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Standard Practice for
Gas Chromatograph Based On-line/At-line Analysis for Sulfur Content of Gaseous Fuels[1]

This standard is issued under the fixed designation D7165; 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 ~~volatile~~ gas phase 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~~ 1 mL sample, is one hundred (100) to one million ~~(1,000,000).~~(1 000 000). This is equivalent to 0.1 to ~~1,000 mg/m3.~~1000 mg/m^3.

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

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.5 *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]

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~~D3609 ~~Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography~~Practice for Calibration Techniques Using Permeation Tubes

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

D4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)

D4150 Terminology Relating to Gaseous Fuels

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

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[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.

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
D6621 Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials
D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
D7493 Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical 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
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

2.2 *ISO ~~Standards~~Standards:*[3]
ISO 7504 Gas Analysis-Vocabulary

3. Terminology

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

3.2 ~~*Definitions:*~~*Definitions of Terms Specific to This Standard:*

~~3.1.1 *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.~~

~~3.1.1.1 *Discussion*—~~

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

~~3.1.2 *direct sampling*—Sampling where there is no direct connection between the medium to be sampled and the analytical unit.~~

~~3.1.3 *in-line instrument*—Instrument whose active element is installed in the pipeline and measures at pipeline conditions.~~

~~3.1.4 *on-line instrument*—Automated instrument that samples gas directly from the pipeline, but is installed externally.~~

~~3.1.5 *at-line instrument*—instrument requiring operator interaction to sample gas directly from the pipeline.~~

~~3.1.6 *continuous fuel monitor (CFM)*—Instrument that samples gas directly from the pipeline on a continuous or semi-continuous basis.~~

~~3.1.7 *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.~~

3.2.1 *near-real time monitoring ~~systems~~—systems, n—*~~Monitoring~~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.~~

3.2.1.1 *Discussion*—

The definition of a near real time monitoring system can be application specific.

~~3.2 *reference gas mixture, n*—a certified gas mixture with known composition used as a reference standard from which other compositional data are derived.~~

~~3.2.1 *Discussion*—~~

~~Reference Gas Mixtures are the analogues of measurement standards of reference standards (reference ISO 7504 paragraph 4.1.1).~~

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[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.

3.3 *Abbreviations:*

3.3.1 *CFM*—continuous fuel monitor

3.3.2 *SRM*—standard reference material

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

5.1 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, D7833, 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.).~~ 0.05 min (3 s). 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 ± 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 × 0.53 mm~~ 60 m × 0.53 mm ID fused silica open tubular column containing a 5 µm 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~~ 1 mV range recording potentiometer or equivalent, with a full-scale response time of ~~2 s~~ 2 s or less can be used. A ~~4-20 mA~~ 4-20 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.

6.4.4 *Data Management Systems*—Data management systems or other data and data processing repositories are sometimes used to collect and process the results from a wide variety of instrumentation at a single facility. The information is then available for rapid dissemination within the organization of the operating facility. Communications protocols with the data management system will dictate the required signal output requirements for the analyzer.

7. Reagents and Materials

NOTE 1—**Warning:** Sulfur compounds contained in permeation tubes or compressed gas cylinders may be flammable and harmful or fatal if ingested or inhaled. Permeation tubes, which emit their contents continuously, 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, hydrogen, argon, nitrogen, or helium can result in an explosion or in creating oxygen deficient atmospheres. Rapid release of argon, nitrogen, or helium can result in asphyxiation. Compressed air supports combustion.

7.1 *Sulfur Standards*—Accurate sulfur standards are required for the quantitation of the sulfur content ~~of natural gas.~~ in natural gas and other fuel type gases. Permeation and compressed gas standards should be stable, and of the highest available accuracy and purity.

7.1.1 *Permeation Devices*—Sulfur standards can be produced on demand using permeation tubes, one for each selected sulfur species, gravimetrically calibrated and certified at a convenient operating temperature. With 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. Permeation devices delivering calibrant at a known high purity must be used since contaminants will adversely impact the calculation of analyte concentration due to error in permeation rate calculated from differential weight measurements of these devices. It is suggested that certified permeation devices be used whenever available. Detailed guidance on calibration using permeation tubes can be found in Practice D3609.

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

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

7.1.1.3 Permeation tube emission rates are expressed in units of mass of the emitted sulfur compound contained inside per unit time, ~~i.e.~~ that is, nanograms of ~~methyl mercaptan~~ analyte per minute. The sulfur emission rate is calculated knowing the molecular formula of the sulfur compound used in the permeation tube.

7.1.1.4 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 ~~D3606~~D3609. These devices are discarded when the liquid contents are reduced to less than ten (10) percent of the initial volume or when the permeation surface is unusually discolored or otherwise compromised.

7.1.1.5 Permeation tubes must be stored in accordance with the manufacturer's recommendation. Improper storage can result in damage ~~and/or~~or a change in the characteristics of the permeation ~~membrane.~~ membrane, or both. Such damage ~~and/or characteristic change~~ or characteristic change, or both, results in an actual permeation rate that differs from the certified permeation rate.

