Designation: D 1072 – 90 (Reapproved 1999)

Standard Test Method for Total Sulfur in Fuel Gases[1]

This standard is issued under the fixed designation D 1072; 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 covers the determination of total sulfur in combustible fuel gases, when present in concentrations between 1 and 30 grains of sulfur per 100 ft^3 (25 and 700 mg/m^3). It is applicable to natural gases, manufactured gases, and mixed gases, such as are distributed by gas utility companies.

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:*

D 1193 Specification for Reagent Water[2]

D 3031 Test Method for Total Sulfur in Natural Gas by Hydrogenation[3]

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry[4]

3. Summary of Test Method

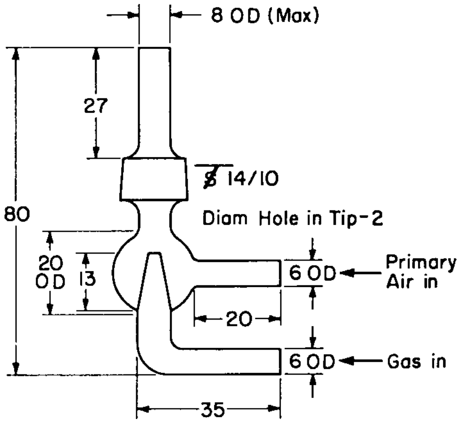
3.1 A metered sample of gas is burned in a closed system in an atmosphere of sulfur-free air. The oxides of sulfur produced are absorbed in sodium carbonate solution, wherein they are oxidized to sulfate. The sulfate in the absorbent solution is subsequently determined by titration with standard barium chloride solution, using tetrahydroxyquinone as an indicator.

4. Apparatus

4.1 *Burner* (Fig. 1), as specified in the AppendixAppendix X1.

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

4.3 *Flowmeter*—A calibrated capillary flowmeter 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 millimetres will then provide a reading precision of ±0.5 %. Other metering devices, such as a rotameter or a dry displacement meter, will be suitable if the precision of reading the scale is equivalent. A flow controlling valve is attached to the inlet connection of the flowmeter.



NOTE 1—All dimensions in millimetres.

FIG. 1 Gas Burner for Sulfur Determination

4.4 *Vacuum System*—A vacuum manifold equipped with a vacuum regulating device, valves, and so forth. A convenient arrangement for multiple tests is shown in Fig. 3, but any other similar system may be used. The system shall be connected to a vacuum pump of sufficient capacity to permit a steady gas flow of 3 L of air per minute through each absorber and to maintain a constant manifold pressure of approximately 40 cm of water below atmospheric.

4.5 *Air-Purifying System*—A device to supply purified air to the burner manifold at a nearly constant pressure of approximately 20 cm of water and to the chimney manifold at a pressure of 1 to 2 cm of water. A convenient arrangement for multiple tests is illustrated in Fig. 4, but any other similar system may be used. The tubing that connects the chimneys to the manifold shall be of an internal diameter not smaller than 0.63 cm to prevent unnecessary restriction of air flow.

4.6 *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 D-3 on Gaseous Fuels and is the direct responsibility of D03.05 on Determination of Special Constituents of Gaseous Fuels.

