



Designation: D8488 – 22

# Standard Test Method for Determination of Hydrogen Sulfide (H<sub>2</sub>S) in Natural Gas by Tunable Diode Laser Spectroscopy (TDLAS)<sup>1</sup>

This standard is issued under the fixed designation D8488; 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 is for the online determination of hydrogen sulfide (H<sub>2</sub>S) in natural gas using tunable diode laser absorption spectroscopy (TDLAS) analyzers also known as a “TDL analyzers.” The particular wavelength for H<sub>2</sub>S measurement varies by manufacturer, typically between 1000 and 10 000 nm with an individual laser having a tunable range of less than 10 nm. The H<sub>2</sub>S concentration ranges can be anywhere from 0-5 ppm(v) to 0-90 % by volume.

1.2 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard. TDLAS analyzers inherently output concentrations in unitless molar ratios such as ppm(v).

NOTE 1—Weight-per-volume units such as milligrams or grains of H<sub>2</sub>S per cubic foot or cubic meter can be derived from ppm(v) at “standard conditions” or standard temperature and pressure.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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:*<sup>2</sup>

- D1945 Test Method for Analysis of Natural Gas by Gas Chromatography
- D4150 Terminology Relating to Gaseous Fuels

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.12 on On-Line/At-Line Analysis of Gaseous Fuels.

Current edition approved Nov. 1, 2022. Published November 2022. DOI: 10.1520/D8488-22.

<sup>2</sup> 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.

- D5503 Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation (Withdrawn 2017)<sup>3</sup>
- D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
- D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
- D6968 Test Method for Simultaneous Measurement of Sulfur Compounds and Minor Hydrocarbons in Natural Gas and Gaseous Fuels by Gas Chromatography and Atomic Emission Detection
- D7551 Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence
- D7833 Test Method for Determination of Hydrocarbons and Non-Hydrocarbon Gases in Gaseous Mixtures by Gas Chromatography

## 3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorption spectroscopy, n*—refers to spectroscopic techniques that measure the absorption of electromagnetic radiation as a function of frequency or wavelength because of its interaction with a sample.

3.2.2 *adsorption, n*—adhesion of molecules to a solid surface forming a molecular or atomic film.

3.2.3 *chemometrics, n*—field of science relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods.

3.2.4 *desorption, n*—phenomenon whereby a substance is released from a surface (the opposite of adsorption).

3.2.5 *heat trace, n*—ribbon-shaped tape that uses electrical resistance or tubing carrying steam to generate heat.

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

3.2.5.1 *Discussion*—Heat trace tape is attached to sample tubing and other sample-conditioning components to avoid condensation and stabilize the temperature of the wetted components and the gas stream.

3.2.6 *selectivity, n*—refers to the extent to which a measurement of concentration can be made in a mixture of various chemicals without significant influence from other components in the mixture.

3.2.7 *tunable diode laser absorption spectroscopy (TDLAS), n*—technique for measuring the concentration of a specific component such as hydrogen sulfide ( $H_2S$ ) in a gaseous sample by absorption spectrometry using tunable diode lasers.

### 3.3 Abbreviations:

3.3.1  $CO_2$ —carbon dioxide

3.3.2  $H_2O$ —water

3.3.3  $H_2S$ —hydrogen sulfide

3.3.4 TDLAS—tunable diode laser absorption spectroscopy

## 4. Summary of Test Method

4.1 A representative sample of the gas is extracted from a process pipe or pipeline and is transferred by a sample transport line through an appropriately designed sample-handling system to the inlet of an analyzer. The sample shall be conditioned with a minimum, preferably negligible, impact on the  $H_2S$  concentration. The gas flows continuously through the analyzer and is vented to atmosphere, or a flare, or back to the process stream depending on application and regulatory requirements.

4.2 The gas sample stream flows through the measurement portion of the analyzer. An overall diagram of a simple TDLAS system is shown in Fig. 1. A solid-state laser with a narrow wavelength range is used as a light source. Electronics drive the laser and a thermoelectric cooler precisely stabilizes the

laser temperature. The laser generates a near-infrared beam of light that passes through the cell window, which is typically reflected using a mirror (or mirrors) within the cell, and then returns through the window and into a photodiode detector. The photodiode signal is used to determine how much light is absorbed at specific wavelengths.

4.3 Fig. 2 is a graph of typical regions in the near-infrared spectrum where  $H_2S$  will be absorbed. In the graph, the x-axis indicates the wavelength. The y-axis indicates the “absorption” of light in which 1.0 (or 100 %) is the maximum. Where the absorption is more than 0,  $H_2S$  is indicated. The vertical lines within the graph indicate the magnitude of absorption at specific wavelengths. Each individual absorption line can be potentially used for TDLAS  $H_2S$  measurement. The actual wavelength used will vary based on manufacturer, background composition, measurement specification requirements, and laser availability.

