Designation: D1072 – 06 (Reapproved 2012)

Standard Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration[1]

This standard is issued under the fixed designation D1072; 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.

1. Scope

1.1 This test method is for the determination of total sulfur in combustible fuel gases, when present in sulfur concentrations between approximately 25 and 700 mg/m^3 (1 to 30 grains per 100 cubic feet). It is applicable to natural gases, manufactured gases, mixed gases, and other miscellaneous gaseous fuels.

1.2 The values stated in inch-pound units are to be regarded as standard.

1.3 *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]

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 A metered sample of gas is burned in a closed system in an atmosphere of sulfur-free air. The oxides of sulfur produced are absorbed in sodium carbonate solution, where they are oxidized to sulfate. The sulfate in the absorbent solution is determined by titration with standardized barium chloride solution, using tetra-hydroxy-quinone (THQ) as an indicator.

4. Interferences

4.1 There are no known interferences for the determination of total sulfur in fuel gases when combustion is followed by barium chloride titration. However, users employing barium chloride titration following collection of sulfur dioxide by alternative procedures are cautioned that ammonia, amines, substances producing water soluble cations, and fluorides will interfere with the titration.

5. Apparatus

5.1 *Burner* (Fig. 1), as specified in the Appendix X1.

5.2 *Chimneys, Absorbers and Spray Traps,* (Fig. 2), as specified in the Appendix X1.

5.3 *Flow meter*—A calibrated capillary flow meter for predetermining and indicating the rate of flow of gas to the burner. The capillary selected should be of such size that at the required rate of flow the differential pressure is at least 20 cm of water. A scale divided into millimeters will then provide a reading precision of ± 0.5 %. Other metering devices, including but not limited to rotameters or dry displacement meters, are suitable provided the reading precision is ± 0.5 % or better. A flow controlling valve is attached to the inlet connection of the flow meter.

5.4 *Vacuum System*—A vacuum manifold equipped with a vacuum regulating device, valves, and other necessary accouterments. An example vacuum system capable of performing multiple test measurements is shown in Fig. 3. Other vacuum system configurations can be used to perform this test method. The vacuum system shall be connected to a vacuum pump capable of providing a steady gas flow of 3 L of air per minute through each absorber and capable of maintaining a constant manifold pressure of approximately 40 cm of water below atmospheric pressure.

5.5 *Air-Purifying System*—A device supplying purified air to the burner manifold at a constant pressure of approximately 200 mm of water and to the chimney manifold at a pressure of 1 to 2 cm of water. An example system configuration for multiple tests is illustrated in Fig. 4; however, other air-purifying system configurations can be used to perform this test method. The tubing that connects the chimneys to the manifold shall be of an internal diameter not smaller than 0.63 cm in order to prevent unnecessary restriction of airflow.

5.6 *Manometer*—A water manometer for indicating the gas pressure at the point of volume measurement. It is connected between the flowmeter and the burner, with one leg open to the atmosphere.

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[1] This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of D03.05 on Determination of Special Constituents of Gaseous Fuels.

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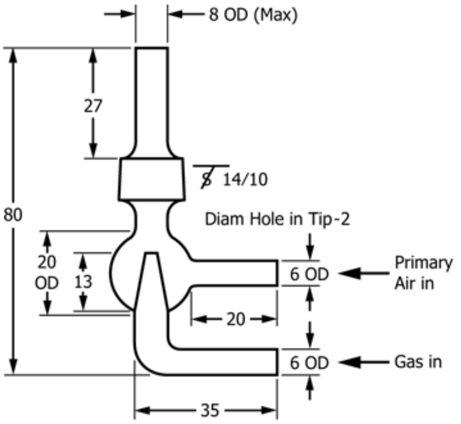
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



NOTE 1—All dimensions in millimetres.

FIG. 1 Gas Burner for Sulfur Determination

6. Reagents and Materials

6.1 *Reagents Purity*—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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without adversely impacting the accuracy of the determination. **Warning—** Sodium hydroxide is corrosive and can cause severe damage to eyes and skin. Inhalation will irritate the nose, throat and lungs. It reacts exothermically with water.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

6.3 *Alcohol*—Ethyl alcohol, denatured by Formula 30 or 3-A, or isopropyl alcohol.

