INTERNATIONAL STANDARD

ISO 6528-2

Second edition
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Rubber — Determination of total sulfur content —

Part 2:
Sodium peroxide fusion method

Caoutchouc — Dosage du soufre total —

Partie 2: Méthode par fusion au peroxyde de sodium

Reference number
ISO 6528-2:1992(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 6528-2 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 6528-2:1983), 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*

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Rubber — Determination of total sulfur content —

Part 2:
Sodium peroxide fusion method

1 Scope

This part of ISO 6528 specifies a sodium peroxide fusion 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, including that contained in barium sulfate which may be used as a filler.

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*.)

2 Principle

A test portion of rubber is oxidized with sodium peroxide, with a few drops of ethylene glycol added, in a suitable bomb reaction vessel. The sulfur is converted to sulfate ions. The sulfate is determined by gravimetric analysis as barium sulfate.

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

Failure to heed the instructions given in this International Standard, or those of the manufacturer of the device used, may result in explosions.

3 Reagents and materials

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

3.1 Ethylene glycol.

3.2 Sodium peroxide, granulated.

3.3 Sodium carbonate, anhydrous.

3.4 Calcium carbonate, anhydrous.

3.5 Hydrochloric acid, solution.

Add 1 volume of concentrated hydrochloric acid ($\rho = 1{,}18$ Mg/m^3) to 4 volumes of water.

3.6 Barium chloride, 50 g/dm^3 solution.

Dissolve 50 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in water, add 0,5 cm^3 of concentrated hydrochloric acid ($\rho = 1{,}18$ Mg/m^3) and dilute to 1 dm^3.

3.7 Acetic acid, 4 mol/dm^3 solution.

3.8 Cupferron (*N*-nitroso-*N*-phenylhydroxylamine, ammonium salt), 60 g/dm^3 solution.

Dissolve 6 g of cupferron in 100 cm^3 of water.

3.9 Silica gel or **calcium chloride**, for use in the desiccator (4.9).

3.10 pH indicator paper.

3.11 Ashless filter paper, high density.

4 Apparatus

Usual laboratory equipment, and

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

4.2 Combustion bomb (Parr or similar), gas- or electrically fired.

WARNING — The bomb must be operated in accordance with the safety instructions given by the manufacturer.

4.3 Nickel crucible with lid, to fit into the bomb (if a gas-fired bomb is used). Suitable dimensions are:

diameter	25 mm;
height	40 mm.

NOTE 1 A fusion cup is used with the electrically fired bomb.

4.4 Safety oven.

4.5 Muffle furnace, capable of being maintained at 600 °C ± 25 °C.

4.6 Filtration equipment.

4.7 Fused-silica filter-crucible, of pore size less than 15 µm, or **fused-silica crucible** of capacity 30 cm^3.

4.8 Nickel crucible, of capacity 30 cm^3.

4.9 Desiccator.

5 Procedure

Carry out at least two determinations.

WARNING — All hazardous operations must be performed behind a safety shield.

5.1 Test portion

Weigh, to the nearest 0,1 mg, 0,05 g to 0,30 g of finely cut or ground test sample.

5.2 Oxidation

Carry out the oxidation using either a gas-fired bomb (see 5.2.1) or an electrically fired bomb (see 5.2.2).

5.2.1 Gas-fired bomb

5.2.1.1 Place 7 g to 7,5 g of sodium peroxide (3.2) in the nickel crucible with lid (4.3). Add the test portion (5.1) and 8 drops (about 150 mg) of ethylene glycol (3.1). Add a further 7 g to 7,5 g of sodium peroxide so that the crucible is filled to about 2 mm from the top. Mix by stirring with a glass rod. Place the crucible in the bomb (4.2).

WARNING — The sodium peroxide must be free from water. If white particles are present, the reagent may ignite on contact with air. This may be prevented by covering the sodium peroxide with a 1 mm layer of sodium carbonate (3.3).

5.2.1.2 Place the lid on the bomb and tighten it by hand.

5.2.1.3 Adjust the flame in the safety oven (4.4), prior to firing the bomb containing the test portion, by placing an empty bomb in the oven and adjusting the flame so that it is a few millimetres from the base of the bomb. Remove the empty bomb and replace it with the bomb containing the test portion, ensuring that the flame is at the same height.

5.2.1.4 Heat the bomb for 3 min after ignition, which usually starts about 10 s to 30 s after placing the bomb above the gas flame, and which can be detected by a cracking sound and the appearance of a red glow on the bottom of the bomb.

5.2.2 Electrically fired bomb

5.2.2.1 Place 7 g to 7,5 g of sodium peroxide (3.2) in the fusion cup. Add the test portion (5.1) and 8 drops (about 150 mg) of ethylene glycol (3.1). Add a further 7 g to 7,5 g of sodium peroxide so that the cup is filled to about 2 mm from the top. Mix by stirring with a glass rod.

