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STANDARD

ISO
7269

Second edition
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Rubber — Determination of free sulfur

Caoutchouc — Dosage du soufre libre



Reference number
ISO 7269:1995(E)

Foreword

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

International Standard ISO 7269 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

This second edition cancels and replaces the first edition (ISO 7269:1987), of which it constitutes a minor revision.

Annex A forms an integral part of this International Standard.

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Introduction

The free-sulfur content of an unvulcanized rubber compound (i.e. the amount of uncombined sulfur present in the compound) should represent all the added, elemental, sulfur. As the vulcanization proceeds and sulfur is gradually combined with the rubber, the free-sulfur content gradually decreases, so its level in any particular product bears some relation to its state of vulcanization, provided the formulation is known and the correct proportion of elemental sulfur (and other ingredients) has been incorporated.

Vulcanizates containing higher proportions of free sulfur than the rubber can dissolve are liable to bloom sulfur, hence certain product specifications include a maximum figure for free sulfur.

Rubber — Determination of free sulfur

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

1.1 This International Standard specifies three methods for the determination of free sulfur in vulcanized rubber: two versions of the copper spiral method, and the sodium sulfite method.

1.2 The copper spiral methods are also applicable, subject to the limitations described in clause 4, to unvulcanized compounds.

1.3 Annex A gives a table listing the sulfur contribution, as a percentage by mass, to these free-sulfur methods for various commercial accelerators.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 383:1976, *Laboratory glassware — Interchangeable conical ground joints.*

ISO 1407:1992, *Rubber — Determination of solvent extract.*

3 Principle

3.1 Copper spiral methods A and B

3.1.1 Method A

The free sulfur in a test portion is extracted with acetone as in the determination of solvent extract, described in ISO 1407, except that a spiral of clean copper gauze is placed in the flask containing the acetone. The copper reacts with the extracted sulfur, forming copper sulfide. When extraction is complete, the acetone solution is drawn off through a filter and discarded. The acetone-insoluble copper and copper sulfide remaining in the flask are treated with hydrochloric acid. The resulting hydrogen sulfide is passed through cadmium acetate solution, and the cadmium sulfide formed is determined iodometrically.

3.1.2 Method B

Rapid copper spiral method B is the same as copper spiral method A except that the extraction time is reduced by using a vapour-jacketed Soxhlet of reduced capacity (6 cm³) to increase the extraction temperature.

3.2 Sulfite method

The free sulfur in a test portion is reacted with aqueous sodium sulfite and the sodium thiosulfate so formed is determined iodometrically.

4 Limitations

4.1 The copper spiral methods generally determine elemental sulfur only, although certain sulfur-donating curatives, such as thiuram disulfide and diaminosulfides, can give rise to slightly high results. In addition, the copper spiral methods are unsuitable for unvulcanized compounds if the added elemental sulfur is of the form insoluble in acetone, i.e. the so-called "insoluble" or amorphous sulfur. The total mass of free sulfur in the test portion shall be in the range 0,2 mg to 10 mg.

4.2 The sulfite method is excessively sensitive to the presence of sulfur-donating curatives and to antioxidants, and shall not be used for unvulcanized compounds.

4.3 In the absence of sulfur-donating curatives, the methods are comparable in accuracy and precision.

NOTE 1 In practice, in addition to determining free elemental sulfur, some coordinately bound reactive sulfur such as that in thiuram disulfide and polysulfides may also give positive responses.

5 Copper spiral method A

5.1 Reagents and materials

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

5.1.1 Acetone.

5.1.2 Cadmium acetate, buffered solution.

Dissolve 25 g of cadmium acetate dihydrate $[(\text{CH}_3\text{COO})_2\text{Cd}\cdot 2\text{H}_2\text{O}]$ and 25 g of sodium acetate trihydrate $(\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O})$ in water, add 100 cm³ of glacial acetic acid and make up to 1 dm³ with water.

5.1.3 Copper gauze, 250 μm to 420 μm (40 mesh to 60 mesh).

5.1.4 Filter paper or polyamide cloth, to wrap the rubber test portion.

5.1.5 Hydrochloric acid, diluted 1 + 1.

Add 1 volume of concentrated [36 % (m/m)] hydrochloric acid, $c(\text{HCl}) = 10 \text{ mol/dm}^3$ ($\rho_{20} = 1,18 \text{ Mg/m}^3$), to 1 volume of water.

