Designation: D 4468 – 85 (Reapproved 2000)

Standard Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry[1]

This standard is issued under the fixed designation D 4468; 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 sulfur gaseous fuels in the range from 0.001 to 20 parts per million by volume (ppm/v).

1.2 This test method may be extended to higher concentration by dilution.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns 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.* Specific precautionary statements are given in 6.7, 6.8, and 7.3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres[3]

3. Summary of Test Method

3.1 The sample is introduced at a constant rate into a flowing hydrogen stream in a hydrogenolysis apparatus. The sample and hydrogen are pyrolyzed at a temperature of 1000°C or above, to convert sulfur compounds to hydrogen sulfide (H_2S). Readout is by the rateometric detection of the colorimetric reaction of H_2S with lead acetate. Units used are ppm/v, which is equivalent to micromoles/mole.

4. Significance and Use

4.1 This test method can be used to determine specification, or regulatory compliance to requirements, for total sulfur in gaseous fuels. In gas processing plants, sulfur can be a contaminant and must be removed before gas is introduced into gas pipelines. In petrochemical plants, sulfur is a poison for many catalysts and must be reduced to acceptable levels, usually in the range from 0.01 to 1 ppm/v. This test method may also be used as a quality-control tool for sulfur determination in finished products, such as propane, butane, ethane, and ethylene.

5. Apparatus [4]

5.1 *Pyrolysis Furnace*—A furnace that can provide an adjustable temperature of 900 to 1300°C in a quartz or ceramic tube of 5 mm or larger tube (ID) is required for pyrolysis of the sample. (See Fig. 1.) The flow system is to be a fluorocarbon or other material inert to H_2S and other sulfur compounds. (See Fig. 1.)

5.2 *Rateometric H_2S Readout*—Hydrogenolysis products contain H_2S in proportion to sulfur in the sample. The H_2S concentration is determined by measuring rate of change of reflectance of a tape impregnated with lead acetate caused by darkening when lead sulfide is formed. Rateometric electronics, adapted to provide first derivative output, allows sufficient sensitivity to measure to 0.001 ppm/v. (See Fig. 2.)

5.3 *Recorder*—A suitable chart recorder may be used for a permanent record of analysis.

6. Reagents and Materials

6.1 *Purity of Chemicals*—Reagent grade unless specified otherwise.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean Type II, reagent grade water, conforming to Specification D 1193.

6.3 *Sensing Tape*—Lead acetate impregnated analytical quality filter paper shall be used.

6.4 *Acetic Acid (5 %)*—Mix 1 part by volume reagent grade glacial acetic acid with 19 parts water to prepare 5 % acetic acid solution.

6.5 *Gastight Syringe*—A gastight 0.1- and 0.5-mL syringe for preparing calibration standard. Volumetric measurement accuracy of the syringe shall be 1 % or better.

6.6 *Piston Cylinder*—Use a 10-L acrylic cylinder with a free moving piston and silicone rubber "O" ring lubricated with a

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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 Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] The apparatus described in 5.1, 5.2, 6.3, 6.5, and 6.6 is similar in specification to the equipment available from Houston Atlas Inc., 22001 N. Park Dr., Kingwood, TX 77339–3804. For further information see U.S. Patent No. 3,756,781, C. L. Kimbell, inventor.

