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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 standard has been approved for use by agencies of the Department of Defense.

^{ε1}Note—Warning notes were editorially moved into the standard text in July 2003.

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 values stated in SI units are to be regarded as the standard.~~

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

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

D 1193 Specification for Reagent Water

~~D 1229 Test Method for Rubber Property—Compression Set at Low Temperatures~~

D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)

~~D 2784 Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)~~² Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

D 6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

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

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² Annual Book of ASTM Standards, Vol 05.01.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard.

E 11 Specification for Wire Cloth and Sieves for Testing Purposes

2.2 ~~Institute of Petroleum Standard~~: Energy Institute Standard:³

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 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.

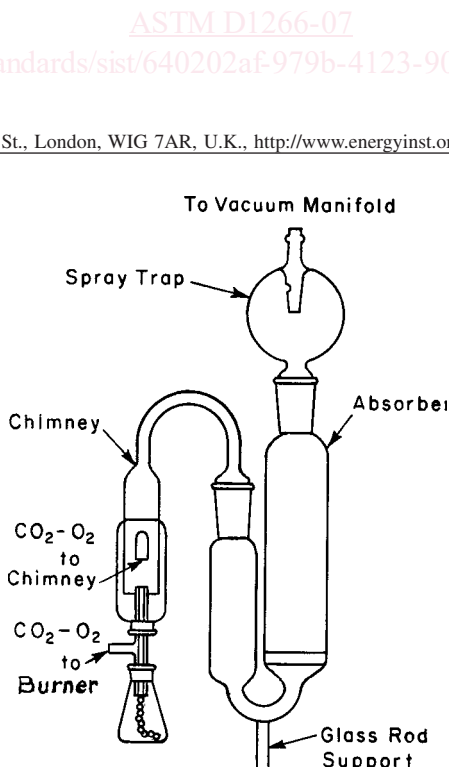


FIG. 1 Illustrative Sketch of the Assembled Lamp Unit

² Annual Book of ASTM Standards, Vol 11.01.

³ Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., <http://www.energyinst.org.uk>.

5.2 *Cotton Wicking*^{4,5}—Clean, unused, uniform, twisted white cotton yarn of good quality. For the burner to burn aromatic samples use long staple, fine-spun, commercial *fine* grade.^{5,6}

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 (CO₂) and 30 % oxygen (O₂) 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.⁷ 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 (CO₂) and the oxygen (O₂) 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, *isooctane*, and absolute ethyl alcohol have been found suitable (Note 9).

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 (H₂O₂, 30 %) with 19 volumes of water. Store in a dark-colored glass-stoppered bottle.

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⁴ Annual Book of ASTM Standards, Vol 09.01.

⁴ The sole source of supply of cotton wicking, yarn, white, 4-strand (2 to 3 mg/cm/strand) known to the committee at this time is 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.

⁵ Annual Book of ASTM Standards, Vol 14.02.

⁵ If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

⁶ Available from Institute of Petroleum (IP), 61 New Cavendish St., London, W1G 7AR, U.K.

⁶ The sole source of supply of fine grade known to the committee at this time is Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0099.

⁷ The sole source of supply of cotton wicking, yarn, white, 4-strand (2 to 3 mg/cm/strand) known to the committee at this time is 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.

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, 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.

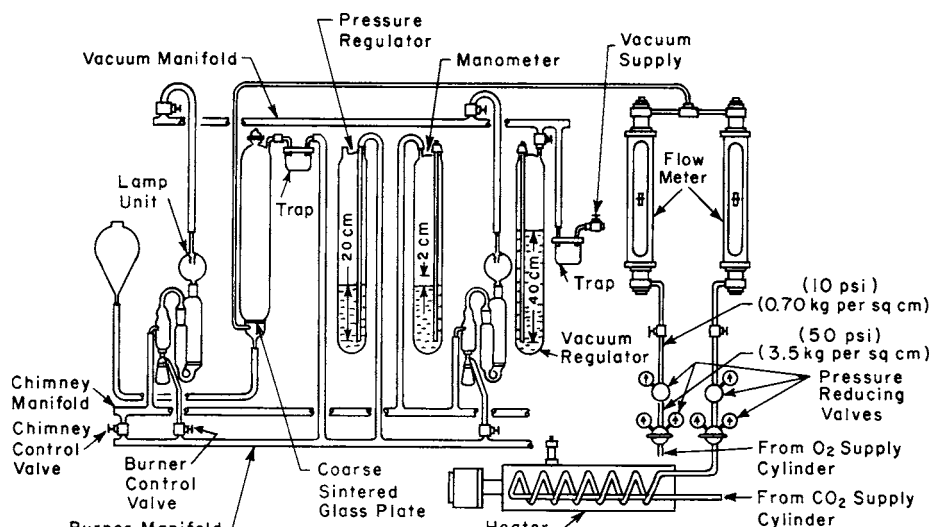


FIG. 2 Schematic Diagram of CO₂-O₂ Supply Manifold and Lamp System

6.7 *Methyl Purple Indicator*—Aqueous solution containing approximately 0.1 % active constituent.⁸ (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 CO₂ from the air. Use only pure 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 16.03M 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 H₂O₂ solution (1 + 19) in the scrubber. Since the manifold manometer also serves as a scrubber at the end of the test to remove CO₂ from the absorbent use H₂O₂ solution (1 + 19) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

7.2 Neutralize the H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 CO₂ and O₂ supplies. (**Warning**—A hazardous (explosive) condition can result if the CO₂ supply is interrupted and the O₂ flow is continued while samples are being burned. The installation of suitable warning or control equipment is recommended.) Adjust the chimney manifold control valve so that, at the required rate of flow through the absorbers, only a small stream of CO₂-O₂ 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 5).

NOTE 5—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 CO₂-O₂ 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 If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

⁸ 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.

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 O₂ content of the combustion atmosphere. Never increase the O₂ 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 6—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 CO₂-O₂ supply to the burners in order to prevent extinction of the flames.

NOTE 7—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 CO₂-O₂ 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 CO₂ and the O₂ 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 CO₂ from the absorbent; then close the vacuum control valve.

NOTE 8—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 CO₂.

TABLE 1 Sample Size for Direct Combustion of Liquid Samples

Sulfur Content, mass percent	Sample Size	
	g	mL
Under 0.05	10 to 15	5 to 10
0.05 to 0.4	10 to 15	20
Under 0.05	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 CO₂-O₂ stream to pass through that absorber until all samples started at one time have finished burning. Turn off the CO₂ and the O₂ 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 CO₂ 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 9—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 10—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 CO₂ and O₂ 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 11—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.

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 12) 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 12—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 13—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.

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