



Designation: **D7493 – 08 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. ~~The~~This test method is applicable to hydrogen sulfide, ~~C1–C4–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~~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 ~~of~~ to the specific EC detector.

1.2 This test method describes a GC-EC method employing packed GC columns and a specific detector ~~as an illustration for~~ natural gas and other gaseous fuel ~~containing~~ composed of mainly light (C4 and smaller) hydrocarbons. Alternative GC columns, detector designs and instrument parameters may be used ~~for the same analysis or for different types of gaseous fuel, provided that appropriate chromatographic separation and optimal detection of these compounds can 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 ~~natural sulfur and sulfur odorant naturally occurring~~ reduced sulfur compounds commonly found in natural gas and fuel gases or employed as an odorous warning agent in fuel odorant in these gases.

1.4 The test method is ~~normally~~typically employed ~~for~~ in repetitive or continuous on-line monitoring of sulfur components in natural gas and fuel gases ~~with using a single sulfur standard. The test method may be employed for laboratory quality measurement with more extensive calibration. (See 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, ISO 6326-2, and or GPA 2199.~~

1.5 The test method can be used for measurement of all ~~listed~~ sulfur compounds listed in Table 1 in air or other gases, gaseous matrices, provided that no compound, which compounds that can interfere with the GC separation and electrochemical detection, is ~~detection are~~ present.

1.6 This test method is written ~~in conjunction with~~ 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

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 21 Typical Retention Times of Sulfur Components of Different GC-ECD Runs

GC-ED instrument	GC-ED #1	GC-ED #2	GC-ED #3
GC-EC instrument	GC-EC #1	GC-EC #2	GC-EC #3
GC-Column and parameters	1/8 in. IDx 70cm L, N ₂ , 12ml/min, 65 °C	1.6 mm IDx 1200 mm L, N ₂ , 100 ml/min, 20 °C	4 mm IDx 400 mm L, N ₂ , 100 ml/min, 20 °C
GC-Column and parameters	1/8 in. IDx 70 cm L, N ₂ , 12 mL/min, 65 °C	1.6 mm IDx 1200 mm L, N ₂ , 100 mL/min, 20 °C	4 mm IDx 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
Hydrogen sulfide, H ₂ S	30	30	30
Methyl mercaptan (MM)	70	66	60
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.

[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](#)

[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](#)

[ISO 6326-2 Gas Analysis – Determination of Sulphur Compounds in Natural gas – Part 2: Gas Chromatographic Method Using an Electrochemical Detector for The Determination of Odoriferous Sulphur Compounds](#)

2.3 GPA Standard⁴

[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 [D4150-3.2](#). Sulfur compounds are commonly referred by their initials (chemical or formula), for example,

3.2 ~~Abbreviations:~~ 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 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. Summary of Test Method

4.1 Gaseous fuel is directly sampled on-line for analysis of ~~specific and normally reactive~~ sulfur compounds. Samples are introduced to ~~an inert~~ the GC instrument through ~~an inert~~ a sampling system. Sulfur compounds are separated by a GC column and measured by an EC detector. The method requires ~~frequent~~ periodic calibration using ~~stable~~ certified standards. The test method conforms to the ~~standard practice of~~ practices stated in Practice [D7165](#).

4.2 A fixed volume of the ~~fuel gas sample~~ (normally 0.25 mL) is injected into ~~an isothermal~~ a gas chromatograph where it is passed through a 1.2 meter, 1.6 mm I.D., Chromosorb W column. A ~~varying amount of sample and other GC columns with or without column back-flush technique can be used for sensitive detection of sulfur with optimal separation.~~ operating isothermally where components are separated using two chromatographic columns.

4.3 ~~Specific~~ GC-separated sulfur compounds are ~~detected by~~ determined using an electrochemical detector utilizing a chromic acid electrolyte. ~~Detectors with different physical designs are commercially available and may be employed.~~

5. Significance and Use

5.1 Gaseous fuels, such as natural gas, petroleum gases and bio-gases, contain ~~varying amounts and types of~~ sulfur compounds: sulfur compounds that are naturally occurring or that are added as odorants for safety purposes. These sulfur compounds are ~~generally~~ odorous, corrosive to equipment, and can inhibit or destroy catalysts employed in gas processing and ~~end use, such as those used in fuel cell.~~ Their ~~accurate on-line measurement is essential~~ 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 ~~4-6 PPMv~~ of of 4 to 6 ppmv) of sulfur odorants are added to natural gas and other fuel gases for safety purposes. Some sulfur odorants ~~can be~~ are reactive, and may be oxidized, forming oxidized to form more stable sulfur compounds having lower odor thresholds. ~~These gaseous thresholds which adversely impact the potential safety of the gas delivery systems and gas users.~~ Gaseous fuels are analyzed for sulfur odorants to help in monitoring 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 ~~and oven~~, automatic injection valve, and software necessary for interfacing to a chromic acid electrochemical detector and ~~designed for the intended application and performance.~~ application. The GC system must be inert, ~~well-conditioned~~ 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 ($\sim 10^\circ\text{C}$) ($\sim 10^\circ\text{C}$) 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 Teflon-polytetrafluoroethylene (PTFE) type tubing are often employed. Different size fixed-volume ~~sample~~ sample loops (0.25 to 10.0 mL) may be used for target concentration ranges, provided with adequate chromatographic separation. 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~~ sample loop to avoid possible decomposition or absorption of reactive species. ~~When necessary, a precision glass syringe with a gas-tight Teflon-seated plunger is used to manually introduce sample or calibration standards through a PTFE septum at the front of GC columns.~~ 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 $0.5^\circ\text{C} \pm 0.5^\circ\text{C}$.

