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Starches and derived products — Determination of sulfur dioxide content — Acidimetric method and nephelometric method

Amidons, fécules et produits dérivés — Détermination de la teneur en dioxyde de soufre — Dosage acidimétrique et dosage par néphélémétrie

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Foreword

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The committee responsible for this document is ISO/TC 93, *Starch (including derivatives and by-products)*.

This second edition cancels and replaces ISO 5379:1983, of which it constitutes a minor revision.

Starches and derived products — Determination of sulfur dioxide content — Acidimetric method and nephelometric method

1 Scope

This International Standard specifies two methods (an acidimetric method and a nephelometric method) for the determination of the sulfur dioxide content of starches and derived products.

2 Acidimetric method

2.1 Reagents

WARNING — All chemicals shall be handled with care. Consult the appropriate material safety data sheet for proper handling and disposal procedures.

All reagents shall be of recognized analytical quality and be sulfate-free.

2.1.1 Water, distilled water or water of at least equivalent purity, recently boiled.

2.1.2 Nitrogen, oxygen-free.

2.1.3 Hydrogen peroxide, solution containing approximately 9 g to 10 g of H_2O_2 per litre {$c(H_2O_2)$ = 0,265 to 0,294 mol/l}.

Place 150 ml of 20 volumes (6 wt %, 2,08 mol/l) hydrogen peroxide solution or 30 ml of 110 volumes (30 wt %, 10,4 mol/l) hydrogen peroxide solution in a 1 l one-mark volumetric flask. Dilute to the mark with water.

This solution should be freshly prepared.

2.1.4 Hydrochloric acid.

To 500 ml of water in a 1 l beaker, slowly add 150 ml of concentrated hydrochloric acid (ρ_{20} 1,18 g/ml; 12 mol/l; 37 wt %) with stirring. Transfer this qualitatively to a 1 l volumetric flask and dilute to the mark.

CAUTION — Never add water to concentrated acid.

2.1.5 Bromophenol blue indicator solution.

Dissolve 100 mg of bromophenol blue [alternative names are α, α-bis(3,5-dibromo-4-hydroxyphenyl) toluene-2, α–sulfone or 3, 3', 5, 5'-tetrabromophenol sulfonephthalein] in 100 ml of 20 % (*V*/ *V*) ethanol.

2.1.6 Tashiro indicator solution.

Dissolve 30 mg of methyl red {2-[[4-(dimethylamino)phenyl]-azo] benzoic acid} and 50 mg of methylene blue [3,7-bis(dimethylamino)phenothiazin-5-ium chloride] in 120 ml of 90 % (*V*/ *V*) ethanol. Dilute to 200 ml with water, mix and filter if necessary.

NOTE The Tashiro indicator can only be used with the titrimetric method (2.3.4). The bromophenol blue indicator is appropriate for the titrimetric method and does not hinder the further use of the nephelometric method (see Clause 3). Nevertheless, with this indicator, it is more difficult to detect the end-point.

2.1.7 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/l; or sodium hydroxide, standard volumetric solution, c(NaOH) = 10 mmol/l.

In order to obtain a sharp end-point, prepare this solution using carbon-dioxide-free water obtained by cooling boiled distilled water (2.1.1) under a flow of nitrogen (2.1.2).

The use of sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/l is recommended and a piston-burette is useful for small volumes. If necessary, increase the mass of the test portion.

2.1.8 Iodine, standard volumetric solution, $c(I_2)$ = 10 mmol/l. Potassium iodate (KIO_3) at the appropriate concentration is a suitable substitute.

2.1.9 Starch, 5 g/l solution.

Dissolve 0,5 g of Lintner starch or similar in 100 ml of water. Heat to boiling while stirring. Add 20 g of sodium chloride, stir and boil until dissolution is complete. Allow to cool to ambient temperature before use.

2.1.10 Sodium metabisulfite ($c(SO_2)$ = 7,8 mmol/l) and **ethylenediaminetetraacetic acid (EDTA), disodium salt** (c(EDTA) = 0,5 mmol/l).[1)]

Dissolve in water 0,74 g of sodium metabisulfite ($Na_2S_2O_5$) and 0,20 g of ethylenediaminetetraacetic acid disodium salt dihydrate ($Na_2H_2EDTA{\cdot}2H_2O$). Transfer the solution quantitatively to a 1 l volumetric flask and make up to the mark with water. For accurate results, minimize exposure of this solution to the atmosphere.

2.2 Apparatus

Glass apparatus should preferably be fitted with ground glass joints. Use ordinary laboratory apparatus, and in particular, the following. See Figure 1.

