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Document Name: ASTM D1266: Standard Test Method for Sulfur in Petroleum Products (Lamp Method)

CFR Section(s): 40 CFR 60.106(j)(2)

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 1266 – 98

An American National Standard

Designation: 107/86

Standard Test Method for Sulfur in Petroleum Products (Lamp Method)[1]

This standard is issued under the fixed designation D 1266; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This test method has been adopted for use by government agencies to replace Method 5201 of Federal Test Method Standard No. 791b

1. Scope

1.1 This test method covers the determination of total sulfur in liquid petroleum products in concentrations from 0.01 to 0.4 mass % (Note 1). A special sulfate analysis procedure is described in Annex A1 that permits the determination of sulfur in concentrations as low as 5 mg/kg.

NOTE 1—The comparable lamp method for the determination of sulfur in liquefied petroleum gas is described in Test Method D 2784. For the determination of sulfur in heavier petroleum products that cannot be burned in a lamp, see the bomb method (Test Method D 129) the quartz tube method (IP 63), or the high-temperature method (Test Method D 1552).

1.2 The direct burning procedure (Section 9) 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 (Section 10) is applicable to the analysis of gas oils and distillate fuel oils, naphthenic acids, alkyl phenols, high sulfur content petroleum products, and many other materials that cannot be burned satisfactorily by the direct burning procedure.

1.3 Phosphorus compounds normally present in commercial gasoline do not interfere. 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.

1.4 The preferred units are acceptable metric units.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[2]

D 1193 Specification for Reagent Water[3]

D 1229 Test Method for Rubber Property—Compression Set at Low Temperatures[4]

D 1552 Test Method for Sulfur in Petroleum Products (High Temperature Method)[2]

D 2784 Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)[5]

E 11 Specification for Wire–Cloth Sieves for Testing Purposes[6]

2.2 *Institute of Petroleum Standard:*[7]

IP 63 Sulfur Content — The Quartz Tube Method

3. Summary of Test Method

3.1 The sample is burned in a closed system, using a suitable lamp (Fig. 1) and an artificial atmosphere composed of 70 % carbon dioxide and 30 % oxygen to prevent formation of nitrogen oxides. The oxides of sulfur are absorbed and oxidized to sulfuric acid by means of hydrogen peroxide solution which is then flushed with air to remove dissolved carbon dioxide. Sulfur as sulfate in the absorbent is determined acidimetrically by titration with standard sodium hydroxide solution, or gravimetrically by precipitation as barium sulfate (see Annex A2).

3.2 Alternatively, the sample may be burned in air, the sulfur as sulfate in the absorbent being determined by precipitation as barium sulfate for weighing (see Annex A2).

NOTE 2—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.

3.3 For sulfur contents below 0.01 mass % it is necessary to

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Feb. 10, 1998. Published April 1998. Originally published as D 1266 – 69 T. Last previous edition D 1266 – 91 (1995).

[2] *Annual Book of ASTM Standards,* Vol 05.01.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 09.01.

[5] *Annual Book of ASTM Standards,* Vol 05.02.

[6] *Annual Book of ASTM Standards,* Vol 14.02.

[7] Available from the Institute of Petroleum, 61 New Cavendish St., London, W.I., England.

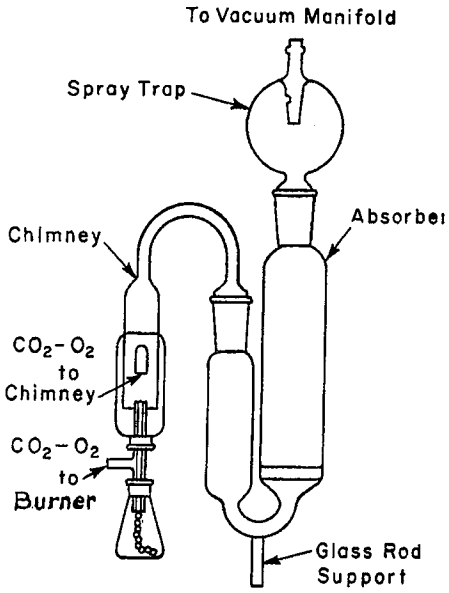


FIG. 1 Illustrative Sketch of the Assembled Lamp Unit

determine the sulfate content in the absorber solution turbidimetrically as barium sulfate (see Annex A1).

4. Significance and Use

4.1 This test method provides a means of monitoring the sulfur level of various petroleum products and additives. This knowledge can be used to predict performance, handling, or processing properties. In some cases the presence of sulfur components is beneficial to the product and monitoring the depletion of sulfur compounds provides useful information. In other cases the presence of sulfur compounds is detrimental to the processing or use of the product.

5. Apparatus

5.1 *Absorbers, Chimneys, Lamps, and Spray Traps* (Fig. 1) as required are described in detail in Annex A3. The standard flask and burner (Fig. A3.1) as shown is not suitable for burning highly aromatic mixtures without blending. The flask and burner for aromatic samples (Fig. A3.1) permits burning these samples directly without blending and may also be used to burn nonaromatic samples; with this lamp, a second port with control valve in the burner manifold is required.