5.1.6 Nitric acid, $c(\text{HNO}_3) = 10 \text{ mol/dm}^3$.

Add 10 volumes of concentrated [70 % (m/m)] nitric acid, $c(\text{HNO}_3) = 16 \text{ mol/dm}^3$ ($\rho_{20} = 1,42 \text{ Mg/m}^3$), to 6 volumes of water.

5.1.7 Iodine solution, $c(\text{I}_2) \approx 0,025 \text{ mol/dm}^3$.

5.1.8 Sodium thiosulfate, accurately standardized solution, $c(\text{Na}_2\text{S}_2\text{O}_3) = 0,05 \text{ mol/dm}^3$.

5.1.9 Starch, 1 g/100 cm³ solution.

5.1.10 Pure nitrogen gas.

5.1.11 Glycerol, general laboratory grade.

5.2 Apparatus

Ordinary laboratory apparatus and the items specified in 5.2.1 to 5.2.10 are required for assembly of the apparatus shown in figures 1 and 2. Substitutions may be made if they perform the same function as the items listed. All ground-glass joints shall comply with the requirements of ISO 383 and shall be sealed by applying glycerol (5.1.11) before assembling.

5.2.1 Extraction flask (A), of capacity 150 cm³, with 34/35 conical ground-glass joint.

5.2.2 Soxhlet extractor (Y), with 34/35 socket and 34/35 cone. Capacity of extractor (P) 20 cm³ to 30 cm³.

5.2.3 Graham condenser (Z), with 34/35 angle drip cone.

5.2.4 Reduction adapter (D), with 14/23 socket, 34/35 cone, and a gas inlet tube to reach to within 3 mm of the bottom of the extraction flask (5.2.1) when assembled.

5.2.5 Conical flask (J), of capacity 250 cm³, with 24/29 conical ground-glass joint.

5.2.6 Gas-washing bottles (K and L).

5.2.7 Receiver adapter (E), with 10/19 socket, 24/29 cone and internal sealed dip-tube.

5.2.8 Condenser, Liebig type (F), effective length approximately 22 cm, with 14/23 angle drip cone, 14/23 socket and side arm with 10/19 cone.

5.2.9 Dropping funnel (G), of capacity 100 cm³, with 14/23 cone, modified stem and 14/23 stopper.

5.2.10 Micro-immersion filter (Emich pattern) (H), stem approximately 75 mm long, diameter of disc 10 mm, porosity grade 3.

5.2.11 Laboratory mill.

5.3 Procedure

5.3.1 Preparation of copper spiral

5.3.1.1 Cut about 5 g of the copper gauze (5.1.3) to form a 10 mm wide strip and loosely roll to form a spiral approximately 20 mm in diameter, the turns being conveniently held in place by a loop of copper wire.

5.3.1.2 Clean the spiral, immediately before use, by dipping in cold dilute nitric acid (5.1.6) for a few seconds, sufficient to cause the copper to become clean and bright. Remove all traces of acid by thoroughly and repeatedly washing in water. Wash with acetone (5.1.1) and dry.

5.3.2 Extraction of free sulfur

5.3.2.1 Prepare the rubber by finely cutting to pass through a 1,70 mm sieve or thinly milling to a thickness not exceeding 0,5 mm and weigh a test portion of approximately 1 g to the nearest 0,1 mg (mass *m*). If there is evidence of sulfur bloom, weigh a 0,5 g test portion to the same tolerance.

If the rubber is unvulcanized, weigh a test portion which will contain not more than 10 mg of free sulfur.

5.3.2.2 Place the copper spiral, prepared as specified in 5.3.1, in the 150 cm³ extraction flask (A) (5.2.1) and extract the test portion for not less than 4 h, following the procedure specified in 5.3.2.3.

5.3.2.3 Roll the weighed test portion in the filter paper or polyamide cloth (5.1.4) (previously extracted with acetone) to form a loose roll from which the rubber cannot fall and so that no part of the rubber is anywhere in contact with any other part of the rubber. Place the roll in the Soxhlet extractor (Y) (5.2.2) and pour into the extraction flask (A) 75 cm³ of acetone. Assemble the apparatus and adjust the rate of heating such that the quantity of acetone distilled will fill the extractor 10 to 20 times per hour.

