INTERNATIONAL STANDARD

ISO 6528-1

Second edition
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Rubber — Determination of total sulfur content —

Part 1:
Oxygen combustion flask method

Caoutchouc — Dosage du soufre total —
Partie 1: Méthode par combustion dans une fiole d'oxygène

Reference number
ISO 6528-1:1992(E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 6528-1 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 6528-1:1984), of which it constitutes a minor revision.

ISO 6528 consists of the following parts, under the general title *Rubber — Determination of total sulfur content*:

— *Part 1: Oxygen combustion flask method*

— *Part 2: Sodium peroxide fusion method*

— *Part 3: Furnace combustion method*

Annex A of this part of ISO 6528 is for information only.

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Rubber — Determination of total sulfur content —

Part 1:
Oxygen combustion flask method

1 Scope

This part of ISO 6528 specifies an oxygen combustion flask method for the determination of the total sulfur content of rubber.

The method is applicable for the determination of all the sulfur present in a rubber or rubber product, except that contained in barium sulfate.

It is applicable to NR, CR, SBR, BR, IR, IIR, EPDM, NBR and ebonite. (The meanings of these designations are given in ISO 1629:1987, *Rubber and latices — Nomenclature*.)

This method gives unreliable (usually low) results in the presence of lead, antimony, zinc, barium and calcium compounds. If calcium carbonate is the only calcium compound present, good results can be obtained by modifying the absorbing solution.

2 Principle

A test portion is ignited in an atmosphere of oxygen in an oxygen combustion flask containing hydrogen peroxide, the carbon and hydrogen of the organic matter being oxidized and the sulfur being converted to sulfuric acid. If necessary, the resulting solution is passed through a cation-exchange column to remove interfering metals. The eluate is titrated with barium perchlorate using thorin indicator.

WARNING — All recognized health and safety precautions shall be observed when carrying out this method of analysis.

3 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

NOTE 1 Two methods are described for the preparation of the indicator (3.8). The analyst may choose that best suited to his experience, equipment and needs.

3.1 Absorbing solution.

3.1.1 Hydrogen peroxide, 2 % (*m*/*m*), absorbing solution.

Dilute 1 volume of 30 % (*m*/*m*) hydrogen peroxide solution (H_2O_2) to 15 volumes with water.

WARNING — 30 % (*m*/*m*) hydrogen peroxide solution is very corrosive to the skin. Wear rubber or plastic gloves and goggles when handling it.

3.1.2 Hydrogen peroxide/hydrochloric acid.

Dilute 4 volumes of 30 % (*m*/*m*) hydrogen peroxide solution (H_2O_2) to 60 volumes with water and add 5 volumes of concentrated hydrochloric acid, (ρ_{20} = 1,18 Mg/m^3), and mix thoroughly.

3.2 Hydrochloric acid, 0,5 mol/dm^3 solution.

3.3 2-Propanol.

3.4 Barium perchlorate, 0,01 mol/dm^3 solution.

3.4.1 Preparation

Dissolve 3,363 g of barium perchlorate [$Ba(ClO_4)_2$] in 200 cm^3 of water. Adjust the pH to about 3,5 with hydrochloric acid solution (3.2). Make up to 1 dm^3 with 2-propanol (3.3).

3.4.2 Standardization

Standardize the barium perchlorate solution as follows.

Weigh, to the nearest 0,1 mg, 0,10 g of anhydrous sodium sulfate (Na_2SO_4) and dissolve the sodium sulfate in 10 cm^3 of water in a 100 cm^3 volumetric flask. Dilute to the mark with water.

Pipette exactly 10 cm^3 of this solution into a small flask or beaker, add 40 cm^3 of 2-propanol (3.3) to make the solution 80 % (V/V) alcoholic and titrate as specified in 7.3.3.

The concentration c of the barium perchlorate solution, expressed in moles per cubic decimetre, is given by the equation

$$c = \frac{0{,}1 \times m_1 \times 1\,000}{142{,}06 \times V_s}$$

where

m_1 is the mass, in grams, of sodium sulfate used;

V_s is the volume, in cubic centimetres, of the barium perchlorate solution required for the titration.

3.4.3 Storage

Barium perchlorate solutions deteriorate on storage and should be standardized sufficiently often so as to be able to detect changes in concentration of 0,000 5 mol/dm^3.

