



# 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 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 ( $\epsilon$ ) 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 [D5504](#), [D5623](#), [D6228](#), [D6968](#), [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 [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:<sup>2</sup>

[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

[D7165](#) Practice for Gas Chromatograph Based On-line/At-line Analysis 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.

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

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 **D4150** 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 **D7165**.

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, cor-

rosive 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.

<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>.

Mass flow controllers, capable of maintaining gas flow constant to  $\pm 1\%$  at the required flow rates can also 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.

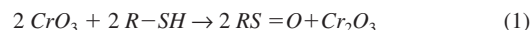
6.1.4 *Detector*—An EC detector using chromic acid chemistry (Fig. 1) is used in this method. The detector is set according to the manufacturer’s specifications for the application. One EC detector is normally employed for measurement. A second EC detector may be employed for simultaneous detection of 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 1Eq 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  $\mu$ m (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

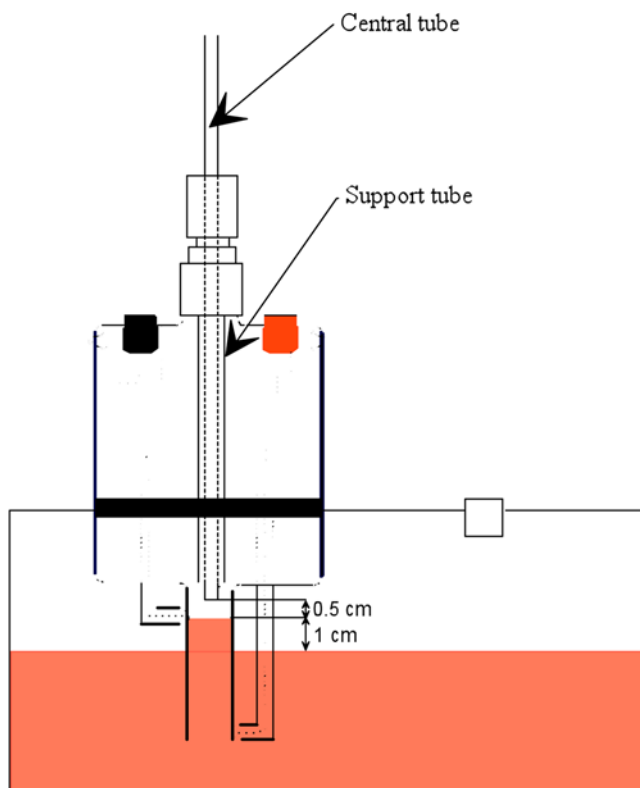


FIG. 1 Typical Electrochemical Detection Cell

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:

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 ED operation, such as gas pressure and flow control.

## 7. Reagents and Materials

7.1 *Compressed Cylinder Gas Standards*—Gas standards should be of high purity with certified stability and accuracy. Blended gaseous sulfur standards may be used if a means to ensure accuracy and stability of the mixture is available. Gas standards can be a source of error if their long term stability during storage cannot be guaranteed.

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. The non-mandatory protocol for compressed gas standard cited in the Appendix X1 of Test Method **D5504** can be used to ensure the quality of standards and to establish traceability to a NIST or NMI standard reference material.

7.1.2 The mix of a multiple sulfur standard should be recommended by a compressed gas standard manufacturer to assure the long term stability of sulfur components. The standard should be re-calibrated as needed.

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.

7.2 *Sulfur Permeation Standards*—Gaseous standards generated from individual or a combination of certified permeation tubes and devices at a constant temperature ( $\pm 0.1$  °C) and a constant flow rate can be used for all 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. Practice **D3609** for calibration techniques using permeation tubes should be enforced.

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

7.3 *Carrier Gas*—Helium, air or nitrogen of high purity (99.999% minimum purity) Air carrier is not recommended if target sulfur compounds may react with air. Additional purification of carrier gas is recommended using molecular sieves or

other suitable agents to remove hydrocarbons or oxygen, or both, in helium and nitrogen. Available carrier gas pressure must be sufficient to ensure a constant carrier gas flow rate (see **6.1.4**).

**NOTE 2—Warning:** Carrier gas employed 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.

## 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 1**.

8.2 *Electrochemical detector*—Place the detector in service according to the manufacturer's step-by-step instructions. In general, carefully remove glass detector assembly from empty chromic acid reservoir. Fill the reservoir with chromic acid solution at the water mark, approximately 3 cm high. Slowly insert the detector in 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 glass detector if air bubbles are present or the solution level in the detector tube is incorrect, or both.