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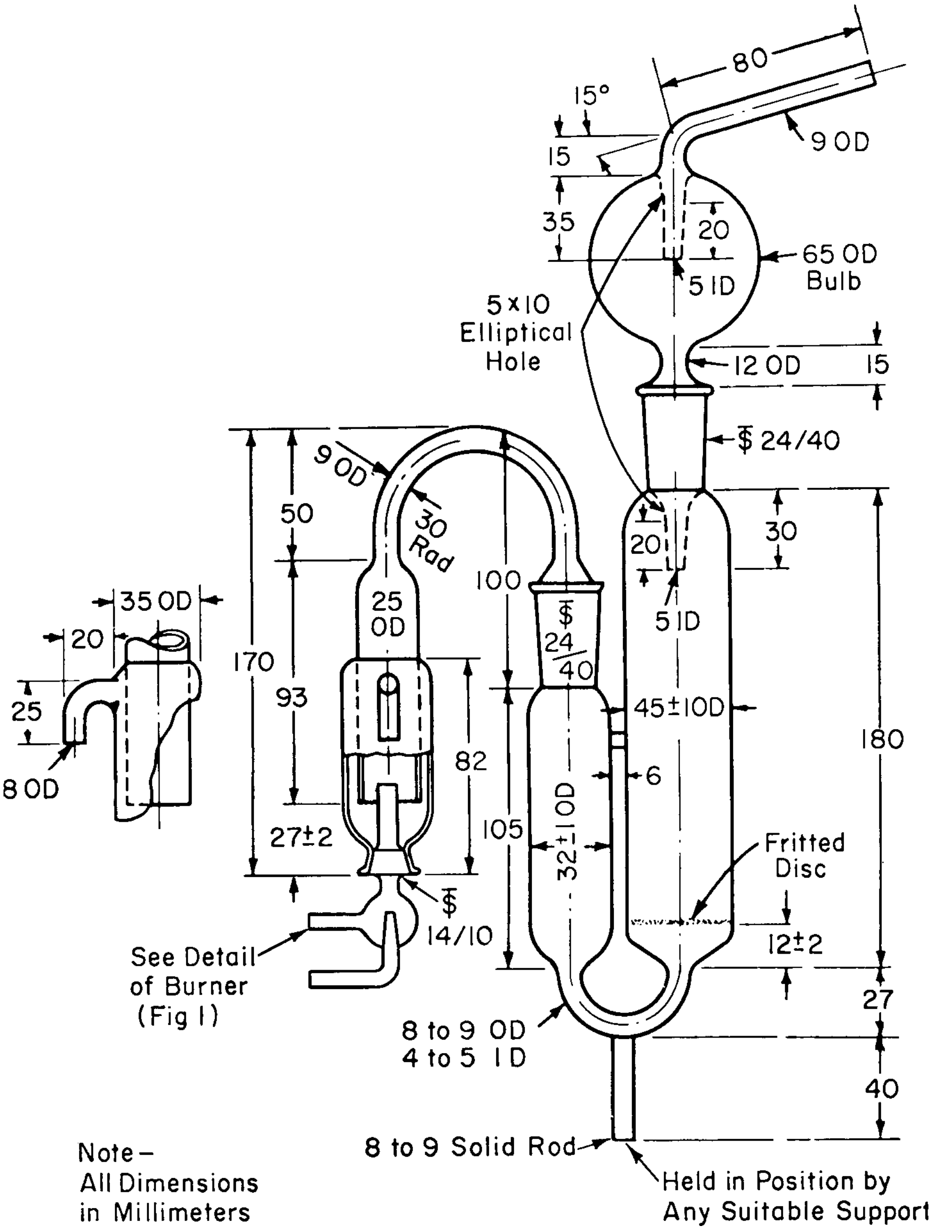
[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Discontinued*—See *1991 Annual Book of ASTM Standards,* Vol 05.05.

[4] *Annual Book of ASTM Standards,* Vol 05.06.



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

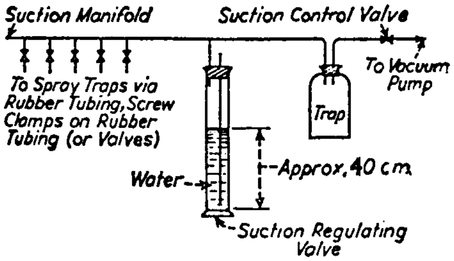


FIG. 3 Suction System for Sulfur Determination

5. Reagents and Materials

5.1 *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.[5] 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming

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[5] *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.

