



## Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)<sup>1</sup>

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 ( $\epsilon$ ) 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/m<sup>3</sup>) 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:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres<sup>3</sup>

D 2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)<sup>4</sup>

D 3609 Practice for Calibration Techniques Using Permeation Tubes<sup>3</sup>

### 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. 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<sup>5</sup> (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 %  $H_2S$ . 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 ft<sup>3</sup>/h) at 70 kPa (approximately 10.15 psig). Gas-wetted parts are to be either aluminum or polytetrafluorethylene (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.<sup>5</sup> (See Fig. 2.)

5.4 *Recorder*, having an adjustable span of 1- to 10-V full scale with an input impedance of 1 M $\Omega$  or higher. A printer or

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>5</sup> A suitable apparatus is available from EnviroTech Controls, Inc., 22001 Northpark Dr., Kingwood, TX 77339-3804.

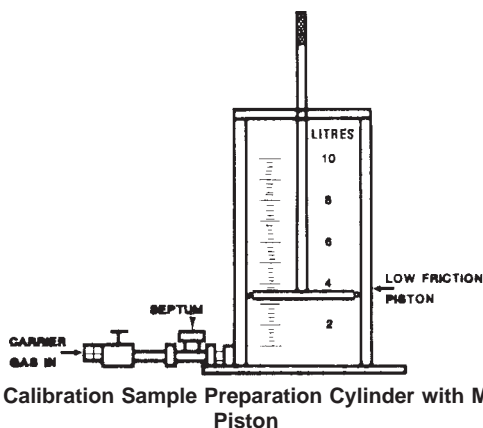


FIG. 1 Calibration Sample Preparation Cylinder with Movable Piston

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 ( $\text{CH}_3\text{COOH}$ ) 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  $\text{H}_2\text{S}$  source is an  $\text{H}_2\text{S}$  mixture obtained using permeation tube procedures. Hydrogen sulfide generated from a solid heated to generate  $\text{H}_2\text{S}$ <sup>5</sup> may be used instead of the lecture bottle of compressed  $\text{H}_2\text{S}$  if desired, as a safety precaution. (**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  $\text{H}_2\text{S}$ -free environment. Commercially available test paper has been found satisfactory.<sup>5</sup>

## 7. Sampling

7.1 Because of the chemical activity and adsorptive properties of  $\text{H}_2\text{S}$ , 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 lead 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  $\frac{1}{3}$  ft<sup>3</sup>) 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  $\text{H}_2\text{S}$  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 ft<sup>3</sup>/h). 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  $\text{H}_2\text{S}$ , that the room air or the carrier gas does not contain  $\text{H}_2\text{S}$ . Absorption on activated charcoal will remove  $\text{H}_2\text{S}$ .

## 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 reference standard described in 11.2 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 of the entire calibration procedure twice a day is normally sufficient for this purpose.

## 11. Preparation of Reference Standard

11.1 Parts per million by volume units, equivalent to micromoles per mole, are used because of the convenience in use of volume measurements rather than weight.

11.2 Prepare a reference standard containing a known volume fraction of  $\text{H}_2\text{S}$ , *D* in ppm by volume units. Inject a known small volume, *V*, of  $\text{H}_2\text{S}$  in millilitre units, of pure  $\text{H}_2\text{S}$  into dilution gas as it fills the 10-L cylinder. A syringe or microlitre valve is used to measure volumetrically small quantities of gas, such as  $\text{H}_2\text{S}$ . The syringe must be filled rapidly five times, from a flowing stream of  $\text{H}_2\text{S}$  gas, to purge the tip volume. The  $\text{H}_2\text{S}$  must be quickly injected into the dilution gas through a septum or equivalent. The time from filling the syringe to injection should be the same as the time from injection to withdrawal of the syringe needle. This compensates for the effect of diffusion

