



# Standard Test Method for Determination of Trace Hydrogen Sulfide, Carbonyl Sulfide, Methyl Mercaptan, Carbon Disulfide and Total Sulfur in Hydrogen Fuel by Gas Chromatography and Sulfur Chemiluminescence Detection<sup>1</sup>

This standard is issued under the fixed designation D7652; 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 describes a procedure primarily for the determination of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and carbon disulfide (**Table 1**) in hydrogen fuels for fuel cell vehicles (FCV) by gas chromatograph with sulfur chemiluminescence detection. The reporting limit is 0.02 ppbv (nanomole per mole as volume), based upon the analysis of a 500 mL hydrogen sample. The procedures described in this method were designed to satisfy sulfur contaminant determination requirements contained in SAE TIRJ2719 and the California Code of Regulations, CFR, Title 4, Division 9, Chapter 6, Article 8, Sections 4180 – 4181.

1.2 This test method can be extended to other sulfur species in hydrogen fuel that are eluted through a chromatographic column.

1.3 This test method can be modified to analyze all sulfur compounds present without chromatographic separation; thus, providing a total sulfur estimation without speciation (**Appendix X1**).

1.4 If any new sulfur compounds need to be analyzed in hydrogen fuel, the calibration or spiking sulfur standards must include these new compounds after their method detection limit study. In addition, no co-elution is allowed in the chromatographic analysis of the calibration standard containing both the newly added and the existing sulfur target compounds. If necessary, the chromatographic conditions may be modified to achieve this goal.

1.5 Although, primarily intended for determining sulfur in hydrogen used as a fuel for fuel cell or internal combustion engine powered vehicles, this test method can also be used to measure sulfur compounds in other gaseous fuels and gaseous matrices provided data quality objectives are satisfied.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.14 on Hydrogen and Fuel Cells.

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1.6 The values stated in SI units are standard. The values stated in inch-pound units are for information only.

1.7 Mention of trade names in this standard does not constitute endorsement or recommendation for use. Other manufacturers of equipment or equipment models can be used.

1.8 *Alternative Detectors*—This test method is written primarily for the use of sulfur chemiluminescent detectors but other detectors can be used provided they can detect hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and carbon disulfide at 0.02 ppbv in hydrogen and meet data quality objectives for the intended use.

1.9 *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.* For safety issues related to liquid nitrogen, refer to material safety data sheet (MSDS) from liquid nitrogen supplier.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

**D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence**

**D7606 Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases**

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

**SAE TIR J2719 Information Report of the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles**

### 2.3 California Code of Regulations:<sup>4</sup>

**California Code of Regulations Title 4, Division 89, Chapter 6, Article 8, Sections 4180–4181.**

<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.

<sup>3</sup> Available from SAE International (SAE), 400 Commonwealth Dr., Warrendale, PA 15096-0001, <http://www.sae.org>.

<sup>4</sup> Available from the Office of Administrative Law, 300 Capitol Mall, Suite 1250, Sacramento, CA 95814-4339.

**TABLE 1 Trace Sulfur Contaminates**

Compound	Formula	MW	BC°C	MP°C	CAS No.
Hydrogen sulfide	H <sub>2</sub> S	34.08	-61	-86	7783-06-4
Carbonyl sulfide	COS	60.07	-50	-139	463-58-1
Methyl maercaptan	CH <sub>3</sub> SH	48.11	6	-123	74-93-1
Carbon disulfide	CS <sub>2</sub>	76	46.5	-111.6	75-15-0

## 2.4 US Code of Federal Regulations.<sup>5</sup>

CFR Title 40, Appendix B, PART 136 (Guideline Establishing Test Procedures for the Analysis of Pollutants)

## 3. Terminology

### 3.1 Definitions:

3.1.1 *absolute pressure*—pressure measured with reference to absolute zero pressure, usually expressed as kPa, mm Hg, bar or psia.

3.1.2 *constituent*—component (or compound) found within a hydrogen fuel mixture.

3.1.3 *contaminant*—impurity that adversely affects the components within the fuel cell system or the hydrogen storage system.

3.1.4 *cryogen*—a refrigerant used to obtain very low temperatures. The cryogen used in this method is liquid nitrogen (bp -195°C).

3.1.5 *dynamic calibration*—calibration of an analytical system using calibration gas standard generated by diluting a known concentration of compressed gas standard with a diluent gas.

3.1.6 *fuel cell grade hydrogen*—hydrogen satisfying the specifications in SAE TIR J2719.

3.1.7 *gaseous fuel*—material to be tested, as sampled, without change of composition by drying or otherwise.

