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## Rubber — Determination of free sulfur

*Caoutchouc — Détermination du soufre libre*

Reference number
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# Foreword

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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.

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# Rubber — Determination of free sulfur

## 0 Introduction

**0.1** The free sulfur[1] content of an unvulcanized rubber 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.

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

## 1 Scope and field of application

**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.

NOTE — The annex gives a table listing the sulfur contribution, as a percentage by mass, to these free sulfur methods for various commercial accelerators.

The table is self-explanatory and is the work of the Tun Abdul Razak Laboratory of the Malaysian Rubber Producers' Research Association.

## 2 References

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

ISO 1382, *Rubber — Vocabulary.*

ISO 1407, *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 $cm^3$) 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 diamino sulfides 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 should be in the range 0,2 to 10 mg.

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1) ISO 1382 gives the following definition for free sulfur :

**sulfur, free** : The uncombined sulfur in a rubber mix or vulcanizate.

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

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

NOTE — 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.

**WARNING — All recognized health and safety precautions shall be in effect when carrying out the operations of this International Standard.**

**5.1.1 Acetone.**

**5.1.2 Cadmium acetate,** buffered solution.

Dissolve 25 g of cadmium acetate dihydrate $[(CH_3COO)_2Cd{\cdot}2H_2O]$ and 25 g of sodium acetate trihydrate $(CH_3COONa{\cdot}3H_2O)$ in water, add 100 $cm^3$ of glacial acetic acid and make up to 1 $dm^3$ with water.

**5.1.3 Copper gauze,** 250 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 hydrochloric acid [36 % $(m/m)$], $c(HCl) = 10$ mol/$dm^3$ ($\varrho_{20} = 1{,}18$ Mg/$m^3$), to 1 volume of water.

**5.1.6 Nitric acid,** $c(HNO_3) = 10$ mol/$dm^3$.

Add 10 volumes of concentrated nitric acid [70 % $(m/m)$], $c(HNO_3) = 16$ mol/$dm^3$, ($\varrho_{20} = 1{,}42$ Mg/$m^3$), to 6 volumes of water.

**5.1.7 Iodine solution,** $c(I_2) \approx 0{,}025$ mol/$dm^3$.

**5.1.8 Sodium thiosulfate,** accurately standardized solution, $c(Na_2S_2O_3) = 0{,}05$ mol/$dm^3$.

**5.1.9 Starch,** 1 g/100 $cm^3$ solution.

**5.1.10 Pure nitrogen gas.**

**5.1.11 Glycerol** (laboratory grade).

### 5.2 Apparatus

Ordinary laboratory apparatus and the items below 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[1] shall be sealed by applying glycerol (5.1.11) before assembling.

**5.2.1 Extraction flask** (A), of capacity 150 $cm^3$, with 34/35 ground glass joint.

**5.2.2 Soxhlet extractor** (Y), with 34/35 socket and 34/35 cone. Capacity of extractor (P) 20 to 30 $cm^3$.

**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, with 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 $cm^3$, with 24/29 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, with 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 $cm^3$, 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

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1) Conical ground glass joints complying with the requirements of ISO 383 and designated as recommended in ISO 383.

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 = $m$ g). 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 specially prepared copper spiral (5.3.1.2) in the 150 cm$^3$ extraction flask (A) of figure 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 apparatus (5.2.2) and pour into the extraction flask (A) 75 cm$^3$ of the acetone. Assemble the apparatus and adjust the rate of heating such that the distilled quantity of acetone 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, a second prepared spiral (5.3.1.2) should be added and the extraction continued 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 cm$^3$ 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 cm$^3$ of the 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 the 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 cm$^3$ of the dilute hydrochloric acid (5.1.5) slowly from the 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 the 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 must 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 the iodine solution (5.1.7) (usually 20 cm$^3$ 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 = $V_1$ cm$^3$) using starch solution (5.1.9) as the indicator.

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 cm$^3$ of the cadmium acetate solution (5.1.2), but omitting the test portion. Volume of standard sodium thiosulfate solution needed = $V_2$ cm$^3$.

**5.3.3.4** 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

The free sulfur content, expressed as a percentage by mass, is given by the formula

$$\frac{3{,}2\,(V_2 - V_1)\,c}{m}$$

where

$V_1$ is the volume of the sodium thiosulfate (5.1.8) reacting with the excess iodine in the determination;

$V_2$ is the volume of the sodium thiosulfate (5.1.8) equivalent to $V$ cm$^3$ of the iodine solution (5.1.7) used for the blank test;

$c$ 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.

# 6 Copper spiral method B

## 6.1 Reagents

See 5.1.

## 6.2 Apparatus

Assemble the following apparatus as shown in figure 3. Substitutions may be made if they perform the same function as the items listed. All ground glass joints shall be sealed by applying glycerol before assembling.

