INTERNATIONAL STANDARD ISO 2192

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

Petroleum products — Determination of sulphur — Lamp method

First edition — 1973-03-01

UDC 662.75 : 543.845

Ref. No. ISO 2192-1973 (E)

Descriptors : petroleum products, chemical analysis, gravimetric analysis, volumetric analysis, determination of content, sulphur.

Price based on 13 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

International Standard ISO 2192 was drawn up by Technical Committee ISO/TC 28, *Petroleum products,* and circulated to the Member Bodies in February 1971.

It has been approved by the Member Bodies of the following countries :

Australia
Austria
Belgium
Brazil
Bulgaria
Chile
Czechoslovakia
Egypt, Arab Rep. of
France
India
Ireland
Italy
Netherlands
Portugal
Romania
South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
United Kingdom
U.S.A.
U.S.S.R.

The Member Bodies of the following countries expressed disapproval of the document on technical grounds :

Germany
New Zealand
Poland

Printed in Switzerland

INTERNATIONAL STANDARD

ISO 2192-1973 (E)

Petroleum products – Determination of sulphur – Lamp method

1 SCOPE AND FIELD OF APPLICATION

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

A special sulphate analysis procedure is described in Annex A that permits the determination of sulphur in concentrations as low as 5 ppm.

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

1.2 The direct burning procedure (see section 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 section 8) is applicable to the analysis of gas oils and distillate fuel oils, high sulphur 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 The test portion is burned in a closed system, using a suitable lamp and an artificial atmosphere composed of 70 % (*V/V*) carbon dioxide and 30 % (*V/V*) oxygen to prevent the formation of oxides of nitrogen. The oxides of sulphur are absorbed and oxidised to sulphuric acid by means of hydrogen peroxide solution which is then flushed with air to remove dissolved carbon dioxide. The sulphur is determined as sulphate 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 the test portion is burned in air, and the sulphur in the absorbent is determined gravimetrically as sulphate by precipitation as barium sulphate (see Annex B).

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

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

3 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to recognized standards for reagent chemicals. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean 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 sulphur 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 solution (100 g/l).

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

3.5 Sodium hydroxide, standard volumetric solution 0,05 N.

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 normality of the sodium hydroxide solution to 0,062 4 ± 0,000 1. Then 1 ml of the sodium hydroxide solution will be equivalent to 0,001 0 g of sulphur. In this case, the factor 16,03 N in the calculation (10.1) becomes 1,000.

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.

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 C.1), as shown, is not suitable for burning highly aromatic mixtures without blending as described in section 8. The flask and burner for aromatic samples (see Figure C.1) 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 40 mbar below atmospheric. The gas mixture in the chimney manifold shall be maintained at a nearly constant pressure of 1 to 2 mbar, and the burner manifold at approximately 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 B.1.

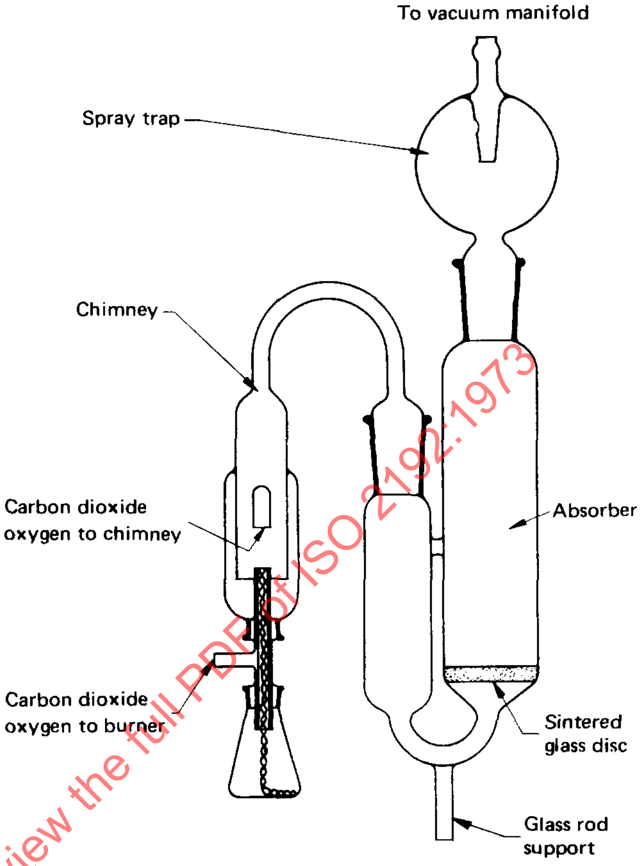

FIGURE 1 — **Sketch of the assembled lamp unit**

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 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.

