BRITISH STANDARD

METHODS OF TESTING VULCANIZED RUBBER

PARTS B 6 TO B 10
DETERMINATION OF SULPHUR

B.S. 903 : Parts B 6 to B 10 : 1958

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The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 5000, indexed and cross-indexed for reference, together with an abstract of each standard, will be found in the Institution's Yearbook, price 15s.

This standard makes reference to the following British Standards:

B.S. 572	Interchangeable conical ground glass joints.
B.S. 1752	Sintered disk filters for laboratory use.

British Standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

The following B.S.I. references relate to the work on this standard:—
Committee references RUC/10–, RUC/10/5
Draft for comment CW(RUC) 9214

CO-OPERATING ORGANIZATIONS

The Rubber Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations :—

Board of Trade
*British Rubber Producers' Research Association
*Federation of British Rubber and Allied Manufacturers
*Institution of the Rubber Industry
*Ministry of Supply
Natural Rubber Development Board
*Research Association of British Rubber Manufacturers
*Rubber Growers' Association

The Government departments and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of the British Standard:—

Admiralty
Air Ministry
Association of British Chemical Manufacturers
British Chemical Plant Manufacturers' Association
British Electrical and Allied Industries Research Association
British Railways, The British Transport Commission
British Rubber and Resin Adhesive Manufacturers' Association
Department of the Government Chemist
General Post Office
Institute of Brewing
Institution of Chemical Engineers
Institution of Mechanical Engineers
Institution of Mechanical Engineers (Automobile Division)
Institution of Municipal Engineers
Institution of Water Engineers
Ministry of Housing and Local Government
National College of Rubber Technology
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FOREWORD

This British Standard has been published under the authority of the Rubber Industry Standards Committee. In deciding to issue a revision of the 1950 edition, the Committee has also considered it desirable to publish B.S. 903 in separate parts and the present parts replace Part 3 of 1950. The group of parts in which the prefix letter ' B ' is used covers chemical methods of testing rubber.

The principal alteration in this document is the replacement of the combustion method for total sulphur by a new method, using a different apparatus.

This part includes methods for the following determinations:—

Part B 6	**Total sulphur**
Section 1	Carius method
Section 2	Fusion method
Section 3	Combustion method
Part B 7	**Extractable sulphur**
Section 1	Copper spiral method
Section 2	Bromine method
Section 3	Nitric acid method
Part B 8	**Rubber-combined sulphur**
Part B 9	**Sulphur in total fillers**
Part B 10	**Sulphide sulphur**

PART B 6. TOTAL SULPHUR

General explanation. ' Total sulphur ' ideally denotes the total amount of sulphur, in whatever form, contained in the sample.

The percentages of total sulphur as determined by the three recommended methods should agree within the usual limits of experimental error, except when the sample contains certain fillers, notably lithopone and barium and calcium sulphates, in which the sulphur may or may not be included in the result according to the method used.

SECTION 1 CARIUS METHOD

1.1 Summary and explanatory note. The rubber is oxidized by heating with fuming nitric acid under pressure in a sealed tube. After dilution and removal of any insoluble matter, the sulphuric acid in the liquid is precipitated as barium sulphate, which is filtered off and weighed. The result will not include the sulphur contained in barium sulphate present as such or as lithopone. It will include the sulphide sulphur present as lithopone, and the sulphur present as calcium sulphate in quantities likely to be met with in practice.

1.2 Reagents. All reagents used shall be of recognized analytical reagent quality and demineralized water shall be used wherever water is specified.

Barium chloride solution: 10 g in 100 ml water.
Hydrochloric acid, concentrated, sp. gr. 1·18.
Nitric acid, fuming, sp. gr. 1·50.
Sodium chloride.

1.3 Procedure. Introduce, by means of a long-stemmed funnel, 5 ml of fuming nitric acid into a bomb-tube 18–24 in. in length and sealed at one end. Withdraw the funnel carefully so as to avoid wetting the side of the tube.

Cautiously slide into the bomb-tube a small ignition tube containing about 0·5 g of the sample (0·1 g in the case of ebonite or thioplasts), taking care that at this stage the rubber does not come into contact with the acid.

Seal the open end of the bomb-tube in a blow-pipe flame by the usual technique, and allow to cool. When cold, place the tube in a bomb furnace. Raise the temperature of the furnace gradually, over a period of three hours, to 230°C, and maintain this temperature for a further three hours.

Allow the tube to cool in the furnace, and when cold release the pressure by carefully heating the tip until the glass is softened and becomes perforated by the escaping gases. Remove the tube from the furnace and open it by making a deep file scratch round the glass and applying the end of a glass rod, heated to redness.

Wash the contents of the bomb-tube into a 600 ml beaker, add 0·5–1·0 g of sodium chloride and evaporate nearly to dryness. Add 10 ml of concentrated hydrochloric acid and evaporate to dryness. Repeat the operation with a further 10 ml of acid. Take up the residue in 200 ml of hot water, containing 1 ml of concentrated hydrochloric acid, filter off any insoluble matter and wash with hot water. Dilute the filtrate and washings (or the unfiltered solution if clear) to 300–350 ml. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5–10 minutes and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity grade No. 4)* which has been previously washed, dried and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

1.4 Expression of results.

$$\text{Total sulphur} = \frac{B \times 13{\cdot}73}{W} \text{ per cent}$$

where B = Corrected weight of barium sulphate, in grammes.
W = Weight of test portion, in grammes.

