

CHL 212 – Quantitative Analysis

Experiment 7 Redox Titration of Vitamin C

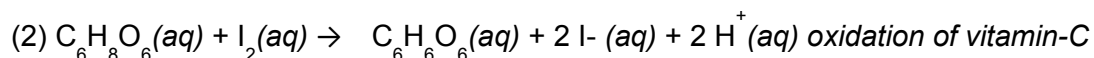
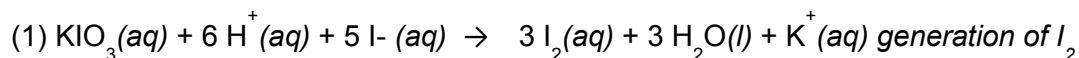
Introduction

In this experiment, you will be acting as the quality control laboratory for a pharmaceutical manufacturer. The product line that you support produces 100-mg Vitamin C supplements. You are to determine the average amount of Vitamin C per tablet in a sample of tablets and report this value and its uncertainty to the product line manager.

As in previous experiments, you will determine the amount of Vitamin C in the tablets using titration. In the case of Acid/Base titration, the acidic or basic sample was neutralized with the appropriate titrant and the amount of sample was determined by measuring the volume of titrant required to reach the end point. In the determination of dissolved Ca^{2+} and Mg^{2+} experiment, you measured the amount of calcium and magnesium dissolved in the laboratory tap water by using a titrant (EDTA) that formed a complex with the ions to be determined.

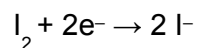
Although new methods and reagents are being discovered and developed continuously, often a titrant solution is not available that reacts directly with the species of interest. In this experiment, we do not have a convenient solution that reacts or complexes directly with the Vitamin C to be analyzed. In these types of cases, we must perform our analysis **indirectly** by analyzing species that *do react or complex* with the species of interest.

Vitamin C (Ascorbic Acid), is a mild reducing agent (it accepts electrons from an electron donor, leaving the Oxidation State of the donor at a value less than original (reduced)). The Ascorbic Acid itself is oxidized to a higher oxidation state. This class of reactions is known as a reduction/oxidation reaction or simply, a *redox* reaction. One such redox reaction is the reduction of the aqueous iodine molecule ($\text{I}_{2(\text{aq})}$) with Ascorbic Acid, as shown below.

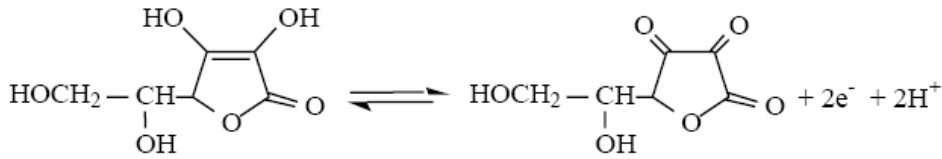


Reaction one generates aqueous iodine, $\text{I}_2(\text{aq})$. This is then used to oxidize vitamin-C (ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$) in reaction two. Both of these reactions require acidic conditions and so dilute hydrochloric acid, $\text{HCl}(\text{aq})$, will be added to the reaction mixture. Reaction one also requires a source of dissolved iodide ions, $\text{I}^-(\text{aq})$. This will be provided by adding solid potassium iodide, $\text{KI}(\text{s})$, to the reaction mixture.

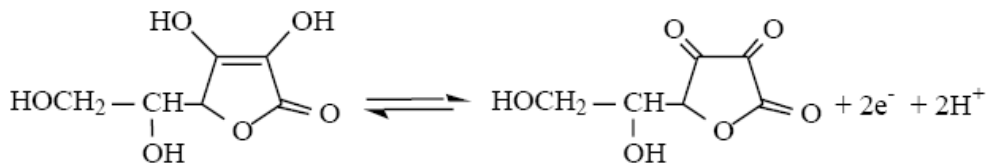
The two relevant half reactions for reaction (2) above are:



Reduction half reaction for Iodine at pH 5



Oxidation half reaction for vitamin-C ($C_6H_8O_6$) at pH 5



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Each of the iodine atoms is reduced to the I^- ion and the Ascorbic Acid gains two electrons to form Dehydroascorbic Acid as in the chemical reaction below:



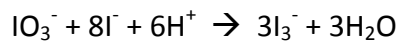
This reaction has a high K value and goes to completion. Unfortunately, the solubility of $I_{2(solid)}$ in water is not very high. The saturated $I_{2(aq)}$ concentration is only 1.3 mM.



