# Digestion Application

## D.2.7 Sulphur dioxide in food

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## 1 Principle

Sulphur dioxide and sulphites are popular preservatives and antioxidants. They are used in numerous food groups. The Acceptable Daily Intake (ADI) is 0.7 mg sulphur dioxide equivalent per kilogram of body weight per day. Due to the allergenic effect, labelling is mandatory in the European Union for concentrations of 10 mg/kg and above. Different limit values are set for different food groups.

When determining the $SO_2$ content, all sulphur dioxide is expelled by adding hydrochloric acid and heat. With the help of the nitrogen stream, the gaseous sulphur dioxide is distilled into hydrogen peroxide. In the process, it reacts to sulphuric acid.

$$H_2O_2 + SO_2 \rightarrow H_2SO_4$$

The amount of acid is determined by titration with sodium hydroxide solution. The $SO_2$ content is directly related to the sulphuric acid formed.

$$H_2SO_4 + 2\,NaOH \rightarrow Na_2SO_4 + 2\,H_2O$$

## 2 Method

This application note is meant to be a guideline for the operation of your C. Gerhardt analysis system and has to be adapted to your sample matrix and the local circumstances in your laboratory.

This document is based on:

- DIN EN 1988-1:1998-05, Lebensmittel - Bestimmung von Sulfit - Teil 1: Optimiertes Monier-Williams-Verfahren
- AOAC 990.28, Sulfites in Foods – Optimized Monier-Williams Method, 1994

## 3 Chemicals and material

Quality grade p. a.

3.1. Water: demineralised or distilled
3.2. Paper weighing boats, weighing paper (Art. 1004939)
3.3. Hydrogen peroxide, w(H2O2) = 3 %.
3.4. Hydrochloric acid, w(HCl) = 15 %
3.5. Nitrogen, high purity
3.6. Ethanol-water mixture φ (ethanol) = 5 %.
3.7. Methyl red indicator
3.8. Sodium hydroxide solution, c (NaOH) = 0.01 mol/l
3.9. Sodium hydroxymethyl sulphonate HMS (standard substance)

## 4 Instruments

- Knife mixer
- Analytical balance (reading accuracy 0.1 mg)
- TURBOTHERM for SO2, 4 x 800 ml (Art. 12-0640)
- Titrator and pH meter (without pH indicator)
- Alternatively, a manual burette (class A, acc. to ISO 385), 50 ml nominal volume, with volume measurement to 0.05 ml

# 5 Procedure

## 5.1 Sample preparation

### 5.1.1 Solid samples

A representative sample quantity is grinded and homogenised**.**

**The sample should be analysed as rapid as possible after grinding.**

Weigh the prepared samples in paper weighing boats (3.2) into the digestion tube. Any sample waste on the wall of the sample tube is rinsed back into the flask with distilled water.

### 5.1.2 Liquid samples

The sample should be as representative and homogeneous as possible.

The sample quantity is based on the sulphur dioxide content. The following quantities are recommended:

| $SO_2$ content [mg/kg] / [mg/l] | ceq (NaOH) [mol/l] | Sample weight [g] / [ml] |
|---|---|---|
| ≤ 10 | 0.01 | ≥ 50 |
| 10 - 20 | | 50 |
| 20 - 50 | | 25 |
| 50 - 100 | | 15 |
| 100 - 200 | | 10 |
| 200 - 500 | | 5 |
| 500 - 1500 | | 2 |
| ≥ 1500 | | 1 |

## 5.2 System preparation

Grease all ground joints and connection points. The 800 ml digestion tubes are filled with 100[1] ml distilled water (3.1) and inserted, the nitrogen introduction tubes are connected and the condenser and the prepared absorption vessels filled with 30 ml hydrogen peroxide solution (3.3) are placed on top. Fill 25 ml hydrochloric acid (3.4) into the dropping funnel and close it with the closed screw cap. Then place the dropping funnel on the third nozzle of the digestion tube. The cooling water is switched on. The nitrogen flow (3.5) is set to 12 l/h and the system is flushed for approx. 15 min.