3.5 Cation exchange resin, strongly acidic, containing nuclear sulfonic acid active groups.

Before filling the column (4.6), allow the resin to stand in a beaker of distilled water to absorb water and become swollen.

Check that the following requirements are fulfilled before use and after regeneration (because of the large capacity of the resin to remove interfering cations, it may be used five to ten times before regeneration becomes necessary):

a) 10 cm^3 of 0,02 mol/dm^3 sulfuric acid solution shall be completely eluted with 15 cm^3 of water (test the last portion of the eluate for the absence of sulfate using thorin solution);

b) the ion exchange column shall be capable of removing 0,1 g of zinc, which is the most commonly interfering cation in rubber analyses.

Regenerate the resin by passing 10 cm^3 of 2 mol/dm^3 hydrochloric acid (3.6) through the resin bed, at the rate of 2 to 3 drops per second, then wash the resin bed with 20 cm^3 of water at a faster rate. Test the last few drops of the washings for the absence of sulfate using thorin solution.

3.6 Hydrochloric acid, 2 mol/dm^3 solution.

3.7 Oxygen, compressed, from a cylinder with an outlet suitable for introduction into the combustion flask (4.1).

3.8 Indicator.

Two types of indicator are described, both of which are suitable for use with the procedure described in this part of ISO 6528, i.e. thorin alone (3.8.1) and thorin plus methylene blue (3.8.2). The thorin used shall be a uniform red powder and shall give a clear, orange, aqueous solution.

3.8.1 Thorin {4-[(2-arsonophenyl)azo]-3-hydroxy-2,7-naphthalenedisulfonic acid, disodium salt}, 0,2 % (m/m) solution.

Dissolve 0,2 g of thorin in 100 cm^3 of water.

3.8.2 Thorin/methylene blue mixed indicator.

3.8.2.1 Thorin, 0,5 % (m/m) solution.

Dissolve 0,5 g of thorin in 100 cm^3 of water.

3.8.2.2 Methylene blue [3,7-bis(dimethylamino)-5-phenothiazinium chloride], CI 52015, 0,012 % (m/m) solution.

Dissolve 0,012 g of methylene blue in 100 cm^3 of water.

3.9 Potassium nitrate (KNO_3), 0,4 % (m/m) solution.

Dissolve 0,4 g of potassium nitrate in 100 cm^3 water.

3.10 Black or white paper, for wrapping the test portions.

NOTE 2 The papers are usually supplied in the form shown in figure 1. For use with smaller platinum baskets, they may be cut as shown in figure 2.

Although most commercial papers are readily combustible, the papers may be cut from regular filter papers and impregnated with the potassium nitrate solution (3.9) to aid combustion of the rubber. Drain the excess solution and dry the papers at

100 °C. If these treated papers are used, the procedure described in 7.3.2.2 shall be followed after the combustion.

NOTES

3 Papers used in electrical ignition units do not require the extension shown in figures 1 and 2.

4 Black papers usually ignite more rapidly with infra-red igniters.

4 Apparatus

Usual laboratory equipment, and

4.1 Oxygen combustion flask (Schöniger flask), thick-walled, of capacity 1 dm^3, with a platinum sample carrier (basket) and a strong pinch clamp or fastening device.

4.2 Combustion device, infra-red safety type with enclosed safety cabinet and door, and with electrical igniter or alcohol burner (see figures 3 and 4).

The infra-red igniter is the preferred apparatus because it is self-contained and properly shields the flask during combustion. All apparatus shall be operated in accordance with the manufacturer's instructions for safe operation.

4.3 Microburette, of capacity 5 cm^3 or 10 cm^3, graduated in 0,01 cm^3 divisions.

4.4 Magnetic stirrer.

4.5 High-intensity lamp (optional).

4.6 Ion-exchange column, comprising a small tube, about 170 mm long with an internal diameter of 10 mm, provided with a stopcock or sintered-glass disc at one end. The bottom shall be filled to a depth of about 10 mm with glass wool, and the rest of the column shall be filled with the resin (3.5).

4.7 Balance, capable of weighing to 0,1 mg.

5 Preparation of test sample

5.1 Finely mill the test sample on a laboratory roll mill and thoroughly homogenize it.

5.2 Due to the small masses of the test portions, the rubber and paper used for wrapping shall be protected from contamination. The use of forceps for handling the test portion and paper reduces the risk of contamination.