SECTION 2 FUSION METHOD

2.1 Summary and explanatory note. The sample is treated with nitric acid-bromine mixture, and after evaporation of the acid the dried residue is fused with an excess of anhydrous sodium carbonate. The melt is leached out with water, the residue filtered off, and the filtrate acidified to decompose the excess of carbonate and evaporated to dryness to precipitate silica. The residue is extracted with water, and after filtration the sulphate present in the filtrate is precipitated as barium sulphate which is weighed. The result will include all the sulphur present as lithopone and as barium and calcium sulphates.

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* B.S. 1752, ' Sintered disk filters for laboratory use '.

2.2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Barium chloride solution: 10 g in 100 ml water.
Hydrochloric acid, concentrated, sp. gr. 1·18.
Methyl orange: 1 g in 100 ml water.
Nitric acid-bromine mixture: nitric acid, sp. gr. 1·42, saturated with bromine.
Potassium nitrate.
Sodium carbonate, anhydrous.

2.3 Procedure. Place 0·5 g of the sample (or 0·1 g in the case of ebonite or thioplasts) in a 75 ml porcelain crucible, add 2–3 g of potassium nitrate and 15 ml of nitric acid-bromine mixture and cover with a small clock-glass.

Heat it gently on a water bath until the reaction commences, then remove from the bath. When the first vigorous reaction has subsided, continue to heat for one hour or until the rubber has completely disintegrated and no globules of sulphur are visible in the liquid. Remove the clock-glass, rinse it with the minimum quantity of water, and evaporate the contents of the crucible to dryness on the water bath.

Moisten the dry residue with 1–2 ml of water and, using a stout glass rod rounded at the end, break up the mass and mix intimately with 5 g of anhydrous sodium carbonate. Transfer the contents of the crucible to a 75 ml nickel crucible using small pieces of moistened filter paper to transfer any material adhering to the porcelain crucible or to the glass rod.

Heat gently in a sulphur free flame or at the mouth of an electric furnace to char the organic matter; subsequently heat more strongly until the contents of the crucible fuse, and maintain in this state for several minutes. Allow to cool, place the crucible on its side in a 250 ml beaker, cover with hot water and set aside on a boiling-water bath or hot plate until the melt has completely disintegrated.

Remove the crucible and rinse thoroughly with hot water. Filter the extract into a 600 ml beaker, wash the residue with hot water until the washings are neutral, collecting the washings with the main filtrate. Allow to cool.

Neutralize the filtrate by the careful addition of concentrated hydrochloric acid using methyl orange as indicator, and add 5 ml of acid in excess. Evaporate to dryness, allow to stand for one hour on the water bath, and repeat the evaporation after the further addition of 10 ml of acid. Add 1 ml of concentrated hydrochloric acid to the dried residue followed by 150 ml of water, and boil for several minutes. Filter if necessary. Dilute the solution to 300–350 ml.

Heat the solution to boiling and, while hot, add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5–10 minutes and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity grade No. 4)* which has previously been washed, and dried at 110°C and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

2.4 Expression of results.

$$\text{Total sulphur} = \frac{B \times 13{\cdot}73}{W} \text{ per cent}$$

where B = Corrected weight of barium sulphate, in grammes.
W = Weight of test portion, in grammes.

SECTION 3 COMBUSTION METHOD

3.1 Summary and explanatory note. The sample is burnt in a stream of oxygen in the presence of a catalyst, the oxides of sulphur are passed into hydrogen peroxide and the resulting sulphuric acid is determined titrimetrically. Alternative finishes are given for samples containing acrylonitrile type polymers and chlorine compounds. In the latter case a small amount of zinc chloride may distil over and this is allowed for by a separate compleximetric titration.

This semi-micro method occupies a total time of about one hour.

The result will include all sulphur present.

3.2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Calcium chloride, *anhydrous*, approx. 14–22 mesh.

Catalyst. Heat some vanadium pentoxide in a shallow dish at 140–160°C for 16 hours and cool in a desiccator. Weigh 0·8 g of the dry vanadium pentoxide and 0·2 g of zinc oxide for each detemination.

Hydrogen peroxide solution: 3 g H_2O_2 in 100 ml water.

Indicator solution: 0·125 g methyl red and 0·083 g methylene blue in 100 ml industrial methylated spirit (I.M.S.).†

Magnesium perchlorate (*anhydrone*), 14–22 mesh.

Supply of oxygen.

Soda asbestos, 14–22 mesh, preferably self-indicating type.

Sodium hydroxide, 0·02N solution.

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* B.S. 1752, 'Sintered disk filters for laboratory use'.

† It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations, 1952 (S.I. 1952, 2230).

Additional reagents for samples containing chlorine compounds and acrylonitrile type polymers.

Ammonium chloride.

Ammonia solution, sp. gr. 0·880.

Barium chloride, 0·01M solution.

Congo red test paper.

Disodium dihydrogen ethylenediaminetetra-acetate (EDTA), 0·01M solution.

Eriochrome Black T or *Solochrome Black WDFA indicator*. Dissolve by warming 0·5 g of Eriochrome Black T or Solochrome Black WDFA in 100 ml of industrial methylated spirit (I.M.S.), and add 4·5 g of hydroxylamine hydrochloride. Allow to stand overnight and centrifuge or filter. This indicator solution should not be kept for more than one month.

Hydrochloric acid, dilute: Dilute 1 vol. of concentrated acid (sp. gr. 1·18) with 3 vol. of water.