5.3.2.4 If, at the end of the extraction period, the spiral is heavily blackened, add a second spiral prepared as specified in 5.3.1 and continue the extraction for a further 2 h. If no blackening is apparent, it will

suffice to add a further piece of copper gauze about 10 mm square and continue the extraction for 1 h.

5.3.2.5 Disconnect the extraction flask, remove the reduction adapter (D) (5.2.4) and filter off the acetone through the micro-immersion filter (H) (5.2.10). Wash the spirals with three portions of about 20 cm³ of hot acetone, removing the washings each time through the micro-immersion filter.

5.3.3 Determination of extracted free sulfur

5.3.3.1 Assemble the extraction flask (A) now containing the copper spirals, together with the micro-immersion filter (H) and reduction adapter (D), into the apparatus of figure 2. Introduce 100 cm³ of cadmium acetate solution (5.1.2) into the receiver (J) (5.2.5) and fill the gas-washing bottles (K and L) (5.2.6) to a depth of about 10 mm with the same solution. Pass a stream of nitrogen (5.1.10) through the apparatus to displace the air and then adjust the flow to about one bubble per second in flask J.

5.3.3.2 Introduce 50 cm³ of dilute hydrochloric acid (5.1.5) slowly from the dropping funnel (G) (5.2.9) into flask A, heat slowly to boiling and continue to boil gently for 20 min to 30 min. Towards the end of this period, increase the flow of nitrogen to sweep over all traces of hydrogen sulfide. The solution in gas-washing bottle K 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 shall be repeated using a smaller test portion or slower rate of gas flow. Disconnect the receiver adapter (E) (5.2.7) from the condenser side arm and, whilst holding it at an angle, add from a pipette a measured volume (*V*) of iodine solution (5.1.7) (usually 20 cm³ is a suitable quantity) to flask J, so that excess iodine is present.

5.3.3.3 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. Cool the solution to approximately 15 °C. Titrate the excess iodine with sodium thiosulfate solution (5.1.8) (volume *V*₁), using starch solution (5.1.9) as the indicator.

5.3.3.4 Carry out a blank test using all the reagents, including a volume *V* (see 5.3.3.2) of iodine solution (5.1.7) and 100 cm³ of cadmium acetate solution (5.1.2), but omitting the test portion. Record the volume of standard sodium thiosulfate solution needed (*V*₂).

5.3.3.5 The difference between the volume of sodium thiosulfate used in the blank test and that used in the determination is equivalent to the iodine which has reacted with the cadmium sulfide.

5.4 Expression of results

Calculate the free-sulfur content, expressed as a percentage by mass, from the formula

$$\frac{1,6(V_2 - V_1)c}{m}$$

where

- V_1 is the volume, in cubic centimetres, of sodium thiosulfate (5.1.8) reacting with the excess iodine in the determination (see 5.3.3.3);
- V_2 is the volume, in cubic centimetres, of sodium thiosulfate (5.1.8) equivalent to V cm³ of the iodine solution (5.1.7) used for the blank test (see 5.3.3.4);
- c is the actual concentration, expressed in moles per cubic centimetre, of the sodium thiosulfate solution (5.1.8) used;
- m is the mass, in grams, of the test portion (see 5.3.2.1).

6 Copper spiral method B

6.1 Reagents and materials

See 5.1.

6.2 Apparatus

Ordinary laboratory apparatus and the items specified in 6.2.1 to 6.2.4 are required for assembly of the apparatus shown in figure 3. Substitutions may be made if they perform the same function as the items listed. All ground-glass joints shall comply with the requirements of ISO 383 and shall be sealed by applying glycerol (5.1.11) before assembling.

6.2.1 Extraction flask (A), of capacity 150 cm³, with 34/35 conical ground-glass joint.

6.2.2 Soxhlet extractor (B), with 19/23 socket and 14/19 cone. Capacity of extraction cup approximately 6 cm³.

As an alternative to a jacketed Soxhlet, the type of Soxhlet depicted in figure 2 of ISO 1407:1992 may be used.

