



Standard Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels¹

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 (ε) 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 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:²

- 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 Standards³

- ISO 7504 Gas Analysis-Vocabulary

3. Terminology

3.1 Definitions:

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.

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.

Current edition approved Jan. 1, 2010. Published February 2010. Originally approved in 2005. Last previous edition approved in 2005 as D7166–05. DOI: 10.1520/D7166-10.

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 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>.

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

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

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

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.

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

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 species 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. Ideally, the analyzer is close coupled to the sample extraction point and there is an insignificant sampling lag time. Normally, the analyzer is mounted at some distance away from the sample extraction point. This increased distance represents increased lag time between when a sample is extracted from a process and when an analytical result is reported. The maximum allowable lag time depends on the specifics of the sampling location relative to the process being sampled. A fast loop sweep can be used to minimize the lag time by creating a bypass loop that flows sample from the process to the analyzer and is then returned to the process or is vented.

8.2 The sample should flow continuously without impediment through the instrument sampling system. The sampling system should be capable of delivering a sample to the detection system in 10 minutes or less.

8.3 A monitoring system pretest of both sampling and analysis functions is critical to determining monitoring system characteristics, identify unforeseen factors affecting measurement and to determine optimal operating conditions for the intended use. This pretest is performed before the system is placed in continuous service and may be performed in a variety of ways including a comparison of results to another instrument already in service, comparison of results to a laboratory sited instrument, analysis of a known gaseous sample etc.

9. Performance Tests

9.1 The following performance tests are suggested as part of an overall QA program. This list is not inclusive. The use of some, or all, of these performance tests, as well as tests not specified, may be required or deemed appropriate and optional by local, regional, state, and federal regulations, or a combination thereof. Also, the user's judgment, manufacturer's recommendations, and application requirements, or a combination thereof, apply. For analyzers installed in remote locations, a sub-set of site and application specific diagnostic tests

and checks, which can be completed during a one day visit to the site, can be performed to verify that the analyzer is operating correctly. A full set of performance tests on the analyzer should be performed at least annually, or more frequently, as required.

9.2 Standard Operating Procedure—Maintain a current and readily available Standard Operating Procedure (SOP) and maintenance log.

9.3 System Blank Test—Periodically perform a system blank test to evaluate the presence of contamination, system leaks or wear on sample valves and related components, or a combination thereof. As necessary, replace components to restore the analytical system to nominal function.

9.4 If the analyzer is equipped with an auto-verification feature, a calibration check, done biannually, daily or at some other interval using a gas standard can be preformed as follows:

9.4.1 Perform consecutive triplicate analysis using the calibration gas .

9.4.2 Discard the first analysis as a conditioning and purging step.

9.4.3 Record the second analysis as the initial data point.

9.4.4 Compare the third analysis against the second analysis. The results of the third analysis should agree with the results of the initial data point to within 5 %.

9.4.5 If the third analysis satisfies criteria under **9.4.4**, record the result of the third analysis.

9.4.6 If the third analysis does not satisfy criteria under **9.4.4**, initiate mitigation steps.

9.4.7 If the analyzer is not equipped with an auto-verification feature, a calibration check can be done following the steps indicated in **9.4** on an as needed basis.

9.5 7-Day Calibration Error Test—At least annually, more frequently as required, and if appropriate for the installation, periodically evaluate the system performance over seven consecutive days. The calibration drift should not exceed 10 percent of the full-scale range for each calibrant. Alternatively, it is possible to specify an appropriate percentage of detector response for each calibrant component, such as a maximum 10 % change in the calibrant response during the course of one week.

9.6 Linearity Check—On a regular basis or as needed and when practicable, perform a three point linearity check. Linearity at the midpoint should not exceed 5% of the expected value.

9.7 Drift Test—It is suggested that a control or drift test be performed on a daily, as practicable or as required basis. Verify that the system response drift for individual species in the test gas does not consistently exceed 10 % of its daily historical value, control chart information, or the most recent validation or control sample results. Adequate system performance is demonstrated by recoveries of 90% to 110% of the theoretical amounts for the individual species in the test gas. Adjustments

made to compensate for successive drifts exceeding 10 % of the daily historical value may be indicative of an operational problem. As necessary, examine the retention time for each individual sulfur specie of interest. Verify that the retention time drift for individual species in the test gas does not consistently exceed 5% for minor components or 2% for major components, such as methane and nitrogen, of its daily historical value, control chart information, or the most recent validation or control sample results. Compare retention times to system programming parameters, such as time gates, to ensure compatibility. These parameters, including the analysis time, on occasion may need to be updated. A drift passing a zero drift test but exceeding the lesser of 10% at the full scale range, or the published manufacturer's specification, may be indicative of an operational problem.