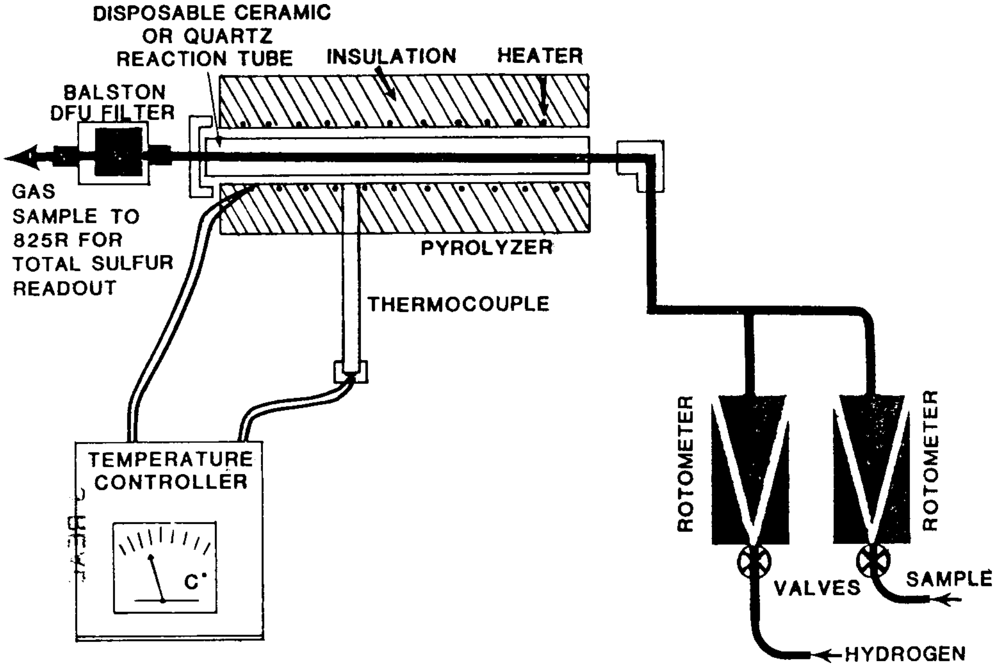

FIG. 1 Hydrogenolysis Flow Diagram

free-flowing silicone lubricant.[5] This cylinder is used to prepare ppm/v calibration samples volumetrically.

6.7 *Carbonyl Sulfide (COS)*—A lecture bottle of COS, 99 % purity, with a needle valve connected to the lecture bottle outlet. Connect 2 ft of tygon tubing to allow insertion of a hypodermic syringe to withdraw pure COS while tubing is purged from the lecture bottle. Other sulfur compounds can be used with adequate odor control. If the sulfur compound has two sulfur atoms per molecule, reduce the volume by one half. (**Warning**—Work with COS should be done in a well-ventilated area, or under a fume hood.)

6.8 *Hydrogen Gas*—Use sulfur-free hydrogen of laboratory grade. (**Warning**—Hydrogen has wide explosive limits when mixed with air. See 1.3 regarding precautions.)

6.9 *Carrier Gas for Calibration Standards*—Use sulfur-free laboratory grade bottled gas of the same type or similar density as the gas to be analyzed or calibrate the flowmeter to establish correct flow setting for an available carrier gas. Test, as in 7.5, adding the carrier gas flow to the hydrogen flow.

6.10 *Purge Gas*—Sulfur-free purge gas, nitrogen, CO_2, or other inert gas. Commercial grade cylinder gas is satisfactory.

7. Preparation of Apparatus

7.1 Turn on the furnace and allow temperature to stabilize at 1000°C. If thiophenic sulfur could be present, use 1300°C temperature setting.

NOTE 1—Reduced operating temperature extends furnace life. Thiophenic compound conversion increases from about 60 % at 1000°C to 100 % at 1300°C.

7.2 Connect all flow tubing between components and fill humidifier inside the cabinet to 30 mL with a 5 % by volume acetic acid solution. Purge all flow systems with inert gas then close valve. Check all connections for leaks with soap solution and repair any leaks. Connect hydrogen and set flow at 200 mL/min and allow temperature to stabilize. Sample flow must be ⅓ or less of the H_2 flow. Total flow can be up to 500 mL/min, except when the sample has thiophenic compounds that require 200 mL/min of H_2 flow for conversion. Make final temperature adjustment to 1000 ± 15°C or a minimum 1300°C if the sample contains thiophenic sulfur compounds.

7.3 Install sensing tape and turn H_2S readout analyzer on. Use adequate safety precautions in handling lead acetate tape.

7.4 Adjust the zero of the analyzer indicator meter (and recorder if used) to desired position with no flow. This should be performed with span at maximum.

7.5 Test hydrogen purity by turning on hydrogen flow and noting any change in zero position after 5 min. If the reading is upscale from the zero set point by greater than 4 %, then the hydrogen source should be suspect as not being sulfur free and should be changed.

7.6 If the change in the recorder zero is less than 4 %, then reset the recorder zero to the desired position while the hydrogen is flowing. This should be performed with the span at maximum.

