International Standard ISO 5522

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Fruits, vegetables and derived products — Determination of total sulphur dioxide content

Fruits, légumes et produits dérivés — Détermination de la teneur en dioxyde de soufre total

First edition — 1981-09-01

UDC 634/635 : 543.845 **Ref. No. ISO 5522-1981 (E)**

Descriptors : agricultural products, fruit and vegetable products, fruits, vegetables, chemical analysis, determination of content, sulphur dioxide.

Price based on 7 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5522 was developed by Technical Committee ISO/TC 34, *Agricultural food products*, and was circulated to the member bodies in July 1979.

It has been approved by the member bodies of the following countries :

- Australia
- Austria
- Brazil
- Bulgaria
- Canada
- Chile
- Cyprus
- Czechoslovakia
- Egypt, Arab Rep. of
- Ethiopia
- France
- Germany, F. R.
- Hungary
- India
- Indonesia
- Israel
- Italy
- Kenya
- Korea, Rep. of
- Libyan Arab Jamahiriya
- Malaysia
- Netherlands
- New Zealand
- Peru
- Philippines
- Poland
- Portugal
- Romania
- South Africa, Rep. of
- Spain
- Thailand
- Turkey
- Yugoslavia

No member body expressed disapproval of the document.

Printed in Switzerland

INTERNATIONAL STANDARD

ISO 5522-1981 (E)

Fruits, vegetables and derived products — Determination of total sulphur dioxide content

1 Scope and field of application

This International Standard specifies a method for the determination of the total sulphur dioxide content of fruits, vegetables and derived products, whatever the sulphur dioxide content.

2 Principle

Acidification and heating of a test portion, then entrainment, in a current of nitrogen, of the sulphur dioxide liberated. Absorption and oxidation of the sulphur dioxide by bubbling it through a neutral, dilute hydrogen peroxide solution. Determination of the sulphuric acid thus formed using standard volumetric sodium hydroxide solution.

Verification of the determination by precipitation of barium sulphate from the resulting solution, and, according to the sulphur dioxide content :

- weighing of the barium sulphate (annex A); or
- nephelometric determination (annex B).

3 Reagents

All reagents shall be of recognized analytical quality. The water used shall be distilled water or water of at least equivalent purity, recently boiled.

3.1 Nitrogen, oxygen free.

3.2 Hydrogen peroxide, 9,1 g/l solution, free from sulphate ions.

3.3 Hydrochloric acid, 100 g/l solution.

Dilute 1 volume of concentrated hydrochloric acid, ϱ_{20} = 1,19 g/ml, with 3 volumes of water.

3.4 Indicator solution.

Dissolve 100 mg of bromophenol blue[1] in 100 ml of 20 % (*V*/*V*) ethanol.

3.5 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0{,}1$ mol/l[2], free from sulphate ions; or

3.6 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0{,}01$ mol/l[3], free from sulphate ions.

3.7 Iodine, standard volumetric solution, $c(1/2\ \text{I}_2) = 0{,}02$ mol/l[4].

3.8 Starch, 5 g/l solution containing 200 g of sodium chloride (as preservative) per litre.

Maintain the solution at boiling point for 10 min during preparation.

3.9 Potassium metabisulphite/EDTA solution.

Dissolve in a little water 1,20 g of potassium metabisulphite ($K_2S_2O_5$) and 0,20 g of the disodium salt of ethylenedinitrilotetraacetic acid[5]. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

3.10 Sucrose, 100 g/l solution.

4 Apparatus

Usual laboratory apparatus not otherwise specified, and in particular :

4.1 Measuring cylinders.

4.2 Pipettes.

---

[1] This indicator has been chosen because it does not give rise to interference in nephelometric determinations.

[2] Hitherto expressed as "0,1 N standard volumetric solution".

[3] Hitherto expressed as "0,01 N standard volumetric solution".

[4] Hitherto expressed as "0,02 N standard volumetric solution".

[5] This product is intended to protect the sulphite ion from oxidation by air by complexing the traces of copper ion.

4.3 Semi-microburette, of capacity 10 ml.

4.4 Burette, of capacity 25 ml.

4.5 Blender.

4.6 *Entrainment* **apparatus,** such as that shown in the figure[1], or equivalent apparatus ensuring the displacement and the entrainment of sulphur dioxide and its absorption in the hydrogen peroxide solution.

4.6.1 Construction of the apparatus

A : round-bottom flask, of capacity 250 ml or more.

B : reflux condenser, of high efficiency, capable of being fitted to the flask (A).

C : dropping funnel, capable of being adapted to the flask (A).