9.8 Carrier Flow Rates—The carrier flow rates should be verified on an as needed basis.

9.9 Audit Test—Calibration, precision, calibration error, and performance audit tests are conducted to determine performance of the monitor. Periodic calibration and maintenance methodology are also specified.

9.10 Validation Test—The validation of a process analyzer is covered in Practices **D3764**, **D6122**, and **D6621**. Application of statistical quality assurance techniques to the performance evaluation of an analytical measurement system is covered in Practice **D6299**. The Additional Reading section contains a list of practices, guides, and procedures related to the performance and validation of analytical measurement systems.

9.11 Lab vs. Process Comparison Test—At start-up and on an annual basis, or on an as-necessary basis, perform a comparison of results from the on-line/at-line/in-line monitor and a laboratory-based analysis of a spot sample. Under certain operational conditions, direct comparison of the analyzer's result to a laboratory-based method may not be valid. In these cases, verification of the analyzer may be performed by comparing the analyzer's results with an appropriate Calibration Gas Mixture or a Reference Gas Mixture. Results consistent with those obtained at instrument start-up constitute acceptable instrument performance.

10. Calculation

10.1 The total sulfur content is calculated from the response of the detector to the sulfur specie being detected using the analyzed gas and the appropriate ASTM method. Software included with the instrumentation may perform the calculation. The user should be satisfied that the software is working properly and is accurately performing calculations. Methods related to determining the relative density of gaseous fuels can be found in Test Methods **D1070**.

11. Keywords

11.1 at-line monitor; continuous fuel monitor; on-line monitor; total sulfur

ADDITIONAL READING

- (1) American Gas Association, *Gas Measurement Manual*, Part 11, Measurement of Gas Properties, Washington, DC.
- (2) American Petroleum Institute, *API 14.1*, Chapter 14, Natural Gas Fluids Measurement; Section 1, Collecting and Handling of Natural Gas Samples for Custody Transfer, Fifth Edition, June 2001.
- (3) American Society of Mechanical Engineers, *Fluid Meters Their Theory and Application*, Sixth Edition, New York, 1971.
- (4) Clevett, Kenneth J., *Process Analyzer Technology*, Wiley-Interscience, New York, 1986.
- (5) Gas Processors Association, GPA-2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography, Tulsa.
- (6) Green, Don W., editor, *Perry's Chemical Engineer's Handbook*, Sixth Edition, McGraw-Hill Book Company, New York, 1984.
- (7) International Organization for Standardization, ISO 10715 Natural Gas Sampling Guide.
- (8) McMillan, Gregory K., and Considine, Douglas M., *Process Instruments and Controls Handbook*, 5th Edition, McGraw-Hill Professional, New York, 1999.
- (9) Miller, Richard W., *Flow Measurement Engineering Handbook*, Third Edition, McGraw-Hill, New York, 1996.
- (10) Nyquist, Harry, "Certain Topics in Telegraph Transmission Theory," *Trans. AIEE*, Vol 47, Apr. 1928, pp. 617-644.
- (11) Shannon, Claude E., "Communication in the Presence of Noise," *Proc. Institute of Radio Engineers*, Vol 37, no. 1, Jan. 1949, pp. 10-21.
- (12) Sherman, R. E., editor, *Analytical Instrumentation*, Instrument Society of America, Research Triangle Park, 1996.

ASTM Standards

- (13) C1068 Standard Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
- (14) D3764 Standard Practice for Validation of the Performance of Process Stream Analyzer Systems
- (15) D6122 Standard Practice for Validation of the Performance of Multivariate Process Infrared Spectrophotometers
- (16) D6299 Standard Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- (17) D6621 Standard Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials
- (18) E1866 Standard Guide for Establishing Spectrophotometer Performance Tests
- (19) E2027 Standard Practice for Performing Proficiency Tests
- (20) E2093 Standard Guide for Optimizing, Controlling and Reporting Test Method Uncertainty
- (21) E2165 Standard Practice for Establishing an Uncertainty Budget for the Chemical Analysis of Metals, Ores and Related Materials—performance methods need an uncertainty budget which includes the variance caused by sampling, sample prep and analysis (with-drawn)
- (22) E2437 Standard Practice for Designing and Validating Performance Based Test Methods
- (23) E2438 Standard Procedure for Implementing Standard Performance Test Methods

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