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## Rubber — Determination of total sulfur content —

## Part 3 :
## Furnace combustion method

*Caoutchouc — Dosage du soufre total —*

*Partie 3 : Méthode par combustion au four*

Reference number
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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 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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6528-3 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Printed in Switzerland

# Rubber — Determination of total sulfur content —

## Part 3 :
## Furnace combustion method

## 0 Introduction

Parts 1 and 2 of ISO 6528 give alternative methods for the determination of the total sulfur content of rubber.

## 1 Scope and field of application

**1.1** This part of ISO 6528 specifies a method for the determination, by combustion in a furnace, of the total sulfur content of raw rubbers, unvulcanized compounded rubbers and vulcanizates, including sulfur present as barium sulfate, calcium sulfate and lithopone.

**1.2** It is applicable to chlorinated rubbers, nitrile rubbers and hydrocarbon rubbers (including natural rubber). The determination is not affected by the presence of metal salts which form insoluble sulfates.

## 2 References

ISO 383, *Laboratory glassware — Interchangeable conical ground joints.*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO 6528, *Rubber — Determination of total sulfur content*

- *Part 1 : Oxygen combustion flask method.*
- *Part 2 : Sodium peroxide fusion method.*

## 3 Principle

**3.1** A test portion is burnt in a stream of oxygen in the presence of a catalyst, the oxides of sulfur are passed into hydrogen peroxide and the resulting sulfuric acid is determined by titration.

**3.2** One of two titration methods is used, depending on the type of rubber combusted. An alkalimetric titration is used when no chlorine or nitrogen combustion products are present and a barium perchlorate titration is used when chlorine and/or nitrogen is present.

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

## 4 Reagents

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

### 4.1 Reagents for the combustion

**4.1.1 Calcium chloride,** anhydrous, particle size approximately 800 to 1 400 µm (14 to 22 mesh ASTM).

**4.1.2 Catalyst.**

Mix together 0,8 g of dry vanadium pentoxide and 0,2 g of zinc oxide for each determination. The vanadium pentoxide shall be previously dried by heating in a shallow dish at 140 to 160 °C for 16 h. It shall be cooled and stored in a desiccator.

**4.1.3 Hydrogen peroxide,** 3 % $(V/V)$ solution.

Carefully mix 1 volume of 30 % hydrogen peroxide with 9 volumes of water.

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

**4.1.4 Magnesium perchlorate,** anhydrous, particle size 800 to 1 400 µm (14 to 22 mesh ASTM).

**WARNING — Magnesium perchlorate can cause irritation of skin and mucous membranes.**

**4.1.5 Supply of oxygen,** e.g. a cylinder with suitable regulator to give a pressure of not less than 35 kPa.

**4.1.6 Carbon dioxide absorbent** (sodium hydroxide absorbed on synthetic silicate), particle size 800 to 1 400 µm (14 to 22 mesh ASTM), preferably of the self-indicating type.

## 4.2 Reagents for titration

**4.2.1 Perchloric acid,** dilute solution.

Carefully mix 1 volume of 50 % perchloric acid ($HClO_4$) solution with 1 volume of water.

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

**4.2.2 2-Propanol.**

Use re-distilled 2-propanol if analytical grade reagent is not available.

**4.2.3 Barium perchlorate,** standard volumetric solution, $c[Ba(ClO_4)_2] = 0{,}01$ mol/dm$^3$.

**4.2.3.1** Preparation

Dissolve 3,363 g of barium perchlorate in 200 cm$^3$ of water. Adjust the pH to about 3,5 with the dilute perchloric acid (4.2.1). Make up to 1 dm$^3$ with the 2-propanol (4.2.2).

