

Application Note

2006

Distillation Unit K-355

SO₂ Determination in Dried Apricots



1 Introduction

SO₂ determination in dried fruits is done by steam distillation, followed by redox titration. Therefore, the distilled SO₂ is collected in an iodine solution and the excess of iodine is titrated back with a standardized sodium thiosulfate solution. The described method shows comparable results to the Monier-Williams method [1,2].

2 Instruments

- Distillation Unit K-355¹ with SO₂ absorption glass (order number 043070)
- Metrohm DMP 785 Titrino²
- Metrohm Pt-Titrode 6.0431.1002²
- Pipettes 1-5 mL / 0.1-1.0 mL
- Beaker 400 mL
- Analytical balance

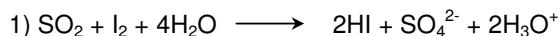


3 Chemicals

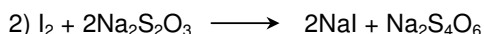
- Sodium thiosulfate 0.1 mol/L Titrisol Na₂S₂O₃, Merck 1.09950
- Sodium thiosulfate 0.01 mol/L; dilute 100 mL sodium thiosulfate solution 0.1 mol/L to 1L with deionized water.
- Hydrochloric acid 25%, Merck 100316
- Iodine-solution 0.05 mol/L, Fluka 35090
- Sulfur dioxide solution 4.5-5.5%, Fluka 00668
- Sulfur dioxide solution approx. 5 mg SO₂/mL; dilute 100 mL sulfur dioxide solution (4.5-5.5%) to 1 L with deionized water.³
- Sulfuric acid 0.5 mol/L, Fluka 35354

4 Reaction

Reaction of SO₂ with iodine solution:



Titration of iodine excess with sodium thiosulfate:



¹ This application can also be performed with all other Büchi Distillation Units.

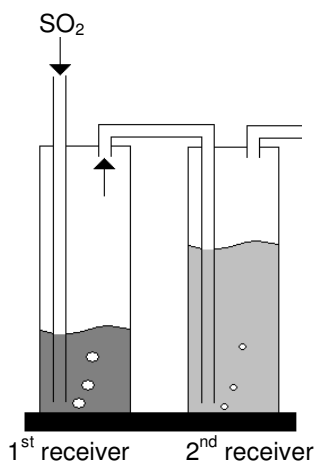
² This application can also be performed with other titrators/electrodes, or manually.

³ The exact concentration of the sulfur dioxide standard solution is determined by titration with a standardized iodine solution.

5 Procedure

5.1 Instrument Settings

| | |
|-----------------------------------|--|
| Sample weight | 4 - 5 g |
| Steam power | 90% |
| Distillation time | 4 - 4.5 min |
| SO ₂ absorption glass: | |
| - 1 st receiver | - 30 mL dest. water - 4 mL iodine solution 0.05 mol/L |
| - 2 nd receiver | - 50 mL dest. water - 1 mL iodine solution 0.05 mol/L |



5.2 Distillation

1. Preheat the K-355 for 5 minutes.
2. Place sample into distillation tube.
3. Place approximately 30 mL of water in the first receiver vessel and 50 mL in the second receiver vessel.
4. Add 4 mL of iodine solution to the first receiver vessel and 1 mL to the second receiver vessel.
5. Add 50 mL hydrochlorid acid 25% to the distillation tube.
6. Start distillation.

5.3 Titration

After distillation, pour the two receiver solutions in a 400 mL beaker. Acidify with 2 mL sulfuric acid 0.5 mol/L. The excess of iodine in the receiver is titrated with standardized sodium thiosulfate 0.01 mol/L.

The redox titrations are carried out with a Metrohm DMP 785 Titrino unit: User Methode: Iodine

A blank titration was performed before each batch of samples.

6 Calculation

Amount of substance in the sample:

$$n(\text{SO}_2)_{\text{sample}} = V(\text{I}_2)_{\text{total;sample}} \cdot c(\text{I}_2) - \frac{V(\text{Na}_2\text{S}_2\text{O}_3)_{\text{sample}} \cdot c(\text{Na}_2\text{S}_2\text{O}_3)}{z^*} \quad [\text{mol}]$$

Amount of substance in the blank:

$$n(\text{SO}_2)_{\text{blank}} = V(\text{I}_2)_{\text{total;blank}} \cdot c(\text{I}_2) - \frac{V(\text{Na}_2\text{S}_2\text{O}_3)_{\text{blank}} \cdot c(\text{Na}_2\text{S}_2\text{O}_3)}{z^*} \quad [\text{mol}]$$

Amount of substance sample effective (sample-blank):

$$n(\text{SO}_2)_{\text{eff}} = n(\text{SO}_2)_{\text{sample}} - n(\text{SO}_2)_{\text{blank}} \quad [\text{mol}]$$

Concentration of SO₂ in the sample g/g:

$$w(\text{SO}_2)_{\text{sample}} = \frac{n(\text{SO}_2)_{\text{eff}} \cdot M(\text{SO}_2)}{m_{\text{sample}}} \quad [\text{g/g}]$$



