INTERNATIONAL STANDARD

ISO
4260

First edition
1987-04-01

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION
МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method

Produits pétroliers et hydrocarbures — Dosage du soufre — Méthode de combustion Wickbold

Reference number
ISO 4260 : 1987 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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 4260 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants.*

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

Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method

CAUTION — The procedure specified in this International Standard includes the combustion of hydrogen in glass apparatus or stainless steel apparatus (in the case of olefins), which is potentially hazardous, and all precautions should be carefully observed.

1 Scope and field of application

This International Standard specifies a method for the determination of total sulfur in petroleum products, natural gas and olefins. The method may be applied to products having sulfur contents in the range 1 to 10 000 mg/kg and is particularly suitable for distillates with total sulfur contents of less than 300 mg/kg. Test samples which are viscous, highly aromatic, or of high sulfur content may be first diluted with a sulfur-free solvent.

The method can be used for the determination of the total sulfur content of natural and refinery gases, also for substances supplied to the burner in the liquid state and for the determination of volatile sulfur in substances supplied to the burner in the gaseous state after vaporization from the liquid phase. It is not suitable for the determination of sulfur in heavy-duty engine oils. For the determination of sulfur in light olefins, see clause 13, special case.

NOTES

1 If required, total chlorine content of petroleum products can be determined by the usual volumetric, gravimetric or potentiometric methods for determination of the chloride ions present in the absorption solution after combustion by this method.

The inorganic bound chlorine has to be removed by water extraction prior to the burning procedure, otherwise interference will occur.

2 When viscous or solid materials, such as bitumen or heavy fuel oils, are burnt in a combustion boat, some of the sulfur may be bound to the ash retained in the boat. If this is the case, the sulfur bound in the ash has to be determined in the residue.

2 References

ISO 641, *Laboratory glassware — Interchangeable spherical ground joints.*

ISO 3170, *Petroleum products — Liquid hydrocarbons — Manual sampling.*

ISO 3171, *Petroleum products — Liquid hydrocarbons — Automatic pipeline sampling.*

ISO 4850, *Personal eye-protectors for welding and related techniques — Filters — Utilisation and transmittance requirements.*

3 Principle

Gaseous or liquid test portions are passed to the oxy-hydrogen flame of a suction burner where they are burnt with considerable excess of oxygen. Viscous or solid test samples are preferably dissolved in light petroleum/toluene blend and treated as liquid test samples or may be burnt in a stream of oxygen in a combustion boat.

The resulting sulfur oxides are converted into sulfuric acid by absorption in hydrogen peroxide solution. Depending on the sulfur content of the test portion, the sulfate ions in the absorption solution are determined using the method of analysis shown in table 1 and set out in clause 9.

Table 1 — Relation between expected sulfur content, mass of test portion, and method of analysis recommended

Expected sulfur content mg/kg	Mass of test portion1) g	Sulfur in absorption solution µg	Aliquot portion of absorption solution	Sulfur in the aliquot portion µg	Method of analysis recommended for different levels of sulfur content		
	100	100	1/2	50	Conductimetric titration (9.4)	Nephelometric titration (9.2)	Turbidimetric titration (9.3)
	50	50	1/1	50			
1	20	20	1/1	20			
5	20	100	1/2	50			
	50	250	1/5	50			
	50	250	1/1	250			
10	5	50	1/1	50	Visual titration (9.1)		
	10	100	1/2	50			
	20	200	1/2	100			
	50	500	1/2	250			
30	5	150	1/2	75			
	10	300	1/2	150			
	20	600	1/2	300			
	50	1 500	1/5	300			
50	5	250	1/2	125			
	10	500	1/2	250			
	30	1 500	1/5	300			
100	2	200	1/2	100			
	5	500	1/2	250			
	10	1 000	1/5	200			
1 000	1	1 000	1/5	200			
	2	2 000	1/5	400			
10 000	1	10 000	1/10	1 000			

1) The volume of a gas test sample required may be calculated with sufficient accuracy from the mass and density of the gas. The precision data in clause 12 do not apply for gas test samples.

4 Reagents and materials

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

Volumetric solutions and other reagents as specified in clause 9 under the individual method of analysis and

4.1 Hydrogen peroxide, 3 % (*m*/*m*) solution, free from sulfur.

4.2 Ethanol, 96 % (*V*/*V*), free from sulfur.

4.3 Blend containing 4 volumes of light petroleum, (boiling range 60 to 80 °C) and 1 volume of toluene, free from sulfur (in the following text referred to as "light petroleum/toluene blend").

4.4 Oxygen, compressed gas, commercial grade, free from sulfur.

4.5 Hydrogen, compressed gas, commercial grade, free from sulfur.

4.6 Hydrochloric acid, concentrated, ϱ_{20} 1,19 g/ml.

4.7 Mercury.

4.8 Dihexyldisulfide or dibenzothiophene reference blend.

Dissolve a known mass of dihexyldisulfide or dibenzothiophene, weighed to the nearest 0,1 mg, in the light petroleum/toluene blend (4.3). The concentration of the product should be chosen from the sulfur concentration in the range shown in column 1 of table 1 according to the finish which will be used.

Dihexyldisulfide contains 27,36 % (*m*/*m*) of sulfur, and dibenzothiophene contains 14,7 % (*m*/*m*) of sulfur.

CAUTION — It is recommended that high-pressure gas cylinders are not stored in the laboratory.

5 Apparatus

NOTE — In order to provide a detailed description of the mode of operation, this International Standard has been based on two types of burners and a single type of absorption train.

Other types of burner using the principle of combustion of a test portion in an oxy-hydrogen flame with excess oxygen may be used (see clause 13). These should be operated as described in the manufacturers' instructions and checked by the combustion of test portions of the standard sulfur-containing reference blends (see clause 10).

Apparatus specified in clause 9 under individual method of analysis and

5.1 Combustion apparatus (see figure 1 for the schematic layout of the apparatus for the combustion of gaseous or liquid test samples and figure 2 for that for the combustion of viscous or solid test samples), consisting essentially of the following components:

5.1.1 Reducing valve (1), with gauge, range 0 to 5 bar (0 to 500 kPa)[1], for oxygen.

5.1.2 Reducing valve (2), with gauge, range 0 to 2 bar (0 to 200 kPa), for hydrogen.

5.1.3 Flowmeter (3), range 20 to 300 l/h, operating on the floating element principle, with precision control valve, for the secondary oxygen line.

5.1.4 Flowmeter (4), range 20 to 200 l/h, operating on the floating element principle, with precision control valve, for the hydrogen line.

5.1.5 Flowmeter (5), range 200 to 2 000 l/h, operating on the floating element principle, with precision control valve, for the primary oxygen line.

5.1.6 Excess-pressure vessels (6), for example wash bottles, containing mercury (4.7) and white oil (see 8.2), or metal pressure safety valves. Three are required. The inlet valves must be of the non-return type.

5.1.7 Flame trap (7), with metal connections.

5.1.8 Flow indicator (8), glass.

5.1.9 Vacuum gauge (11), range from approximately 0,6 to 1,1 bar (60 to 110 kPa) absolute.

5.1.10 Vacuum line (12), with vacuum valve (9), and branch line to vacuum gauge (11), and a branch line with stopcock (10) to the flow indicator (8).

5.1.11 Narrow-necked one-mark volumetric flask (13), 100 or 250 ml capacity, with spherical ground glass joint, ISO 641-S29/15.

