



Designation: D7493 – 22

Standard Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection¹

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1. Scope

1.1 This test method is for on-line measurement of gas phase sulfur-containing compounds in gaseous fuels by gas chromatography (GC) and electrochemical (EC) detection. This test method is applicable to hydrogen sulfide, C1 to C4 mercaptans, sulfides, and tetrahydrothiophene (THT).

1.1.1 Carbonyl sulfide (COS) is not measured according to this test method.

1.1.2 The detection range for sulfur compounds is approximately from 0.1 to 100 ppm(v) (mL/m^3) or 0.1 to 100 mg/m^3 at 25 °C, 101.3 kPa. The detection range will vary depending on the sample injection volume, chromatographic peak separation, and the sensitivity of the specific EC detector.

1.2 This test method describes a GC-EC method using capillary GC columns and a specific detector for natural gas and other gaseous fuels composed of mainly light (C4 and smaller) hydrocarbons. Alternative GC columns including packed columns, detector designs, and instrument parameters may be used, provided that chromatographic separation, quality control, and measurement objectives needed to comply with user or regulator needs, or both, are achieved.

1.3 This test method does not intend to identify and measure all individual sulfur species and is mainly employed for monitoring naturally occurring reduced sulfur compounds commonly found in natural gas and fuel gases or employed as an odorant in these gases.

1.4 This test method is typically employed in repetitive or continuous on-line monitoring of sulfur components in natural gas and fuel gases using a single sulfur calibration standard. Guidance for producing calibration curves specific to particular analytes or enhanced quality control procedures can be found in Test Methods D5504, D5623, D6228, D6968, ISO 19739, or GPA 2199.

¹ 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.

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1.5 The test method can be used for measuring sulfur compounds listed in Table 1 in air or other gaseous matrices, provided that compounds that can interfere with the GC separation and electrochemical detection are not present.

1.6 This test method is written as a companion to Practices D5287, D7165 and D7166.

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

1.8 *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.*

1.9 *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

D3609 Practice for Calibration Techniques Using Permeation Tubes

D4150 Terminology Relating to Gaseous Fuels

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5287 Practice for Automatic Sampling of Gaseous Fuels

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

D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection

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.

TABLE 1 Example Retention Times of Sulfur Components Observed for Several Column and Detector Sizes

GC-EC instrument	GC-EC #1	GC-EC #2	GC-EC #3	GC-EC #4
GC-Column and parameters	1/8 in. ID × 70 cm L, N ₂ , 12 mL/min, 65 °C	1.6 mm ID×1200 mm L, N ₂ , 100 mL/min, 20 °C	4 mm ID× 400 mm L, N ₂ , 100 mL/min, 20 °C	0.53 mm ID× 30 m, N ₂ , 4 mL/min, 58 °C
Detector Size	5×20 mm	5×20 mm	30×25 mm	5×20 mm
Sulfur Compound	RT (sec.)	RT (sec.)	RT (sec.)	RT (sec.)
Hydrogen sulfide, H ₂ S	30	30	30	98
Methyl mercaptan (MeSH)	70	66	60	141
Ethyl mercaptan (EtSH)	105	150	80	203
Dimethyl sulfide (DMS)	120	200	80	...
i-Propyl mercaptan (IPM)	160	240	160	268
t-Butyl mercaptan (TBM)	220	342	240	330
n-Propyl mercaptan (NPM)	265	426	290	375
i-Butyl mercaptan (IBM)	440	...	560	...
n-Butyl mercaptan (NBM)	585
Thiophane (THT)	900 ^A	720 ^A	2100	39 ^B
s-Butyl mercaptan (SBM)	548

^A The shorter GC column is employed for simultaneous accelerated analysis of THT.

^B Dual use of a second shorter column is used to elute THT as the first analyte.

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

D7165 Practice for Gas Chromatograph Based On-line/At-line Analysis for Sulfur Content of Gaseous Fuels

D7166 Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *ISO Standard*.³

ISO 19739 Natural Gas – Determination of Sulfur Compounds using Gas Chromatography

2.3 *GPA Standard*.⁴

GPA 2199 Determination - Determination of Specific Sulfur Compounds by Capillary Gas Chromatography and Sulfur Chemiluminescence Detection

3. Terminology

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

3.2 *Abbreviations*: Abbreviations are commonly used when discussing sulfur compounds. The following list of abbreviations is for sulfur compounds that can be determined according to this method.