**6.2.1 Extraction flask** (A), of capacity 150 cm$^3$, with 34/35 ground glass joint.

**6.2.2 Soxhlet extractor** (B), with 19/23 socket and 14/19 cone. Capacity of extraction cup approximately 6 cm$^3$.

As an alternative to a jacketed Soxhlet, the type of Soxhlet depicted in figure 2 of ISO 1407 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 specially prepared copper spiral in the 150 cm$^3$ extraction flask (A) of figure 3 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, a second prepared spiral should be added and the extraction continued 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 cm$^3$ 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.

**WARNING — All recognized health and safety precautions shall be in effect when carrying out the operations of this International Standard.**

**7.1.1 Sodium sulfite,** solution.

Dissolve 50 g of anhydrous sodium sulfite ($Na_2SO_3$) or 100 g of sodium sulfite heptahydrate ($Na_2SO_3 \cdot 7H_2O$) in 1 dm$^3$ 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 to 300 °C for 45 min.

**7.1.4 Formaldehyde,** 300 to 400 g/dm$^3$ solution.

**7.1.5 Acetic acid,** glacial.

**7.1.6 Iodine,** solution, $c(I_2) \approx 0{,}025$ mol/dm$^3$.

**7.1.7 Sodium thiosulfate,** accurately standardized solution, $c(Na_2S_2O_3) = 0{,}05$ mol/dm$^3$.

**7.1.8 Starch,** 1 g/100 cm$^3$ solution.

**7.1.9 Diatomaceous earth**[1], filter aid.

### 7.2 Apparatus

Ordinary laboratory apparatus and

**7.2.1 Conical flask,** borosilicate, of capacity 500 cm$^3$.

**7.2.2 Büchner funnel,** 60 mm.

**7.2.3 Büchner flask.**

**7.2.4 Hot-plate.**

**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 cm$^3$ of the sodium sulfite solution (7.1.1) and, to prevent frothing, 3 to 5 cm$^3$ of the liquid paraffin (7.1.2). Cover the mouth of the flask with a clock glass and boil gently on the hot-plate (7.2.4) for 4 h.

**7.3.2** Cool, add 5 g of the 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 cm$^3$ volumes of hot water, collecting the filtered washings in the Büchner flask (7.2.3). Wash the filter residue with a further 25 cm$^3$ of hot water.

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[1] Celite 545, or an equivalent product, available commercially, is suitable. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of this product by ISO.

**7.3.4** Add 10 $cm^3$ of the formaldehyde solution (7.1.4) to the filtrate in the Büchner flask, allow to stand for 5 min and add 5 $cm^3$ of the glacial acetic acid (7.1.5). Swirl to mix, cool to approximately 15 °C and add an accurately measured volume of the iodine solution (7.1.6), so that excess iodine is present. Mix thoroughly, add a few drops of the starch solution (7.1.8) and titrate the excess iodine with the sodium thiosulfate solution (7.1.7) (volume = $V_3$ $cm^3$).

**7.3.5** Carry out a blank test on the reagents. Volume of standard sodium thiosulfate solution needed = $V_4$ $cm^3$.

### 7.4 Expression of results

The free sulfur content, expressed as a percentage by mass, is given by the formula

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

where

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

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

$c$ 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) all details necessary for the complete identification of the sample;

b) reference to this International Standard;

c) the method used — copper spiral method A or B, or the sulfite method;

d) result of the determination;

e) any deviations from the standard procedure or unusual features noted during the determinations, which might influence the results;

f) date of test.