6.4 *Barium Chloride,(CAS No: 10361-37-2), Standard Solution* (1 mL = 1 mg S)—Dissolve 7.634 g of barium chloride ($BaCl_2{\cdot}2H_2O$) in water and dilute to 1 L. The solution is standardized gravimetrically by precipitation as barium sulfate or by titration against sulfuric acid (see 6.12)

6.5 *Hydrochloric Acid (CAS No 7647-01-0)* (2.275-g HCl/L)—Titrated against Na_2CO_3 solution (see 6.15), using methyl orange indicator. Adjusted such that 1 mL of HCl solution is equivalent to 1 mL of Na_2 CO_3 solution.

6.6 *Hydrogen Peroxide* (*30 %*) (H_2O_2;CAS No: 7722-84-1).

6.7 *iso-Propanol (CAS No. 67630)*

6.8 *Potassium Hydrogen Phthalate (KHP; CAS No 877-24-7)* —Dry use.

6.9 *Phenolphthalein (CAS No 77-09-8)*

6.10 *Methyl Orange (CAS No 547-58-0) Indicator Solution*—Dissolve 0.1 g of methyl orange in 100 mL of water.

6.11 *Silver Nitrate (CAS No 7761-88-8)Solution* (17-g $AgNO_3$/L)—Dissolve 1.7 g of silver nitrate ($AgNO_3$) in 100 mL of water. Store in a brown bottle.

6.12 *Sodium Carbonate (CAS No 5968-11-6) Solution* (3.306-g Na_2CO_3/L)—Dissolve 3.306 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

6.13 *Sodium Hydroxide Solution (CAS No 1310-73-2)* (100-g NaOH/L)—Dissolve 100 g of technical grade sodium hydroxide (NaOH) pellets in water and dilute to 1 L. Standardize against potassium hydrogen phthalate (See 6.1)

6.14 *Sulfuric Acid(CAS No 7664-93-9)* (*1 + 16*)—Mix 60 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 960 mL of water.

6.15 *Tetrahydroxyquinone Indicator* (*THQ* CAS No. 5676-48-2), in powdered form.

6.16 *Thorin indicator*— (CAS No. 132-33-2)

7. Calibration and Standardization

7.1 *Sodium Hydroxide Solution Standardization*— The following provides an example procedure for standardization; other quantities of reagents, as convenient, can be used. Dry and crushed potassium hydrogen phthalate (KHP) is heated in an oven at 105 °C for 2 hours and allowed to cool to room temperature in a desiccator. KHP (950 ± 50 mg weighed to the nearest 0.1 mg) is placed in an Erlenmeyer flask. Water (70 mL) and 2-4 drops of phenolphthalein are added. Titrate the KHP solution with the sodium hydroxide solution prepared under 6.13 to a faint pink color. Repeat the titration using a second portion of KHP. Titrate a 70 mL water blank containing 1-4 drops of phenolphthalein to a faint pink color using the sodium hydroxide solution prepared under 6.13. Repeat this procedure and average the results. For both the water blank and the KHP titration replicates should agree to 0.05 mL titrant. For each KHP trial, independently calculate the normality for the sodium hydroxide solution according to the following equation:

$$\text{Normality of NaOH} = \frac{\text{mg KHP/204.23}}{(\text{mL NaOH} - \text{avg. mL blank})} \qquad (1)$$

Values for the two KHP trials should agree within ± 0.5 percent. If they do not, repeat the titrations or identify the cause for the excessive discrepancy, or both.

7.2 *Sulfuric Acid Standardization*— The following provides an example procedure for standardization; other quantities of reagents, as convenient, can be used. Titrate the sulfuric acid solution prepared under 6.14 against the sodium hydroxide standardized in 7.1 using 2-4 drops of phenolphthalein as the indicator. Repeat and average the result for the normality of the sulfuric acid. Values for the two trials should agree within ± 0.5 percent. If they do not, repeat the titrations or identify the cause for the excessive discrepancy, or both.

7.3 *Barium Chloride Solution Standardization*— – Titrate the barium chloride solution against the previously standardized sulfuric acid solution (see 7.2). This can be conveniently accomplished by transferring 10.0 mL sulfuric acid to a flask