Zinc disodium ethylenediaminetetra-acetate. Dissolve by warming 5·0 g disodium dihydrogen ethylenediaminetetra-acetate dihydrate in 100 ml water. Add 1·5 g zinc oxide to the hot solution, stir and heat to boiling to dissolve as much as possible of the zinc oxide. Cool to room temperature and filter the excess of zinc oxide. Evaporate the solution to dryness on a water bath with occasional stirring.

3.3 Apparatus. The assembly of the apparatus is shown in Fig. 1.

A. Flow meter. To indicate 50–60 ml per minute.

B & C. Purifying train.

D. Silica combustion tube with heater for bent end. Total horizontal length 650–670 mm.

E. Silica rod with handle and button. Diameter of rod 7–8 mm. Diameter of button 12–13 mm. Overall length 125 mm.

F. Magnetic stainless steel cylinder block. Diameter 13–14 mm. Length 10–11 mm.

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

H. Combustion furnace (electric) with temperature indicator and controller. Length about 320 mm.

J. Primary absorbing vessel (see Fig. 2).

K. Secondary absorbing vessel.

L. Calcium chloride tube.

M. Needle valve.

Magnet capable of moving cylinder F from outside silica combustion tube.

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* It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations, 1952 (S.I. 1952, 2230).

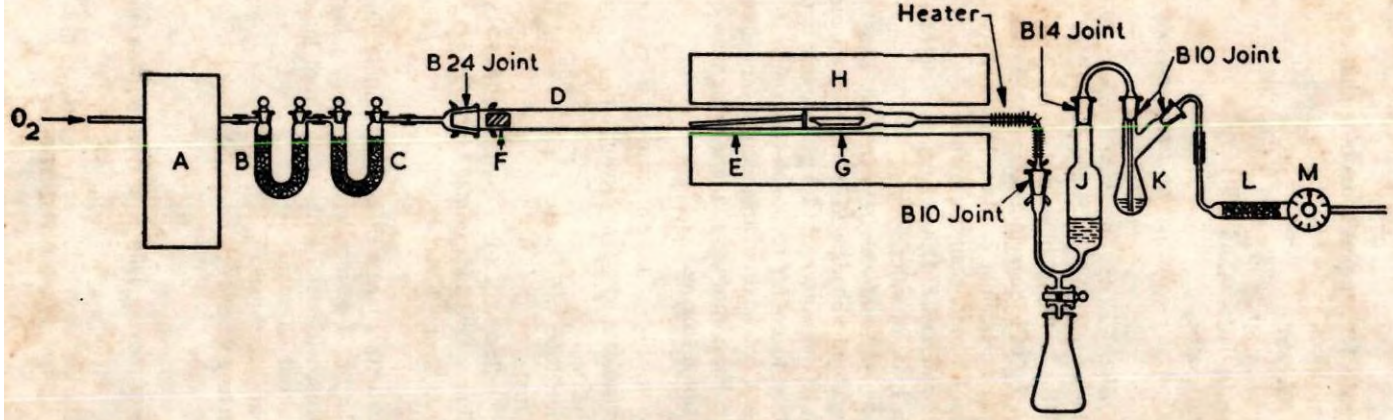

Fig. 1. Apparatus for the determination of total sulphur by the combustion method

