



Designation: D4084 – 23

Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)¹

This standard is issued under the fixed designation D4084; 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 determination of hydrogen sulfide (H_2S) in gaseous fuels. It is applicable to the measurement of H_2S in natural gas, liquefied petroleum gas (LPG), substitute natural gas, landfill gas, sewage treatment off gasses, recycle gas, flare gasses, and mixtures of fuel gases. This method can also be used to measure the hydrogen sulfide concentration in carbon dioxide. Air does not interfere. The applicable range is 0.1 to 16 parts per million by volume (ppm/v) (approximately 0.1 to 22 mg/m³) and may be extended to 100 % H_2S by manual or automatic volumetric dilution.

1.2 *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.*

1.3 *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

D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres

D2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)

D3609 Practice for Calibration Techniques Using Permeation Tubes

¹ This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.06.03 on Analysis by Spectroscopy.

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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.

D4150 Terminology Relating to Gaseous Fuels

D7166 Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels

E2165 Practice for Establishing an Uncertainty Budget for the Chemical Analysis of Metals, Ores, and Related Materials (Withdrawn 2007)³

3. Terminology

3.1 For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

4. Summary of Test Method

4.1 Measurement of H_2S is accomplished by ratiometrically comparing a reading of an unknown sample with that of a known standard using a differential colorimetric detection. Pure H_2S is used as a primary standard and mixed volumetrically with a sulfur free matrix gas that is ideally similar in composition to the sample gas. A gaseous sample at constant flow is humidified and passed over lead-acetate-impregnated paper. H_2S reacts with lead acetate to form a brown stain on the paper. The rate of reaction and resulting rate of color change is proportional to the concentration of H_2S in the sample. The analyzer is comprised of an optical system, a photon detection system, a signal differentiation system of first order, and a signal output system. When there is no change in the color of the tape, and no resulting change in photodetector output, E , the first derivative, dE/dt , is zero. This results in an analyzer that automatically zeroes when there is no H_2S .

5. Significance and Use

5.1 This test method is useful in determining the concentration of hydrogen sulfide in gaseous samples and in verifying compliance with operational needs and/or environmental limitations for H_2S content. The automated performance operation of this method allows unattended measurement of H_2S concentration. The user is referred to Practice D7166 for unattended on-line use of instrumentation based upon the lead acetate reaction rate method.

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

6. Apparatus

6.1 *Volumetric Measuring Devices*—A graduated 10-L cylinder (see Fig. 1) having a movable piston for volumetrically measuring test gas. Gastight syringes of 0.1-mL and 0.5-mL volume for volumetrically measuring 100 % H₂S. Gas tight syringes of other volumes can be used. These graduated 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.

6.2 *Sample Pump*—A pump capable of providing more than 8 mL/s (approximately 1 ft³/h) or less than 1 mL/s at 70 kPa (approximately 10.15 psig). Gas-wetted parts are ideally constructed from either aluminum or polytetrafluorethylene (PTFE). Stainless steel may be used when higher safety than afforded by aluminum or PTFE is required.

6.3 *Colorimetric Rate of Reaction Sensor*—Select a device of sufficient sensitivity to measure a minimum rate of change of color density corresponding to 0.1-ppm H₂S by volume in the sample gas. (See Fig. 2.)

6.4 *Recorder*, having an adjustable span of 1-V to 10-V full scale with an input impedance of 1 MΩ or higher. A printer or other output means, such as a data logger or Distributed Control System (DCS), can be used.

7. Reagents and Materials

7.1 **Warning**—Hydrogen Sulfide contained in lecture bottles, permeation tubes or compressed gas cylinders may be flammable and harmful or fatal if ingested or inhaled. 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 gases can result in asphyxiation. Compressed air supports combustion.

7.2 *Acetic Acid Solution*—Add 50 mL of glacial acid (CH₃COOH) to distilled water or dionized water to make 1 L of solution (5 %). Type II distilled water as specified in Specification D1193 is satisfactory for the dilution. Water dionized to 1 megaohm-centimeter is also satisfactory for the dilution.