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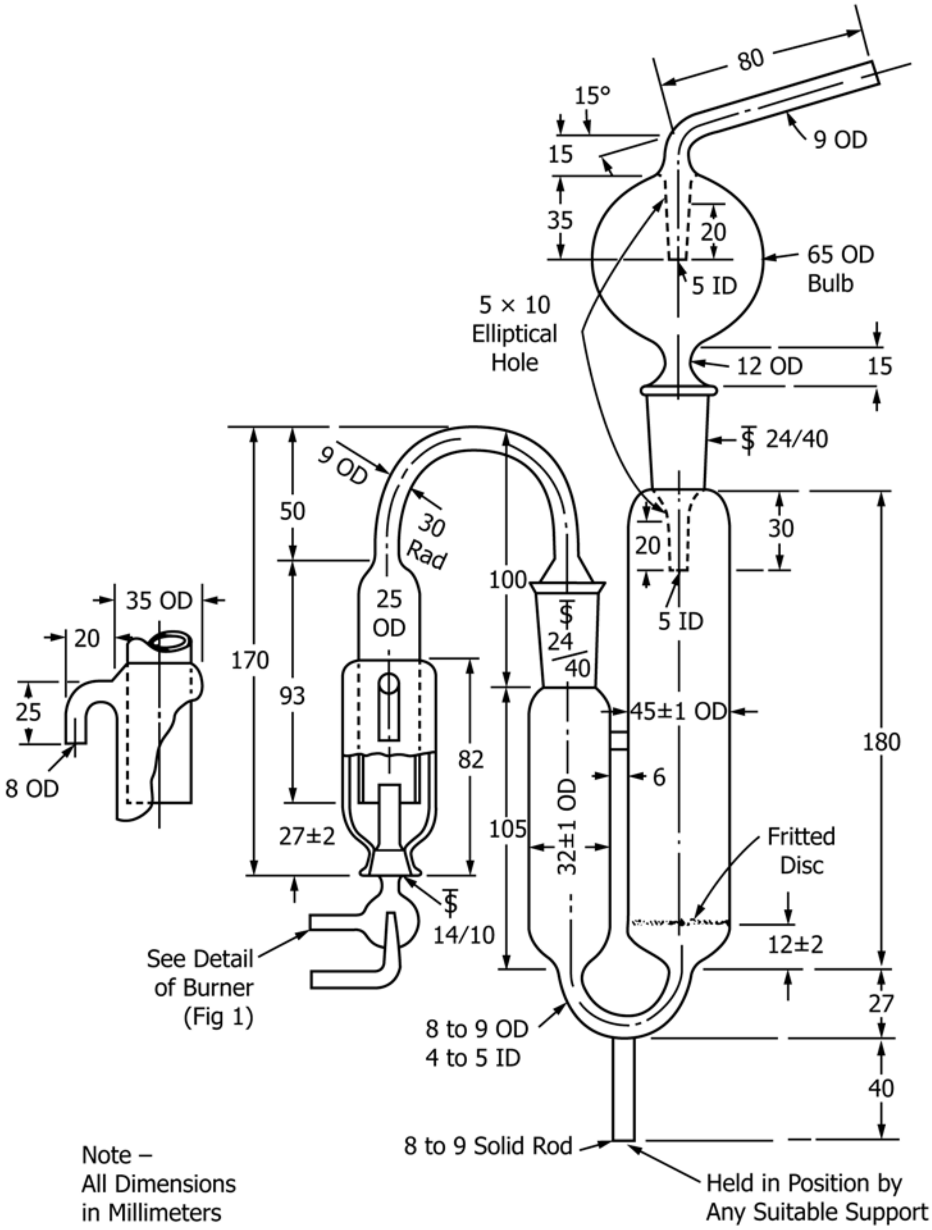
[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States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



NOTE 1—In the case of those dimensions for which no specific tolerances are designated above, the permissible variation is ±10 % to the nearest 1 mm, provided, however, that in no case shall the deviation be greater than 5 mm.

FIG. 2 Detailed Drawing of Combustion and Absorption Apparatus for Sulfur Determination

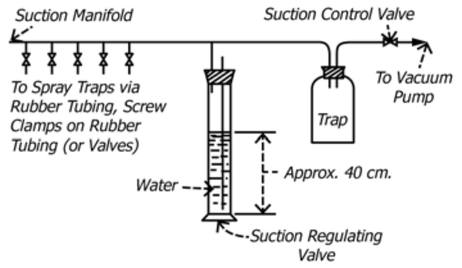


FIG. 3 Suction System for Sulfur Determination

where 40 mL iso-propanol and 2-4 drops thorin indicator are added. This is titrated to a pink end point using the barium chloride solution. Repeat the titration and average the results. The replicate titrations should agree within 0.5 percent. If they do not, repeat the titrations or identify the cause for the excessive discrepancy, or both. Using this same procedure, perform duplicate blank titrations using water in place of sulfuric acid solution. The replicate titrations should agree within 0.5 percent. Calculate the normality of the barium chloride solution according to the following equation:

$$\text{Normality of Barium Chloride} = \frac{10.0\text{ mL x N Sulfuric Acid}}{(\text{avg. mL} - \text{avg. blank})} \qquad (2)$$