To increase the solubility of the I_2 molecule, we can create a complex between the $I_{2(aq)}$ and the iodide ion (I^-) as below:



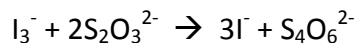
The I_3^- complex is known as *triiodide*. Rather than starting with solid I_2 and taking the time to dissolve it in solution, triiodide can also be produced by reacting iodate ion (IO_3^-) with iodide (I^-) as below:



Triiodide is reduced by Ascorbic acid in the same way that the $I_{2(aq)}$ species reacted:



It is this reaction that we use to measure indirectly the amount of Ascorbic Acid in the sample. We do have a titration solution and indicator that can measure the amount of I_3^- in the sample. The titration solution is sodium thiosulfate (thigh-o-sul-fate), $Na_2S_2O_3$, and it reacts with the triiodide species in the 1:2 reaction below:



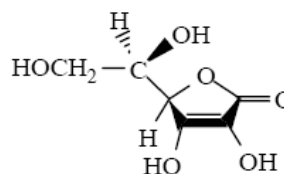
The indicator used is a starch solution. In the presence of the triiodide, starch and triiodide form a complex that is intensely dark blue in color. In the absence of triiodide, the starch indicator is a milky-white.

Vitamin-C: An Important Chemical Substance

Vitamin-C, *known chemically as ascorbic acid*, is an important component of a healthy diet. The history of vitamin-C revolves around the history of the human disease scurvy, probably the first human illness to be recognized as a deficiency disease. Its symptoms include exhaustion, massive hemorrhaging of flesh and gums, general weakness and diarrhea. Resultant death was common. Scurvy is a disease unique to guinea pigs, various primates, and humans. All other animal species have an enzyme which catalyzes the oxidation of L-gluconactone to L-ascorbic acid, allowing them to synthesize vitamin-C in amounts adequate for metabolic needs.

As early as 1536, Jacques Cartier, a French explorer, reported the miraculous curative effects of infusions of pine bark and needles used by Native Americans. These items are now known to be good sources of ascorbic acid. However, some 400 years were to pass before vitamin-C was isolated, characterized, and synthesized. In the late 1700's, the British Navy ordered the use of limes on ships to prevent scurvy. This practice was for many years considered to be quackery by the merchant marines, and the Navy sailors became known as "Limeys". At that time scurvy aboard sailing vessels was a serious problem with often up to 50% of the crew dying from scurvy on long voyages.

The RDA (*Recommended Daily Allowance*) for vitamin-C put forward by the Food and Nutrition Board of the National Research Counsel is 60 mg/day for adults. It is recommended that pregnant women consume an additional 20 mg/day. Lactating women are encouraged to take an additional 40 mg/day in order to assure an adequate supply of vitamin-C in breast milk. Medical research shows that 10 mg/day of vitamin-C will prevent scurvy in adults. There has been much controversy over speculation that vitamin-C intake should be much higher than the RDA for the prevention of colds and flu. Linus Pauling, winner of both a Nobel Prize in Chemistry and the Nobel Peace Prize, has argued in his book, *Vitamin-C and the Common Cold*, that humans should be consuming around 500 mg of vitamin-C a day (considered by many doctors to be an excessive amount) to help ward off the common cold and prevent cancer.



L-Ascorbic Acid -- Vitamin-C

Vitamin-C is a six carbon chain, closely related chemically to glucose. It was first isolated in 1928 by the Hungarian-born scientist Szent-Gyorgi and structurally characterized by Haworth in 1933. In 1934, Reichstein worked out a simple, inexpensive, four-step process for synthesizing ascorbic acid from glucose. This method has been used for commercial synthesis of vitamin-C. Vitamin-C occurs naturally primarily in fresh fruits and vegetables.

Vitamin-C content of some foodstuffs

Vitamin-C (mg/100g)	Foods
100 – 350	Chili peppers, sweet peppers, parsley, and turnip greens
25 – 100	Citrus juices (oranges, lemons, etc.), tomato juice, mustard greens, spinach, brussels sprouts
10 – 25	Green beans and peas, sweet corn, asparagus, pineapple, cranberries, cucumbers, lettuce
< 10	Eggs, milk, carrots, beets, cooked meat

From Roberts, Hollenberg, and Postman, *General Chemistry in the Laboratory*.

