TC 28

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Petroleum products — Determination of total sulfur content — Lamp method

Produits pétroliers — Dosage du soufre total — Méthode à la lampe

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Foreword

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Petroleum products — Determination of total sulfur content — Lamp method

1 Scope and field of application

1.1 This International Standard specifies a method for the determination of the total sulfur content of liquid petroleum products in concentrations above 0,002 % (*m*/*m*).

A special sulfate analysis procedure is described in annex A that permits the determination of sulfur in concentrations as low as 5 mg/kg.

In the basic procedure, sulfate is determined acidimetrically by titration with sodium hydroxide; an alternative gravimetric procedure (precipitation as barium sulfate) is described in annex B.

1.2 The direct burning procedure (see clause 7) is applicable to the analysis of such materials as gasoline, kerosine, naphtha, and other liquids that can be burned completely in a wick lamp.

The blending procedure (see clause 8) is applicable to the analysis of gas oils and distillate fuel oils, high sulfur content petroleum products, and many other materials that cannot be burned satisfactorily by the direct burning procedure. It is not suitable for heavy residues such as residual fuel oils, bitumens and tars.

1.3 Phosphorus compounds normally present in commercial gasoline do not interfere in the determination. A correction is given for the small amount of acid resulting from the combustion of the lead anti-knock fluids in gasolines.

Appreciable concentrations of acid-forming or base-forming elements from other sources interfere when the titration procedure is employed since no correction is provided in these cases.

2 Principle

2.1 Burning of a test portion in a closed system, using a suitable lamp and an artifical atmosphere composed of 70 % (*V*/*V*) carbon dioxide and 30 % (*V*/*V*) oxygen to prevent the formation of oxides of nitrogen. Absorption of the oxides of sulfur and oxidation to sulfuric acid by means of hydrogen peroxide solution which is then flushed with air to remove dissolved carbon dioxide. Determination of the sulfur as sulfate in the absorbent, either acidimetrically by titration with standard sodium hydroxide solution, or gravimetrically by precipitation as barium sulphate (see annex B).

2.2 Alternatively, burning of the test portion in air, and gravimetric determination of the sulfur in the absorbent as sulfate by precipitation as barium sulfate (see annex B).

NOTE — In the absence of acid-forming or base-forming elements, other than sulfur, results by the volumetric and gravimetric finishes described are equivalent within the limits of precision of the method.

2.3 For sulfur contents below 0,002 % (*m*/*m*), it is necessary to determine the sulfate content in the absorber solution turbidimetrically as barium sulfate (see annex A).

3 Reagents

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

3.1 **Carbon dioxide** (CO_2) and **oxygen** (O_2), both at least 99,5 % (*V*/*V*) pure and meeting the requirements specified in 7.5.

3.2 **Diluent,** having a sulfur content less than 0,001 % (*m*/*m*), completely miscible with the sample to be analysed, and permitting burning at a moderate rate without smoking. *n*-Heptane, *iso*-octane and absolute ethanol have been found suitable.

3.3 **Hydrogen peroxide,** solution (1 + 19).

Mix 1 volume of concentrated hydrogen peroxide [H_2O_2, 30 % (*m*/*m*)] with 19 volumes of water.

Store in a dark-coloured glass-stoppered bottle.

3.4 **Sodium hydroxide,** 100 g/l solution.

Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 l.

3.5 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0{,}05$ mol/l.

Dilute 2,8 ml of saturated sodium hydroxide solution to 1 l (see note 1), using the clear saturated solution decanted after standing long enough to permit any precipitate to settle out.

Standardize by titration against a standard volumetric solution of acid, using the methyl purple indicator (3.6).

Store in an alkali-resistant glass bottle (see note 2) and protect to minimize contamination by carbon dioxide from the air.

Use only pure gum rubber tubing for connections between the storage bottles and burettes.

NOTES

1 The calculation of results may be simplified by adjusting the concentration of the sodium hydroxide solution to 0,062 4 ± 0,000 1 mol/l. Then 1 ml of the sodium hydroxide solution will be equivalent to 0,001 0 g of sulfur. In this case, the value of $1{,}603c$ in the calculation (10.1) becomes 0,1.

2 A bottle of a suitable plastics materials is permitted as an alternative to glass.

3.6 Methyl purple indicator, aqueous solution containing approximately 0,1 % active constituent.

NOTE — Methyl violet indicator is not suitable as an alternative to methyl purple.