3.1.8 *poisoning*—process by which catalysts are made inoperative due to the activity of substances such as hydrogen sulfide or other sulfur substances that can bind to the catalyst used in the fuel cell.

3.1.9 *qualitative accuracy*—the ability of an analytical system to correctly identify compounds without necessarily providing a precise concentration.

3.1.10 *quantitative accuracy*—the ability of an analytical system to measure the concentration of an identified compound to a specified degree of accuracy.

3.1.11 *static calibration*—calibration of an analytical system using standards in a matrix, state or manner different than the samples to be analyzed.

3.1.12 *reporting limit*—The limit is reported for each sample analysis. The spike analysis at the reporting limit (10.7) must be performed to demonstrate the reporting limit can be reached. The reporting limit is 0.02 ppbv for each sulfur target compound analyzed by this method.

3.1.13 *method detection limit*—The method detection limit is described in US Code of Federal Regulations, CFR Title 40, Appendix B, PART 136 (Guidelines Establishing Test Procedures for the Analysis of Pollutants). For this method, seven replicates of each sulfur target compound at the reporting limit, 0.02 ppbv, in hydrogen are analyzed to establish the method detection limits (10.5).

### 3.2 Acronyms:

3.2.1 *FCV*—Fuel Cell Vehicle.

3.2.2 *PEMFC*—proton exchange membrane fuel cell.

## 4. Summary of Test Method

4.1 The analysis of sulfur compounds at trace level in hydrogen is challenging due to the reactivity of these substances, especially hydrogen sulfide. These substances can be absorbed by or out gas from metal surfaces such as stainless steel. Absorption and reaction with metals impacts both sampling and analysis of sulfur compounds in gaseous streams. An 1800 psi rated sampling cylinder is used for the sample collection as described in Practice D7606. The cylinder is internally coated with an inert material, such as silicon oxide, to reduce the surface adsorption and reactivity of sulfur compounds on the metal surface. Analytic systems must also be passivated against sulfur loss and reactivity. Passivation can be provided by using TFE-fluorocarbon, silica or glass, or surface treated metal in the analytic system as well as any transfer lines from the sample to the analysis system.

4.1.1 The diagram for analysis of H<sub>2</sub>S, COS, CH<sub>3</sub>SH, CS<sub>2</sub> and total sulfur in Hydrogen is shown in Fig. 1, in which the sulfur analysis is performed by concentrating and analyzing a 500 mL of sample taken from sample container by a 500 mL gas tight syringe with plunger tip covered with TFE-fluorocarbon. Due to high hydrogen pressure, it is difficult to take hydrogen sample directly into a syringe. One method is to use a short clean thick wall TFE-fluorocarbon tube (minimum 0.185 cm wall thickness) as a medium for sample transfer, as shown in Fig. 2 and described in the following passage. A short thick wall TFE-fluorocarbon tube is connected to one valve (Valve 1, Fig. 2) on a hydrogen fuel sample bottle. The other end of the short TFE-fluorocarbon tube is connected to another valve (Valve 2, Fig. 2) with a septum on the other end to accept a needle of a 500 mL gas tight syringe. With Valve 2 closed, open Valve 1 to pressurize the TFE-fluorocarbon tube. Close Valve 1 first and then open Valve 2 slowly to release the pressurized hydrogen sample into a 500mL syringe. **Warning**—Please allow syringe plunger to expand freely to avoid pressure inside the syringe over 30 psi when the syringe plunger stops. For the first time only, remove the hydrogen sample from syringe. Repeat the procedure several times to achieve a 500 mL sample in the syringe. If the sample

<sup>5</sup> Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, <http://dodssp.daps.dla.mil>.

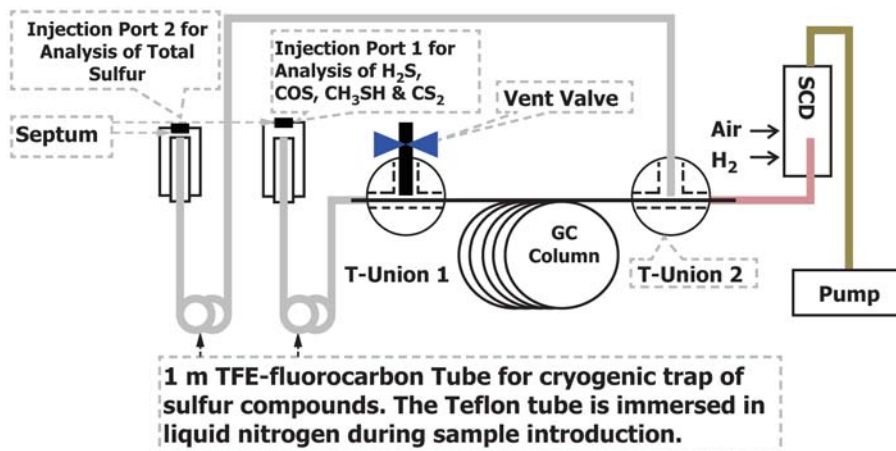


FIG. 1 Diagram for Analysis of H<sub>2</sub>S, COS, CH<sub>3</sub>SH, CS<sub>2</sub> and Total Sulfur in Hydrogen