3.2.1 *DES*—diethyl disulfide

3.2.2 *DI-TBDS*—di-tert-butyl-disulfide

3.2.3 *DMDS*—dimethyl disulfide

3.2.4 *DMS*—dimethyl sulfide

3.2.5 *EtSH*—ethyl mercaptan

3.2.6 *H₂S*—hydrogen sulfide

3.2.7 *IBM*—iso-butyl mercaptan

3.2.8 *IPM*—iso-propylmercaptan

3.2.9 *MeSH*—methyl mercaptan

3.2.10 *NBM*—n-butyl mercaptan

3.2.11 *NPM*—n-propyl mercaptan

3.2.12 *SBM*—sec-butyl mercaptan

3.2.13 *TBM*—tert-butyl mercaptan

3.2.14 *THT*—tetrahydrothiophene or thiophane

4. Summary of Test Method

4.1 Gaseous fuel is directly sampled on-line for analysis of sulfur compounds. Samples are introduced to the GC instrument through a conditioned or passivated sampling system. Sulfur compounds are separated by a GC column and measured by an EC detector. The method requires periodic calibration using certified standards. The test method conforms to the procedures stated in Practice **D7165**.

4.2 A fixed volume of the sample (normally 0.15 mL) is injected into a gas chromatograph operating isothermally where components are separated using two chromatographic columns in parallel.

4.3 GC-separated sulfur compounds are determined with an electrochemical detector using a chromic acid electrolyte in aqueous solution between 9 % and 10 %.

5. Significance and Use

5.1 Gaseous fuels, such as natural gas, petroleum gases and bio-gases, contain sulfur compounds that are naturally occurring or that are added as odorants for safety purposes. These sulfur compounds are odorous, toxic, corrosive to equipment, and can inhibit or destroy catalysts employed in gas processing and other end uses. Their accurate continuous measurement is important to gas processing, operation and use, and is frequently of regulatory interest.

5.2 Small amounts (typically, total of 4 to 6 ppm(v)) of sulfur odorants are added to natural gas and other fuel gases for safety purposes. Some sulfur odorants are reactive and may be oxidized to form more stable sulfur compounds having higher

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>.

⁴ Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, <http://www.gasprocessors.com>.

odor thresholds which adversely impact the potential safety of the gas delivery systems and gas users. Gaseous fuels are analyzed for sulfur compounds and odorant levels to assist in pipeline integrity surveillance and to ensure appropriate odorant levels for public safety.

5.3 This method offers an on-line method to continuously identify and quantify individual target sulfur species in gaseous fuel with automatic calibration and validation.

6. Apparatus

6.1 *Chromatograph*—Industrial gas chromatograph with an isothermal oven, automatic injection valve, and software necessary for interfacing to a chromic acid electrochemical detector and designed for the intended application. The GC system must be inert, well-conditioned and passivated with a gas containing the sulfur compounds of interest to ensure reliable results.

6.1.1 *Sample Inlet System*—The gas sample is introduced to the GC by sample loop injection. An automated non-reactive gas sampling valve is employed for a fixed sample loop injection. The sample injection port must be heated continuously at a temperature significantly ($\sim 10\text{ }^{\circ}\text{C}$) above the temperature at which the gas is sampled to avoid sample condensation and discrimination. Inert tubing made of non-permeable, non-sorbing and non-reactive materials, as short as possible and heat traced at the same temperature, is employed for transferring the sample from a sample source to the gas sampling valve and to the GC inlet system. Silica-coated 316 stainless steel (s.s.) and non-permeable polytetrafluoroethylene (PTFE) type tubing are often employed. Different size fixed-

volume sample loops (0.05 to 0.15 mL) may be used to target multiple concentration ranges for components in a gas, provided chromatographic separation and quality control objectives are obtained. The same non-reactive materials are used for the sample loop to minimize decomposition or absorption of reactive species. The sampling and GC inlet system must be well conditioned or passivated and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds, such as tert-butyl mercaptan (TBM). A programmable and computer-controlled multi-stream sample selector can be used to sample fuel gases and calibration gases.

6.1.2 *Column Temperature*—The GC must be capable of maintaining an isothermal temperature, normally at $58\text{ }^{\circ}\text{C}$, with temperature variation not exceeding $\pm 0.5\text{ }^{\circ}\text{C}$.