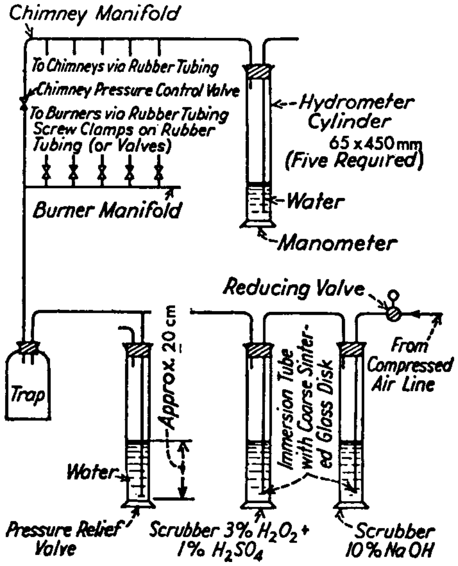

FIG. 4 Purified Air System for Sulfur Determination

to Specification D 1193.

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

5.4 *Barium Chloride, 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. Standardize the solution gravimetrically by precipitation as barium sulfate.

5.5 *Hydrochloric Acid* (2.275-g HCl/L)—Compare this solution by titration with the Na_2CO_3 solution (see 5.9), using methyl orange indicator. Adjust, if necessary, so that 1 mL of HCl solution is equivalent to 1 mL of Na_2CO_3 solution.

5.6 *Hydrogen Peroxide* (*30 %*) (H_2O_2).

5.7 *Methyl Orange Indicator Solution*—Dissolve 0.1 g of methyl orange in 100 mL of water.

5.8 *Silver Nitrate Solution* (17-g $AgNO_3$/L)—Dissolve 1.7 g of silver nitrate ($AgNO_3$) in 100 mL of water. Keep in a brown bottle.

5.9 *Sodium Carbonate 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.

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

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

5.12 *Tetrahydroxyquinone Indicator* (*THQ*), in powdered form.[6]

6. Preparation of Apparatus

6.1 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 (1 + 16), and 30 mL of H_2O_2 (30 %)) in the second scrubber. Replace these solutions whenever the volume becomes less than two thirds of the original.

6.2 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.

6.3 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.

6.4 When first assembling the apparatus, connect the gas sample line by means of 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.

6.5 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 by means of rubber or plastic tubing. Close the chimney opening by means of a cork.

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.

7. Procedure

7.1 Before the beginning of 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 6.4. Adjust the primary air flow so that a soft blue flame is obtained, with no yellow tip.

7.2 To start a determination, the suction on the absorber and the air flow having been adjusted, insert the burner into the

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[6] Tetrahydroxyquinone Indicator (THQ) is obtainable from the Betz Laboratories, Inc., Gillingham and Worth Sts., Philadelphia, PA 19124.

chimney, fastening it in place with rubber bands or springs. Check, and readjust if necessary, the indicated rate of gas flow and the primary air flow 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.

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

7.4 Unless an integrating-type meter is used for gas measurements, disconnect the burner from the flowmeter. Attach in its place 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 7.3 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.

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

$$V = (t_d/10t_c) \times (520/T_d) \times [P + (m/13.6) - w]/(30 - 0.522) \quad (1)$$

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, and is believed to be more precise.

7.4.2 Calculate the volume in standard cubic metres as follows:

$$V = (t_d/t_c) \times [288/(273 + T_d)] \times [P + (m/13.6) - w]/(760 - 12.788) \quad (2)$$

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.

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

$$V = V_m (520/T_d) \times [P + (m/13.6) - w']/(30 - 0.522) \quad (3)$$

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 6.4.

$$V = V_m \times [273/(273 + T_d)] \times [P + (m/13.6) - w']/(760 - 12.788) \quad (4)$$

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.

8. Analysis of Absorbent

8.1 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.

8.2 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 tetrahydroxyquinone 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.

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

9. Calculation

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

$$S = [(A - 0.2)/V] \times 1.543 \quad (5)$$

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

$$S = [(A - 0.2)/V] \times 3531 \quad (6)$$

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

NOTE 7—The 0.2 mL subtracted from the $BaCl_2$ titer is a blank allowance for the titration end point.

10. Precision and Bias

10.1 The accuracy of the results of a determination depends on the accuracy with which the sample volume is metered as well as on the accuracy of the titration procedure.

10.1.1 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.

10.1.2 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.

11. Keywords

11.1 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.