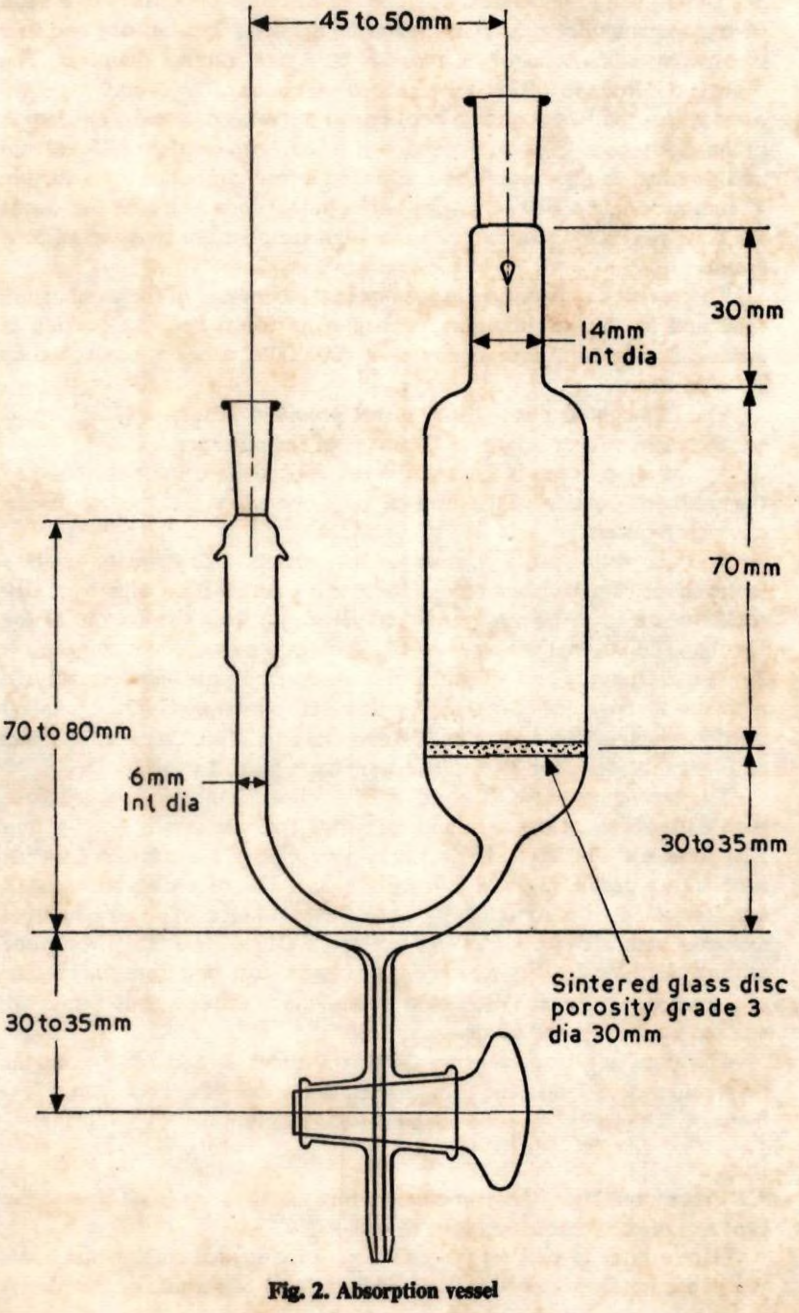

Fig. 2. Absorption vessel

3.4 Description of apparatus. The combustion tube D consists of a satin or transparent silica tube 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 B24 cone provided with hooks. The overall measurement across the B24 cone and hooks must not exceed 30 mm. The length of the wide tube is 480 mm; the narrower tube is horizontal for 170–190 mm and then bends downwards at a right angle and continues for a further 77 mm including a B10 cone with hooks in the same plane as the bend: the cone is greased with sulphur-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 400–500°C which is controlled by suitable means.

The B24 cone is fitted with a socket provided with hooks, and this is connected by rubber tubing to U-tube C of the purifying train.

An asbestos screen is fixed at the exit end of the combustion tube so that radiated heat from the furnace does not affect the solution in the absorbing vessels.

The absorption train consists of two vessels. The primary vessel J is the shape of a U-tube and is joined to the combustion tube by a B10 socket which is 70–80 mm (measured vertically) from the bottom of the U-tube. The internal diameter of this limb is 6 mm and the stopcock is 30–35 mm from the bottom of the tube. A sintered glass disk (porosity 3), 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 diameter. This limb then narrows to 14 mm diameter for 30 mm and terminates in a B14 socket.

The secondary vessel K consists of a 20 or 25 ml pear shaped flask with B10 sockets at the neck and side arm. The side arm is fitted with a B10 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 B14 cone at one end and a B10 cone and delivery tube at the other. 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.

The purifying train consists of two U-tubes B and C. B contains magnesium perchlorate and is connected to the exit of the calibrated flow meter A. The second U-tube contains soda asbestos.

3.5 Procedure. Heat the combustion furnace to 1000 ± 20°C, and the bent end of the combustion tube to 400–500°C.

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

Connect the absorbing vessels to the combustion tube, remove the inverted U-tube and from a graduated pipette add 15 ml of hydrogen peroxide solution to the primary absorbing vessel via the B14 socket and 5 ml to the secondary absorbing vessel. Replace the inverted U-tube and connect the side arm of the secondary absorbing vessel via the calcium chloride tube to the needle valve attached to the suction line.

Connect the oxygen to the flow meter and purifying train and adjust the supply of oxygen so that the rate of flow is 50 ml per minute. To ensure a steady stream of oxygen a pressure of not less than 25 lb/sq. in. should be shown on the pressure gauge of the cylinder. Disconnect the oxygen from the flow meter without changing the setting of the oxygen regulator.

Insert the boat in the mouth of the combustion tube followed by the silica rod and steel cylinder. Close the combustion tube with the B24 socket and connect to the purifying train and flow meter. Adjust the suction to draw purified air through the combustion tube and absorbing vessels at a rate of 60 ml per minute as indicated by the flow meter. Connect the oxygen to the flow meter so that the previously adjusted oxygen is drawn through the combustion tube and absorption train.

By means of the magnet (steel cylinder and silica rod) slide the boat to a position 1 cm from the furnace and leave it for two minutes. In order to maintain a steady combustion rate propel the boat slowly forward (about 0·5 cm per minute) to the hottest zone of the furnace. (If the advance of the boat into the hot zone is too rapid excessive fluctuations of the flow meter level 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 flow meter, continue the combustion for a further 30 minutes to ensure decomposition of alkaline earth sulphates.

Switch off the current to the bent end heater, disconnect the oxygen from the flow meter, and cool the hot B10 joint of the primary absorbing vessel to room temperature, e.g. 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.*

Connect 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 B10 joint. Carefully open the stopcock, allow the liquid to run slowly into a flask and continue

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* In order 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 silica, applying heat to the boat if necessary. Suspend the cool boat in warm concentrated hydrochloric acid, then remove all traces of acid by washing with water, and ignite.

blowing until all the solution is transferrred. For samples containing no chlorine compounds or acrylonitrile-type polymers, collect the solution in a 100 ml conical flask. For samples containing these compounds collect the solution in a 50 ml volumetric flask.

Add about 8 ml 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 B10 joint and collect the washings in the flask. Disconnect the apparatus at the B14 joint and rinse down the side of the wide limb of the U-tube with 10 ml of water. Replace the B14 joint and force the liquid into the U-tube and thence through the stop cock into the flask. Repeat the washing with a further 10 ml of water and then titrate according to the appropriate finish.

Make a blank determination on the reagents by carrying out the complete procedure using the appropriate titrimetric finish and calculate the sulphur content from the corrected titration figure.

3.6 Titrimetric finish for samples containing no acrylonitrile type polymers or chlorine compounds. Add to the liquid in the 100 ml conical flask two drops of methyl red/methylene blue indicator solution and titrate using 0·02N sodium hydroxide from a 10 ml micro burette.