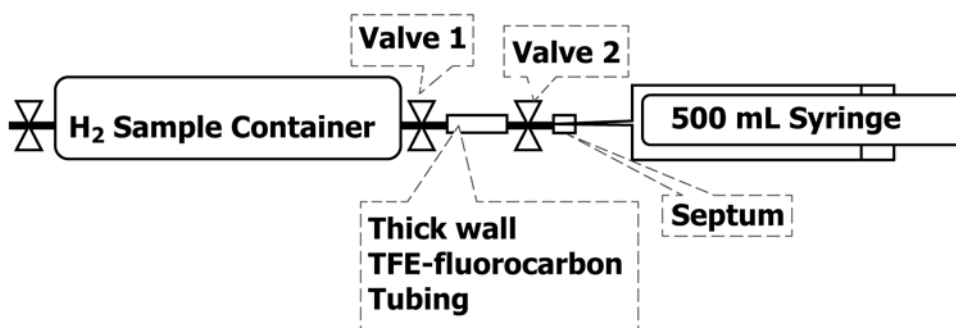


FIG. 2 Hydrogen Sample from a High Pressure Sample Container

pressure is less than 200 psi, a 500 mL sample can be directly taken from the sample bottle through a septum. Alternative methods can be used other than a gas tight syringe for sampling. These methods could include automated gas valves. Other sampling devices are acceptable as long as they are constructed of appropriate passivated materials and can introduce a sample of at least 500 mL.

4.1.2 A 500 mL sample of hydrogen is introduced into a TFE-fluorocarbon tube that is suspended over a bath of liquid nitrogen using syringe injection of the sample through Injection Port 1 of Fig. 1. All sulfur compounds are trapped while hydrogen is expelled through the vent valve of T-Union 1 shown in Fig. 1. The trap is warmed to room temperature by immersing it into a water bath at room temperature. Trapped sulfur compounds are desorbed onto a capillary column for separation. The sulfur compounds eluting from the capillary column are detected by sulfur chemiluminescence detection. Alternative trapping methods and devices may be used provided sensitivity requirements as defined in SAE J2719 and the California Code of Regulations, Title 4, Division 9, Chapter 6, Article 8, Sections 4180 – 4181. These Alternative methods may or may not require the use of a cryogen.

## 5. Significance and Use

5.1 Low operating temperature fuel cells such as proton exchange membrane fuel cells (PEMFCs) require high purity hydrogen for maximum material performance and lifetime. Sulfur compounds are present in many of the materials used in

hydrogen production and small quantities typically remain after processing and purification. Part-per-billion concentrations of sulfur gases such as hydrogen sulfide (H<sub>2</sub>S), carbonyl sulfide (COS) and mercaptans diminish single fuel cell capacity.

## 6. Apparatus

NOTE 1—Additional details on general sulfur gas determination can be found in Test Method D5504.

6.1 *Gas chromatography (GC)*—A gas chromatograph of standard manufacture, with hardware necessary for interfacing to a sulfur chemiluminescence detector, possessing an inlet system as described in 6.2, and containing all other features necessary for measuring sulfur compounds in hydrogen can be used.

6.2 *Sample Inlet System*—A sample inlet system capable of cryogenic or ambient concentration of sulfur compounds in a TFE-fluorocarbon tube or appropriate trapping device without loss of analytes is required. The inlet system must be evaluated frequently for possible sulfur contamination. The injection and concentration systems must transfer all compounds of interest to the GC column without loss or absorption. Since stainless steel can adsorb or off gas sulfur compounds, it must be limited in its use within the sample concentration system or it must be treated specifically for use with sulfurs. The injection system insert can either be made of glass, TFE-fluorocarbon, or other appropriate material which does not adsorb or off gas sulfur compounds. Fig. 1 shows a configuration that has been

successfully used in this application. As shown in Fig. 1, Injector Port 1 is connected to a T-Union 1 using a one meter TFE-fluorocarbon tube with an approximate 1 mm ID. The remaining two openings of T-Union 1 are connected to a 75 m 0.53 mm ID 3 micron DB-624 capillary column and a vent valve. The TFE-fluorocarbon tube is used as a cryogenic trap for the sulfur compounds in hydrogen. The vent valve is used to rapidly release hydrogen after cryogenically trapping the analytes in the TFE-fluorocarbon tube during introduction of a 500 mL hydrogen sample. After sample introduction, the valve is closed, the TFE-fluorocarbon trap is removed from liquid nitrogen to ambient air and the GC/SCD run starts.