THE PLAN

So here goes...

The starch indicator is readily biodegraded, so we will need a fresh solution of starch indicator at the start of each lab period.

We will make a standard solution of IO_3^- by weighing out a known amount of KIO_3 and dissolving it in a volumetric flask having a known volume to obtain the known molarity of the IO_3^- solution.

Then we will make a solution of sodium thiosulfate that is around 0.07 M. We need to buffer the pH of this solution so we will also add some Na_2CO_3 .

We will then take a known amount of IO_3^- and add a large (excess) amount of I^- to produce a known amount of triiodide (I_3^-) – note the 1:3 stoichiometry. We will titrate this known amount of triiodide with the sodium thiosulfate solution using the starch indicator (1:2 reaction). This will permit us to find the exact concentration of the sodium thiosulfate solution. With this known concentration, we can then determine the amount of triiodide in a sample.

Then (FINALLY!) we will dissolve some Vitamin C tablets. We will then add a known amount of the standard IO_3^- solution and an excess of I^- to produce a known total amount of triiodide. The Ascorbic Acid will react with **some** of the triiodide, resulting in a small amount of triiodide remaining in the sample. We will use the sodium thiosulfate solution and the starch indicator to determine the amount of triiodide remaining (1:2 reaction).

With the knowledge of how much triiodide we started with and the amount of triiodide remaining after reaction with all of the ascorbic acid (1:1), we can determine the amount of ascorbic acid contained in the tablets.

The following indicator will be used for the titration:

Starch solution

dark blue (complexed with iodine) → milky-white (uncomplexed)
end point is disappearance of dark blue

Procedure

The procedure for this experiment has been adapted from experiment 13 on the following website: www.whfreeman.com/qca, "Iodometric Titration of Vitamin C".

SAFETY NOTE

*The sulfuric acid used in this experiment **WILL CAUSE INJURY** if in contact with the skin. The proper use of laboratory **SAFETY GLASSES** and/or **SPLASH GOGGLES** and **GLOVES** will be expected and strictly monitored.*

Reagents

Starch Solution	Sodium Carbonate (Na_2CO_3)
0.5 M Sulfuric Acid (H_2SO_4)	0.3 M Sulfuric Acid (H_2SO_4)
Potassium Iodide (KI)	Potassium Iodate (KIO_3)
100 mg Vitamin C Tablets	
Sodium Thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	

Standardization of Sodium Thiosulfate Solution

Preparation of Starch Indicator

1. Clean and rinse a 100-mL beaker with DI water. Fill the beaker to the 100-mL mark and place on a hot plate until boiling.
2. Weigh out around 1 gram of soluble starch and slowly add to the beaker of boiling water with stirring. Continue boiling until the solution is clear.

Preparation of Sodium Thiosulfate Solution

3. Clean and rinse a 500-mL beaker with DI water. Fill the beaker to the 500-mL mark and place on a hot plate. Boil the water for 5 minutes to expel dissolved CO_2 gas. Allow solution to cool.
4. Weigh out around 0.05 g of Na_2CO_3 and place into the 500-mL beaker of boiled water.
5. Weigh out around 8.7 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and dissolve into the 500-mL beaker of boiled water buffered with Na_2CO_3 .
6. Clean and rinse a 1-L brown plastic bottle with DI water. Rinse the bottle with a small amount of the sodium thiosulfate solution. Transfer the remainder of the sodium thiosulfate solution to the brown plastic bottle. Label this bottle "Sodium Thiosulfate Solution" and keep this bottle tightly capped when not in use.

Preparation of Standard Iodate Solution

7. Clean and rinse a 500-mL volumetric flask with DI water. Fill the clean flask with around 400 mL of DI water.
8. Accurately weigh out around 1 gram of KIO_3 using the analytical electronic balance and record the mass to four decimal places.
9. Dissolve the KIO_3 into the DI water contained in the 500-mL volumetric flask. After all of the solid has dissolved, fill the volumetric flask to the mark with DI water. Using the following atomic masses, determine the exact molarity of this solution. K: 39.0983 I: 126.90447 O: 15.9994
10. Clean and rinse a 1-L white plastic bottle with DI water. Rinse the bottle with a small amount of standard KIO_3 solution. Transfer the remainder of the KIO_3 solution from the volumetric flask into the white plastic bottle. Label this bottle "Standard KIO_3 Solution".