5.2 *Cotton Wicking*—Clean, unused, uniform, twisted white cotton yarn of good quality.[8] For the burner to burn aromatic samples use long staple, fine-spun, commercial *fine* grade.[9]

5.3 *Manifold System* consisting of a vacuum manifold with regulating device, valves, and so forth (Fig. 2) and a dual manifold (burner and chimney) supplying a gas mixture of approximately 70 % carbon dioxide (CO_2) and 30 % 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 cm of water below atmospheric. The gas mixture in the chimney manifold shall be maintained at a nearly constant pressure of 1 to 2 cm of water and the burner manifold at approximately 20 cm of water. A suitable arrangement is shown in Fig. 2 and described in Annex A3, but any other similar system can be used. Modifications of the manifold and associated equipment for burning samples in air are shown in Fig. A2.1 and described in Annex A2.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[10] 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II or Type III of Specification D 1193.

6.3 *Carbon Dioxide and Oxygen*—The carbon dioxide (CO_2) and the oxygen (O_2) shall each be at least 99.5 % pure. These gases shall meet the requirements of 9.5.

6.4 *Diluent*—The diluent used shall have a sulfur content less than 0.001 mass %, be completely miscible with the sample to be analyzed, and permit burning at a moderate rate without smoking. Normal heptane, *iso*octane, and absolute ethyl alcohol have been found suitable (Note 10).

6.5 *Hydrochloric Acid (1 + 10)*—Mix 1 volume of concentrated hydrochloric acid (HCl, relative density 1.19) with 10 volumes of water.

6.6 *Hydrogen Peroxide Solution (1 + 19)*—Mix 1 volume of concentrated hydrogen peroxide (H_2O_2, 30 percent) with 19 volumes of water. Store in a dark-colored glass-stoppered bottle.

6.7 *Methyl Purple Indicator*—Aqueous solution containing approximately 0.1 % active constituent.[11] (Not methyl violet.)

6.8 *Sodium Hydroxide Solution (100 g/L)*—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

6.9 *Sodium Hydroxide, Standard Solution* (0.05 *M*)—Dilute 2.8 mL of saturated NaOH solution to 1 L (Note 3), using for this purpose the clear saturated solution decanted after standing long enough to permit any precipitate to settle out. Standardize by titration against standard acid, using the methyl purple indicator. Store in an alkali-resistant glass bottle and protect to minimize contamination by CO_2 from the air. Use only pure

[8] Yarn, white, 4-strand (2 to 3 mg/cm/strand), available from Koehler Instrument Co., 1595 Sycamore Ave., Bohemia, NY 11716, or the type marketed by various suppliers in the United Kingdom as 13s/14 ends, scoured, and bleached has been found suitable for this purpose.

[9] Available from Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0099.

[10] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[11] Fleisher Methyl Purple Indicator, U. S. Patent No. 2416619 may be obtained from Harry Fleisher Chemical Co., Benjamin Franklin Station, Washington, DC 20044, or from any chemical supply company handling Fleisher Methyl Purple.

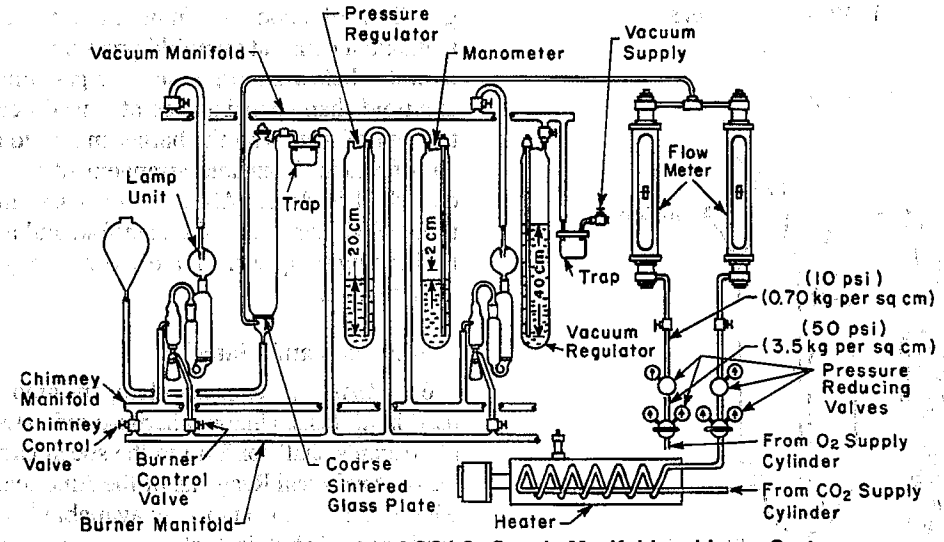


FIG. 2 Schematic Diagram of CO_2-O_2 Supply Manifold and Lamp System

gum rubber tubing for connections between the storage bottles and burets.

NOTE 3—The calculation of results can be simplified by adjusting the molarity of the NaOH solution to 0.0624 ± 0.0001. Then 1 mL of the NaOH solution will be equivalent to 0.0010 g of sulfur. In this case, the factor 16.03*M* in the calculation (see 12.1) becomes 1.000.

