



Designation: D7165 – 06

Standard Practice for Gas Chromatograph Based On-line/At-line Analysis for Sulfur Content of Gaseous Fuels¹

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1. Scope

1.1 This practice is for the determination of volatile sulfur-containing compounds in high methane content gaseous fuels such as natural gas using on-line/at-line instrumentation, and continuous fuel monitors (CFMS). It has been successfully applied to other types of gaseous samples including air, digester, landfill, and refinery fuel gas. The detection range for sulfur compounds, reported as picograms sulfur, based upon the analysis of a 1 cc sample, is one hundred (100) to one million (1,000,000). This is equivalent to 0.1 to 1,000 mg/m³.

1.2 This practice does not purport to measure all sulfur species in a sample. Only volatile compounds that are transported to an instrument under the measurement conditions selected are measured.

1.3 The values stated in SI units are standard. The values stated in inch-pound units are for information only.

1.4 *This practice 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 practice to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

[D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration](#)

[D1945 Test Method for Analysis of Natural Gas by Gas Chromatography](#)

[D3606 Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography](#)

¹ This practice 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.

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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.

- [D4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels \(Lead Acetate Reaction Rate Method\)](#)
- [D4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry](#)
- [D4626 Practice for Calculation of Gas Chromatographic Response Factors](#)
- [D4810 Test Method for Hydrogen Sulfide in Natural Gas Using Length-of-Stain Detector Tubes](#)
- [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](#)
- [E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography](#)

3. Terminology

3.1 Definitions:

3.1.1 *direct sampling*—Sampling where there is no direct connection between the medium to be sampled and the analytical unit.

3.1.2 *in-line instrument*—Instrument whose active element is installed in the pipeline and measures at pipeline conditions.

3.1.3 *on-line instrument*—Automated instrument that samples gas directly from the pipeline, but is installed externally.

3.1.4 *at-line instrument*—instrument requiring operator interaction to sample gas directly from the pipeline.

3.1.5 *continuous fuel monitor (CFM)*—Instrument that samples gas directly from the pipeline on a continuous or semi-continuous basis.

3.1.6 *total reduced sulfur (TRS)*—Summation of sulfur species where the sulfur oxidation number is -2 , excluding sulfur dioxide, sulfones, and other inorganic sulfur compounds. This includes but is not limited to mercaptans, sulfides, and disulfides.

3.1.7 *near-real time monitoring systems*—Monitoring system where measurement occurs soon after sample flow through the system or soon after sample extraction. The definition of a near real time monitoring system can be application specific.

4. Summary of Practice

4.1 A representative sample of the gaseous fuel is extracted from a process pipe or pipeline and is transferred in a timely manner to an analyzer inlet system. The sample is conditioned with minimum impact on sulfur content. A precisely measured volume of sample is injected into the analyzer. Excess process or pipeline sample is vented or is returned to the process stream dependant upon application and regulatory requirements.

4.2 Sample containing carrier gas is fed to a gas chromatograph where the components are separated using either a packed or capillary column. Measurement is performed using a suitable sulfur detection system.

4.3 Calibration, precision, calibration error, performance audit tests, maintenance methodology and miscellaneous quality assurance procedures are conducted to determine analyzer performance characteristics and validate both the operation and the quality of generated results.

5. Significance and Use

On-line, at-line, in-line, CFMS, and other near-real time monitoring systems that measure fuel gas characteristics, such as the sulfur content, are prevalent in the natural gas and fuel gas industries. The installation and operation of particular systems vary on the specific objectives, contractual obligations, process type, regulatory requirements, and internal performance requirements needed by the user. This standard is intended to provide guidelines for standardized start-up procedures, operating procedures, and quality assurance practices for on-line, at-line, in-line, CFMS, and other near-real time gas chromatographic based sulfur monitoring systems used to determine fuel gas sulfur content. For measurement of gaseous fuel properties using laboratory based methods the user is referred to Test Methods [D1072](#), [D1945](#), [D4084](#), [D4468](#), [D4810](#) and Practices [D4626](#), [E594](#).

6. Apparatus

6.1 *Instrument*—Any gas chromatographic based instrument of standard manufacture, with hardware necessary for interfacing to a natural gas or other fuel gas pipeline and containing all features necessary for the intended application(s) can be used.

6.1.1 The chromatographic parameters must be capable of obtaining retention time repeatability of 0.05 min. (3 sec.). Instrumentation must meet the performance characteristics for repeatability and precision without encountering unacceptable interference or bias. The components coming in contact with sample, such as tubing and valving, must be passivated or constructed of inert materials to ensure an accurate sulfur gas measurement.

6.2 *Sample Inlet System*—A sample inlet system capable of operating continuously above the maximum column temperature is necessary. A variety of sample inlet configurations can be used including but not limited to on-column systems and split/splitless injection system capable of splitless operation and split control from 10:1 up to 50:1. An automated gas sampling valve is required for many applications. The inlet system must be constructed of inert material and evaluated frequently for compatibility with reactive sulfur compounds.

The sampling inlet system is heated as necessary so as to prevent condensation. All wetted sampling system components must be constructed of inert or passivated materials. Sample delivered to the inlet system should be in the gas phase free of particulate or fluidic matter.

6.2.1 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical for optimum and consistent analytical performance. Control is achieved by use of pressure regulators and fixed flow restrictors. The gas flow is measured by appropriate means and adjusted, as required, to the desired value. Mass flow controllers, capable of maintaining a gas flow constant to within $\pm 1\%$ at the flow rates necessary for optimal instrument performance can be used.

6.2.2 *Detector*—Sulfur compounds can be measured using a variety of detectors including but not limited to: sulfur chemiluminescence, flame photometric, electrochemical cell, oxidative cell and reductive cells. In selecting a detector, the user should consider the linearity, sensitivity, and selectivity of particular detection systems prior to installation. The user should also consider interference from substances in the gas stream that could result in inaccurate sulfur gas measurement due to effects such as quenching.

6.3 *Columns*—A variety of columns can be used to separate the sulfur compounds in the sample. Typically, a 60 m \times 0.53 mm ID fused silica open tubular column containing a 5 μ m film thickness of bonded methyl silicone liquid phase is used. The selected column must provide retention and resolution characteristics that satisfy the intended application. The column must be inert towards sulfur compounds. The column must also demonstrate a sufficiently low liquid phase bleed at high temperature such that a loss of the instrument response is not encountered while operating the column at elevated temperatures.

6.4 *Data Acquisition*—Data acquisition and storage can be accomplished using a number of devices and media. Following are some examples.

6.4.1 *Recorder*—As an example, a 0 to 1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less can be used. A4-20 mA range recorder can also be used.

6.4.2 *Integrator*—An electronic integrating device or computer can be used. For GC based systems, it is suggested that the device and software have the following capabilities:

6.4.2.1 Graphic presentation of chromatograms.

6.4.2.2 Digital display of chromatographic peak areas.

6.4.2.3 Identification of peaks by retention time or relative retention time, or both.

6.4.2.4 Calculation and use of response factors.

6.4.2.5 External standard calculation and data presentation.

6.4.3 *Distributed Control Systems (DCS)*—Depending on the site requirements, the analytical results are sometimes fed to a distributed control system. The information is then used to make the appropriate adjustments to the process. Signal isolation between the analyzer and the distributed control network is most often required. Communications protocols with the DCS will dictate the required signal output requirements for the analyzer.