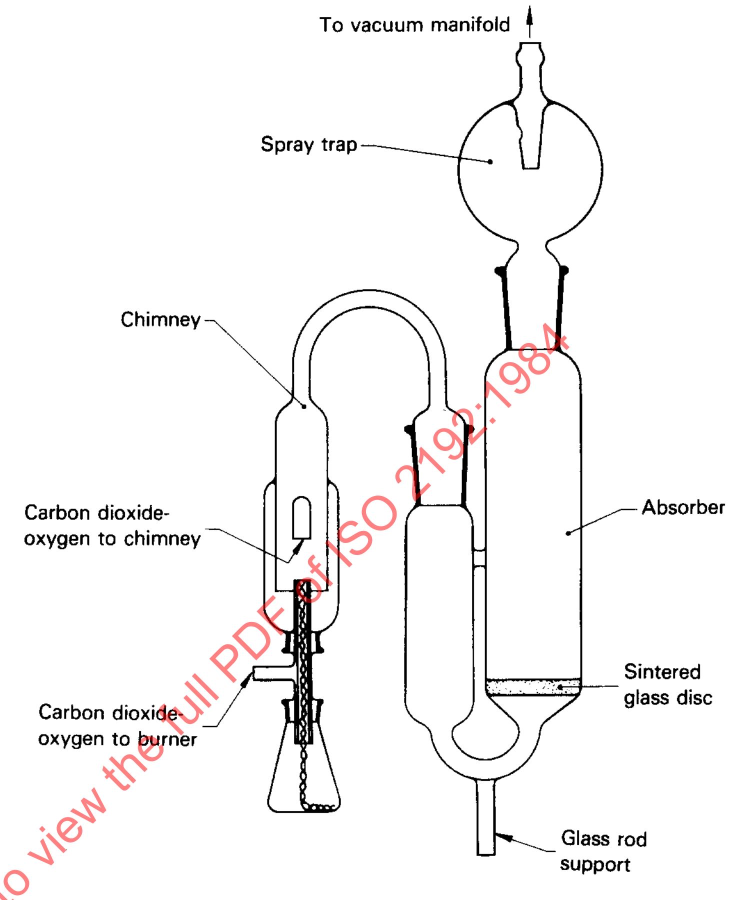

Figure 1 — Sketch of the assembled lamp unit

4 Apparatus

4.1 Lamps, chimneys, absorbers and spray traps (see figure 1), as described in detail in annex C.

The standard flask and burner (see figure 4), as shown, is not suitable for burning highly aromatic mixtures without blending as described in clause 8. The flask and burner for aromatic samples (see figure 4) permits burning these samples directly without blending and may also be used to burn non-aromatic samples; with this lamp, a second port with control valve in the burner manifold is required.

4.2 Cotton wicking. Clean, unused, uniform, twisted white cotton yarn of good quality.[1] To enable the burner to burn aromatic samples use long staple, fine spun, commercial fine grade cotton.

4.3 Manifold system, consisting of a vacuum manifold with regulating device, valves, etc. (see figure 2) and a dual manifold (burner and chimney) supplying a gas mixture of approximately 70 % (V/V) carbon dioxide (CO_2) and 30 % (V/V) oxygen (O_2) at regulated pressures. The vacuum manifold shall be connected to a pump of sufficient capacity to permit a steady gas flow of about 3 l/min through each absorber and to maintain a constant manifold pressure of approximately 4 kPa (40 mbar) below atmospheric. The gas mixture in the chimney manifold shall be maintained at a nearly constant pressure of 100 to 200 Pa (1 to 2 mbar), and the burner manifold at approximately 2 kPa (20 mbar). A suitable arrangement is shown in figure 2 and described in annex C, but any other similar system may be used. Modifications of the manifold and associated equipment for burning samples in air are described in annex B and shown in figure 3.

5 Preparation of apparatus

5.1 When the apparatus is first assembled, charge the absorber with 30 ± 2 ml of water. Adjust the individual valves between the vacuum manifold and spray traps so that approximately 3 l/min of air will be drawn through each absorber when the chimney outlets are open to the atmosphere, while maintaining the pressure in the vacuum manifold at approximately 4 kPa (40 mbar) below atmospheric. When all adjustments have been made, remove the water from the absorbers. The height of the liquids in the pressure and vacuum regulators shall be as indicated in figure 2, and during operation a slow leak of gas shall be maintained through them.

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[1] Rug yarn, white, 4-strand (2 or 3 mg/cm per strand), or equivalent material has been found satisfactory for this purpose.