6.1.3 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is necessary for optimal and consistent analytical performance. Control is best provided by use of pressure regulators like Piezo valves and fixed flow restrictors. Piezo valves allow for remote adjustments when needed. The gas flow is measured using a gas flow meter either volumetrically or based upon mass flow rates. Mass flow controllers, capable of maintaining gas flow constant to $\pm 1\%$ at the required flow rates are used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa greater than the regulated gas at the instrument to compensate for system back pressure.

6.1.4 *Detector*—An EC detector, whose operation is based upon the reduction/oxidation reaction between reduced sulfur compounds and a solution of chromic acid (Fig. 1), is used in

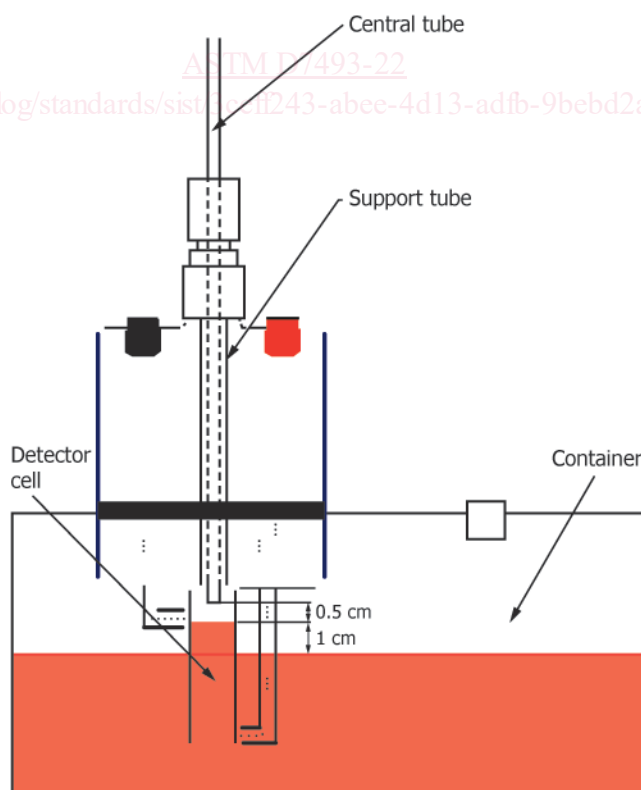


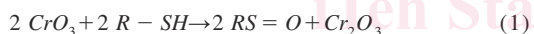
FIG. 1 Typical Electrochemical Detection Cell

this method. The detector is set according to the manufacturer's specifications for this application.

6.1.4.1 The detector consists of an electrochemical system made of glass and a container made of glass or methyl polymethacrylate. The electrodes, two pieces of platinum gauze grids, are arranged vertically in parallel, and are welded in a borosilicate glass tube. These grids are isolated from each other and other conductive materials and connected to an amplifier for data acquisition.

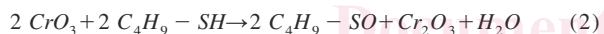
6.1.4.2 The electrolyte, a solution of chromium (VI) oxide in distilled or deionized water (100 g/L or 0.66 mole/L), is contained in an acid-resistant vessel. A tube fitted with the electrodes is dipped into the solution such that the liquid is retained by capillary action within the tube at a level approximately midway between two grids.

6.1.4.3 The gas flow from the GC column is discharged through a narrow glass or PTFE tube (0.7 mm ID) immediately above the upper grid center (normally 5 mm). Each sulfur compound sequentially elutes and reacts with chromic acid. Possible reaction mechanisms are illustrated as Eq 1 and Eq 2. The redox reaction occurs on the electrode surface, creating a potential difference between the two electrodes, thus causing a current to be measured (using a low resistance measuring circuit). For example, TBM is oxidized to t-butyl sulfoxide and chromium oxide (Eq 2).



where:

R = organic moieties, such as C_xH_y.