6.2.3 Graham condenser (C), with 19/26 angle drip cone.

6.2.4 Reduction adapter (X), with 34/35 cone and 14/19 socket.

6.3 Procedure

This is identical to 5.3 except that 5.3.2.2 shall read

“Place the copper spiral, prepared as specified in 5.3.1, in the 150 cm³ extraction flask (A) (6.2.1) and extract the test portion for not less than 1 h, following the procedure specified in 5.3.2.3.”

5.3.2.4 shall read

“If, at the end of the extraction period, the spiral is heavily blackened, add a second spiral prepared as specified in 5.3.1 and continue the extraction for a further 10 min. If no blackening is apparent, it will suffice to add a further piece of copper gauze about 10 mm square and continue the extraction for 10 min.”

and 5.3.2.5 shall read

“Disconnect the extraction flask, remove the reduction adapter (X) (6.2.4) and filter off the acetone through the micro-immersion filter (H) (5.2.10). Wash the spirals with three portions of about 20 cm³ of hot acetone, removing the washings each time through the micro-immersion filter.”

6.4 Expression of results

See 5.4.

7 Sulfite method

7.1 Reagents and materials

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

7.1.1 Sodium sulfite, solution.

Dissolve 50 g of anhydrous sodium sulfite (Na₂SO₃) or 100 g of sodium sulfite heptahydrate (Na₂SO₃·7H₂O) in 1 dm³ of water.

This solution shall be made up freshly once a week.

7.1.2 Liquid paraffin.

7.1.3 Charcoal, granular, activated for gas adsorption by heating at 250 °C to 300 °C for 45 min.

7.1.4 Formaldehyde, 300 g/dm³ to 400 g/dm³ solution.

7.1.5 Acetic acid, glacial.

7.1.6 Iodine, solution, $c(I_2) \approx 0,025$ mol/dm³.

7.1.7 Sodium thiosulfate, accurately standardized solution, $c(Na_2S_2O_3) = 0,05$ mol/dm³.

7.1.8 Starch, 1 g/100 cm³ solution.

7.1.9 Diatomaceous earth¹⁾, for use as filter material.

7.2 Apparatus

Ordinary laboratory apparatus, plus the following:

7.2.1 Conical flask, borosilicate, of capacity 500 cm³.

7.2.2 Büchner funnel, 60 mm.

7.2.3 Büchner flask.

7.2.4 Hotplate.

7.2.5 Laboratory mill.

7.3 Procedure

7.3.1 Prepare the rubber, by finely cutting to pass through a 1,70 mm sieve or thinly milling to a thickness not exceeding 0,5 mm, and weigh a test portion of approximately 2 g to the nearest 0,1 mg. Transfer to the borosilicate conical flask (7.2.1) and add 100 cm³ of sodium sulfite solution (7.1.1) and, to prevent frothing, 3 cm³ to 5 cm³ of liquid paraffin (7.1.2). Cover the mouth of the flask with a watch glass and boil gently on the hotplate (7.2.4) for 4 h.

7.3.2 Cool, add 5 g of activated charcoal (7.1.3) and allow to stand for 30 min, during which time accelerator residues are adsorbed on the charcoal.

7.3.3 Remove any insoluble matter by filtering, under vacuum, through the Büchner funnel (7.2.2) containing a filter bed, approximately 5 mm thick, of the diatomaceous earth (7.1.9) supported on qualitative grade filter paper. Wash the conical flask with three successive 25 cm³ volumes of hot water, collecting

the filtered washings in the Büchner flask (7.2.3). Wash the filter residue with a further 25 cm³ of hot water.

7.3.4 Add 10 cm³ of formaldehyde solution (7.1.4) to the filtrate in the Büchner flask, allow to stand for 5 min and add 5 cm³ of glacial acetic acid (7.1.5). Swirl to mix, cool to approximately 15 °C and add an accurately measured volume of iodine solution (7.1.6), so that excess iodine is present. Mix thoroughly, add a few drops of starch solution (7.1.8) and titrate the excess iodine with sodium thiosulfate solution (7.1.7) (volume V_3).