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 hydrogen peroxide solution (3.3) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

---

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

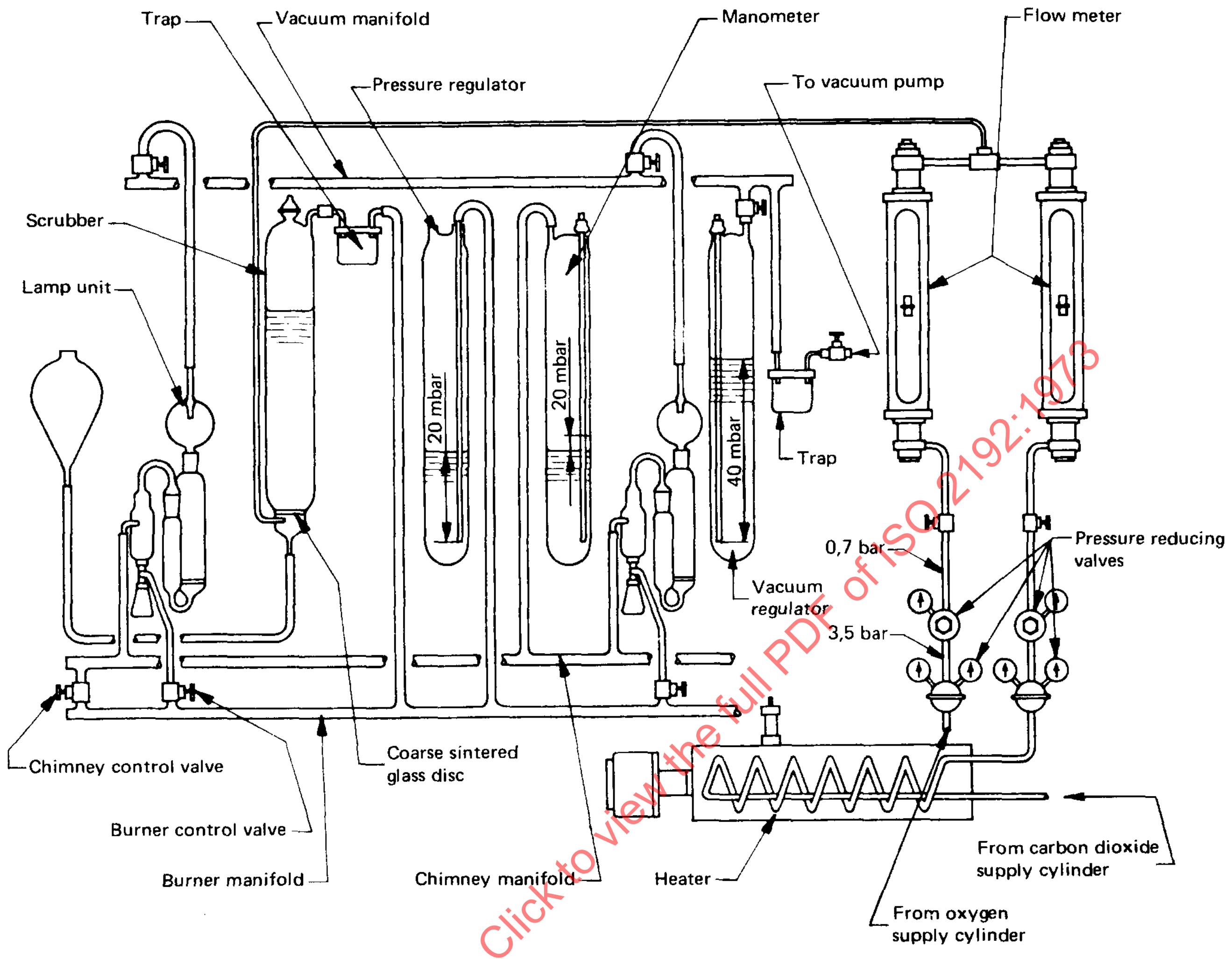

FIGURE 2 – **Schematic diagram of carbon dioxide-oxygen supply manifold and lamp system**