6.3 *Sulfur Chemiluminescence Detector (SCD)*—The specification of SCD is the same as those in 5.1.3.2 of Test Method D5504.

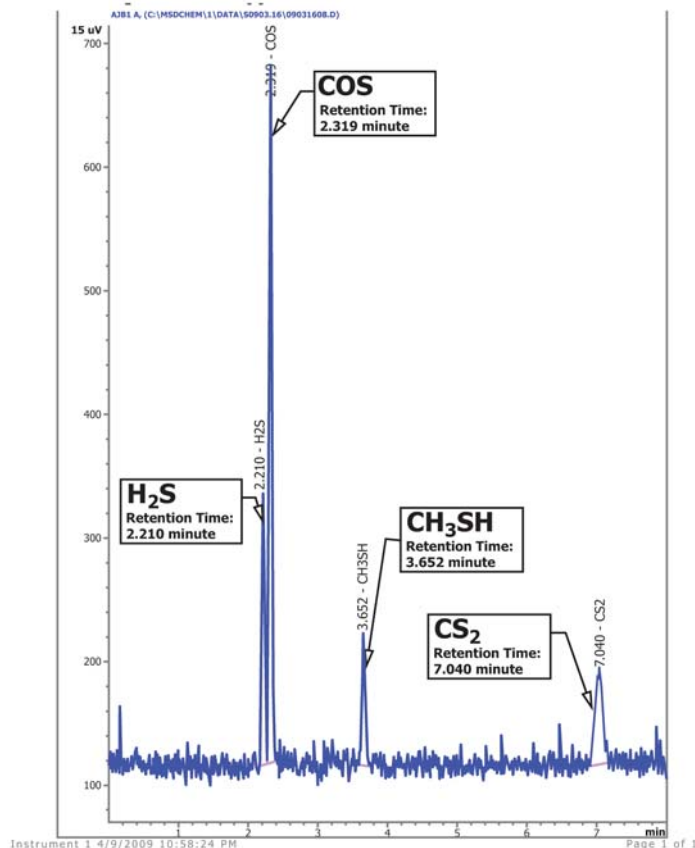
6.4 *Data Acquisition*—A computer or other data recorder loaded with appropriate software for data acquisition, data reduction, and data reporting and possessing the following capabilities is required.

- 6.4.1 Graphic presentation of the chromatogram.
- 6.4.2 Digital display of chromatographic peak areas.
- 6.4.3 Identification of peaks by retention time or relative retention time, or both.
- 6.4.4 Calculation and use of response factors.
- 6.4.5 External standard calculation and data presentation.

6.5 *Hydrogen fuel collection vessels*—Any collection vessel with working pressures up to 1800 psi can be used provided the vessel internal surface is inert towards sulfur compounds. A 1-liter 1800 psi pressure proof stainless steel container with two valves on opposite ends and silicon coating on the inside surface has been successfully used in this application. The vessel must have a DOT 3A1800 label (United States Department of Transportation mandated label) affixed to the outside surface for transportation of hydrogen samples.

6.6 *Carrier Gas Control*—Constant flow control of carrier and detector gases is critical for optimum and consistent analytical performance. Control is achieved by use of pressure regulators and fixed flow restrictors. Mass flow controllers or electronic pressure controllers can be used for optimal instrument performance.

6.7 *Chromatographic Column*—A variety of columns have been used successfully for the determination of trace sulfur compounds in hydrogen fuel. Typically, a 0.53 mm ID fused silica open tubular column of bonded methyl silicone liquid phase is used. The selected column must provide baseline separation of hydrogen sulfide and carbonyl sulfide at the reporting limit level (10µL injection of 1 ppmv sulfur calibration standard, as shown in Fig. 3). An example of the chromatographic conditions is listed in Table 2.



The chromatographic conditions are listed in Table 2.