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

8.4 *Chromatography*—A chromatogram of typical sulfur analysis at PPMv levels is illustrated in Figure 2 (relative response vs. retention time) and their retention times are listed in Column 1 of **Table 2**. The retention times of selected sulfur compounds using different instrument settings are listed for reference in **Table 2**. They may vary considerably depending on the chromatographic conditions. The eluting sequence and spread of sulfur peaks should remain roughly the same. Adequate resolution defined as baseline separation of adjacent peaks shall be attempted, although the characteristic GC peak broadening is the trait of EC detector and significant peak

**TABLE 1 Typical Gas Chromatographic Operating Parameters**

Gap Sample Loop:	0.25 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 EC detector
Column Oven:	Isotherm, 65 °C
Detector:	Reagent and instrument operating parameters as recommended by the GC-EC manufacturer



**TABLE 2 Typical Retention Times of Sulfur Components of Different GC-ECD Runs**

GC-ED instrument	GC-ED #1	GC-ED #2	GC-ED #3
GC-Column and parameters	1/8 in. ID× 70cm L, N <sub>2</sub> , 12ml/min, 65 °C	1.6 mm ID× 1200 mm L, N <sub>2</sub> , 100 ml/min, 20 °C	4 mm ID× 400 mm L, N <sub>2</sub> , 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 <sub>2</sub> S	30	30	30
Methyl mercaptan (MM)	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 <sup>A</sup>	720 <sup>A</sup>	2100

<sup>A</sup>The shorter GC column is employed for simultaneous accelerated analysis of THT.

overlaps are often observed. The complete baseline separation of two peaks is normally defined as the specific ED signal of the first compound returns to a point at least below 5% of the smallest peak of two. Less than baseline separation may lead to poorer precision and larger bias. GC-ED chromatograms should be examined thoroughly with sample injections. An abnormally high concentration of hydrocarbon components may interfere with the measurement, although typical natural gas hydrocarbon concentrations have not previously shown any interference with the sulfur measurement. Tests can be conducted to verify possible chromatographic and detector interferences.

8.5 *Detector Response Calibration*—Analyze calibration gases to obtain the chromatograms and peak areas for response factor calculation as Equation 3 Eq 3 (Practice D4626). Response factors of different sulfur compounds vary considerably as shown in Table 3. Determine the linear range of detector

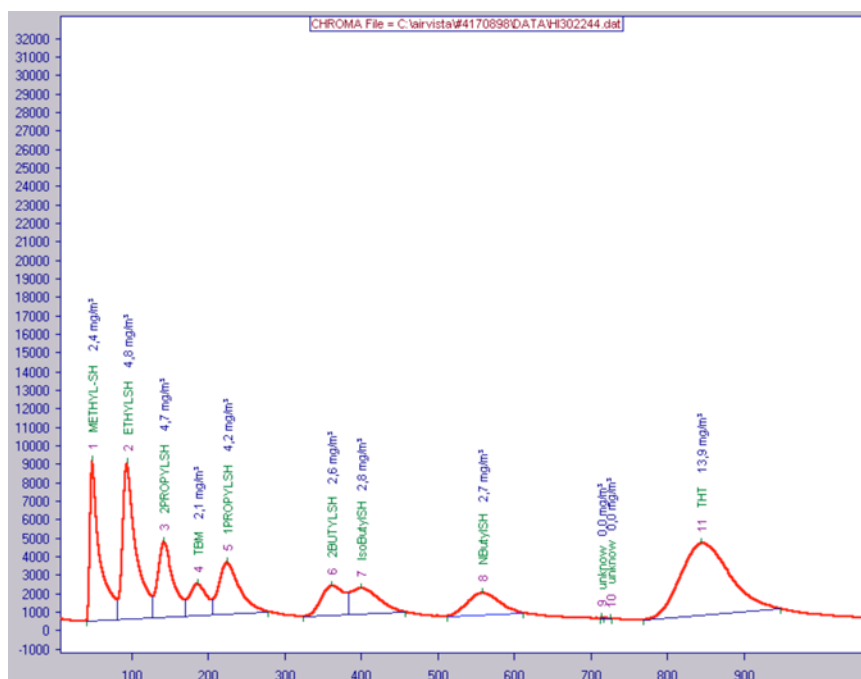
**TABLE 3 Typical Gas Chromatographic Operating Parameters**

Compound	Relative RF vs. DMS
Hydrogen Sulfide, H <sub>2</sub> S	2.3
Methyl mercaptan (MM)	0.75
Dimethyl sulfide (DMS)	1
i-Propyl mercaptan (IPM)	2.12
t-Butyl mercaptan (TBM)	1.8
Thiophane (THT)	0.94

response toward each sulfur compound. A linear standard curve is constructed with the linear correlation factor calculated. Detector linearity is essential to on-line measurement accuracy and should be verified at a frequency recommended by instrument manufacturers.