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 methyl purple indicator solution (3.6) for each 100 ml of hydrogen peroxide solution and then add 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 (3.3) 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 sulphur-free rubber tubing. Close the chimney openings by means of corks (see Note).

NOTE – Suitable sulphur-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 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 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 section 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 throroughly 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 sulphur 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 sulphur 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**

Sulphur content % (*m/m*)	**Test portion size**	
	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 sulphur-free rubber tubing. Light the burner with a sulphur-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 section 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 directed in section 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 section 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 sulphur-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 sulphur-free diluent (3.2) and proceed as described in section 7.

TABLE 2 – **Test portion size for testing blended samples**

Sulphur content % (*m/m*)	**Test portion size**	
	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 described 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 rinsings to the absorbers and titrate as directed in section 9.

9 TITRATION OF ABSORBENT SOLUTION

Add 3 to 4 drops of methyl purple indicator solution (3.6) to the liquid in each absorber. Titrate the absorbent solution by introducing 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 sulphur 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 sulphur content of the test portion, as a percentage by mass, as follows :

$$S\,\%\,(m/m) = 1{,}603 \times \frac{VT}{m}$$

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;

T is the normality of the sodium hydroxide solution (see Note 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 sulphur content for lead anti-knock fluids (see Note below), calculate the corrected value of the sulphur content as follows :

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

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 sulphur 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 following criteria shall be used for judging the acceptability of results (95 % confidence level) as applied to the direct burning of liquid samples in the range of 0,01 to 0,4 % sulphur.

11.1 Repeatability

Duplicate results by the same operator using the same apparatus shall be considered suspect if they differ by more than the following amount :

	Repeatability
Sulphur content	0,005

11.2 Reproducibility

The results submitted by each of two laboratories shall be considered suspect if they differ by more than the following amount :

	Reproducibility
Sulphur content	0,010 + 0,025 S

where S is the total sulphur content of the sample, as a percentage by mass.

12 TEST REPORT

The test report shall give the results of the tests for sulphur in liquid fuels to the nearest 0,01 % for sulphur contents at the level of 0,05 % and higher, reference being made to this International Standard.

ANNEX A

METHOD OF TEST FOR TRACE QUANTITIES OF SULPHUR

A.1 SCOPE AND FIELD OF APPLICATION

This Annex describes a procedure for extending the lamp method of test for sulphur to the analysis of samples having sulphur contents as low as 5 ppm (see Note 1 below). The procedure is not applicable for the determination of less than 300 ppm of sulphur in liquids containing lead anti-knock compounds (see Note 2 below).

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

A test portion of suitable size is burned as described in the main method. Sulphate ion in the absorber solution is determined by precipitation as barium sulphate, and the turbidity of a suspension of the precipitate, stabilized by the addition of ethanol and glycerin, is measured by 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, $d = 1{,}19$) in a 1 l volumetric flask and dilute to the mark with deionized water (A.3.6).

A.3.4 Hydrochloric acid solution (1 + 215)

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

A.3.5 Sulphuric acid standard solution (1 ml = 0,100 mg of sulphur)

Dilute 6,24 ± 0,01 ml of 1 N sulphuric acid (H_2SO_4) to exactly 1 l with deionized water. Check the dilution by titration against sodium hydroxide standard volumetric solution of about the same normality and adjust the concentration, if necessary, so that each millilitre of this solution is equivalent to 0,100 mg of sulphur.

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 Photometer. Preferably a spectrophotometer having an effective band width of about 50 nm and equipped with a blue-sensitive phototube for use at 450 nm, or alternatively a filter photometer equipped with a colour filter having a maximum transmission at approximately 450 nm.