6.10 Quality Control (QC) Sample(s), preferably are portions of one or more liquid petroleum materials or product standards of known sulfur content that were not used in the generation of the instrument calibration curve. These (QC) samples are to be used to check the validity of the testing process as described in Section 12. An ample supply of QC sample material shall be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

7. Preparation of Apparatus

7.1 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 of air per minute 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 cm of water 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 is indicated in Fig. 2, and during operation a slow leak of gas should be maintained through them.

NOTE 4—In use, place 300 to 400 mL of H_2O_2 solution (1 + 19) in the scrubber. Since the manifold manometer also serves as a scrubber at the end of the test to remove CO_2 from the absorbent use H_2O_2 solution (1 + 19) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

7.2 Neutralize the H_2O_2 solution (1 + 19) immediately before use. As 30 mL of the solution is needed, transfer to a beaker multiples of 30 mL sufficient for the number of absorbers to be used simultaneously. Add 1 drop of methyl purple indicator solution for each 100 mL of H_2O_2 solution and then add 0.05 *N* NaOH solution dropwise until the color changes from purple to light green.

7.3 Introduce 30 ± 2 mL of the freshly neutralized H_2O_2 solution (1 + 19) into the larger bulb of each absorber. In addition, for each set of samples 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.

7.4 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 cm of water below atmospheric, turn on the CO_2 and O_2 supplies (**Warning**—see Note 5). Adjust the chimney manifold control valve so that, at the required rate of flow through the absorbers, only a small stream of CO_2-O_2 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 cm of water. Minor adjustment of the vacuum regulator and vacuum control valve may be necessary to achieve this condition (Note 6).

NOTE 5—**Warning:** A hazardous (explosive) condition can result if the CO_2 supply is interrupted and the O_2 flow is continued while samples are being burned. The installation of suitable warning or control equipment is recommended.

NOTE 6—It is convenient to balance the gas flow system by regulating the pressure in the vacuum manifold. This is done by raising or lowering the air inlet tube in the vacuum regulator by sliding it in a rubber sleeve.

7.5 Cut the wicking to 30-cm lengths. Use the number of lengths dictated by the sample (see Section 8); fold the wicking once to give a 15-cm 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 the 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.

8. Control of Combustion

8.1 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 CO_2-O_2 flow.

8.2 Highly volatile samples require a tight-fitting wick, the top of which can 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 can require warming.

8.3 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 should be 8 mm or more for benzene and 4 mm for toluene; a slight heating of the upper end of the burner will be helpful in starting vaporization of heavier materials.

8.4 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 vapor 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.

8.5 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.

8.6 Satisfactory combustion of materials difficult to burn can sometimes be obtained by increasing the O_2 content of the combustion atmosphere. Never increase the O_2 content of the combustion atmosphere to more than 40 %.

8.7 Before extinguishing the flames, allow the sample 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 a short time after the flask appears dry because of the sample in the wick. For example, for gasoline samples, which burn with a high flame, the flame should 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 samples are not burned until the flask is apparently dry, erratic results may be obtained. In the case of volatile samples, any unburned sample will escape from the burner during weighing. When elemental sulfur is present, it is particularly important that the sample 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 seem to burn first, possibly concentrating sulfur compounds in the material remaining behind.

9. Procedure for Direct Combustion of Liquid Samples (see also Annex A2)

9.1 By means of an appropriate pipet, introduce into the flask of each lamp an approximate quantity of sample as indicated in Table 1. Stopper the flasks with clean, numbered corks. Weigh each flask and its burner to the nearest 0.005 g.

NOTE 7—While the stoppered flasks and prepared burners can all be weighed separately, it is usually more convenient to place each flask and its burner on the balance pan and obtain the combined weight in a single weighing.

9.2 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 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 7). During the burning, and particularly during the latter stages when the flame becomes small, decrease the CO_2-O_2 supply to the burners in order to prevent extinction of the flames.

NOTE 8—When incomplete combustion occurs, the absorber liquid will foam excessively.

9.3 When the burning of each sample is complete, as evidenced by the flame becoming small owing to depletion of the sample, remove the burner and flask from the chimney, extinguish the flame, shut off the CO_2-O_2 supply to the burner and stopper the chimney opening. Immediately reweigh the flask, burner, and numbered cork. When all combustions have been completed, turn off the CO_2 and the O_2 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 CO_2 from the absorbent; then close the vacuum control valve.

NOTE 9—If it is desired to conserve the combustion atmosphere, the gas flow through each individual absorber can 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 gases at the rotameters 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 removal of dissolved CO_2.

TABLE 1 Sample Size for Direct Combustion of Liquid Samples

Sulfur Content, mass percent	Sample Size	
	g	mL
Under 0.05	10 to 15	20
0.05 to 0.4	5 to 10	10

9.4 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 rinsing to the absorbers, and titrate as directed in Section 11.

9.5 *Blank*—Leave the chimney of the blank absorber (see 7.3) stoppered, and allow the CO_2-O_2 stream to pass through that absorber until all samples started at one time have finished burning. Turn off the CO_2 and the O_2 supplies and aerate the blank absorber in the same manner as the sample absorbers (see 9.3). Titrate the absorber liquid as directed in Section 11. Normally, the combustion atmosphere blank will be small, but if the titration requires more than 0.1 mL of 0.05 *N* NaOH solution discard the determination and replace the CO_2 cylinder.

