



Designation: **D7493–14 (Reapproved 2018) D7493 – 22**

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

This standard is issued under the fixed designation D7493; 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 test method is for on-line measurement of ~~volatile 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 covered in measured according to this test method.

1.1.2 The detection range for sulfur compounds is approximately from 0.1 to 100 ~~ppm~~ **ppm(v)** (mL/m³) or 0.1 to 100 mg/m³ at 25 °C, 101.3 kPa. The detection range ~~may will~~ vary depending on the sample injection volume, chromatographic peak separation, and the sensitivity ~~to of~~ the specific EC detector.

1.2 This test method describes a GC-EC method ~~employing packed~~ using capillary GC columns and a specific detector for natural gas and other gaseous ~~fuel 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~~ user or regulator needs, or both, are achieved.

1.3 This test method does not intend to identify and measure all individual sulfur ~~species~~ 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 ~~The~~ 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. ~~Need for a multipoint calibration curve or~~ Guidance for producing calibration curves specific to particular analytes or enhanced quality control procedures can be satisfied by making use of procedures delineated found in Test Methods **D5504, D5623, D6228, D6968**, ISO 19739, or GPA 2199.

1.5 The test method can be used for ~~measurement of all~~ measuring sulfur compounds listed in **Table 1** in air or other gaseous matrices, provided that ~~no~~ 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 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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TABLE 1 Typical Retention Times of Sulfur Components of Different GC-ECD Runs

GC-ECD instrument	GC-ECD #1	GC-ECD #2	GC-ECD #3
GC-Column and parameters	1/8 in. ID x 70 cm L, N ₂ , 12 mL/min, 65 °C	1.6 mm ID x 1200 mm L, N ₂ , 100 mL/min, 20 °C	4 mm ID x 400 mm L, N ₂ , 100 mL/min, 20 °C
Detector Size	5x20 mm	5x20 mm	30x25 mm
Sulfur Compound	RT (sec.)	RT (sec.)	RT (sec.)
Hydrogen sulfide, H ₂ S	30	30	30
Methyl mercaptan (MeSH)	70	66	60
Ethyl mercaptan (EtSH)	105	150	80
Dimethyl sulfide (DMS)	120	200	80
i-Propyl mercaptan (IPM)	160	240	160
t-Butyl mercaptan (TBM)	220	342	240
n-Propyl mercaptan (NPM)	265	426	290
i-Butyl mercaptan (IBM)	440	...	560
n-Butyl mercaptan (NBM)	585
Thiophane (THT)	900 ^A	720 ^A	2100

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

GC-ECD instrument	GC-ECD #1	GC-ECD #2	GC-ECD #3	GC-ECD #4
GC-Column and parameters	1/8 in. ID x 70 cm L, N ₂ , 12 mL/min, 65 °C	1.6 mm ID x 1200 mm L, N ₂ , 100 mL/min, 20 °C	4 mm ID x 400 mm L, N ₂ , 100 mL/min, 20 °C	0.53 mm ID x 30 m, N ₂ , 4 mL/ min, 58 °C
Detector Size	5x20 mm	5x20 mm	30x25 mm	5x20 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

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

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

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
- D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric 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.

[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 Standards:~~Standard.³

~~ISO 19739 Natural gas~~Gas – Determination of sulfur compounds by gas chromatographySulfur Compounds using Gas Chromatography

2.3 ~~GPA Standard~~Standard.⁴

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

3. Terminology

3.1 ~~Common terminology used in this method are cited in~~For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology ~~D4150~~. Sulfur compounds are commonly referred by their initials (chemical or formula), for example,

3.2 ~~Abbreviations:~~

hydrogen sulfide	= H ₂ S
methyl mercaptan	= MeSH (MM)
ethyl mercaptan	= EtSH (EM)
dimethyl sulfide	= DMS
i-Propyl mercaptan	= IPM
n-Propyl mercaptan	= NPM
t-Butyl mercaptan	= TBM
tetrahydrothiophene	= THT or Thiophane

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 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>.

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 practices/procedures stated in Practice **D7165**.

4.2 A fixed volume of the sample (normally ~~0.25 mL~~) 0.15 mL) is injected into a gas chromatograph operating isothermally where components are separated using two chromatographic ~~columns~~ columns in parallel.

4.3 GC-separated sulfur compounds are determined using with an electrochemical detector utilizing using a chromic acid ~~electrolyte~~ 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 utilization use, and is frequently of regulatory interest.

5.2 Small amounts (typically, total of 4 to ~~6 ppm(v)~~) 6 ppm(v)) of sulfur odorants are added to natural gas and other fuel gases for safety purposes. Some sulfur odorants are reactive reactive and may be oxidized to form more stable sulfur compounds having ~~lower~~ higher 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 technique/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 (~10 °C) above the temperature at which the gas was 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, ~~should be~~ 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 (~~0.25 to 10.0 mL~~) (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 ~~avoid possible~~ 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~~ 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 gas chromatograph GC must be capable of maintaining an isothermal temperature, normally at 65°C ; 58°C , with temperature variation not exceeding $\pm 0.5^{\circ}\text{C}$.