5.1.12 Combustion chamber[2] (20), of transparent fused quartz, **cooler (19), absorber tower (17), frit-type filter, pore size index 1,6 mm (16), drip chamber (15), three-way stopcock (14), and ground glass spherical joint,** ISO 641-S29/15, assembled into a single unit. The combustion chamber, cooler and absorber tower are enclosed in a water-cooled jacket.

5.1.13 Burner[2] (21), of stainless steel or transparent fused quartz. The burner should be of the suction type (see figure 1) for the combustion of gaseous or liquid products. A stainless steel burner may be used as an alternative and such a burner shall be used for light olefins (see figure 3).

5.1.14 Stopcock (18), fitted in the line connecting the absorption solution flask and absorber tower (17).

5.1.15 Test portion container (22). The assembly of the combustion equipment shown in figure 1 uses a test portion container, for example a conical flask, approximately 100 ml capacity. (See also 8.6.1 to 8.6.4.) When testing highly volatile test samples, the conical flask should be enclosed by a vacuum jacketed vessel or other similar device. The flask is held in place by means of an adjustable support.

The assembly of the combustion equipment shown in figure 2 uses a combustion boat as the test portion container.

5.1.16 Gas sample meter. A dry gas meter connected to a precision type valve for measuring the quantity of test portion for gas samples shall be used, unless this is to be determined gravimetrically. The range of the meter shall be appropriate for the quantity of sample to be burned and the meter shall be recently calibrated.

5.1.17 Connectors. For connecting the hydrogen and oxygen cylinders with flowmeters (3), (4), and (5), use high-pressure metal piping. The remaining piping in the system may be made of elastomers, such as silicone rubber.

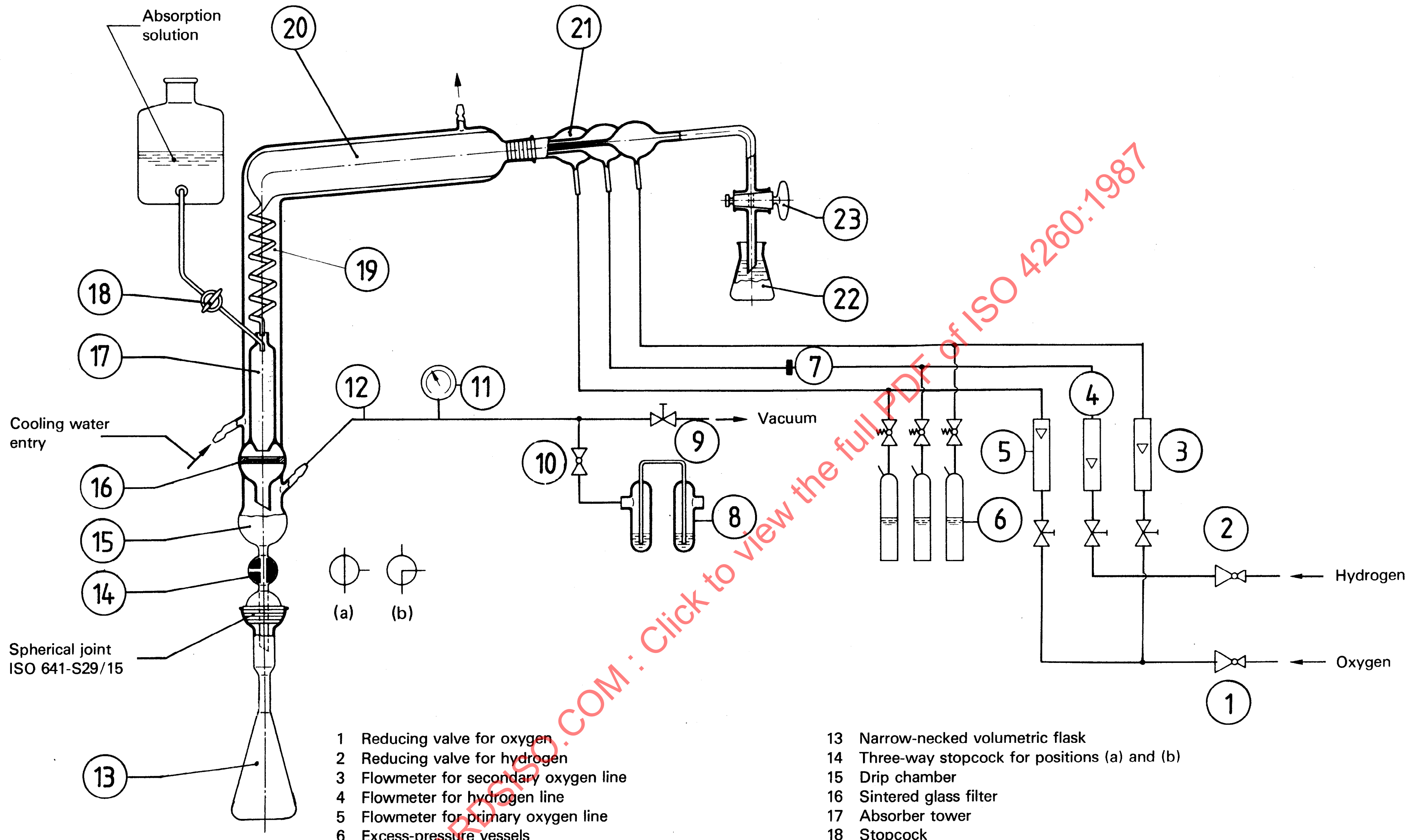
5.1.18 Bunsen burner.