10. Procedure for Blending and Combustion of Liquid Samples

10.1 Add 6 mL of sulfur-free diluent to each flask. Stopper the flasks with numbered corks and weigh to the nearest 0.005 g. By means of a pipet, introduce into the flask of each burner an approximate quantity of sample as indicated in Table 2; swirl to mix thoroughly, and reweigh.

NOTE 10—Alternatively, make a quantitative 40 % blend of the sample in sulfur-free diluent and proceed as described in Section 9.

10.2 Insert the burner and burn as described in 9.2. 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 one more time so that a total of 10 mL of diluent has been burned.

NOTE 11—In this case, it is desirable that a 10-mL diluent blank be run; the titration of the absorber solution from this blank, shall not exceed 0.1 mL of 0.05 *M* NaOH solution.

10.3 After all lamps have completed burning, turn off the CO_2 and O_2 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 11.

11. Titration of Absorbent Solution

11.1 Add 3 to 4 drops of methyl purple indicator solution to the liquid in each absorber. Titrate the absorbent solution by introducing 0.05 *N* NaOH solution from a buret into the smaller bulb of the absorber. Use a 10-mL microburet 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 12—When incomplete combustion of the sample occurs, the air drawn through the absorber during the titration will have a characteristic taste or odor and the end point will be broad. In these cases, discard the determination.

TABLE 2 Sample Size for Testing Blended Liquid Samples

Sulfur Content, mass percent	Sample Size	
	g	mL
0.4 and under	3 to 4	5

12. Calculations

12.1 Calculate the sulfur content of liquid samples as follows:

$$\text{Sulfur content, mass percent} = 16.03\, M \times (A/10\, W) \quad (1)$$

where:

A = millilitres of NaOH solution required to titrate the acid in the absorbent solution from the burned sample,
M = molarity of the NaOH solution (see Note 3), and
W = grams of sample burned.

12.2 When it is required by specifications to correct the sulfur content (Note 13) for lead antiknock fluids, calculate the corrected values as follows:

$$\text{Corrected sulfur content, mass percent} = S - LF \quad (2)$$

where:

F = 0.0015 if the sample contains aviation lead antiknock fluid or 0.0035 if the sample contains tetraethyllead, tetramethyllead, or the mixed lead alkyl antiknock fluid,
L = lead content, g/U.S. gal, and
S = sulfur content, mass %.

NOTE 13—These corrections are based on experiments of burning fuels blended with antiknock fluid containing tetraethyllead and ethylene halide in commonly-used combinations. Tetramethyllead and the mixed lead alkyl antiknock fluids contain the same ethylene halide combination as the tetraethyllead fluid.

NOTE 14—To convert grams of lead per Imperial gallon into grams per U.S. gallon, multiply by 0.8326. Multiply by 3.7853 to convert grams of lead per litre into grams per U.S. gallon.

13. Report

13.1 Report the results of the test to the nearest 0.01 % for sulfur at a level of 0.05 % and higher, and the specific test procedure used.

14. Quality Control

14.1 Confirm the performance of the apparatus or the procedure, or both, each day it is in use by analyzing a QC sample (6.10) that is representative of samples typically analyzed. Increase the analysis frequency of the QC sample if a large number of samples are analyzed. Analysis of the result(s) from the QC sample(s) can be carried out using control charts[12], or other statistically equivalent techniques, to ascertain the control status of the total testing process. Any out of control data should trigger investigation for root cause. The QC sample precision shall be checked against the ASTM method precision to ensure data quality.

15. Precision and Bias

15.1 The precision of this test is not known to have been obtained in accordance with currently accepted guidelines (for example, in Committee D-2 Research Report RR-D-2-1007, "Manual on Determining Precision Data for ASTM Methods

[12] ASTM Manual 7, *Manual on Presentation of Data and Control Chart Analysis*, 6th edition, available from ASTM Headquarters.

on Petroleum Products and Lubricants").[13]

15.1.1 *Repeatability*—The difference between two 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 following values only in one case in twenty:

Repeatability	0.005

15.1.2 *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 following values only in one case in twenty:

Reproducibility	$0.010 + 0.025S$

where:

S = the total sulfur content, mass percent, of the sample.

15.2 *Bias*—It is not practicable to specify bias of Test Method D 1226 for measuring sulfur becuase the responsible subcommittee, after diligent search, was unable to attract volunteers for an interlaboratory study.

16. Keywords

16.1 lamp; sulfur

[13] *Annual Book of ASTM Standards*, Vol 05.03.

ANNEXES

(Mandatory Information)

A1. TEST METHOD OF TEST FOR TRACE QUANTITIES OF SULFUR

A1.1 Scope

A1.1.1 This annex describes a procedure for extending the lamp method of test for sulfur to the analysis of samples having sulfur contents as low as 5 ppm (Note A1.1): The procedure is not applicable for the determination of less than 300 mg/kg of sulfur in liquids containing lead antiknock compounds.

A1.1.1.1 Only by the exercise of the most scrupulous care and attention to details can reliable results be obtained by this method. Before placing new glassware into use 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.

