The Determination of Ascorbic Acid in Vitamin Tablets

INTRODUCTION

The ascorbic acid or vitamin C ($C_6H_8O_6$) content of vitamin tablets can be determined by a variety of techniques. This experiment will utilize a series of redox steps for analysis. Interesting oxidation/reduction chemistry can be studied along the way. A back titration will be necessary for the final step.

This experiment will require three standard solutions, KIO_3 (potassium iodate, a strong oxdizer), $KBrO_3$ (potassium bromate, a strong oxdizer), and $Na_2S_2O_3$ (sodium thiosulfate). The first two can be obtained as solids in pure forms that can be easily dried (without decomposition) and weighed and therefore make excellent primary standards. Sodium thiosulfate, however, is usually obtained in the pentahydrate form, $Na_2S_2O_3 \cdot 5H_2O$. The crystalline lumps are usually at least partially opaque due to significant losses of the waters of hydration which increase (but not quantitatively) with heating. Therefore, since the exact composition is not known, it cannot be used as a primary standard and must be titrated to determine the concentration.

Part I.

In the first part of the experiment, a standardized sodium thiosulfate solution is prepared using KIO_3 as the primary standard. A standard amount of KIO_3 is added to an excess of KI to generate the triiodide ion according to the reaction

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \qquad (1)$$

The I_3^- (often referred to as an iodine solution even though elemental I_2 is only very slightly soluble in water) is the major species when I_2 is in an aqueous solution of I^-.

$$I_2 + I^- \rightarrow I_3^- \qquad K = 720 \qquad (2)$$

The triiodide ion is a weak (and therefore selective) oxidizing agent

$$I_3^- + 2e^- \rightarrow 3I^- \qquad E° = +0.54V \qquad (3)$$

and can be used without an indicator if the concentration is high enough since the triiodide ion is deep red-brown at high concentrations and the iodide ion is colorless. In dilute solutions, however, the transition color becomes pale yellow to clear and is hard to detect. Starch and the triiodide ion make a deep blue colored complex, which can be used to enhance the endpoint detection (now the deep blue to colorless). BEWARE: starch decomposes quickly and MUST be prepared fresh daily. Check the preparation date on the stock bottle.

The amount of triiodide ion formed from reaction (1) is determinable if a known mass (and therefore moles) of the primary standard KIO_3 is reacted with excess I^- since this reaction goes quantitatively. The I_3^- produced can then be used to standardize a thiosulfate solution by the following equation:

$$I_3^- + 2Na_2S_2O_3 \rightarrow S_4O_6^{2-} + 3I^- + 4Na^+ \qquad E° = +0.46V \qquad (4)$$

This reaction is run in the presence of starch. Since both the thiosulfate and the tetrathionate ($S_4O_6^{2-}$) ions are colorless, the endpoint can be detected as the blue to colorless change due to the disappearance of the triiodide-starch complex. The triiodide-starch complex is very strong and therefore is slow to dissociate as the stoichiometric point nears. Therefore time must be allowed for its dissociation. The E° value is large enough to ensure quantitative results. NOTE: the blue color may reappear with time due to the air oxidation of the iodide ion.

Solutions of $Na_2S_2O_3$ are prepared from the solid and include a small amount of Na_2CO_3, which raises the solution *p*H to improve the stability and to precipitate out any trace amounts of copper(II) that might be present since this ion acts as a catalyst in the decomposition of thiosulfate ion. It is also a good idea to store the solution in the dark to slow its decomposition. Unlike most standard acids and bases, solutions of $Na_2S_2O_3$ have a limited shelf life.

NOTE: The stoichiometry for the calculations must involve a combination of that from (1) and (4) with KIO_3 as the limiting reagent.

Part II.

Now that the $Na_2S_2O_3$ has been standardized, it can be used to determine the vitamin C content of vitamin tablets. First the tablets must be crushed and the mass determined. Often binders are present and remain suspended but do not affect the results. In some tablets, the binder may be starch so that the characteristic color of the complex with $\mathbf{I}_3^-$ may be seen early in the analysis, but this will not affect the results.

An excess of Br^- is added to the tablets and reacted with primary standard $KBrO_3$. The product, Br_2, in turn reacts with vitamin C to oxidize it.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (5)$$

$$Br_2 + (VitC)_{reduced} \rightarrow (VitC)_{oxidized} + 2Br^- + 2H^+ \qquad (6)$$

An excess of BrO_3^- is added so that all of the vitamin C reacts and a quantitative excess of Br_2 remains. This amount must now be determined.

Excess KI is added to this to form the triiodide ion

$$Br_2 + 3I^- \rightarrow 2Br^- + I_3^- \qquad (7)$$

which is titrated with the thiosulfate from Part I above.

$$I_3^- + 2Na_2S_2O_3 \rightarrow S_4O_6^{2-} + 3I^- + 4Na^+ \qquad (8)$$

The endpoint is visually seen as the disappearance of the blue triiodide-starch complex color.

This experimental procedure assumes that the unknown samples will contain about 100 mg of vitamin C. This is the approximate contents of 1 cup (250 mL) of orange juice, 1 cup of broccoli (extracted), one multiple vitamin (beware of other species in a multiple vitamin mix that might interfere with the analysis), or one 100 mg vitamin C tablet. The current RDA value for vitamin C is 60 mg.

EXPERIMENTAL

Part I.

1. Preparation of 0.1 M $Na_2S_2O_3$. Boil 150-mL of water for 15 minutes and allow it to cool to room temperature. To this water, add an appropriate amount of $Na_2S_2O_3 \cdot 5H_2O$ and 0.20 g of Na_2CO_3 and stir well. Transfer to a 250-mL bottle and store in the dark. Do not let excess light to reach the solution.

2. Preparation of 100-mL 0.01 M KIO_3. Estimate the amount of KIO_3(s) that is needed for this experiment. Transfer this amount into a small glass bottle without contaminating the compound (i.e., do not put your spatula in the reagent bottle or return any unused solid to the bottle. Also, make certain to leave the lid on as much as possible so it does not absorb water). Dry this compound for 1 hour at 110°C. Measure to the nearest 0.1 mg of an appropriate amount of the cooled KIO_3(s) and transfer quantitatively to a volumetric flask (what size?). Dissolve and dilute to the mark. Calculate the molarity of KIO_3(aq). WARNING: KIO_3(s) is a strong oxidizer and can cause fires if allowed extended contact with oxidizable materials such as wood or paper towels. When disposing of excess solid, place it in a large container. Add water and save to collect with the rest of your waste from this experiment.

3. Indicator. The starch solution was prepared for you by dissolving 1 gram of soluble starch in 15-mL of water to make a paste. It was diluted to 500-mL with boiling water and heated until clear. A pinch of HgI_2 (TOXIC) was added to keep bugs from growing. Keep the bottle tightly stoppered.

4. Standardization of Sodium Thiosulfate Solution. Pipet 25-mL of the standard iodate solution into a 125-mL Erlenmeyer flask. Add 1 gram of iodate-free KI and swirl to dissolve. Add 1-mL of 6 M HCl and titrate immediately with the thiosulfate solution until the red-brown color fades to a pale yellow color (this occurs just prior to the stoichiometric point). Add 5-mL of starch solution (it must turn blue now or you added too much thiosulfate) and titrate slowly until the blue color just disappears. Relate these steps to some of the reactions mentioned above

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$$
$$I_3^- + 2Na_2S_2O_3 \rightarrow S_4O_6^{2-} + 3I^- + 4Na^+$$

plus the fact that

I_3^- is red-brown at high concentration and pale yellow at low concentration.

$I_3^- + \text{starch} \rightarrow \text{Blue complex}$

$S_4O_6^{2-}$ and I^- are colorless

5. Repeat the standardization two more times. Process each sample completely before beginning the next one. This is to minimize air oxidation of the iodide ion.

6. Calculate the concentration of the $Na_2S_2O_3$ solution.

7. Waste Treatment. Collect all waste solutions in the hazardous waste container provided.

Part II.

1. Preparation of 100-mL 0.009 M $KBrO_3$(s). Without contaminating the reagent grade $KBrO_3$(s), transfer an appropriate amount of this compound into a small glass bottle. Dry it for an hour at 110°C. Measure the appropriate amount to 0.1 mg of the cooled $KBrO_3$(s) and transfer quantitatively to a volumetric flask (what size?). Dissolve and dilute to the mark. Calculate the molarity of this solution. WARNING: Solid $KBrO_3$ can cause fire if it comes in contact with damp organic materials, such as paper towels. When disposing of excess solid, place it in a large container. Add water and save to collect with the rest of your waste from this experiment. Check with your TA if you have any questions and always notify your TA if there is a spill.

2. Preparation of Sample for Analysis. Obtain a vitamin tablet and record its mass and the nominal mass of vitamin C on the label. Pulverize the tablet in a clean mortar and use the resulting powder that is equivalent to a nominal mass of 100-mg for this experiment. Weigh and record the mass of your sample carefully. Wash the mortar and leave it to dry in the balance room.

Quantitatively transfer the weighed pulverized powder sample to a 100-mL volumetric flask. Add a spatula-tip full of solid EDTA disodium salt (Na_2-EDTA). This is used to tie up traces of Cu^{2+} that may be present in the solution. Cu^{2+} can catalyze the decomposition of vitamin C. Dilute to the mark with 1.5 M H_2SO_4.

3. Do the following process completely for each sample before proceeding to the next one.

3a. Proceed with a 25-mL aliquot of the sample solution. Add 2.5 g KBr (this amount is excess and need not be exact) and immediately add 25-mL of the standard $KBrO_3$. A faint (but definite) yellow color must be seen (due to excess Br_2). If not, add more (a known amount, of course) of $KBrO_3$ until yellow.

3b. Add 1.5 g of KI (not critical and need not be exact) and 5-mL of starch solution and back titrate with the standard thiosulfate solution slowly and carefully.

3c. Repeat Steps 3a and 3b with your second sample and then with your third.

4. Calculate the mass, in mg, of ascorbic acid per tablet.

5. Waste Treatment. Collect all waste solutions in the hazardous waste container provided.

Have you

1. **wipe down all benchtops, including the sink, hood, and balance areas?**
2. **return all stock chemicals to their proper locations?**
3. **return all equipment to your drawer or general supply area?**
4. **lock your desk drawer?**