4.4 The sensitivity of the measurement is determined by the absorption as well as the length of the laser beam path (path length) within the sample cell. The path length is fixed and can range from about 30 cm to 30 m depending on the measurement range and the wavelength used. By optimizing the path length and wavelength, linearity less than 0.1 % can be readily achieved. The TDLAS manufacturer must be consulted for actual linearity specifications.

4.5 This test method can be used as a guideline for producing  $H_2S$  measurement data of a known and defensible quality when using a TDLAS analyzer. A procedure is outlined below for validating measurement integrity.

## 5. Significance and Use

5.1  $H_2S$  measurements in natural gas are performed to ensure concentrations satisfy gas purchase contract criteria and to prevent pipeline and associated component corrosion.

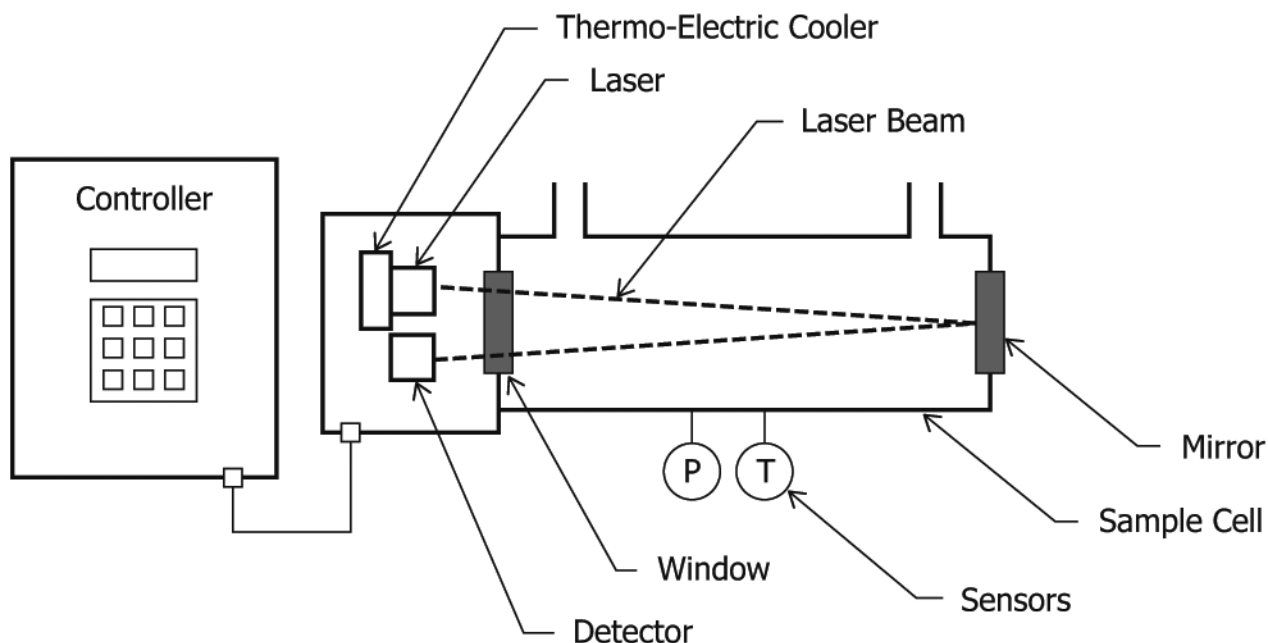


FIG. 1 Main Components of the TDLAS System

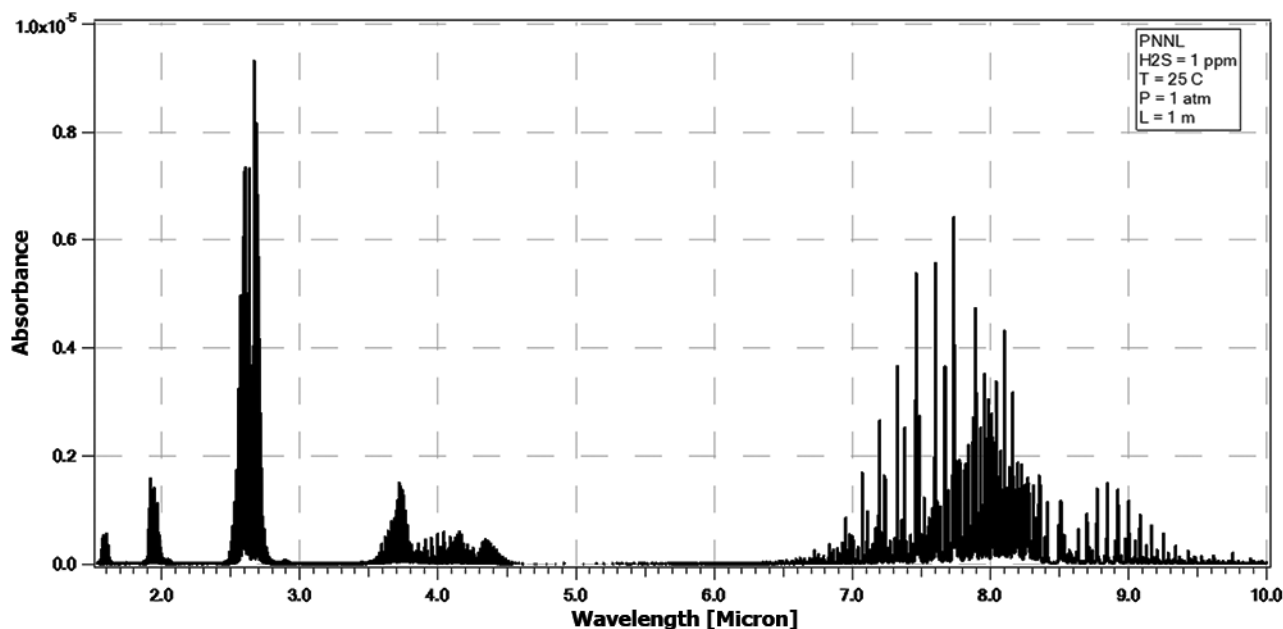


FIG. 2 H<sub>2</sub>S Absorption in the Near Infrared (NIR) Spectrum (Source: Pacific Northwest National Laboratory Northwest Infrared Database)

5.2 Using TDLAS for the measurement of H<sub>2</sub>S in natural gas enables a high degree of selectivity with minimal interference from common constituents in natural gas streams. The TDLAS analyzer can detect changes in concentration with a relatively rapid response compared to other methods so that operators may take swift action when designated H<sub>2</sub>S concentrations are exceeded.

5.3 Primary applications covered in this test method are listed in 5.3.1 and 5.3.2. Each application may have differing requirements and methods for gas sampling. Additionally, different natural gas applications may require unique spectroscopic considerations.

5.3.1 Raw natural gas is found in production, gathering sites, and inlets to gas-processing plants characterized by potentially high levels of water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), H<sub>2</sub>S, and heavy hydrocarbons. Gas-conditioning plants and skids are normally used to remove H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, and other contaminants.

5.3.2 High-quality “sales gas” is found in transportation pipelines, natural gas distribution (utilities), and natural gas power plant inlets. The gas is characterized by a very high percentage of methane (90 to 100 %) with small quantities of other hydrocarbons and trace levels of contaminants.