A1.2 Summary of Test Method

A1.2.1 A sample of suitable size is burned as described in Section 9. Sulfate ion in the absorber solution is determined by precipitation as barium sulfate and measurement of the turbidity of a suspension of the precipitate. The suspension is stabilized by the addition of alcohol and glycerin, and its turbidity is measured by use of a spectrophotometer or filter photometer.

A1.3 Additional Apparatus

A1.3.1 *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 color filter having a maximum transmission at approximately 450 nm.

A1.3.2 *Absorption Cells* having optical path lengths of 5 cm are preferred. 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 following cleaning.

NOTE A1.1—The procedure as written assumes an absorbance change of about 0.100 for each 0.1 mg of sulfur in 50 mL of solution measured in a 5-cm cell. Photometers employing cells of shorter optical paths give proportionately poorer precision.

A1.3.3 *Scoop*, capable of dispensing 0.30 ± 0.01 g of barium chloride dihydrate as specified in A1.4.2.

A1.3.4 *Magnetic Stirrer*, equipped with tetrafluoroethylene covered stirring bars about 32 mm (1¼in.) long.

A1.3.5 *Lamp Assembly*, as described in Annex A3. Reserve complete units consisting of flask, burner, chimney, absorber, and spray trap for use in this procedure only.

A1.4 Additional Reagents[14]

A1.4.1 *Alcohol-Glycerin Mixture*—Mix 2 volumes of denatured ethyl alcohol conforming to Formula No. 3A of the U.S. Bureau of Internal Revenue or ethyl alcohol (95 % by volume) with 1 volume of glycerin.

A1.4.2 *Barium Chloride Dihydrate* ($BaCl_2 \cdot 2H_2O$)—Crystals passing an ASTM E 11 20-mesh sieve or a BS 18-mesh sieve and retained on an ASTM E11 30-mesh sieve or a BS 30-mesh (See Specification E 11).

NOTE A1.2—The crystal size of the $BaCl_2 \cdot 2H_2O$ is an important variable that affects the development of turbidity.

A1.4.3 *Hydrochloric Acid* (*1 + 12*)—Add 77 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to a 1-L volumetric flask and dilute to the mark with deionized water.

A1.4.4 *Hydrochloric Acid* (*1 + 215*)—Add 60 mL of 1 + 12 HCl to a 1-L volumetric flask and dilute to the mark with deionized water.

A1.4.5 *Sulfuric Acid* (*1 mL = 0.100 mg S*)—Dilute 6.24± 0.01 mL of 1 *N* sulfuric acid (H_2SO_4) to exactly 1 L with deionized water. Check the dilution by titration against standard NaOH 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 S.

[14] For Purity of Reagents, see 6.1.

A1.4.6 *Water, Deionized Distilled*—Percolate water through a column of mixed anion and cation exchange resins.

NOTE A1.3—A means for determining when to replace the exchange resins should be supplied. Use of a simple electrical conductivity meter has been found satisfactory for this purpose.

A1.5 Calibration

A1.5.1 Into 50-mL volumetric flasks introduce, by means of a buret, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00, and 5.00 mL of H_2SO_4 (1 ml = 0.100 mg S). Add 3.0 mL of HCl (1 + 12) to each flask, dilute to volume with water, and mix thoroughly. Prepare a reagent blank standard in a similar way, omitting the H_2SO_4.

A1.5.2 Pour the entire contents of each flask into a 100-mL beaker, add by means of a pipet 10 ± 0.1 mL of alcohol-glycerin mixture, and mix for 3 min on the magnetic stirrer. Select a stirring speed just below that which might cause loss of sample through splashing. Maintain this speed throughout the entire procedure.

A1.5.3 Allow the solution to stand undisturbed for 4 min. Transfer to an absorption cell and measure the initial absorbance, using water as reference.

A1.5.4 Return the solution to the beaker and add 0.30± 0.01 g of $BaCl_2 \cdot 2H_2O$ crystals, either by weighing this amount or by use of the scoop. 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.

A1.5.5 Following steps described in A1.5.2-A1.5.4, obtain a reagent blank reading by subtracting the initial absorbance of the reagent blank standard from that obtained after addition of $BaCl_2 \cdot 2H_2O$. This reading should not exceed 0.005.

A1.5.6 Obtain the net absorbance for each standard by subtracting the initial absorbance and reagent blank reading from the absorbance obtained in accordance with A1.5.4. Plot the net absorbance of each standard against milligrams of sulfur contained in 50 mL of solution, and draw a smooth curve through the points.

A1.5.7 Check the calibration curve daily by making single determinations to detect possible shifts.

A1.6 Procedure for Combustion of Samples

A1.6.1 Prepare the combustion apparatus and burn between 5 and 30 g of sample depending on the expected sulfur level (Note A1.5). Follow the general procedures described in Sections 7, 8, and 9 of the main method. The requirements for initial neutralization of the H_2O_2 solution (see 7.2) and for final removal of dissolved CO_2 from this solution (see 9.3, and 10.3), 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 9.4), 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.

A1.6.1.1 A sample 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 described in A1.6.3 and A1.7 and will avoid the necessity for 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 sample sizes, a burner flask of suitable size must be fabricated to replace the standard 25-mL flask. In recognition of the larger size of the flask, it is preferable to use 18 cm of wicking rather than the 15 cm specified in 7.5. To avoid excessive depletion of absorber liquid caused by the longer burning time for larger samples, it is preferable to charge the absorbers with 50 mL of the hydrogen peroxide solution instead of the 30 mL specified in 7.2.

