



Designation: D 4084 – 05

Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)¹

This standard is issued under the fixed designation D 4084; 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 hydrogen sulfide (H_2S) in gaseous fuels. It is applicable to the measurement of H_2S in natural gas, liquefied petroleum gas (LPG), substitute natural gas, and mixtures of fuel gases. Air does not interfere. The applicable range is 0.1 to 16 parts per million by volume (ppm/v) (approximately 0.1 to 22 mg/m³) and may be extended to 100 % H_2S by manual or automatic volumetric dilution.

1.2 *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 1193 Specification for Reagent Water

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

D 2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)

D 3609 Practice for Calibration Techniques Using Permeation Tubes

D 5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

3. Summary of Test Method

3.1 Measurement of H_2S is accomplished by ratiometrically comparing a reading of an unknown sample with that of a known standard sample using a colorimetric analysis method.

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 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.

Pure H_2S is used as a primary standard and mixed volumetrically with a sulfur free carrier gas that is of the same type as the gas to be analyzed. A gaseous sample at constant flow is humidified and passed over lead-acetate-impregnated paper. H_2S reacts with lead acetate to form a brown stain on the paper. The rate of reaction and resulting rate of color change is proportional to the concentration of H_2S in the sample. An optical system, photodetectors, a means to obtain the first derivative of the photodetector signal, and a means to obtain an output from the differentiation process comprises the analyzer. When there is no change in the color of the tape, and no resulting change in photodetector output, E , the first derivative, dE/dt , is zero. This results in an analyzer that automatically zeroes when there is no H_2S .

4. Significance and Use

4.1 This test method is useful in determining the concentration of hydrogen sulfide in gaseous samples to verify that limits set for H_2S in the product gas are complied with. The automatic operation of this method allows unattended measurement of H_2S concentration.

5. Apparatus

5.1 *Volumetric Measuring Devices*—a graduated 10-L cylinder (see Fig. 1) having a movable piston for volumetrically measuring test gas. Gastight syringes of 0.1- and 0.5-mL volume for volumetrically measuring 100 % H_2S . Gas tight syringes of other volumes can be used. These graduated devices are not needed if the permeation tube method of dynamic mixing is used to prepare the reference sample as this method may be used to generate reference mixture.

5.2 *Sample Pump*—a pump capable of providing more than 8 mL/s (approximately 1 ft³/h) or less than 1 mL/s at 70 kPa (approximately 10.15 psig). Gas-wetted parts are to be either aluminum or polytetrafluoroethylene (PTFE). Stainless steel is less preferable but may be used for the purpose of improving safety if applicable.

5.3 *Colorimetric Rate of Reaction Sensor*—select a device of sufficient sensitivity to measure a minimum rate of change of color density corresponding to 0.1-ppm H_2S by volume in the sample gas. (See Fig. 2.)

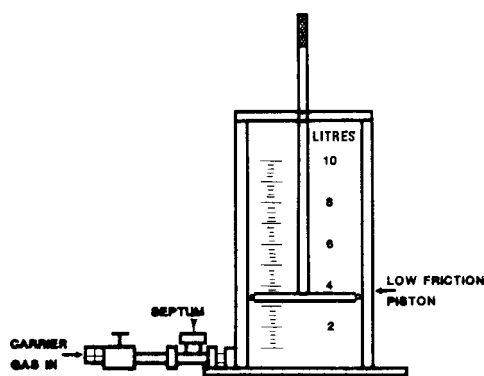


FIG. 1 Calibration Sample Preparation Cylinder with Movable Piston

5.4 Recorder, having an adjustable span of 1- to 10-V full scale with an input impedance of 1 MΩ or higher. A printer or other output means can be used with digital and computerized rate of reaction sensors.

6. Reagents and Materials

6.1 Acetic Acid Solution—Add 50 mL of glacial acid (CH₃COOH) to distilled water to make 1 L of solution (5%). Type II distilled water as specified in Specification D 1193 is satisfactory for the dilution.