5.1.19 Analytical balance.

---

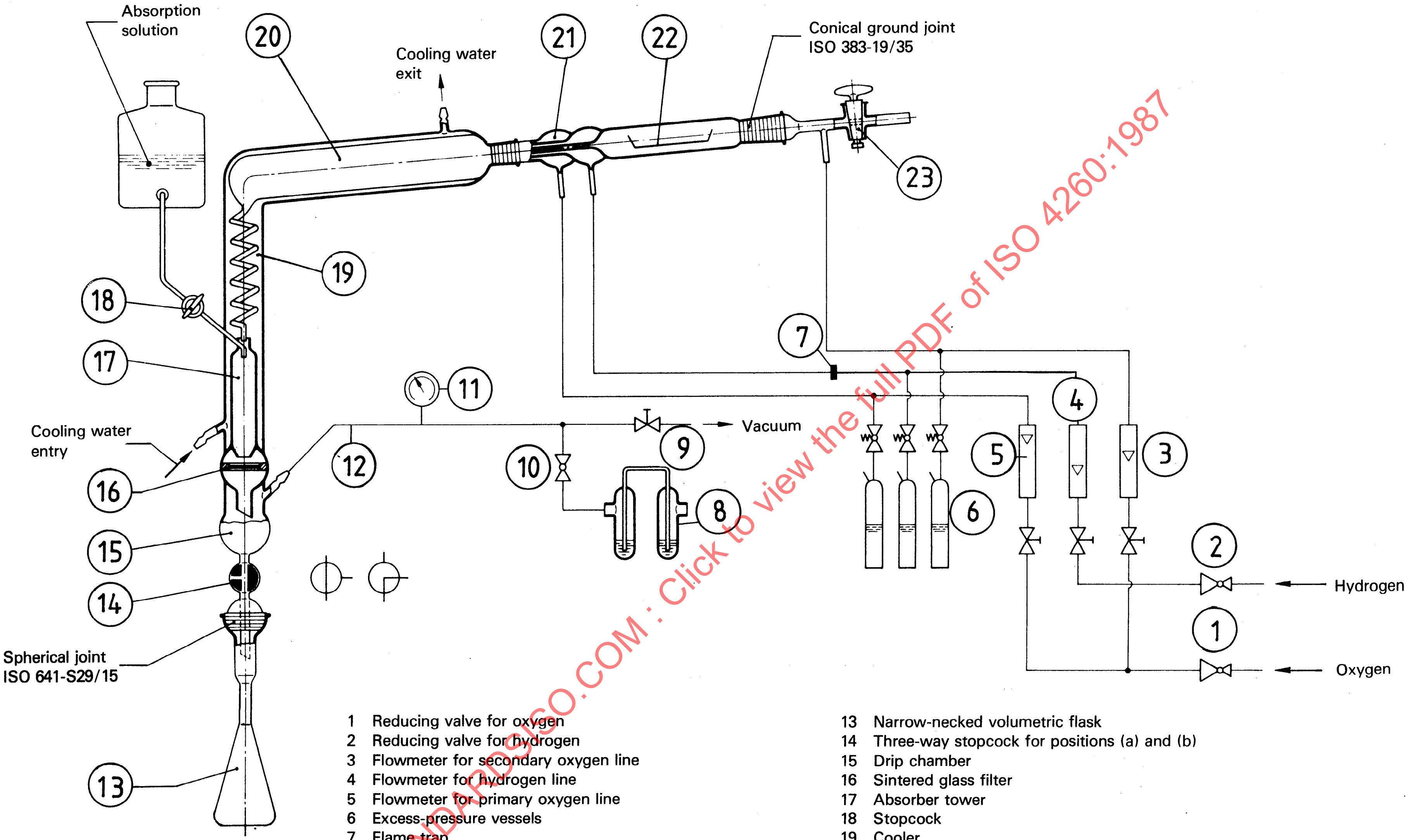
[1] 1 Pa = 1 N/m^2 = 10^{-5} bar

[2] The burner and combustion chamber as shown are claimed to be the subject of patents in some countries. Information on the patent position should be sought from local suppliers. However, most of these patents are unlikely to be still current.



1	Reducing valve for oxygen
2	Reducing valve for hydrogen
3	Flowmeter for secondary oxygen line
4	Flowmeter for hydrogen line
5	Flowmeter for primary oxygen line
6	Excess-pressure vessels
7	Flame trap
8	Flow indicator
9	Vacuum valve
10	Stopcock
11	Vacuum gauge
12	Vacuum line
13	Narrow-necked volumetric flask
14	Three-way stopcock for positions (a) and (b)
15	Drip chamber
16	Sintered glass filter
17	Absorber tower
18	Stopcock
19	Cooler
20	Combustion chamber
21	Suction-type burner
22	Test portion container
23	Stopcock

Figure 1 — Schematic layout of apparatus for combustion of gaseous or liquid test samples



1	Reducing valve for oxygen	13	Narrow-necked volumetric flask
2	Reducing valve for hydrogen	14	Three-way stopcock for positions (a) and (b)
3	Flowmeter for secondary oxygen line	15	Drip chamber
4	Flowmeter for hydrogen line	16	Sintered glass filter
5	Flowmeter for primary oxygen line	17	Absorber tower
6	Excess-pressure vessels	18	Stopcock
7	Flame trap	19	Cooler
8	Flow indicator	20	Combustion chamber
9	Vacuum valve	21	Solid product burner
10	Stopcock	22	Test portion container
11	Vacuum gauge	23	Stopcock
12	Vacuum line		

Figure 2 — Schematic layout of apparatus for combustion of viscous or solid test samples

5.2 Safety appliances

5.2.1 A screen, for example of safety glass, or fine-mesh wire gauze or suitable transparent plastics material or equivalent, to screen off the burner, combustion chamber and absorber tower.

5.2.2 Protective glass filter goggles, capable of absorbing harmful radiation given off during combustion, shall be worn to protect the operator's eyes. Oxy-acetylene welding goggles are suitable (see ISO 4850).

5.2.3 Safety electrovalves, capable of shutting off the hydrogen stream: one on the cold-water circuit, which operates only in the event that admission of water stops, and the other in the vacuum line (12) which operates only in case of variation in the low pressure in the combustion chamber.

6 Sampling

Test samples shall be taken following the appropriate good practice for sampling petroleum products. Suitable procedures for sampling from bulk storage are specified in ISO 3170 and for automatic sampling from pipe-lines are specified in ISO 3171. For gaseous products, on-line sampling and testing is recommended.

7 Size of test portion

The size of the test portion required depends on the sulfur content of the test sample and on the method of analysis employed to determine the sulfur content. The quantities of test portion required for different combinations of sulfur content and methods of analysis are set out in table 1.

8 Combustion procedure

8.1 Cleaning of apparatus

Scrupulous cleanliness of test portion containers and apparatus is required throughout. Wash the test portion containers, lines, valves, and connectors used for gas and LPG test samples with light petroleum/toluene blend (4.3) until the sulfur content of the washings as determined according to the procedure for liquid test samples is negligible. Ensure that the containers are solvent-free before taking test portions. Glassware and silicaware can be cleaned with concentrated detergent but must finally be thoroughly washed with water to remove sulfur compounds. More rigorous cleaning can be accomplished with dichromate/nitric acid cleaning agent. Silicaware can be cleaned by heating in a muffle furnace.

It is preferable to reserve a set of test portion containers and the silica and glassware equipment for low sulfur content test samples and to keep another set for high sulfur content test samples.

NOTE — After each combustion or series of combustions, the combustion chamber should be cleaned by washing carefully with the hydrochloric acid (4.6), diluted (1 + 1), and with water.

8.2 Assembly of apparatus

For testing gaseous or liquid test samples, assemble the carefully cleaned apparatus as shown in figure 1, or for viscous and solid test samples as shown in figure 2.

Fill the three excess-pressure vessels (6) with the mercury (4.7) up to a level of approximately 300 mm and float approximately 20 mm of white oil on top of the mercury or adjust the safety valves to an equivalent relief pressure.

Fill the flow indicator (8) with water until the level in both compartments is about 30 mm.

In the assembly shown in figure 1, support the suction burner (21) with a wire or wire coil of suitable length.

Ensure that the safety devices (see 5.2) are in place.

8.3 Preparation of apparatus

Pass a rapid stream of cold water in the direction shown in figures 1 and 2, through the cooling jacket enclosing the combustion chamber, cooler and absorber tower.

Fill the absorption solution reservoir with the hydrogen peroxide solution (4.1).

Adjust the oxygen pressure reducing valve (1) to 1 bar (100 kPa) and the hydrogen pressure reducing valve (2) to 0,5 bar (50 kPa). Ensure that the valves of meters (3), (4) and (5) are closed. Turn the three-way stopcock (14) to position (a).

Remove the burner (21) and open the stopcock (10) upstream of the flow indicator (8). Open the valve upstream of flowmeter (5) to allow an oxygen stream of 600 to 800 l/h to pass through the primary oxygen line, and open the valve upstream of flowmeter (3) to allow 100 to 200 l/h of oxygen to flow through the secondary oxygen line. Re-introduce the burner (21) and, at the same time, open the vacuum valve (9) until the flow indicator (8) drops back to zero. Close the stopcock (10).

Set the vacuum valve (9) so that the vacuum gauge (11) indicates a pressure of 0,135 to 0,35 bar (13,5 to 35 kPa) absolute.