A1.6.2 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 HCl (1 + 12) to the flask, make up to volume with water, and mix thoroughly.

A1.6.3 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 volumetric flask and dilute the solution in both flasks to volume with HCl (1 + 215). 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. Analyze the solutions as described in A1.7.

A1.7 Procedure for Analysis of Solutions

A1.7.1 Pour the entire contents of the 50-mL volumetric flask containing the solution to be analyzed into a 100-mL beaker and proceed as directed in A1.5.2-A1.5.4. 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 addition of $BaCl_2 \cdot 2H_2O$.

NOTE A1.4—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 reagents are at fault. Place 30 mL of the H_2O_2(1.5 percent) in the 50-mL volumetric flask, dilute to the mark with HCl (1 + 215), and proceed as described in A1.5.5. If this reagent blank reading exceeds 0.010, results should not be considerable reliable.

A1.7.2 Obtain the net absorbance of the analysis solution by subtracting the initial absorbance and the combustion atmosphere-reagent blank reading from that obtained after addition of $BaCl_2 \cdot 2H_2O$.

A1.7.3 Convert net absorbance to milligrams of sulfur by using the calibration curve.

A1.8 Calculation

A1.8.1 Calculate the amount of sulfur in the sample as follows:

$$\text{Sulfur content, mg/kg} = (A/WF) \times 1000 \quad \text{(A1.1)}$$

where:

A = milligrams of sulfur read from the calibration curve,

W = grams of sample burned, and
F = aliquot fraction of the sample solution used for analysis.

A1.9 Precision and Bias

A1.9.1 The following criteria should be used for judging the acceptability of results (95 % confidence):

A1.9.1.1 *Repeatability*— Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Sulfur Content, mg/kg	Repeatability
5 to 80	0.116 × mg/kg *S*
Over 80 to 280	(0.01 × mg/kg *S*) + 8.5

A1.9.1.2 *Reproducibility*— The results submitted by each of two laboratories should be considered suspect if the two results differ by more than the following amounts:

Sulfur Content, mg/kg	Reproducibility
5 to 125	0.145 × mg/kg *S*
Over 125 to 280	(0.508 × mg/kg *S*) − 45.4

NOTE A1.5—For the determination of trace quantities of sulfur by a rapid burning method see Test Method D 2785.

A1.9.2 *Bias*—It is not practicable to specify the bias of Test Method D 1266, Annex A1 for measuring trace quantities of sulfur because the responsible subcommittee, after diligent search, was unable to attract volunteers for an interlaboratory study.

A2. AIR BURNING OF SAMPLE, GRAVIMETRIC FINISH

A2.1 Scope

A2.1.1 This procedure is recommended only for analyzing liquid petroleum samples that can be burned with a wick lamp.

A2.2 Apparatus

A2.2.1 The mainfold system described in 5.3 may be used with only a slight modification. Substitute filtered air for the CO_2-O_2 supply train and add a second sintered-plate scrubber to the incoming air line as shown in Fig. A2.1.

A2.3 Additional Reagents

A2.3.1 *Barium Chloride Solution (100 g/L)*—Dissolve 100 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 litre.

A2.3.2 *Hydrochloric Acid (relative density 1.19)*—Concentrated hydrochloric acid (HCl).

A2.3.3 *Hydrogen Peroxide Solution (30 %)*—Concentrated hydrogen peroxide (H_2O_2).

A2.3.4 *Sodium Hydroxide Solution (100 g/L)*—Dissolve 100 g of technical grade sodium hydroxide (NaOH) pellets in water and dilute to 1 L.

A2.3.5 *Sulfuric Acid (1 + 16)*—Mix 60 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 960 mL of water.

A2.4 Preparation of Apparatus

A2.4.1 Place 300 to 400 mL of NaOH solution in the first scrubber (Fig. A2.1) and the same amount of H_2O_2-H_2SO_4 solution (300 mL of H_2O, 30 mL of H_2SO_4 (1 + 16), and 30 mL of H_2O_2(30 %)) in the second scrubber. For apparatus in daily use, replace these solutions two times each week or whenever the volume becomes less than two thirds of the original.

A2.4.2 Make other preparations as described in Section 7, except that the H_2O_2 solution (1.5 %) need not be neutralized.

A2.5 Procedure for Combustion

A2.5.1 Burn the sample as described in Section 9, controlling combustion as described in Section 8. Use a sample size as prescribed in Table A2.1. Analyze the absorber solutions from the samples and blank as described in A2.6.1.

