International Standard ISO 5379

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

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

First edition — 1983-08-15

UDC 664.2 : 543.24 : 546.224-31 Ref. No. ISO 5379-1983 (E)

Descriptors : carbohydrates, starches, food starch, tests, determination of content, sulfur dioxide.

Price based on 6 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (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 authorized 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 5379 was developed by Technical Committee ISO/TC 93, *Starch (including derivatives and by-products)*, and was circulated to the member bodies in June 1982.

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

Australia	Iran	Romania
Canada	Korea, Rep. of	South Africa, Rep. of
Chile	Mexico	Spain
Egypt, Arab Rep. of	Netherlands	USA
France	Peru	USSR
Germany, F. R.	Poland	

No member body expressed disapproval of the document.

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

1 Scope and field of application

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 References

ISO 1227, *Starch, including derivatives and by-products — Vocabulary.*

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Entrainment in a current of nitrogen of the sulfur dioxide extracted from the acidified and heated product, and fixing and oxidation of the sulfur dioxide by bubbling through a dilute solution of neutral hydrogen peroxide. Titration of the sulfuric acid formed with standard volumetric sodium hydroxide solution or nephelometric determination in the case of low sulfur dioxide contents.

4 Acidimetric method

4.1 Reagents

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

4.1.1 Nitrogen, oxygen-free.

4.1.2 Hydrogen peroxide, solution containing approximately 9 to 10 g of H_2O_2 per litre.

Place 150 ml of 20 volumes hydrogen peroxide solution or 30 ml of 30 % (*m/m*) (110 volumes) hydrogen peroxide solution in a 1 000 ml one-mark volumetric flask. Dilute to the mark with water.

NOTE — This solution should be freshly prepared.

4.1.3 Hydrochloric acid.

Place 150 ml of concentrated hydrochloric acid, (ϱ_{20} = 1,19 g/ml) in a 1 000 ml one-mark volumetric flask. Dilute to the mark with water.

4.1.4 Bromophenol blue indicator solution.

Dissolve 100 mg of bromophenol blue [α, α-bis(3,5-dibromo-4-hydroxyphenyl) toluene-2,α-sultone] in 100 ml of 20 % (*V/V*) ethanol.

4.1.5 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.

NOTE — The Tashiro indicator (4.1.5) can only be used with the titrimetric method (4.3.4). The bromophenol blue indicator (4.1.4) is appropriate for the titrimetric method and does not hinder the further use of the nephelometric method (see clause 5). Nevertheless, with this indicator, it is more difficult to detect the end-point.

4.1.6 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/l[1]; or

4.1.7 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,01 mol/l.[2]

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

NOTE — The use of solution (4.1.6) is recommended and a piston-burette is useful for small volumes. If necessary, increase the mass of the test portion.

1) Hitherto designated as "0,1 N standard volumetric solution".

2) Hitherto designated as "0,01 N standard volumetric solution".

4.1.8 Iodine, standard volumetric solution, $c(I_2) = 0{,}01$ mol/l.[1)]

4.1.9 Starch, 5 g/l solution.

Dissolve 0,5 g of Lintner starch (see ISO 1227) 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.

4.1.10 Potassium disulfite and ethylenediaminetetraacetic acid (EDTA), disodium salt.[2)]

Dissolve in water 0,87 g of potassium disulfite ($K_2S_2O_5$) and 0,20 g of disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2edta). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

4.2 Apparatus

Glass apparatus should preferably be fitted with ground glass joints.

Ordinary laboratory apparatus, and in particular

4.2.1 One-mark volumetric flasks, of capacity 1 000 ml, complying with the requirements of ISO 1042, class A.

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

4.2.3 Semi-microburette, of capacity 10 ml, complying with the requirements of ISO 385/2, class A.

4.2.4 Burettes, of capacities 25 and 50 ml, complying with the requirements of ISO 385/2, class A.

4.2.5 Analytical balance.

4.2.6 Magnetic stirrer, efficient, with heating, for use with the flask (A) (see 4.2.7.1).

4.2.7 Entrainment apparatus, as shown in the figure[3)] or equivalent equipment for ensuring the displacement and entrainment of sulfur dioxide and its absorption in a solution of hydrogen peroxide.

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

4.2.7.1 Composition of apparatus

A : round-bottom flask, of capacity 250 ml or greater, with a ground tubulure 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 and E′ : 2 bubblers in series, connected to the condenser (B).

F : thermometer.

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

4.2.7.2 Check tests

The apparatus shall satisfy the following requirements :

4.2.7.2.1 Place in the flask (A) 100 ml of water and proceed as specified in 4.3.3.

The contents of the bubblers shall remain neutral.