2.2.1 One-mark volumetric flasks, of capacity 1 l, complying with the requirements of ISO 1042, class A.

2.2.2 One-mark pipettes, of capacities 0,1 –1 –2 –3 –5 and 20 ml, complying with the requirements of ISO 648, class A.

2.2.3 Burettes, with capacities of 10 ml, 25 ml and 50 ml, complying with ISO 385, smallest scale division, accuracy class A or AS.

2.2.4 Analytical balance, capable of weighing to the nearest 10 mg.

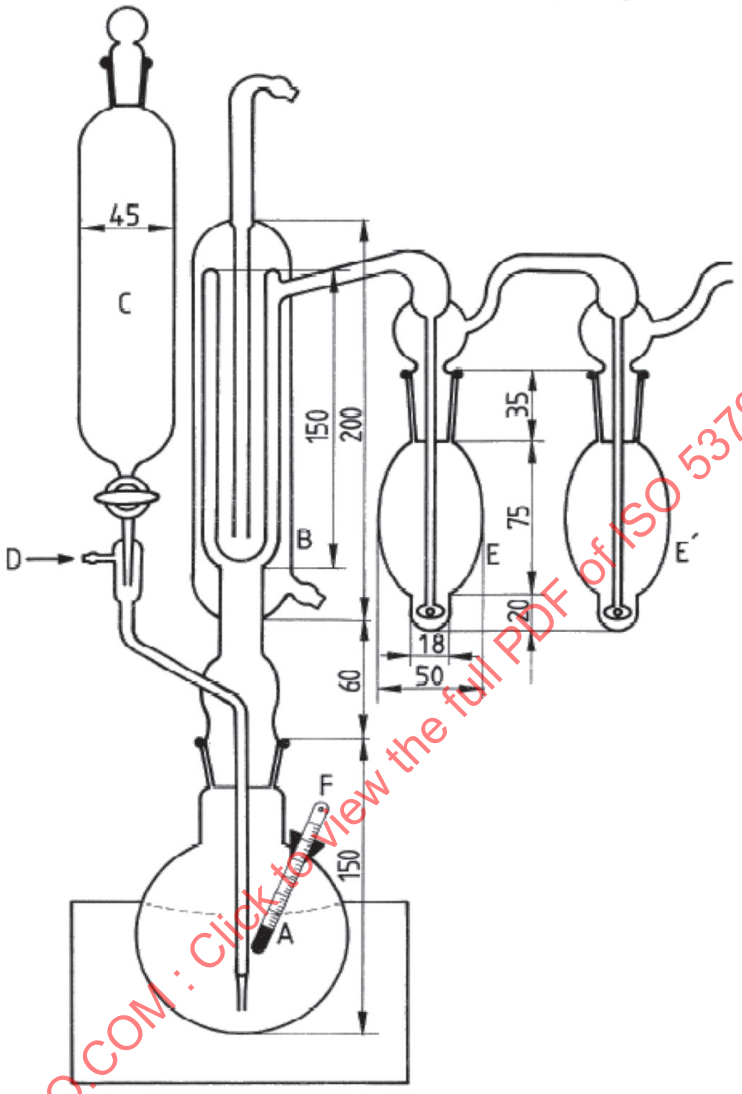
2.2.5 Magnetic stirrer, efficient, with heating, for use with the flask (A) (see Figure 1).

2.2.6 Entrainment apparatus, as shown in the Figure 1, or equivalent equipment for ensuring the displacement and entrainment of sulfur dioxide and its absorption in a solution of hydrogen peroxide.

Avoid making connections with tubes between the condenser and the bubblers as this could lead to absorption of sulfur dioxide.

1) EDTA is used to retard any oxidation of sulfite by air in the presence of trace amounts of copper ion.

Dimensions in millimetres



Key

A round-bottom flask, of capacity 250 ml or greater, with a ground tubular allowing the introduction of a thermometer

B vertical condenser of high efficiency, to fit the flask (A)

C separating funnel, fitted to the flask (A)

D nitrogen inlet with an absorber containing an alkaline solution of pyrogallol

E, E' 2 bubblers in series, connected to the condenser (B)

F thermometer

Between two determinations, if the entrainment is sufficiently slow and moderate, only flask (A) need be cleaned.

Figure 1 — Diagram of entrainment apparatus (Lieb and Zaccheri type)

2.2.7 Check tests

The apparatus shall satisfy the following requirements.

a) Place in the flask (A) 100 ml of water and proceed as specified in 2.3.3. The contents of the bubblers shall remain neutral.

b) Carry out the following operations.