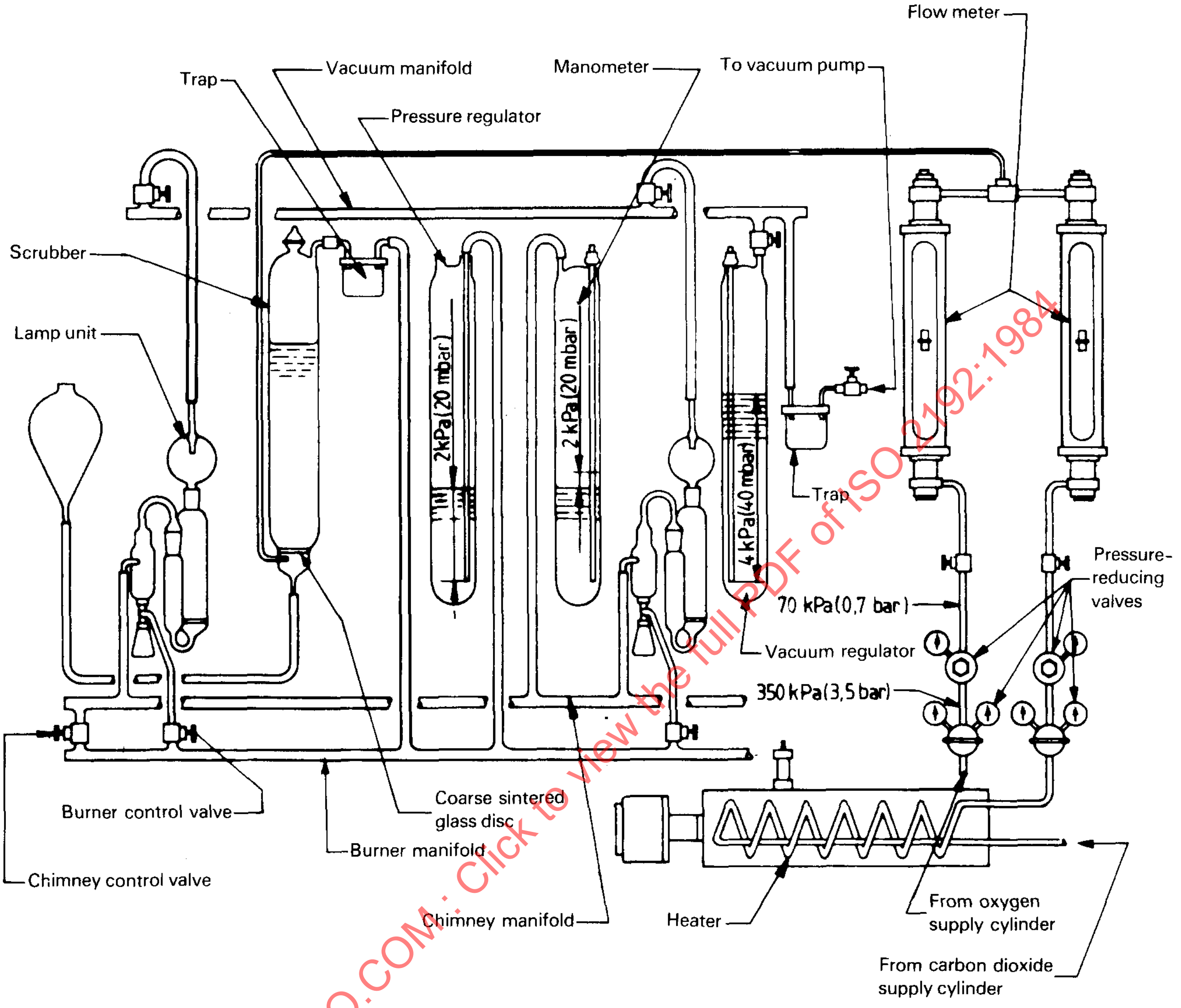

Figure 2 — Schematic diagram of carbon dioxide-oxygen supply manifold and lamp system

NOTE — In use, place 300 to 400 ml of hydrogen peroxide solution (3.3) in the scrubber. As the manifold manometer also serves as a scrubber at the end of the test to remove carbon dioxide from the absorbent, use the hydrogen peroxide solution (3.3) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

5.2 Neutralize the hydrogen peroxide solution (3.3) immediately before use. As 30 ml of the solution is needed, transfer to a beaker a multiple of 30 ml sufficient for the number of absorbers to be used simultaneously. Add 1 drop of the methyl purple indicator solution (3.6) for each 100 ml of hydrogen peroxide solution and then add the sodium hydroxide standard volumetric solution (3.5) drop by drop until the colour changes from purple to light green.

5.3 Introduce 30 ± 2 ml of the freshly neutralized hydrogen peroxide solution (5.2) into the larger bulb of each absorber. In addition, for each set of test portions burned, prepare an extra absorber for use as a control blank. Attach the spray traps and chimneys, and connect them to their respective manifolds by means of sulfur-free rubber tubing. Close the chimney openings by means of corks.

NOTE — Suitable sulfur-free rubber or plastics bungs are permitted as an alternative to corks.

5.4 With the burner control valves closed, the valve to the vacuum regulator fully open, and the pressure in the vacuum manifold adjusted to approximately 4 kPa (40 mbar) below atmospheric, turn on the carbon dioxide and oxygen supplies.

CAUTIONARY NOTE — A hazardous (explosive) condition may result if the carbon dioxide supply is interrupted and the oxygen flow is continued while test portions are being burned. The installation of suitable warning or control equipment is recommended.

5.5 Adjust the chimney manifold control valve so that, at the required rate of flow through the absorbers, only a small stream of carbon dioxide-oxygen gas escapes at the pressure regulator, a small stream of air enters at the vacuum regulator, and the pressure in the chimney manifold is 100 to 200 Pa (1 to 2 mbar). Minor adjustment of the vacuum regulator and vacuum control valve may be necessary to achieve this condition.

NOTE — It is convenient to balance the gas flow system by regulating the pressure in the vacuum manifold. This shall be done by raising or lowering the air inlet tube in the vacuum regulator by sliding it in a rubber sleeve.

5.6 Cut the cotton wicking (4.2) into 300 mm lengths. Use the number of lengths required for the sample (see clause 6); fold the wicking once to give a 150 mm long bundle for threading the burners. Thread the required number of burners by inserting the looped ends into the top of the inner tube of each burner. Draw the wicking through by means of a metal hook. Trim the wick as close as possible to the top of the burner with a pair of sharp scissors. It is essential that thoroughly cleaned burners and new wicking be used for each test.