D : nitrogen inlet.

E and E' : 2 bubblers, in series, capable of being fitted to the condenser (B).

F : disk, of sheet-iron or asbestos, diameter 150 mm, having a central hole of diameter 40 mm. This disk is intended to prevent any pyrogenation, particularly of the extractable matter in the product.

NOTE — Between tests, if the entrainment is sufficiently slow and gentle, only the flask (A) need be cleaned.

4.6.2 Check tests

The apparatus shall satisfy the following three check tests :

4.6.2.1 Introduce into the flask (A) 100 ml of water and 5 ml of the hydrochloric acid solution (3.3). Heat the flask under reflux, while passing a current of nitrogen, for 1 h, with the bubblers (E and E') each containing 5 ml of water and 0,1 ml of the indicator solution (3.4).

The contents of each bubbler shall remain neutral.

4.6.2.2 Introduce into the flask (A) 20 ml of the sucrose solution (3.10). Heat the flask under reflux, while passing a current of nitrogen, for 1 h.

The sucrose solution shall remain colourless, and there shall be no deposition of caramel on the walls of the flask. (The test is intended to check the intensity of heating.)

4.6.2.3 Carry out the following two operations :

a) By means of a pipette (4.2), introduce into the flask (A) 20 ml of the potassium metabisulphite/EDTA solution (3.9) and 5 ml of the hydrochloric acid solution (3.3). Carry out the entrainment and determination of sulphur dioxide under the same conditions as the determination proper, but without adding hydrochloric acid solution (i.e. as specified in 5.3.1, 5.3.2, 5.3.5 and 5.4).

b) Introduce into a 100 ml conical flask, 20 ml of the potassium metabisulphite/EDTA solution (3.9), and add 5 ml of the hydrochloric acid solution (3.3) and 1 ml of the starch solution (3.8).

Titrate, using the burette (4.4) containing the iodine solution (3.7) until the first appearance of a blue colour.

The sulphur dioxide content obtained in a) shall be within ± 1 % of that obtained in b).

Procedure b) shall not be carried out more than 15 min after terminating procedure a), in order to avoid a possible change in the sulphur dioxide content of the metabisulphite solution.

4.7 Balance.

5 Procedure

5.1 Preparation of test sample

Remove seeds and hard seed-cavity walls if necessary, and blend the sample carefully.

Allow frozen or deep-frozen products to thaw in a closed container, and add the liquid formed during this process to the product before blending.

5.2 Test portion

Weigh, to the nearest 0,01 g, 10 to 100 g of the test sample (5.1), according to the expected sulphur dioxide content, so that the test portion contains not more than 10 mg of sulphur dioxide; transfer the test portion to the flask (A) of the entrainment apparatus (4.6).

5.3 Entrainment

5.3.1 Place in each bubbler (E and E') 3 ml[2] of the hydrogen peroxide solution (3.2) and 0,1 ml of the indicator solution (3.4), and neutralize the hydrogen peroxide solution with the 0,01 mol/l sodium hydroxide solution (3.6).

---

[1] Apparatus of the Lieb and Zaccherl type.

[2] This quantity is theoretically sufficient to oxidize 51 mg of sulphur dioxide, but an excess is essential.

5.3.2 Connect the dropping funnel (C), the reflux condenser (B) and the bubblers (E and E′) to the flask (A); pass a current of nitrogen to drive out the air from the flask (A) and the whole of the apparatus.

5.3.3 Place 100 ml of water and 5 ml of the hydrochloric acid solution (3.3) in the dropping funnel (C).

5.3.4 Allow the dilute hydrochloric acid solution contained in the dropping funnel (C) to run into the flask (A) (if necessary, interrupting the nitrogen current momentarily).

5.3.5 Bring the contents of the flask slowly to the boil, and maintain at the boiling point, allowing the nitrogen to circulate regularly throughout to give one or two bubbles per second, for about 30 min.

5.4 Titration

Transfer the contents of the second bubbler (E′) to the first and titrate the sulphuric acid formed with the 0,01 mol/l (3.6) or 0,1 mol/l (3.5) sodium hydroxide solution, according to the expected sulphur dioxide content.

5.5 Verification

5.5.1 If the volume V of 0,01 mol/l sodium hydroxide solution required exceeds 10 ml (or 1 ml in the case of 0,1 mol/l sodium hydroxide solution), carry out the gravimetric determination specified in annex A.

5.5.2 If the volume V is less than 10 ml, carry out the nephelometric determination specified in annex B.

If the volume V is less than 5 ml, only the nephelometric method may be used. For a test portion of 100 g, this 5 ml limit corresponds to a sulphur dioxide content of 16 mg/kg.