7.3.5 Carry out a blank test on the reagents. Record the volume of standard sodium thiosulfate solution needed (V_4).

7.4 Expression of results

Calculate the free-sulfur content, expressed as a percentage by mass, from the formula

$$\frac{3,2(V_3 - V_4)c}{m}$$

where

V_3 is the volume, in cubic centimetres, of sodium thiosulfate (7.1.7) used for titration of the test portion (see 7.3.4);

V_4 is the volume, in cubic centimetres, of sodium thiosulfate (7.1.7) used in the blank test (see 7.3.5);

c is the actual concentration, expressed in moles per cubic decimetre, of the sodium thiosulfate solution (7.1.7) used;

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

8 Test report

The test report shall include the following information:

- a reference to this International Standard;
- all details necessary for the complete identification of the sample;
- the method used — copper spiral method A or B, or the sulfite method;
- the result of the determination;

1) Celite 545, available commercially, is suitable. This information is given for the convenience of users of this International Standard 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.

- e) any unusual features noted during the determination;
- f) any operation not included in this International Standard or in the International Standards to which reference is made, as well as any operation regarded as optional;
- g) the date of the test.

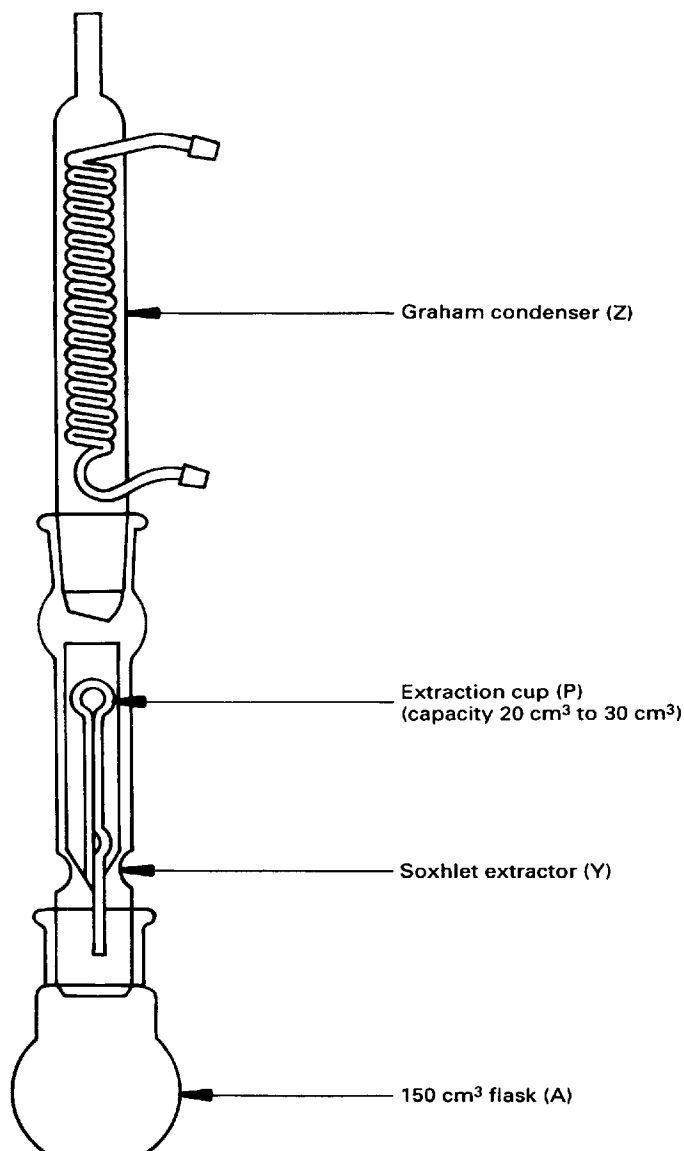


Figure 1 — Typical apparatus for extraction of free sulfur by copper spiral method A