7.3 Reference Gas:

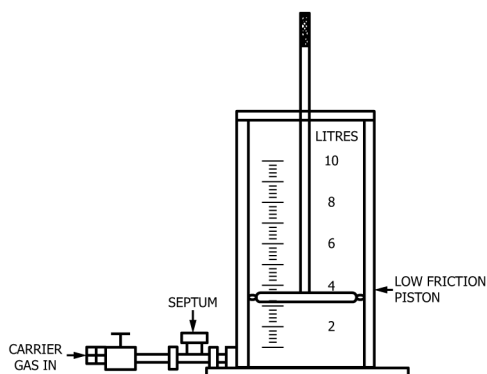


FIG. 1 Calibration Sample Preparation Cylinder with Movable Piston

7.3.1 *Hydrogen Sulfide Source*—99.5 % by volume purity or better. An alternative H₂S source is an H₂S mixture obtained using permeation tube procedures. Hydrogen sulfide generated from a solid heated to generate H₂S may be used instead of a H₂S source if desired. H₂S contained in permeation tubes or compressed gas cylinders may be flammable and harmful or fatal if ingested or inhaled. Permeation tubes and compressed gas standards should only be handled in well ventilated locations away from sparks and flames. (**Warning**—Hydrogen sulfide is an extremely toxic gas.)

7.3.2 *Dilution Gases*—Chemically pure grade or purified gas. Blend or obtain a sulfur-free gas of the same relative density as the sample gas to be analyzed. Blends of gases, of similar composition to the sample gas, are prepared from pure gases by mixing, using a 10-L cylinder with piston. Pipeline gas scrubbed through activated charcoal and sodium hydroxide-asbestos absorbent is satisfactory.

7.3.3 *Gas Mixtures*—Another alternative H₂S source is a certified H₂S mixture obtained from a gas standard vendor. Such mixtures are in a sulfur free carrier gas that is of the same type, or a close approximation, as the gas to be analyzed. 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 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. In the event of a discrepancy, H₂S mixtures prepared from a 99.5 % by volume or better purity H₂S lecture bottle or obtained using permeation tube procedures must be used.

7.3.3.1 *Compressed Gas Standards*—The protocol for compressed gas standards contained in the appendix can be used to ensure uniformity in compressed gas standard manufacture and provide for traceability to a NIST or NMi reference material.

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

7.4 *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, and/or federal environmental regulations.

7.5 *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.

