



Designation: ~~D7675~~—~~11~~ D7675 – 15

Standard Test Method for Determination of Total Hydrocarbons in Hydrogen by FID ~~Based~~ FID-Based Total Hydrocarbon (THC) Analyzer¹

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) measurement in hydrogen intended as a fuel for fuel cells on a ~~C1 Basis. Total Hydrocarbons methane (C1) basis.~~ The determination of total hydrocarbons on a C1 basis is an analytical technique where ~~total carbon is determined and~~ all of the hydrocarbons are assumed to have the same response as ~~Methane. methane.~~ Sensitivity from 0.1 part per million (~~ppm~~;(ppm(v), μ mole/mole) up to 1000 parts per million (~~ppm~~;(ppm(v), μ mole/mole) concentration are 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 ~~FID-based~~ FID-based hydrocarbon analysis method without the use of separation ~~columns;~~ therefore, columns. Therefore, this method does not provide speciation of individual hydrocarbons. ~~Varieties~~ Several varieties of instruments are manufactured and can be used for this method.

1.2.1 This method provides a measure of total hydrocarbons “as ~~methane~~,” methane,” because all hydrocarbon species are quantified the same as methane response, which is the sole species used for calibration. ~~Therefore C2 and above hydrocarbons are quantified.~~ 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 total hydrocarbon result as if all carbon atoms are from aliphatic, aromatic, olefinic, or acetylenic compounds, where the detector response caused by these atoms are 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 total hydrocarbon 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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

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

F307D7606 Practice for Sampling Pressurized Gas for Gas Analysis of High Pressure Hydrogen and Related Fuel Cell Feed Gases

F1398D7892 Test Method for Determination of Total Hydrocarbon Contribution by Gas Distribution System Components Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry

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.

2.2 EPA Standards:³

[EPA 40 CRF Part 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit](#)

2.3 SAE Standards:⁴

[SAE TIR-J2719 Information Report of the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles](#)

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 ~~C1 Hydrocarbon~~—Hydrocarbon, *n*—general hydrocarbon containing one Carbon atom; a hydrocarbon carbon content expressed in terms of methane.

3.1.2 ~~C2 Hydrocarbon~~—Hydrocarbon, *n*—general hydrocarbon containing two Carbon atoms; a hydrocarbon carbon content expressed in terms of ethane.

3.1.3 ~~contaminant~~—contaminant, *n*—impurity that or foreign material that makes a product less suitable or even unsuitable for the intended use or that adversely affects the components within the fuel-cell system or the hydrogen storage system; processing, storage, or distribution systems.

3.1.4 ~~dynamic calibration~~—calibration, *n*—calibration of an analytical system using calibration gas standard concentrations generated by diluting known concentration compressed gas standards with purified inert gas.

3.1.5 ~~fuel-cell grade hydrogen~~—hydrogen satisfying the specifications in SAE TIR-J2719.

3.1.5 ~~gaseous fuel~~ —, *n*—hydrogen used as a fuel source for the operation of the flame ionization detector.

3.1.6 ~~gauge pressure~~—pressure, *n*—pressure measured above ambient atmospheric pressure. Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

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

3.1.8 ~~Shewart Control Chart~~—Chart, *n*—statistical tool for monitoring and improving quality, originated by Walter Shewart in 1924 for the manufacturing environment and later extended to quality improvement in all areas of an organization.1924.

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

3.1.10 ~~student *t*-test~~, *n*—a *t*-test is any statistical hypothesis test in which the test statistic follows a student's *t* distribution if the null hypothesis is supported.

4. Summary of Test Method

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

4.2 ~~The Total Hydrocarbon Analyzer~~—The total hydrocarbon 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 methane. 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 $50^{\circ}\text{C} \pm 1^{\circ}\text{C}$ 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 methane. Therefore, if the THC result is 1 ppm v/v and the hydrocarbon was methane (CH_4) there would be $1 \mu\text{mole}$ of methane/mole of hydrogen. However, if the THC result is 1 ppm v/v and as an example, the hydrocarbon was propane (C_3H_8), there would be $0.33036 \mu\text{mole}$ of propane/mole of propane per mole of hydrogen.

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

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

5. Significance and Use

5.1 Low operating temperature fuel cells such as proton exchange membrane fuel cells (PEFCs)(PEM-FC) require high purity hydrogen for maximum material performance and lifetime. Analysis to 0.1 part per million (ppm)(ppm(v)) concentration of total hydrocarbons (measured as methane) in hydrogen is necessary for assuring 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 total hydrocarbon 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) total hydrocarbons) to achieve a result of the total hydrocarbon content by applying the appropriate dilution factor to the result. Samples that contain total hydrocarbon concentrations greater than 1000 ppm(v) may be determined, although results will likely 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 total hydrocarbon 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 total hydrocarbon determination of nitrogen, the instrument zero point must be determined with a high purity grade of nitrogen (99.999 % and < 0.1 ppm(v) total hydrocarbons) and the instrument calibration must be done with a certified standard of methane 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-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. (See Fig. 1.)

6.1.2 The burner jet and the collector function as electrodes. The jet is connected to the positive terminal of the 90 VDC a polarizing voltage. The collector is connected to the signal amplifier. The two polarized electrodes establish an electrostatic field in the vicinity of the flame. The field causes the charged particles formed during combustion to migrate. Electrons go to the burner jet; positive ions go to the collector. Thus a small ionization current flows between the two electrodes. Magnitude of the current depends on the concentration of carbon atoms in the sample. The burner current serves as the input signal to the electronic measuring circuitry.