6.1.3 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is necessary for ~~optimum~~optimal and consistent analytical performance. Control is best provided by the use of pressure regulators like Piezo valves and fixed flow restrictors. Piezo valves allow for remote adjustments when needed. The gas flow rate 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 $\pm 1\%$; $\pm 1\%$ at the required flow rates should be are used. The supply pressure of the gas delivered to the gas chromatograph must be at least ~~69~~69 kPa (10 psi); ~~69~~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 this method. The detector is set according to the manufacturer's specifications for this particular application. ~~One EC detector is normally employed for measurement. A second column is employed for detection of late-eluting sulfur compounds, such as THT. application.~~

6.1.4.1 The detector consists of ~~a~~an electrochemical system made of glass and a container made of glass or methyl polymethacrylate ~~container. 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~~100 g ~~g/L~~ or 0.66L or 0.66 mole ~~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 (~~2 mm~~0.7 mm ID) immediately above the upper grid center (normally ~~5 mm~~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, ~~t-butyl mercaptan~~TBM is oxidized to t-butyl sulfoxide and chromium oxide (Eq 2).

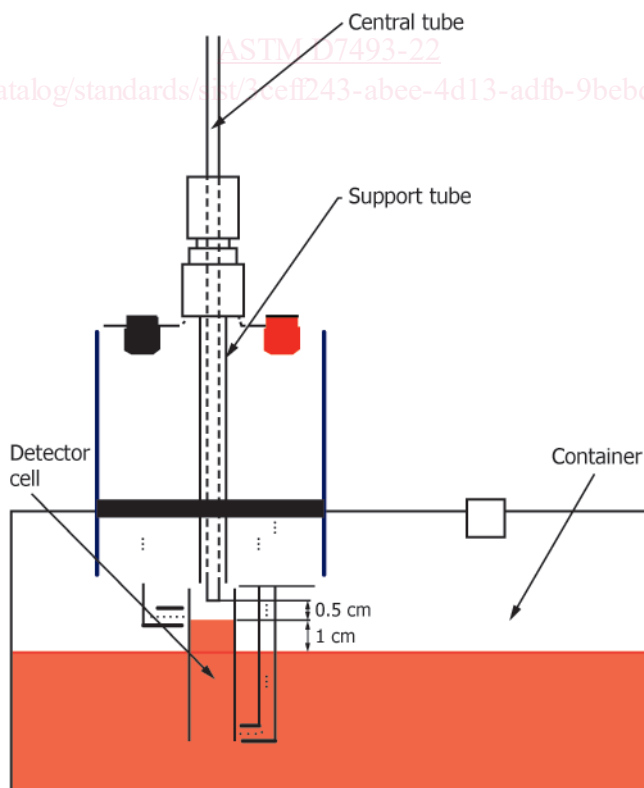


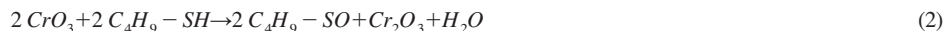
FIG. 1 Typical Electrochemical Detection Cell



where:

R = ~~organic moieties, such as C_xH_y~~

R = organic moieties, such as C_xH_y.



6.2 ~~Column—1200 mm of 1.6 mm ID glass or PTFE tubing packed with 150 to 180 μm (80 to 100 mesh) Chromosorb W support~~ 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. ~~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 increased speed 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 give 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 ~~instability in their storage and use.~~ 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~~) or other (~~NIST~~), national metrology institute (~~NMI~~) (~~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~~ long-term stability of sulfur ~~components~~ 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 ~~inert~~, appropriate for the delivery of sulfur gases and well ~~passivated~~ 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~~ 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 %~~ 0.1 % of the permeated sulfur species. Permeation devices shall be discarded when the liquid content is reduced to less than ~~10 %~~ 10 % of the initial volume. See Practice **D3609** for further information on the proper use of permeation devices.

~~NOTE 1—Warning: Sulfur compounds may be flammable and may be harmful if ingested or inhaled.~~

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

~~7.3 Carrier Gas—Helium, air, Helium or nitrogen of high purity (99.999 % minimum purity), 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 6.1.46.1.3).~~

~~NOTE 2—Warning: Carrier gas employed may be from a source of compressed gases under high pressure.~~

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).

~~NOTE 3—Warning: Toxic chemical, handling with rubber gloves and caution. Waste reagent should be chemically reduced and properly disposed.~~

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.

TABLE 2 Typical Gas Chromatographic Operating Parameters

Gap	
Sample Loop:	0.25 mL at 10 °C above GC column oven temperature
Gap	
Sample Loop:	0.15 mL at 10 °C above GC column oven temperature
Injection Type:	Sampling Loop
Carrier Gas:	Helium, air or nitrogen at 12 mL/min with micro-EG detector
Carrier Gas:	Nitrogen, air, or helium at 4 mL/min with micro EC detector
Column Oven:	Isotherm, 65 °C
Column Oven:	Isotherm, 58 °C
Detector:	Reagent and instrument operating parameters as recommended by the GC-EC manufacturer