



Designation: ~~D4323~~—15 D4323 – 21

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

This standard is issued under the fixed designation D4323; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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, studies, fence-line monitoring, and other source emission monitoring.

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

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* (See Section 9 for specific safety precautionary statements.)

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- D1193 Specification for Reagent Water
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)
- D2725 Test Method for Hydrogen Sulfide in Natural Gas (Methylene Blue Method) (Withdrawn 1996)³
- D3609 Practice for Calibration Techniques Using Permeation Tubes
- D4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)
- D4323 Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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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.

³ The last approved version of this historical standard is referenced on www.astm.org.

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356.

4. Summary of Test Method

4.1 Hydrogen sulfide is determined by use of the reaction of H_2S with lead acetate-impregnated paper tape and by comparing a reading of an unknown sample with that of a known standard using a differential colorimetric detection. Detection of the rate of change of reflectance provides measurement in ppb/v ranges with an analysis time appropriate for the application. (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. H_2S reacts with lead acetate to form a brown stain on the paper. The resultant change in reflectance is detected by a photon detection system. The rate of change of reflectance is proportional to H_2S concentration. The analyzer is composed of an optical system, a photon detection system, a signal differentiation system of first order, and a signal output system.

5. Significance and Use

5.1 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, environmental justice based monitoring, and for plume characterization. This test method is intended for hydrogen sulfide content up to 3000 ppbv. Measurement of hydrogen sulfide above this concentration in gaseous fuels, carbon dioxide or other gaseous matrices is described in Test Method D4084. Equipment described is suitable for fixed site or for mobile monitoring.

6. Interferences

6.1 In applications of this method, high levels of some interfering compounds can result in instrument response. Methyl mercaptan, when 1000 times the H_2S concentration can affect response equal to H_2S result in a significant H_2S response. Arsine,

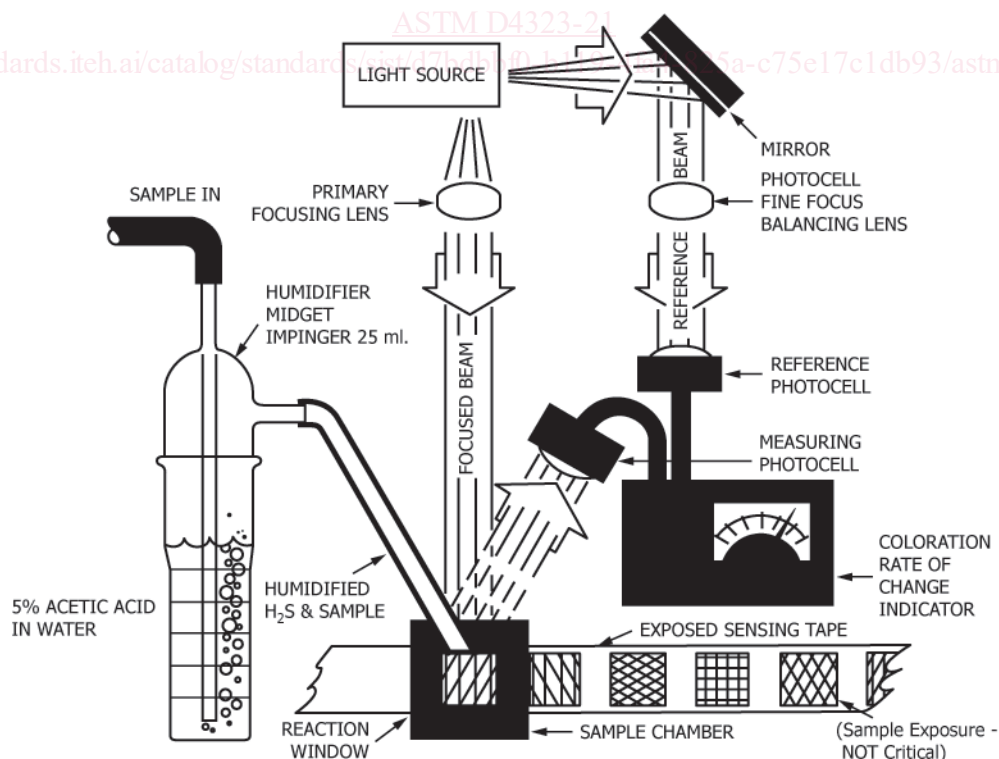


FIG. 1 Typical Rate of Change of Reflectance Type H_2S System

phosphine, and free sulfur have been reported as causing response. The operator response as well. The user should take required precautions action if the above materials are expected to be present in the sample.

6.2 In the event SO₂ ~~may be is~~ 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.⁴ Hydrogen sulfide and SO₂ react spontaneously and prepared samples cannot be stored more than a few ~~minutes~~minutes.

7. Apparatus⁵

7.1 *Rate-of-Reaction H₂S 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 components~~ consist of a flowmeter, humidifier, sensing surface exposure chamber, optical system, and electronic system. (See Fig. 1.) ~~A complete analysis results from use of~~ Results are based upon 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 a reflectance change, and this rate measurement is a measure of H₂S concentration. A new ~~section~~portion of sensing material is drawn into the sensing chamber to provide a new independent measurement.

7.2 *Recorder*—A method of recording the electronic signal is required. A printer or other output means, such as a microprocessor, data logger, or data collection system (DCS), can be used.

7.3 Reference Gas Preparation:

7.3.1 *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~~ Construction materials 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~~suitable in many applications. Concentration remains stable to within 1 % over a 1-h period. Alternatively, a reference mixture can be prepared by dilution using a commercially available diluter with passivated components and diluent gas. These devices are not needed when the permeation tube method of dynamic mixing is used to prepare the reference sample since this method will generate a reference mixture.

7.3.2 *Hypodermic Syringe*—Gas-tight syringes of 10 and ~~50-μL~~50-μL 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.

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

8. Reagent and Materials

8.1 *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.⁶

8.2 *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 **D1193**.

8.3 *Sensing Tape*—Prepare sensing tape as described in Test Method **D2420** or use commercial sensing tape⁶ that has been prepared in a similar manner. Keep sensing tape in a sealed container to prevent exposure to ambient H₂S.

8.4 *Hydrogen Sulfide (99.5 %)*—Commercially available H₂S has been found to be insufficiently pure. Purity certification is

⁴ Smith, A. F., Jenkins, D. G., and Cunningworth, P. E., *Journal of Applied Chemistry*, Vol 11, 1961, pp. 317.

⁵ Kimbell, C. L. and Drushel, H. V., "Trace Sulphur Determination in Petroleum Fractions," *Analytical Chemistry*, Vol 50, 1978, p 26.

⁶ *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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~~Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

recommended or use of H₂S generators using permeation devices may be used. Alternatively, a certified H₂S mixture at concentrations as low as 1000 ppbv can be obtained from a gas standard vendor in an air or nitrogen matrix. 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 piston~~ or commercially available dilution apparatus, 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 certification period.

8.4.1 *Compressed Gas Standards*—The protocol for compressed gas standards contained in **Appendix X3** can be used to ensure uniformity in compressed gas standard manufacture and provide for traceability to a NIST or other standard reference materials.

8.4.1.1 Compressed gas standard regulators must be appropriate for the delivery of sulfur gases and attached fittings must be passivated or inert to sulfur gases.

8.4.2 *Permeation Devices*—Hydrogen ~~Sulfide~~sulfide standards can be prepared using a permeation tube gravimetrically calibrated and certified at a convenient operating temperature. At constant temperature, calibration gases covering a wide range of concentration can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the ~~analyzer~~analyzer.

8.4.2.1 *Permeation System Temperature Control*—Permeation devices are maintained at the calibration temperature within ~~0.1°C~~0.1 °C.

8.4.2.2 *Permeation System Flow Control*—The permeation flow system measures diluent gas flow over the permeation tubes within ~~±2 percent~~±2 %.

8.4.2.3 Permeation tubes are inspected and weighed to the nearest 0.01 mg ~~on at least a monthly basis~~ using a balance calibrated against NIST traceable “S” class weights or the equivalent. Analyte concentration is calculated by weight loss rate and dilution gas flow rate as in accordance with Practice **D3609**. These devices are discarded when the liquid contents are reduced to less than ten percent of the initial volume or when the permeation surface is unusually discolored or otherwise compromised. Used permeation tubes should be disposed of in accordance with local, state, or federal environmental regulations, or combination thereof.

8.5 *Dilution Gas*—A chemically pure grade or purified gas similar to the gas to be sampled, H₂S-free. Mixture can be prepared using the 10-L cylinder or commercially available diluter as described in 7.3.1.

<https://standards.iteh.ai/catalog/standards/sist/d7bdbbf0-b119-4fa4-825a-c75e17c1db93/astm-d4323-21>

8.6 *Lead Acetate Sensing Paper*—Prepare in accordance with Test Method **D2420**, using appropriate size strips and drying in an H₂S-free environment. Commercially available test paper has been found satisfactory. Used Lead Acetate Sensing Paper should be disposed of in accordance with local, state, or federal environmental regulations, or combination thereof.

9. Hazards

9.1 Hydrogen ~~Sulfide~~sulfide contained in lecture bottles, permeation tubes or compressed gas cylinders may be flammable and harmful or fatal if ingested or inhaled. 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 **6.1** and **6.2** on Interferences.)

9.2 Lecture bottles, permeation tubes and compressed gas standards should only be handled in well ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing air, nitrogen, or hydrocarbons can result in explosion. Rapid release of nitrogen or hydrocarbon gasses can result in asphyxiation.

9.3 Compressed air supports combustion.

9.4 Concentrated acetic acid fumes are an irritant and can cause damage to skin and mucus membrane. Handle carefully to avoid injury.

9.5 Lead acetate is a cumulate poison; wash hands after handling and do not breathe ~~any~~ dust containing lead acetate.

10. Sampling

10.1 Sample lines and containers must not absorb sample H₂S. Suitable materials are fluorocarbon resins, aluminum, borosilicate glass, silica lined metal tubing, and suitable inactive acrylic. Stainless steel (Type 316) may be used when required by regulations but is not preferred.

10.2 Avoid materials containing copper, brass, or having petroleum lubricant coatings.

11. Calibration and Standardization

11.1 *Reference Standard*—Reference standards are prepared by volumetric measurement or reference standard dilution to the desired concentration 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.

11.2 *Calibration*—*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 7.3.1. To calculate microlitres of H₂S required in a 10-L mixture, use the following equation:

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

11.2.1 *Volumetric Measurement*—For example, to prepare 1000 ppb/v sample by volumetric measurement, add 10 μL of H₂S to make a 10-L sample carrier mixture using the 10-L acrylic cylinder described in 7.3.1. To calculate microlitre of H₂S required in a 10-L mixture, use the following equation:

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

where: p = microlitre 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.

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11.2.2 *Permeation Devices*—Hydrogen sulfide standards can be prepared using a permeation tube gravimetrically calibrated and certified at a convenient operating temperature. At constant temperature, calibration gases covering a wide range of concentration can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the analyzer. 8.4.2 presents parameters critical for generating standards of known concentration with accuracy suitable for use under this standard. See Practice D3609 for details on performing calibrations using permeation devices.

11.2.3 *Dilution of Primary H₂S Cylinder Gas Standard*—As necessary, a H₂S calibration standard is prepared by dilution to the desired concentration of a NIST traceable gas standard with diluent using a commercially available gas calibration dilution system (GCDS) which is within certification.

12. Procedure

12.1 Turn the analyzer power on, install sensing tape, and add 50 mL/L 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