Designation: D4323 – 15

Standard Test Method for
Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance[1]

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D2725 Test Method for Hydrogen Sulfide in Natural Gas (Methylene Blue Method) (Withdrawn 1996)[3]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

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.

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[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.

Current edition approved April 1, 2015. Published April 2015. Originally approved in 1984. Last previous edition approved in 2009 as D4323 – 84 (2009). DOI: 10.1520/D4323-15.

[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.

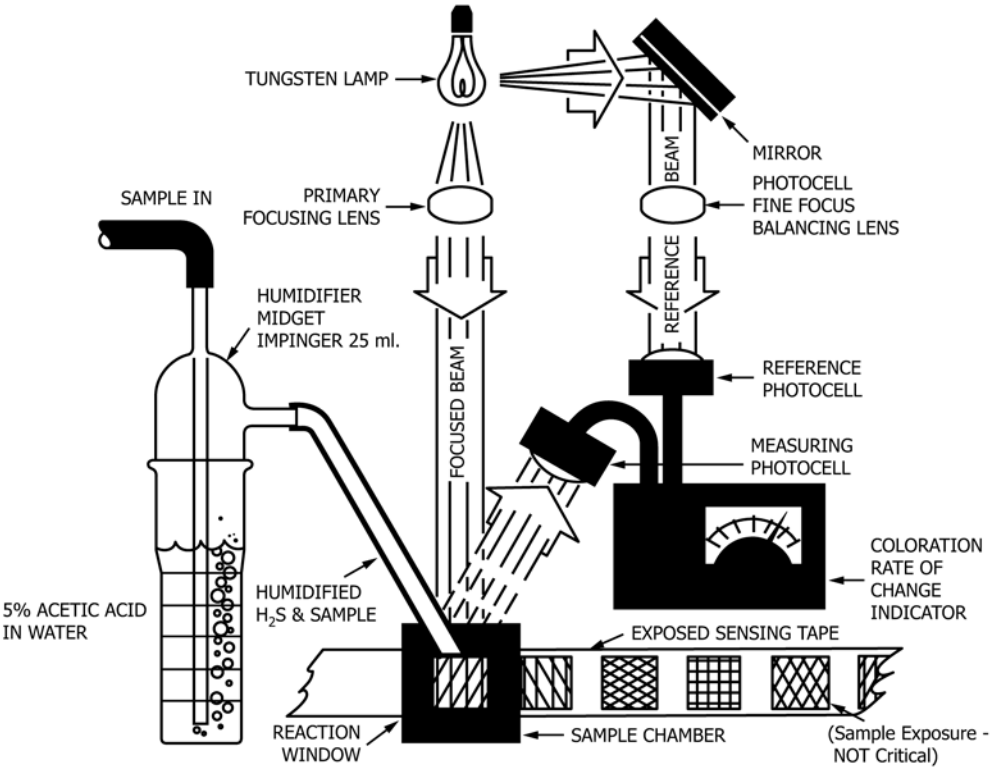

FIG. 1 Typical Rate of Change of Reflectance Type H_2S System

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 H_2S concentration can affect response equal to H_2S 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 SO_2 may be present, a solution of barium acetate may be substituted for the acetic acid solution to scrub out the SO_2 component without removing H_2S. Use 3 % by weight barium acetate in deionized water.[4] Hydrogen sulfide and SO_2 react spontaneously and prepared samples cannot be stored more than a few minutes

7. Apparatus[5]

7.1 *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 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 H_2S 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 H_2S 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-µl capacity. A side port is convenient for purging. Avoid Luer tip syringes made of plated brass as H_2S reacts with brass. Other convenient small volume measurement devices such as a microlitre valve may be used.

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[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.

7.3.3 *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_2S and not lead to a deterioration of the sample.

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 (CH_3COOH), 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 tape[6] that has been prepared in a similar manner. Keep sensing tape in a sealed container to prevent exposure to ambient H_2S.

8.4 *Hydrogen Sulfide* (99.5 %)—Commercially available H_2S has been found to be insufficiently pure. Purity certification is recommended or use of H_2S generators using permeation devices may be used. Alternatively, a certified H_2S 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 H_2S concentration using a 10-L cylinder with a piston, or a standard in a pressurized cylinder containing the desired H_2S concentration. Because of the potential for degradation, H_2S 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 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

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

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 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, H_2S-free. Mixture can be prepared using the 10-L cylinder described in 7.3.1.

8.6 *Lead Acetate Sensing Paper*—Prepare in accordance with Test Method D2420, using appropriate size strips and drying in an H_2S-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 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 H_2S in cylinders is handled. Sense of smell may be lost on exposure to H_2S 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 H_2S. 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.

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[6] *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.

11. Calibration and Standardization

11.1 *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 H_2S 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, H_2S 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*—To prepare 1000 ppb/v sample add 10µ L of H_2S to make a 10-L sample carrier mixture using the 10-L acrylic cylinder described in 7.3.1. To calculate microlitres of H_2S 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 H_2S-free carrier gas. Purge the microlitre syringe with H_2S. Gradually fill the 10-L cylinder with carrier gas as the syringe is adjusted for the proper quantity of H_2S. Insert the syringe quickly into the cylinder septum and inject the aliquot of H_2S into the flowing carrier gas. Turn off the carrier gas when 10 L are obtained. Withdraw the syringe quickly after injection to prevent residual H_2S 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.

