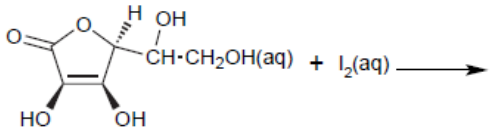
# Redox Titration of Vitamin C

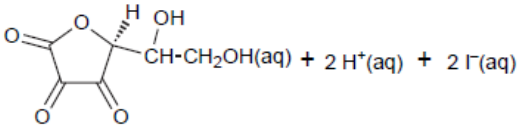
This is the first experiment that we'll do that comes a little closer to the real job of an analytical chemist. Chapter 1 in Harvey describes the process of analysis in a more comprehensive way than we usually do in this class – including things like selection of method, sampling, control of chemical form, elimination of interferences, and finally analysis including data workup. We will work with a "real world" sample here and incorporate the pre-treatment and sampling steps into the procedure. In many cases, the quality and reproducibility of the analyst's work during these procedures limits the accuracy and precision of the whole analysis, but this one works pretty well.

In this experiment, we will determine the amount of ascorbic acid (the active ingredient) in commercial vitamin C tablets. You may bring your own vitamin tablets from home if you wish, but be forewarned that the quality of the results can vary depending on the formulation (presence of binders and additives, etc.) Bring 2 tablets in case you run into problems.

Ascorbic acid (MW 176 g/mol) is a mild reducing agent that reacts rapidly with iodine (Reaction 1) or similarly with triiodide (producing three iodide anions). In this experiment, we will generate a known excess of $I_3^-$ by the reaction of a measured amount of iodate with excess iodide (Reactions 2 and 3), allow the reaction with ascorbic acid to proceed, and then back titrate the excess $I_3^-$ with thiosulfate (Reaction 4) using starch as an indicator for iodine/$I_3^-$.




Ascorbic acid ($C_6H_8O_6$)




Dehydroascorbic acid ($C_6H_6O_6$)

(Rxn 1)

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O \qquad \text{(Rxn 2)}$$

$$I_2 + I^- = I_3^- \qquad \text{(Rxn 3)}$$

$$I_3^- + 2S_2O_3^{2-} = 3\ I^- + S_4O_6^{2-} \qquad \text{(Rxn 4)}$$

Note the complex stoichiometry for the procedure: three iodine/triiodide ions are formed per iodate used, and each triiodide ion (or iodine) oxidizes one ascorbic acid, then the excess triiodide ion is determined by titration with a standardized sodium thiosulfate solution with a 1:2 stoichiometry. (Thiosulfate ion is a common reducing agent that in neutral or acidic solution is oxidized to the tetrathionate ion. Some of you may remember doing a similar procedure to determine hypochlorite in bleach in GenChem lab.) It may help to draw a diagram for yourself and/or write down what is being measured and the relationships between those species and the analyte.

## Apparatus

Hot plate, 400 mL beaker, Buret and stand, 250 mL volumetric flask, 25 mL volumetric pipet, mortar and pestle, 10 mL graduated cylinders, 250 mL Erlenmeyer flasks

## Solution Available

The starch indicator is prepared ahead of time for you via the following procedure:
(Make a paste of 5 g of soluble starch in 50 mL of DI water, dissolve in 500 mL of boiling water and boil until solution is clear.)
*You should need no more than 10 mL for all of the titrations. Fill a 10 mL graduated cylinder at the beginning of the lab and keep it at your station, being careful not to knock it over.

## Solutions to Prepare

1. Prepare 0.035 M $Na_2S_2O_3$

Dissolve 2.18 g of $Na_2S_2O_3 \cdot 5H_2O$ in 250 mL of freshly boiled (Note 1) DI water containing 0.02g of $Na_2CO_3$. Store this solution in a tightly capped brown bottle.

2. Prepare 0.01 M $KIO_3$

**Accurately** weigh (to 0.1 mg) 0.5 g of dried solid reagent $KIO_3$ and dissolve it in 250 mL of DI water (use your volumetric flask). Using the molar mass of $KIO_3$ (214.00 g/mol), calculate the molarity of this solution, which should be near 0.01 M.