Standardize the Sodium Thiosulfate Solution

11. Clean and rinse a 50-mL buret with DI water.
12. Rinse the 50-mL buret with a small amount of the Sodium Thiosulfate solution. Fill the buret with the Sodium Thiosulfate solution.
13. Clean and rinse a 250-mL flask with DI water.
14. Accurately pipet 50.00 mL of standard KIO_3 solution into the flask.
15. Weigh out around 2 grams of KI and place into the flask.
16. Add 10 mL of 0.5 M H_2SO_4 to the flask.
17. The solution should start out as a "red-ish" solution due to the presence of the triiodide. Titrate the solution with the Sodium Thiosulfate until the solution has lost most of the red-ish color (should be a pale yellow). At this point add 2 mL of the starch indicator (may turn smoky-blue or remain yellowish). Carefully add Sodium Thiosulfate until the solution turns colorless (may be a milky-white). Record this volume as the end point.

The indicator is not added until just before the end point as the triiodide/starch complex can "hold on to" the triiodide in concentrated solutions and prevent it from reacting with the Sodium Thiosulfate.

18. Repeat this titration (steps 13 – 17) two more times to obtain 3 good values for the volume of Sodium Thiosulfate required to titrate the sample of KIO_3 .
19. Using the known stoichiometry, calculate the molarity of the Sodium Thiosulfate solution.

Analysis of Vitamin C

React Triiodide with Ascorbic Acid

20. Clean and rinse a 250-mL flask with DI water.
21. Place 60 mL of 0.3 M H₂SO₄ into the clean flask.
22. Add 2 Vitamin C tablets to the flask and dissolve in the sulfuric acid. You can use a clean glass stirring rod to help break up the solid tablets. Some solid binding material may not dissolve.
23. Accurately pipet 50.00 mL of standard KIO₃ solution into the flask.
24. Weigh out around 2 grams of KI and place into the flask.
25. Gently swirl the flask for 1 minute to insure complete formation of the triiodide complex and complete reaction between the triiodide and the Vitamin C.

Titrate Solution with Sodium Thiosulfate

26. The solution should start out as a “red-ish” solution due to the presence of the triiodide. Titrate the solution with the Sodium Thiosulfate until the solution has lost most of the red-ish color (should be a pale yellow). At this point add 2 mL of the starch indicator (may turn smoky-blue or remain yellowish). Carefully add Sodium Thiosulfate until the solution turns colorless (may be a milky-white). Record this volume as the end point.

The indicator is not added until just before the end point as the triiodide/starch complex can “hold on to” the triiodide in concentrated solutions and prevent it from reacting with the Sodium Thiosulfate.

27. Repeat this titration (steps 20 – 26) two more times to obtain 3 good values for the volume of Sodium Thiosulfate required to titrate the remaining triiodide.

Q (90%)	Number of Observations
0.94	3
0.76	4
0.64	5

$$Q_{calc} = \frac{gap}{range}$$

Data Analysis

1. Use your buret calibration graph created in Experiment I to correct your final buret readings.
2. Using the formula weight of KIO_3 , calculate the molarity of your standard IO_3^- solution.
3. Using the known stoichiometry of the Sodium Thiosulfate/ IO_3^- reaction, calculate the molarity of your Sodium Thiosulfate solution. Calculate the average and standard deviation of the concentration.
4. Using the known stoichiometries of the Sodium Thiosulfate/ IO_3^- and Ascorbic Acid/ IO_3^- reactions, calculate the average number of moles of Ascorbic Acid contained in each Vitamin C tablet.
5. Using the formula weight of Vitamin C ($\text{C}_6\text{H}_8\text{O}_6$, FW = 176.13), calculate the average number of milligrams of Vitamin C contained in each tablet along with the standard deviation.

Report

Report the concentration of your standard IO_3^- solution.

Report the average concentration with both absolute error and % relative error of your standardized Sodium Thiosulfate solution.

Report the calculated average concentration with both absolute error and % percent relative error of the determined mass in milligrams of Vitamin C per tablet.

Include the manufacture's brand and label information from the bottle of Vitamin C tablets.

Question: Why is sulfuric acid used in the titrations?