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 SO_2). Turn on H_2S-free carrier gas having a composition as near as possible to the sample matrix composition by pumping or from a pressurized source at a constant rate of 300 mL/min flow ±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 12.4.

12.2 Calibrate the analyzer with a freshly prepared reference sample of the concentration expected in samples, as noted in 11.2. Adjust the flow rate to 300 mL/min ± 3 % and record the analyzer reading, r, in 12.4.

12.3 Connect the sample to the analyzer to adjust flow rate at 300 mL/min ± 3 %. Record the analyzer reading, u, in 12.4.

12.4 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.

13. Quality Control (QC)

13.1 The following quality assurance (QA) procedures are recommended and may be required in certain applications. Additional quality control information is contained in Appendix X2.

13.2 *Blank Analysis*—Confirmation of a lack of significant carry-over or contamination is recommended. This is accomplished through analysis of a blank in a nitrogen, air, or other gas matrix that is representative of the sample being analyzed. The significance of observed carryover is defined by the users need and should be determined before performance of this method.

13.3 *Sample Analysis*—The analysis of each sample in duplicate is strongly suggested and may be required for certain applications. Duplicate sample analysis will verify adequate system passivation/conditioning and performance.

13.4 *Control Sample or Calibration Standard Reanalysis*—A control is analyzed or a standard is reanalyzed after samples as part of a QA/QC program. The hydrogen sulfide concentration should be within 2 % of the theoretical amounts based on the original standards. Unacceptable results are indicative of a system malfunction and will require the user to perform corrective action to restore the system to nominal performance.

13.5 *Linearity Verification*—Quantitative dilution of a known hydrogen sulfide in gas calibration standard and subsequent analysis provides information regarding the linearity of the analyzer. Linearity data that falls outside of the manufacturer's specifications is indicative of a system malfunction and will require the user to perform corrective action to restore the system to nominal performance.

13.6 *Drift Check*—Extended steady state response data for a fixed stable hydrogen sulfide in gas calibration standard can provide information on the stability of the analyzer. Upward or downward drift as well as variations outside of the manufacturer's published repeatability specification are indicative of a system malfunction and will require the user to perform corrective action to restore the system to nominal performance.

14. Report

14.1 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/m^3), 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 H_2S.

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

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

15. Precision and Bias

15.1 The information in this section is derived from data collected by ASTM Committees D02 and D22 using a similar type analyzer.

15.1.1 *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.

15.1.2 *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.

15.1.3 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.

15.1.4 *Hydrogen Sulfide Reference*—Reference samples were prepared from a compressed gas cylinder containing a nominal 99 % nitrogen, and 1 % H_2S by volume. At the end of the testing the concentration was measured by the Methylene Blue Method at 0.92 % H_2S by volume. Bias of prepared samples depend on reagent purity and care in sample preparation. Test Method D2725 (Methylene Blue Method) may be used to check prepared samples above 16 ppm [23 mg/cm^3].

16. Keywords

16.1 atmospheres; hydrogen sulfide; tape sampler

APPENDIXES

(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.

X2. QUALITY CONTROL (QC)

X2.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X2.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practices D6299 and D6792).

X2.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practices D6299 and D6792). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X2.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the users' needs, the demonstrated stability of the testing process, and any other regulatory or process control requirements. Generally, a QC sample is analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X2.5 It is recommended that, if possible, the types of QC sample that are regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practices D6299 and D6792 for further guidance on QC and control charting techniques.

X3. PROTOCOL FOR COMPRESSED GAS CALIBRATION STANDARDS

X3.1 This protocol was developed to assist compressed gas sulfur standard users. It can provide calibration gas traceability to a NIST, NMi, or similar standard reference material. This protocol requires the determination of hydrogen sulfide using a NIST or NMi hydrogen sulfide SRM or a NTRM as the primary reference. This procedure will insure uniformity in measurement of the hydrogen sulfide content. This protocol should be submitted to vendors when calibration gas is ordered.

X3.1.1 A standard is analyzed according to Test Method D4323. A minimum of three consecutive data points are collected with the necessary precision to support the reported analytical accuracy. The necessary precision is achieved with a percent relative standard deviation (% RSD) calculated from a minimum of three consecutive data points, less than or equal to two percent.

X3.1.2 A hydrogen sulfide standard reference material is analyzed under identical conditions used in the analysis of the standard. Acceptable hydrogen sulfide reference standards include NIST or NMi traceable SRMs or NTRMs. A minimum three consecutive data points are collected with the necessary precision to support the reported analytical accuracy. An average area of the hydrogen sulfide is calculated using all consecutive analysis.

X3.2 The hydrogen sulfide analysis is performed at least twice, with a minimum 48 hour incubation period between the two analyses. The difference in percent between the two values must be less than 2 %. This is necessary to assure product stability. The reported hydrogen sulfide concentration is the value obtained in the second analysis.

X3.3 The value for the hydrogen sulfide concentration is reported on the certificate of analysis as follows:

X3.3.1 The value for the hydrogen sulfide concentration from both the first and second analysis in Section X3.2, along with the date of analyses.

X3.3.1.1 The cylinder number, concentration and NIST or NMi SRM/NTRM batch ID from the NIST reference standard used in the standard analysis.