6 Safety precautions

The oxygen combustion flask has been in use in many laboratories for a number of years and has an excellent safety record. Provided that the safety precautions are rigorously observed, there is little danger of explosion.

6.1 Flasks of capacity 1 dm^3 shall not be used for test portions of mass greater than 80 mg.

Larger flasks are available for larger test portions, but successive burning in the same flask over the same liquid is effectively the same as using a larger flask and larger test portions. It is also safer.

6.2 Flasks shall be inspected for minute cracks before use. Destroy imperfect flasks.

6.3 The flask shall contain no residues of organic solvent or vapours. This could cause an explosion. Any such solvents used for cleaning shall be repeatedly rinsed out with water.

6.4 Pressure, generated by the rapid combustion of organic material, could cause the flask to explode, and combustion shall, therefore, be carried out behind a safety shield or hood. The hands and face of the operator shall be behind a shield before the flame reaches the test portion. Goggles or a face shield shall be worn during combustion. A self-contained safety chamber is, therefore, highly recommended.

6.5 The flask shall be left in the safety chamber until the last spark is extinguished. When it is removed, goggles or a face shield are recommended, since a slight vacuum is formed.

7 Procedure

Carry out the determination in duplicate.

7.1 Test portion

Weigh 40 mg to 80 mg of the test sample (see clause 5) [for sulfur contents up to about 4 % (m/m)] or an appropriately smaller mass in the case of higher sulfur contents. (The test portion shall not contain more than 3 mg of sulfur.)

7.2 Preparation of the apparatus

If calcium carbonate is absent, place 5 cm^3 of hydrogen peroxide absorbing solution (3.1.1) in the combustion flask (4.1). If the presence of calcium carbonate is suspected, place 5 cm^3 of hydrogen peroxide/hydrochloric acid absorbing solution (3.1.2) in the combustion flask. If using a stirring bar, place the stirring bar in the flask.

Wrap the test portion (see 7.1) in the paper (3.10) and fold so that the test portion is adequately contained and the paper extension extends above the platinum basket when placed therein. Do not allow the paper to become wet with absorbing solution.

Insert a tube from the oxygen cylinder (3.7) almost to the bottom of the flask and blow in oxygen strongly for at least 30 s. (Avoid splashing the absorbing solution.) Quickly remove the oxygen tube, close the flask with the combustion device and firmly attach the pinch clamp or fastening device.

7.3 Determination

7.3.1 Combustion

Place the flask in the safety chamber with the paper extension in line with the focal point of the infra-red igniter beam. Ensure that the paper does not touch the side of the flask. If using electrical ignition, attach the flask to the proper connections.

Ignite the paper and allow combustion to proceed to completion. When the test portion and paper have been completely incinerated, remove the flask from the safety chamber and examine for black carbon deposits. If these are noted, repeat the whole procedure using a new test portion. (The object of combustion is to attain as high a temperature as possible and to burn the paper and test portion completely.)

When proper combustion has been achieved, place the sealed flask on the magnetic stirrer (4.4), if one is being used, and stir for 1 h. If no stirrer is used, allow the flask to stand for 2 h, to allow the gases to be absorbed by the absorbing solution. Occasional shaking may speed up absorption.

7.3.2 Elimination of interfering substances

7.3.2.1 If interfering cations are absent, pour the contents of the flask into a 250 cm^3 beaker or flask. Wash down the sides of the combustion flask and sample carrier with 5 cm^3 of water and collect the washings in the same 250 cm^3 container. Repeat the washing twice more. Collect the solution and water from the washings in a 100 cm^3 conical flask and boil to decompose the excess hydrogen peroxide. Evaporate the solution to 5 cm^3 to 10 cm^3 volume and then proceed with the titration (see 7.3.3).

7.3.2.2 If there are interfering substances, pass the solution through the ion-exchange column (4.6). Allow the solution to pass through the column at a rate of about 2 to 3 drops per second into a 250 cm^3 flask. Regulate the stopcock to obtain this rate. Wash the sides of the flask, the stopper and the platinum basket three times with 5 cm^3 portions of water, pouring each successive washing through the column and collecting the washings in the same container. Elute the last of the washings using pressure or vacuum.

7.3.3 Titration

7.3.3.1 Add sufficient 2-propanol (3.3) to make the test solution 70 % (V/V) to 90 % (V/V) alcoholic. Insert a stirring bar, and place the flask on a magnetic stirrer.