FIG. 3 Sulfur Calibration Standard at Detection Limit: 10µL injection of 1 ppmv Sulfur Calibration Standard



**TABLE 2 Example GC and SCD Operating Parameters**

Gas Chromatograph	
Column:	75m 0.53mm ID 3µm DB-624 fused silica column.
Carrier Gas:	Nitrogen
Flow Rate:	4 cm <sup>3</sup> /min
Sample Size:	500mL
Isothermal Column Temperature:	35 or 40°C
Sulfur Chemiluminescence	
Detector Hydrogen flow:	40mL/minute
Air Flow:	65mL/min
Detector Temperature:	800 °C

6.8 *Sample Introducer*—Any device capable of successfully introducing a specific amount of gaseous sample, typically 500 mL, to the GC/SCD without sample contamination or sample loss. A 500 mL glass tight syringe with a plunger covered with TFE-fluorocarbon has been used successfully.

6.9 *Sample container cleaning system*—For the cleaning of several sample containers simultaneously, the following is required:

6.9.1 *Vacuum Pump*—capable of evacuating sample vessel(s) to an absolute pressure of less than 0.05 mmHg.

6.9.2 *Vacuum Gauge*—capable of measuring vacuum down to an absolute pressure of 0.01 mm Hg or less.

6.9.3 *Pressure Gauges*—the pressure gauge 0 to 1000 psig to monitor UHP hydrogen pressure.

6.9.4 *Pressure Regulator*—regulates pressure of UHP hydrogen into sample container.

6.9.5 *Isothermal Oven*—used to heat container(s) to 80°C during cleaning, if the sample vessel contained high concentrations of sulfurs or hydrocarbons in the previous sample.

## 7. Reagents and Materials

### 7.1 Compressed Gas Standards:

7.1.1 A compressed gas standard containing hydrogen sulfide, carbonyl sulfide and methyl mercaptan in nitrogen can be used. In this application, an additional gas standard containing carbon disulfide is also required. Care must be exercised in the use of compressed gas standards since they can introduce errors in measurement due to sulfur gas losses or changes over time. The compressed gas standards should be re-certified as recommended by the manufacturer or as needed to insure accuracy.

7.1.2 Alternative approaches for generation of calibration standards are acceptable as long as accuracy and stability can be verified.

7.2 *Carrier Gas*—Sulfur free hydrogen, helium or nitrogen can be used. The total sulfur concentrations in carrier gas should be less than 0.01 ppbv. Nitrogen from a liquid nitrogen tank was used as carrier gas for the analysis, as illustrated in Fig. 3.

7.3 *Hydrogen*—UHP hydrogen containing total sulfur concentration <0.01 ppbv must be used.

7.4 *Air*—Ultrahigh purity zero air is used.

7.5 *Liquid Nitrogen*—maybe required for cryogenic cooling.

7.6 *Sample Container*—The cleaning procedure for the sample container is described in the following passage. For new sample containers with internal surfaces coated with

silicon, the sample container is evacuated to less than 0.1 torr using a vacuum pump. The sample container is then pressurized with ultrahigh purity (UHP) hydrogen to approximate 400 psi. After verifying the absence of leaks using a hydrogen leak detector, the sample container is stored at 400 psi hydrogen at room temperature for at least two hours. The hydrogen is then released and the sample container pumped down below 0.1 torr before being used to collect a hydrogen fuel sample. Hydrogen pressurization of the sample container provides hydrogen permeation and equilibration with the inside surface of the container; thereby, allowing sulfur compounds time to be desorbed from the vessel surfaces. For the sample containers previously containing high concentration of sulfurs, such as 1 ppbv hydrogen sulfide, the sample containers must be treated using the above-mentioned procedure. In addition, the sample container must be analyzed to make sure there are no sulfurs above 0.02 ppbv before being used for sampling of hydrogen fuel. The sample containers used for hydrogen fuel sampling must not be used for sampling of either natural gas or LPG since both gases contains more than 1 ppmv of mercaptans.

## 8. Equipment Preparation

8.1 *GC/SCD*—Place in service in accordance with the manufacturer's instructions. Many operating conditions can be used to perform speciation and quantitation of sulfur compounds in hydrogen and related fuel cell feed gases. Typical, minimal performance criteria for chromatographic conditions are:

8.1.1 The chromatographic conditions must elute and separate all species of interest in calibration, especially baseline separation of hydrogen sulfide and carbonyl sulfide at a 10µL injection size of 1 ppmv sulfur gaseous standards (Fig. 3).

8.1.2 *Sulfur Chemiluminescence Detector (SCD)*—The SCD should be set up according to manufacturer instruction. The temperature of SCD, flow rate of hydrogen and air should be set to reach highest sensitivity and lowest noise. An example of these conditions is shown in Table 2. Both the hydrogen and oxygen may be filtered to lower the SCD noise.

