



Designation: D7493 – 14

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 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 this test method.

1.1.2 The detection range for sulfur compounds is approximately from 0.1 to 100 ppmv (mL/m^3) or 0.1 to 100 mg/m^3 . The detection range may vary depending on the sample injection volume, chromatographic peak separation and the sensitivity to the specific EC detector.

1.2 This test method describes a GC-EC method employing packed GC columns and a specific detector for natural gas and other gaseous fuel composed of mainly light (C4 and smaller) hydrocarbons. Alternative GC 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 The 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 quality control procedures can be satisfied by making use of procedures delineated in Test Methods D5504, D5623, D6228, D6968, ISO 19739, or GPA 2199.

1.5 The test method can be used for measurement of all 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 present.

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

1.7 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

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

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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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 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× 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 |
| Detector Size | 5×20 mm | 5×20 mm | 30×25 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 |

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

[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](#)

2.2 *ISO Standards*:³

[ISO 19739 Natural gas – Determination of sulfur compounds by 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 Common terminology used in this method are cited in Terminology [D4150](#). Sulfur compounds are commonly referred by their initials (chemical or formula), for example,

3.2 *Abbreviations*:

| | |
|----------------------------|--------------------|
| <i>hydrogen sulfide</i> | = H ₂ S |
| <i>methyl mercaptan</i> | = MeSH (MM) |
| <i>ethyl mercaptan</i> | = EtSH (EM) |
| <i>dimethyl sulfide</i> | = DMS |
| <i>i-Propyl mercaptan</i> | = IPM |
| <i>n-Propyl mercaptan</i> | = NPM |
| <i>t-Butyl mercaptan</i> | = TBM |
| <i>tetrahydrothiophene</i> | = THT 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 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 stated in Practice [D7165](#).

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>.

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

4.3 GC-separated sulfur compounds are determined using an electrochemical detector utilizing a chromic acid electrolyte.

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, 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, and is frequently of regulatory interest.

5.2 Small amounts (typically, total of 4 to 6 ppmv) 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 lower 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 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 ($\sim 10^\circ\text{C}$) 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 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) 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 decomposition or absorption of reactive species. The sampling and GC inlet system must be well conditioned and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds, such as tert-butyl mercaptan. 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 must be capable of maintaining an isothermal temperature, normally at 65°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 and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. 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 $\pm 1\%$ at the required flow rates should be used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa (10 psi) 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.

6.1.4.1 The detector consists of a glass or methyl polymethacrylate container. 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 (2 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.

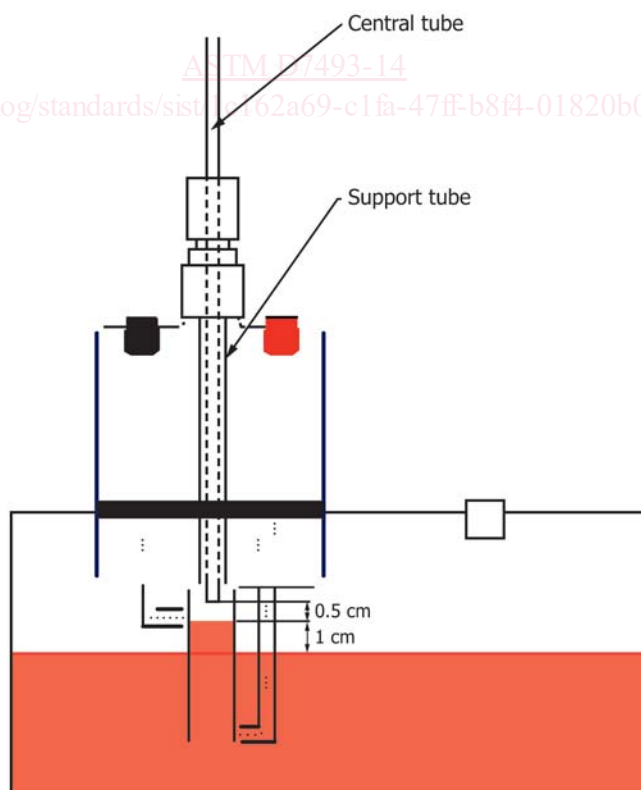


FIG. 1 Typical Electrochemical Detection Cell