## Standardize the thiosulfate solution

Pipet 25 mL of $KIO_3$ solution into a flask using your calibrated pipet. Add 1 g of solid KI and 5 mL of 0.5 M $H_2SO_4$. (Note 2) **Immediately** titrate with thiosulfate until the solution has lost almost all of its color (it turns a pale yellow). Then add about 1 mL of starch indicator and complete the titration (the dark solution will become colorless at the endpoint). Repeat the titration with two additional 25 mL aliquots of the $KIO_3$ solution. Calculate the average molarity (and the relative standard deviation) of thiosulfate and verify that it is near the nominal value given above.

## Analysis of Vitamin C Tablets

This procedure is designed for commercial vitamin C tablets containing 500 mg per tablet; it should be adjusted for more or less concentrated tablets or powders if you brought your own samples. You will perform the analysis in triplicate, using powdered portions of one crushed vitamin C tablet. You will report the mean and relative standard deviation for the number of milligrams of vitamin C *per tablet* so you will need to be able to scale your result up. (Note 3)

1. Obtain an accurate mass for one vitamin C tablet (or an amount of your own tablets or powder that roughly corresponds to 500 mg ascorbic acid). Crush the tablet (Note 4) and prepare three accurately weighed powder samples of about 0.1 g each in 250 mL Erlenmeyer flasks.

2. Use your calibrated pipet to add 25 mL of standard $KIO_3$ to **one** of the 250 mL flasks and swirl to dissolve the vitamin C powder (some solid binding material will probably be present and will not dissolve). Add 1 g of solid KI and 5 mL of 0.5 M $H_2SO_4$ and titrate immediately with standard thiosulfate as you did above. Add the 1 mL of starch indicator just before the end point (pale yellow color) and finish the titration to the starch endpoint. Repeat for the other two samples.

## REQUIRED MEASUREMENTS

Report the average and CV (a.k.a. percent RSD) for <u>both</u> the concentration of your thiosulfate solution <u>and</u> the number of mg Ascorbic acid per vitamin C tablet. If any of the trials appear odd, you can apply the Q test. Calculate the relative error from the nutritional information on the label.

**Sample Results Table**

| | Concentration | StDev | CV(%) |
|---|---|---|---|
| $Na_2S_2O_3$ | | | |
| Vc (mg) | | | |

## How the Q-test is applied

When you have a set of data, you sometimes encounter numbers that seem to be outliers, but you do not know that you made any errors. (On the other hand, if you went past the titration end point and you knew it, that number is not a valid member of the statistical sample.) The Q-test is a useful tool that helps you draw a conclusion that is more statistically and scientifically supportable about outliers.

The test is very simple and it is applied as follows:

(1) The N data values that compose the set of observations under examination are arranged in ascending order:

$$x_1 < x_2 < \ldots < x_N$$

(2) The statistic Q is then calculated. It is the ratio of the difference between the suspect value and its nearest neighbor divided by the *range* or *spread* of the values (Q refers to rejection *quotient*). For example, to test whether $x_1$ is a statistical outlier we use the following Q expression:

$$Q = \frac{Gap}{Range}$$

$$Q = \frac{X_2 - X_1}{X_N - X_1}$$

(3) The obtained Q statistic is then compared to a critical Q-value ($Q_{crit}$) found in tables (like the one in your textbook). This critical value is a function of the confidence level (CL) that is chosen (usually: CL=95%). If Q exceeds the critical value, it can be treated as an outlier.

## NOTES

(1) It takes a while to get the water boiling, try to get that going ASAP.

(2) Weigh out 6 one-gram portions of KI in advance. Exposure to air over time will lead to inaccurate results for the redox titration, so as soon as you add the KI and $H_2SO_4$, you should start the titration.

(3) To scale up from each trial to a whole tablet, you need to obtain the initial mass of the tablet before crushing, and the mass of each sample used. Then calculate the scale factor for each solid sample and multiply it by the Vc mass (in mg) from the relevant titration to obtain the mass result for that trial.

$$scale\ factor = \frac{mass\ of\ whole\ tablet}{mass\ of\ each\ trial}$$

(4) Folding the tablet in a piece of paper and using a solid object to crush it will usually produce an adequately fine powder. Try your best to pick a homogeneous part of the sample in order to avoid binding and coating materials that sometimes affect the results.