8. Standardization

8.1 With hydrogen flow at 200 mL/min, advance tape to an unexposed area and note baseline.

8.2 Prepare a reference standard as described in Section 9. Connect the reference sample to the pump and the pump to the analyzer. When a stable reading is obtained, record this value (*C* in 11.1). Advance the tape and introduce reference sample gas flow with a sulfur concentration near that expected in the unknown (see 9.2). Adjust the sample flow to 65 mL/min. After about 4 min, adjust the recorder span such that the recording

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[5] Dow Corning 200 silicone grease has been found to be satisfactory for this application.

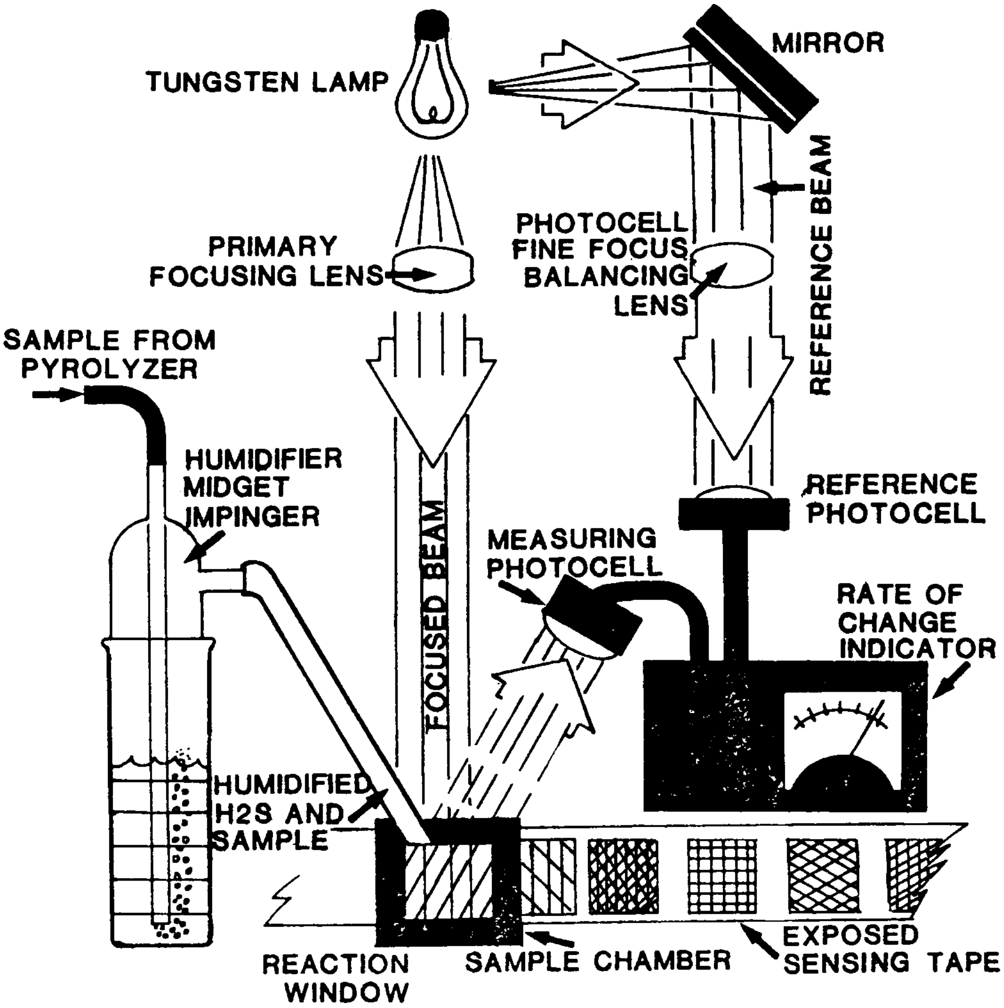

FIG. 2 Photorateometry H_2S Readout

indicates to desired response. The response is linear. A calibration standard, such as 0.8 ppm/v, can be prepared and the recorder span adjusted to 80 % of full scale so that full scale is 1 ppm/v and any lower value can be read directly on a scale divided into 100 parts.