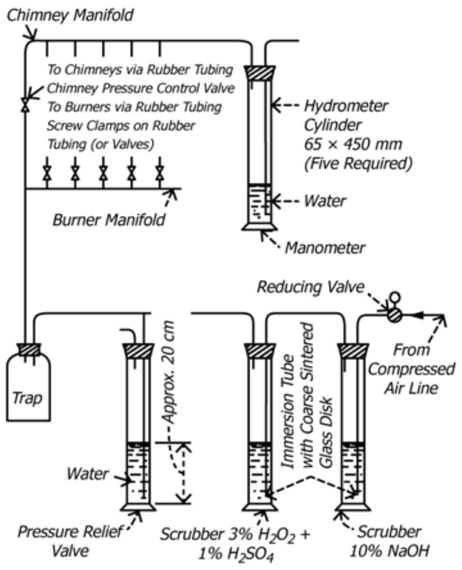


FIG. 4 Purified Air System for Sulfur Determination

7.4 An auto titration can be used to determine the concentration of both sodium hydroxide and sulfuric acid.

8. Preparation of Apparatus

8.1 Place 300 to 400 mL of NaOH solution in the first scrubber (Fig. 4) and the same amount of H_2O_2-H_2SO_4 solution (300 mL of water, 30 mL of H_2SO_4 , and 30 mL of H_2O_2 (30 % w/w)) in the second scrubber. Replace these solutions whenever the volume becomes less than two thirds of the original.

8.2 When the apparatus is first assembled, adjust the valve between the vacuum manifold and the spray trap so that approximately 3 L of air per minute will be drawn through the absorber when the chimney outlet is open to the atmosphere, the absorber is charged with 30 ± 2 mL of water, and the pressure in the vacuum manifold is maintained at approximately 40 cm of water below atmospheric. When all adjustments have been made, remove the water from the absorbers.

8.3 With the burner control valve 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 purified air. Adjust the chimney manifold control valve so that, at the required flow through the absorber, only a small stream of air escapes at the pressure-relief valve, 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 1—It is convenient to balance the air-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.

8.4 When first assembling the apparatus, connect the gas sample line using glass or aluminum tubing to the inlet of the flowmeter. Connect the outlet of the flowmeter in a similar way to the lower side arm of the burner. Adjust the valve for controlling the rate of flow of gas so that gas is burned at a rate to liberate approximately 250 to 500 Btu/h (Note 2). This rate should be indicated by two index marks on the columns of the flowmeter U-tube or timing a rate-index device. Make the primary air connection from the purified air line to the upper side arm of the burner by means of rubber or plastic tubing.

NOTE 2—Using this gas rate, the chimney and absorber should not become overheated during a test. The appropriate volumetric rate of gas flow will therefore depend on the heating value of the gas being tested.

8.5 Wash the spray trap, absorber, and chimney well with water before each test. Charge the larger bulb of the absorber with 10 mL of Na_2CO_3 solution (Note 3) and 20 mL of water. Attach the spray trap and chimney, and connect them, respectively, to the vacuum line and to the purified air line using rubber or plastic tubing. Close the chimney opening using a cork or other suitable plug.

NOTE 3—This quantity of Na_2CO_3 solution is adequate to absorb the SO_2 from the combustion products of 1 ft^3 of gas containing 15 grains of sulfur per 100 ft^3 (0.03 m^3 of gas containing 350 mg/m^3 of sulfur.) For higher concentrations of sulfur in the gas, the volume of Na_2CO_3 solution should be proportionately increased, but the total initial liquid volume in the absorber should not exceed 30 mL.

9. Procedure

9.1 Prior to each test, purge the flowmeter, burner, and connection with the gas sample, and light the flame on the burner. Adjust the gas-flow rate by its valve to conform with the requirements prescribed in 8.4. Adjust the primary air flow so that a soft blue flame is obtained, with no yellow tip.

9.2 To start a determination, insert the burner into the chimney, fastening it in place with rubber bands or springs. Check, and readjust if necessary, gas flows to obtain a stable flame. Note the time at which the burner was inserted, or note the meter reading if an integrating meter is used.