**4.2.3.2** Standardization

Standardize the barium perchlorate by weighing, to ± 0,1 mg, approximately 0,10 g anhydrous sodium sulfate and dissolving it in 10 cm$^3$ of water in a 100 cm$^3$ one-mark volumetric flask. Make up to the mark with water. Pipette exactly 10 cm$^3$ of this solution into a small flask or beaker, add 40 cm$^3$ of the 2-propanol to make the solution 80 % alcohol by volume and titrate to the same end-point as will be used in the analysis of rubbers, using the same indicator system (see 7.2).

Determine the molar concentration, $c_1$, of the barium perchlorate solution, expressed in moles of $Ba(ClO_4)_2$ per cubic decimetre, from the formula

$$\frac{0{,}1 \times m_s \times 1\,000}{142{,}06 \times V_s}$$

where

$m_s$ is the mass, in grams, of sodium sulfate;

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

**4.2.3.3** Storage

Preparations of barium perchlorate deteriorate on storage and should be standardized often enough to detect a change in concentration of 0,000 5 mol/dm$^3$.

**4.2.4 Sodium hydroxide solution,** $c(NaOH) = 0{,}02$ mol/dm$^3$, accurately standardized or commercial solution.

**4.2.5 Indicator systems for barium perchlorate titrations.**

Two systems are given, both suitable for use in this part of ISO 6528.

**4.2.5.1 Thorin indicator.**

Dissolve 0,2 g of Thorin[1] in 100 cm$^3$ of water.

The reagent shall be a uniform red powder and produce a clear orange aqueous solution.

**4.2.5.2 Thorin and methylene blue indicator.**

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

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

**4.2.6 Indicator system for alkalimetric titration.**

Dissolve 0,125 g of methyl red and 0,04 g of methylene blue in 100 cm$^3$ of methanol.

**4.2.7 Hydrochloric acid,** $c(HCl) = 2$ mol/dm$^3$.

Dilute 1 volume of hydrochloric acid ($\varrho = 1{,}18$ Mg/m$^3$) with 5 volumes of water.

**4.2.8 Cation exchange resin,** strongly acidic, containing nuclear sulfonic acid active groups.[2]

Before filling the column (5.6) 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 sulfuric acid solution, $c(H_2SO_4) = 0{,}02$ mol/dm$^3$, 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 (4.2.5.1);

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.

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1) Thorin is 2,2-hydroxy-3,6-disulfo-1-naphthyl-azobenzene-arsonic acid.

2) There are many types and particle size ranges of resin available. DOWEX 50W-8X spheres 75 to 150 µm (100 to 200 mesh) from J.T. Baker Company, 222 Red School Lane, Phillipsburg, New Jersey 088 65, USA, has been found satisfactory. This information is given for the convenience of users of this part of ISO 6528 and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Regenerate the resin by passing 10 $cm^3$ of the hydrochloric acid (4.2.7) through the resin bed, at the rate of 2 or 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 (4.2.5.1).

## 5 Apparatus

Ordinary laboratory apparatus, glassware having joints complying with the requirements of ISO 383, and

**5.1 Combustion apparatus** (see figure 1).

**5.1.1 Flowmeter (A),** to indicate 0,8 to 1 $cm^3/s$.

**5.1.2 Purifying train,** consisting of two U-tubes (B and C) with side arms, connected to the calibrated flowmeter (A).

**5.1.2.1 U-tube (B),** with side arms, contains the magnesium perchlorate (4.1.4).

**5.1.2.2 U-tube (C),** with side arms, contains the carbon dioxide absorbent (4.1.6).

**5.1.3 Silica combustion tube,** with heater for bent-end (D). The total horizontal length is 650 to 670 mm. It consists of a satin or transparent silica tube of 16 mm internal diameter fused at one end to a transparent silica tube, which narrows to 7 mm internal diameter. The other end is fused to a 24/29 cone provided with hooks. The overall measurement across the 24/29 cone and hooks shall not exceed 30 mm. The length of the wide tube is 480 mm; the narrower tube is horizontal for 170 to 190 mm and then bends downwards at a right angle and continues for a further 77 mm, including a 10/19 cone with hooks in the same plane as the bend. The cone is greased with sulfur-free high-temperature-resisting silicone grease. To prevent condensation of vapour in the bent-end of the combustion tube and in the neighbouring ground glass joint, the bent portion is electrically heated to a temperature of 400 to 500 °C which is controlled by suitable means.