6 Control of combustion

6.1 Most types of liquid samples burn with a luminous yellow flame, the size and shape of which is dependent on the gas flow to the burner, the volatility of the material, the tightness of the fit of the wick in the burner tube, and the position of the top of the wick relative to the top of the burner. It is preferable that the latter two variables be fixed with relation to the first before burning is started so that the flame can be controlled by variation in the rate of carbon dioxide-oxygen flow.

6.2 Highly volatile samples require a tight-fitting wick, the top of which may need to be several millimetres below the top of the burner, and in extreme cases may have to be cooled in ice during the burning. Less volatile materials require a more loosely fitting wick and may require warming.

6.3 After trimming, draw the wick down until the trimmed edge is flush with, or just a little below, the top of the burner. With the burner for aromatic samples, the distance from the top of the burner to the top of the wicking shall be 8 mm or more for benzene, and 4 mm for toluene; a slight heating of the upper end of the burner is helpful in starting vaporization of heavier materials.

6.4 To use the standard lamp, light the wick and then slowly admit combustion atmosphere to the burner to obtain a smoke-free flame. To use the burner for aromatic samples, introduce a small amount of combustion atmosphere into the flask to provide sufficient vapour for lighting the burner. After lighting the burner, introduce combustion atmosphere directly into the burner to prevent smoking and to adjust the flame size. If the flame is accidentally snuffed out, relight.

6.5 A short burning period (1 to 2 min is usually sufficient) at low flame height is necessary to allow combustion to reach equilibrium before the flame size can be increased without causing a smoky flame. In adjusting the standard lamp, the entire control is at the burner. For the burner for aromatic samples, first adjust the flow of gas to the flask and then reduce the flow of gas to the burner as required. In any case, it is essential that the flame burn smoothly and symmetrically and without jets in the inner cone or smoke on the outer fringes.

6.6 Satisfactory combustion of materials which are difficult to burn can sometimes be obtained by increasing the oxygen content of the combustion atmosphere. However, never increase the oxygen content of the combustion atmosphere to more than 40 %.

6.7 Before extinguishing the flame, allow the test portion to burn until the flask and wicking appear to be dry and the flame has reduced considerably in size; frequently the flame continues to burn for a short time after the flask appears dry because of the liquid in the wick. For example, for gasoline samples which burn with a high flame, the flame shall be extinguished when it is only 3 to 4 mm high. If the flame is permitted to burn until it goes out, partially oxidized substances (probably organic acids) are produced; as a result, broad, indistinct end points are obtained. When test portions are not burned until the flask is apparently dry, erratic results may be obtained. In the case of volatile samples, any unburned test portion will escape from the burner during weighing. When elemental sulfur is present it is particularly important that the test portion be burned to apparent dryness and that the wick be maintained flush with the top of the burner to ensure complete combustion. With mixtures containing light and heavy hydrocarbons, the more volatile materials appear to burn first, possibly concentrating sulfur compounds in the remaining material.

7 Procedure for direct combustion of samples (see also annex B)

7.1 By means of an appropriate pipette, introduce into the flask of each lamp an approximate quantity of the sample as shown in table 1. Stopper the flasks with clean, numbered corks. Weigh each flask and its burner to the nearest 0,005 g.

NOTE — Although the stoppered flasks and prepared burners may all be weighed separately, it is usually more convenient to place each flask and its burner on the balance pan and obtain the combined mass in a single weighing.

Table 1 — Test portion size for direct combustion of samples

Sulfur content	Test portion size	
% (*m*/*m*)	g	ml
under 0,05	10 to 15	20
0,05 to 0,3	5 to 10	10
0,3 to 1	3 to 5	5
over 1	2 to 3	3

7.2 Handling each lamp individually, insert the burner in the flask. As soon as the sample has risen by capillary action to the top of the wick, connect the side tube of the burner to the burner manifold by means of sulfur-free rubber tubing. Light the burner with a sulfur-free flame (such as an alcohol lamp) and insert the burner into the chimney, pinching off the connection between the chimney and the chimney manifold during the insertion if the flame tends to be blown out. At the same time, adjust the gas flow to the burner so that the flame is maintained at a point just below smoking and has a steady symmetrical appearance. Continue in this manner until all lamps have been placed in the chimneys. Make any minor adjustment of the chimney manifold control valve necessary to maintain the required pressure (see clause 5). During the burning, and particularly during the latter stages when the flame becomes small, decrease the carbon dioxide-oxygen supply to the burners in order to prevent extinction of the flames.

NOTE — When incomplete combustion occurs, the absorber liquid will foam excessively.

7.3 When the burning of each sample is complete, as shown by the flame becoming small owing to depletion of the sample, remove the burner and flask from the chimney, extinguish the flame, turn off the carbon dioxide-oxygen supply to the burner and stopper the chimney opening. Immediately re-weigh the flask, burner, and numbered cork. When all the combustions have been completed, turn off the carbon dioxide and the oxygen main supplies, close the chimney control valve, and close the connection to the vacuum regulator; this will cause air to be drawn into the chimney manifold through the manometer. Allow air to be drawn through the absorbers in this manner for 5 min to remove dissolved carbon dioxide from the absorbent; then close the vacuum control valve.