Above this limit, the acidimetric determination is sufficient.

5.6 Number of determinations

Carry out two determinations on the same test sample (5.1).

6 Expression of results

6.1 Method of calculation and formula

The sulphur dioxide content, expressed in milligrams per kilogram of product, is given by the formula[1]

$$0{,}32 \times \frac{V}{m} \times 10^3 = 320 \times \frac{V}{m}$$

where

m is the mass, in grams, of the test portion (5.2);

V is the volume, in millilitres, of the 0,01 mol/l sodium hydroxide solution (3.6) used for the titration (5.4);

0,32 is the mass, in milligrams, of sulphur dioxide corresponding to 1 ml of 0,01 mol/l sodium hydroxide solution.

Take as the result the arithmetic mean of the two determinations (5.6), provided that the requirement for repeatability (see 6.2) is satisfied.

6.2 Repeatability

The difference between the results of two determinations, carried out simultaneously or in rapid succession by the same analyst, shall not exceed ± 5 % of the mean value.

7 Test report

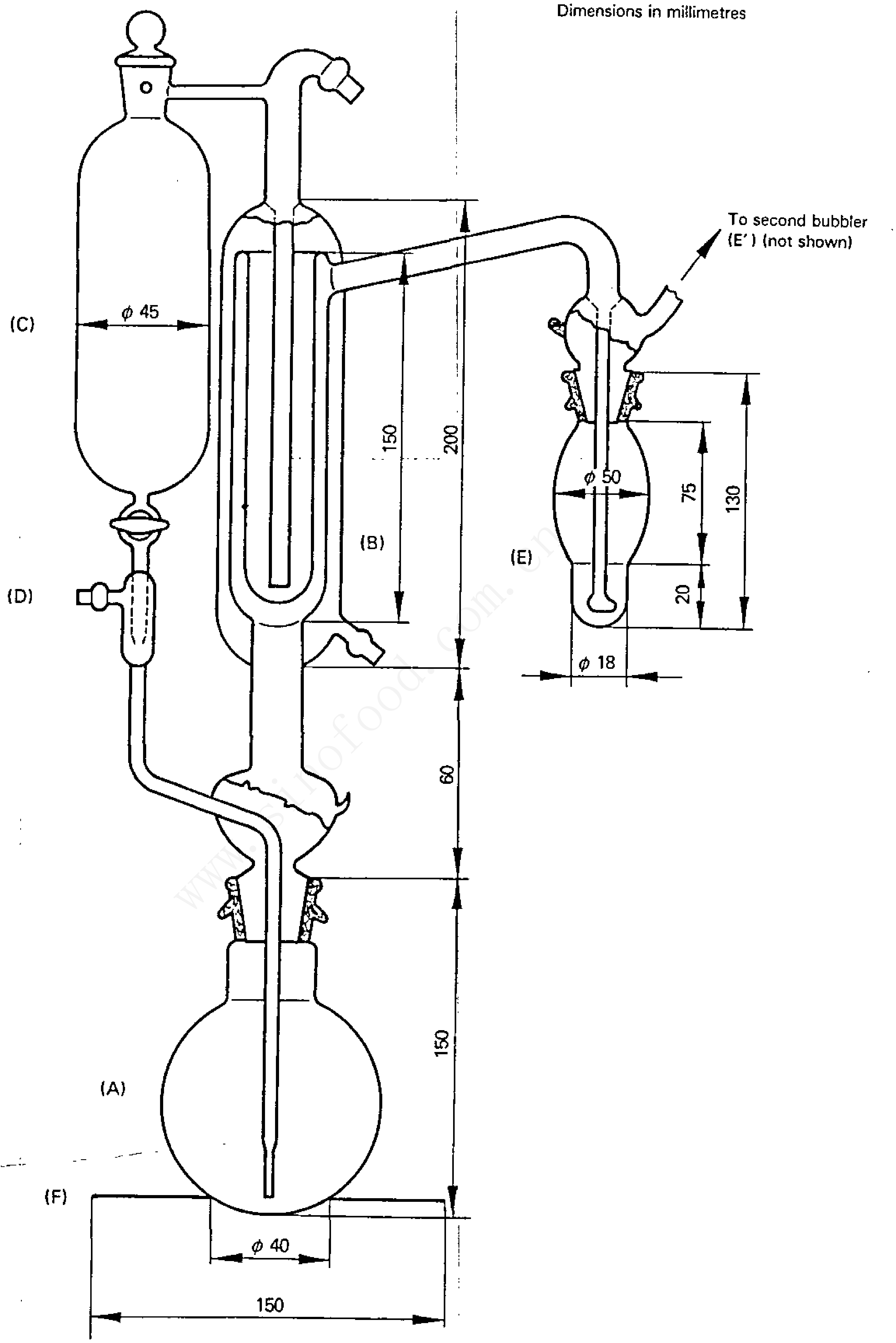
The test report shall show the method used and the result obtained. It shall also mention any operating conditions not specified in this International Standard, or regarded as optional, as well as any circumstances that may have influenced the result.