4.2.7.2.2 Carry out the following operations :

a) Place in the flask (A) 100 ml of water. Introduce, using a pipette, 20 ml of the solution (4.1.10). Carry out the entrainment and the determination of sulfur dioxide as specified in 4.3.3 and 4.3.4.

b) Transfer, using a pipette, 20 ml of the iodine solution (4.1.8), 5 ml of the hydrochloric acid (4.1.3) and 1 ml of the starch solution (4.1.9) into a 100 ml conical flask (4.1).

Titrate, using a burette (4.2.4), with the solution (4.1.10) until the first coloration is discharged.

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

Operation b) shall not be carried out more than 15 min after completion of operation a) in order to avoid a possible change in the amount of sulfur dioxide contained in the potassium disulfite/Na_2H_2edta solution.

1) Hitherto designated as "0,02 N standard volumetric solution".

2) This product is intended to protect the sulfite ion from oxidation by air by complexing traces of copper ion.

3) Apparatus of the Lieb and Zaccherl type.

4.3 Procedure

4.3.1 Preparation of test sample

Thoroughly mix the laboratory sample.

4.3.2 Test portion

Weigh, to the nearest 0,01 g, a mass of the test sample (see 4.3.1) as specified in the following table.

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

This quantity may be increased, in particular 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[1] and mix well by shaking.

4.3.3 Entrainment

4.3.3.1 Place in the funnel (C) 50 ml of the hydrochloric acid (4.1.3).

4.3.3.2 In each of the bubblers (E and E′), place, by means of a pipette, 3 ml of the hydrogen peroxide solution (4.1.2), 0,1 ml of the bromophenol blue indicator solution (4.1.4) (see the note to 4.1.5) and neutralize the hydrogen peroxide solution with the sodium hydroxide solution (4.1.7).

4.3.3.3 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.

4.3.3.4 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).

4.3.3.5 Bring the mixture to boiling point in 30 min. Boil for 30 min, while passing a current of nitrogen and stirring with the stirrer (4.2.6).

4.3.4 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 (4.1.6 or 4.1.7) depending on the expected sulfur dioxide content.

NOTE — 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.

4.3.5 Check

If the volume V is less than 5 ml when the 0,01 mol/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 5).

4.3.6 Number of determinations

Carry out two determinations on the same test sample (4.3.1).

4.4 Expression of results

4.4.1 Method of calculation and formulae

If determination by the nephelometric method is not necessary (see 4.3.5), the sulfur dioxide content, expressed in milligrams per kilogram of sample, is given by the formula

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

where

m_0 is the mass, in grams, of the test portion (4.3.2);

V is the volume, in millilitres, of 0,01 mol/l (4.1.7) or 10 times the volume of 0,1 mol/l (4.1.6) sodium hydroxide solution used.

Take as the result the arithmetic mean of the values obtained in the two determinations (4.3.6), provided that the requirement for repeatability (see 4.4.2) is satisfied.

4.4.2 Repeatability[2]

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.

1) 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) See ISO 5725.

4.4.3 Reproducibility[1)]

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.

5 Nephelometric method

If the volume V was less than 5 ml when the 0,01 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.

5.1 Reagents

All reagents shall be of recognized analytical quality and sulfate free. The water shall be distilled water or water of equivalent purity, recently boiled.

5.1.1 Sulfuric acid, standard solution.

Place in a 1 000 ml 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.

5.1.2 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.

NOTE — Fresh solution should be prepared every week.

5.1.3 Barium chloride, stock solution.

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

5.1.4 Mixed solution.

Place in a 100 ml glass bottle (5.2.4) 15 ml of the barium chloride solution (5.1.3)[2)], 64 ml of water, 15 ml of 95 % (V/V)[2)] ethanol and 5 ml of the PVP solution (5.1.2)[2)].

Mix and bring to 20 °C using the water bath (5.2.3). Add, by means of a pipette, 30 min before the reagent is required for use, 1 ml of the sulfuric acid solution (5.1.1). Mix thoroughly.

5.2 Apparatus

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

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

5.2.3 Water bath, maintained at 20 ± 1 °C.

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

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

5.3 Procedure

5.3.1 Calibration curve

Into six 50 ml one-mark volumetric flasks (5.2.1), introduce 0 — 2 — 4 — 8 — 12 and 16 ml of the standard sulfuric acid solution (5.1.1), 20 ml of water, 0,1 ml of the bromophenol blue indicator solution (4.1.4), 1 ml of the hydrochloric acid (4.1.3) and 5 ml of the mixed solution (5.1.4), corresponding to 0 — 0,2 — 0,4 — 0,8 — 1,2 and 1,6 mg of sulfur dioxide, respectively. Dilute to the mark with water and mix.

Between 15 and 20 min after adding the reagent (5.1.4), measure the absorbance at 650 nm using the spectrometer (5.2.5).

Plot a calibration curve of the measured absorbances as a function of the masses of sulfur dioxide, in milligrams.

5.3.2 Determination

After the titration (4.3.4), pour the contents of the bubbler and the water used for washing it into a 50 ml one-mark volumetric flask (5.2.1), add 1 ml of the hydrochloric acid (4.1.3) and 5 ml of the mixed solution (5.1.4). Dilute to the mark with water and mix.