NOTE — If it is desired to conserve the combustion atmosphere, the gas flow through each individual absorber may be turned off upon completion of the burning period. To accomplish this, pinch off the rubber tubing connecting the spray trap to the vacuum manifold, reduce the flow of mixed gas at the flowmeters proportionately, and readjust the vacuum control valve and the chimney control valve. When the burning of all samples has been completed, it is necessary to remove the pinch clamps and readjust the vacuum control valve in order to draw air at the required rate through the absorbers for the removal of dissolved carbon dioxide.

7.4 Rinse the chimneys and spray traps three times, using about 10 ml of water each time. When the sample contains lead anti-knock fluids, use hot water to rinse the chimneys. Add the rinsings to the absorbers, and titrate as specified clause 9.

7.5 For the blank test, leave the chimney of the blank absorber (see 5.3) stoppered, and allow the carbon dioxide-oxygen stream to pass through that absorber until all the samples started at one time have finished burning. Turn off the carbon dioxide and the oxygen supplies and aerate the blank absorber in the same manner as the sample absorbers (see 7.3). Titrate the absorber liquid as directed in clause 9. Normally, the combustion atmosphere blank will be small, but if the titration requires more than 0,1 ml of sodium hydroxide standard volumetric solution (3.5), discard the determination and replace the carbon dioxide cylinder.

8 Procedure for blending and combustion of samples

8.1 Add 6 ml of the sulfur-free diluent (3.2) to each flask. Stopper the flasks with numbered corks and weigh to the nearest 0,005 g. By means of a pipette, introduce into the flask of each burner an approximate quantity of the sample as shown in table 2. Swirl to mix thoroughly, and re-weigh.

NOTE — Alternatively, make a quantitative 40 % blend of the sample in sulfur-free diluent (3.2) and proceed as described in clause 7.

Table 2 — Test portion size for testing blended samples

Sulfur content	Test portion size	
% (*m*/*m*)	g	ml
up to and including 0,5	3 to 4	5
over 0,5	2 to 3	3

8.2 Insert the burner and carry out the combustion as specified in 7.2. Remove each lamp from its chimney as the flame nears extinction and extinguish the flame. Add 2 ml of diluent, allowing the diluent to rinse down the walls of the flask. Burn the additional diluent and repeat the addition of diluent and burning once more so that a total of 10 ml of diluent has been burned.

NOTE — In this case, a 10 ml diluent blank test shall be carried out; the titration of the absorber solution from this blank shall not exceed 0,1 ml of sodium hydroxide standard solution (3.5).

8.3 After all lamps have completed burning, turn off the carbon dioxide and oxygen supplies, close the connection to the vacuum regulator, draw air through the absorbers for 5 min and finally close the vacuum control valve. Rinse the chimneys and spray traps three times, using about 10 ml of water each time. Add the rinsing to the absorbers and titrate as specified in clause 9.

9 Titration of absorbent solution

Add 3 to 4 drops of the methyl purple indicator solution (3.6) to the liquid in each absorber. Titrate the absorbent solution by introducing the sodium hydroxide standard volumetric solution (3.5) from a burette into the smaller bulb of the absorber. Use a 10 ml microburette if less than 10 mg of sulfur is expected to be present in the absorber. Stir during the titration by applying suction intermittently to the top of the larger bulb.

NOTE — When incomplete combustion of the test portion occurs, the air drawn through the absorber during the titration will have a characteristic odour and the end point will be broad. In these cases, discard the determination.

10 Calculation and expression of results

10.1 Calculate the sulfur content, S, of the test portion, as a percentage by mass, from the equation

$$S = 1{,}603 \times \frac{Vc}{m}$$

where

V is the volume, in millilitres, of sodium hydroxide standard volumetric solution required to titrate the acid in the absorbent solution from the burned test portion;

c is the concentration, in moles per litre, of the sodium hydroxide solution (see note 1 to 3.5);

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

10.2 When it is required by specifications to correct the sulfur content for lead anti-knock fluids (see the note) calculate the corrected value of the sulfur content from the equation

corrected value, % $(m/m) = S - (3{,}785\ 4\ LF)$

where

F = 0,001 5 if the sample contains aviation lead anti-knock fluid, or 0,003 5 if the sample contains tetraethyl lead, tetramethyl lead, or the mixed lead alkyl anti-knock fluid;

L is the lead content, in grams per litre;

S is the sulfur content, as a percentage by mass, calculated as specified in 10.1.

NOTE — These corrections are based on experiments using burning fuels blended with anti-knock fluid containing tetraethyl lead and ethylene halide in commonly used combinations. Tetramethyl lead and the mixed lead alkyl anti-knock fluids contain the same ethylene halide combination as the tetraethyl lead fluid.

11 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

11.1 Repeatability

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the value 0,005 only in one case in 20.

11.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the value $0{,}010 + 0{,}025\ S$ only in one case in 20.

12 Test report

The test report shall contain at least the following information:

a) the type and identification of the product tested;

b) a reference to this International Standard;

c) the result of the test;

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

Annex A

Determination of trace quantities of sulfur — Spectrophotometric method

(This annex forms an integral part of the Standard.)