The 24/29 cone is fitted with a socket provided with hooks, and this is connected by rubber tubing to the U-tube (C) of the purifying train.

A screen of heat-resistant, thermally insulating material is fixed at the exit end of the combustion tube so that radiated heat from the furnace does not affect the solutions in the absorbing vessels.

**5.1.4 Silica rod with handle and button (E).** The diameter of the rod shall be 7 to 8 mm and the diameter of the button 12 to 13 mm. The overall length is 125 mm.

**5.1.5 Magnetic stainless steel cylinder (F).** The diameter is 13 to 14 mm, the length 10 to 11 mm. Also, a magnet capable of moving the cylinder (F) from outside the silica combustion tube (D) is required.

**5.1.6 Combustion boat (transparent silica) with handle (G).** Outside measurements: overall length 53 to 55 mm, width 11 to 13 mm and depth 7 to 9 mm.

**5.1.7 Electric combustion furnace with temperature indicator and controller (H),** about 320 mm long, capable of maintaining a temperature of 1 000 ± 20 °C.

**5.2 Absorption train.**

**5.2.1 Primary absorbing vessel (J)** (see figure 2).

This is in the shape of a U-tube and is joined to the combustion tube by a 10/19 socket which is 70 to 80 mm (measured vertically) from the bottom of the U-tube. The internal diameter of this limb is 6 mm and the stopcock is 30 to 35 mm from the bottom of the tube. A sintered glass disc (porosity grade P 40, see ISO 4793), diameter 30 mm, is sealed in the other limb at the lower end of the expanded portion, which is 70 mm long and 30 mm in diameter. This limb then narrows to 14 mm diameter for 30 mm and terminates in a 12/13 socket.

**5.2.2 Secondary absorbing vessel (K).**

This consists of a 20 or 25 $cm^3$ pear-shaped flask with a 10/19 socket at the neck and side arm. The side arm is fitted with a 10/19 cone and delivery tube which is connected via a calcium chloride tube (L) to a needle valve (M) and suction line. The two absorbing vessels are connected to each other by an inverted U-tube of 7 mm internal diameter with a 12/13 cone at one end and a 10/19 cone and delivery tube at the other end. The delivery tube ends not more than 1 mm from the bottom of the secondary vessel. All ground glass joints of the absorption train are secured by springs and no grease is used.

**5.2.3 Calcium chloride tube (L).**

**5.2.4 Needle valve (M).**

**5.3 Burette,** 10 $cm^3$ capacity, reading to 0,01 $cm^3$.

**5.4 Magnetic stirrer,** (desirable, but not essential).

**5.5 Daylight matching lamp** (desirable, but not essential).

**5.6 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 (4.2.8).

## 6 Preparation of test sample

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

**6.2** Due to the small masses of the test portions, the rubber shall be protected from contamination. The use of forceps for handling the test portion reduces the risk of contamination.

## 7 Procedure

### 7.1 Combustion

**7.1.1** Heat the combustion furnace (5.1.7) to 1 000 ± 20 °C and the bent-end of the combustion tube (5.1.3) to 400 to 500 °C.

**7.1.2** Place a layer of about 0,3 g of the catalyst (4.1.2) in the previously ignited combustion boat (5.1.6). Weigh accurately about 50 ± 0,1 mg (10 ± 0,1 mg in the case of ebonite or thioplasts) of the test sample and distribute this test portion in the prepared boat. Cover the test portion with the remainder of the catalyst.