9. Calibration and Standardization

9.1 *Reference Standard*—Reference standards are prepared by volumetric measurement at the time the reference material is to be used. (See Fig. 3.) This minimizes deterioration of the sample. Normally this reference standard will deteriorate less than 1 % in 15 min. Small volumes of pure sulfur compound are measured using a gastight syringe. Dilution gas is measured using a 10-L graduated cylinder having a movable piston. When ppm/v samples are prepared for immediate use by volumetric measurement, no correction for temperature and pressure changes are needed in a laboratory environment. Temperature and pressure correction will be needed if conversion to weight units is desired.

9.2 *Preparation*—To prepare 1-ppm/v sample, add 10 µL (0.01 mL) of COS to make a 10-L sample carrier mixture. Inject COS through the septum on the 10-L acrylic cylinder as it is filled with carrier gas. Swirling of the carrier provides mixing. To calculate millilitres of sulfur compound required in a 10-L mixture, use the following equation:

$$p = \text{ppm/v} \times 10^{-2} \qquad (1)$$

where: p = millilitres of sulfur compound. (This applies to gas-phase material only.)

9.2.1 Prepare a reference standard of a concentration slightly higher than may be anticipated in the sample. Purge the 10-L cylinder with sulfur-free carrier gas. Connect the tygon tubing to the COS lecture bottle and insert end into a beaker of water. Open valve while observing bubbles to adjust tubing purge flow rate. Insert gastight hypodermic needle into the wall of the tygon tubing. Raise and lower plunger slowly several times to purge the syringe. Start filling the 10-L cylinder with carrier gas and inject desired quantity of sulfur compound through the septum. Withdraw the syringe quickly after injection to prevent residual gas in the needle tip from diffusing into the flowing gas. Turn off the carrier gas when 10 L are obtained. The reference standard is now ready for use in calibrating the analyzer. For samples less than 1 ppm/v, secondary volumetric dilution may be used. As an example, to get a 0.2-ppm/v sample, exhaust the cylinder filled with 10 L of 1-ppm/v gas to 2 L, then fill again to 10 L with diluent gas.