3.7 Titrimetric finish for samples containing acrylonitrile type polymers and chlorine compounds. Make up the liquid in the 50 ml volumetric flask to the mark with water and proceed as follows:—

a. For samples containing acrylonitrile type polymers. Pipette 20 ml of the solution into a 100 ml conical flask, add a small piece of congo red indicator paper and neutralize with 0·02N sodium hydroxide. Add 5 drops of dilute hydrochloric acid, heat to boiling, add by pipette 5 ml of 0·01M barium chloride and boil for one minute. Cool the solution to 15 ± 2°C and add 0·1 g ammonium chloride,* 0·02 g zinc EDTA complex,* 5 ml ammonia solution, and 5 drops of Eriochrome Black T or Solochrome Black WDFA. Titrate to the first pseudo end point with 0·01M EDTA, add a further 5 ml of ammonia solution and titrate to the blue end point (Y ml).

Carry out a blank titration using the same quantities of reagents as above (X ml).

b. For samples containing chlorine compounds with or without acrylonitrile type polymers. Proceed exactly as described under *a.* with the following addition.

Pipette a further 20 ml into a 100 ml conical flask, add 5 drops of dilute hydrochloric acid and boil for one minute. Cool the solution to

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* The weights of ammonium chloride and zinc EDTA complex may be added by means of measuring spatulas.

15 ± 2°C, add 0·1 g ammonium chloride, 5 ml ammonia solution and 5 drops of Eriochrome Black T or Solochrome Black WDFA indicator. Titrate as described in *a*. with 0·01M EDTA (Z ml).

3.8 Expression of results.

3.81 *Samples containing no acrylonitrile type polymers or chlorine compounds.*

$$\text{Total sulphur} = \frac{V \times 0{\cdot}032}{W} \text{ per cent}$$

where V = Corrected volume of 0·02N sodium hydroxide, in millilitres.
W = Weight of test portion, in grammes.

3.82 *Samples containing acrylonitrile type polymers.*

$$\text{Total sulphur} = \frac{0{\cdot}08\,(X - Y)}{W} \text{ per cent}$$

where W = Weight of test portion, in grammes.

3.83 *Samples containing chlorine compounds with or without acrylonitrile type polymers.*

$$\text{Total sulphur} = \frac{0{\cdot}08\,(X + Z - Y)}{W} \text{ per cent}$$

where W = Weight of test portion, in grammes.

PART B 7. EXTRACTABLE SULPHUR

General explanation. A sulphur determination is made on the matter extracted from the rubber by acetone. Depending on the method used, the result of this determination (often termed ' free sulphur ') usually represents an intermediate value between the following two extremes: (i) the elemental sulphur extractable by boiling acetone (true free sulphur), and (ii) the total sulphur (elemental and combined) in the extract. It is not yet known precisely what forms of sulphur are included in the sulphur as determined by the three methods described in Sections 1, 2 and 3, but the copper spiral method approximates more nearly to the elemental sulphur content.

The bromine and nitric acid methods give similar results for sulphur in the acetone extract of any factice present (either brown or white), but it is not known how much of this is combined sulphur.

SECTION 1 COPPER SPIRAL METHOD

1.1 Summary and explanatory note. The rubber is extracted with acetone as in normal estimation of acetone extract, except that a spiral of clean copper gauze is placed in the flask containing the acetone. The copper reacts with the extracted sulphur, forming copper sulphide. When extraction is complete the acetone solution is drawn off and the flask and its contents are treated with hydrochloric acid. The resulting hydrogen sulphide is passed through cadmium acetate solution, and the cadmium sulphide formed is determined iodometrically. This method is commonly regarded as giving elemental sulphur only, but too high a result may be obtained in the presence of compounds such as tetramethyl thiuram disulphide containing co-ordinated sulphur.

The method as given is suitable for determination of amounts of sulphur not exceeding 10 milligrammes.

1.2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Acetone.

Cadmium acetate, buffered solution: 25 g cadmium acetate $(CH_3COO)_2Cd \cdot 2H_2O$, 25 g sodium acetate $CH_3COONa \cdot 3H_2O$ and 100 ml glacial acetate acid, made up to 1000 ml with water.

Copper gauze, 40–60 mesh per linear inch.

Hydrochloric acid, dilute: 1 vol. of concentrated acid (sp. gr. 1·18) with 1 vol. of water.

Nitric acid, dilute: 1 vol. of concentrated acid (sp. gr. 1·42) with 1 vol. of water.

Iodine solution, approximately 0·05N.

Sodium thiosulphate solution, 0·05N.

Starch solution.

Supply of nitrogen or carbon dioxide.

1.3 Apparatus. *Preparation of spiral.* Cut about 5 g of 40–60 mesh copper gauze to form a 1 cm wide strip and loosely roll to form a spiral approximately 2 cm in diameter, the turns being conveniently held in place by a loop of copper wire.

Clean the spiral immediately before use by washing in hot concentrated hydrochloric acid. If tarnished after this treatment immerse for a few seconds in dilute nitric acid. Remove all traces of acid by thorough washing with water and finally with acetone.

The assembly of the apparatus is shown in Fig. 3. It consists of:—

1 150 ml B34* extraction flask.
1 Adapter, B14* socket, B34* cone with gas inlet tube.
1 Condenser, Liebig type, effective length approximately 22 cm, with B14* cone angle drip, B14* socket and side arm with B10* cone.
1 Dropping funnel 100 ml with B14* cone, modified stem and B14* stopper.
1 250 ml B24* conical flask.
1 Receiver adapter, B10* socket, B24* cone with internal sealed dip-tube.
1 Micro-immersion filter (Emich pattern), stem approximately 75 mm, diameter of disc 10 mm, porosity grade No. 3.†
2 Arnold bubblers.

