SULPHUR DIOXIDE IN FOOD

1. Introduction

VAPODEST speeds up significantly the stripping of sulphur dioxide in comparison to the classical method. There are several methods to be used for the detection of sulphur dioxide. The acidimetric determination is done by using hydrogen peroxide in the receiver, sulphur dioxide undergoes oxidation to sulphuric acid which is titrated with a lye. When using the iodometric determination a iod solution is used, which is then titrated back with sodium thiosulphate solution.

The selection of the method to be used depends very much on the matrix to be examined. Samples with other water steam volatile contents for example with volatile acids should be tested using the iod metric method. In this case there is no risk, that acid like substances are detected with lye.

This application document consists of two parts:
A. Procedure for the acidimetric determination of the sulphur dioxide content
B. Procedure for the iodometric determination of the sulphur dioxide content

A. Acidimetric Method

A.1. Principle

SO_2 is stripped using phosphoric acid and water steam, received in a hydrogen peroxide solution (6 %) and then, determined titrimetrically.

A.2. Area of Usage

Food, preferably without volatile acids

A.3. Chemicals

A.3.1. Phosphoric acid w = 60 %
A.3.2. Peroxide/Indicator solution w = 6 %:
200 ml Aquadest, 50 ml hydrogen peroxide w = 30 % ; 2.5 ml methyl orange indicator solution (alternatively bromocresol blue or bromocresol pink) in 0.1 % alcoholic solution.
The pH-value should be between 3.3 und 3.4.
A.3.3. $Na_2S_2O_5$ sodium disulphate p. a. (standard solution)
A.3.4. Sodium hydroxide solution c_{NaOH} = 0.1 mol/l or 0.01 mol/l depending on the content range of the sample

A.4. Instruments

A.4.1. VAP 20s - 45s, acid resistant, with titrator for endpoint titration
A.4.2. Erlenmeyer flask, wide neck opening 300 ml

A.5. Analysis

A.5.1. Sample Preparation

The sample weight depends on the matrix to be determined. The comminuted and homogenized sample is weighed into a Kjeldahl flask; solid samples are covered with 100 ml Aquadest.
Depending on the used model, the following program parameters are recommended for operating the VAPODEST. These are only meant to serve as guide lines for the analysis and might have to be adapted to other requirements.

A.5.2. Programming of VAPODEST

	VAP 20s	VAP 30s	VAP 45s
H_2O Addition	-	0 s	0 s
NaOH (phosphoric acid) Addition	20 ml	20 ml	20 ml
Reaction Time	0 s	0 s	0 s
Distillation Time	360 s	360 s	360 s
Steam Power	100 %	100 %	100 %
Suction Sample	manual	30 s	30 s

A.5.3. Distillation

Use the VAPODEST following the instruction manual. As a start run a blank distillation in order to heat up and clean the instrument. Check whether all chemicals are present in the required quantities.

The flask is put into the VAPODEST and 25 ml of the peroxide/indicator solution is put into the 300 ml Erlenmeyer flask. The outlet tubing of the distillate has to be immerged in this solution. After the distillation the Erlenmeyer flask is taken out and the distillate is titrated with sodium hydroxide solution c = 0.01 mol/l to the pH-endpoint, which has been determined from the blank value (endpoint determination).

Blank value: 100 ml Aquadest are put into the distillation flask and 25 ml of the hydrogen peroxide solution are put into the receiver. The hydrogen peroxide solution will be diluted by the distillate which leads to an increase of the pH value of the receiver solution (from about 3.3. to 4.3.).
The samples to be analyzed are titrated back to this pH-value.

A.6. Evaluation

Reaction equation:

1. $H_2O_2 + SO_2 \longrightarrow H_2SO_4$

2. $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

$$m\ (SO_2) = \frac{(V - V_{Bl}) \cdot c_{NaOH} \cdot M_{SO2}}{2}$$

1 ml 0.01n NaOH = 0.32 mg SO_2

meaning:
V = Consumption standard solution sodium hydroxide solution [ml]
V_{Bl} = Blank value consumption of standard solution [ml]
c_{NaOH} = Concentration of sodium hydroxide solution [mmol/ml] (normality 0.01)
M = molar mass sulphur dioxide [mg/mmol]
m = mass SO_2 [mg]

At the end of this application, you find a sample of a lab report (Application Shortnote) enclosed.