A.1 Scope and field of application

This annex specifies a spectrophotometric method for extending the lamp method of test for sulfur to the analysis of samples having sulfur contents as low as 5 mg/kg (see note 1). The method is not applicable for the determination of less than 300 mg/kg of sulfur in liquids containing lead anti-knock compounds (see note 2).

NOTES

1 Only by the exercise of the most scrupulous care and attention to details may reliable results be obtained by this method. Before using new glassware, and thereafter as required, wash the glassware with concentrated nitric acid. Rinse three times with tap water, followed by three rinsings with deionized distilled water. Reserve units of glassware for use in this method alone.

2 The extent of application of the method is under study.

A.2 Principle

Burning of a test portion of suitable size as specified in the main method.

Determination of the sulfate ion in the absorber solution by precipitation as barium sulfate, and measurement of the turbidity of a suspension of the precipitate, stabilized by the addition of ethanol and glycerin, using a spectrophotometer or filter photometer.

A.3 Additional reagents[1]

A.3.1 Ethanol-glycerin mixture.

Mix 2 volumes of ethanol [95 % (*V*/*V*)] with 1 volume of glycerin.

A.3.2 Barium chloride dihydrate ($BaCl_2.2H_2O$), crystals, pulverized if necessary, passing an 850 µm sieve and retained on a 600 µm sieve.

NOTE — The crystal size of the barium chloride dihydrate is an important variable that affects the development of turbidity.

A.3.3 Hydrochloric acid, solution (1 + 12).

Place 77 ml of concentrated hydrochloric acid (HCl, ϱ = 1,19 g/ml) in a 1 000 ml one-mark volumetric flask and dilute to the mark with the deionized water (A. 3.6).

A.3.4 Hydrochloric acid, solution (1 + 215).

Place 60 ml of the hydrochloric acid solution (A.3.3) in a 1 000 ml one-mark volumetric flask and dilute to the mark with the deionized water (A.3.6).

A.3.5 Sulfuric acid, standard solution corresponding to 0,1 g of S per litre (1 ml ≙ 0,100 mg of sulfur).

Dilute 6,24 ± 0,01 ml of sulfuric acid, $c(1/2\ H_2SO_4)$ = 1 mol/l, to exactly 1 000 ml, with the deionized water (A.3.6). Check the dilution by titration against sodium hydroxide standard volumetric solution of about the same concentration and adjust the concentration, if necessary, so that each millilitre of this solution is equivalent to 0,100 mg of S.

A.3.6 Water, deionized.

Percolate water through a column of mixed anion and cation exchange resins.

NOTE — A means for determining when to replace the exchange resins shall be provided. The use of a simple electrical conductivity meter has been found satisfactory for this purpose.

A.4 Additional apparatus

A.4.1 Spectrophotometer, having an effective band width of about 50 nm and equipped with a blue-sensitive phototube for use at 450 nm, or

A.4.2 Filter photometer, equipped with a colour filter having a maximum transmission at approximately 450 nm.

A.4.3 Absorption cells, preferably having optical path lengths of 50 mm. With use, the cells may become coated with a film. To remove this film, wash the cells with a detergent using a soft brush. Rinse thoroughly with deionized water after cleaning.

NOTE — The procedure as given assumes an absorbance change of about 0,100 for each 0,1 mg of sulfur in 50 ml of solution measured in a 50 mm cell. Instruments employing cells of shorter optical paths give proportionately poorer precision.

A.4.4 Scoop, capable of dispensing 0,30 ± 0,01 g of the barium chloride (A.3.2).

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[1] For purity of reagents, see clause 3.

A.4.5 Magnetic stirrer, fitted with polytetrafluoroethylene-covered stirring bars about 30 mm long.

A.4.6 Lamp assembly, as described in annex C. Reserve complete units consisting of flask, burner, chimney, absorber, and spray trap for use in this procedure only.

A.5 Calibration

A.5.1 Into a series of eight 50 ml one-mark volumetric flasks introduce, by means of a burette, 0,25 — 0,50 — 0,75 — 1,00 — 1,50 — 2,00 — 3,00 and 5,00 ml of the sulfuric acid solution (A.3.5). Add 3,0 ml of the hydrochloric acid solution (A.3.3) to each flask, dilute to the mark with water and mix thoroughly. Prepare a reagent blank standard in a similar way, omitting the sulfuric acid solution (A.3.5).

A.5.2 Pour the entire contents of each flask into a 100 ml beaker, add by means of a pipette 10 ± 0,1 ml of the ethanol-glycerin mixture (A.3.1) and mix for 3 min on the magnetic stirrer (A.4.5). Select a stirring speed just below that which might cause loss of sample through splashing. Maintain this speed throughout the entire procedure.

A.5.3 Allow the solution to stand undisturbed for 4 min. Transfer to an absorption cell (A.4.2) and measure the initial absorbance in the spectrophotometer (A.4.1) or the filter photometer (A.4.2), using water (A.3.6) as reference.

A.5.4 Return the solution to the beaker and add 0,30 ± 0,01 g of the barium chloride (A.3.2), either by weighing this amount or by use of the scoop (A.4.4). Stir with the magnetic stirrer for exactly 3 min. Allow to stand for an additional 4 min, transfer to the cell, and again measure the absorbance relative to water.