7.3.3.2 If using the thorin solution (3.8.1), add 2 or 3 drops of the indicator solution, and place the beaker in the light beam of the high-intensity lamp (4.5), if being used. Titrate with the barium perchlorate solution (3.4), dropwise from the microburette (4.3), to the end-point (stable pink colour). Read the volume of barium perchlorate solution used to 0,01 cm^3.

7.3.3.3 If using the thorin/methylene blue solution (3.8.2), add 1 drop of the thorin solution (3.8.2.1) and sufficient of the methylene blue solution (3.8.2.2) to change the colour from orange to yellow. Do not add excess methylene blue, which would impart a green colour to the solution. Titrate with the barium perchlorate solution (3.4), dropwise from the microburette (4.3), to the end-point (stable pink colour). Read the volume of barium perchlorate solution used to 0,01 cm^3. As the end-point is approached, allow 2 s to 3 s between adding each increment and mix thoroughly after each addition.

7.4 Blank test

Carry out a blank test by repeating the procedure, but omitting the test portion.

8 Expression of results

8.1 Calculation

The total sulfur content, expressed as a percentage by mass, is given by the formula

$$\frac{(V_t - V_b) \times 0{,}032\ 1 \times c \times 100}{m_2}$$

where

V_b is the volume, in cubic centimetres, of barium perchlorate solution required for titration in the blank test;

V_t is the volume, in cubic centimetres, of barium perchlorate solution required for titration of the test portion;

c is the concentration, in moles per cubic decimetre, of the barium perchlorate solution;

m_2 is the mass, in grams, of the test portion;

0,032 1 is the mass, in grams, corresponding to 1 mmol of sulfur.

Calculate the result for each determination to the nearest 0,01 % (m/m) sulfur.

Take as the result the arithmetic mean of the results of two determinations provided that the requirements for repeatability (see 8.2) are satisfied.

Express the mean value to the nearest 0,05 % (m/m) sulfur.

8.2 Repeatability

The results of two determinations obtained by the same operator are acceptable if they comply with the requirements given in table 1.

Table 1 — Repeatability data

Mean of determined total sulfur contents, % (m/m)	Deviation from the mean
< 1	± 0,1
1 to 5	± 0,2
> 5	± 0,3

EXAMPLE

Test result No. 1:	total sulfur content 2,8 % (m/m)
Test result No. 2:	total sulfur content 3,2 % (m/m)
Mean:	total sulfur content 3,0 % (m/m)

The test results are acceptable because they do not differ by more than ± 0,2 from the mean value for a total sulfur content of 3 % (m/m).

9 Test report

The test report shall include the following information:

a) all details necessary for the complete identification of the sample;

b) a reference to this part of ISO 6528;

c) any deviations from the procedure specified, as well as any unusual incidents noted during the determinations which might have influenced the results;

d) the mean value of the results of the two determinations.

Dimensions are approximate and in millimetres

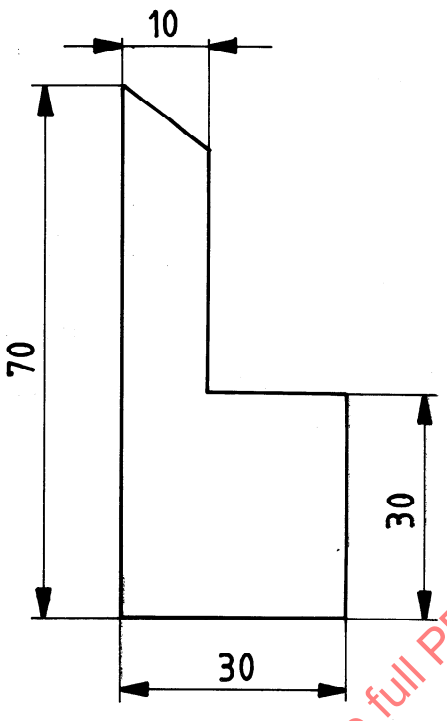

Figure 1 — Form of paper for wrapping test portions

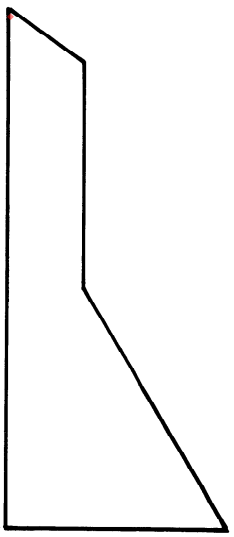

Figure 2 — Cut form of paper for wrapping test portions (for use with smaller platinum baskets)