A.7. Standard Recovery / Quality Assurance

Preparation of a standard solution 1000 ppm or 1000 mg/kg sulphur dioxide

Dissolve 0.475 g $Na_2S_2O_5$ in 1000 ml Aquadest

M ($Na_2S_2O_5$) = 190.1 g/mol
M (SO_2) = 64.06 g/mol

$\longrightarrow$ 1 mol sodium disulphite contains 2 mol SO_2
$\longrightarrow$ 190.12 g $Na_2S_2O_5$ contain 128.14 g SO_2

Calculation:

190.12 g $Na_2S_2O_5$ = 128.14 g SO_2
0.475 g $Na_2S_2O_5$ = 0.32 g SO_2

Sulphur dioxide content of the solution:
0.32 g SO_2 in 1000 ml (1 kg) Aquadest
320 mg SO_2 in 1.000 kg (ppm = mg/kg)

Depending on the measuring range of the customer, take an aliquot part

10 ml contain 3.2 mg SO_2

Distillation and titration according to the lab directive.

Calculation Example:

Reaction equation:

1. $H_2O_2 + SO_2 \longrightarrow H_2SO_4$

2. $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

$$m\ (SO_2) = \frac{(V - V_{Bl}) \cdot c_{NaOH} \cdot M_{SO2}}{2}$$

$$m\ (SO_2) = \frac{(20.4ml - 0.42ml) \cdot 0.05mmol/ml \cdot 64.07mg/mmol}{2} = 32\ mg$$

Theoretic value: 20 ml

Recovery > 85 %, Standard deviation +/-5 %

Comments: This solution should always be made freshly.

B. Iodometric Method

B.1. Principle

SO_2 is stripped with hydrochloric acid and water steam and collected in a sodium hydroxide solution.
The distillate is acidified and the standard iodine solution is added. The excessive iodine is titrated back with sodium thiosulphate solution.

B.2. Area of Usage

Foods and beverages.

B.3. Chemicals

B.3.1. Hydrochloric acid, w ≅ 5 %
B.3.2. Sodium hydroxide solution c_{NaOH} = 1 mol/l or 0.1 mol/l depending on the content range of the sample
B.3.3. Solution 1: Iodine solution $c_{KI2/I}$ = 0.05 mol/l
B.3.4. Solution 2: Sodium thiosulphate solution c = 0.1 mol/l
B.3.5. Starch solution: 1 g soluble potato starch in 500 ml water, boiled 5 minutes, filtrated and let cool off
B.3.6. Standard solution sodiumdisulphite ≅ 4.75 g (0.475 g) in 1000 ml

B.4. Instruments

as described under A. Acidimetric Method.

B.5. Analysis

B.5.1. Sample Preparation

The sample weight depends on the matrix to be determined. The comminuted and homogenized sample is weighted into a Kjeldahl flask; solid samples are covered with 100 ml Aquadest.
Depending on the model used, the following program parameters are recommended for operating the VAPODEST. These are only meant to serve as guide lines for the analysis and might have to be adapted to other requirements.

B.5.2. Programming of VAPODEST

	VAP 20s	VAP 30s	VAP 45s
H_2O Addition	-	0 s	0 s
NaOH (HCl) Addition	20 ml	20 ml	20 ml
Reaction Time	0 s	0 s	0 s
Distillation Time	360 s	360 s	360 s
Steam Power	90 %	90 %	90 %
Suction Sample	manual	30 s	30 s

B.5.3. Distillation

Use the VAPODEST following the instruction manual. As a start run a blank distillation in order to heat up and clean the instrument. Check whether all chemicals are present in the required quantities.

10 ml of the sample to be analyzed are pipetted into a digestion tube of the VAPODEST and 10 ml water are added. A 300 ml Erlenmeyer flask filled with 5 ml sodium hydroxide solution (B.3.2.) and 20 ml water is used as a receiver. The outlet tubing of the distillate has to be immersed in the solution.
2 ml of the hydrochloric acid (B.3.1.) are added to the sample and the digestion tube is put immediately into the VAPODEST. Then the program is started and the distillation is run.
After that, the distillate is acidified with approx. 5 ml partly concentrated hydrochloric acid (B.3.1.) - check the pH value! - and 10 ml iodine solution (B.3.3.) are added. The excessive iod is titrated back with sodium thiosulphate solution (B.3.4.) against starch.
A blank is done in an analogue way.