A.5.5 Following the procedure specified in A.5.2, A.5.3 and A.5.4, obtain a reagent blank reading by subtracting the initial absorbance of the reagent blank standard from that obtained after the addition of the barium chloride (A.3.2). This reading shall not exceed 0,005.

A.5.6 Obtain the net absorbance for each standard by subtracting the initial absorbance and reagent blank reading from the absorbance obtained in accordance with A.5.4. Plot the net absorbance of each standard against the number of milligrams of sulfur contained in 50 ml of solution, and draw a smooth curve through the points.

A.5.7 Check the calibration curve daily by making single determinations to detect possible shifts.

A.6 Procedure for combustion of samples

A.6.1 Prepare the combustion apparatus and burn between 5 and 30 g of sample depending on the expected sulfur level (see the note). Follow the general procedures described in clauses 5, 6 and 7 of the main method. The requirements for initial neutralization of the hydrogen peroxide solution (see 5.2) and for final removal of dissolved carbon dioxide from this solution (see 7.3 and 8.3) may be omitted. Draw combustion atmosphere through one absorber of a set to serve as a blank on the purity of this atmosphere. Reserve all glassware exclusively for use with this trace procedure to avoid any possible contamination from other sources. Transfer the absorber solution, containing rinsings from the spray trap and chimney (see 7.4), to a 250 ml beaker, rinse the absorber two or three times with 10 ml portions of water, and add the rinsings to the solution in the beaker.

NOTE — A test portion size that will yield between 0,15 and 2,5 mg of sulfur in the absorber must be selected. This will then allow subsequent direct application of the procedures specified in A.6.3 and clause A.7 and will avoid the necessity of using less than a one-fifth aliquot of the absorber solution for analysis. When the sulfur level of the sample is about 15 mg/kg or less, at least 30 g of sample must be burned. To accommodate the large test portion sizes, a burner flask of suitable size must be fabricated to replace the standard 25 ml flask. In view of the larger size of the flask, it is preferable to use 180 mm of wicking rather than the 150 mm specified in 5.6. To avoid excessive depletion of absorber liquid caused by the longer burning time for larger test portions, it is preferable to charge the absorbers with 50 ± 3 ml of the hydrogen peroxide solution (3.3) instead of the 30 ± 2 ml specified in 5.3.

A.6.2 Reduce the volume of the absorber solution to about 20 ml by evaporation on a hot-plate. Quantitatively transfer the resulting solution to a 50 ml one-mark volumetric flask, rinsing the beaker with several small portions of water. Add 3 ml of the hydrochloric acid solution (A.3.3) to the flask, make up to volume with water, and mix thoroughly.

A.6.3 If the sulfur content of the absorber solution is known to be less than 0,5 mg, use the entire contents of the volumetric flask for analysis. If the approximate sulfur content is unknown or is expected to exceed 0,5 mg, transfer a 10 ml aliquot to a second 50 ml one-mark volumetric flask and dilute the solution in both flasks to volume with the hydrochloric acid solution (A.3.4). Use the more dilute solution first and, if less than 0,05 mg of sulfur is found, then use the more concentrated solution. Prepare a dilution of the combustion atmosphere blank similar to the solution used for analysis. Analyse the solutions as specified in clause A.7.

A.7 Procedure for analysis of solutions

A.7.1 Pour the entire contents of the 50 ml one-mark volumetric flask containing the solution to be analysed into a 100 ml beaker and proceed as specified in A.5.2, A.5.3 and A.5.4. Treat the combustion atmosphere blank in the same way and obtain a combustion atmosphere-reagent blank reading by subtracting its initial absorbance from that obtained after the addition of the barium chloride (A.3.2).

NOTE — Should the blank reading exceed 0,020, the precision obtainable will be impaired. In this event, make an analysis of the reagents alone to determine whether the atmosphere or the reagents are at fault. Place 30 ml of the hydrogen peroxide solution (3.3) in the 50 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid solution (A.3.4), and proceed as specified in A.5.5. If this reagent blank reading exceeds 0,010, results shall not be considered reliable.

A.7.2 Obtain the net absorbance of the analysis solution by subtracting the initial absorbance and the combustion atmosphere-reagent blank reading from that obtained after the addition of the barium chloride (A.3.2).

A.7.3 Convert net absorbance to milligrams of sulfur by using the calibration curve (A.5.6).

A.8 Expression of results

Calculate the sulfur content, S, of the test portion, in milligrams per kilogram, from the equation

$$S = \frac{m_1}{m_2 V'} \times 1\,000$$

where

m_1 is the sulfur content, in milligrams, of the analysis solution read from the calibration curve;

m_2 is the mass, in grams, of the test portion burned;

V' is the aliquot fraction of the absorber solution used for analysis.

A.9 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

A.9.1 Repeatability

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values shown in table 3 only in one case in 20.

Table 3

Sulfur content	Repeatability
mg/kg	mg/kg
5 to 80	$0{,}116 \times S$
Over 80 to 280	$(0{,}01 \times S) + 8{,}5$

A.9.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values shown in table 4 only in one case in 20.