1.4 Procedure. Extract a 1 g test portion of the rubber (0·5 g if there is evidence of sulphur bloom) with acetone as described in B.S. 903, Part B.2, but with modifications in procedure as follows:—

Place the specially prepared copper spiral in a 150 ml extraction flask and extract the test portion for not less than four hours.

If, at the end of the extraction period the spiral is heavily blackened, a second prepared spiral should be added and the extraction continued for a further two hours. If no blackening is apparent it will suffice to add a further piece of copper gauze about 1 cm square and continue the extraction for one hour.

Disconnect the extraction flask and filter off the acetone through a porosity No. 3 filter stick. Wash the spiral with three portions of about 20 ml of hot acetone, removing the washings each time through the filter stick. Assemble the flask A containing copper spiral and filter stick into the apparatus (see Fig. 3).

Introduce about 300 ml cadmium acetate solution into the receiver B and fill the Arnold bubblers C and D to a depth of about 1 cm with the same solution. Pass a stream of pure nitrogen or carbon dioxide through the apparatus to sweep out the air and then adjust the flow to about one bubble per second in flask B.

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* B.S. 572, ' Interchangeable conical ground glass joints '.

† B.S. 1752, ' Sintered disk filters for laboratory use '.

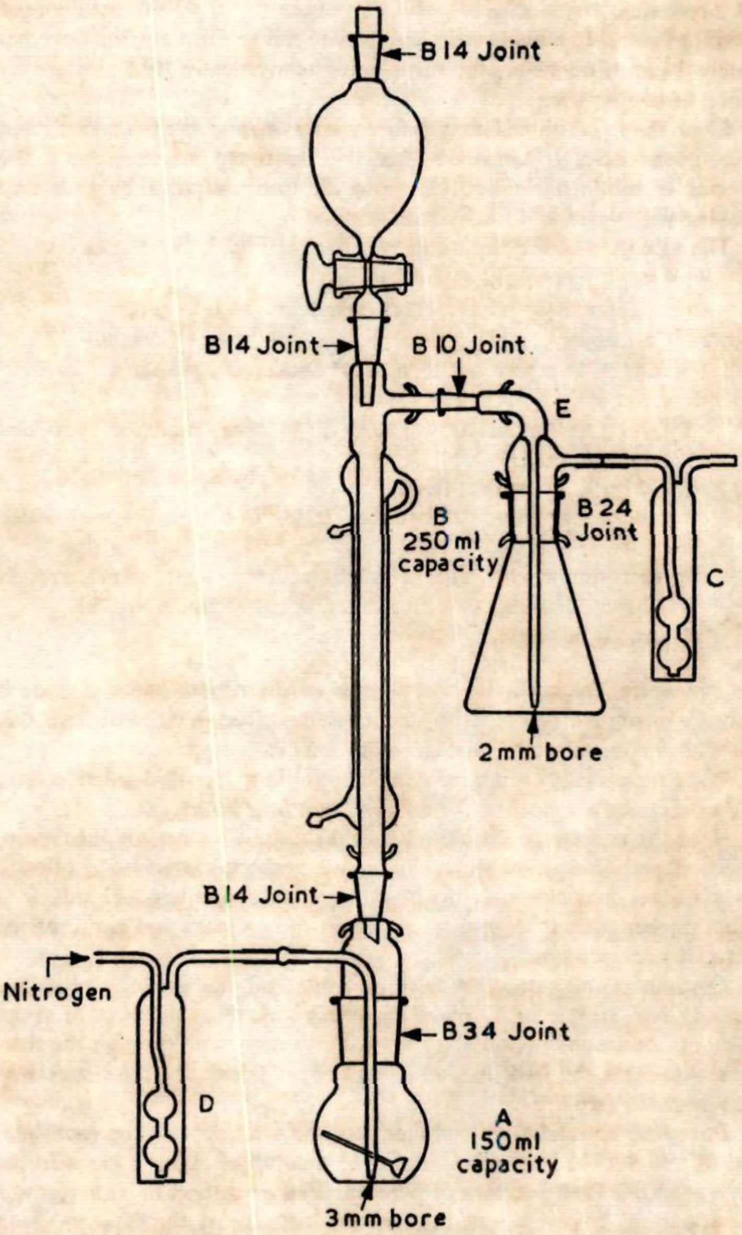

Fig. 3. Determination of extractable sulphur by the copper spiral method

Run in 50 ml of dilute hydrochloric acid slowly from the funnel, heat slowly to boiling and continue to boil gently for 20 to 30 minutes. Towards the end of the period increase the flow of inert gas to sweep over all traces of hydrogen sulphide. The solution in the Arnold bubbler C should be clear and colourless; if this is not so, it is an indication that the gas flow has been too rapid, and the determination must be repeated using a smaller test portion or slower rate of gas flow. Disconnect the receiving flask adapter E from the delivery tube and, whilst held at an angle, add from a pipette a measured volume (V ml) of 0·05N iodine solution (usually 20 ml is a suitable quantity) to flask B, so that excess of iodine is present.