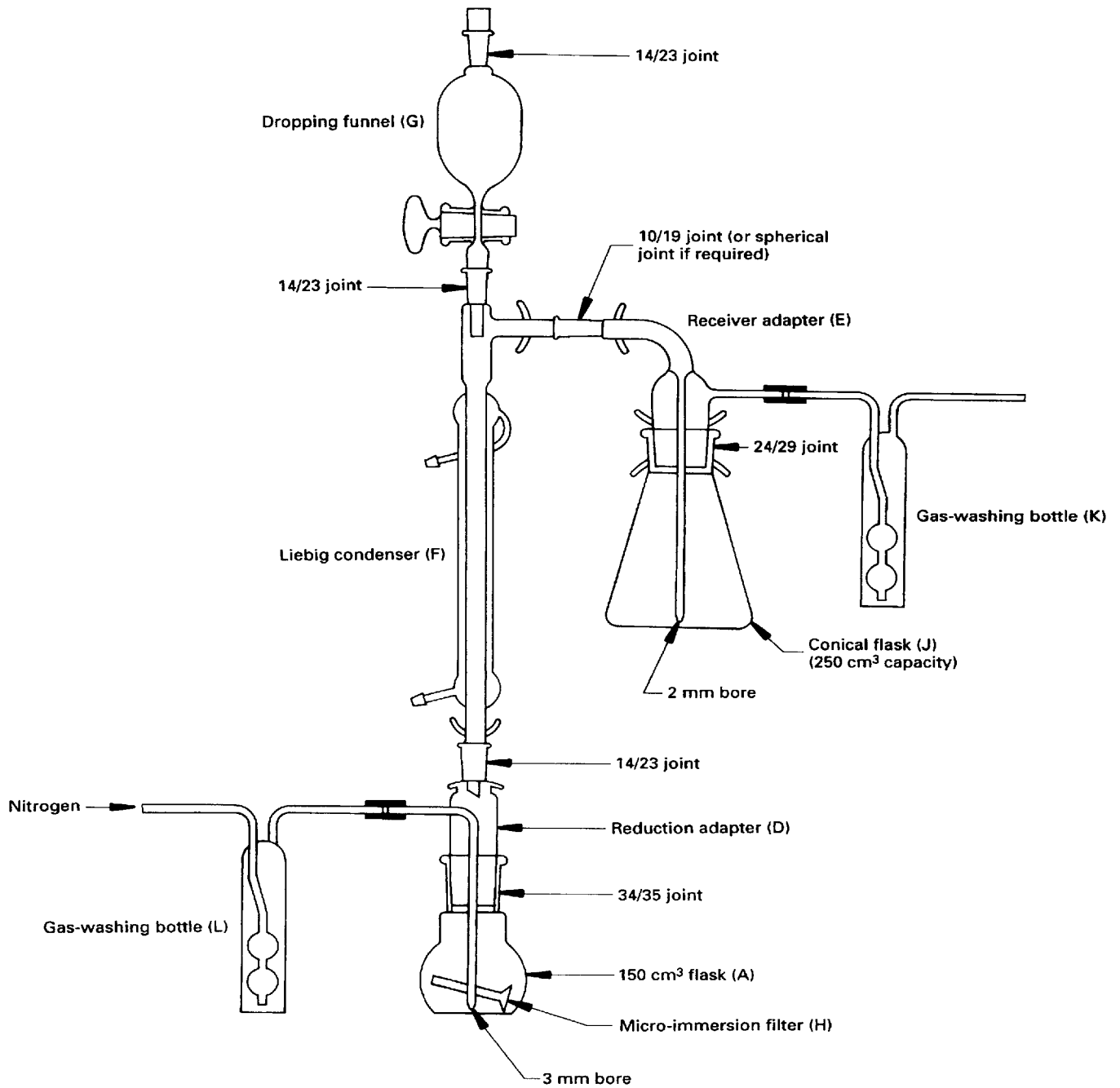


Figure 2 — Typical apparatus for determination of free sulfur by copper spiral method A