Table 4

Sulfur content	Reproducibility
mg/kg	mg/kg
5 to 125	$0{,}145 \times S$
Over 125 to 280	$(0{,}508 \times S) - 45{,}4$

Annex B

Air burning of sample — Gravimetric finish

(This annex forms an integral part of the Standard.)

B.1 Scope and field of application

This annex specifies a barium sulfate gravimetric method for the determination of the total sulfur content of petroleum products.

This procedure is recommended only for analysing liquid petroleum samples that can be burned with a wick lamp.

B.2 Additional reagents[1]

B.2.1 Barium chloride, 100 g/l solution.

Dissolve 100 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in water and dilute to 1 l.

B.2.2 Hydrochloric acid, (HCl, ϱ = 1,19 g/ml).

B.2.3 Hydrogen peroxide (H_2O_2), 30 % (*m*/*m*) solution.

B.2.4 Sodium hydroxide, 100 g/l solution.

Dissolve 100 g of technical grade sodium hydroxide (NaOH) pellets in water and dilute to 1 l.

B.2.5 Sulfuric acid, solution (1 + 16).

Mix 60 ml of concentrated sulfuric acid, (H_2SO_4, ϱ = 1,84 g/ml), with 960 ml of water.

B.3 Apparatus

The manifold system described in 4.3 may be used with only a slight modification. Substitute filtered air for the carbon dioxide-oxygen supply train and add a second sintered disc scrubber to the incoming air line as shown in figure 3.

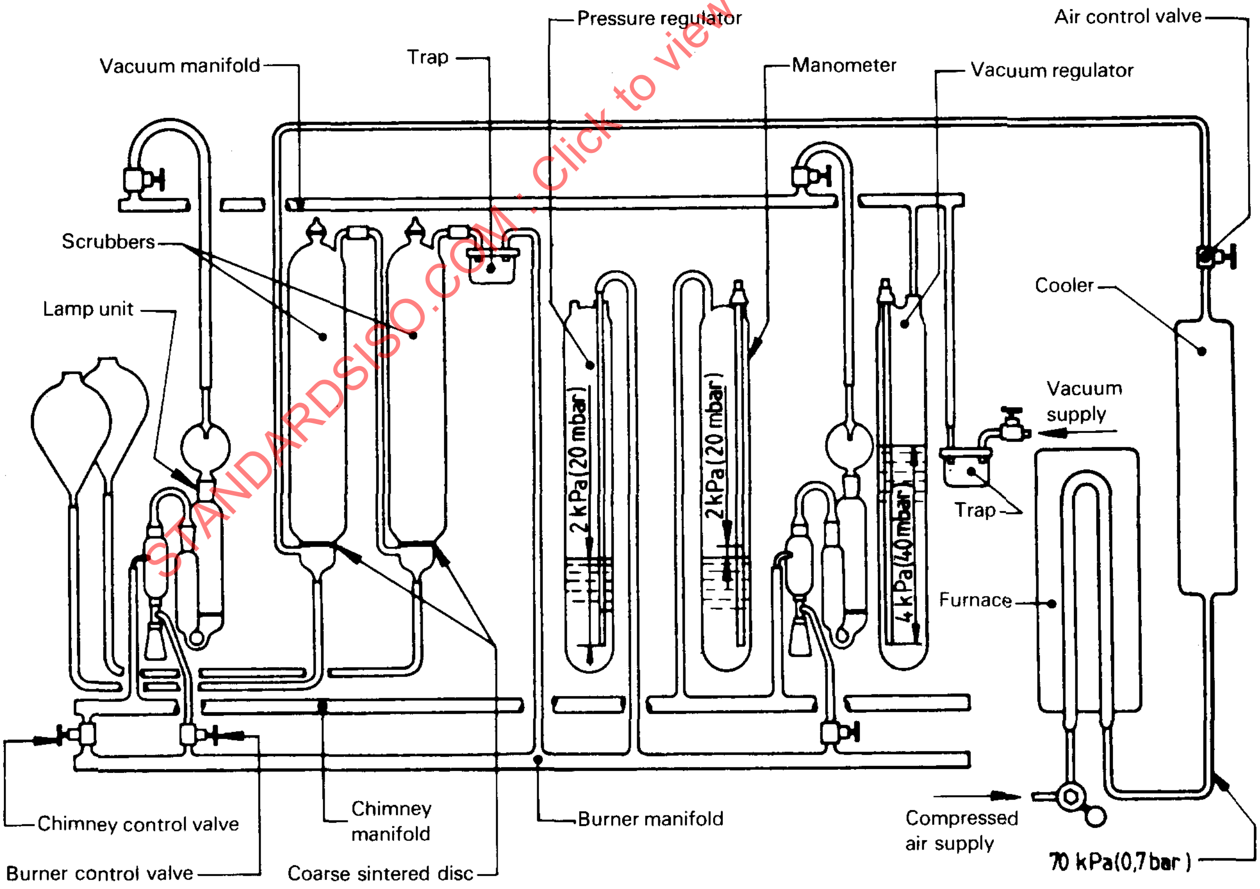

Figure 3 — Schematic diagram of purified air supply manifold and lamp system

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[1] For purity of reagents, see clause 3.