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

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

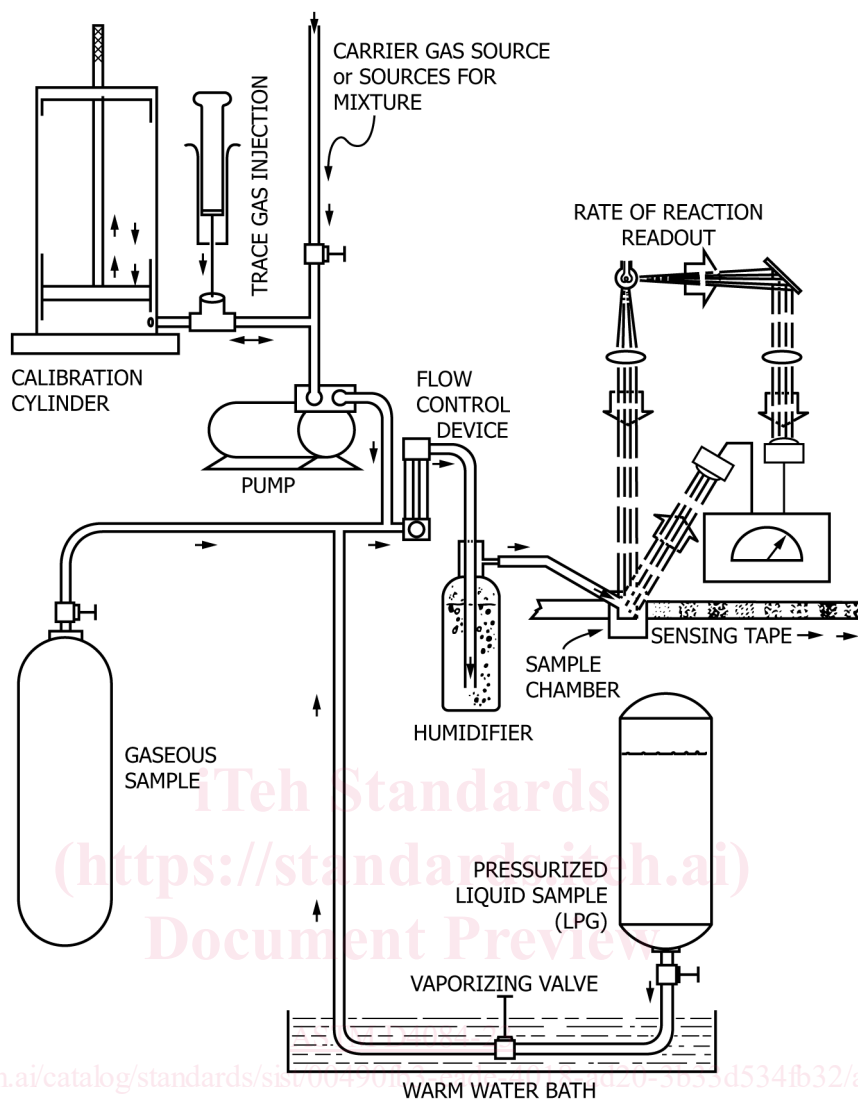


FIG. 2 Flow System for H₂S Measurement Showing Calibration, LPG, and Gaseous Sample Connections

7.5.3 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 per Practice D3609. These devices are discarded when the liquid contents are reduced to less than ten (10) % 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, and/or federal environmental regulations.

8. Sampling

8.1 Because of the chemical activity and adsorptive properties of H₂S, it is highly desirable to connect the test apparatus directly to the sample source using minimum lengths of stainless steel, hastalloy, aluminum or fluorocarbon sample lines. Do not use copper containing, that is, brass or copper flow system parts. In the event that direct sampling is not practical, clean aluminum, stainless steel, or fluorocarbon lined sample containers may be used. Tedlar bags with inert fittings

such as polypropylene or equivalent and silica lined sample containers can also be used for sample collection. Tedlar bags containing sample require protection from light and heat. The collection of samples that are either in two phases or that will form two phases before analysis can be performed must be avoided. The presence of liquids causes H₂S to partition unequally between the liquid and gas phases. Such a partition of H₂S results in inaccurate measurement of H₂S content. Samples must be analyzed with as little delay as possible and reported as “proximate analyses from cylinders” with length of residence time noted. Because of the broad reactivity of H₂S, an extended delay between obtaining the sample and analyzing the sample can result in inaccurate results.

NOTE 1—Each new sample container to be used for a test specimen can be filled with a sample and analyzed over a period of time and the resulting data examined to determine the rate of deterioration of the sample. Repeated filling with a representative sample will tend to passivate a container. Approximately 10 L (approximately 1/3 ft³) of sample, at atmospheric pressure, is convenient for analysis and will normally not deteriorate appreciably within 1 h. Slow instrument response to changes in H₂S concentration indicates the need for a thorough cleaning

of the flow system. (See [Appendix X1](#) for a suggested cleaning procedure.) Errors caused by ambient temperature and pressure changes are compensated for by comparison to a reference standard prepared at the time of analysis. Preparation of the reference sample is described in [Section 12](#).

9. Instrument Preparation

9.1 Fill a humidifier or humidifying bubbler to the full mark with acetic acid solution. The acetic acid minimizes some interfering species. Set the range of the analyzer for the range expected in the sample. Connect the pump and set the flowmeter for a nominal flow of 8 mL/s (approximately 1 ft³/h). Note: analyte gas can also be delivered to the analyzer by use of a compressed gas cylinder or a permeation tube device. Alternative flow settings, such as a nominal 1 mL/s, can be used. Obtain a blank reading by flowing dilution gas through the analyzer. Record the reading of the blank sample as *B* in [13.1](#). Do not adjust the instrument zero until verification is obtained, that the room air or the carrier gas does not contain H₂S. Verification is accomplished by analyzing a room air or carrier gas sample after it has been passed through an activated charcoal filter absorbent.