WARNING — See WARNING note to 5.2.1.1.

5.2.2.2 Assemble the bomb and tap it gently to settle the contents.

5.2.2.3 Carry out the oxidation following the manufacturer's instructions for safe operation.

5.3 Determination

5.3.1 In the case of a gas-fired bomb, cool the bomb, open it and remove the crucible.

WARNING — If the bomb is cooled in water, take care that water does not reach the joint between the plug and the bomb.

Alternatively, dismantle the electrically fired bomb.

5.3.2 Place the crucible and lid, or the contents of the electrically fired bomb together with the head and fusion cup, in a 600 cm^3 beaker, completely flood them with water, and immediately cover the beaker with a watch glass.

WARNING — If doubt exists as to whether the bomb has been successfully fired, do not place the contents of the bomb in water, but spread them on dry sand and spray with water from a safe distance.

Wash with copious amounts of water. FAILURE TO FOLLOW THESE PRECAUTIONS MAY RESULT IN AN EXPLOSION DUE TO THE VIOLENT REACTION OF SODIUM PEROXIDE WITH WATER.

5.3.3 When the reaction is complete, heat the beaker and its contents, then cool. Rinse the crucible and lid, or the fusion cup, etc., with water as it is removed from the beaker.

5.3.4 Slowly add acetic solution (3.7) until the pH is about 4, checking by means of the pH indicator paper (3.10). Heat to boiling and filter into another 600 cm^3 beaker. Wash the filter paper with 20 cm^3 of water acidified with 1 cm^3 of acetic acid solution, collecting the washings in the beaker containing the filtrate. If there is no residue proceed directly to 5.3.7.

5.3.5 If there is a residue, transfer it to the nickel crucible (4.8), add 0,5 g of sodium carbonate (3.3) and 0,5 g of calcium carbonate (3.4) and heat to a clear melt. Cool the crucible and place it in 100 cm^3 of water in a 200 cm^3 beaker. Heat to about 50 °C for 10 min, then filter. Wash the residue with water. Acidify the filtrate with hydrochloric acid solution (3.5) until the pH is about 4.

5.3.6 If titanium is present, indicated by a yellow-orange colour of the solution, cool, then add, while stirring, 5 cm^3 of cupferron solution (3.8). Titanium salts will precipitate. Allow the solution to stand for 30 min and filter. Wash with water, and combine the washings and the filtrate with that obtained in 5.3.4.

5.3.7 Dilute the combined filtrate(s) and washings to 300 cm^3 to 400 cm^3, heat to boiling and add 10 cm^3 of hot barium chloride solution (3.6). Allow to stand for 5 min, then add, dropwise, additional barium chloride solution to ascertain whether the reaction is complete. If additional precipitation is noted, add more barium chloride until precipitation ceases. Allow the solution and precipitate to stand for at least 4 h.

5.3.8 Heat the fused-silica filter-crucible or fused-silica crucible (4.7) in the muffle furnace (4.5) maintained at 600 °C, cool in the desiccator (4.9) and weigh.

5.3.9 Collect the precipitate obtained in 5.3.7 on the ashless filter paper (3.11) or in the filter-crucible (4.7) and wash with warm water.

If the precipitate was collected on the filter paper, transfer to the crucible prepared in 5.3.8, ignite the filter paper and place the crucible in the muffle furnace (4.5), maintained at 600 °C, for 30 min.

If the precipitate was collected in the filter-crucible, place the filter-crucible in the muffle furnace (4.5), at 600 °C, for 30 min.

5.3.10 Remove the crucible and its contents from the muffle furnace, place in the desiccator (4.9), cool to room temperature and weigh to the nearest 0,1 mg.

5.3.11 Repeat the operations of heating in the muffle furnace, cooling in the desiccator and weighing until the mass of the crucible and its contents does not differ by more than 0,3 mg, or 0,5 % of the mass of the ash, in successive weighings.

5.4 Blank test

Carry out a blank test using the same reagents in the same quantities, in the same crucible or filter-crucible and using the same procedures, but omitting the test portion.

6 Expression of results

6.1 Calculation

Calculate the total sulfur content, expressed as a percentage by mass, using the formula

$$\frac{(m_2 - m_1) \times 0{,}137\,4 \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the empty crucible or filter-crucible;

m_2 is the mass, in grams, of the crucible or filter-crucible and the barium sulfate obtained in the determination, corrected for the value in the blank test.

Take as the result the arithmetic mean of at least two determinations, provided that the requirements for repeatability (see 6.2) are satisfied.

6.2 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 $\pm$ 0,2 from the mean value for a total sulfur content of 3 % (m/m).

7 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.