A2.6 Procedure for Analysis of Absorber Solution

A2.6.1 Transfer the absorber liquid to a 400-mL beaker. Rinse the absorber and chimney thoroughly with water and add the rinsings to the beaker. Filter the solution to remove any foreign material, receiving the filtrate in a 400-mL beaker having a mark to indicate 75 mL. Add 2 mL of HCl, heat to boiling, and add 10 mL of $BaCl_2$ solution, either in a fine

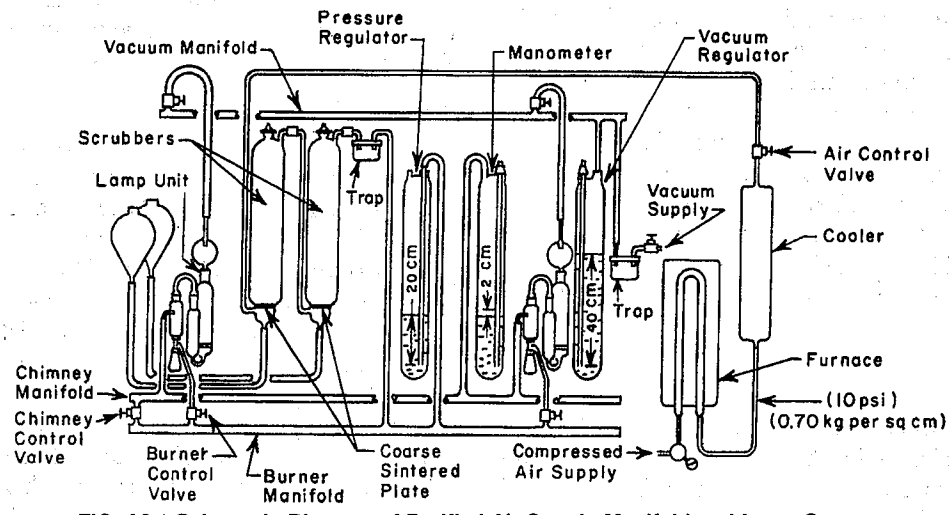


FIG. A2.1 Schematic Diagram of Purified Air Supply Manifold and Lamp System

TABLE A2.1 Sample Size for Air Burning of Liquid Samples

Sulfur Content, weight percent	Sample Size	
	g	mL
0.5 and under	5 to 10	10
Over 0.5	3 to 5	5

stream or dropwise. Stir the solution during the addition and for 2 min thereafter.

A2.6.2 Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume of approximately 75 mL, as indicated by the mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow to cool 1 h before filtering.

A2.6.3 Filter the supernatant liquid through a close-texture, ashless filter paper. Wash the precipitate with water, first by decantation and then on the filter paper, until free of chloride ion. Transfer the paper and precipitate to a suitable weighed crucible, and dry at low heat until the moisture hasevaporated. Char the paper completely without igniting it, and finally ignite at a bright red heat until the precipitate is burned white (Note A2.1). After ignition is complete, allow the crucible to cool to room temperature and weigh.

NOTE A2.1—A satisfactory means of accomplishing these operations is to place the uncovered crucible containing the wet filter paper in a cold electric muffle furnace and turn on the current. Drying, charring, and ignition usually occur at the desired rate.

A2.7 Calculation

A2.7.1 Calculate the sulfur content of the sample as follows:

$$\text{Sulfur content, mass percent} = [(w - b) \times 13.73]/W \quad \text{(A2.1)}$$

where:

w = grams of barium sulfate ($BaSO_4$) precipitate in the absorber solution from the burned sample,

b = grams of $BaSO_4$ precipitate from the corresponding blank absorber solution (Note A2.2), and

W = grams of sample burned.

NOTE A2.2—The determination should be discarded if the blank correction used in the calculation exceeds 1.5 mg of $BaSO_4$. Frequently, impure reagents are the cause of this difficulty.

A2.8 Precision

A2.8.1 See Section 15 for recommended data.

A3. APPARATUS DETAIL

A3.1 Flask and Burner for Nonaromatic Samples

A3.1.1 A lamp of chemically resistant glass, consisting of a 25-mL Erlenmeyer flask and a burner that conforms to the dimensions shown in Fig. A2.1, shall be used. The burner consists of two concentric glass tubes, the external tube having a sidearm and standard-taper glass joints for connection with the flask and the chimney. The upper ends of both burner tubes shall be polished and shall have plane surfaces that are in the same horizontal plane. The burner shall have a 1-mm opening near its base to allow equalization of pressure between the chimney and the flask. When connected with the chimney, the lamp shall be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

A3.2 Flask and Burner for Aromatic Samples

A3.2.1 A lamp of chemically resistant glass, consisting of a 25-mL Erlenmeyer flask with a side-arm and a burner that conforms to the dimension shown in Fig. A2.1, shall be used. The burner consists of two concentric glass tubes, the external tube having a sidearm and standard-taper glass joints for connecting the burner with the flask and the chimney. The upper ends of both burner tubes shall be polished and shall have plane surfaces that are in the same horizontal plane. When connected with the chimney, the lamps shall be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

A3.3 Chimney

A3.3.1 A chimney of chemically resistant glass, conforming to the dimensions shown in Fig. A2.1 and provided with standard-taper glass joints for connection with the burner and absorber, shall be used.