Note: This system preparation must be carried out before **every** analysis.

[1] In the case of muddy or particularly sticky samples, an amount of 200 ml distilled water may be better for the analytical procedure.

*TURBOTHERM für $SO_2$*

### 5.3 Distillation

After flushing the system with nitrogen for 15 minutes, the condenser is placed in the condenser holder and the sample is transferred to digestion tubes and 100 ml of ethanol mixture (3.6) is added. Replace the condenser. Add all but 2-3 ml of the hydrochloric acid (3.4) and close the tap and protective cap.

Bring the sample to the boiling point and adjust the reflux to 80-90 drops per minute. For heating with TURBOTHERM for $SO_2$ we recommend the following programme parameters:

| Note | Step | hh:mm | Power [%] |
|---|---|---|---|
| Heating up the system | 1/3 | 00:07 | 100 |
| Further heating up to boiling point | 2/3 | 00.05 | 70 |
| Reflux 80 - 90 drops/min | 3/3 | 1:45 | 50 |
| Digestion done | | - | - |
| | | | |

This programme can only serve as an orientation. The programme steps may have to be adapted to the respective sample material.

After completion of the boiling phase, the absorption vessel is immediately removed and the hydrogen peroxide solution is quantitatively transferred into an Erlenmeyer flask. Titration is then carried out immediately.

After the sample tubes have cooled down, the cooling water is turned off and the condenser is rinsed with distilled water and placed in the condenser holder. The nitrogen introduction tubes are disconnected from the Steckmatic connection and the insert rack with sample tubes, dropping funnels and nitrogen introduction tubes are removed from the TURBOTHERM. All parts must be carefully cleaned **after each analysis** performed.

**The absorption tubes must always be removed before the nitrogen tap is turned off.**

### 5.4 Titration

Add 3 - 4 drops of methyl red indicator (3.7) to the receiver and titrate with caustic soda (3.8) until the colour changes from red to yellow. If the end point is determined with a pH meter or titrator, the additive of the indicator is omitted. The titration is carried out to the pH value of the transition point. This is determined before the first use - normally this point is around 6.0.

### 5.5 Blank value

For each analysis, the blank value of the chemicals is determined by titration with caustic soda. The blank value with a freshly prepared hydrogen peroxide solution is normally 0.35 ml to 0.60 ml.

### 5.6 Performance check

To check the analytical performance of the system, the recovery rate of a standard solution of sodium hydroxymethyl sulphonate (HMS) with 100 ppm $SO_2$ is determined. For this purpose, 0.209 g HMS (3.9) are weighed out and dissolved in 1000 ml distilled water. The solution should always be prepared fresh. An aliquot is taken on the basis of the measuring range. 10 ml contain 1 mg $SO_2$. The recovery rate should be at least 80 %.

## 6 Calculation

The mass fraction of $SO_2$ expressed in mg/kg is calculated as follows:

$$\omega = \frac{32{,}03 * (V_1 - V_0) * 1000 * c_{eq,soll} * t}{m}$$

ω = Mass fraction of $SO_2$ [mg/kg]
32,03 = milliequivalent weight of $SO_2$ [g/mol]
$V_1$ = Volume of the standard solution used for the sample [ml]
$V_0$ = volume of the standard solution used for the blank test [ml]
1000 = factor for converting milliequivalents into microequivalents
$c_{eq,soll}$ = concentration of the sodium hydroxide standard solution [mol/L]
t = titre of the standard solution
m = weight of the sample [g]

## COMPREHENSIVE APPLICATION DATA BASE

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- Nitrogen in food and feed samples according to Kjeldahl and Dumas
- Crude fibre, ADF and NDF in feed
- Fat in food and feed
- Alcohol determination
- Total cyanide in water
- Trace metal in soil and sludge
- COD determination in water
- Total nitrogen determination in water, soil and plants
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