8.4 Ignition of oxy-hydrogen flame

8.4.1 Suction burner (see figure 1)

Remove the suction burner (21) from the combustion chamber (20). Open the valve upstream of flowmeter (4) so that a hydrogen flow of approximately 200 l/h is admitted, (see note 2). Allow hydrogen to flow freely for approximately 30 s before igniting the oxy-hydrogen flame with a wax taper or electrical ignition device. Matches shall not be used.

CAUTION — Use safety goggles (see 5.2.2).

NOTES

1 This procedure is modified when burning certain gaseous samples (see 8.6.1).

2 When the burner is being flushed with hydrogen, care should be exercised that the hydrogen leaving the burner mouth does not pass into the combustion chamber, otherwise damage may occur when the burner is lit.

Replace the suction burner (21), avoiding contact between the combustion chamber joint (20) and the oxy-hydrogen flame. With the aid of the valve upstream of flowmeter (4), adjust the hydrogen flow so as to obtain an oxy-hydrogen flame length of 10 to 20 mm. This will produce a drop in pressure at the vacuum gauge (11). Readjust the vacuum to 0,135 to 0,35 bar (13,5 to 35 kPa) by means of vacuum valve (9). It is important to maintain this vacuum level to achieve steady combustion.

If it is intended to carry out a blank test on the gases the duration of the combustion should be noted.

8.4.2 Solid products burner (see figure 2)

Sub-clause 8.4.1 applies equally to the ignition of the oxy-hydrogen flame in the solid products burner (21).

8.5 Control of absorption solution supply

Turn the stopcock (18) so that the supply of absorption solution is adjusted to a rate of 1 to 5 drops per second.

8.6 Combustion of test portion

8.6.1 Gaseous test samples (general)

8.6.1.1 In the general procedure, the samples are burnt in the oxy-hydrogen flame; however, samples of natural gas frequently have very low sulfur contents (approximately 1 mg/kg) and it is necessary to burn larger test portions. For such samples, there is no need for an oxy-hydrogen flame as a back-up flame for burning the gas and these gases can be burnt directly in the oxygen stream as in 8.6.2.

NOTE — The procedures in 8.6.1 and 8.6.2 relate to test portions taken direct from a bulk sample or from a large sample container. Alternatively, the test portion may be the entire contents of a suitable gas sample container; the quantity of the test portion may then be determined by weighing the container before and after the combustion procedure. It is important to ensure that all of the test portion has been transferred to the combustion chamber.

8.6.1.2 Allow the test portion of gaseous sample to flow from the sample container through a precision-type valve and a dry gas meter into the test portion supply line of the suction burner (21). A safety pressure-relief valve may be included before the gas meter.

Adjust the vacuum valve (9) and stopcock (23) so that a flame approximately 3/4 of the length of the combustion chamber (20) is obtained. Care shall be taken that the flame does not extend to touch the condenser coil.

Ensure that during the combustion process the vacuum gauge (11) indicates a steady vacuum.

8.6.1.3 When a sufficient volume of the test portion (see table 1) has been burnt, close the gas meter valve. Pinch off the connection between the gas meter and the test portion supply line to allow any residual gas in the test portion supply line to be drawn into the suction burner (21) and burnt. Close stopcock (18) to shut off the flow of absorption solution.

NOTE — If the test portion is the contents of a gas sample cylinder, when the test portion is completely burnt, two portions, each of a volume corresponding to approximately 2 % of the volume of the cylinder of the light petroleum/toluene blend (4.3) should be introduced into the cylinder to dissolve any residual part of the test portion and each portion burnt in the oxy-hydrogen flame.

8.6.1.4 Shut off the hydrogen stream by closing the valve upstream of flowmeter (4). When the burner tip is visibly free from glowing particles, shut off both oxygen streams by closing the valves upstream of the flowmeters (3) and (5) and immediately remove the suction burner from the combustion chamber.

8.6.1.5 Spray several jets of distilled water from a wash bottle onto the interior walls of the combustion chamber in order to wash any residual combustion products through the cooler and absorber tower into the narrow-necked volumetric flask (13).

8.6.1.6 Turn the three-way stopcock (14) to position (b) to relieve the vacuum in the narrow-necked flask (13) and then remove it. Close vacuum valve (9) and open stopcock (10).

NOTE — If a series of test portions is to be burnt, neither the oxy-hydrogen gas flame nor the vacuum need be shut off after combustion of each portion to prepare equipment for further combustion. After the initial test portion has been burnt, shut off supply of absorption solution, and remove the lighted burner (21) from combustion chamber (20). After spraying distilled water through the combustion chamber (see 8.6.1.5), replace narrow-necked volumetric flask (13) by another one and re-insert the burner into the combustion chamber.

8.6.2 Gaseous test samples (low sulfur content)

8.6.2.1 Remove the hydrogen supply line to the suction burner (21) and in its place connect the test portion supply line for the gas. This supply line shall include a precision-type valve and a dry gas meter (5.1.16) and may include a safety pressure relief valve before the meter. Prepare the apparatus as specified in 8.1 to 8.3 but do not ignite the burner as specified in 8.4.

8.6.2.2 Remove the suction burner (21) from the combustion chamber (20), allow the gaseous test sample to flow through the precision-type valve and the dry gas meter into the burner. Keep the stopcock (23) closed. Allow the gas to flow freely for approximately 30 s before igniting the flame, use a wax taper or an electrical ignition device. Matches shall not be used. Replace the burner in the combustion chamber, avoiding contact between the combustion chamber joint and the flame. Adjust the vacuum valve (9) and the precision-type valve of the gas test portion supply line so that a flame approximately 3/4 of the length of the combustion chamber (20) is obtained. Care shall be taken so that the flame does not extend to touch the condenser coil. Ensure that during the combustion process the vacuum gauge (11) indicates a steady vacuum.

8.6.2.3 When a sufficient volume of test portion (see table 1) has been burnt, close the precision-type valve, pinch off the connections between the gas meter and the supply line to allow any residual gas in the supply line to be drawn to the suction burner and as much as possible burnt. With test samples having low sulfur contents, the unburnt portion will not be sufficient to introduce significant error. Close stopcock (18) to shut off the flow absorption solution.

NOTE — If the test portion is the contents of a gas sample cylinder, proceed as described in the note in 8.6.1.3.

8.6.2.4 When the burner tip is visibly free from glowing particles, shut off both oxygen streams by closing the valves upstream of the flowmeters (3) and (5) and immediately remove the suction burner from the combustion chamber. Proceed as in 8.6.1.5 and 8.6.1.6 (the note does not apply).

8.6.3 Liquefied petroleum gas test samples

Transfer a test portion of the test sample in its liquid form from its container to a test sample cylinder. From the latter, pass the liquid through a vaporizer coil at a temperature of 60 to 80 °C, and pass the resulting gas through the test portion supply line to the suction burner (21).

Adjust the flame size as indicated in 8.6.1.2 (in this case the first paragraph of 8.6.1.2 does not apply), readjust the oxygen flow rate if necessary and complete the combustion (see the note in 8.6.4.2). Proceed as in 8.6.1.3 to 8.6.1.6.

Calculate the quantity of the test portion used from the difference between the apparent masses of the empty and full test sample cylinder. Generally a 30 to 50 g test portion will suffice.

8.6.4 Liquid test samples

Liquid petroleum hydrocarbon fractions, up to and including light fuel oil, may be burnt by feeding directly into the oxy-hydrogen flame. Lubricating oils free from ash-forming additives and petroleum hydrocarbons with higher viscosities than light fuel oil may also be burnt in the assembly shown in figure 1 after dilution with the specified light petroleum/toluene blend (4.3).