7.2 *Compressed Gas Standards*—Alternatively, blended gaseous sulfur standards in nitrogen, helium, or methane base gas may be used. Care must be exercised in the use of compressed gas standards since they can introduce errors in measurement due to lack of uniformity in their manufacture or instability in their storage and use. Standards should be blended such that components will not condense under storage or while the standard is in use. 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 (Nederlands Meetinstituut) reference material.~~ NIST, NMi (Nederlands Meetinstituut), or similar provider of standard reference materials (SRMs).

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

7.2.2 All compressed gas standards must be re-certified as recommended by the manufacturer or as needed to ~~insure~~ensure accuracy.

7.3 The following sulfur compounds, including the molecular formula and the CAS number, are commonly found or are added to natural gas and related fuel gases and may be useful as calibrants for on-line and at-line monitors:

7.3.1 Hydrogen sulfide (H_2S) (7783-06-4)

7.3.2 Methyl mercaptan (CH_3SH) (74-93-1)

7.3.3 Ethyl mercaptan (CH_3CH_2SH) (75-08-1)

7.3.4 1-propanethiol ($CH_3CH_2CH_2SH$) (107-03-9)

7.3.5 2-propanethiol ($CH_3CHSHCH_3$) (75-33-2)

7.3.6 Dimethyl sulfide (CH_3SCH_3) (75-18-3)

7.3.7 Dimethyl disulfide (CH_3SSCH_3) (624-92-0)

7.3.8 Tetrahydrothiophene (THT) (110-01-0)

7.3.9 t-butyl mercaptan ($(CH_3)_3CSH$) (75-66-1)

7.4 Many applications require the periodic preparation of a calibration curve or a linearity verification as part of a QA program. To satisfy this need, three calibration standards can be used consisting of ~~volatile~~ gas phase sulfur species at:

7.4.1 10-30 percent of calibrated range

7.4.2 40-60 percent of calibrated range

7.4.3 80-100 percent of calibrated range

7.5 For applications where periodic preparation of a calibration curve is not required, a compressed gas standard certified at 80 % of the maximum expected concentration of analyte and analyzed periodically as a control or check standard is suggested as part of the users QA program.

8. Equipment Siting and Installation

~~The siting and installation of an at-line or on-line monitor is critical for collecting representative information on sulfur gas 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, the electrical classification of the area and the analyzer, appropriateness of samples from a sampling location, and, of course safety, issues.~~

8.1 The siting and installation of an at-line or on-line monitor is critical for collecting representative information on sulfur gas 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, the electrical classification of the area and the analyzer, appropriateness of samples from a sampling location, and, of course, safety issues.

8.2 An appropriate sample probe should be used for extracting a representative sample for transport to the analyzer.

8.3 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 less than 5 min or as necessary to meet the intended need.

8.4 Pretest sampling and analysis is critical to determining monitoring system characteristics, identify unforeseen factors affecting measurement, and to determine optimal operating conditions for the intended use.

8.5 The sampling system should be designed to maintain the integrity of the sample so that the analytical result truly represents the conditions existing in the process at the sample location.

8.6 The sampling system should provide for the necessary filtration, pressure reduction, and temperature adjustment to deliver a representative sample to the analyzer.

8.7 The sampling point must be carefully selected to ensure the collection of a representative sample.

8.8 The sample must be in the gas state at the sampling point, throughout the sampling system and instrument sample introduction system. The presence of solid or liquid material could result in collection of an unrepresentative gas sample or could interfere with the performance of the monitoring instrumentation.

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 ideally 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 *Daily Calibration Check*—It is recommended that instruments possessing auto calibration capability are calibrated ~~daily.~~ daily when in use. If the analyzer is equipped with an auto-verification feature, a calibration check, done biannually, daily, or at some other interval consistent with the intended use of the analyzer, using an appropriate Calibration Gas Mixture, should be performed. A calibration check can be performed as follows:

9.4.1 Perform consecutive triplicate injections using the appropriate Calibration Gas Mixture.

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

9.4.3 Record the second injection as the initial data point.

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

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

9.4.6 If the third injection does not satisfy criteria under 9.4.4, initiate ~~mitigation steps.~~investigation and corrective action as necessary.

9.4.7 Repeat steps 9.4.1 through 9.4.6, as required, for the low-span and high-span Calibration Gas Mixtures.

9.4.8 More than three injections may be used in some applications. In this case, the final two injections are used as per 9.4.3 through 9.4.7.

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 %~~ 10 % change in the calibrant response ~~during the course of~~ over 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%~~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 %~~ 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%~~90 % to ~~110%~~110 % of the theoretical amounts for the individual species in the test gas. Adjustments made to compensate for successive drifts exceeding ~~10 %~~ 10 % of the daily historical value may be indicative of an operational problem. As necessary, examine the retention time for each individual sulfur ~~specie~~species of interest. Verify that the retention time drift for individual species in the test gas does not consistently exceed ~~5%~~5 % for minor components or ~~2%~~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%~~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.