**7.1.3** Connect the absorbing vessels (5.2.1 and 5.2.2) to the combustion tube, remove the inverted U-tube and from a graduated pipette add 15 cm$^3$ of the hydrogen peroxide solution (4.1.3) to the primary absorbing vessel via the 12/13 socket and 5 cm$^3$ to the secondary absorbing vessel. Put the inverted U-tube back in place and connect the side arm of the secondary absorbing vessel via the calcium chloride tube (5.2.3) to the needle valve (5.2.4) attached to the suction line.

**7.1.4** Connect the oxygen supply (4.1.5) to the flowmeter (5.1.1) and purifying train (5.1.2), and adjust the rate of flow to 0,8 cm$^3$/s. To ensure a steady stream of oxygen, a pressure of not less than 35 kPa shall be shown on the delivery pressure gauge of the oxygen cylinder. Disconnect the oxygen from the flowmeter without changing the setting of the oxygen regulator.

**7.1.5** Insert the boat in the mouth of the combustion tube, followed by the silica rod (5.1.4) and steel cylinder (5.1.5). Close the combustion tube with the 24/29 socket and connect to the purifying train and flowmeter. Adjust the suction to draw purified air through the combustion tube and absorbing vessels at a rate of 1 cm$^3$/s as indicated by the flowmeter. Connect the oxygen to the flowmeter so that the previously adjusted oxygen is drawn through the combustion tube and absorption train.

**7.1.6** By means of the magnet, steel cylinder and silica rod, slide the boat to a position 10 mm from the furnace and leave it for 2 min. In order to maintain a steady combustion rate, propel the boat slowly forward at a rate of about 0,5 cm/s to the hottest zone of the furnace. (If the advance of the boat into the hot zone is too rapid, excessive fluctuations of the flowmeter will be noted.) Withdraw the steel cylinder to the mouth of the tube immediately the boat reaches the hottest zone of the furnace. When destruction of the organic material is complete, as indicated by stability of the flowmeter, continue the combustion for a further 30 min to ensure decomposition of alkaline earth sulfates.

**7.1.7** Switch off the current to the bent-end heater, disconnect the oxygen from the flowmeter, and cool the hot 10/19 joint of the primary absorbing vessel to room temperature, for example with a jet of compressed air. Then disconnect the suction from the side arm of the secondary absorbing vessel and remove the silica rod and boat.

NOTE — To clean the boat for further determinations, it is advisable to withdraw the boat while the contents are still molten and quickly pour the molten mass into a beaker containing sand, applying heat to the boat if necessary. Suspend the boat in warm concentrated hydrochloric acid and then wash with water to remove all traces of acid and finally ignite.

**7.1.8** Connect a hand bellows to the side arm and gently blow the liquid from the secondary absorbing vessel into the primary absorbing vessel and round the lower U-tube until it is just above the 10/19 joint. Carefully open the stopcock, allow the liquid to run slowly into a flask and continue blowing until all the solution is transferred. Collect the absorbing solution in a 250 cm$^3$ conical flask.

**7.1.9** Add about 8 cm$^3$ of water through the side arm of the secondary absorbing vessel and with the hand bellows transfer the liquid to the primary vessel, wash the U-tube just above the 10/19 joint and collect the washings in the conical flask (already containing the absorbing solution). Disconnect the apparatus at the 12/13 joint and rinse down the side of the wide limb of the U-tube with 10 cm$^3$ of water. Put the 12/13 joint back in place and force the liquid into the U-tube and thence through the stopcock into the conical flask. Repeat the washing with a further 10 cm$^3$ of water, combining all washes in the flask.

**7.1.10** If the rubber contains chlorine, a small amount of zinc chloride will distil over. This zinc interference shall be removed by percolating the solution of 7.1.9 through the ion exchange column (5.6). Allow the solution to trickle through the prepared column at a rate of about 2 or 3 drops per second into a second 250 cm$^3$ conical flask. Adjust the stopcock to obtain this rate. Wash the sides of the first flask with water, pouring each successive washing through the column and collecting the washings in the second flask. Force out the last of the washings with pressure or vacuum.