CAUTION — Liquids of volatility comparable with that of isopentane may cause explosions. Such test samples should be blended before combustion with a high boiling solvent, for example iso-octane.

8.6.4.1 Weigh a test portion (see table 1) to the nearest 0,05 g into the pre-weighed container (22). Place the container with the test portion on an adjustable support under the free end of the supply line to the suction burner (21). Raise the container until the supply line reaches the bottom of the container.

8.6.4.2 Increase the vacuum carefully with the aid of vacuum valve (9) so that the test portion is slowly drawn into the oxy-hydrogen flame. Adjust the vacuum valve (9) until the combustion flame fills approximately 3/4 of the length of the combustion chamber (20) corresponding to a combustion rate of approximately 3 to 5 ml/min. Ensure that the flame is completely smoke-free and does not extend into the condenser coil.

NOTE — If a test portion does not burn readily, check the pressure reading of the vacuum gauge (11). Combustion can be improved by adjusting the valve upstream of flowmeter (3) so as to increase the flow rate of secondary oxygen. Readjust the pressure at the vacuum gauge (11).

Alternatively, combustion can be improved by reducing the liquid flow using the stopcock (23) in the test portion supply line.

8.6.4.3 When the test portion is completely burnt, introduce two portions, each of 2 ml, of the ethanol (4.2) into the test portion container (22) to wash down unburnt residues and burn each portion in the oxy-hydrogen flame. To wash down higher boiling petroleum products, use the light petroleum/toluene blend (4.3).

8.6.4.4 Shut off the hydrogen and oxygen streams following the procedure of 8.6.1.4, and detach the flask (13). Close the vacuum valve (9) and open stopcock (10). Proceed as in 8.6.1.5 and 8.6.1.6.

NOTE — For combustion of a series of samples. see the note in 8.6.1.6.

8.6.5 Leaded gasoline samples (see the note in 12.2)

8.6.5.1 Alternative procedures

If the lead content of the sample is accurately known, the direct combustion procedure specified in 8.6.5.3 may be employed.

If, however, the amount of lead present is unknown or if it is known and the value of the term

$$\text{lead concentration} \times \frac{32}{207}$$

is significant with respect to the concentration of sulfur sought, the use of the extraction method 8.6.5.2 is preferred.

NOTE — If the procedure in 8.6.5.3 is used, lead oxide produced during combustion may condense on the burner and result in erratic burning; in addition, traces of lead oxide may remain in the system and will interfere with subsequent tests on lead-free samples if the Thorin method (9.1) is used.

8.6.5.2 Gasoline of unknown lead content

Introduce a test portion of approximately 100 ml and 50 ml of the hydrochloric acid solution (4.6) into an extraction apparatus (see figure 4). To avoid any loss of volatile constituents, pass a stream of ice water through the reflux condenser. Extract for approximately 5 min from initial time of boiling. After cooling and allowing the phases to separate, draw off the hydrochloric acid layer and reject it. Wash the gasoline layer with water until the washings are neutral to methyl orange. The gasoline layer is then burnt as a liquid test sample.

NOTE — If it is intended to use the turbidimetric titration described in 9.3, the extraction step may be omitted and the test portion burned as a liquid test sample (see 8.6.4). If the extraction is omitted, only the turbidimetric titration shall be used.

8.6.5.3 Gasoline of known lead content

Burn the test portion without extraction and use the Thorin method (9.1). Apply the correction for lead content in 9.1.7.2 to the calculated sulfur content (see 9.1.7.1).

8.6.6 Viscous or solid test samples

Burn viscous or solid test portions in the assembly shown in figure 2 using a combustion boat (22) and a direct flow of oxygen unless it is preferred to dilute the test portion with the light petroleum/toluene blend (4.3) and burn it as a liquid (see 8.6.4). Cut-back bitumens and similar materials which contain solvents shall always be burned as liquids after dilution.

Weigh into a combustion boat an appropriate test portion (see table 1). Ignite the oxy-hydrogen flame as described in 8.4.2. Detach the ground glass joint of the secondary oxygen supply line from the solid matter burner (21) while stopcock (23) is in the open position. Place the combustion boat in the solid product burner and, with the aid of a pusher, push it approximately half way up the burner. Re-establish the connection between the secondary oxygen supply line and the solid product burner. Close stopcock (23) and place the Bunsen burner (5.1.18) with a hot flame underneath the solid product burner so that the Bunsen burner flame is approximately 20 mm in front of the combustion boat. After a few seconds, the solid product burner tube will glow. The heat radiated from the glowing part of the tube will vaporize and ignite the test portion near the pointed end of the combustion boat. The test portion will burn in the oxygen stream within a few seconds.

In order to prevent possible entrainment of unburnt solid matter into the capillary upstream of combustion chamber, a pad of silica wool may be inserted into the tapering section between the combustion chamber and burner capillary.

Depending on the volatility and ignition temperature of the product it may be necessary to change the distance between the Bunsen burner flame and the combustion tube so as to initiate combustion of the test portion.

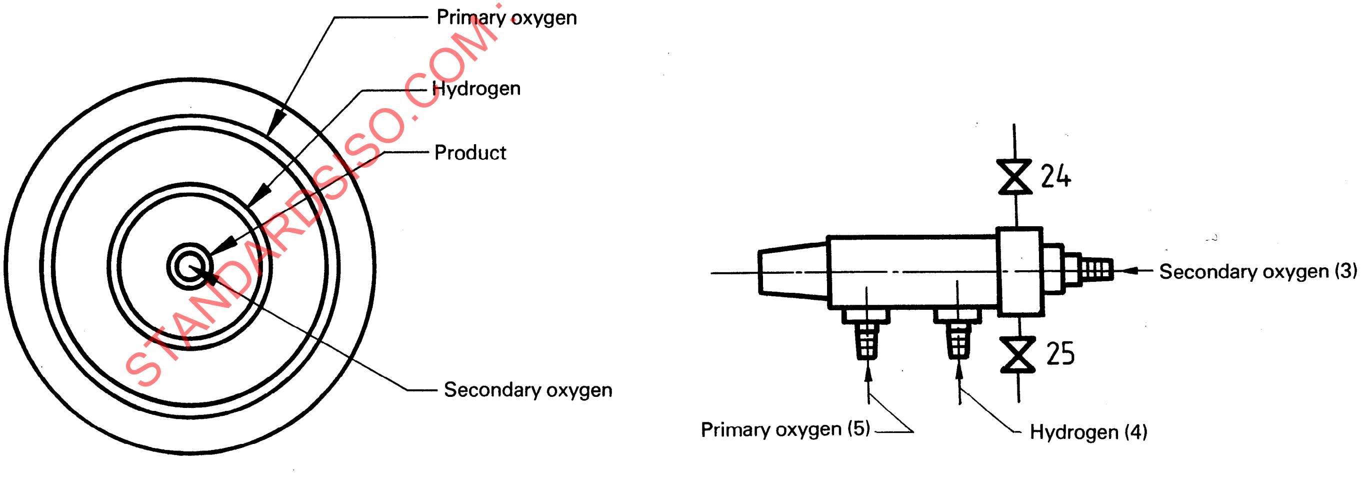
After combustion of the test portion in the combustion boat, move the Bunsen burner along the tube of the solid product burner so as to burn off any residual sulfur.

In order to speed up heating the solid product burner tube, a second Bunsen or similar burner may be used.

8.6.6.1 When combustion of the test portion is complete, close stopcock (18) to shut off the absorption solution stream; then open stopcock (23) in order to vent the combustion chamber. Remove the combustion boat from the solid product burner through the opened ground glass joint.

