



Designation: D 4323 – 84 (Reapproved 1997)^{ε1}

Standard Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance¹

This standard is issued under the fixed designation D 4323; 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.

^{ε1} NOTE—Editorial corrections were made throughout in November 1997.

1. Scope

1.1 This test method covers the automatic continuous determination of hydrogen sulfide (H_2S) in the atmosphere or in gaseous samples in the range from one part per billion by volume (1 ppb/v) to 3000 ppb/v. Information obtained may be used for air-pollution studies and to monitor for emission sources.

1.2 The range may be extended by appropriate dilution techniques or by equipment modification.

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.* (See 6.2, 6.3, and 6.4 for specific safety precautionary statements.)

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)³

D 2725 Test Method for Hydrogen Sulfide in Natural Gas (Methylene Blue Method)⁴

3. Summary of Test Method

3.1 Hydrogen sulfide is determined by use of the reaction of H_2S with lead acetate-impregnated paper tape. Detection of the rate of change of reflectance provides measurement in ppb/v ranges with an approximate 3-min analysis cycle time. (See Fig. 1.) Sample gas is passed through a flowmeter and a humidifier; then across lead acetate-treated paper tape. A constant humidity is required for a constant reaction rate of H_2S with lead acetate. The resultant change in reflectance is detected by a photocell. The rate of change of reflectance is

proportional to H_2S concentration.

4. Significance and Use

4.1 Hydrogen sulfide is an odorous substance which is offensive even at low concentrations in the atmosphere and toxic at higher levels. It may be a product of biological processes in the absence of oxygen, as may occur in municipal garbage landfills. It is emitted from geothermal sources, occurs in oil and gas, and may be emitted from industrial processes. Measurement is required for air pollution studies, for pollution control, and for plume characterization. Equipment described is suitable for fixed site or for mobile monitoring.

5. Apparatus^{5,6}

5.1 *Rate-of-Reaction H_2S Analyzer*—Sample is passed across a lead acetate-treated surface causing a reflectance change. Hydrogen sulfide is determined by measuring the rate of change of reflectance resulting from darkening when lead sulfide is formed. Equipment consists of a small flowmeter, humidifier, sensing surface exposure chamber, optical system, and electronic system. (See Fig. 2.) A complete analysis in about 1 min results from use of the rate of change of color rather than magnitude of cumulative color development. The electronic system provides an output that is proportional to the derivative of the photocell signal, caused by reflectance change, and this rate measurement is a measure of H_2S concentration. A new section of sensing material is drawn into the sensing chamber at approximately 3-min intervals to provide a new independent measurement.

5.2 *Recorder*—A method of recording the electronic signal is required. This may take any form that is suitable for the record required. A typical system recorder will accept a range from 0 to 10 V from an output impedance of 1000 Ω (maximum). An attenuator or amplifier (usually incorporated

¹ This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres.

Current edition approved March 1, 1984. Published May 1984.

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

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.05.

⁵ The sole source of supply of the apparatus described in 5.1, 5.3, and 6.3 known to the committee at this time is Houston Atlas, Inc., 22001 N. Park Dr., Houston, TX 77339-3809. If you are aware of alternate suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

⁶ Kimbell, C. L. and Drudhel, H. V., "Trace Sulphur Determination in Petroleum Fractions," *Analytical Chemistry*, Vol 50, 1978, p 26.

