Designation: D7675 – 22

Standard Test Method for Determination of Total Hydrocarbons in Hydrogen by FID-Based Total Hydrocarbon (THC) Analyzer[1]

This standard is issued under the fixed designation D7675; 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 for total hydrocarbons (THC's) measurement in hydrogen intended as a fuel on a methane (C_1) basis. The determination of THC on a C_1 basis is an analytical technique where all the hydrocarbons are assumed to have the same response as methane (CH_4). Sensitivity from 0.1 parts per million by volume (ppm(v), µmol/mol) up to 1000 ppm(v) concentration is achievable. Higher concentrations can be analyzed using appropriate dilution techniques. This test method can be applied to other gaseous samples requiring analysis of trace constituents provided an assessment of potential interferences has been accomplished.

1.2 This test method is a Flame Ionization Detector-based (FID-based) hydrocarbon analysis method without the use of separation columns. Therefore, this method does not provide speciation of individual hydrocarbons. Several varieties of instruments are manufactured and can be used for this method.

1.2.1 This method provides a measure of THC "as CH_4," because all hydrocarbon species are quantified the same as CH_4 response, which is the sole species used for calibration. Magnitude of the FID response to an atom of carbon is dependent on the chemical environment of this atom in the molecule. This method provides the THC result as if all carbon atoms are from aliphatic, aromatic, olefinic, or acetylenic compounds, where the detector response caused by these atoms is approximately relative to the number of carbon atoms present in the molecule. Other types of molecules, including those containing oxygen or chlorine atoms, will respond differently and usually much lower than the corresponding aliphatic hydrocarbon. Therefore, other methods (Test Methods D7653, D7892, or equivalent) must be utilized to determine the exact constituents of the THC response determined by this method.

1.3 The proper handling of compressed gas cylinders containing air, nitrogen, hydrogen, or helium requires the use of gas regulators to preclude over-pressurization of any instrument component

1.4 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4150 Terminology Relating to Gaseous Fuels

D7653 Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy

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

D7892 Test Method for Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry

2.2 *EPA Standard:*[3]

40 CFR Part 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit

[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.

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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.

[3] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

2.3 *SAE Standard:*[4]
SAE J2719 Hydrogen Fuel Quality for Fuel Cell Vehicles

3. Terminology

3.1 *Definitions*—For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *C_1 Hydrocarbon, n*—a hydrocarbon carbon content expressed in terms of CH_4.

3.2.2 *pressurized sampling, n*—collection of a sample in a container with a (final) container pressure above atmospheric pressure.

3.2.3 *Shewart Control Chart, n*—statistical tool for monitoring and improving quality, originated by Walter Shewart in 1924.

3.3 *Abbreviations:*

3.3.1 *C_1*—Methane basis

3.3.2 *CH_4*—Methane

3.3.3 *FID*—Flame Ionization Detector

3.3.4 *MDL*—Method Detection Limit

3.3.5 *ppm(v)*—parts per million by volume

3.3.6 *THC*—Total Hydrocarbon

4. Summary of Test Method

4.1 A hydrogen gas sample is analyzed via appropriate gas inlet system by a THC analyzer and compared to a reference standard mixture of known composition.

4.2 The THC analyzer utilizes the flame ionization method of detection. The sensor is a burner in which a regulated flow of sample gas passes through a flame sustained by regulated flows of air and a fuel gas (hydrogen or a hydrogen/diluent mixture). Within the flame, the hydrocarbon components of the sample stream undergo a complex ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through electronic measuring circuitry. The ionization current is proportional to the rate at which carbon atoms enter the burner, and is therefore a measure of the concentration of hydrocarbons in the original sample, present as CH_4. The analyzer provides a readout on a front panel digital display and a selectable output for an accessory recorder.

4.3 To ensure stable, drift-free operation, particularly in high-sensitivity applications, an internal temperature controller maintains the analyzer interior at a constant temperature. A temperature of 50 ± 1 °C is appropriate. This feature minimizes temperature-dependent variations in electronic current measuring circuitry and adsorption/desorption equilibrium of background hydrocarbons within the internal flow system.

4.4 To minimize system response time, an internal sample bypass feature provides high velocity sample flow through the analyzer.

4.5 This test method determines total carbon, and all of the hydrocarbons are assumed to have the same response as CH_4. Therefore, if the THC result is 1 ppm(v) and the hydrocarbon was CH_4, there would be 1 µmole of CH_4/mole of hydrogen. However, if the THC result is 1 ppm(v) and as an example, the hydrocarbon was propane (C_3H_8), there would be 0.36 µmole of propane per mole of hydrogen.

5. Significance and Use

5.1 Low operating temperature fuel cells such as proton exchange membrane fuel cells (PEM-FC) require high purity hydrogen for maximum material performance and lifetime. Analysis to 0.1 part per million (ppm(v)) concentration of THCs (measured as CH_4) in hydrogen is necessary for ensuring a feed gas of sufficient purity to satisfy fuel cell system needs as defined in SAE J2719 or as specified in regulatory codes.

5.2 Dynamic dilution techniques using highly accurate mass flow controllers can be used with test samples that have THC content exceeding the upper limit of the instrument's linear range, without the need to recalibrate the instrument using higher levels of calibration standards. The sample can be diluted with a high purity grade of hydrogen (99.999 %, so long as it contains < 0.1 ppm(v) THCs) to achieve a result of the THC content by applying the appropriate dilution factor to the result. Samples that contain THC concentrations greater than 1000 ppm(v) may be determined, although results will likey be achieved with reduced precision and should be analyzed by the dilution method.

5.3 Although not intended for application to gases other than hydrogen, techniques within this test method can be applied to other non-hydrocarbon gas samples requiring THC content determination. This can be achieved by using a zero gas and a calibration gas that consist of the same background gas as the actual sample. As an example, for the THC determination of nitrogen, the instrument zero point must be determined with a high purity grade of nitrogen (99.999 % and < 0.1 ppm(v) THCs) and the instrument calibration must be done with a certified standard of CH_4 in nitrogen in the appropriate range. This will correct for any interferences caused by the background gas.

6. Apparatus

6.1 *Instrument*—Any instrument of standard manufacture, with hardware necessary for interfacing to a pressurized hydrogen sample and containing all the features necessary for the intended application(s) can be used.

6.1.1 This method uses a Flame Ionization Detector (FID). The principle components of the burner are the manifold, burner jet, and the collector. Streams of sample, fuel, and air delivered by the analyzer flow system are routed through internal passages in the manifold and into the interior of the burner (see Fig. 1). Here the sample and fuel pass through the burner jet and into the flame; the air stream flows around the periphery of the flame.

6.1.2 The burner jet and the collector function as electrodes. The jet is connected to the positive terminal of a polarizing voltage. The collector is connected to the signal amplifier. The two polarized electrodes establish an electrostatic field in the

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