8.2 *Liquid nitrogen tank*—A 160 – 230 L liquid nitrogen tank with head pressure of 22 psi may be required.

8.3 *A liquid nitrogen dewar*—A dewar is used to store liquid nitrogen from a liquid nitrogen tank. The dewar serves as a liquid nitrogen bath for cryogenic cooling of TFE-fluorocarbon tubes during sample concentration (4.1.2, 6.2, and 10.4).

## 9. Calibration

9.1 This test method uses external calibration to quantitate the sulfur compounds.

9.1.1 Calibration of target compounds (H<sub>2</sub>S, COS, CH<sub>3</sub>SH and CS<sub>2</sub>) is performed daily before sample analysis and the response factors (RF) are calculated according to the methodology in 9.1.2

9.1.2 A typical example of an initial calibration consists of analysis of 1000, 500, 250, 200, 100, 50, and 10 μL volumes of 1 ppmv sulfur calibration standards containing sulfur compounds of interest. The standard analytical procedure is identical to that of sample concentration and analysis in 10.4, in which the calibration standard is analyzed with 500 mL sulfur free hydrogen.

9.1.3 From the analysis of each calibration standard, the response factor (RF) of each sulfur compound is calculated as in Eq 1. The volume (μL) of sulfur compound injected in Eq 1 is calculated as in a following example. A 10 μL injection of 1 ppmv sulfur standard is the injection of 10μL × 1/1000,000 = 1.0 × 10<sup>-5</sup> μL of each sulfur compound. The average RF and its percentage relative standard deviation (% RSD, standard deviation divided by average) of the daily initial calibration are calculated. The linearity requirement is that the % RSD of the daily initial calibration of each sulfur compound should not be more than 30%. The average RF of the daily initial calibration is used for the concentration calculation of samples analyzed following this initial calibration, as shown in Eq 2. An example of a daily initial calibration is shown in Fig. 4.

9.1.4 A 10 μL injection of 1 ppmv sulfur calibration standard must be analyzed after sample analysis as the sequence-ending standard, whose response factors should not deviate more than 40% from the corresponding average RF of the initial calibration in the same sequence.

$$\text{Response Factor (RF)} = \frac{\text{Volume } (\mu\text{L}) \text{ of the Sulfur Compound Injected}}{\text{Peak Area of the Sulfur Compound}} \quad (1)$$

### 10. Laboratory Procedures

10.1 *Summary of Criteria of Sulfur Analysis*—As stated in 6.7, the analytical conditions of sulfur analysis must baseline separate hydrogen sulfide and carbonyl sulfide at the lowest calibration level, as shown in Fig. 3. In addition to linearity requirements delineated in 9.1.2, the RF of each sulfur compound of a 10μL injection of 1 ppmv calibration standard after sample analysis (9.1.3) should not deviated more than 40% from the corresponding average RF of the initial calibration in the same sequence.

10.2 *Sampling Procedure*—This is performed according to D7606.

10.3 *Sample Receipt*—Examine the overall condition of each sample container; perform leak checks and record observations in a dedicated logbook. Each container must possess an attached sample identification tag that includes the weight of sampled hydrogen, the place, date and time of sample collection and approximate pressure of hydrogen in the container.

10.4 *Sample Concentration and Analysis*—The sample concentration and analysis has been described in 4.1.2, which is described in detail as following. In order to lower the reporting limit of sulfur compounds to the required level, a large sample volume of sample (typically 500 mL) is taken from the sample container using a 500 mL glass syringe with TFE-fluorocarbon plunger tip or other appropriate sampling device. (4.1.1 and