1) Place in the flask (A) 100 ml of water. Introduce, using a pipette, 20 ml of the solution. Carry out the entrainment and the determination of sulfur dioxide as specified in 2.3.3 and 2.3.4.

2) Transfer, using a pipette, 20 ml of the iodine solution, 5 ml of the hydrochloric acid and 1 ml of the starch solution into a 100 ml conical flask.

Titrate, using a burette, with the solution until the first coloration is discharged. The sulfur dioxide (SO_2) content can be calculated according to the below chemical equation:

$$SO_2 + I_2 + 2\,H_2O \rightarrow SO_4^{2-} + 4\,H^+ + 2\,I^-$$

where

I_2 is the chemical formula for iodine;

H_2O is the chemical formula for water;

SO_2 is the chemical formula for sulfur dioxide;

H^+ is the chemical symbol for the hydrogen ion;

I^- is the chemical symbol for the iodide ion;

SO_4^{2-} is the chemical symbol for the sulfate ion.

The difference between the sulfur dioxide contents determined in Operations 1) and 2) shall not exceed 1 % of their arithmetic mean.

Operation 2) shall not be carried out more than 15 min after completion of Operation 1) in order to avoid a possible change in the amount of sulfur dioxide contained in the sodium metabisulfite/ Na_2H_2EDTA solution.

2.3 Procedure

2.3.1 Preparation of test samples

Thoroughly mix the laboratory sample.

2.3.2 Test portion

Weigh, to the nearest 10 mg, a mass of the test sample (see 2.3.1) as specified in Table 1.

Table 1 — Mass of test sample

Expected sulfur dioxide content	Approximate mass of test portion
mg/kg	g
< 50	100
50 to 200	50

This quantity may be increased, particularly in the case of D-glucose.

If the expected content is greater than 200 mg/kg, reduce the test portion accordingly so that it does not contain more than 10 mg of sulfur dioxide and transfer it quantitatively to the flask (A). In the case of certain derived products, the mass of the test portion can be determined by difference by weighing of the container. Add 100 ml of water to the test portion and mix well by shaking. [In the case of a test portion of more than 100 g (for example D-glucose), the quantity of water added should be equal to that of the test portion.]

2.3.3 Entrainment

2.3.3.1 Place in the funnel (C) 50 ml of the hydrochloric acid.

2.3.3.2 In each of the bubblers (E and E'), place, by means of a pipette, 3 ml of the hydrogen peroxide solution, 0,1 ml of the bromophenol blue indicator solution (see the note to 2.1.6 Tashiro indicator solution) and neutralize the hydrogen peroxide solution with the sodium hydroxide solution.

2.3.3.3 Connect the condenser (B) and the bubblers (E and E') to the apparatus, and slowly pass a current of nitrogen to expel the air from the whole equipment. Start the flow of water to the condenser.

2.3.3.4 Allow the hydrochloric acid contained in the funnel (C) to flow into the flask (A) (if necessary interrupt the flow of nitrogen for a moment).

CAUTION — With D on, there is positive pressure in the assembly which may expel hydrochloric acid from C causing injury. D should be off when C is on.

2.3.3.5 Bring the mixture to boiling point in 30 min. Boil for 30 min, while passing a current of nitrogen and stirring with the magnetic stirrer.

CAUTION — This involves boiling an acidic mixture under slightly positive pressure. The entrainment apparatus should be assembled in a fume hood and all joints should be leak-proof.

2.3.4 Titration

Add quantitatively the content of the second bubbler to the content of the first bubbler, and titrate the sulfuric acid formed with the sodium hydroxide solution depending on the expected sulfur dioxide content.

If the end point is not sharp, owing to the presence of volatile organic acids, boil for 2 min and cool to room temperature before titrating.

2.3.5 Check

If the volume V is less than 5 ml when the 10 mmol/l sodium hydroxide solution is used, or less than 0,5 ml when the 0,1 mol/l sodium hydroxide solution is used, carry out the determination by the nephelometric method (see Clause 3).

2.3.6 Number of determinations

Carry out two determinations on the same test sample (2.3.1)

2.4 Expression of results

2.4.1 Method of calculation and formulae

If determination by the nephelometric method is not necessary (see 2.3.5), the sulfur dioxide content, expressed in milligrams per kilogram of sample, is given by the formula:

$$\frac{0,320\,3 \times V\ 1\,000}{m_0} = \frac{320,3 \times V}{m_0}$$

where

m_0 is the mass, in grams, of test portion (2.3.2);

V is the volume, in milliliters, of 10 mmol/l sodium hydroxide, standard volumetric solution, or 10 times the volume of 0,l mol/l sodium hydroxide, standard volumetric solution used.