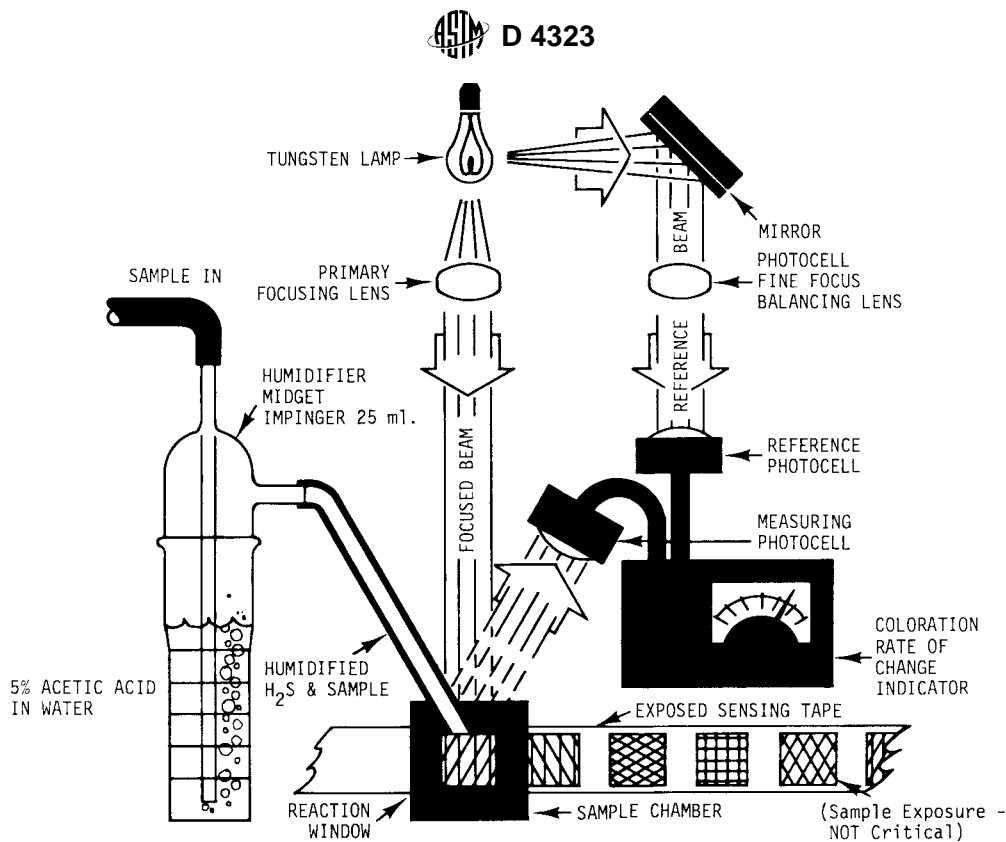


FIG. 1 Rate of Change of Reflectance Type H₂S Readout System

into the recorder) may be used for other sensor signal levels. A chart speed of 1 cm/min is suitable for short term analyses. A chart speed of 1 to 5 cm/h is preferable for long-term sampling. Electronic processing, such as integrators, may be added when concentration averages over an interval of time are desirable.

5.3 Reference Gas Preparation:

5.3.1 *Mixing*—A calibrated 10-L cylinder having a movable piston for use in making volumetric mixtures of gases in the ppb/v range may be used. Materials of construction must be inert to H₂S and not lead to a deterioration of prepared samples. A cylinder of acrylic lubricated with silicone grease and using a silicone O-ring has been found to be suitable. Concentration remains stable to within 1 % over a 1-h period.

5.3.2 *Hypodermic Syringe*—Gas-tight syringes of 10 and 50- μ l capacity. A side port is convenient for purging. Avoid Luer tip syringes made of plated brass as H₂S reacts with brass. Other convenient small volume measurement devices such as a microlitre valve may be used.

5.3.3 *Pump*—A sample pump capable of providing 500 mL/min flow at approximately 35 kPa (5 psi). The pump wetted parts must be inert to H₂S and not lead to a deterioration of the sample.

6. Reagent and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise noted, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such

specifications are available.⁷

6.2 *Acetic Acid Solution (50 mL/L)*—Dilute 50 mL of glacial acetic acid (CH₃COOH), reagent grade, to make 1 L of solution using Type III water prepared as described in Specification D 1193. **Caution:** Concentrated acetic acid fumes are an irritant and can cause damage to skin and mucus membrane. Handle carefully to avoid injury.

6.3 *Sensing Tape*—Prepare sensing tape as described in Test Method D 2420 or use commercial sensing tape⁵ that has been prepared in a similar manner. Keep sensing tape in a sealed container to prevent exposure to ambient H₂S. **Caution:** Lead acetate is a cumulative poison; wash hands after handling and do not breathe any dust containing lead acetate.

6.4 *Hydrogen Sulfide (99.5 %)*—Commercially available H₂S has been found not to be sufficiently pure. Purity certification is recommended or a commercially available H₂S generator may be used. **Caution:** Hydrogen sulfide is toxic at levels above 10 000 ppb/v. Use only under an appropriate fume hood. Use protective glasses if liquid H₂S in cylinders is handled. Sense of smell may be lost on exposure to H₂S and is unreliable as a warning of danger. (See Appendix X1.1 and X1.2 on Interferences.)