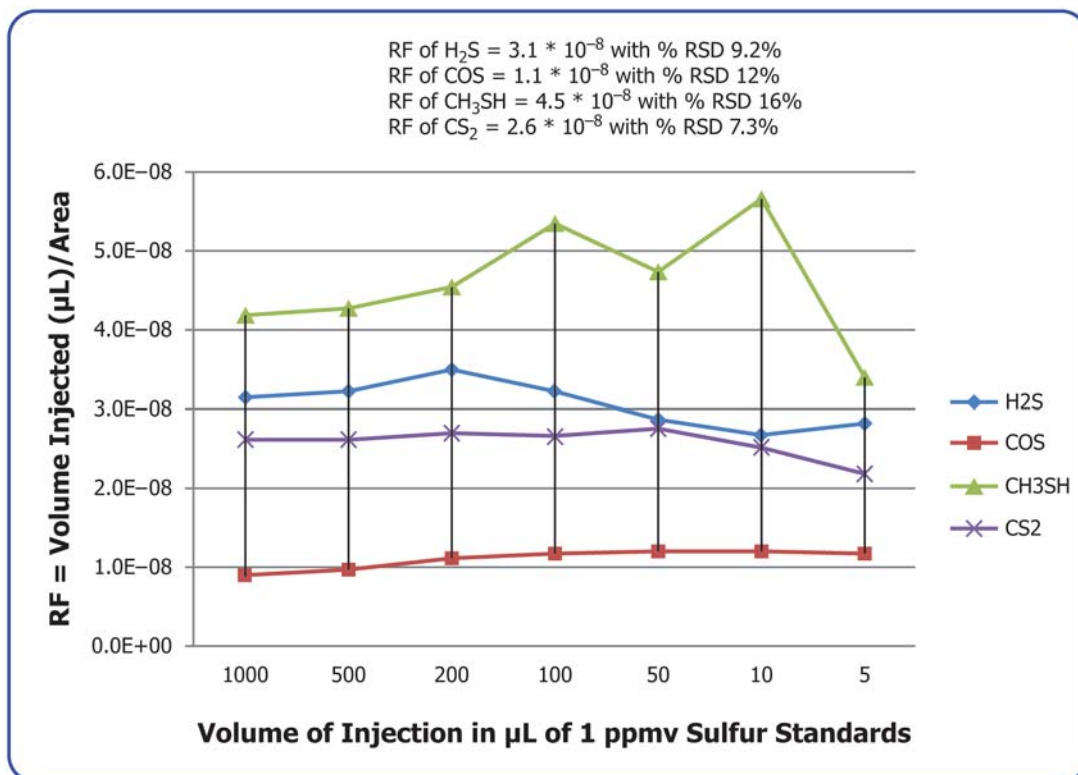


FIG. 4 Examples of RF of Initial Calibration

**Fig. 2).** More than 40 cm of TFE-fluorocarbon tube connected to Injection Port 1 (**Fig. 1**) is immersed into liquid nitrogen in a Dewar. With Vent Valve (**Fig. 1**) opened, the 500mL of the hydrogen sample is introduced through Injector Port 1 and the sulfur compounds are trapped while the hydrogen exits through the vent valve. The sample concentration process is completed in approximate 2 min. The concentration process may also be completed using other types of trapping concentrating devices that may or may not require the use of a cyrogen. The vent valve is closed 15 s after the completion of sample introduction to allow the entire hydrogen sample to flow through the TFE-fluorocarbon tube. The TFE-fluorocarbon tube is then removed from the liquid nitrogen bath and allowed to warm to ambient temperature or immersed in a water bath at room temperature. Data acquisition is started. The liquid nitrogen trapped sulfur compounds are transferred onto the capillary column. Results for individual analyses are processed in three phases: data acquisition, data reduction, and data reporting. Primary identification is performed based upon retention time. However, if the retention times shift, the analysis of the sample co-injected with standard as in 10.7 should be performed to identify sulfur compounds through co-elution. In general, most of hydrogen fuel sulfur analyses will show the presence of hydrogen sulfide, carbonyl sulfide or carbon disulfide, or a combination thereof. If the peak areas of these sulfur compounds are less than the corresponding peak areas of the calibration standard at lowest injection volume, the sample analysis may be repeated to confirm the sulfur concentrations lower than reporting limit. However, if at least one of the peak areas of the sulfur compounds is greater than the corresponding one of the calibration standard at lowest injection volume, the sample analyses must be repeated until the peak areas can be duplicated within 30%.

10.5 *Method Detection Limit Study (2.2.15)*— Before any sample analysis, each laboratory should demonstrate their ability to perform this test method and satisfy sensitivity and repeatability requirements. The capability is demonstrated by seven repetitive analyses of a 10 $\mu$ L injection of 1 ppmv standard co-injected with 500 mL of sulfur free hydrogen or hydrogen sample at the spiking concentration of 0.02 ppbv ((10 $\mu$ L  $\times$  1/1,000,000) / (500mL  $\times$  1,000 $\mu$ L/mL) = 0.02 ppbv). In each analysis, all the sulfur peaks should be clearly identified and their concentrations calculated. The method detection limit for each sulfur compound is three times the standard deviation of the concentrations obtained from seven replicate analyses.

10.6 *Blank Analysis*—500 mL sulfur free hydrogen must be analyzed before the sample analysis to demonstrate that sulfur compounds are present at less than the lowest concentration calibration standard, (10 $\mu$ L of 1 ppmv standard).