Between 15 and 20 min after adding the reagent (5.1.4), measure the absorbance at 650 nm using the spectrometer (5.2.5).

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

5.3.3 Number of determinations

Carry out the determination on the two solutions titrated in 4.3.4.

1) See ISO 5725.

2) Using a pipette.

5.4 Expression of results

The sulfur dioxide content, expressed in milligrams per kilogram of sample, is given by the formula

$$\frac{m_1 \times 1\,000}{m_0}$$

where

m_0 has the same meaning as in 4.4.1;

m_1 is the mass, in milligrams, of sulfur dioxide, corresponding to the absorbance measured in 5.3.2 and read from the calibration curve.

Take as the result the arithmetic mean of the values obtained in the two determinations (5.3.3).

6 Test report

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

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

Dimensions in millimetres

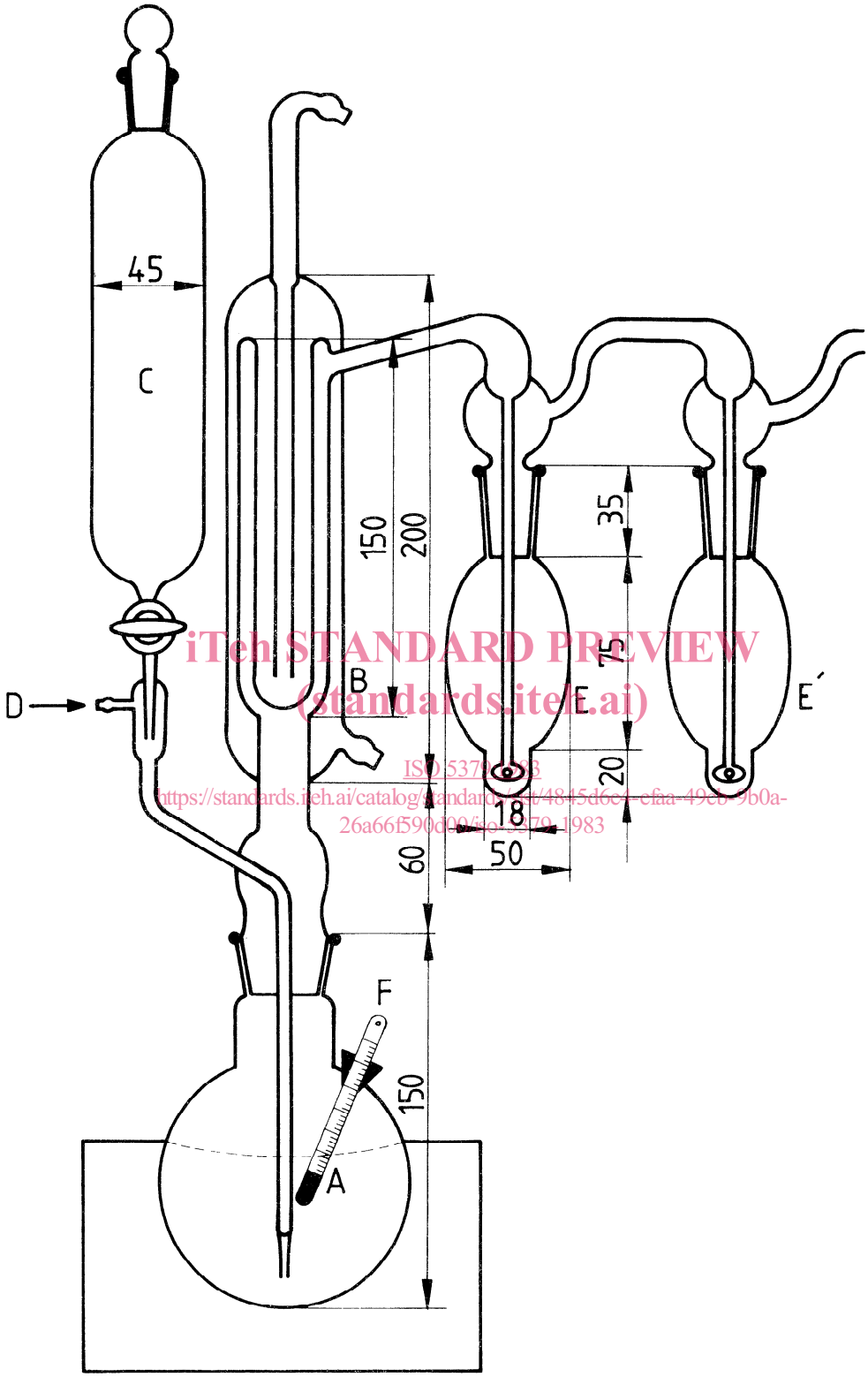

Figure — Diagram of entrainment apparatus