6.2 *Column*—30 m of 0.53 mm ID metallic capillary column with 3 μm film thickness of 624 or equivalent stationary phase has been successfully used in performance of this test method. However, other columns including packed columns that provide adequate retention and resolution characteristics under the experimental conditions as described in 8.1 can be used. A second GC column of the same ID and phase, but of a shorter length, can be employed for faster measurement of late-eluting sulfur compounds such as THT. In this case, two columns are connected to the GC injection system using a 10-port valve to direct sample flow through the appropriate column and then onto the EC detector; thus, allowing measurement of low molecular weight sulfur gases and high molecular weight sulfur gases such as THT from a single sample injection, THT may exit first in such mounting of columns if a dual column (column commutation) is used. The elution of high molecular weight sulfur gases such as THT may also be accelerated by sped up carrier gas flow rate after the elution of TBM. When samples may contain high boiling or instrument damaging substances, a backflush column may be employed to remove these materials before they reach the chromatographic column and EC detector. The performance of GC columns shall provide adequate separation of target sulfur compounds for the particular application.

6.3 Data Acquisition

6.3.1 The device and software must have the following capabilities:

- 6.3.1.1 Graphic presentation of the chromatogram.
- 6.3.1.2 Digital display of chromatographic peak areas.
- 6.3.1.3 Identification of peaks by retention time or relative retention time, or both.
- 6.3.1.4 Calculation and use of response factors.
- 6.3.1.5 External standard calculation and data presentation.
- 6.3.1.6 Instrument control for electrochemical detector operation, such as gas pressure and flow control.

7. Reagents and Materials

7.1 *High-pressure Cylinder Reference Gas Standards*—Gas standards of high purity with certified stability and accuracy are used.

7.1.1 *Sulfur Gas Standards*—Single or multiple sulfur compounds in a compressed gas of high purity 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 analyte instability. The non-mandatory protocol for compressed gas standards cited in Appendix X1 of Test Method D5504 can be used to ensure the quality of standards and to establish traceability to a National Institute of Standards and Technology (NIST), national metrology institute (NMI), or other standard reference material (SRM).

7.1.2 Multiple sulfur gas standard mixes should be used as recommended by a compressed gas standard manufacturer to assure the long-term stability of sulfur compounds. The standard should be re-certified as per manufacturers' recommendations or as needed for regulatory compliance.

7.1.3 *Compressed Gas Standard Delivery System*—Pressure regulators, gas lines, and fittings must be appropriate for the delivery of sulfur gases and well passivated or inert.

7.2 *Sulfur Permeation Standards*—Gaseous standards generated from individual or a combination of certified permeation tubes and devices at a constant temperature (±0.1 °C) and a constant flow rate can be used for calibrations. The standard concentration is calculated by mass loss at a fixed temperature and dilution gas flow rate. Permeation devices should be calibrated gravimetrically to the nearest 0.01 mg. Impurities permeated from each device must be detected, measured, and accounted for in the mass loss if they are present above a level of 0.1 % of the permeated sulfur species. Permeation devices shall be discarded when the liquid content is reduced to less than 10 % of the initial volume. See Practice D3609 for further information on the proper use of permeation devices.

7.2.1 **Warning**—Sulfur compounds may be flammable and may be harmful if ingested or inhaled.

7.3 *Carrier Gas*—Helium or nitrogen with a minimum purity of 99.999 % with maximum concentrations of 1 ppm(v) oxygen, 1 ppm(v) water, and 0.5 ppm(v) total hydrocarbons. Use of air as a carrier gas is not recommended since many sulfur compounds react with air. Additional purification of carrier gas is recommended using molecular sieves or other suitable agents to remove hydrocarbons, oxygen, or both, in helium and nitrogen. If a purifier is used, the maximum allowable concentrations of oxygen, water and total hydrocarbons at the outlet of the purifier must be specified. A dual stage

regulator and a carrier gas pressure sufficiently high to ensure a constant carrier gas flow rate are needed (see 6.1.3).

7.3.1 **Warning**—Carrier gas may be from a source of compressed gases under high pressure.

7.4 *Chromium Oxide*—Reagent grade (99.9 % minimum purity).

7.4.1 **Warning**—Toxic chemical, handle with rubber gloves and caution. Waste reagent should be chemically reduced and properly disposed.

8. Preparation of Apparatus and Calibration

8.1 *Chromatograph*—Place in service according to the manufacturer’s instructions. Typical operating conditions are shown in Table 2.

NOTE 1—DMDS, DES, DI-TBDS, IBM, and NBM can be analyzed with appropriate selection of chromatographic conditions.