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 by any appropriate means and the required gas flow indicated by the use of a pressure gauge, 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 ~~can also should~~ be used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa (10 psig) greater than the regulated gas at the instrument to compensate for the system back pressure.

6.1.4 *Detector*—An EC ~~detector using chromic acid chemistry~~ 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 ~~the~~ this particular application. One EC detector is normally employed for

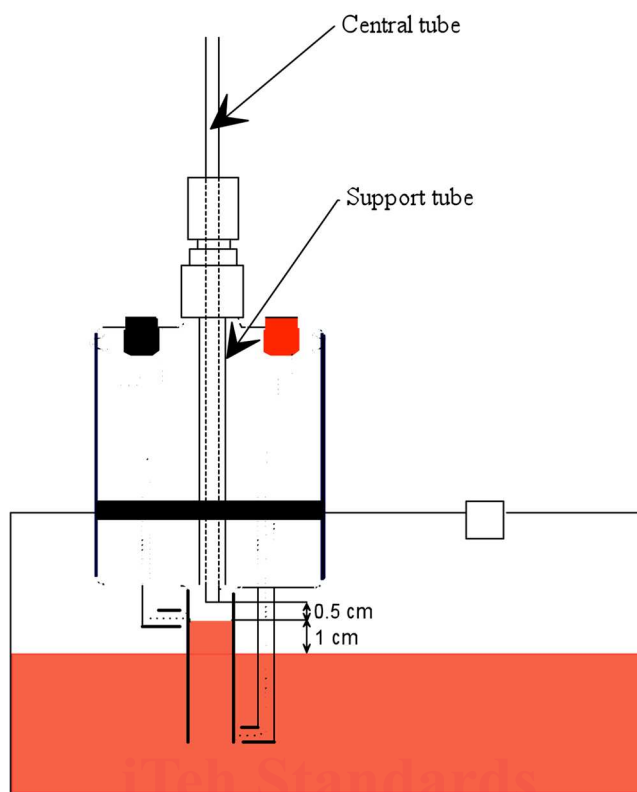


FIG. 1 Typical Electrochemical Detection Cell

(<https://standards.iteh.ai>)

measurement. A second EC detector may be employed for simultaneous detection of late-eluting sulfur compound, such as THT, using a shorter GC column and/or at different optimal separation conditions.

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

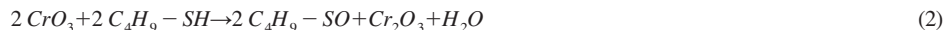
6.1.4.2 The electrolyte, a solution of chromium (VI) oxide in distilled or deionized water (100 g/L or 0.66 mole/L), is contained in an acid-resistant vessel. A tube fitted with the electrodes dips into the solution such that the liquid is retained by capillary action within the tube at a level approximately at 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. The redox reaction occurs on the electrode surface, creating a potential difference between the two electrodes, thus causing a current which is to be measured in (using a low resistance measuring circuit). For example, *t*-butyl mercaptan is oxidized to *t*-butyl sulfoxide and chromium oxide (Eq 2).



where:

R = organic moieties, such as C_xH_y



6.2 Column—A 1200 mm of 1.6 mm ID glass or PTFE tubing packed with 150-180 μm (80-100-150 to 180 μm (80 to 100 mesh) Chromosorb W support is used. The column shall have been successfully used in performance of this test method. However, other columns that provide adequate retention and resolution characteristics under the experimental conditions as described in 8.1. Other columns that can provide equivalent or desirable separation can be employed as well. For example, a 400 mm of 4 mm ID tubing packed with the same support has been used with different detector designs. can be used. A second GC column of the same ID and phase with phase, but of a shorter length is often length, can be employed for faster measurement of late-eluting sulfur compounds, compounds such as THT. Two GC columns can be plumbed. In this case, two columns are connected to the GC injection system using a 10-port valve to direct light sulfur compounds and THT sequentially for complete detection using one or two EC detectors. 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. The elution of high molecular weight sulfur gases such as THT may also be accelerated by increased carrier gas flow rate after the elution of