Spray several jets of distilled water from a wash bottle through the solid product burner into the flame in order to wash any residual particles adhering to the burner capillary into the oxy-hydrogen flame.

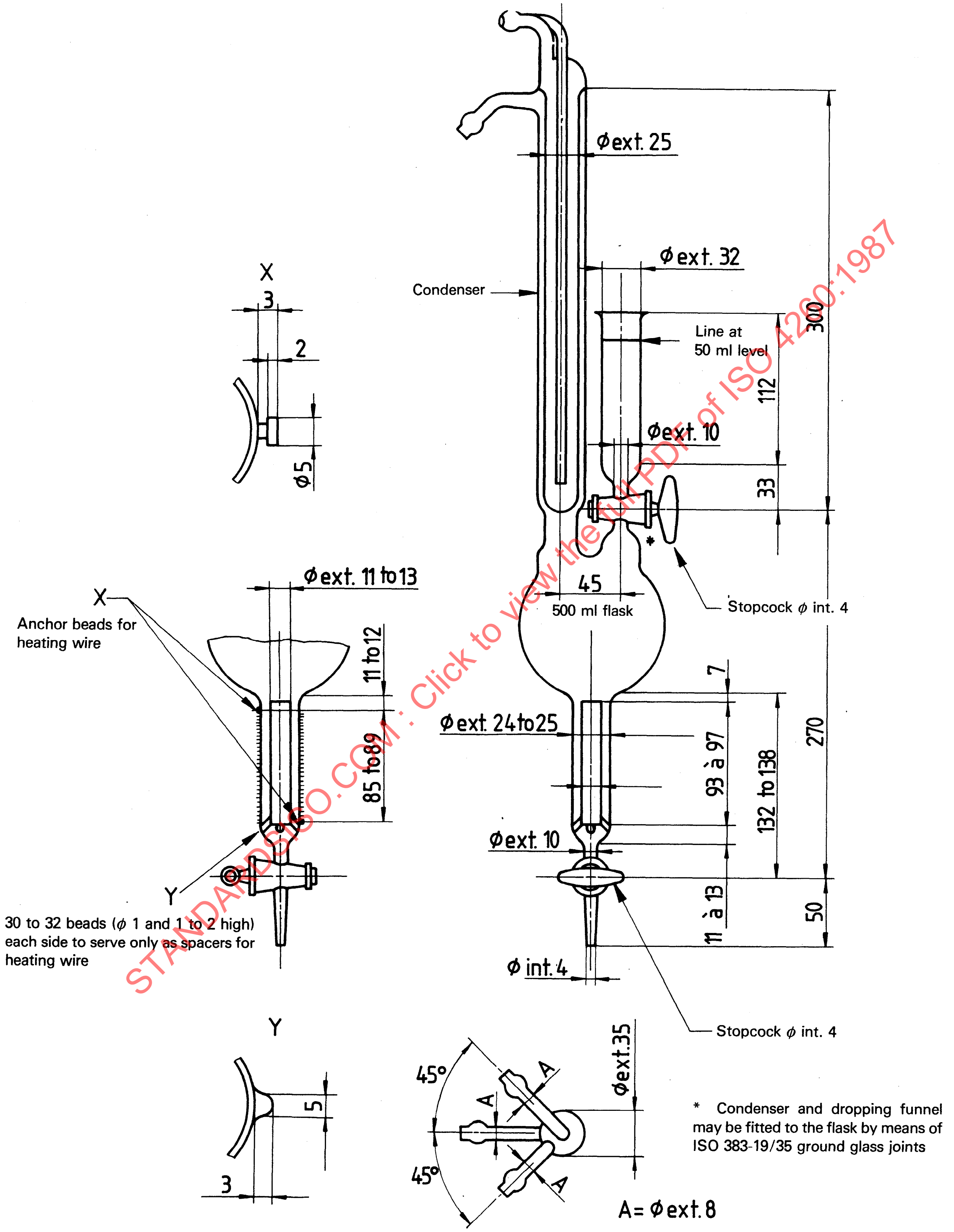
8.6.6.2 Shut off the oxygen and hydrogen streams following the procedure in 8.6.1.4 and proceed as in 8.6.1.5 and 8.6.1.6.



Enlarged cross-section

Figure 3 — Stainless steel burner for olefins

Dimensions in millimetres



* Condenser and dropping funnel may be fitted to the flask by means of ISO 383-19/35 ground glass joints

Figure 4 — Extraction apparatus

9 Determination of absorbed sulfur

Depending on the sulfur content of the test sample or the presence of interfering ions, determine the sulfate ions in the absorption solution by visual titration (9.1), by nephelometric method (9.2), by turbidimetric titration (9.3) or by conductimetric titration (9.4).

The most rapid determination is visual titration as in 9.1. However, a pre-requisite for its application is the absence of cations in the absorption solution. Should cations be present they shall be removed by means of a cation exchanger. Visual titration cannot be used in the presence of phosphate ions; interference by other anions is negligible and may be ignored.

9.1 Visual titration

9.1.1 Range

See table 1.

9.1.2 Interferences

Using the Thorin method, chlorine and nitrogen in the test sample may exceed the sulfur concentration by several times without causing interference. Fluorine interferes if present in concentrations higher than 30 % of the sulfur content. Phosphorus and cations interfere. Sodium, potassium, zinc, magnesium and ammonium ions reduce results by 2 to 3 % due to co-precipitation, cations forming insoluble sulfates interfere quantitatively and many other metal ions interfere by forming coloured complexes with Thorin in alcoholic solutions. In the amounts present in most products these interferences are not significant but they preclude the use of this finish on most lubricating oils containing additives.

9.1.3 Reagents

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

9.1.3.1 2-propanol (*Iso*propyl alcohol).

9.1.3.2 Barium perchlorate, standard volumetric solutions.

a) Standard volumetric solution (1). Weigh 10,6 g of barium perchlorate [$Ba(ClO_4)_2$] or 12,2 g of barium perchlorate trihydrate [$Ba(ClO_4)_2 \cdot 3H_2O$] and dissolve in 200 ml of water; dilute to 1 000 ml with the 2-propanol (9.1.3.1) and adjust to a pH of 3,5 with perchloric acid. Standardize the solution against a standard volumetric solution of sulfuric acid $c(H_2SO_4)$ = 0,005 mol/l.

1 ml of this standard volumetric solution is equivalent to approximately 1 mg of sulfur.

b) Standard volumetric solution (2). Dilute accurately the standard volumetric solution (1) according to the relation (1 + 19).

1 ml of this standard volumetric solution is equivalent to approximately 50 µg of sulfur.

9.1.3.3 Indicator solutions.

a) Thorin, disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphtylazo) benzenearsonic acid, 0,2 % (m/m) aqueous solution.

WARNING — Thorin is toxic by inhalation and by contact with the skin.

b) Methylene blue (C.I. 52015), 0,01 % (m/m) aqueous solution.

NOTE — As an alternative to indicators a) and b), it is possible to use dimethylsulfonazo III [2,7-bis (4-methyl-2-sulfonylazo) chromotropic acid].

Store the indicator solutions in silica or polyethylene bottles.