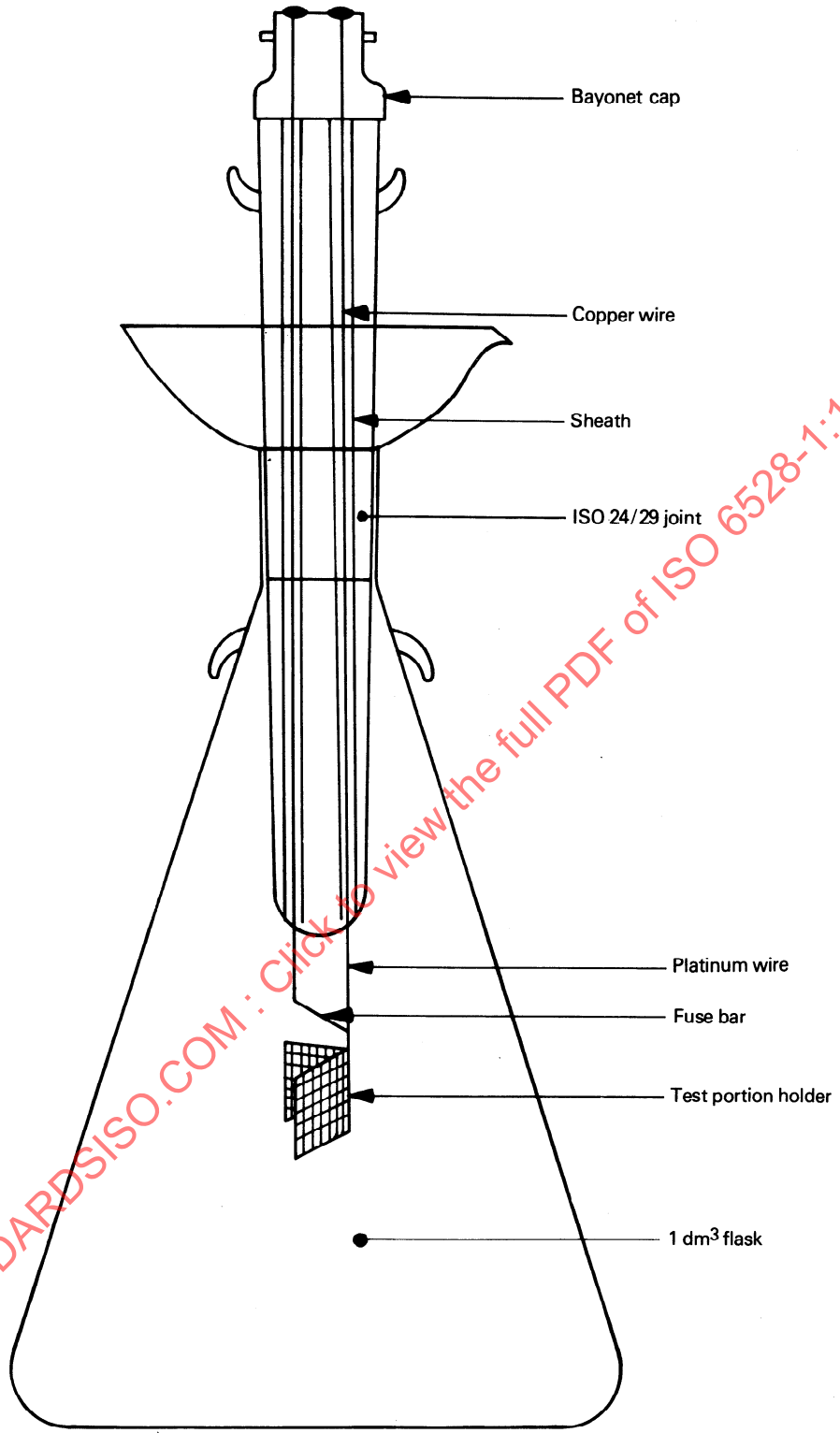

Figure 3 — Typical combustion apparatus for the determination of sulfur by the oxygen combustion flask method