9.3 Continue the test until approximately 0.03 m^3 (1 ft^3) of gas is burned. Maintain the flowmeter differential at a constant value during this period. Note the time, or the meter reading when using an integrating meter, and remove the burner from the chimney, replacing it with the cork or other suitable plug, and continuing the suction on the absorber until the latter attains room temperature. Extinguish the flame.

9.4 Unless an integrating-type meter is used for gas measurements, disconnect the burner from the flowmeter. Replace it with a connection to a calibrated wet-test meter that has been purged with 5 ft^3 (0.15 m^3) of the gas being tested. Adjust the flowmeter differential and the manometer reading to that existing during the determination in 9.3 and time with a stopwatch one complete revolution of the wet-test meter. A needle value may be required at the inlet of the wet-test meter to adjust the pressure and flow of gas so that both the flowmeter and the manometer indicate the same values, respectively, that existed during the determination.

9.4.1 Calculate the volume of gas in standard cubic feet burned during the determination as follows:

$$V = (t_d/10t_c) \times [519.67/459.67 + T_d] \times [P + (m/13.6) - w]/(30 - 0.522) \quad (3)$$

where:

V = volume of sample burned, in standard cubic feet at 60°F, 30 in. Hg, saturated;
t_d = time for determination, s;
t_c = time of one revolution of wet test meter during calibration, s;
T_d = meter temperature, °F absolute;
P = barometric pressure, in. Hg;
m = manometer reading, in. water; and
w = vapor pressure of water at meter temperature, in. Hg.

NOTE 4—This calibration procedure avoids the necessity of calculating corrections of the flowmeter calibration for each gas tested.

9.4.2 Calculate the volume in standard cubic metres as follows:

$$(4) V = (t_d/t_c) \times [288.15/(273+15+T_d)] \times [P+(m/13.6) - w]/(760 - 12.788) \quad (4)$$

where:

V = volume in cubic metres at standard conditions (15°C and 101.325 kPa);
t_d = time of determination, s;
t_c = time of calibration, s/m^3;
T_d = meter temperature, °C;
P = barometric pressure, mm Hg;
m = manometer reading, mm H_2O; and
w = vapor pressure of H_2O in mm Hg.

NOTE 5—The calculated results in inch-pound and metric conditions are not directly convertible. The calculation equations for inch-pound and metric results are based on differing base conditions of temperature and pressure (inch-pound – 60°F, 30 in. Hg or 14.73 psia; Metric—288.15 K (+ 15°C), 101.325 kPa). Any conversion must take these differences into account.

9.5 If a calibrated integrating dry displacement meter is used for gas measurement, calculate the volume as follows:

$$V = V_m [519.67/(459.67+T_d)] \times [P+(m/13.6) - w']/(30 - 0.522) \quad (5)$$

where:

V_m = meter reading at end of determination minus the meter reading at the start of the determination, ft^3 and
w' = actual partial pressure of water vapor in gas at dry-meter temperature, and all other symbols are defined as in 8.4.

$$V = V_m \times [288.15/(273.15+T_d)] \times [P+(m/13.6) - w']/(760 - 12.788) \quad (6)$$

where:

V_m = meter reading at end of determination minus the meter reading at the start of the test and
w' = actual partial pressure of water vapor in gas at dry-meter temperature.

9.6 A duplicate test is suggested to assure the user that representative results are obtained for a particular fuel sample. Values for the two tests should agree within ± 0.5 percent. If they do not, identify the cause for the excessive discrepancy, mitigate the cause and re-perform the test(s).

10. Analysis of Absorbent

10.1 When the absorber has cooled to room temperature, wash the chimney and trap with the smallest possible quantity of water, and add the washings to the solution in the absorber. Add three drops of methyl orange indicator to the solution. Titrate the excess Na_2CO_3 in the absorber with HCl to the methyl orange end point, mixing the solution after each addition of acid by alternate sucking and blowing on one end of the absorber.

10.2 Discharge the tan color of the acid methyl orange with a few drops of Na_2CO_3 solution and add 50 mL of ethyl or isopropyl alcohol. Add about 0.5 g of tetra-hydroxy-quinone indicator (THQ). After mixing the solution well, titrate with $BaCl_2$ solution. After 1 or 2 mL of the $BaCl_2$ solution have been added, add 1 mL of 0.1*N* $AgNO_3$ solution, and continue titration to the end point. The end point is reached when the color of the solution changes from yellow to rose, which is persistent with good mixing. Note and record the volume of $BaCl_2$ solution required to produce the red color.