The test report shall include all details required for complete identification of the sample.

---

[1] If the 0,1 mol/l sodium hydroxide solution (3.5) is used, replace the coefficient 320 by 3 200.

Dimensions in millimetres



NOTE – The internal diameters of the four concentric tubes which serve as the condenser are 45, 34, 27 and 10 mm, respectively. It is advantageous to replace the two ground conical surfaces by spherical ones.

Figure – Schematic diagram of an apparatus for entrainment

Annex A

Gravimetric verification of the acidimetric determination of the sulphate ion formed

A.1 Reagents

All reagents shall be of recognized analytical quality. The water used shall be distilled water or water of at least equivalent purity, recently boiled.

A.1.1 Barium chloride, 100 g/l solution.

A.1.2 Concentrated hydrochloric acid, ϱ_{20} = 1,19 g/ml.

A.1.3 Washing solution for the barium sulphate precipitate.

Dissolve in water, in a 1 000 ml one-mark volumetric flask, 26 mg of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), add 1 ml of the concentrated hydrochloric acid (A.1.2) and dilute to the mark with water.

A.2 Apparatus

Usual laboratory apparatus not otherwise specified, and in particular :

A.2.1 Conical flasks, of capacity 50 ml.

A.2.2 Volumetric pipettes, of appropriate capacities.

A.2.3 Ash-less filter paper.

A.2.4 Oven, capable of being controlled at 800 ± 25 °C.

A.2.5 Incineration dishes.

A.2.6 Desiccator, containing an efficient desiccant (other than sulphuric acid).

A.2.7 Analytical balance.

A.3 Procedure

A.3.1 After the titration (see 5.4), transfer the contents of the bubbler (E), and the water used for washing, to a conical flask (A.2.1); the total volume shall be approximately 25 ml. Add 1 ml of the concentrated hydrochloric acid (A.1.2) and bring to the boil.

Add, drop by drop, 2 ml of the barium chloride solution (A.1.1), stir, then allow to cool and stand for 12 h. Quantitatively collect the precipitate formed, on the filter paper (A.2.3), previously moistened with boiling water. Wash the precipitate once with 20 ml of tepid distilled water, then five times with 20 ml portions of tepid washing solution (A.1.3). Drain and dry.

Place the filter paper and precipitate in the incineration dish (A.2.5), previously dried and tared to the nearest 1 mg, and incinerate in the oven (A.2.4), controlled at 800 ± 25 °C, for 2 h. Remove from the oven. After cooling in the desiccator (A.2.6), weigh the dish and its contents to the nearest 1 mg.

Determine by difference the mass of barium sulphate obtained.

A.3.2 Carry out gravimetric verifications of both the determinations specified in 5.6.

A.4 Expression of results

A.4.1 Method of calculation and formula

The sulphur dioxide content, expressed in milligrams per kilogram of product, is given by the formula

$$\frac{0{,}274\,5\, m_1}{m} \times 10^3$$

where

m_1 is the mass, in milligrams, of barium sulphate obtained (see A.2.6);

m has the same meaning as in 6.1;

0,274 5 is the mass, in milligrams, of sulphur dioxide corresponding to 1 mg of barium sulphate.

Take as the result the arithmetic mean of the two determinations, provided that the requirement for repeatability (see A.4.2) is satisfied.

A.4.2 Repeatability

The difference between the results of the two determinations, carried out simultaneously or in rapid succession by the same analyst, shall not exceed ± 5 % of their mean value.

A.5 Agreement of results

The result obtained shall not differ by more than 5 % from that obtained using the acidimetric method.

In the case where the difference in results obtained by the acidimetric method and the gravimetric method is greater than 5 %, only the result obtained by the gravimetric method shall be reported.

Annex B

Nephelometric verification of the acidimetric determination of the sulphate ion formed

B.1 Reagents

B.1.1 Sulphuric acid, standard solution.