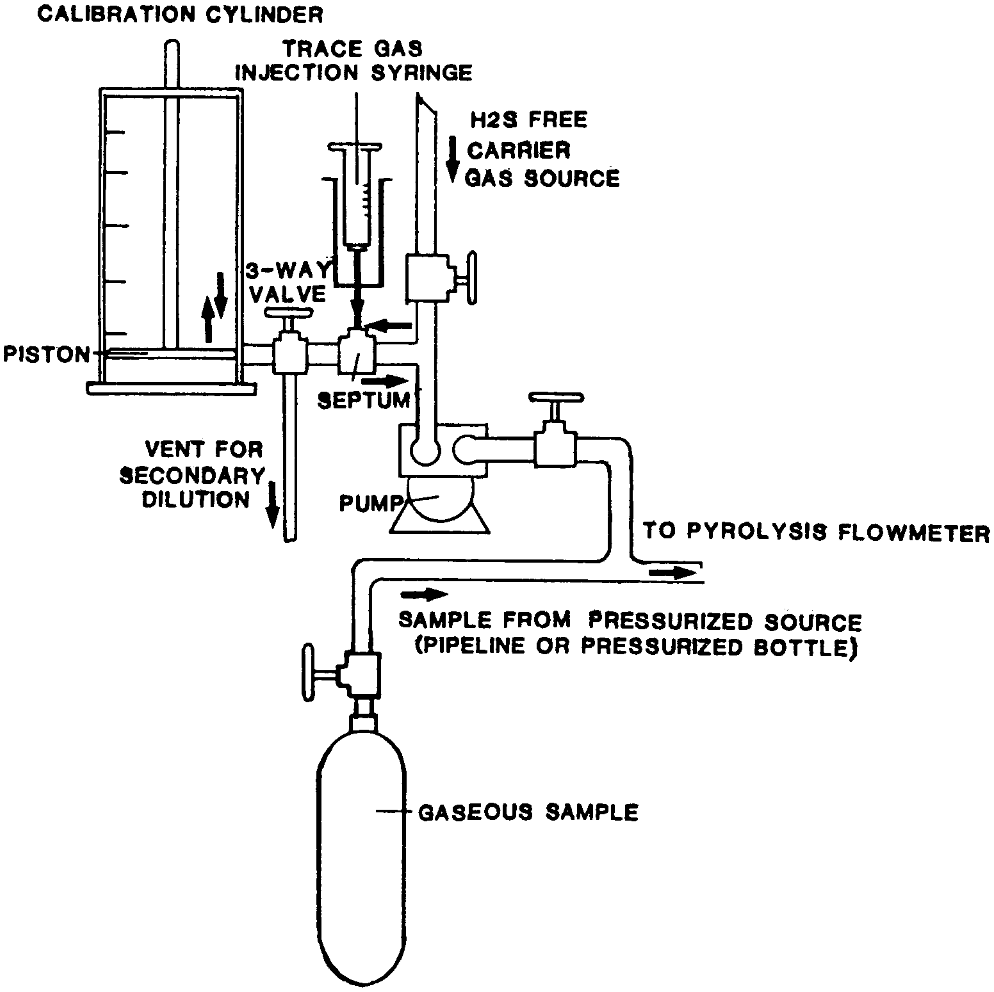

FIG. 3 Flow System for Gas Sample and Calibration Reference

10. Sample Measurement Procedure

10.1 Connect the sample to the analyzer and adjust the flow rate to approximately 65 mL/min. This flow must be maintained constant during testing. After the response is observed to be stable, record the reading *A* (see 11.1). The reference standard described in 9.2 must be prepared and run to establish the analyzer span frequently enough to allow compensation for changes in temperature and atmospheric pressure. When samples are within 25 % of the reference standard, repeating the entire calibration procedure twice a day is normally sufficient for this purpose.

11. Calculation

11.1 Calculate concentration of an unknown sample in ppm/v as follows:

$$X = (A - B)D/(C - B) \tag{2}$$

where:

A = scale reading for the unknown sample at ambient temperature and pressure,
B = blank scale reading,
C = scale reading obtained from the prepared reference standard at ambient temperature and pressure,
D = fraction of sulfur compound in reference standard in units of ppm/v, and
X = fraction of sulfur compound in the unknown sample in ppm/v.

11.2 Conversion from volume fraction to mass concentration *W* of sulfur compound in milligrams per cubic metre at 25°C and 760 mm Hg (101.3 kPa) is obtained by multiplying ppm by molecular weight and dividing by 24.450 as shown in Practice D 1914. For carbonyl sulfide:

$$W = 2.46X \tag{3}$$

where:

W = mass concentration, mg/m^3;
X = fraction of sulfur compound by volume in the unknown sample, ppm by volume; and
M = molecular weight.

Make appropriate correction for other temperatures and pressures.

12. Precision

12.1 The information in this section is derived from data collected by ASTM Committees D03 and D22, using a similar type analyzer to measure H_2S.

12.1.1 *Repeatability*—At the 95 % confidence level, the difference as a result of test error obtained between two results from the same sample at the same laboratory should be considered suspect if greater than as follows:

Full-Scale Range, ppm/v	Repeatability Piston Cylinder Reference (Manual) Deviation, (ppm/v)	PPM Generator Reference (Automatic) Deviation, ppm/v
1.0	0.014	0.017
0.1	0.002	0.002

12.1.2 *Reproducibility*—At the 95 % confidence level, the difference caused by test error obtained between two results from the same sample from different laboratories should be considered suspect if greater than as follows:

Full-Scale Range, ppm/v	Reproducibility Piston Cylinder Reference (Manual) Deviation, ppm/v	PPM Generator Reference (Automatic) Deviation, ppm/v
1.0	0.050	0.141
0.1	0.006	0.008

12.1.3 For sulfur compounds other than H_2S, the repeatability and reproducibility are as follows:[6]

Full-Scale Reading, ppm/v	Repeatability, ppm/v	Reproducibility, ppm/v
1.0	0.16	0.26
0.1	0.051	0.082

13. Keywords

13.1 gaseous fuels; sulfur

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[6] Refer to Test Method D 4045 for "Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry," *Annual Book of ASTM Standards*, Vol 05.02.

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