



Designation: D 4323 – 84 (Reapproved 1997)<sup>ε1</sup>

## Standard Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> 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 Water<sup>2</sup>

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

D 2725 Test Method for Hydrogen Sulfide in Natural Gas (Methylene Blue Method)<sup>4</sup>

### 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<sup>5,6</sup>

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  $\Omega$  (maximum). An attenuator or amplifier (usually incorporated

<sup>1</sup> 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.

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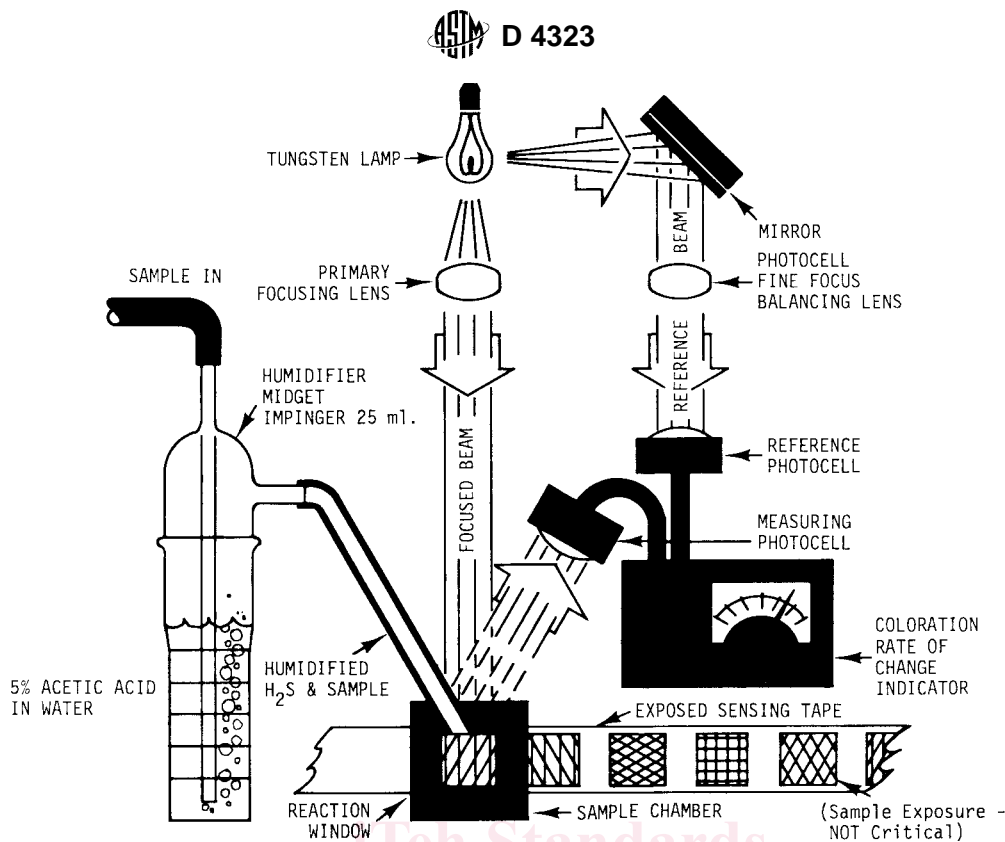
<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.05.

<sup>5</sup> 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 committee<sup>1</sup>, which you may attend.

<sup>6</sup> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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- $\mu$ l capacity. A side port is convenient for purging. Avoid Luer tip syringes made of plated brass as H<sub>2</sub>S 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 H<sub>2</sub>S 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.<sup>7</sup>

**6.2 Acetic Acid Solution (50 mL/L)**—Dilute 50 mL of glacial acetic acid (CH<sub>3</sub>COOH), 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 tape<sup>5</sup> that has been prepared in a similar manner. Keep sensing tape in a sealed container to prevent exposure to ambient H<sub>2</sub>S. **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 H<sub>2</sub>S has been found not to be sufficiently pure. Purity certification is recommended or a commercially available H<sub>2</sub>S 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 H<sub>2</sub>S in cylinders is handled. Sense of smell may be lost on exposure to H<sub>2</sub>S 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,

<sup>7</sup> *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.