					
sample 3					

Results

Give the following as 95% confidence intervals.

Concentration of H_2O_2 in disinfectant, mg/mL:	
Ascorbic acid in vitamin C tablets	w/w %:
	mg/tablet:

Give the results of your hypothesis tests:

Comparison of H_2O_2 concentration with nominal value of 30 mg/mL –

Comparison of ascorbic acid concentration with nominal value of 500 mg/tablet –