## 6. Interferences

6.1 TDLAS analyzers can be highly selective. They can measure target component with very little interference from background composition with some limitations. There may be some interference from background components, for example, at some wavelengths, methane, ethane, and carbon dioxide may absorb at the same wavelength as H<sub>2</sub>S. If interferences exist at a particular wavelength, a different wavelength can be used and other techniques such as chemometrics, compensation algorithms, vacuum pumps (to separate the spectroscopy peaks), or differential measurements (a technique using an H<sub>2</sub>S

scrubber) may be used. Since hundreds of possible wavelengths are available in the near-infrared band for measuring H<sub>2</sub>S, it is not practical to list the potential interferences. The manufacturer should indicate the intended stream composition for the analyzer and the allowable variations in the stream to the end user.

6.2 Protection from liquid carryover such as from heavy hydrocarbons, amines, and water in the sample lines is necessary to prevent liquid pooling in the cell or the sample system components. Liquid carryover is especially a concern on the outlet of gas-sweetening processes that use aqueous solutions such as amines.

## 7. Apparatus

7.1 A TDLAS analyzer system includes the following sub-systems: (1) sample extraction, (2) sample transport, (3) sample-conditioning system, (4) TDLAS analyzer, and (5) vent line.

7.1.1 *Sample Extraction Hardware*—Sample extraction is required to obtain a representative sample from the pipeline. To maximize the response speed, it is recommended to reduce the pressure at the sample point. To avoid condensation that may occur from expanding the gas when it is depressurized (especially when the pipeline pressure is high), it is important to understand the phase diagram of all the components in the gas (for example, hydrocarbons, alcohols, and water). Use an extraction probe and a regulator as shown in Fig. 3 mounted so that the tip of the probe is in the center third of the pipe diameter. If the dew point of the gas is lower than the ambient temperature after consideration for temperature reduction because of gas expansion through the regulator (approximately 3 °C per 6 bar), all sampling apparatus such as the probe and regulator may need to be heat traced or enclosed in a heated chamber, or both. According to Practice D5503, “vapor sample