B.6. Evaluation

Reaction equation:

1. $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

2. $SO_3^{2-} + J_2 + H_2O \rightarrow SO_4^{2-} + 2J^- + 2H^+$

3. $S_2O_3^{2-} + J_2 \rightarrow S_4O_6^{2-} + 2J$ (solution must be neutral or weakly acidic)

The SO_2 content is calculated using the following equation:

SO_2 content [mg/l] = $M \cdot (a - b) \cdot 0.05 \cdot 100$

M = Molecular weight of SO_2
a = Consumption of $Na_2S_2O_3$ solution (blank)
b = Consumption of $Na_2S_2O_3$ solution (sample)

Standard recovery / Quality control
Observing the directive and the measuring range of the samples, the analysis of a standard is done.
Also see A. Acidimetric Method

APPLICATION SHORTNOTE VAPODEST

SULFHUR DIOXIDE IN DRIED FRUITS

1. Aim of the Destillation:
quantitative determination of sulphur dioxide in dried fruits (free and combined sulphur dioxide)

2. According to which method are you working? e. g. DIN, DEV, ISO, §35, operating instruction, etc.
C. Gerhardt application "Sulphur Dioxide in Food", Acidimetric Method

3. Sample Details:

Type of Sample	Amount of Sample [g]	Content or Recovery free SO_2 [ppm]	combined SO_2 [ppm]
dried fruits	6 - 18	3500; 3530; 3490	3740; 3670; 3710
dried fruits	6 - 8	3455; 3410; 3480	3530; 3515; 3530
dried apples	7 - 12	602; 611; 601	601;*)
dried fruits	20 - 30	319; 312; 320	377; 347; 369
dried apricots	20 - 30	1500; 1580; 1540	1830; 1700; 1700
dried peaches	10 - 15	1690; 1690; 1710	1790; 1805; 1810

*) content of free SO_2 is the same as content of combined SO_2

4. Chemicals:
4.1. Phosporic acid, 85 %
4.2. Hydrogen peroxide solution, 6 %
4.3. Sodium hydroxide solution c = 0.1 mol/l
4.4. Aquadest

5. Type of Instrument and Supply:
VAPODEST model: VAP 45, with titrator Schott Titro Line easy
Special modification: acid resistant pump
Type of glasses: Kjeldahl flask with enlarged neck, 500 or 750 ml
Set of storage tanks: no

6. Sample Preparation:
100 to 200 g of the sample material are comminuted (e. g. with a moulinette). Depending on the sample type, a suitable amount of sample is weighed into the Kjeldahl flask.

7. Analysis
For the determination of free SO_2 only aquadest (4.4.) is added. For the determination of combined SO_2, aquadest (4.4.) and phosporic acid (4.1.) are added.
The blank value serves for the determination of the titration endpoint: 100 ml aquadest are put into the distillation flask and 25 ml of the hydrogen peroxide solution (4.2.) are filled into the receiver. The hydrogen peroxide solution will be diluted by the distillate which leads to an increase of the pH value of the receiver solution.
The samples to be analyzed are titrated back to this pH value (automatically done by a Schott tritrator with fixed endpoint).

Pogramm Settings VAPODEST

	VAP 10	VAP 20	VAP 30	free SO_2 VAP 45	combined SO_2 VAP 45
H_2O Addition				7 s	7 s
NaOH (phosphoric acid) Addition*				0 s	2 s
Reaction Time				0 s	0 s
Destillation Time				390 s	390 s
Steam Power				100 %	100 %
Suction Sample	manual	manual		0 s	0 s
H_3BO_3 (hydrogen peroxide solution) Addition	manual	manual	manual	6 - 7 s	6 - 7 s
Suction Receiver	manual	manual	manual	20 s	20 s
Titration (NaOH c = 0.1 mol/l)	manual	manual	manual	automatic	automatic
Calculation	manual	manual	manual	manual	manual

8. Remarks:
* Should the Vapodest not be equipped with an acid resistant pump, the (20 ml) phosphoric acid (4.1.) are filled by hand directly into the distillation flask and the distillation is started without delay in order to prevent any loss of SO_2.

9. Work finished at:

Date: 23.9.05 Signature: F. Merklin