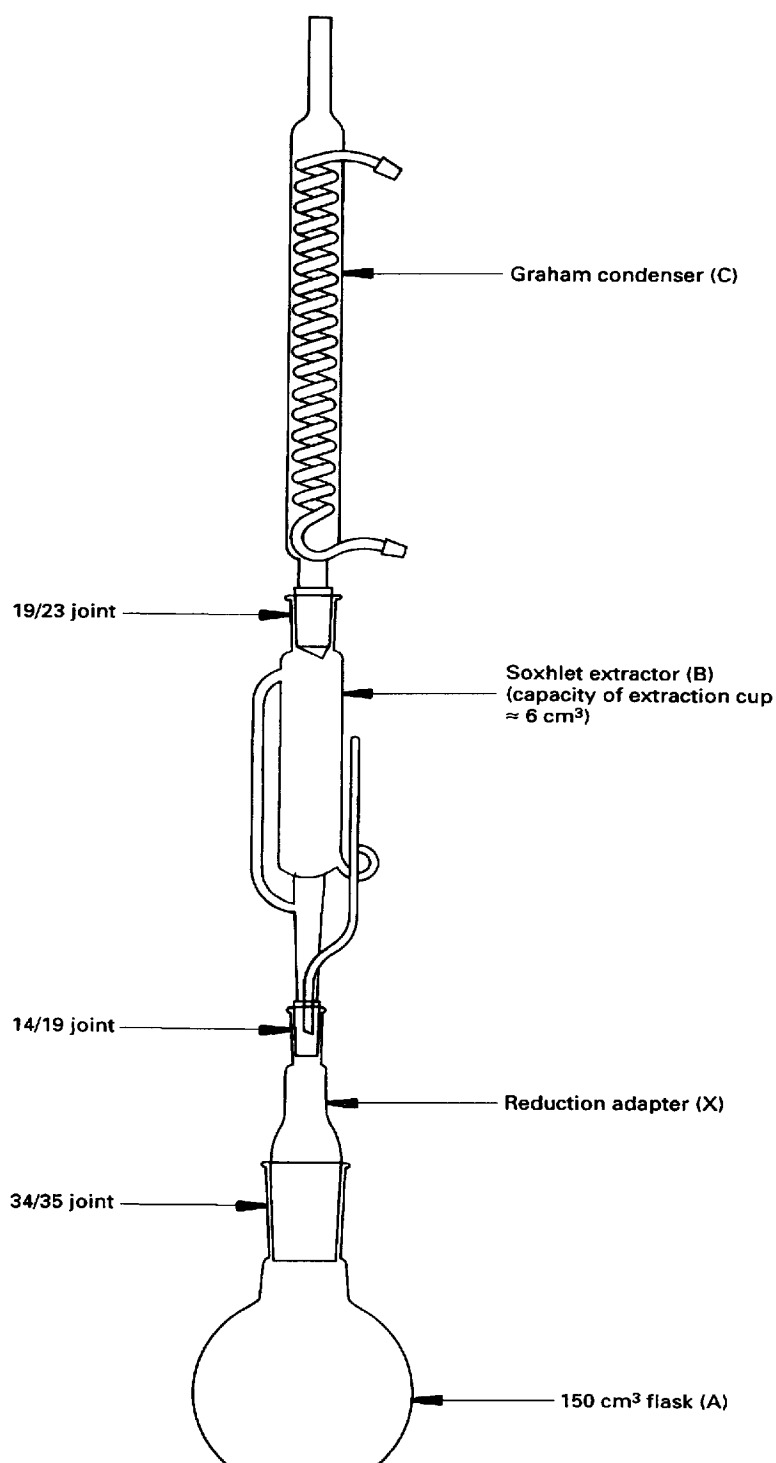


Figure 3 — Typical apparatus for determination of free sulfur by copper spiral method B

Annex A (normative)

Determination of free-sulfur content — Effect of various commercial accelerators on the copper spiral and sulfite methods of analysis

(Information provided by the Tun Abdul Razak Laboratory of the Malaysian Rubber Producers' Research Association)

Accelerator	Apparent free S % Cu spiral methods	Apparent free S % sulfite method
Dipentamethylene thiuram hexasulfide	22,5	26,4
Dipentamethylene thiuram tetrasulfide	20,0	20,3
4,4'-Dithiomorpholine	10,3	21,0
4-Morpholinyl-2-benzothiazolyl disulfide	6,1	20,0
Zinc isopropyl xanthate	4,6	3,5
Tetramethyl thiuram disulfide	1,4	38,6
Dimethyldithiocarbamyl sulfenamide	0,92	16,6
Tetramethyl thiuram monosulfide	< 0,01	33,3
Zinc dimethyl dithiocarbamate	< 0,01	21,4
Zinc 2-mercaptobenzothiazole	< 0,01	5,1
Ethylene thiourea	< 0,01	7,6
Dicyclohexylamine salt of di- <i>n</i> -butyl-dithiophosphoric acid	< 0,01	8,0
<i>N</i> -cyclohexyl-benzothiazole-sulfenamide-2	< 0,01	0,7
2-Mercaptobenzothiazole	< 0,01	12,5
2-2'-Dibenzothiazyl disulfide	< 0,01	11,2

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Descriptors: rubber, vulcanized rubber, chemical analysis, determination of content, sulphur, test equipment.

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