9.1.4 Apparatus

9.1.4.1 One-mark pipette(s), for transfer of the aliquot portion.

9.1.4.2 Conical flask, wide neck, of capacity 250 ml.

9.1.4.3 Burette, 25 ml, graduated in 0,05 ml, or an **automatic titrator.**

9.1.5 Procedure

Make up the absorption solution in the narrow-necked volumetric flask (13) to the mark with water and mix well. By means of pipette(s) (9.1.4.1), transfer an aliquot portion (see table 1) of the absorption solution to the conical flask (9.1.4.2) and add four times its volume of 2-propanol (9.1.3.1). Add 4 drops of Thorin indicator solution [9.1.3.3 a)]; up to 5 drops of the methylene blue solution [9.1.3.3 b)] may also be added for each 50 ml of absorption solution.

The ratio of Thorin indicator [9.1.3.3 a)] to methylene blue solution [9.1.3.3 b)] may be modified by the operator as and when required.

Titrate with the barium perchlorate standard volumetric solution [9.1.3.2 1) or 2)] according to the concentration of sulfate ions, to a colour change from yellow to a permanent pink or, in the presence of methylene blue, from green to purple/grey.

The Thorin end point is very difficult to see in some types of light, particularly fluorescent lighting and direct sunlight. Good results can be obtained by titrating in front of a daylight lamp.

The colour change can be readily detected spectrometrically at a wavelength of 520 nm.

9.1.6 Determination of reagent blank

Carry out a blank determination by burning the oxygen and hydrogen for the same time as taken to burn a test portion, and carry out the procedure specified in 9.1.5.

9.1.7 Calculation

9.1.7.1 Lead absent

Calculate the sulfur content S, in milligrams per kilogram (parts per million) using equation (1), or in milligrams per cubic metre at 0 °C and 1 013 mbar (101,3 kPa) pressure using equation (2), or as a percentage by mass using equation (3).

$$S = \frac{(V_1 - V_0) \times T}{m_0} \times \frac{V_3}{V_2} \quad \text{(mg/kg)} \qquad \dots (1)$$

$$S = \frac{(V_1 - V_0) \times T}{V_4} \times \frac{V_3}{V_2} \quad \text{(mg/m}^3\text{)} \qquad \dots (2)$$

$$S = \frac{(V_1 - V_0) \times T}{m_0 \times 10^4} \times \frac{V_3}{V_2} \quad [\% \ (m/m)] \qquad \dots (3)$$

where

V_0 is the volume, in millilitres, of barium perchlorate solution used for the blank test;

V_1 is the volume, in millilitres, of barium perchlorate solution used for the absorption solution;

V_2 is the volume, in millilitres, of the aliquot taken;

V_3 is the total volume, in millilitres, of the absorption solution;

V_4 is the volume, in litres, at 0 °C and 1 013 mbar (101,3 kPa) pressure, of the test portion;

T is the sulfur equivalent, in micrograms per millilitre, of the barium perchlorate solution used;

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

9.1.7.2 In the presence of lead

If the amount of lead present is known, the result should be calculated using equation (4):

$$S = S\,\text{(apparent)} + (172{,}7 \times Pb) \qquad \dots (4)$$

where

S (apparent) is the sulfur content, in milligrams per kilogram, calculated according to the equation (1);

Pb is the lead content, in grams per litre.

This method of correction for the lead content of test samples should not be used for test samples containing less than 50 mg/kg of sulfur.

9.2 Nephelometric method

9.2.1 Range

See table 1.

9.2.2 Reagents

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

9.2.2.1 Ethanol/glycerol mixture.

Mix 2 volumes of 99 % (V/V) ethanol (C_2H_5OH) with 1 volume of glycerol [$C_3H_6O(OH)_2$].

9.2.2.2 Barium nitrate.

Carefully and thoroughly sift barium nitrate crystals [$Ba(NO_3)_2$] through a sieve with nominal aperture size between 300 and 150 µm. Do not grind, and avoid the development of a powdery component as the crystal size of the barium nitrate is an important variable that affects the development of turbidity.

9.2.2.3 Hydrochloric acid, solution.

Dilute 77 ml of concentrated hydrochloric acid (HCl), ϱ_{20} 1,19 g/ml, to 1 000 ml with water.

9.2.2.4 Sulfur, standard solutions.

a) Solution A: Introduce 62,4 ml of standard volumetric solution of sulfuric acid $c(H_2SO_4)$ = 0,050 mol/l into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

1 ml of this standard solution is equivalent to approximately 100 µg of sulfur.

b) Solution B: Introduce 10,00 ml of solution A into a 100 ml one-mark volumetric flask and make up to the mark with water

1 ml of this standard solution is equivalent to approximately 10 µg of sulfur.

9.2.3 Apparatus

9.2.3.1 Nephelometer and **galvanometer.** The nephelometer shall be fitted with a filter having a maximum transmission at approximately 415 nm. Cells of suitable size for the volume of the test solution used shall be provided.

9.2.3.2 Burette, 10 ml, graduated every 0,05 ml.

9.2.3.3 Beaker, tall-form, with spout, of capacity 250 ml.

9.2.3.4 One-mark volumetric flasks, of capacity 50 ml.

9.2.3.5 One-mark pipette(s), for transfer of the aliquot portion.

9.2.3.6 One-mark pipette, of capacity 10 ml.

9.2.4 Preparation of calibration curve

9.2.4.1 Into a series of eight 50 ml one-mark volumetric flasks, introduce, by means of the burette, 0,25 — 0,50 — 0,75 — 1,00 — 1,50 — 2,00 — 3,00 and 5,00 ml of the standard sulfur solution A (9.2.2.4). Add 1,0 ml of the dilute hydrochloric acid (9.2.2.3) to each flask, make up to the mark with water and mix thoroughly. Carry out the blank test by burning the oxygen and hydrogen for the same time as taken to burn the test portion and, if the volume of the absorption solution is sufficiently low, transfer it quantitatively to a 50 ml one-mark volumetric flask and follow the procedure specified in paragraphs 1 and 3 of 9.2.5. If it is necessary to reduce the volume, follow the procedures specified in paragraphs 2 and 3 of 9.2.5. Pour the contents of each flask, including the blank, into a series of nine 100 ml beakers.

9.2.4.2 Add to each beaker 10,0 ± 0,1 ml of ethanol/glycerol mixture (9.2.2.1) by means of a pipette and mix for 3 min with a magnetic stirrer. Select a stirring speed slow enough to avoid liquid loss by splashing. Maintain this speed throughout the entire procedure. Allow each solution to stand undisturbed for 4 min and add to one of them 0,30 g of barium nitrate (9.2.2.2). The exact amount of barium nitrate is not critical and it may be added from a small scoop. Stir with the magnetic stirrer for 1 min and allow to stand for 4 min. Transfer to a nephelometer cell (or cuvette) and read the galvanometer immediately.

9.2.4.3 Repeat the procedure on the other seven calibration standards and on the blank.

Prepare a graph plotting the sulfur contents, in micrograms, against the nephelometer readings. A straight line plot should be obtained.

If the sulfur contents to be determined are extremely low, prepare a calibration curve according to the above procedure but making the calibration standards from solution B [9.2.2.4 b)] using 1,0 — 2,0 — 3,0 — 4,0 — 5,0 — 8,0 — 10 ml volumes and plotting the sulfur contents in micrograms against the nephelometer readings.

To check possible drift, check the calibration curve daily by making a single measurement using a standard near the middle range of whichever curve is in use.

9.2.5 Procedure

If the whole of the absorption solution in the narrow-necked volumetric flask (13) is required, and the volume is not too great, transfer it quantitatively to a 50 ml one-mark volumetric flask. If necessary, the volume shall be reduced by the procedure specified below. If an aliquot portion (see table 1) of the absorption solution is required, make up the volume in the narrow-necked volumetric flask (13) to the mark with the water and mix well. If the volume of the aliquot portion is not too great, transfer it by means of a pipette to a 50 ml one-mark volumetric flask.

