Experiment A4: Iodometric Titration

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Full title: Determination of vitamin C content in commercial vitamin C tablets.

Demonstrator:

Group: 7

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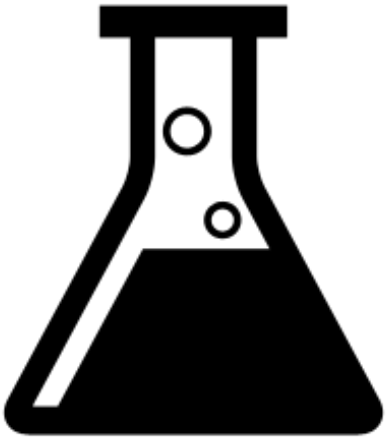

Aims

1. Standardization of a thiosulphate solution ($\approx 0.007M$) by:
   (a) Titration with KIO_3 standard solution with added KI, using a starch indicator.
2. Determination of mass of Vitamin C (Ascorbic acid) in commercial vitamin C tablets, using the KIO_3 standard in a redox titration with the tablet dissolved in sulfuric acid solution.

Introduction

Ascorbic acid commonly known as Vitamin C, is an important dietary component which helps to protect against cancer cardiac disease and scurvy, however as modern diets may be lacking in sufficient natural sources of Vitamin C such as fresh fruit and vegetables, commercially available vitamin C supplements are often taken. (Carr *et al*, 1999). As Ascorbic acid can act as a reducing agent, and all non-trace components of the supplement tablets are chemically inactive substances such as cellulose (Descombes and Hanck,1993), the amount of ascorbic acid present in a given commercial sample can be readily assessed by means of a redox titration.

There are several different redox systems available but iodometric titrations are often favored as the provide a fast accurate and low cost, (both in terms of materials used and equipment required) determination method, (Verdini and Lagier, 2000). In the case of an reducing analyte as ascorbic acid there are two possible determination paths. Firstly analyte may be directly titrated with standard I_2 solution.Secondly known excess KIO_3 may first be reduced and combined with I^- in strong acid to generate I_2. The I_2 generated may then be reacted *in situ* with the analyte sample, and the excess I_2 back titrated against a standard solution of a suitable reducing agent such as thiosulphate solution, (Ciesielski and Zakrzweski, 2006).The molar amount of I_2 reduced by Ascorbic acid in the sample,and hence the mass of ascorbic acid can then be inferred. In this case the reactions involved are as follows (Silva, 1999):

1. The formation of I_2 from excess KIO_3 and KI.
   $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$
2. The reduction of I_2 by ascorbic acid
   $C_6H_8O_6 + I_2 + H_2O \rightarrow 2I^- \rightarrow C_6H_8O_7 + 2I^- + 2H^+$
3. The reduction of I_2 by thiosulphate in the back titration step.
   $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + [O_3S - S - S - SO_3]^{2-}$

In the back titration I_2 combines with I^- ions to give an stable I_3^- complex, $(I_2 + I^- \rightarrow I_3)$ which leads to a dark brown color fading to a pale yellow as its concentration is reduced in the titration. Near the end of the back titration addition of a starch indicator leads to the formation of an intense blue-black starch I_3- complex. The final conversion of this dark blue solution to a clear solution as all the available I_2 is reacted marks the end point of the titration (Rundle and Edwards, 1943).

In this experiment standardization of the Thiosulphate solution was required. This standardization proceeded along the same principles outlined above, by back titration with thiosulphate solution, of I_2 formed by reaction of known quantities of $KIO_3(aq)$ and $KI(s)$ ion excess acid. (Schroeder, 1950). The concentration of the standard solution may then be inferred.

Experimental Procedure

See second year analytic laboratory manual, pages 32-33 for full procedure. The following changes were made to the procedure:

1. Distilled water was used in place of deionised water in the preparation of the KIO_3 standard
2. The Vitamin C tables used were first crushed in filter paper before solvation.