Place 31,2 ml of standard volumetric sulphuric acid solution, $c(1/2\ H_2SO_4) = 0{,}1$ mol/l[1], in a 1 000 ml one-mark volumetric flask, and make up to the mark with water.

1 ml of this solution corresponds to 0,1 mg of SO_2.

B.1.2 Polyvinyl pyrolidone, 50 g/l solution, free from sulphate ions (mean relative molecular mass 85 000).

B.1.3 Barium chloride and polyvinyl pyrolidone, mixed solution.

Mix 80 ml of 100 g/l barium chloride solution with 20 ml of the polyvinyl pyrolidone solution (B.1.2).

B.1.4 Hydrochloric acid solution (see 3.3).

B.1.5 Indicator solution (see 3.4).

B.2 Apparatus

B.2.1 One-mark volumetric flasks, of capacity 50 ml, complying with the requirements of ISO 1042.

B.2.2 Pipettes, or burettes, to deliver 2 — 4 — 8 — 12 — 16 and 25 ml.

B.2.3 Spectrophotometer, suitable for measurements at a wavelength of 650 nm.

B.3 Procedure

B.3.1 Preparation of the calibration curve

Into a series of six 50 ml one-mark volumetric flasks (B.2.1), place 0 — 2 — 4 — 8 — 12 and 16 ml of the standard sulphuric acid solution (B.1.1), 20 ml of water, 0,1 ml of the indicator solution (B.1.5), 1 ml of the hydrochloric acid solution (B.1.4) and 5 ml of the mixed solution (B.1.3). Make up to the mark with water and mix.

The solutions obtained correspond respectively to 0 — 0,2 — 0,4 — 0,8 — 1,2 and 1,6 mg of sulphur dioxide.

After 15 to 20 min of having added the mixed solution (B.1.3), measure the absorbance of each solution at 650 nm using the spectrophotometer (B.2.3).

Plot the calibration curve of absorbance as a function of the sulphur dioxide content, in milligrams per litre.

B.3.2 Determination

B.3.2.1 Case where the volume *V* of 0,01 mol/l sodium hydroxide solution is less than 5 ml

After the titration (see 5.4), transfer the contents of the bubbler (E), and the water used for washing, to a 50 ml one-mark volumetric flask (B.2.1). Add 1 ml of the hydrochloric acid solution (B.1.4) and 5 ml of the mixed solution (B.1.3). Make up to the mark with water and mix.

After the titration (see 5.4), transfer the contents of the bubbler (E), and the water used for washing, to a 50 ml one-mark volumetric flask (B.2.1). Make up to the mark with water and mix.

B.3.2.2 Case where the volume *V* of 0,01 mol/l sodium hydroxide solution is between 5 and 10 ml

After the titration (see 5.4), transfer the contents of the bubbler (E), and the water used for washing, to a 50 ml one-mark volumetric flask (B.2.1). Make up to the mark with water and mix.

Transfer 25 ml of this solution to another 50 ml one-mark volumetric flask (B.2.1). Add 1 ml of the hydrochloric acid solution (B.1.4) and 5 ml of the mixed solution (B.1.3). Make up to the mark with water and mix.

After 15 to 20 min of having added the mixed solution (B.1.3), measure the absorbance of the solution at 650 nm using the spectrophotometer (B.2.3).

B.3.3 Number of determinations

Carry out nephelometric verifications of both the determinations specified in 5.6.

---

[1] Hitherto expressed as "0,1 N standard volumetric solution".

B.4 Expression of results

B.4.1 If verification was carried out in accordance with B.3.2.1, the sulphur dioxide content, expressed in milligrams per kilogram of product, is given by the formula

$$c \times \frac{1\,000}{m}$$

where

c is the sulphur dioxide concentration, in milligrams per litre, read from the calibration curve (B.3.1) and corresponding to the absorbance measured in B.3.2.1;

m has the same meaning as in 6.1.

B.4.2 If verification was carried out in accordance with B.3.2.2, the sulphur dioxide content, expressed in milligrams per kilogram of product, is given by the formula

$$c \times \frac{1\,000}{m} \times 2$$

where

c has the same meaning as in B.4.1, and corresponds to the absorbance measured in B.3.2.2;

m has the same meaning as in 6.1.

B.4.3 Take as the result the arithmetic mean of the two determinations, provided that the requirement for repeatability (see 6.2) is satisfied.

B.5 Agreement of results

The result obtained shall not differ by more than 5 % from that obtained using the acidimetric method.

In the case where the difference in results obtained by the acidimetric method and the nephelometric method is greater than 5 %, only the result of the nephelometric method shall be reported.