Take as the result the arithmetic mean of the values obtained in two determinations (2.3.6), provided that the requirement for repeatability (see 2.4.2) is satisfied.

2.4.2 Repeatability

The absolute difference between the results of two determinations carried out simultaneously or in rapid succession by the same analyst on the same test sample shall not exceed 5 % of the mean value of the two determinations. (See ISO 5725-2.)

2.4.3 Reproducibility

The difference between the results of two determinations carried out in different laboratories on the same test sample shall not exceed 10 % of the mean value of the two determinations. (See ISO 5725-2.)

3 Nephelometric method

If the volume V was less than 5 ml when the 10 mol/l sodium hydroxide solution was used or was less than 0,5 ml when the 0,1 mol/l sodium hydroxide solution was used, determination only by the nephelometric method is valid. For a test portion of 100 g, this limit of 5 ml corresponds to a content of 16 mg of sulfur dioxide per kilogram. Above this limit, the acidimetric method is satisfactory.

3.1 Reagents

All reagents shall be of recognized analytical quality and sulfate-free. The following reagents shall be used.

3.1.1 Water, distilled water or water of equivalent purity, recently boiled.

3.1.2 Sulfuric acid, standard solution.

Place in a 1 l one-mark volumetric flask, 31,2 ml of 0,1 mol/l standard volumetric sulfuric acid solution and dilute to the mark with water. 1 ml of this solution is equivalent to 0,1 mg of SO_2.

3.1.3 Polyvinylpyrrolidone (PVP) solution.

Dissolve in water 5,0 g of polyvinylpyrrolidone (relative molecular mass 44 000 or 85 000) in a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix. Filter through a fine filter paper and store in a brown glass bottle. Fresh solution should be prepared every week.

3.1.4 Barium chloride, stock solution.

Dissolve in water 122,14 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix. Filter through a fine filter paper.

3.1.5 Mixed solution.

Place in a 100 ml glass bottle (3.2.1) 15 ml of the barium chloride solution, 64 ml of water, 15 ml of 95 % (*V*/ *V*) ethanol and 5 ml of the PVP solution (3.1.3) using a pipette. Mix and bring to 20 °C using the water bath (3.2.2) Add, by means of a pipette, 30 min before the reagent is required for use, 1 ml of the sulfuric acid solution. Mix thoroughly.

3.2 Apparatus

3.2.1 One-mark volumetric flasks, of capacities 50 ml, 100 ml and 1 000 ml, complying with the requirements of ISO 1042, class A.

3.2.2 Pipettes or **burettes,** to deliver 2 ml, 4 ml, 8 ml, 12 ml, 16 ml and 25 ml.

3.2.3 Water bath, maintained at (20 ± 1) °C.

3.2.4 Glass bottle, of capacity 100 ml, with a ground glass stopper.

3.2.5 Spectrometer, suitable for making measurements at a wavelength of 650 nm, provided with cells of optical path length 10 mm.

3.3 Procedure

3.3.1 Calibration curve

Into six 50 ml one-mark volumetric flasks, introduce 0 ml, 2 ml, 4 ml, 8 ml, 12 ml and 16 ml of the standard sulfuric acid solution, 20 ml of water, 0,1 ml of the bromophenol blue indicator solution, 1 ml of the hydrochloric acid and 5 ml of the mixed solution, corresponding to 0 mg, 0,2 mg, 0,4 mg, 0,8 mg, 1,2 mg and 1,6 mg of sulfur dioxide, respectively. Dilute to the mark with water and mix. Between 15 min and 20 min after adding the mixed solution, measure the absorbance at 650 nm using the spectrometer. Plot a calibration curve of the measured absorbance as a function of the mass of sulfur dioxide, in milligrams.

3.3.2 Determination

After the titration (2.3.4), pour the contents of the bubbler and the water used for washing it into a 50 ml one-mark volumetric flask add 1 ml of the hydrochloric acid and 5 ml of the mixed solution. Dilute to the mark with water and mix. Between 15 min and 20 min after adding the reagent, measure the absorbance at 650 nm using the spectrometer.

The calibration and the determination should be carried out at the same temperature, which should not exceed (25 ± 1) °C.

3.3.3 Number of determinations

Carry out the determination on the two solutions titrated in 2.3.4.