**7.1.11** If the combustion products contain chlorine and/or nitrogen, proceed according to 7.2. If neither chlorine nor nitrogen combustion products are present, proceed according to 7.3, for titration with sodium hydroxide.

### 7.2 Titration with barium perchlorate

**7.2.1** The amount of sulfur present in the test portion shall not exceed 3 mg. If the amount of sulfur is found to exceed this figure, repeat the determination using a smaller test portion.

NOTE — A test portion of the recommended size of 50 mg will contain 3 mg of sulfur when the sample contains 6 % (*m*/*m*) sulfur.

**7.2.2** Reduce the volume of the test portion solution obtained as described in 7.1.9 or 7.1.10 to 10 to 20 cm$^3$ by boiling, taking care to avoid losses by splashing by placing a funnel in the neck of the flask. Add sufficient 2-propanol (4.2.2) to make the test solution 70 to 90 % (*V*/*V*) alcoholic.

**7.2.3** If using the indicator system of 4.2.5.1, add 2 or 3 drops of Thorin solution and titrate with barium perchlorate drop by drop, to the pink end-point. Read the burette to the nearest 0,01 cm$^3$.

**7.2.4** If using the indicator system of 4.2.5.2, add 1 drop of Thorin solution and sufficient methylene blue solution to change the colour from orange to yellow.

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

Titrate the barium perchlorate (4.2.3), drop by drop, to the permanent pink end-point. Read the burette to the nearest 0,01 $cm^3$.

**7.2.5** For both indicator systems, a magnetic stirrer (5.4) and a daylight matching lamp (5.5) may be used, if desired. Additional assistance in determining the end-point may be obtained by using a piece of diazochrome blue film[1] in front of the titration flask.

**7.2.6** Calculate the sulfur content according to 8.1, using the volume of barium perchlorate to reach the end-point obtained with either indicator system.

### 7.3 Titration with sodium hydroxide

**7.3.1** Using the solution obtained as described in 7.1.9, add 2 drops of methyl red/methylene blue indicator solution (4.2.6) and titrate using the sodium hydroxide solution (4.2.4), reading the burette to the nearest 0,01 $cm^3$.

**7.3.2** Proceed to 8.2 for calculation of the sulfur content.

### 7.4 Blank test

Carry out a blank test by following exactly the same procedure, using the same quantities of reagents, but omitting the test portion.

## 8 Expression of results

**8.1** The percentage, by mass, of the total sulfur, rounded off to the nearest 0,01 % is given by the following formula for test portions containing chlorine and/or nitrogen :

$$\frac{(V_t - V_b) \times 0{,}032\,1 \times c_1 \times 100}{m}$$

where

$V_t$ is the volume, in cubic centimetres, of barium perchlorate solution (4.2.3) required for the determination;

$V_b$ is the volume, in cubic centimetres, of barium perchlorate solution (4.2.3) required for the blank test;

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

$c_1$ has the same meaning as in 4.2.3.2.

**8.2** The percentage, by mass, of the total sulfur, rounded off to the nearest 0,01 %, is given by the following formula for test portions containing no chlorine or nitrogen :

$$\frac{3{,}2\,(V_t - V_b)c_2}{m}$$

where

$V_t$ is the volume, in cubic centimetres, of sodium hydroxide solution (4.2.4) required for the determination;

$V_b$ is the volume, in cubic centimetres, of sodium hydroxide solution (4.2.4) required for the blank test;

$c_2$ is the actual concentration, in moles of NaOH per cubic decimetre, of the sodium hydroxide solution (4.2.4);

$m$ has the same meaning as in 8.1.

**8.3** Take as the result the mean value of the results of two determinations, provided that the requirements for repeatability (see 9.1) are satisfied. Express the mean value to the nearest 0,05 % (*m*/*m*) sulfur.