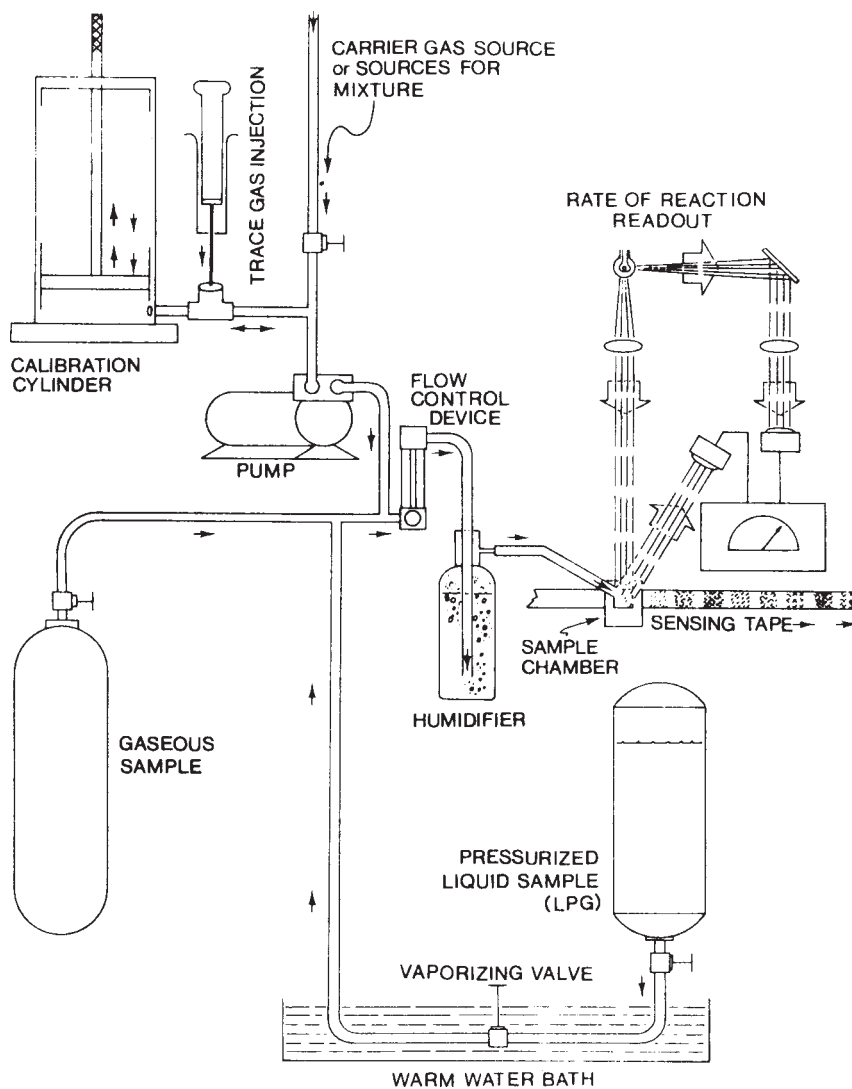


FIG. 2 Flow System for H<sub>2</sub>S Measurement Showing Calibration, LPG, and Gaseous Sample Connections

from the syringe needle. The formula used to calculate the quantity of H<sub>2</sub>S required to prepare a given sample in the 10-L calibration cylinder is as follows:

$$V = 0.01D$$

where:

$V$  = a known small volume of pure H<sub>2</sub>S in mL and  
 $D$  = fraction of H<sub>2</sub>S in reference standard in units of ppm by volume.

*Example*—To prepare a 10-ppm/v sample in sulfur-free carrier gas, inject from a hypodermic syringe 0.1 mL of H<sub>2</sub>S into 10 L of dilution gas as the calibration cylinder is filled. Never pump the syringe at this stage as errors are caused by the added volume in the needle tip.

## 12. Calculation

12.1 Calculate concentration of an unknown sample in ppm by volume as follows:

$$X = (A - B)D / (C - B)$$

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 H<sub>2</sub>S in reference standard in units of ppm by volume, and  
 $X$  = fraction of H<sub>2</sub>S in the unknown sample in ppm by volume. Computerized analyzers may run this calculation internally.

12.2 Conversion from volume fraction to mass concentration of  $W$  of H<sub>2</sub>S 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 H<sub>2</sub>S:

$$W = 1.394 X$$

where:

$W$  = mass concentration,  $\text{mg}/\text{m}^3$ , and

$X$  = fraction of  $\text{H}_2\text{S}$  in the unknown sample, ppm by volume.

Make appropriate correction for other temperatures and pressures.

### 13. Precision

13.1 The following data should be used to judge acceptability of test results:

13.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than indicated in Fig. 3.

13.1.2 *Reproducibility*—Results submitted by different laboratories, using samples of the same concentration, should be considered suspect if they differ by more than indicated in Fig. 3.

### 14. Keywords

14.1 gaseous fuels

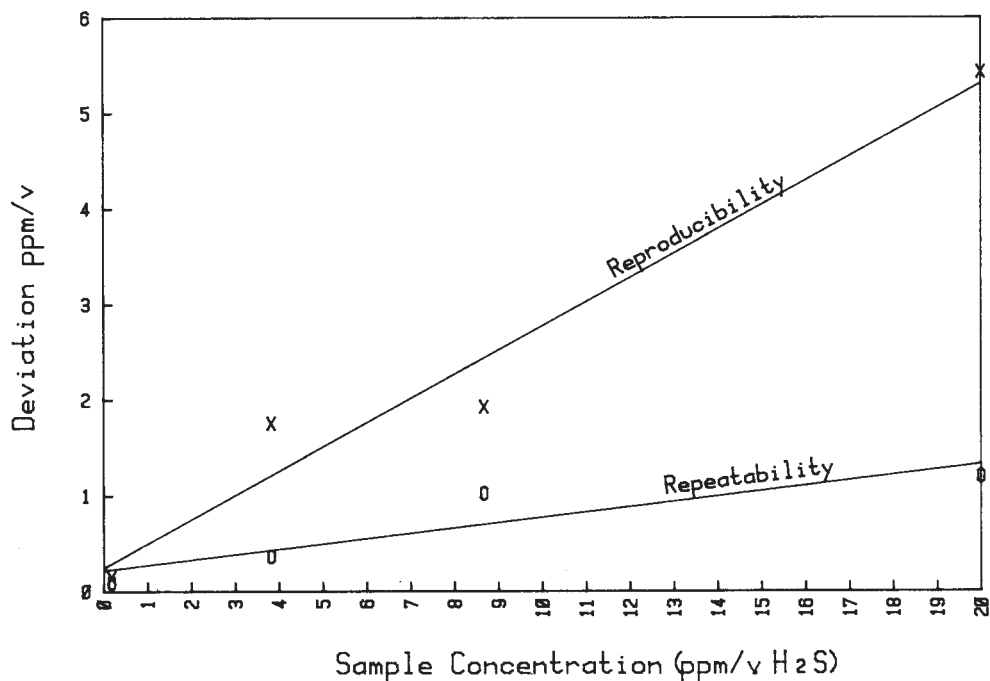


FIG. 3 Graph of Reproducibility and Repeatability

## APPENDIX

(Nonmandatory Information)

### X1. CLEANING PROCEDURE FOR SAMPLE FLOW SYSTEM

X1.1 Use isopropyl alcohol as a solvent and flush the flow system, then thoroughly dry before use.

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