10. Calibration

10.1 Immediately after preparing the calibration standard, obtain its response on the analyzer. Practice [D3609](#) is acceptable as an alternative method for preparation of a reference standard. Certified compressed gas calibration standards obtained from a gas standard vendor can also be used to calibrate the analyzer. The analyzer response is recorded as *C* in [13.1](#). At least twenty (20) discrete response replicates should be obtained to adequately demonstrate the statistical repeatability of the analyzer at two times the standard deviations about the mean. If the analyzer repeatability response fall outside of the published repeatability specifications then appropriate corrective action must be taken and the repeatability response of the analyzer must be redetermined.

11. Sample Measurement Procedure

11.1 *Sampling and Preparation of Samples*—Appropriate sampling procedures are critical for meaningful hydrogen sulfide determinations and must be tailored to the particular sample source.

11.1.1 *Samples*—Samples are delivered to the laboratory in Tedlar bags with polypropylene fittings or other inert fittings at atmospheric pressure, protected from heat and light. Samples are normally analyzed within 24 h of sampling to ensure accurate measurement of hydrogen sulfide in the sample. The holding time can be extended to the limits of existing data when hydrogen sulfide gas retention in a specific matrix is available. Alternatively, samples are delivered to the laboratory in passivated/lined vessels demonstrated to not demonstrate significant hydrogen sulfide losses in samples over 24 h. As part of a QA/QC program, passivated or lined vessels should periodically be examined for continued hydrogen sulfide gas stability and acceptable sample carryover characteristics. Passivated or lined vessels may allow for reliable sample analysis after more than 24 h. In such cases, analysis is recommended within a time frame supported by hydrogen sulfide retention data.

11.2 *External Calibration*—Procedures delineated in [10.1](#) validate the use of a single-point calibration. At least once a day, analyze the calibration standard and determine standard response factors. Typically, standards are analyzed until three (3) consecutive trials yield a maximum range consistent with [Section 14](#), Precision.

11.3 *Blank Analysis*—Confirmation of a lack of significant carry-over or contamination is recommended and may be required for certain applications. 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.

11.4 *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 conditioning and performance.

11.5 *Quality Assurance*—The following quality assurance (QA) procedures are suggested and may be required in certain applications.

11.5.1 *Spiked Samples*—A spiked sample is analyzed each day as part of a QA/QC program. Spikes are prepared by quantitative addition of hydrogen sulfide in a gas to a known volume of sample gas. An acceptable recovery should match the theoretical amounts of H₂S in the spiked sample within a tolerance consistent with [Section 14](#), Precision, to verify nominal performance. Unacceptable recoveries indicate system malfunction and will require the user to perform mitigative action to restore the system to nominal performance.

11.5.2 *Calibration Standard Reanalysis*—A standard is re-analyzed after samples every day as part of a QA/QC program. The hydrogen sulfide concentration should match the theoretical amounts based on the original standards within a tolerance consistent with [Section 14](#), Precision. Unacceptable results are indicative of a system malfunction and will require the user to perform mitigative action to restore the system to nominal performance.

11.5.3 *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 mitigative action to restore the system to nominal performance.

11.5.4 *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. Typically a drift test lasts two (2) h with data collection occurring once per minute. 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 mitigative action to restore the system to nominal performance.

11.6 Connect the sample to the analyzer and adjust the flow rate to approximately 8 mL/s. This flow must be maintained constant during testing. After the recording is observed to be stable, record the reading *A*, see [13.1](#). Prepare a reference

standard sample as described in 12.2. Connect the reference sample to the pump and the pump to the analyzer. When a stable reading is obtained, record this value (C in 13.1). The reference standard described in 12.2 must be prepared and run to establish the analyzer span frequently enough to allow compensation for changes in temperature and atmospheric pressure. Reference standards as certified gas mixtures or obtained using a permeation tube device are also acceptable alternatives to a reference standard prepared according to 12.2. When samples are within 25 % of the reference standard, repeating the calibration procedure twice a day is normally sufficient for determining any compensation needed to account for changes in temperature and atmospheric pressure.

12. Reference Standard Preparation

12.1 Parts per million by volume (ppmv) units, equivalent to micromoles per mole, are used because these units are easier to use than parts per million by weight in the typical application of this method.