10.3 Using this same procedure as 10.2, perform a blank titration using water in place of the sample solution.

NOTE 6—The $AgNO_3$ intensifies the rose color at the end point.

11. Calculation

11.1 Calculate the concentration of sulfur from the results of the $BaCl_2$ titration, as follows (see Note 5):

$$S = [(A - B)/V] \times 1.543 \quad (7)$$

where:

S = sulfur concentration in grains/100 standard ft^3,
A = millilitres of $BaCl_2$ solution used for sample titration,
B = millilitres of $BaCl_2$ solution used for blank titration,
V = volume in ft^3.

NOTE 7—One grain=64.799 milligrams; 1ft^3= 0.0283 m^3

$$S = [(A - B)/V] \times 3531 \quad (8)$$

where:

S = sulfur concentration in mg/m^3,
A = millilitres of $BaCl_2$ used for titration,
B = millilitres of $BaCl_2$ used for blank titration,
V = volume in m^3.

NOTE 8—The amount of $BaCl_2$ solution used in the blank titration (*B*) can be substituted with 0.2 mL as an approximate blank allowance for the titration end point when the intended use of the data is not adversely impacted.

12. Quality Assurance

12.1 *Sulfuric Acid Control*—A typical sulfuric acid control procedure is as follows. Titrate 10.0 mL of 0.1N H_2SO_4 with every set of samples, or every ten samples, whichever occurs first. Results should be within ± 5 percent of the theoretical value. If results are outside of the accepted range, re-standardize the NaOH and recalculate the results. If the recalculated results do not fall within range, investigate the procedure until it is under control, and reanalyze the samples.

12.2 *Sulfate Analysis Control*—Analyze an EPA SO_2 Quality Assurance vial or other suitable known standard with every set of samples or every ten samples, whichever occurs first. Results should be within ± 5 percent of theoretical. If results do not fall within the accepted range, re-standardize the $BaCl_2$ and recalculate the results. If the recalculated results fall outside of the accepted range, investigate the procedure until it is under control, and reanalyze the sample(s).

13. Precision and Bias

13.1 The accuracy of the results for a determination is dependant on the accuracy with which the sample volume is metered and the accuracy of the titration procedures.

13.1.1 When 1 ft^3 of gas is burned, an absolute precision equivalent to ±0.1 grain of sulfur per 100 ft^3 of gas should be attainable in the $BaCl_2$ titration, independent of the total quantity of sulfate present in the absorber. The overall accuracy should therefore be between ±0.1 and ±0.7 grains of sulfur per 100 ft^3, if metering accuracy of ±2 % is attained, over the concentration range to which the procedure is adaptable.

13.1.2 When 1 m^3 of gas is burned, an absolute precision equivalent to ±0.06 mg/m^3 should be attainable in the $BaCl_2$ titration, independent of the total quantity of sulfate in the absorber. The overall accuracy should therefore be between ±0.06 and ±0.42 mg/m^3, if metering accuracy of ±2 % is attained, over the concentration range to which the procedure is adaptable.

14. Keywords

14.1 gaseous fuels

APPENDIX

(Nonmandatory Information)

X1. APPARATUS

X1.1 *Burner*, of chemically resistant glass that conforms with the dimensions shown in Fig. 1. It consists of a burner tube to which the gas sample is admitted through a side arm and orifice at the lower end. Surrounding the gas orifice tip is a spherical enlargement of the burner tube into which purified primary air for combustion is admitted. The burner tube is provided with a standard-taper glass joint for connection with the chimney. The upper end of the burner tube shall be polished. When connected with the chimney, the burner shall be held in position by rubber bands or metal springs stretched between glass hooks on the burner and chimney.

X1.2 *Chimney*, of chemically resistant glass conforming to the dimensions shown in Fig. 2, provided with standard-taper glass joints for connection with the burner and absorber.

X1.3 *Absorber*, of chemically resistant glass conforming to the dimensions shown in Fig. 2, provided with standard-taper glass joints for connection with the chimney and spray trap. A fritted disk with average pore diameter from 150 to 200 µm shall be sealed in the larger of the two bulbs of the absorber. The fritted disk should be of such a permeability 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.

X1.4 *Spray Trap*, of chemically resistant glass conforming to the dimensions shown in Fig. 2, provided with a standard-taper glass joint for connection with the absorber.