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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

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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 6528/1 was developed by Technical Committee ISO/TC 45, *Rubber and rubber products*, and was circulated to the member bodies in May 1982.

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

Australia	Indonesia	Spain
Belgium	Italy	Sri Lanka
Canada	Korea, Rep. of	Sweden
China	Malaysia	Thailand
Czechoslovakia	Netherlands	Turkey
Denmark	New Zealand	United Kingdom
France	Nigeria	USA
Germany, F.R.	Poland	USSR
Hungary	Romania	
India	South Africa, Rep. of	

No member body expressed disapproval of the document.

Rubber — Determination of total sulfur content

Part 1: Oxygen combustion flask method

1 Scope and field of application

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 ebonite¹⁾.

This method gives unreliable (usually low) results in the presence of lead, antimony, 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

Ignition of a test portion 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, passage of the resulting solution through a cation-exchange column to remove interfering metals, such as zinc. Titration of the eluate with barium perchlorate using thiorin indicator.

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

3 Reagents²⁾

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

NOTE — Two methods are described for the preparation of the indicator. 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, $\rho_{20} = 1,18 \text{ Mg/m}^3$, and mix thoroughly.

3.2 Perchloric acid solution.

Mix 1 volume of 50 % (m/m) perchloric acid ($HClO_4$) solution with 1 volume of water.

WARNING — Perchloric acid should be handled with extreme caution. Contact with dust or organic particulates may, in many cases, cause ignition. Contact with organic materials must be avoided.

3.3 2-Propanol.

3.4 Barium perchlorate, 0,01 mol/dm³ solution.

3.4.1 Preparation

Dissolve 3,363 g of barium perchlorate [$Ba(ClO_4)_2$] in 200 cm³ of water. Adjust the pH to about 3,5 with the perchloric acid solution (3.2). Make up to 1 dm³ with the 2-propanol (3.3).

3.4.2 Standardization

Standardize the barium perchlorate solution as follows.

1) See ISO 1629, *Rubber and latices — Nomenclature*.

2) The term millilitre (ml) is commonly used as a special name for the cubic centimetre (cm³), in accordance with a decision of the Twelfth Conférence générale des Poids et Mesures. The term millilitre is acceptable, in general, for references in International Standards to capacities of volumetric glassware and to liquid volumes.

Weigh, to the nearest 0,1 mg, 0,10 g of anhydrous sodium sulfate (Na_2SO_4) and dissolve in 10 cm³ of water in a 100 cm³ volumetric flask. Dilute to the mark with water.

Pipette exactly 10 cm³ of this solution into a small flask or beaker, add 40 cm³ 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

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

where

m 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/dm³.

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

NOTE — There are many types and particle size ranges of resins available. Details of one type of resin which has been found to be satisfactory may be obtained from the Secretariat of ISO/TC 45 (BSI) or from ISO Central Secretariat.

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):

- 10 cm³ of 0,02 mol/dm³ sulfuric acid solution should be completely eluted with 15 cm³ of water. Test the last portion of the eluate for the absence of sulfate using thorin solution;
- the ion exchange column should 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 cm³ of 2 mol/dm³ hydrochloric acid through the resin bed, at the rate of 2 to 3 drops per second, then wash the resin bed with 20 cm³ 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, $c(\text{HCl}) = 2 \text{ mol/dm}^3$.

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-arsenophenyl)azol-3-hydroxy-2,7-naphthalenedisulfonic acid, disodium salt]}, 0,2 % (m/m) solution.

Dissolve 0,2 g of thorin in 100 cm³ 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 cm³ 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 cm³ of water.

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

Dissolve 0,4 g of potassium nitrate in 100 cm³ of water.

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

NOTES

1 Details of suitable, commercially available material may be obtained from the Secretariat of ISO/TC 45 (BSI) or from ISO Central Secretariat.

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.

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 must be followed after the combustion.

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 dm³, 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, 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 according to the manufacturer's instructions for safe operation.

4.3 Microburette, of capacity 5 or 10 cm³, graduated in 0,01 cm³ 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 0,000 1 g.

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 dm³ 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 should 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 to 80 mg of the test sample (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 cm³ of hydrogen peroxide absorbing solution (3.1.1) in the combustion flask (4.1). If the presence of calcium carbonate is suspected, place 5 cm³ 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 (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 splattering 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 sides 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, 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 interferences

7.3.2.1 If interfering cations are absent, pour the contents of the flask into a 250 cm³ beaker or flask. Wash down the sides of the combustion flask and sample carrier with 5 cm³ of water and collect the washings in the same 250 cm³ container. Repeat the washing twice more and then proceed with the titration (see 7.3.3).

7.3.2.2 If doubt exists about the presence of interfering cations, if potassium nitrate impregnated papers have been used in the combustion, or if zinc or other cations are thought to be present, 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 cm³ flask. Regulate the stopcock to obtain this rate. Wash the sides of the flask, the stopper and the platinum basket three times with 5 cm³ 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 to make the test solution 70 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 to 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).

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.

NOTE — Do not add excess methylene blue, which would impart a green colour to the solution.

7.3.3.4 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 cm³. As the end-point is approached, allow 2 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

$$\frac{(V_t - V_b) \times 0,0321 \times c \times 100}{m}$$

where

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

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

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

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

0,0321 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 mean value 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 the table.

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 %
Test result No. 2:	total sulfur content 3,2 %
Mean:	total sulfur content 3,0 %

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 %.

9 Test report

The test report shall include the following information:

- all details necessary for the complete identification of the sample;
- a reference to this part of ISO 6528;
- any deviations from the procedure specified or any unusual incidents noted during the determinations which might have influenced the results;
- the mean value of the results of the two determinations.

Dimensions are approximate and in millimetres

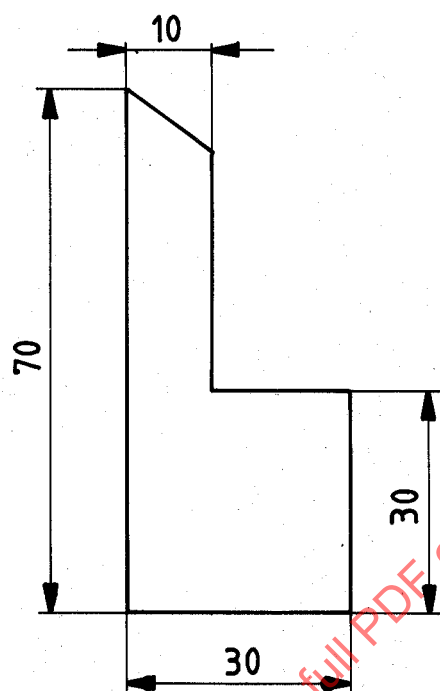


Figure 1 — Form of paper for wrapping test portions

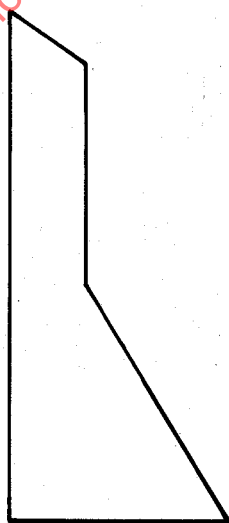


Figure 2 — Cut form of paper for wrapping test portions (for use with smaller platinum baskets)

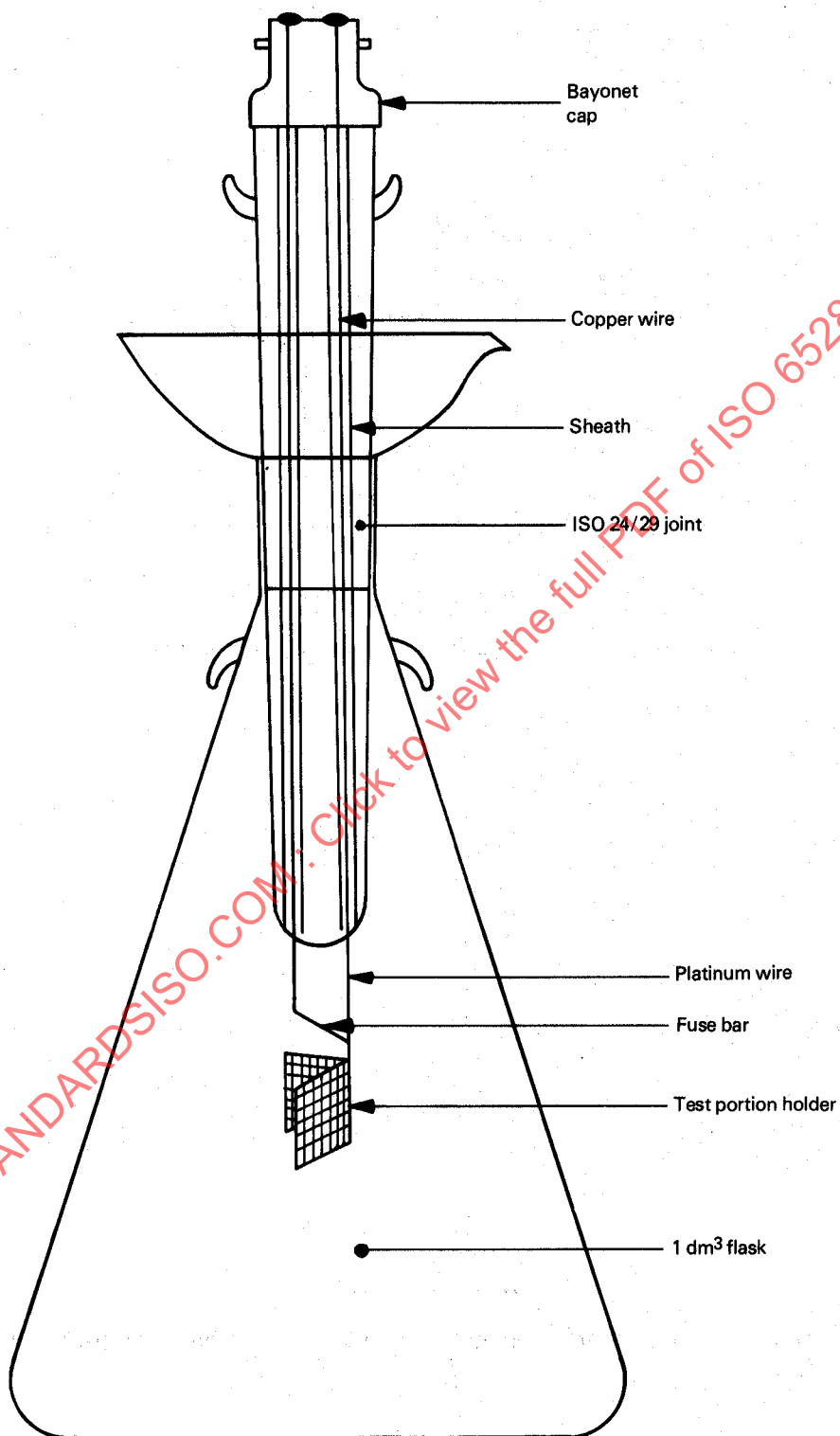


Figure 3 — Typical combustion apparatus for the determination of sulfur by the oxygen combustion flask method