If the volume of the absorption solution or of the required aliquot portion is too great to transfer to the 50 ml volumetric flask, quantitatively transfer the whole volume of aliquot portion as required to a 250 ml beaker (9.2.3.3) and evaporate it over a hot-plate (DO NOT EVAPORATE OVER A FLAME) until the volume is reduced to approximately 25 ml. Transfer the reduced volume quantitatively to a 50 ml one-mark volumetric flask.

In each case add 1 ml of the hydrochloric acid solution (9.2.2.3) and make up to the mark.

Pour the entire contents of the flask into a 100 ml beaker and proceed as specified for the calibration standards 9.2.4.2.

Convert the nephelometer readings to mass of sulfur by using whichever of the two calibration curves is appropriate.

NOTE — If the sulfur content of the reagent blank reading exceeds 4 µg of sulfur, the results should not be considered reliable.

9.2.6 Calculation

Calculate the sulfur content S, in milligrams per kilogram (parts per million) using equation (5), or in milligrams per cubic metre at 0 °C and 1 013 mbar (101,3 kPa) pressure using equation (6), or as a percentage by mass using equation (7).

$$S = \frac{m_1}{m_0} \times \frac{V_3}{V_2} \qquad \text{(mg/kg)} \qquad \ldots (5)$$

$$S = \frac{m_1}{V_4} \times \frac{V_3}{V_2} \qquad (\text{mg/m}^3) \qquad \ldots (6)$$

$$S = \frac{m_1}{m_0} \times \frac{1}{10^4} \times \frac{V_3}{V_2} \qquad [\%\ (m/m)] \qquad \ldots (7)$$

where

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

m_1 is the mass, in micrograms, of sulfur obtained from the calibration curve;

V_2 is the volume, in millilitres, of the aliquot portion taken;

V_3 is the total volume, in millilitres, of the absorption solution;

V_4 is the volume, in litres, at 0 °C and 1 013 mbar (101,3 kPa) pressure, of the test portion;

9.3 Turbidimetric titration

9.3.1 Range

See table 1.

9.3.2 Reagents

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

9.3.2.1 Barium chloride, standard volumetric solution.

Dissolve 0,38 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in water in a 1 000 ml one-mark volumetric flask and make up to the mark.

To standardize the barium chloride solution, pipette 2,00 ml of standard volumetric $c(H_2SO_4) = 0{,}002\,5$ mol/l sulfuric acid solution into a 250 ml conical flask containing about 25 ml of water. Add 1,0 ml of the sodium chloride solution (9.3.2.4) and proceed with the evaporation and subsequent titration procedure as detailed in 9.3.4. Calculate the sulfur equivalent of the barium chloride solution.

1 ml of this standard volumetric solution is equivalent to approximately 50 µg of sulfur.

9.3.2.2 Coagulant solution.

Dissolve 20 g of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and 3,5 g of ammonium chloride (NH_4Cl) in 1 000 ml of water. Adjust to a pH of 8,0 to 8,2 with concentrated ammonium hydroxide (NH_4OH) solution.

9.3.2.3 Methanol.

9.3.2.4 Sodium chloride, 100 g/l solution.

Dissolve 100 g of sodium chloride (NaCl) in 1 000 ml of water.

9.3.3 Apparatus

9.3.3.1 Molecular absorption spectrometer, having an effective band width of about 50 nm, and equipped with a blue-sensitive photocube for use at 450 nm, or alternatively a filter spectrometer equipped with a colour filter having a maximum transmission at approximately 450 nm.

9.3.3.2 Optical cells, with a thickness of 50 mm.

9.3.3.3 One-mark pipette(s), for transfer of the aliquot portion.

NOTE — The procedure described assumes an absorbance change of about 0,10 for each 100 µg of sulfur in 50 ml of solution measured in a 50 mm cell. Spectrometers employing cells of lesser thickness will not give the precision of measurement stated in this method.

9.3.4 Procedure

Make up the absorption solution in the narrow-necked volumetric flask (13) to the mark with water and mix well. By means of pipette(s) (9.3.3.3), transfer an aliquot portion (see table 1) of the absorption solution to a 250 ml beaker. Add 1 ml of the sodium chloride solution (9.3.2.4). Evaporate over a hotplate (DO NOT EVAPORATE OVER A FLAME) until the contents reach a small volume which shall be not less than 1 ml.

Allow the beaker and contents to cool, then add 5 ml of the coagulant solution (9.3.2.2) and ensure that the contents dissolve thoroughly. Add 20 ml of the methanol (9.3.2.3) and transfer the contents of the beaker quantitatively to the cell. Rinse the beaker with three 10 ml portions of methanol, add the rinsings to the cell and mix thoroughly with a paddle.

NOTE — Turbidity in the solution at this stage may be caused by the precipitation of magnesium phosphate, and should not interfere with the turbidimetric titration.

Insert the cell into the spectrometer (9.3.3.1) and record the initial galvanometer reading. From the burette, add the barium chloride solution (9.3.2.1) in small, equal increments. In the case of sulfur contents below 0,05 mg, add 0,1 ml at a time; in the case of sulfur contents up to 0,15 mg, add 0,2 ml at a time; in the case of sulfur contents of more than 0,2 mg, add 0,5 ml at a time. After each addition, mix the liquid contents of the cell thoroughly with the paddle, then observe and record the galvanometer reading. Add at least five equal increments before the inflection point, and four increments subsequently. To eliminate, as far as possible, the effect of outside light, it is recommended that the cell be covered after stirring, following each addition of solution.

9.3.5 Determination of reagent blank

Carry out a blank test by burning the oxygen and hydrogen for the same time as taken to burn the test portion and then determine and record the volume of the barium chloride solution (9.3.2.1) used by the procedure specified in 9.3.4.

9.3.6 Calculation

Plot the volumes, in millilitres, of the barium chloride solution (9.3.2.1) added against the corresponding galvanometer readings. Join the plotted points. The resulting curve consists of two sections; the intersection point of the tangents to the two branches is the equivalence point.

Calculate the sulfur content S, in milligrams per kilogram (parts per million) using equation (8), or in milligrams per cubic metre at 0 °C and 1 013 mbar (101,3 kPa) pressure using equation (9), or as a percentage by mass using equation (10).

$$S = \frac{(V_1 - V_0) \times T}{m_0} \times \frac{V_3}{V_2} \quad \text{(mg/kg)} \quad \ldots (8)$$

$$S = \frac{(V_1 - V_0) \times T}{V_4} \times \frac{V_3}{V_2} \quad (\text{mg/m}^3) \quad \ldots (9)$$

$$S = \frac{(V_1 - V_0) \times T}{m_0 \times 10^4} \times \frac{V_3}{V_2} \quad [\% \ (m/m)] \quad \ldots (10)$$

where

V_0 is the volume, in millilitres, of the barium chloride solution used for the blank;

V_1 is the volume, in millilitres, of the barium chloride solution at the equivalence point;

V_2 is the volume, in millilitres, of the aliquot portion taken;

V_3 is the total volume, in millilitres, of absorption solution;

V_4 is the volume, in litres, at 0 °C and 1 013 mbar (101,3 kPa) pressure, of the test portion;

T is the sulfur equivalent, in micrograms per millilitre, of the barium chloride solution;

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

9.4 Conductimetric method

9.4.1 Range

See table 1.

9.4.2 Reagents

During the analysis, use only reagents of recognized analytical grade.