8.2 *Electrochemical Detector*—Place the detector in service according to the manufacturer’s instructions. In general, carefully remove the glass detector assembly from the empty chromic acid reservoir. Fill the reservoir with chromic acid solution to the mark, approximately 3 cm high. Slowly insert the detector into the reservoir until chromic acid solution reaches and passes the upper grid. Very slowly lift the detector until the level of the solution is at 1 cm below the upper grid. The solution should suspend in the detector tube by capillary action. Repeat the insertion of the glass detector if air bubbles are present or the solution level in the detector tube is incorrect, or both.

8.2.1 **Warning**—Handle chromic acid with extreme care. Chromic acid is carcinogenic and corrosive. Contact can severely irritate and burn skin and eyes with possible eye damage. Breathing Chromic Acid can irritate the nose, throat, and lungs causing coughing, wheezing, or shortness of breath, or a combination thereof. Wear appropriate personal protective equipment including rubber gloves and plastic aprons.

8.3 *Sample Injection*—A fixed size sample loop is used to conduct a performance check. A linear calibration curve may be determined by using standards of varying concentrations or different sample loop sizes.

8.4 *Chromatography*—A typical chromatogram for sulfur compounds present at ppm(v) levels is shown in Fig. 2. Retention times for compounds in this chromatogram are listed

in Column 4 of Table 1. The typical cycle time is 12 min. The retention times of selected sulfur compounds using alternative instrument settings are listed for reference in Table 1. The elution sequence and distribution of sulfur peaks, except THT, should remain approximately the same under these alternative conditions. Acceptable resolution defined as baseline separation of adjacent peaks is the goal for chromatographic separation, although GC peak broadening is a characteristic of EC detectors with peak overlap occasionally observed. Baseline separation of two peaks using EC detection is normally defined as the EC detector signal of the lead compound returning to a point at least 5 % below the top of the smallest peak. Less than baseline separation may lead to poorer precision and larger bias than baseline separated peaks. Each GC-EC chromatogram should be examined thoroughly. High concentrations of some hydrocarbons may interfere with measurements; although, typical natural gas hydrocarbon concentrations have not been reported to show interference with sulfur gas measurement. Matrix studies can be conducted to ascertain whether a particular gas composition results in chromatographic or detector interferences, or both. For high sulfur compound concentrations, a smaller volume sample loop can be used to improve chromatographic peak separation.

8.5 *Detector Response Calibration*—Analyze calibration gases to obtain the chromatograms and peak areas for response factor determination as per Eq 3 (Practice D4626). Response factors of different sulfur compounds vary considerably as shown in Table 3. Therefore, response factors for each component of interest are necessary for the accurate determination of specific species. Determine the linear range of detector response toward each sulfur compound. A linear standard curve is constructed, and the linear correlation factor is calculated. Detector linearity based upon a multi-point calibration curve is essential for on-line measurement accuracy and should be verified at a frequency recommended by the instrument manufacturer, as required by regulation or as required for process control.

$$RF = C_n/A_n \tag{3}$$

where:

- RF = response factor of sulfur compound,
- C_n = concentration of the compound in the sampled gas on a common measurement unit, and
- A_n = peak area of the compound measured.

NOTE 2—Typically, instrument manufacturers design GC-EC systems under standardized temperatures and pressures. Therefore, users are advised to ensure the temperature and gas pressure used during calibration is comparable to that of sampled gas. Analytic results can be corrected for inconsistencies by employing the gas law.

NOTE 3—The instrument response should be linear for ppbv and ppm(v) range concentrations without linearization. If linear response is not observed, perform corrective action or contact the instrument manufacturer.

8.5.1 *Example*—Consider a 1.0 ppm(v) of dimethyl sulfide (DMS) in natural gas injected onto a GC with a 0.15 mL fixed sample loop producing a sulfur response of 2000 counts.

$$1 \text{ PPM}_v \text{ DMS} = 1 \text{ PPM}_v \text{ Sulfur}$$

TABLE 2 Typical Gas Chromatographic Operating Parameters

Gap Sample Loop:	0.15 mL at 10 °C above GC column oven temperature
Injection Type:	Sampling Loop
Carrier Gas:	Nitrogen, air, or helium at 4 mL/min with micro EC detector
Column Oven:	Isotherm, 58 °C
Detector:	Reagent and instrument operating parameters as recommended by the GC-EC manufacturer