



**Designation: D7166-05** ~~Designation: D7166 – 10~~

## Standard Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels<sup>1</sup>

This standard is issued under the fixed designation D7166; 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.

### 1. Scope

1.1 This practice is for the determination of total sulfur from volatile sulfur-containing compounds in high methane or hydrogen content gaseous fuels using on-line/at-line instrumentation.

~~1.2 The values stated in SI units are standard. Values stated in other units are for information only.~~

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

D1070 Test Methods for Relative Density of Gaseous Fuels

D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration

D3246 Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry

D3609 Practice for Calibration Techniques Using Permeation Tubes

D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems

D4298 Guide for Intercomparing Permeation Tubes to Establish Traceability

D4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry

D5287 Practice for Automatic Sampling of Gaseous Fuels

D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence

D5503 Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation

D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

D6122 Practice for Validation of the Performance of Multivariate Process Infrared Spectrophotometer Based Analyzer Systems

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6621 Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials

D6667 Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence

D6920 Test Method for Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection

#### 2.2 ISO Standards<sup>3</sup>

ISO 7504 Gas Analysis-Vocabulary

### 3. Terminology

#### 3.1 Definitions:

<sup>1</sup> 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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<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.

<sup>3</sup> Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, <http://www.iso.ch>.

3.1.1 *at-line instrument*—instrumentation requiring operator interaction that samples gas directly from the pipeline.

3.1.2 *calibration gas mixture, n*—a certified gas mixture with known composition used for the calibration of a measuring instrument or for the validation of a measurement or gas analytical method.

3.1.2.1 *Discussion*—Calibration Gas Mixtures are the analogues of measurement standards in physical metrology (reference ISO 7504 paragraph 4.1).

3.1.3 *continuous fuel monitor*—instrument that samples gas directly from the pipeline on a continuous or semi-continuous basis.

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

3.1.2

3.1.5 *in-line instrument*—instrument with an active element installed in a pipeline, which is used to measure pipeline contents or conditions.

3.1.3

3.1.6 *on-line instrument*—instrument that samples gas directly from a pipeline, but is installed externally.

3.1.4 *at-line instrument*—instrumentation requiring operator interaction that samples gas directly from the pipeline.

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

3.1.6

3.1.7 *reference gas mixture, n*—a certified gas mixture with known composition used as a reference standard from which other compositional data are derived.

3.1.7.1 *Discussion*—Reference Gas Mixtures are the analogues of measurement standards of reference standards (reference ISO 7504 paragraph 4.1.1).

3.1.8 *total reduced sulfur (TRS)*—concentration summation of all volatile sulfur species with a  $-2$  sulfur oxidation number, excluding sulfur dioxide, sulfones and other inorganic sulfur compounds.

3.1.7

3.1.9 *total sulfur*—concentration summation of all volatile sulfur species in a sample.

3.1.8

3.1.10 *volatile*—molecular characteristic wherein the sulfur specie exists in the gas phase at the operating conditions of the process or pipeline.

#### 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 through an appropriately designed sampling system to the inlet of a total sulfur analyzer. The sample is conditioned with a minimum, preferably negligible, impact on the sulfur content. A precisely measured volume of sample is either injected, or allowed to flow continuously, either directly into the analyzer or into a carrier gas, as required by the analyzer. Some total sulfur analyzer systems are configured such that sample gas flows directly into the analyzer detection system. Excess process or pipeline sample is vented to atmosphere, to flare or to the process stream dependant upon application and regulatory requirements.

4.2 Sample containing carrier gas is fed to a furnace operating at an elevated temperature where sulfur compounds are converted into detectable species. The conversion reaction may be oxidative or reductive and may require the introduction of additional carrier or other supply gases.

4.3 Furnace exit gasses are conditioned as required with respect to temperature and water content and are introduced into the detector where quantification of the total sulfur content occurs.

4.4 Calibration, maintenance, quality assurance and performance protocols provide a means to validate the analyzer operation and the generated results.

#### 5. Significance and Use

5.1 On-line, at-line, in-line and other near-real time monitoring systems that measure fuel gas characteristics such as the total 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 protocol is intended to provide guidelines for standardized start-up procedures, operating procedures, and quality assurance practices for on-line, at-line, in-line and other near-real time total sulfur monitoring systems.

#### 6. Apparatus

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

6.1.1 *Specific Sulfur Specie Detection Systems*—The operating parameters employed generally must be capable of converting all of the volatile sulfur species in the sample into a single detectable species such as sulfur dioxide or hydrogen sulfide. Instrumentation must satisfy or exceed other analytic performance characteristics for accuracy and precision for the intended application without encountering unacceptable interference or bias. In addition, components in contact with sample streams such as tubing and valving must be constructed of suitable inert, or passivated, materials to ensure constituents in the fuel stream do not degrade these components or alter the composition of the sampled gas.