## 9 Precision and accuracy

### 9.1 Repeatability

Two test results, obtained by the same operator, are acceptable if they conform to the following :

| Total sulfur found<br>% (*m*/*m*) | Deviation from the mean<br>% (*m*/*m*) |
|---|---|
| Less than 1 | ± 0,1 |
| 1 to 5 | ± 0,2 |
| More than 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 % (*m*/*m*) from the mean value for a total sulfur content of 3 % (*m*/*m*).

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[1] Suitable film in different sizes may be obtained from Gordon Audio Visual Ltd., 28-30 Market Place, Oxford Circus, London W1N 8PH. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this particular product. Equivalent products may be used if they can be shown to lead to the same results.

### 9.2 Reproducibility

This part of ISO 6528 has not been tested for interlaboratory reproducibility.

### 9.3 Accuracy

This part of ISO 6528 has not been tested for accuracy.

## 10 Test report

The test report shall include the following information :

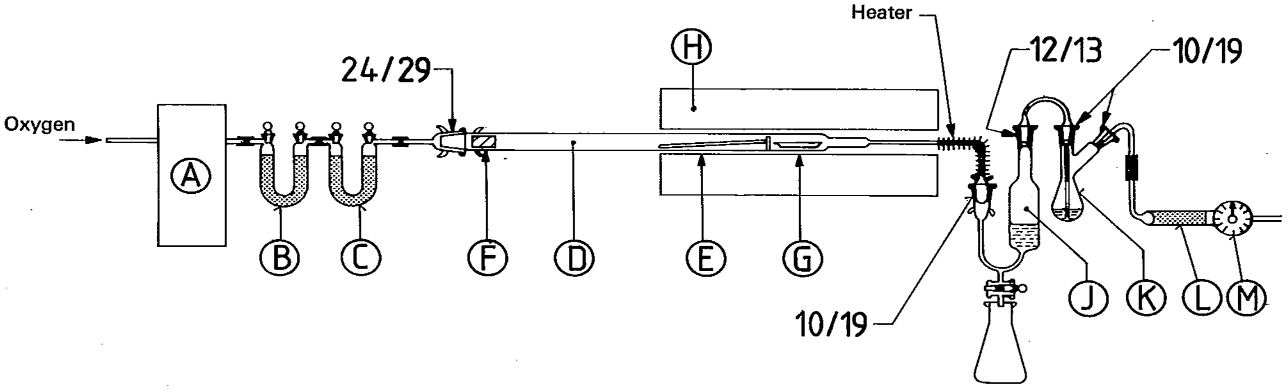
a) all details necessary for full identification of the sample;

b) reference to this International Standard;

c) the mean value of the results of two determinations;

d) any operation, not included in this part of ISO 6528, which might have affected an individual test;

e) date of test.



| | |
|---|---|
| Ⓐ | Calibrated flowmeter |
| Ⓑ | U-tube containing magnesium perchlorate |
| Ⓒ | U-tube containing a carbon dioxide absorbent |
| Ⓓ | Silica combustion tube |
| Ⓔ | Silica rod with handle and button |
| Ⓕ | Magnetic stainless steel cylinder |
| Ⓖ | Transparent silica combustion boat with handle |
| Ⓗ | Electric combustion furnace with temperature indicator and controller |
| Ⓙ | Primary absorbing vessel |
| Ⓚ | Secondary absorbing vessel |
| Ⓛ | Calcium chloride tube |
| Ⓜ | Needle valve |