Allow the iodine to react with any precipitate adhering to the entry tube and when all the precipitate has dissolved remove and rinse the tube and titrate the excess iodine with 0·05N sodium thiosulphate solution using starch as indicator in the usual manner (Y ml). Determine the concentration of iodine solution in terms of millilitres of standard sodium thiosulphate by titrating V ml of iodine solution with the standard sodium thiosulphate in the presence of 100 ml of buffered cadmium acetate (X ml).

The difference between the volume of sodium thiosulphate used in the standardization and that used in the determination is equivalent to the iodine which has reacted with the cadmium sulphide.

1.5 Expression of results.

$$\text{Extractable sulphur} = \frac{0{\cdot}08\,(X - Y)}{W}\ \text{per cent}$$

where W = Weight of test portion, in grammes.

SECTION 2 BROMINE METHOD

2.1 Summary and explanatory note. The acetone extract is oxidized by bromine in presence of water, and the resulting sulphuric acid is precipitated as barium sulphate, which is weighed. This method gives all the elemental sulphur, and part, but not all, of the sulphur in sulphur-containing accelerators; it is not known whether the result includes any combined sulphur from other sources, e.g. sulphur reaction products of rubber ‘ resins ’.

2.2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Barium chloride solution: 10 g in 100 ml water.
Bromine.
Hydrochloric acid, concentrated, sp. gr. 1·18.

2.3 Procedure. Extract a weighed test portion of the rubber with acetone by the method described in B.S. 903 : Part B.2; add to the dried extract 50 ml of water and 1–3 ml of bromine, and cover with a watch glass.

Allow the vessel to stand for at least 30 min in a water-bath at about 70°C, then remove the watch glass and heat cautiously without boiling until the solution is almost colourless. Add 1 ml concentrated hydrochloric acid, filter the solution and dilute to 250 ml with water. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5–10 min and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity grade No. 4)* which has previously been washed, dried at 110°C and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

2.4 Expression of results.

$$\text{Extractable sulphur} = \frac{B \times 13{\cdot}73}{W} \text{ per cent}$$

where B = Corrected weight of barium sulphate, in grammes
W = Weight of test portion, in grammes.

SECTION 3 NITRIC ACID METHOD

3.1 Summary and explanatory note. The acetone extract is oxidized by heating with nitric acid and potassium chlorate. The resulting sulphuric acid is precipitated as barium sulphate, which is weighed. This method gives all the elemental sulphur, part or all of the sulphur from sulphur-containing accelerators (usually a higher proportion than by the bromine method), and part, but not all, of the sulphur that has entered into combination with rubber 'resins.'

3.2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Barium chloride solution: 10 g in 100 ml water.
Hydrochloric acid, concentrated, sp. gr. 1·18.
Nitric acid, concentrated, sp. gr. 1·42.
Potassium chlorate.

3.3 Procedure. Extract a weighed test portion of the rubber with acetone by the method described in B.S. 903, Part B.2. To the vessel containing

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* B.S. 1752, 'Sintered disk filters for laboratory use'.

the dried extract add 30 ml of concentrated nitric acid, cover with a watch glass, and heat on a steam bath for four hours, or for a longer period if necessary, until most of the organic matter is destroyed. After the first hour add, at intervals and in small portions, 2·5 g of potassium chlorate in order to accelerate oxidation. Do not allow the temperature to rise sufficiently to melt the sulphur into globules as these oxidize extremely slowly. Evaporate the liquid to dryness, add 3 ml of concentrated hydrochloric acid, and again evaporate to dryness; repeat the evaporation with further 3-ml portions of hydrochloric acid until no more brown fumes are evolved when the hydrochloric acid is added. Dissolve the residue in a mixture of 50 ml of hot water and 1 ml of concentrated hydrochloric acid, filter, and dilute to 250 ml with water. Heat the solution to boiling, and while hot add slowly a slight excess of hot barium chloride solution. Continue to boil the liquid for 5–10 minutes and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity grade No. 4)* which has previously been washed, dried at 110°C and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

3.4 Expression of results.

$$\text{Extractable sulphur} = \frac{B \times 13{\cdot}73}{W} \text{ per cent}$$

where B = Corrected weight of barium sulphate, in grammes.
W = Weight of test portion, in grammes.

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* B.S. 1752, ' Sintered disk filters for laboratory use '.

PART B 8. RUBBER-COMBINED SULPHUR

The rubber-combined sulphur should be estimated indirectly by determining the total sulphur, using one of the methods given in Part B 6, on a sample of rubber previously extracted with acetone, chloroform and alcoholic potash, as described in B.S. 903, and correcting for the sulphur present in the total fillers (determined by the method given in Part B 9).

PART B 9. SULPHUR IN 'TOTAL FILLERS'

1 Summary. The 'total fillers', separated from the rubber by treatment with a high-boiling solvent, is treated with nitric acid-bromine mixture and subsequently fused with sodium carbonate to convert all sulphur into a soluble sulphate, following the procedure described in Part B 6, Section 2.

2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Barium chloride solution: 10 g in 100 ml water.
Hydrochloric acid, concentrated, sp. gr. 1·18.
Methyl orange: 1 g in 100 ml water.
Nitric acid-bromine mixture: nitric acid concentrated, sp. gr. 1·42.
Sodium carbonate, anhydrous.

3 Procedure. Transfer to a 75 ml porcelain crucible the insoluble residue of fillers separated as described in B.S. 903, Part B 13. Add cautiously a few drops of concentrated nitric acid-bromine mixture and heat on a steam bath until the mass is substantially dry. Thoroughly mix this residue with 5 g of anhydrous sodium carbonate and transfer the contents of the porcelain crucible to a 75 ml nickel crucible using small pieces of moistened filter paper to transfer any material adhering to the porcelain crucible or to the glass rod.