6.2 Hydrogen Sulfide, Lecture Bottle Size—99.5% by volume purity or better. An alternative H₂S source is an H₂S mixture obtained using permeation tube procedures. Hydrogen sulfide generated from a solid heated to generate H₂S may be used instead of the lecture bottle of compressed H₂S if desired, as a safety precaution. H₂S contained in permeation tubes or compressed gas cylinders may be flammable and harmful or fatal if ingested or inhaled. Permeation tubes and compressed gas standards should only be handled in well ventilated locations away from sparks and flames. Test Method D 5504 contains additional information on permeation tubes devices and pressurized cylinders. (**Warning**—Hydrogen sulfide is an extremely toxic gas.)

6.3 Dilution Gases—Chemically pure grade or purified gas. Blend or obtain a sulfur-free gas of the same relative density as the sample gas to be analyzed. Blends of gases, of similar composition to the sample gas, are prepared from pure gases by mixing, using a 10-L cylinder with piston. Pipeline gas scrubbed through activated charcoal and sodium hydroxide-asbestos absorbent is satisfactory.

6.4 Lead Acetate Sensing Paper—Prepare in accordance with Test Method D 2420, using appropriate size strips and drying in an H₂S-free environment. Commercially available test paper has been found satisfactory.

6.5 Gas Mixtures — Another alternative H₂S source is a certified H₂S mixture obtained from a gas standard vendor. Such mixtures are in a sulfur free carrier gas that is of the same type, or a close approximation, as the gas to be analyzed. These mixtures can be either a primary standard, which is then diluted to the desired H₂S concentration using a 10-L cylinder with a piston, or a standard in a pressurized cylinder containing the desired H₂S concentration. Because of the potential for degradation, H₂S mixtures obtained from a gas standard vendor must

be properly stored and used only within the stated validity period. In the event of a discrepancy, H₂S mixtures prepared from a 99.5% by volume or better purity H₂S lecture bottle or obtained using permeation tube procedures must be used.

7. Sampling

7.1 Because of the chemical activity and adsorptive properties of H₂S, it is highly desirable to connect the test apparatus directly to the sample source using minimum lengths of aluminum or fluorocarbon sample lines. Do not use brass or copper flow system parts. In the event that direct sampling is not practical, clean aluminum, stainless steel, or fluorocarbon lined sample containers may be used. Sample in containers must be analyzed with as little delay as possible and reported as “proximate analyses from cylinders” with length of residence time noted.

NOTE 1—Each new sample container to be used for a test specimen can be filled with a sample and analyzed over a period of time and the resulting chart recording examined to determine the rate of deterioration of the sample. Repeated filling with a representative sample will tend to stabilize a container. Approximately 10 L (approximately 1/3 ft³) of sample, when at atmospheric pressure, is convenient for analysis and will normally not deteriorate appreciably within 1 h. Slow instrument response to changes in H₂S concentration indicates the need for thorough cleaning of the flow system. (See Appendix X1 for cleaning procedure.) Errors caused by ambient temperature and pressure changes are compensated by comparison to a reference standard prepared at the time of analysis. Preparation of the reference sample is described in Section 11. An approximate sample concentration is indicated by the procedure in Section 10.

8. Preparation of Instrument

8.1 Fill the humidifier bubbler to the full mark with acetic acid solution. The acetic acid minimizes interference from mercaptans. Set the range of the analyzer for the range expected in the sample. Connect the pump and set the flowmeter for a nominal flow of 8 mL/s (approximately 1 ft³/h). Alternative flow settings, such as a nominal 1 mL/s, can be used. Obtain a blank reading by flowing dilution gas through the analyzer. Record the reading of the blank sample as B in 12.1. Do not adjust the instrument zero until verification is obtained, by scrubbing out H₂S, that the room air or the carrier gas does not contain H₂S. Absorption on activated charcoal will remove H₂S.

9. Calibration

9.1 Immediately after having prepared a calibration standard, obtain its response on the analyzer. Practice D 3609 is acceptable as an alternative method for preparation of a reference standard. The analyzer response is recorded as C in 12.1.

10. Sample Measurement Procedure

10.1 Connect the sample to the analyzer and adjust the flow rate to approximately 8 mL/s. This flow must be maintained constant during testing. After the recording is observed to be stable, record the reading A, see 12.1. Prepare a reference standard sample as described in 11.2. Connect the reference sample to the pump and the pump to the analyzer. When a stable reading is obtained, record this value (C in 12.1). The