Designation: D7652 – 11

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[1]

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 (ε) 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.

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:*[2]

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:*[3]

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

2.3 *California Code of Regulations:*[4]

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

[1] 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.

Current edition approved March 1, 2011. Published March 2011. DOI 10.1520/D7652–11.

[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.

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

[4] 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_2S	34.08	-61	-86	7783–06–4
Carbonyl sulfide	COS	60.07	-50	-139	463–58–1
Methyl maercaptan	CH_2SH	48.11	6	-123	74–93–1
Carbon disulfide	CS_2	76	46.5	-111.6	75–15–0

2.4 *US Code of Federal Regulations:*[5]

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_2S, COS, CH_3SH, CS_2 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

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