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

where:



**FIG. 2 Typical GE-ED sulfur Chromatogram of a Mixed Sulfur Standard**

$F_n$  = response factor of a sulfur compound  
 $C_n$  = concentration of the compound in the sampled gas on a common measurement unit  
 $A_n$  = peak area of the compound measured

8.5.1 Example: Assume 1.0 PPMv of dimethyl sulfide (DMS) injected onto GC with a 0.25 mL fixed sample loop. The peak areas of its sulfur responses are 2,000 counts.

$$1 \text{ PPMv DMS} = 1 \text{ PPMv Sulfur}$$

$$\begin{aligned} \text{DMS Response Factor (RF}_{\text{DMS}}) &= 1 \text{ PPMv} / 2000 \\ &= 0.0005 \text{ PPMv DMS per area count} \end{aligned}$$

A single component calibration standard or a control standard or sample should be used daily to verify the response factor of target sulfur compounds. The day to day variation of retention time should not exceed  $\text{RSD} \pm 1\%$ . The day-to-day variation of  $F_n$ 's should not be greater than 5%. The detector electrolytic level should be maintained and the detector should be re-calibrated for optimal sensitivity if  $F_n$ 's exceeds this limitation. Auto calibration at a specific interval is strongly recommended for continuous on-line monitoring.

## 9. Procedure

### 9.1 Sampling and Preparation of Sample Aliquots:

9.1.1 *Gas Samples*—Sample is transported from a gas source to the GC-EC instrument using an adequate and inert on-line sampling system as described in or Practice **D7165** and **D7166**, or both. Samples may be brought to the laboratory in specially conditioned high-pressure sample containers or in Tedlar bags at atmospheric pressure for off-line analysis.

9.2 *Instrument Setup*—Set up the GC-ED according to the chromatograph operating parameters listed in **Table 1**.

9.3 *Instrument Performance Check*—Analyze selected control standards or samples, in replicates if necessary, to verify the chromatographic performance (see **8.1**) retention times (RT) (**Table 1**), and response factors (RF) (see **8.5**). Components present in controls must be identified correctly based on RTs. The day to day variation of response factors should not exceed 5%. System maintenance and re-calibration are required if these criteria cannot be met.

9.4 *External Standard Calibration*—At least twice a day or as frequently as necessary, analyze the calibration standard mix to verify the calibration curve determined in **8.5**. and determine the standard response factors for the sample analysis. The difference of response factors found at the beginning and the end of each run or series of runs within 24-hour period should not exceed 5%

9.5 *Sample Analysis*—Purge the sampling lines from the sample receiving point through the sample loop in the gas chromatograph. Inject 0.25 mL in loop with a gas-sampling valve. If the sample size gives results beyond the linear range of the detector, change the sample size using a smaller or larger sampling loop. Run the analysis per the conditions specified in **Table 1**. Obtain the chromatographic data via a computer-based chromatographic data system. Examine the graphic display for any errors (for example, over-range component data), and repeat the injection and analysis if necessary. The difference

between corresponding peak areas of repeated runs should not exceed 5% for compounds present at concentrations equal to or higher than 50 times of their corresponding detection limits. Standard addition and matrix dilution should be carried out to identify possible interferences and improve qualitative and quantitative determination.

## 10. Calculation

10.1 Determine the chromatographic peak area of each component and use the response factor (Eq 4) obtained from the calibration run to calculate the amount of each sulfur compound present.

$$C_n = A_n \times F_n \quad (4)$$

where:

$C_n$  = concentration of the compound in the gas on a common unit basis (PPMv, mg/M3 etc.)  
 $A_n$  = peak area of the compound measured  
 $F_n$  = response factor of the compound (PPMv, mg/M3 per unit area)

## 11. Report

11.1 Report the identification and concentration of each individual sulfur compound in common units.

## 12. Precision and Bias

12.1 *Precision*—This standard has not yet undergone an interlaboratory study to substantiate the listed precision data. The statistical examination of the laboratory test results is as follows:

12.1.1 *Repeatability (Single Operator and Apparatus)*—The difference between successive test results obtained by an automatic online GC-EC analyzer on a single sulfur compound under a constant operating condition on an identical testing sample would, in the long run, in the normal and correct operation of the test method, exceed the following values by only one case in twenty. See **Table 4**.

12.1.2 *Reproducibility (Different Operators, Apparatus and sites)*—The difference between two single and independent results obtained by different operators working on different online GC-EC analyzers using an identical test sample would, in the long run, exceed the following values only one case in twenty. (Experimental results to be determined.)

12.2 *Bias*—Since there is no accepted true sulfur reference material for determining the bias of sulfur measurement, no statement on this can be made.

## 13. Keywords

13.1 electrochemical detection; gas chromatography; odorants; on-line measurement; sulfur compounds

**TABLE 4 Repeatability of Specific Sulfur Compounds Measurement in Nitrogen**

Compound	PPMv	Repeatability
H <sub>2</sub> S	5.85	± 0.047
MM	6.34	± 0.046
IPM	1.15	± 0.016
TBM	2.49	± 0.011
THT	4.91	± 0.070

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