10.7 *Analysis of Spike at Reporting Limit*—For each analytical sequence, the analysis of a 10 $\mu$ L injection of 1 ppmv standards co-injected with a 500 mL of sulfur free hydrogen or hydrogen sample should be performed before the sequence-ending standard (9.1.4). The spiking concentration is typically

0.02 ppbv as determined from the following calculation:- (10 $\mu$ L  $\times$  1/1,000,000) / (500mL  $\times$  1,000 $\mu$ L/mL) = 0.02 ppbv = 0.00002 ppmv. The spike recovery of each sulfur compound is measured and should not be more than 40% different than the theoretical amount. This spike analysis demonstrates the analytical capability to reach the reporting limit of 0.02 ppbv for each analyte and to meet measurement precision requirements.

## 11. Calculation

11.1 From the analysis of each calibration standard, the response factor (RF) of each sulfur compound is calculated as in Eq 1 (9.1).

11.2 The sample concentration of the identified sulfur compound in ppmv is calculated as in Eq 2.

$$\begin{aligned} & \text{Concentration (ppmv) of Identified Sulfur Compound} \quad (2) \\ &= \frac{\text{Peak Area of Identified Sulfur Compound} \times \text{Average RF}}{\text{Total Volume of Sample (500mL)} \times 1000\mu\text{L/mL}} \\ & \quad \times 1000000 \end{aligned}$$

## 12. Report

12.1 Report the concentrations of identified sulfur compounds in ppmv, as calculated by Eq 2. For the sulfur compounds not detected, the reporting limit of this sulfur compound is reported. The reporting limit is 10 $\mu$ L  $\times$  1/1,000,000 / (500mL  $\times$  1,000 $\mu$ L/mL) = 0.02 ppbv = 0.00002 ppmv for the analysis of a 500mL.

## 13. Precision and Bias

13.1 *Precision*—The estimate of the repeatability for impurities present in H<sub>2</sub> fuel gas, is based upon the standard deviation of 7 successive test results multiplied by a factor of 2.77 which represent that difference between two such single and independent results as would be exceeded in the long run in only 1 case in 20 in the normal and correct operation of the test method result in the following:

Target Constituents	Estimated Repeatability at Average (ppbv)
Hydrogen Sulfide	0.037 at 0.10
Carbonyl Sulfide	0.015 at 0.02
Methyl Mercaptan	0.005 at 0.007
Carbon Disulfide	0.005 at 0.004

13.2 *Reproducibility*—The reproducibility of this test method for measuring impurities present in H<sub>2</sub> fuel gas, is being determined and will be available within five years of the publication of this standard, based upon the results of inter-laboratory testing.

13.3 *Bias*—The bias for each component analyzed will be determined by experimental results within five years of the release of this standard.

## 14. Keywords

14.1 sulfur chemiluminescence detection; gas chromatography; sulfur compounds; concentration of sulfur compounds in 500mL or larger volume of hydrogen fuel using liquid nitrogen.

**APPENDIX**
**(Nonmandatory Information)**
**X1. Total Sulfur**

X1.1 The total sulfur content is determined in the same manner as stated in the body of this standard, except that a column is not used. Instead, all sulfur compounds are trapped using liquid nitrogen followed by injection into a SCD without chromatographic separation. This is accomplished by replacing the analytical column described in 4.1.2 with a short un-coated

silica-column. The diagram depicting this configuration is shown in Fig. 1. Calibration using this configuration has been accomplished by 10 $\mu$ L injection of 1 ppmv standards. Post analysis drift assessment is performed by analysis of the same 10 $\mu$ L injection of a 1 ppmv standard after sample analysis.

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- (2) D1946 Practice for Analysis of Reformed Gas by Gas Chromatography
- (3) D4150 Terminology Relating to Gaseous Fuels
- (4) D5287 Practice for Automatic Sampling of Gaseous Fuels
- (5) D4626 Practice for Calculation of Gas Chromatographic Response Factors
- (6) F307 Practice for Sampling Pressurized Gas for Gas Sampling  
*IEC Standard*<sup>6</sup>
- (7) IEC 60079-29-2: 2007 Selection, installation, use and maintenance of detectors for flammable gases and oxygen

*ISO Standards*<sup>7</sup>

- (8) ISO 14687-2 Hydrogen Fuel- Product Specification- Part 2: Proton Exchange Membrane (PEM) fuel cell applications for road vehicles.
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- (10) ISO/TR 26142 Hydrogen detection apparatus  
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<sup>6</sup> Available from International Electrotechnical Commission (IEC), 3 rue de Varembe, Case postale 131, CH-1211, Geneva 20, Switzerland, <http://www.iec.ch>.

<sup>7</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>.

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