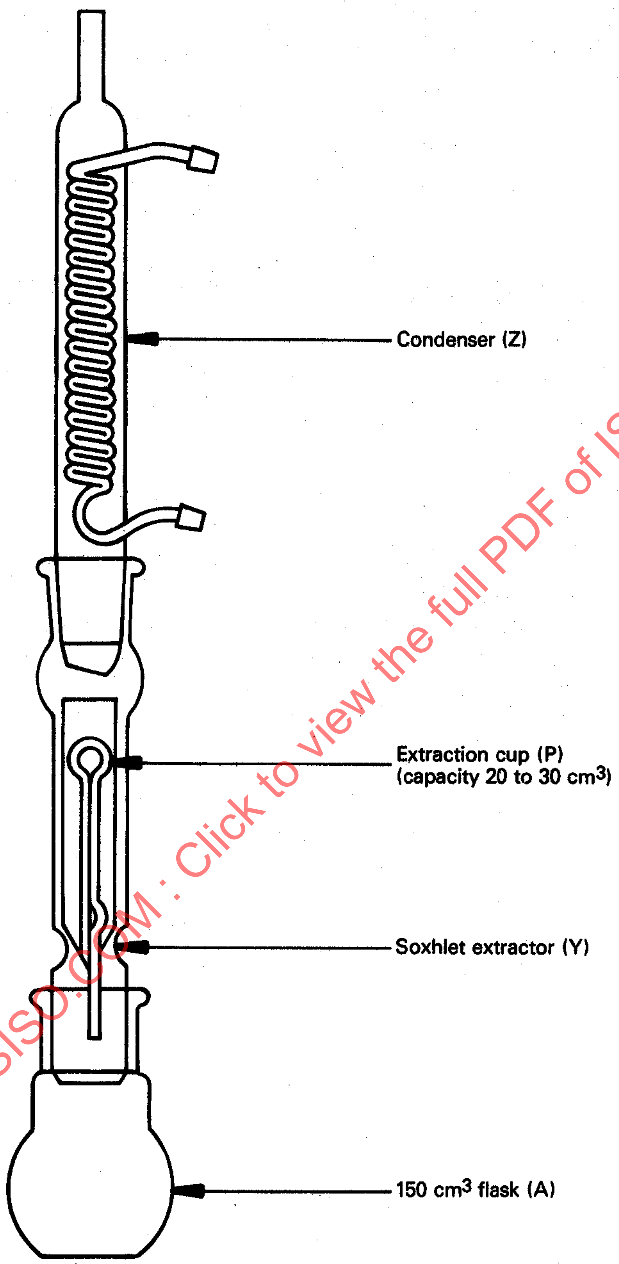

Figure 1 — Typical apparatus for extraction of free sulfur by the Copper Spiral Method A

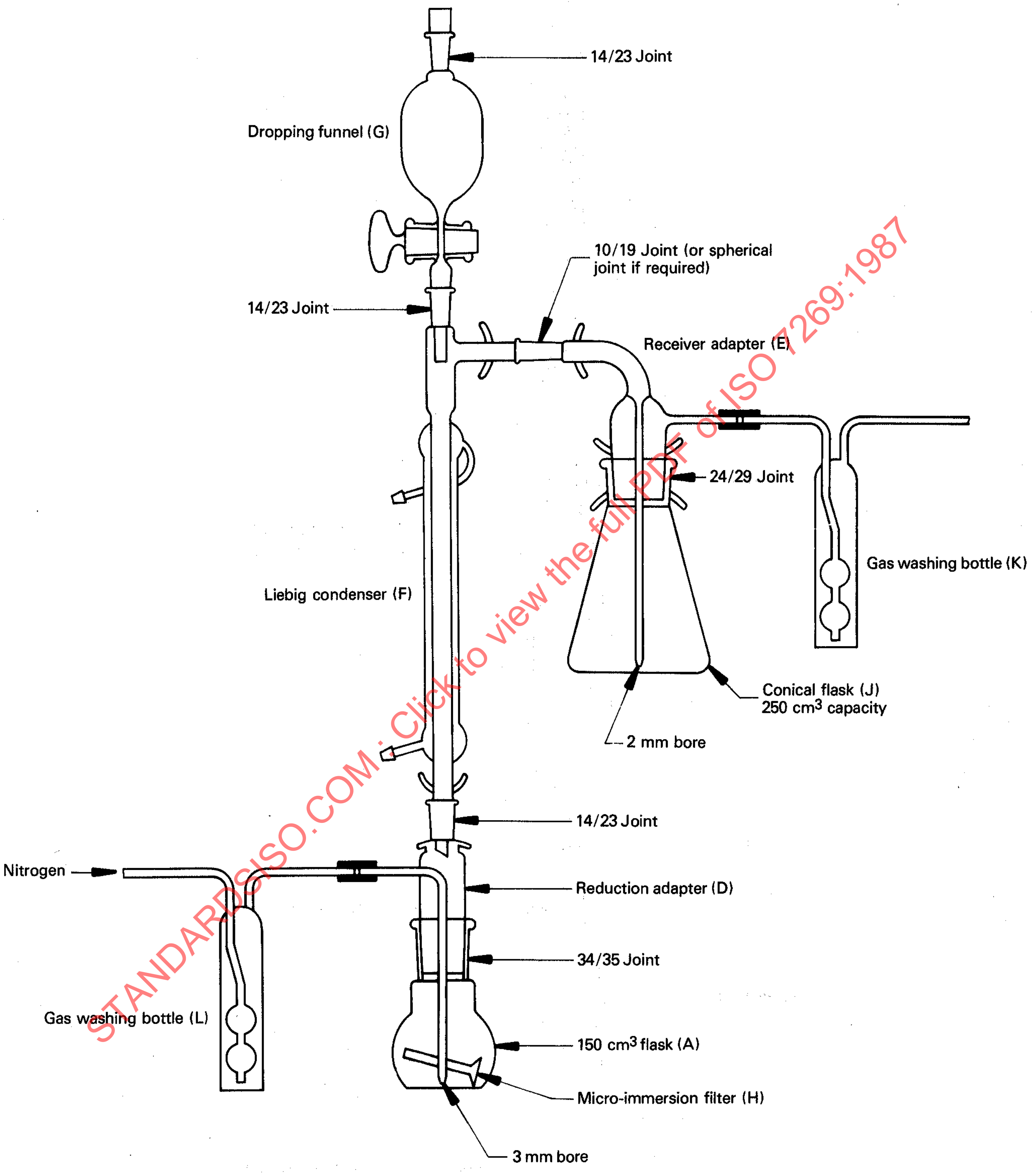

**Figure 2 — Typical apparatus for determination of free sulfur by the Copper Spiral Method A**