Heat gently in a sulphur-free flame or at the mouth of an electric furnace to char the organic matter; subsequently heat more strongly until the contents of the crucible fuse, and maintain in this state for several minutes. Allow to cool, place the crucible on its side in a 250 ml beaker, cover with hot water and set aside on a boiling-water bath or hot plate until the melt has completely disintegrated.

Remove the crucible and rinse thoroughly with hot water. Filter the extract into a 600 ml beaker, wash the residue with hot water until the washings are neutral, collecting the washings with the main filtrate. Allow to cool.

Neutralize the filtrate by the careful addition of concentrated hydrochloric acid using methyl orange as indicator, and add 5 ml of acid in excess. Evaporate to dryness, allow to stand for one hour on the water bath, and repeat the evaporation after the further addition of 10 ml of acid. Add 1 ml of concentrated hydrochloric acid to the dried residue, followed by 150 ml of water, and boil for several minutes. Filter if necessary. Dilute the solution to 300–350 ml.

Heat the solution to boiling and, while hot, add slowly a slightly excess of hot barium chloride solution. Continue to boil the liquid for 5–10 minutes and allow to stand for at least one hour at 90–100°C.

Filter through a sintered glass or silica crucible (porosity grade No. 4)* which has previously been washed, and dried at 110°C and weighed. After the filtration wash the crucible and the precipitate with hot water until the washings are free from chloride, dry at 110°C for one hour, cool in a desiccator and weigh.

Carry out a blank determination on every batch of reagents, using the same quantities and the same conditions of test, and apply the resulting correction to the final weight obtained above.

4 Expression of results.

$$\text{Sulphur in total fillers} = \frac{B \times 13{\cdot}73}{W} \text{ per cent}$$

where B = Corrected weight of barium sulphate, in grammes.
W = Weight of test portion, in grammes.

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* B.S. 1752, ' Sintered disk filters for laboratory use '.

PART B 10. SULPHIDE SULPHUR

1 Summary. The rubber is treated with hydrochloric acid to decompose metallic sulphides. The resulting hydrogen sulphide is absorbed in cadmium acetate solution, and the cadmium sulphide thus formed is determined iodometrically.

2 Reagents. All reagents used shall be of recognized analytical reagent quality, and demineralized water shall be used wherever water is specified.

Cadmium acetate, buffered solution: 25 g cadmium acetate $(CH_3COO)_2Cd . 2H_2O$, 25 g sodium acetate $CH_3COONa . 3H_2O$ and 100 ml glacial acetic acid, made up to 1000 ml with water.

Hydrochloric acid, dilute: 1 vol. of concentrated acid (sp. gr. 1·18) to 1 vol. of water.

Iodine solution, approximately 0·05N.

Sodium thiosulphate solution, 0·05N.

Starch solution.

Supply of nitrogen or carbon dioxide.

3 Apparatus. The assembly of the apparatus is shown in Fig. 3. It consists of:—

1 150 ml B34* extraction flask.
1 Adapter, B14* socket, B34* cone with gas inlet tube.
1 Condenser, Liebig type, effective length approximately 22 cm with B14* cone angle drip, B14* socket and side arm with B14* cone.
1 Dropping funnel 100 ml with B14* cone, modified stem and B14* stopper.
1 250 ml B24* conical flask.
1 Receiver adapter, B10* socket, B24* cone with internal sealed dip-tube.
1 Micro-immersion filter (Emich pattern), stem approximately 75 mm, diameter of disc 10 mm, porosity grade No. 3.†
2 Arnold bubblers.

4 Procedure. Extract a weighed test portion of the rubber, about 0·5 g, with acetone by the method described in B.S. 903, Part B 2, and transfer it to flask A of the apparatus shown in Fig. 3. Introduce about 100 ml cadmium acetate solution into the receiver B and half fill the Arnold bubblers C and D with the same solution. Pass a rapid stream of pure nitrogen or carbon dioxide through the apparatus to sweep out the air and then adjust the flow to about one bubble per second in flask B.

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* B.S. 572, 'Interchangeable conical ground glass joints'.

† B.S. 1752, 'Sintered disk filters for laboratory use'.

Run in 50 ml of dilute hydrochloric acid slowly from the funnel, heat slowly to boiling and continue to boil gently for 30–40 minutes. Towards the end of the period increase the flow of inert gas to sweep over all traces of hydrogen sulphide. The solution in the Arnold bubbler C should be clear and colourless; if this is not so, it is an indication that the gas flow has been too rapid, and the determination must be repeated using a smaller test portion or slower rate of gas flow. Disconnect the receiving flask adapter E from the delivery tube and, whilst held at an angle, add from a pipette a measured volume (V ml) of 0·05N iodine solution (usually 20 ml is a suitable quantity) to flask B, so that excess of iodine is present. Allow the iodine to react with any precipitate adhering to the entry tube and when all the precipitate has dissolved remove and rinse the tube and titrate the excess iodine with 0·05N sodium thiosulphate solution using starch as indicator in the usual manner (Y ml). Determine the concentration of iodine in terms of millilitres of standard sodium thiosulphate by titrating V ml of iodine solution with the standard sodium thiosulphate (X ml).

The difference between the volume of sodium thiosulphate used in the standardization and that used in the determination is equivalent to the iodine which has reacted with the cadmium sulphide.

5 Expression of results.

$$\text{Sulphide sulphur} = \frac{0{\cdot}08\,(X - Y)}{W}\ \text{per cent}$$

where W = Weight of test portion, in grammes.

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