



# Standard Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection<sup>1</sup>

This standard is issued under the fixed designation D 7493; 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 ( $\epsilon$ ) 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 test method is applicable to hydrogen sulfide, C1-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 or 0.1 to 100 mg/m<sup>3</sup>. The detection range may vary depending on the sample injection volume, chromatographic peak separation and the sensitivity of 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 mainly light 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 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 compounds commonly found in fuel gases or employed as an odorous warning agent in fuel gases.

1.4 The test method is normally employed for repetitive on-line monitoring of sulfur components in fuel gases with a single sulfur standard. The test method may be employed for laboratory-quality measurement with more extensive calibration. (See Test Methods [D 5504](#), [D 5623](#), [D 6228](#), [D 6968](#), [ISO 19739](#), [ISO 6326-2](#), and [GPA 2199](#).)

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

1.6 This test method is written in conjunction with Practices [D 5287](#), [D 7165](#) and [D 7166](#).

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:*<sup>2</sup>

[D 3609 Practice for Calibration Techniques Using Permeation Tubes](#)

[D 4150 Terminology Relating to Gaseous Fuels](#)

[D 4626 Practice for Calculation of Gas Chromatographic Response Factors](#)

[D 5287 Practice for Automatic Sampling of Gaseous Fuels](#)

[D 5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence](#)

[D 5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection](#)

[D 6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection](#)

[D 6968 Test Method for Simultaneous Measurement of Sulfur Compounds and Minor Hydrocarbons in Natural Gas and Gaseous Fuels by Gas Chromatography and Atomic Emission Detection](#)

[D 7165 Practice for Gas Chromatograph Based On-line/At-line Analysis for Sulfur Content of Gaseous Fuels](#)

[D 7166 Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels](#)

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

## 2.2 ISO Standards:<sup>3</sup>

**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 Standard<sup>4</sup>

**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 **D 4150** 3.2 Sulfur compounds are commonly referred by their initials (chemical or formula), for example,

### 3.2 Abbreviations:

<i>hydrogen sulfide</i>	= H <sub>2</sub> 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 specific and normally reactive sulfur compounds. Samples are introduced to an inert GC instrument through an inert sampling system. Sulfur compounds are separated by a GC column and measured by an EC detector. The method requires frequent calibration using stable standards. The test method conforms to the standard practice of Practice **D 7165**.

4.2 A fixed volume of the fuel gas (normally 0.25 mL) is injected into an isothermal 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.

4.3 Specific GC-separated sulfur compounds are detected by an electrochemical detector utilizing 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. 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 to gas processing, operation and utilization, and of regulatory interest.

5.2 Small amounts (typically, total 4-6 PPMv) of sulfur odorants are added to natural gas and other fuel gases for safety purposes. Some sulfur odorants can be reactive, and may be oxidized, forming more stable sulfur compounds having lower odor thresholds. These gaseous fuels are analyzed for sulfur odorants to help in monitoring 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 isothermal oven and automatic injection valve and software necessary for interfacing to a chromic acid electrochemical detector and for the intended application and performance. 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 by sample loop injection. An automated non-reactive gas sampling valve is employed for 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 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 type tubing are often employed. Different size fixed-volume sampling loops (0.25 to 10.0 mL) may be used for target concentration ranges, provided with adequate chromatographic separation. The same non-reactive materials are used for the sampling 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 °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. Mass flow controllers, capable of maintaining gas flow constant to ± 1 % at the required flow rates can also be used. The supply pressure of the gas delivered to the gas chromatograph

<sup>3</sup> 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>.

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

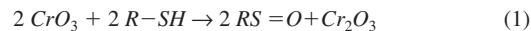
must be at least 69 kPa (10 psig) greater than the regulated gas at the instrument to compensate for the system back pressure.

6.1.4 *Detector*—An EC detector using chromic acid chemistry (Fig. 1) is used in this method. The detector is set according to the manufacturer’s specifications for the application. One EC detector is normally employed for 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 arranged vertically in parallel, are welded in a borosilicate glass tube and separately connected to an amplifier for data acquisition.

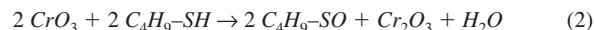
6.1.4.2 The electrolyte, a solution of chromium (VI) oxide in distilled or deionized water (100 g/L or 0.66 mole/L), is contained in a vessel. A tube with the electrodes dips into the solution such that the liquid is retained by capillary within the tube at a level approximately at midway between two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

6.1.4.3 The gas flow from the GC column is discharged through a narrow glass or Teflon tube (2 mm ID) immediately above the upper grid centre (normally 5 mm). Each sulfur compound sequentially elutes and reacts with chromic acid. Possible reaction mechanisms are illustrated as Equation 1 Eq 1 and 2Eq 2. The redox reaction occurs on the electrode surface creating a potential difference between the two electrodes, thus causing a current which is measured in a low resistance measuring circuit. For example, to t-butyl mercaptan is oxidized t-butyl sulfoxide and chromium oxide (Equation 2Eq 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 um (80-100 mesh) Chromosorb W support is used. The column shall provide adequate retention and resolution characteristics under the experimental conditions 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. A second GC column of the same ID and phase with a shorter length is often employed for faster measurement of late-eluting sulfur compounds, such as THT. Two GC columns can be plumbed using a 10-port valve to direct light sulfur compounds and THT sequentially for complete detection using one or two EC detectors. The elution of THT may also be accelerated by increased carrier gas flow rate after the elution of TBM. A back-flush column is not described in this method although back-flushing technique may be employed to remove high boiling and possible harmful gas components, which may have undesirable effects on the analyzing GC column and the electrochemical detector. The performance of GC columns shall give adequate separation of target sulfur compounds for desired accuracy and precision.

### 6.3 Data Acquisition

6.3.1 The device and software must have the following capabilities:

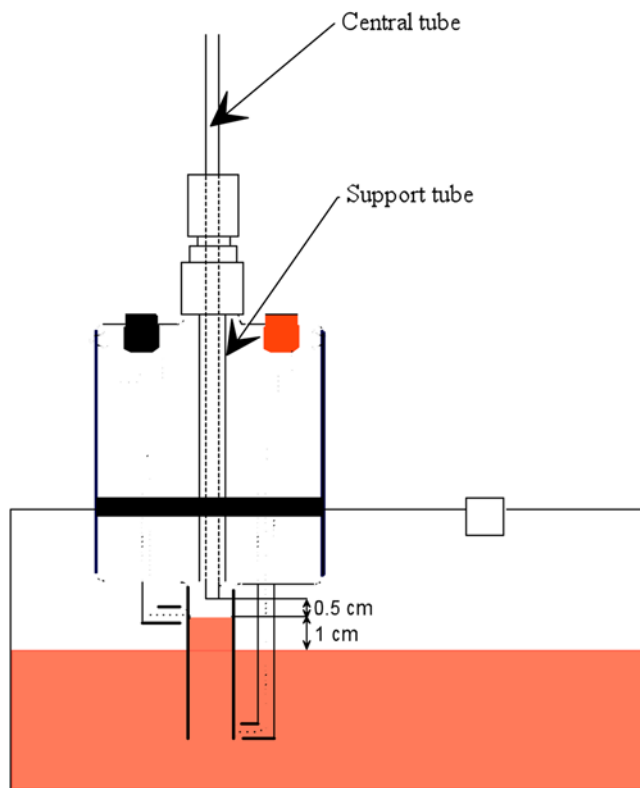


FIG. 1 Typical Electrochemical Detection Cell