A.4.2 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 sulphur in 50 ml of solution measured in a 50 mm cell. Photometers employing cells of shorter optical paths give proportionately poorer precision.

A.4.3 Scoop, capable of dispensing 0,30 ± 0,01 g of the barium chloride (A.3.2).

A.4.4 Magnetic stirrer, fitted with polytetrafluoroethylene-covered stirring bars about 30 mm long.

A.4.5 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.

---

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

A.5 CALIBRATION

A.5.1 Into a series of eight 50 ml 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 sulphuric acid (A.3.5). Add 3,0 ml of hydrochloric acid (A.3.3) to each flask, make up to volume with water and mix thoroughly. Prepare a reagent blank standard in a similar way, omitting the sulphuric acid (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.4.4). 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 using water (A.3.6) as reference.

A.5.4 Return the solution to the beaker and add 0,30 ± 0,01 g of barium chloride (A.3.2), either by weighing this amount or by use of the scoop (A.4.3). 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 steps described in A.5.2, A.5.3, 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 milligrams of sulphur 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 sulphur level (see Note, below). Follow the general procedures described in sections 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 sulphur in the absorber must be selected. This will then allow subsequent direct application of the procedures described in A.6.3 and section A.7 and will avoid the necessity of using less than a one-fifth aliquot of the absorber solution for analysis. When the sulphur level of the sample is about 15 ppm 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 volumetric flask, rinsing the beaker with several small portions of water. Add 3 ml of hydrochloric acid (A.3.3) to the flask, make up to volume with water, and mix thoroughly.

A.6.3 If the sulphur 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 sulphur content is unknown or is expected to exceed 0,5 mg, transfer a 10 ml aliquot to a second 50 ml volumetric flask and dilute the solution in both flasks to volume with hydrochloric acid (A.3.4). Use the more dilute solution first and, if less than 0,05 mg of sulphur 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 described in section A.7.

A.7 PROCEDURE FOR ANALYSIS OF SOLUTIONS

A.7.1 Pour the entire contents of the 50 ml volumetric flask containing the solution to be analysed into a 100 ml beaker and proceed as directed in A.5.2, A.5.3, 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 volumetric flask, dilute to the mark with hydrochloric acid (A.3.4), and proceed as described 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 sulphur by using the calibration curve.

A.8 CALCULATION AND EXPRESSION OF RESULTS

Calculate the sulphur content of the test portion, in parts per million by mass, as follows :

$$\text{S ppm } (m/m) = \frac{m_1}{m_2 F} \times 1\,000$$

where

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

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

F is the aliquot fraction of the absorber solution used for analysis.

A.9 PRECISION

The following criteria shall be used for judging the acceptability ot results (95 % confidence level).

A.9.1 Repeatability

Duplicate results by the same operator shall be considered suspect if they differ by more than the following amounts :

Sulphur content ppm	**Repeatability**
5 to 80	0,116 × ppm S
Over 80 to 280	(0,01 × ppm S) + 8,5

A.9.2 Reproducibility

The results submitted by each of two laboratories shall be considered suspect if they differ by more than the following amounts :

Sulphur content ppm	**Reproducibility**
5 to 125	0,145 × ppm S
Over 125 to 280	(0,508 × ppm S) – 45,4

ANNEX B

AIR BURNING OF SAMPLE – GRAVIMETRIC FINISH

B.1 SCOPE AND FIELD OF APPLICATION

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

B.2 ADDITIONAL REAGENTS[1]

B.2.1 Barium chloride solution (100 g/l)

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

B.2.2 Hydrochloric acid (HCl, *d* = 1,19).

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

B.2.4 Sodium hydroxide solution (100 g/l).

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

B.2.5 Sulphuric acid (1 + 16).

Mix 60 ml of concentrated sulphuric acid (H_2SO_4 *d* = 1,84) 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 B.1.