6.2 *Detector Gas Control*—Constant flow control of detector gases is critical for optimum and consistent analytical performance. Control is achieved by use of pressure regulators and flow controllers. The gas flow is measured by appropriate means and adjusted as necessary.

6.3 *Data Acquisition*—Data acquisition and storage can be accomplished using a number of devices and media. Following are some examples.

6.3.1 *Recorder*—A 0 to 1 mV range recording potentiometer or equivalent can be used.

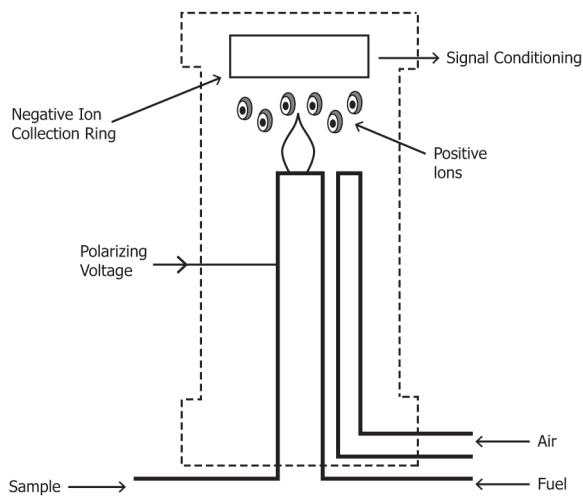


FIG. 1 Typical FID Burner Diagram

6.3.2 *Data Storage*—Most instruments come equipped with an RS-232 port. This allows the instrument to report its data to a computer or to a serial printer for data storage.

7. Reagents and Materials

NOTE 1—The use of oxygen scrubbers, water dryers, and hydrocarbon scrubbers are used in all gases supplied to the total carbon analysis system. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

NOTE 2—Compressed gas standards should only be handled in well-ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing air, nitrogen, hydrogen, or helium can result in explosion. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion. The hydrogen delivery system must be leak free or a flammable situation could occur.

7.1 *Ultra-High Purity (UHP) Hydrogen, 99.999% minimum purity, <0.1 ppmv* A high purity grade of hydrogen that meets 99.999 % minimum purity and <0.1 ppm(v) total hydrocarbon content. (**Warning**—Extremely flammable gas under high pressure.)

7.2 *Ultra Zero Grade Air, A high purity grade of compressed air with less than 0.1 ppmv* A high purity grade of compressed air with less than 0.1 ppm(v) total hydrocarbon content. (**Warning**—Compressed gas under high pressure that supports combustion.)

7.3 *Reference Standards*—The calibration standards used for this test method are NIST traceable standard mixtures of Methane in Hydrogen. Methane-methane in hydrogen traceable to NIST or another national metrology institute. Recommended methane concentrations used in this test method are listed below in Table 1. Accuracy of the standard must be 1% or better. (**Warning**—Extremely flammable gas under high pressure.)

ZERO Certified UHP Hydrogen-99.999%	SPAN 10± 2ppm Methane Balance Hydrogen
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TABLE 1 Zero Span Gas Used for Calibration

ZERO Hydrogen—99.999%; <0.1 ppm(v) THC	SPAN 10± 2 ppm(v) Methane Balance Hydrogen
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7.4 Other multi-component gases concentrations of methane in hydrogen as needed.

7.5 The use of oxygen scrubbers, water dryers, and hydrocarbon scrubbers are used in all gases supplied to the total hydrocarbon analysis system. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

8. Hazards

8.1 Compressed gas cylinders should only be handled in well-ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing air, nitrogen, hydrogen, or helium can result in explosion. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion.

8.2 The hydrogen delivery system must be leak-free or a flammable situation could occur. Safety measures such as hydrogen monitors are recommended to ensure that potentially combustible gas mixtures do not come in contact with any ignition source

9. Preparation of Apparatus

9.1 Set up the instrumentation and optimize the FID in accordance with the manufacturer's instruction or as specified herein. Optimization of the FID and a check of linearity (see 10.1.1 if optional) should occur after installation and after any maintenance is performed on the instrument. If applicable on the specific instrument, use the maximum sensitivity settings to achieve the lowest possible detection limit.

9.1.1 Start-up instrument according to manufacturer's specifications.

9.1.2 Turn on the hydrogen fuel and air cylinders to detector. Ensure flow settings are according to manufacturer specifications. Typical flow settings for flame ionization detectors are 25 mL/min for hydrogen and 250 mL/min for air.

9.1.3 Ignite detector. Flame ignition is indicated by a low popping sound. Allow sufficient time for the instrument and electronics to stabilize.

9.1.4 Proceed to calibration and sample analysis.

10. Calibration and Standardization

10.1 *Calibration*—The instrument is calibrated daily "on-use" shall be calibrated each day that it is used with zero gas (UHP Hydrogen, 99.999% (hydrogen, 99.999 % min purity, < 0.1 ppm(v) THC) and span gas certified standards. Most instruments make it is possible to adjust the zero and span gain so that the displayed percent of full scale is the same as the ppm(v) concentration in the standards. In most cases, a standard of 10 ppm(v) CH₄ balance H₂ This obviates the need for mathematical calculation and expedites THC analysis; with 1% accuracy is used for the span gas. This will provide a full scale reading of 0 to 10 ppm(v).

10.1.1 At regular intervals according to the manufacturer's recommendation, or whenever maintenance is performed, a linearity verification should be performed. This is accomplished by analyzing a minimum of three known concentrations of methane in hydrogen standards according to the following procedure. For each concentration of methane, the standard is analyzed and