6.2 *Sample Probes/Sample Extraction*—The location and orientation of sampling components are critical for ensuring that a

representative sample is analyzed. The locations and orientation of sampling components should be selected based upon sound analytic and engineering considerations. Sampling practices for gaseous fuels can be found in Practice D5287.

6.3 *Sample Inlet System*—The siting and installation of an at-line or on-line monitor is critical for collecting representative information on sulfur content. Factors that should be considered in siting an instrument include ease of calibration, ease of access for repair or maintenance, sample uniformity at the sampling point, appropriateness of samples from a sampling location, ambient conditions, and of course safety issues. An automated gas sampling valve is required in many applications. All sampling system components in contact with the fuel stream must be constructed of inert or passivated materials. Care should be taken to ensure that the extracted sample is maintained as a particulate and condensate free gas. Heating at the point of pressure reduction or along the sample line to the analyzer and the use of a filter may be required to ensure that the sample is maintained in the gas phase. The need for heat tracing and the extent to which it is required will be site and application specific. In general, considerations impacting heat tracing decisions include sample compositions and the expected variations, ambient temperature fluctuations, operating pressures, anticipated pressure differentials in sample system components, and safety considerations. Sample filtration should be utilized as required to remove particulate matter from the extracted sample. The sampling frequency relative to the process bandwidth is critical to ensuring that the reported analytical results adequately represent the process being monitored. The Nyquist-Shannon sampling criterion of a sampling frequency that exceeds twice the process bandwidth can be used to establish a minimum analytical cycle time. Sample handling and conditioning system practices can be found in Practice D5503.

6.3.1 *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 as well as rotameters. Temperature control is generally vital for ensuring consistent operation of these devices. The gas flow is measured by appropriate means and adjusted as necessary. Mass flow controllers, capable of maintaining a gas flow constant to within  $\pm 1\%$  at the flow rates necessary for optimal instrument performance are typically used.

6.3.2 *Detectors*—Common detectors used for total sulfur determinations include chemiluminescence (Test Method D5504), microcoulometry (Test Method D3246), electrochemical (Test Method D6920), lead acetate (Test Method D4468), titration, such as barium chloride (Test Method D1072), ultra-violet fluorescence (Test Methods D5453 and D6667), both continuous and pulsed. Other detectors can be used provided they have appropriate linearity, sensitivity, and selectivity for the selected application. 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.

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

6.4.1 *Recorder*—A 0 to 1 mV range recording potentiometer or equivalent can be used.

6.4.2 *Communications*—Efficient communications between the analyzer and the host depend on resolving any and all interface issues. Signals to and from the host are typically optically isolated from each other.

## 7. Reagents and Materials

**NOTE 1—Warning:** Compressed gas standards should only be handled in well ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing calibration standards, air, nitrogen, hydrogen, argon or helium can result in explosion. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion. Sulfur species and radiation sources can be toxic.

7.1 *Standards*—Accurate sulfur standards are required for the determination of total sulfur. Standards are available as prepared standards in the form of a compressed gas or as a preparable standard in the form of a permeation tube calibration device.

7.2 *Prepared Standards*—Compressed gas standards should be stable, of the highest available accuracy and purity and used in accordance with the manufacturer's recommendations. The matrix components in the reference standard can be representative of the monitored gas. Alternatively, a simplified matrix can be used if the analyzer can be calibrated in accordance with the manufacturer's specifications. Sulfur concentrations are dependent on the detector linearity and are typically selected between one half and twice their expected concentration in the monitored gas. Alternatively, a critical value of sulfur concentration, such as an alarm limit, can be used to identify the desired total sulfur concentration of the standard. Using a sulfur specie that differs from what the detector sees allows for a total analyzer system performance check. Standards must be maintained within the temperature range specified by the manufacturer to ensure accuracy and stability.

7.3 *Permeation Devices*—Permeation devices contain an aliquot of a specific compound that continuously diffuses at a determined rate through a permeable medium. A dry inert carrier gas flows at a constant rate across the medium at a constant temperature consistent with the manufacturer's recommendations to create a calibration gas that then flows to the analyzer. Proper storage, in accordance with the manufacturer's recommendations, is required to prevent damage to the membrane. A sufficiently long equilibration time is required when the permeation device temperature is changed to ensure the reestablishment of a constant permeation rate. Calibration devices using permeation tubes contain a temperature controlled oven and employ flow control to maintain a constant diluent flow rate. Practice D3609 and Guide D4298 contain additional information on permeation tubes.

## 8. Equipment Siting and Installation

8.1 A sample inlet system capable of operating continuously and delivering a gas phase sample to the analyzer is necessary. The location of the sample inlet to the analyzer relative to the sample extraction point is critical to obtaining timely analytical results.