Results

Experimental Data

1) Standardisation of ≈ 0.07M NaS_2O_3 solution using KIO_3

Mass of KIO_3 used to prepare the standard solution= 1.4564

a) KI used in standardisation

Table 1: Masses of KI used for standardisation of Thiosulphate solution using starch indicator

Analysis Number	1	2	3
Weighing bottle+KI powder/g	11.4956	11.5495	10.1493
Weighing bottle+residue/g	9.5070	9.5740	7.9490
Mass of KI used/g	1.9886	1.9755	2.2003

b) Standardisation using starch indicator

Table 2: Volumes of thiosulphate solution titrated in the standardisation of the thiosulphate solution

Titration Number	1	2	3
Final Reading/ml	0.19	0.02	0.21
Initial Reading/ml	30.76	29.77	29.80
Volume of Thiosulphate solution delivered/ml	30.57	29.75	29.59

2) Analysis of commerical Vitamen C tablets using thiosulphate standard solution.

a) KI used in Analysis

Table 3: Masses of KI used in the titration of dissolved vitamen C tablets with standardised thiosulphate, using a starch indicator

Analysis Number	1	2	3
Weighing bottle+KI powder/g	11.5200	11.5820	9.949
Weighing bottle+residue/g	9.5106	9.5734	7.898
Mass of KI used/g	2.0094	2.0086	2.051

a) Vitamen C tablets analysed

Table 4: Masses of Vitamen C tablets analysed

Tablet	1	2	3	4
Weighing bottle+Tablet/g	8.4615	8.4415	10.2272	0.9005
Weighing bottle+Residue/g	8.1707	8.1691	9.9443	0.6031
Mass of Tablet/g	0.2908	0.2724	0.2829	0.2974

c) Titration with Thiosulphate standard using starch indicator.

Table 5: Volumes of standardised thiosulphate solution titrated in the reduction of each dissolved vitamen C tablet.

Titration Number	1	2	3	4
Final Reading/ml	0.3	0.11	0.21	0.02
Initial Reading/ml	25.8	21.13	21.40	21.29
Volume of Thiosulphate solution delivered/ml	25.5	21.02	21.19	21.27

Calculations

Molarity of KIO_3 solution prepared

Mass of KIO_3 used = 1.4564g
Volume of final solution $500.0ml = 0.5000L$ Molecular mass of KIO_3=$214.001g \cdot mol^{-1}$

$c = \frac{m}{vM} = \frac{1.4564g}{(0.5000L)(214.001)g \cdot mol^{-1}} = 0.01361mol \cdot L^{-1}$

Molarity of standardised $Na_2S_2O_3$ solution

Inital reaction:

$IO_3 + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Moles of I_2 produced=$3 \cdot$ Moles of KIO_3^- used $= 3 \cdot 0.01361mol \cdot L^{-1} \cdot 0.025L = 0.0010208mol$

Back Titration

Reaction:
$I_2 + 2S_2O_3^{2-} \rightleftharpoons 2I^- + [O_3S - S - S - SO_3]^{2-}$

Titration 1

Concentration of $N_2S_2O_3$ solution $= \frac{\text{Moles of } 2S_2O_3^{2-}}{\text{Volume}} = \frac{2 \cdot \text{Moles of } I_2}{\text{Volume}} = \frac{0.0010208mol}{0.03057L} = 0.06678mol \cdot L^{-1}$

Titration 2

Concentration of $N_2S_2O_3$ solution $= \frac{\text{Moles of } 2S_2O_3^{2-}}{\text{Volume}} = \frac{2 \cdot \text{Moles of } I_2}{\text{Volume}} = \frac{0.0010208mol}{0.02975L} = 0.06862mol \cdot L^{-1}$

Titration 3

Concentration of $N_2S_2O_3$ solution $= \frac{\text{Moles of } 2S_2O_3^{2-}}{\text{Volume}} = \frac{2 \cdot \text{Moles of } I_2}{\text{Volume}} = \frac{0.0010208mol}{0.02959L} = 0.06899mol \cdot L^{-1}$

Average concentration

Titration one is not included as it was a rough titration only:

Average concentration of $N_2S_2O_3$ solution=$0.068805\, mol \cdot L^{-1}$

Relative standard error

$RDS = \frac{s}{\bar{x}} \cdot 100\% = \frac{2.616 \times 10^{-4}}{0.068805} \cdot 100\% = 0.3802\%$

Ascorbic Acid Present in commercial Vitamen C tablet

Inital reaction:

$IO_3 + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Moles of I_2 produced=$3 \cdot$ Moles of KIO_3^- used $= 3 \cdot 0.01361 mol \cdot L^{-1} \cdot 0.025 L = 0.0010208 mol$

First Tablet

Moles of I_2 Reduced by thiosulphate during titration=(Volume of $S_2O_3^{2-}$ titrated) $\cdot$ (Concentration of $S_2O_3^{2-}$ solution) $\cdot \frac{1}{2}$=8.773×10^{-4}

Moles of I_2 Reduced by Ascorbic acid in tablet=1.4349×10^{-4}

Reaction of ascorbic acid with iodine

1 Ascorbic Acid + $I_2 \rightarrow$ Dehydroascorbic acid + $2I^- + 2H^+$

Mass of Ascorbic acid Present= Moles of I_2 reduced $\cdot$ Molecular mass of Ascorbic acid=$0.02527 g$=$25.27 mg$

Percentage Ascorbic acid=$\frac{\text{mass of Ascorbic Acid}}{Massoftablet}$=$\frac{0.0253 g}{0.2908 g} \cdot 100\% = 8.69\%$

Second Tablet

Moles of I_2 Reduced by thiosulphate during titration=(Volume of $S_2O_3^{2-}$ titrated) $\cdot$ (Concentration of $S_2O_3^{2-}$ solution) $\cdot \frac{1}{2}$=7.231×10^{-4}

Moles of I_2 Reduced by Ascorbic acid in tablet=2.9761×10^{-4}

Reaction of ascorbic acid with iodine

1 Ascorbic Acid + $I_2 \rightarrow$ Dehydroascorbic acid + $2I^- + 2H^+$

Mass of Ascorbic acid Present= Moles of I_2 reduced $\cdot$ Molecular mass of Ascorbic acid=$0.05242 g$=$52.42 mg$

Percentage Ascorbic acid=$\frac{\text{mass of Ascorbic Acid}}{Massoftablet}$=$\frac{0.0524 g}{0.2724 g} \cdot 100\% = 8.69, 19.242\%$

Third Tablet

Moles of I_2 Reduced by thiosulphate during titration=(Volume of $S_2O_3^{2-}$ titrated) $\cdot$ (Concentration of $S_2O_3^{2-}$ solution) $\cdot \frac{1}{2}$=7.29×10^{-4}

Moles of I_2 Reduced by Ascorbic acid in tablet=2.9761×10^{-4}

Reaction of ascorbic acid with iodine

1 Ascorbic Acid + $I_2 \rightarrow$ Dehydroascorbic acid + $2I^- + 2H^+$

Mass of Ascorbic acid Present= Moles of I_2 reduced $\cdot$ Molecular mass of Ascorbic acid=$0.05139 g$=$51.39 mg$

Percentage Ascorbic acid=$\frac{\text{mass of Ascorbic Acid}}{Massoftablet}$=$\frac{0.0514 g}{0.2829 g} \cdot 100\% = 8.69, 19.242, 18.164\%$

Fourth Tablet

Moles of I_2 Reduced by thiosulphate during titration=(Volume of $S_2O_3^{2-}$ titrated) $\cdot$ (Concentration of $S_2O_3^{2-}$ solution) $\cdot\frac{1}{2}$=7.317×10^{-4}

Moles of I_2 Reduced by Ascorbic acid in tablet=2.9761×10^{-4}

Reaction of ascorbic acid with iodine

1 Ascorbic Acid + $I_2 \rightarrow$ Dehydroascorbic acid + $2I^- + 2H^+$

Mass of Ascorbic acid Present= Moles of I_2 reduced $\cdot$ Molecular mass of Ascorbic acid=$0.0509g$=$50.9mg$

Percentage Ascorbic acid=$\frac{\text{mass of Ascorbic Acid}}{Massoftablet}$=$\frac{0.0509g}{0.2974g} \cdot 100\% = 8.69, 19.242, 18.164, 17.115\%$

Average Mass

Titration 1 was excluded as a rough titration.

Average Mass of ascorbic acid per tablet=$51.57mg$

Relative standard error

$RDS = \frac{s}{\bar{x}} \cdot 100\% = \frac{7.736\times10^{-4}}{0.0515679} \cdot 100\% = 1.5\%$

Average Percentage

Titration 1 was excluded as a rough titration.

Average Percentage of ascorbic acid in vitamin C tablets=18.17%

Relative standard error

$RDS = \frac{s}{\bar{x}} \cdot 100\% = \frac{1.0634785}{18.1739579} \cdot 100\% = 5.852\%$

Discussion

In the standardization of Thiosulphate solution the relative standard error achieved in the two accurate titrations performed was less that 0.5% suggesting a reasonably high level of precision for the average concentration of the thiosulphate solution calculated, $0.068805\,mol \cdot L^{-1}$. However this value differs considerably from the $\approx 0.07M$ concentration expected from $8.68 \pm 0.02g$ of $Na_2S_2O_3.5H_2O$ used in the preparation of the standard. This difference is perhaps best accounted for by inaccuracies in the level of hydration of the thiosulphate salt, as partial dehydrating could explain the unusually high morality of the standard produced.

In the actual analysis of the commercial Vitamin C tablets, the relative standard error, excluding the first rough titration was also relatively low, below 2%, again suggesting a reasonable level of precision. The first rough titration, although not included in any calculations differed so seriously from the subsequent titrations as to suggest some serious flaw occurred in the experimental procedure, such as perhaps loss of powdered vitamin C tablet through tares developed in filter paper during crushing process. This error may be avoided by using a double layer of filter paper in the crushing. There is also a considerably larger relative standard error in the percentage vitamin C calculated. although this high error could be taken as an indication of inaccuracy it may be more likely that it is as a result of variance in the weight of tablets related to different amounts of cellulose substrate in each tablet, as the production process may well involve precise addition of the active component to each tablet will far less precise addition of the general substrate of the tablets.

The accuracy of the Vitamin C content determined appears highly dubious as the average mass of vitamin C calculated $5.1567892 \times 10^{-5} mg$ differs by almost 80% from the true value. The high precision and low accuracy are indicative of a serious systematic error in either the experimental procedure or in the standard solution used. One potential source of error might be the distilled water used in preparation of standards. If this water was contaminated by mineral ions such as Fe^{3+}, at some point after the distillation process these ions may well have engaged in redox reactions with the I^- in the iodometric system resulting in inaccurately low measures for the Ascorbic acid content of the commercial samples. Carbonate ions resulting from solvation of atmospheric CO_2 into the KIO_3 standard solution could also potentially have reduced I^- ions present lower the calculated Ascorbic acid content.

In conclusion, the standard solution prepared was of higher than expected concentration, perhaps due to dehydration of thiosulphate salt used in preparation, but was still standardized with a relatively high precision. The determination of Ascorbic acid was also achieved with relatively high precision, however only low overall accuracy was achieved, with the average calculated mass of ascorbic acid per tablet $5.1567892 \times 10^{-5} mg$ far lower than the true value of 250mg. This inaccuracy must have resulted from a serious systematic error in the determination perhaps due to interference in the redox system by atmospheric of other electrically active contaminants.

References

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Questions

The satrch indicator is only added to the solution close to the end of the titration why?

The starch Iodine inclusion complex is relatively stable, so at high I_2 concentrations its dissociation to provide I_2 for the continued redox reaction occurring during the process of the titration is relatively slow. This slow

speed of release may well lead to a positive error in the titration volume due to a delay in the color change as despite sufficient reducing agent already present in the solution, not all starch iodine complex molecules are dissociated and their associated deep blue color remains. In order to perform a time effective and accurate titration addition of starch indicator should be left until very near the end point of titration at which point low I_2 concentrations in solution can act to drive the dissociation of the inclusion complex.

Why is sodium carbonate added to the sodium thiosulphate solution.

Under acidic conditions thiosulphate is unstable and can undergo a decomposition reaction as follows:
$S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$

The addition of Na_2CO_3 acts to increase the alkalinity of the standard solution as $Na(aq)$ forms a strong base $NaOH$ where as CO_3 form a weak acid H_2CO_3. This increased alkalinity reduces the H^+ concentration pulling the above equilibrium to the left and stabilizing the $S_2O_3^{2-}$ concentration in the standard solution.