Legend:

| Symbol | Text | Unit | Example |
|--|---|-------|---|
| $n(\text{SO}_2)_{\text{sample}}$ | Amount of substance of SO ₂ in the sample | mol | |
| $V(\text{I}_2)_{\text{total;sample}}$ | Volume iodine solution in sample determination | L | 0.005 L |
| $c(\text{I}_2)$ | Concentration of iodine solution | mol/L | 0.05 mol/L |
| $V(\text{Na}_2\text{S}_2\text{O}_3)_{\text{sample}}$ | Volume sodium thiosulfate solution | L | |
| $c(\text{Na}_2\text{S}_2\text{O}_3)$ | Concentration of sodium thiosulfate solution | mol/L | 0.01 mol/L |
| z^* | Valency of reaction | - | 2 2 Na ₂ S ₂ O ₃ = 1 I ₂ |
| $n(\text{SO}_2)_{\text{blank}}$ | Amount of substance of SO ₂ in the blank determination | mol | |
| $V(\text{I}_2)_{\text{total;blank}}$ | Volume iodine solution in blank determination | L | 0.005 L |
| $V(\text{Na}_2\text{S}_2\text{O}_3)_{\text{blank}}$ | Volume sodium thiosulfate solution in blank determination | L | |
| $n(\text{SO}_2)_{\text{eff}}$ | Amount of substance of SO ₂ effective | mol | |
| $M(\text{SO}_2)$ | Relative molar mass of SO ₂ | g/mol | 64.06 g/mol |
| m_{sample} | Weight of sample used for analysis | g | |
| $w(\text{SO}_2)_{\text{sample}}$ | Mass concentration of SO ₂ in the sample in g/g | g/g | |

7 Verification

For verification, the determinations were carried out with commercial samples.

7.1 Results

According to preliminary testing the blank was 0.6 mg SO₂ (RSD 3.3%, n=3).

| | Sample ⁴ | Spiked Samples | |
|-----------------------------|--------------------------|--|--|
| | [mg SO ₂ /kg] | Spike included [mg SO ₂ /kg] | Spike subtracted [mg SO ₂ /kg] |
| Dried apricots ⁵ | 1602 | 2009 | 1608 |
| | 1604 | 2028 | 1672 |
| | 1679 | 2032 | 1633 |
| Mean value | 1628 | | 1638 |
| RSD [%] | 2.7 | | 1.9 |

The samples were spiked with 0.5 ml of a sulfur dioxide solution containing 3.5 mg SO₂/mL).

7.2 Summary

The results of a threefold determination of the SO₂-content of dried apricots gives a mean value of 1628 mg SO₂/kg with a small RSD of 2.7%. Using spiked samples the same amount of SO₂ can be found after subtraction of the spike (mean value: 1638 mg SO₂/kg, RSD 1.9%).

8 Comparison to the standard methods

There are at least 11 different methods for sulfite determination described in the *Official Methods of Analysis of AOAC International, 16th Edition*. All of the methods introduced since 1987, as well as AOAC Methods 892.02 and 962.16, take advantage of the fact that the addition of water and strong mineral acids to the food will cause all of the various forms of sulfite to be converted to sulfur dioxide. Afterwards the sulfur dioxide can be conveniently removed from the bulk of the food components, captured in a solution and analyzed by variety of means.

The U.S. Food and Drug Administration (FDA) has established that the Optimized Monier-Williams method (AOAC 990.28) will be used for official samples.

As for the Optimized Monier-Williams method the sample is heated in this application with refluxing HCl to convert sulfite to sulfur dioxide. Instead of a N₂-stream (Optimized Monier-Williams method) the air inside the distillation unit is dispersed by a water steam stream. In the absorption glass (SO₂-receiver) the sulfur dioxide is finally titrated with an iodine-iodate solution according to the "Ripper" method (AOAC 892.02).

⁴ The dried apricots are cut in small pieces.

⁵ Average values in the literature show 1500-2000 mg SO₂/kg. In Switzerland and the European Union (directive 95/2/EG) the low allows to add up to 2000 mg SO₂/kg.

9 References

- Manuals
 - Büchi Distillation Unit K-355
 - Metrohm DMP 785 Titrino
- Standard Methods
 - AOAC 990.28
 - AOAC 892.02
- Literature
 - [1] Monier-Williams method. Official Methods of Analysis (1984) n. 20.123 and n.20.124 A.O.A.C. Association of Official Analytical Chemists. Arlington. VA. U.S.A.
 - [2] De Vries J.W., H. Ge, F.J. Ebert, J.M. Magnuson, M.K. Ogawa, J. A.O.A.C. 69:827-80 (1986).



Replaces the official Büchi Application No. K-355-002, Version A.

BÜCHI Labortechnik AG
CH-9230 Flawil 1/Switzerland
T +41 71 394 63 63
F +41 71 394 65 65

www.buchi.com

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