6.5 *Dilution Gas*—A gas similar to the gas to be sampled,

⁷ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

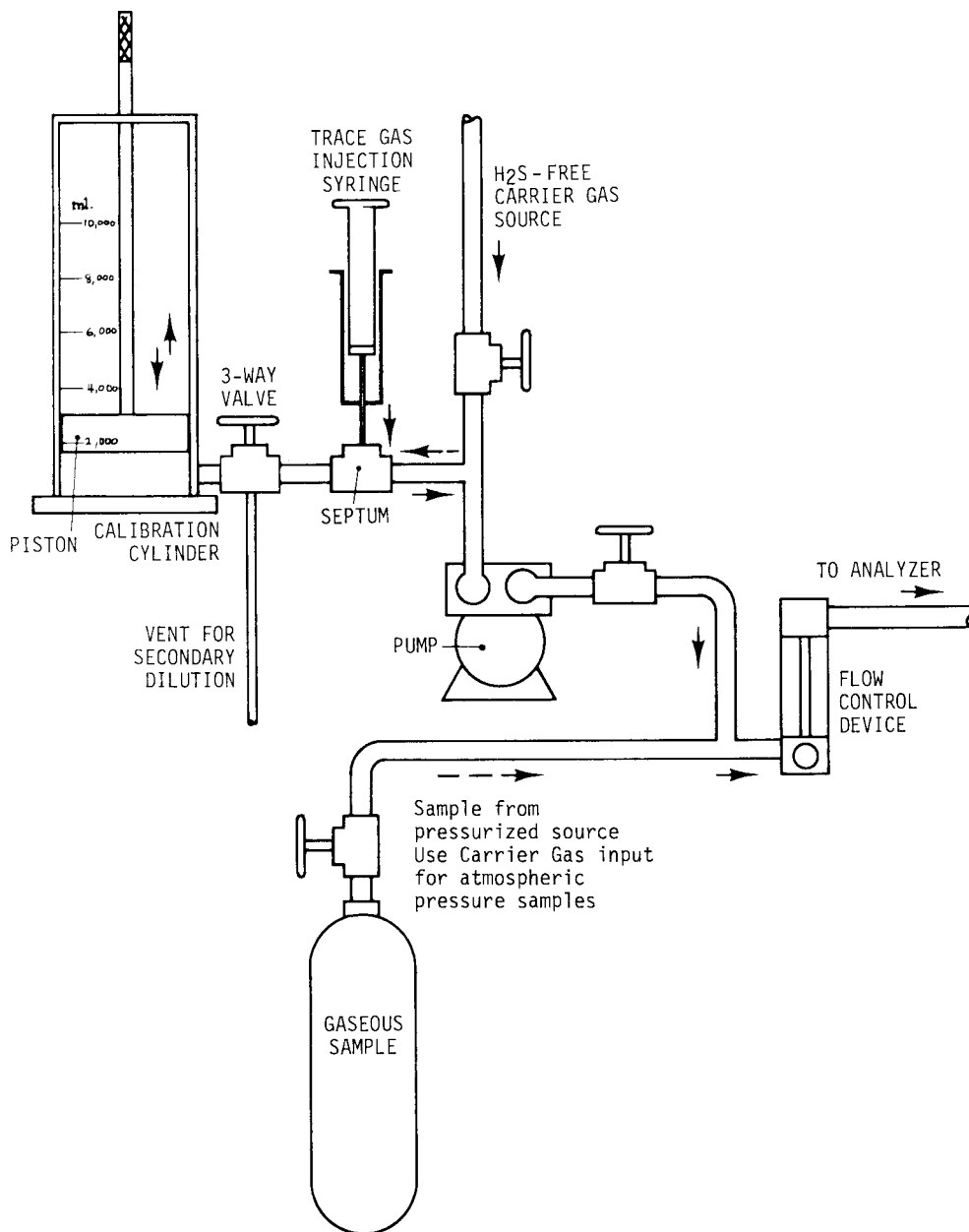


FIG. 2 Flow System for Gas Sample and for Calibration Reference

H₂S-free. Mixture can be prepared using the 10-L cylinder described in 5.3.1.

TABLE 1 Repeatability

Full Scale Range ppm/v	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

7. Sampling

7.1 Sample lines and containers must not absorb sample H₂S. Suitable materials are fluorocarbon resins, aluminum,

TABLE 2 Reproducibility

Full Scale Range ppm/v	Piston Cylinder Reference (Manual) Deviation, ppm/v	PPM Generator Reference (Automatic) Deviation, ppm/v
1.0	0.050	0.141
0	0.006	0.008

borosilicate glass, and suitable inactive acrylic. Stainless steel (Type 316) may be used when required by regulations but is not preferred.

7.2 Avoid materials containing copper or having petroleum lubricant coatings.

8. Calibration and Standardization

8.1 *Reference Standard*—Reference standards are prepared by volumetric measurement at the time the reference material

is to be used. This minimizes deterioration of the sample. The permeation tube method or compressed gas cylinders certified as to concentration by the manufacturer may be used as a reference standard. Small volumes of pure H₂S are measured using a gas-tight syringe. Dilution gas is measured using a 10-L graduated cylinder having a movable piston. As a syringe needle has appreciable volume, H₂S can escape by diffusion from the needle tip. Therefore, a smooth fast work routine must be established to prevent delays and loss of sample.

8.2 *Calibration*—To prepare 1000 ppb/v sample add 10 μL of H₂S to make a 10-L sample carrier mixture using the 10-L acrylic cylinder described in 5.3.1. To calculate microlitres of H₂S required in a 10-L mixture, use the following equation:

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

where: p = microlitres of pollutant used. Prepare a reference standard of a concentration slightly higher than may be anticipated in the sample. Purge the 10-L cylinder with H₂S-free carrier gas. Purge the microlitre syringe with H₂S. Gradually fill the 10-L cylinder with carrier gas as the syringe is adjusted for the proper quantity of H₂S. Insert the syringe quickly into the cylinder septum and inject the aliquot of H₂S into the flowing carrier gas. Turn off the carrier gas when 10 L are obtained. Withdraw the syringe quickly after injection to prevent residual H₂S in the needle tip from diffusing into the flowing gas. The reference standard is now pumped into the analyzer to calibrate it. For samples less than 1000 ppb/v, secondary volumetric dilution will be required. For 500 ppb/v samples, exhaust a cylinder filled with 10 L of 1000 ppb/v gas to 5 L, then fill again to 10 L with diluent gas.

9. Procedure

9.1 Turn the analyzer power on, install sensing tape, and add 5 % acetic acid by volume in water to the bubbler (3 % by weight barium acetate solution may be used to remove SO₂). Turn on H₂S-free carrier gas having a composition as near as possible to the sample composition by pumping or from a pressurized source at a constant rate of 300 mL/min flow \pm 3 %. This flow must be held constant during all testing. After 30 min, adjust the analyzer zero. Record this as the recorder blank reading, b , in 9.4.

9.2 Calibrate the analyzer with a freshly prepared reference sample of the concentration expected in the unknown, as noted in 8.2. Adjust flow rate to 300 mL/min \pm 3 % and record the analyzer reading, r , in 9.4.

9.3 Connect the sample to the analyzer to adjust flow rate at 300 mL/min \pm 3 %. Record the analyzer reading, u , in 9.4.

9.4 Calculate the concentration of the unknown sample as follows:

$$x = c(u - b)/(r - b) \quad (2)$$

where:

x = concentration of sample under test, ppb/v,

b = blank analyzer reading, percent of scale,

u = unknown sample analyzer reading, as received, percent of scale,

r = reference standard analyzer reading, percent of scale, and

c = concentration of reference standard, ppb/v.

10. Report

10.1 Report the results in ppb/v or apply the appropriate conversion if other units are required. The procedure is self-compensating for temperature and pressure. If data are desired in weight units of milligrams per cubic metre (mg/m³), apply the following equation:

$$\text{ppb/v} \times 1.395 \times 10^{-3} = \text{mg/m}^3 \quad (3)$$

NOTE 1—This equation is based on the ideal gas density computed by dividing molecular weights by molar volume at 25°C and 760 mm Hg (101.3 kPa). Weight is weight of H₂S.

11. Precision and Bias

11.1 The information in this section is derived from data collected by ASTM Committees D-2 and D-22 using a similar type analyzer.

11.1.1 *Repeatability*—At the 95 % confidence level the difference due to test error obtained between two results from the same sample at the same laboratory should be considered suspect if greater than shown in Table 1.

11.1.2 *Reproducibility*—At the 95 % confidence level the difference due to test error obtained between two results from the same sample from different laboratories should be considered suspect if greater than shown in Table 2.

11.1.3 The precision studies were conducted by six laboratories. There were twelve samples associated with the piston-cylinder and nine samples associated with the ppm generator methods of sample preparations.

11.1.4 *Hydrogen Sulfide Reference*—Reference samples were prepared from a compressed gas cylinder containing a nominal 99 % nitrogen, and 1 % H₂S by volume. At the end of the testing the concentration was measured by the Methylene Blue Method at 0.92 % H₂S by volume. Bias of prepared samples depend on reagent purity and care in sample preparation. Test Method D 2725 (Methylene Blue Method) may be used to check prepared samples above 16 ppm (23 mg/cm³).

12. Keywords

12.1 atmospheres; hydrogen sulfide; tape sampler



APPENDIX

(Nonmandatory Information)

X1. INTERFERENCES

X1.1 In applications of this method, high levels of some compounds can result in instrument response. Methyl mercaptan, when 1000 times the H₂S concentration can affect response equal to H₂S response. Arsine, phosphine, and free sulfur have been reported as causing response. The operator should take required precautions if the above materials are expected to be present in the sample.

X1.2 In the event SO₂ may be present, a solution of barium acetate may be substituted for the acetic acid solution to scrub

out the SO₂ component without removing H₂S. Use 3 % by weight barium acetate in deionized water.⁸ Hydrogen sulfide and SO₂ react spontaneously and prepared samples cannot be stored more than a few minutes.

⁸ Smith, A. F., Jenkins, D. G., and Cunningworth, P. E., *Journal of Applied Chemistry*, Vol 11, 1961, pp. 317.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).