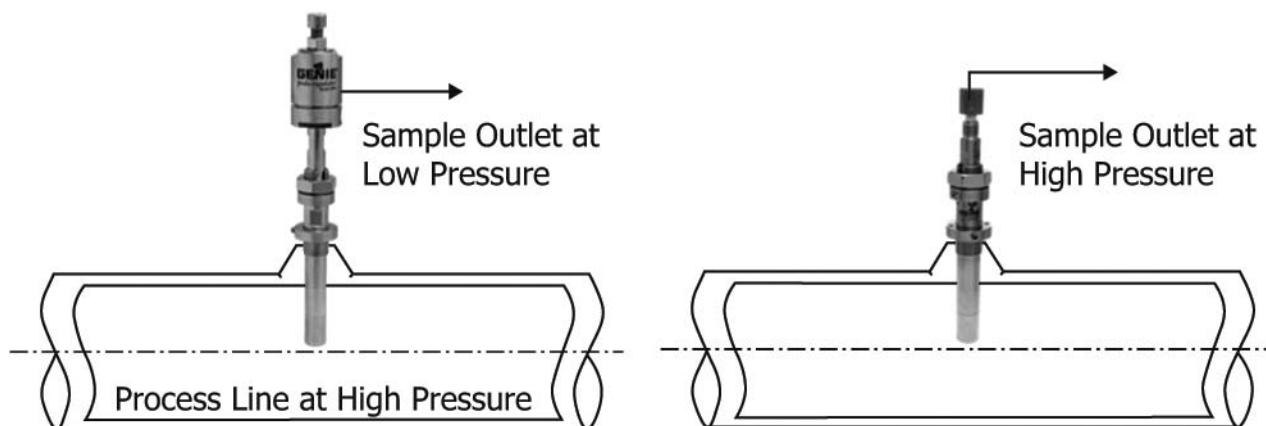


FIG. 3 Sample Probe with Integrated Pressure Regulator (Left) and Sample Probe with No Regulator (External Pressure Regulator to be Used) (Right)

must be kept at least 10 °C above the hydrocarbon dew point temperature to prevent condensation of the sample.”

**7.1.2 Sample Transport Hardware**—The sample transport line carries the sample from the sample extraction point to the analyzer. The length of the sample transport tubing should be as short as possible. Heat trace is necessary if the environmental temperature is close to the dew point of the sample gas. Heat trace prevents liquid condensation and adsorption and desorption of H<sub>2</sub>S from the walls of the tubing caused by ambient temperature changes (Fig. 4). When heat trace is used, the entire length of tubing shall be heated and insulated with no gaps. Electropolished tubing is recommended for use in analytical sample transport to reduce adsorption and desorption effects and optimize speed of response in the sample transport. Silica-lined tubing may also be used.

**7.1.3 Sample-Conditioning System Hardware**—The sample-conditioning system is typically installed immediately before the analyzer and contains a regulator to perform a final pressure drop, a means to control and measure flow, and filters to remove particulates and trap liquids. Additionally, the sample-conditioning system may provide a means for bypassing the analyzer to connect a reference gas for validating or challenging the analyzer and an outlet for venting the gas. Sample system recommendations are described in detail in Practice D5503.

**7.1.3.1** Similar to the sample transport line, the sample-conditioning system may require heat tracing to eliminate condensation and reduce erratic readings caused by adsorption/

desorption affects. Typically, if heat tracing is required, a sample panel will be installed in a heated building or a heated enclosure. Components such as valves, regulators, and fittings that are used in the sample extraction, sample transport, and sample conditioning shall be designated as “instrument or analytical grade.” If the sample gas may contain an unsafe level of H<sub>2</sub>S, the sample system and the heated enclosure shall have the appropriate purge ports and warning system to prevent accidental exposure during repair and maintenance.

**7.1.3.2** The sample vent line transports the sample from the analyzer to a safe location or back into the process stream. It should be an unrestricted line. Many users vent the analyzer to a high point. If so, appropriate equipment may be used to protect against lightning strikes at the vent. Also, a 180° bend with at least a 30 mm radius should be applied to the end of the vent to minimize rain and wind intrusion. Additionally, a screen of some kind on the end should be used to discourage insects that might plug the vent. Never vent the analyzer inside a building or enclosure.

**7.1.4 Reference Standard Hardware**—A binary gas mixture (for example, H<sub>2</sub>S in methane) can be used to validate a TDLAS analyzer. In Fig. 5, a simple setup is shown. The analyzer may have a validation gas inlet built into the sample-conditioning system, so the three-way ball valve is optional. All the components used must minimize the retention of the analyte of interest between the condensate or filter material and the effluent gas. Finer surface finish, electropolished stainless



FIG. 4 Heat-Trace Tubing with Self-Regulating Heat Tape Bundled with Insulation and Protective Jacket