A3.4 Absorber

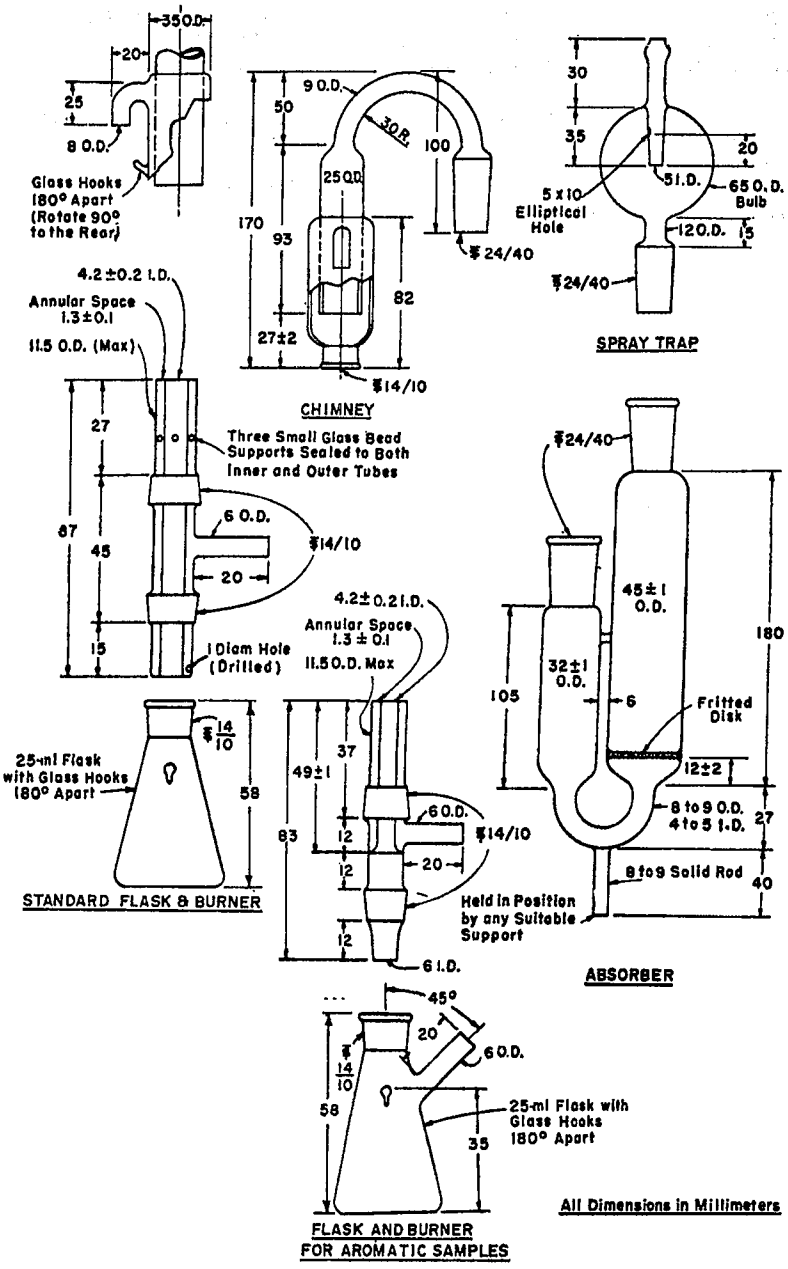
A3.4.1 An absorber of chemically resistant glass conforming to the dimensions shown in Fig. A3.1 and provided with standard-taper glass joints for connection with the chimney and spray trap, shall be used. A fritted disk with average pore diameter from 150 to 200 μm shall be sealed in the larger of two bulbs of the absorber. The fritted disk should be of such a porosity that, when 50 mL of water is placed in the absorber and air is passed through at the rate of 3.0 L/min in the forward direction, the pressure differential between the two sides of the absorber is between 15 and 23 cm of water and the air is dispersed uniformly.

A3.5 Spray Trap

A3.5.1 A spray trap of chemically resistant glass conforming to the dimensions shown in Fig. A2.1 and provided with a standard-taper glass joint for connection with the absorber, shall be used.

A3.6 Manifold System

A3.6.1 A satisfactory vacuum and combustion atmosphere manifold and supply system for supplying the required CO_2-O_2 mixture to the lamp assemblies is shown diagrammatically in Fig. 2. The gases are supplied from commercial cylinders, the pressure of each gas being adjusted to 10 ± 2 psig (0.70 ± 0.14 kg/cm ^{2}) by means of two single-stage regulating valves to ensure constant pressure at the flow-regulating needle valves. It is necessary to pass the CO_2 through a heat exchanger installed ahead of the regulating valves to prevent freezing of the valves. The gases are passed through a metering system consisting of two calibrated rotameter flow meters to indicate the proportion of the two gases mixed in the surge tank. Any number of lamp assemblies can be operated as a unit, the throughput of the flow



NOTE 1—Standard tapers 14/10, 24/40, or equivalent.

NOTE 2—The fritted disk shown in the drawing of the absorber shall be of such a porosity that, when 50 mL of water is placed in the absorber and air is passed through at the rate of 3.0 litres/min in the forward direction, the pressure differential between the two sides of the absorber is between 15 and 23 cm of water and the air is dispersed uniformly.

FIG. A3.1 Detailed Drawing of Combustion and Absorption Apparatus

meters being chosen accordingly. The tubing that connects the chimney manifold to the chimneys should have an internal diameter not smaller than 6.4 mm (¼ in.) in order to prevent unnecessary restriction in gas flow. The scrubber should have a capacity of about 1 litre.