**Figure 1 — Apparatus for the determination of total sulfur by the furnace combustion method**

Dimensions in millimetres

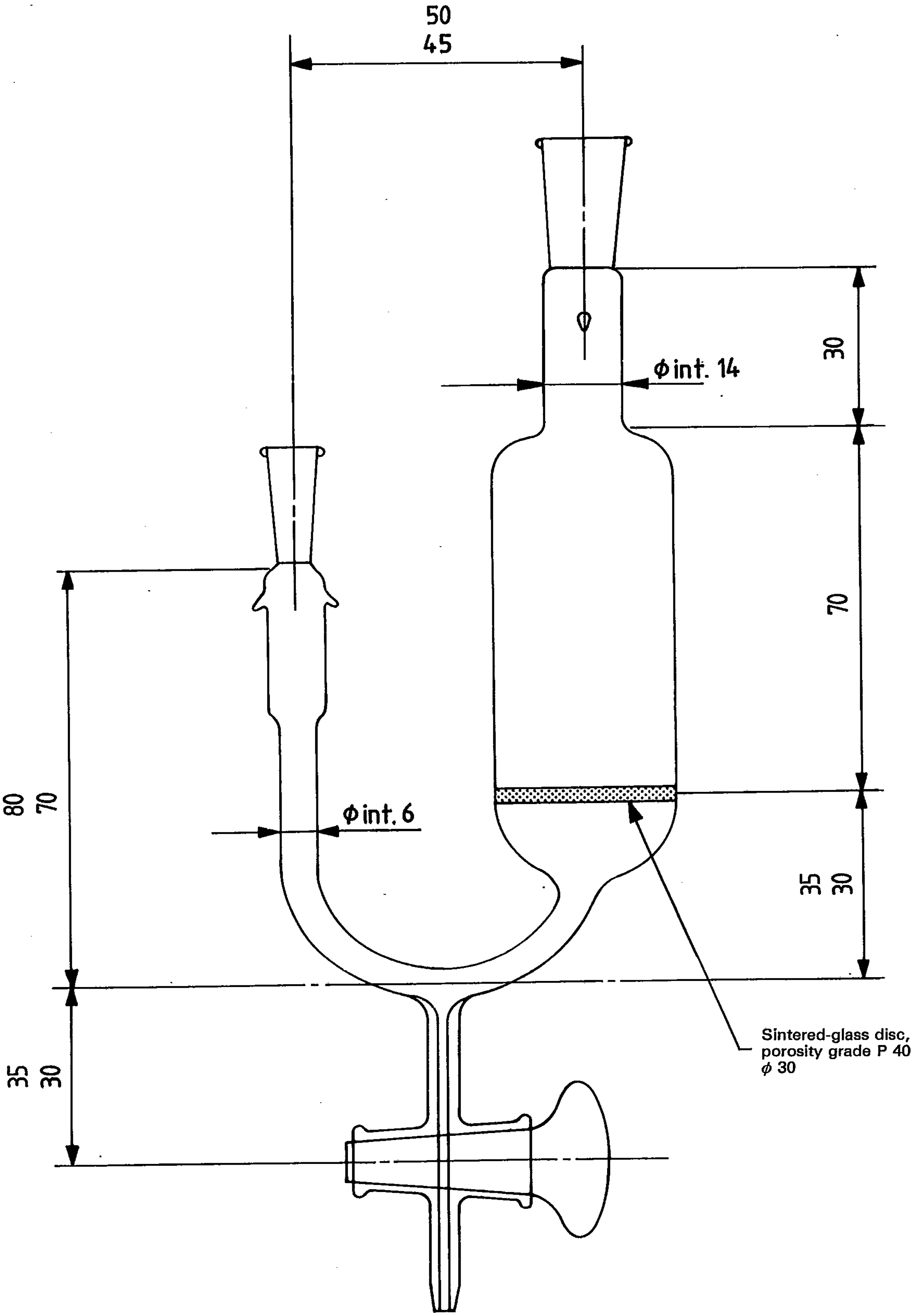


Figure 2 — Absorption vessel for use in the determination of total sulfur by the furnace combustion method

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**Descriptors :** rubber, tests, chemical analysis, determination of content, sulphur, combustion analysis.

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