12.2 Prepare a reference standard containing a known volume fraction of H_2S , D in ppmv. Inject a known small volume, V , of H_2S in milliliter units, of pure H_2S into dilution gas as it fills a 10-L cylinder. A syringe or microliter valve is used to volumetrically measure small quantities of H_2S . The syringe must be filled rapidly five times, from a flowing stream of H_2S gas, to purge the tip volume. The H_2S must be quickly injected into the dilution gas through a septum or equivalent. The time from filling the syringe to injection should be the same as the time from injection to withdrawal of the syringe needle. This compensates for the effect of diffusion from the syringe needle. The formula used to calculate the quantity of H_2S required to prepare a given sample in the 10-L calibration cylinder is as follows:

$$V = 0.01D$$

where:

V = a known small volume of pure H_2S in mL, and
 D = fraction of H_2S in reference standard in units of ppmv.

12.2.1 *Example*—To prepare a 10-ppmv, D , sample in sulfur-free carrier gas, inject from a hypodermic syringe 0.1 mL, V , of H_2S into 10 L of dilution gas as it fills the calibration cylinder. Never pump the syringe at this stage as errors are caused by the added volume in the needle tip.

12.3 When using a primary standard, the formula used to calculate the quantity of primary standard required to prepare a given sample in the 10-L calibration cylinder is as follows:

$$V^* = 10^6 \frac{V}{P} \quad (1)$$

V^* = a known volume of primary standard containing H_2S in mL, and

P = fraction of H_2S in the primary standard in units of ppmv.

12.3.1 *Example*—To prepare a 10-ppmv, D , sample in sulfur-free carrier gas, inject from a hypodermic syringe 1.0 mL, V^* , of a primary standard containing 100 000 ppmv H_2S , P , into 10 L of dilution gas as the calibration cylinder is filled. Never pump the syringe at this stage as errors are caused by the added volume in the needle tip.

12.4 *Reference Standard Concentration Uncertainty*—The user is referred to Practice E2165 for establishing an ISO 10725 compliant uncertainty budget.

12.4.1 *Compressed Gas Standard*—The uncertainty in the H_2S concentration of a compressed gas calibration standard is determined by, and should be obtainable from, the vendor.

12.4.2 *Dilution from H_2S Source*—The uncertainty in the H_2S concentration of a standard prepared by diluting pure H_2S arises from three main sources: (1) the uncertainty in the purity of the H_2S , (2) the uncertainty in the H_2S volume measurement, and (3) the uncertainty in the final mixture volume measurement.

12.4.3 *Dilution of Primary H_2S Gas Standard*—The uncertainty in the H_2S concentration of a standard prepared by diluting a primary H_2S gas standard arises from three main sources: (1) the uncertainty in the H_2S concentration of the primary gas standard, (2) the uncertainty in the primary gas calibration standard volume measurement, and (3) the uncertainty in the final mixture volume measurement. The uncertainty in the H_2S concentration of the primary gas standard is determined by, and should be obtainable from, the vendor.

12.4.4 *Permeation Tube Devices*—The uncertainty in the H_2S concentration of a standard prepared by using a permeation tube device arises from three main sources: (1) the uncertainty in the permeation rate of the tube, (2) the uncertainty of the diluent volumetric flow rate, and (3) the uncertainty in the oven temperature. The uncertainty in the permeation rate is determined by, and should be available from, the vendor. Flow rate measurement and oven temperature set point uncertainties are determined from the specifications of the flow measuring and temperature control devices.

12.4.5 *Material Compatibility and Line Conditioning*—The uncertainty in the measured H_2S concentration can be affected by wetted material incompatibilities and inadequate line conditioning. Copper containing materials react with H_2S . Appropriate materials are listed in 8.1. Because of the broad reactivity of H_2S , some finite amount of absorption still occurs when compatible materials are in contact with H_2S . Calibration standards should be run for a sufficient period of time to ensure that a stable H_2S concentration output is obtained. The required line conditioning time should be determined as part of a QA/QC program.

13. Calculation

13.1 Calculate concentration of an unknown sample in ppm by volume as follows: