



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 reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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

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[D2725 Test Method for Hydrogen Sulfide in Natural Gas \(Methylene Blue Method\)](#) (Withdrawn 1996)³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](#)

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.

[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 System in Petroleum Products and Lubricants Testing Laboratories](#)

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, and for plume characterization. This test method is intended for hydrogen sulfide content up to 3000 ppbv.

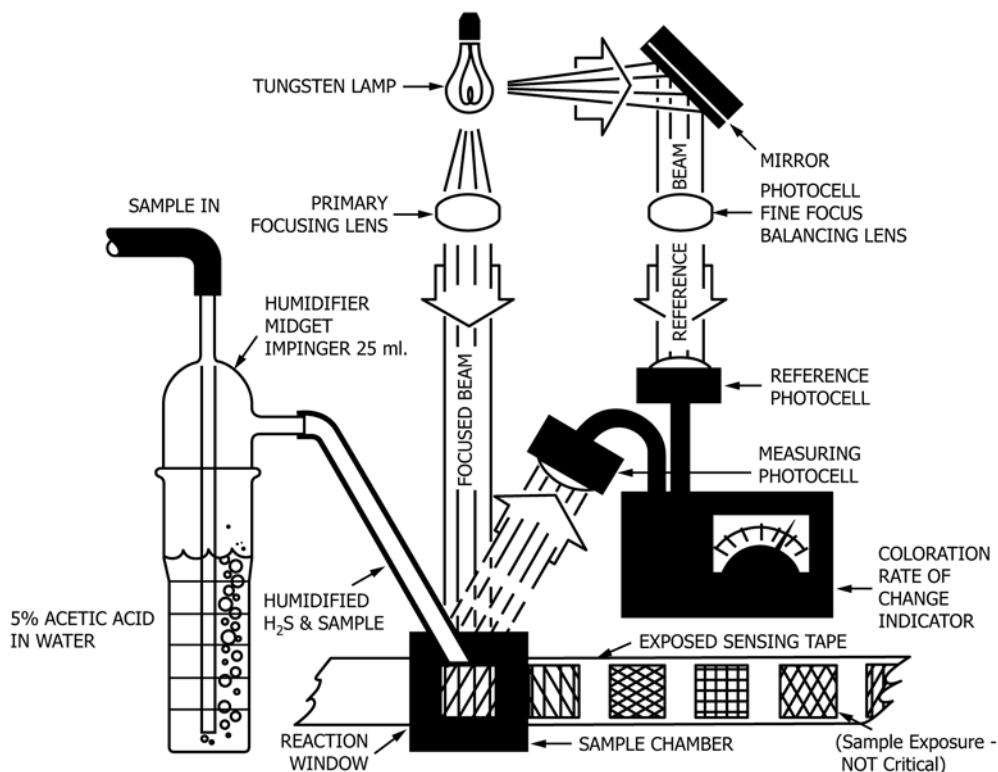


FIG. 1 Typical Rate of Change of Reflectance Type H₂S System

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 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.

6.2 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.⁴ Hydrogen sulfide and SO₂ react spontaneously and prepared samples cannot be stored more than a few 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 of a flowmeter,

humidifier, sensing surface exposure chamber, optical system, and electronic system. (See Fig. 1.) A complete analysis 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 a reflectance change, and this rate measurement is a measure of H₂S concentration. A new section 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 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. 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- 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.

⁴ Smith, A. F., Jenkins, D. G., and Cunninghamworth, 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.