B.4 PREPARATION OF APPARATUS

B.4.1 Place 300 to 400 ml of sodium hydroxide solution (B.2.4) in the first scrubber (see Figure B.1) and the same amount of hydrogen peroxide-sulphuric acid solution (300 ml of water, 30 ml of sulphuric acid (B.2.5) and 30 ml of hydrogen peroxide (B.2.3) in the second scrubber. For apparatus in daily use, replace these solutions twice each week or whenever the volume becomes less than two-thirds of the original.

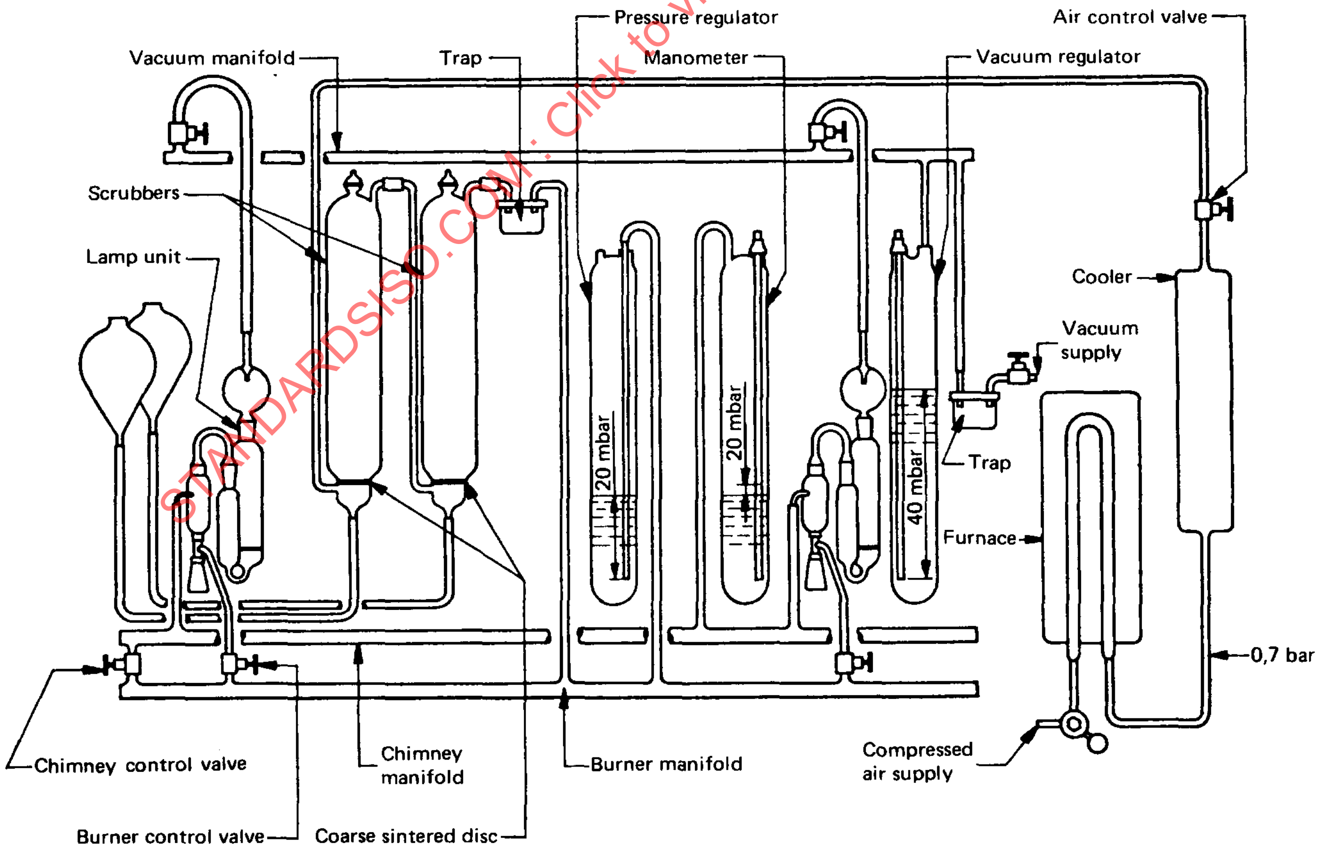

FIGURE B.1 – **Schematic diagram of purified air supply manifold and lamp system**

---

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