Designation: D7675 – 15

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) measurement in hydrogen intended as a fuel for fuel cells on a methane (C1) basis. The determination of total hydrocarbons on a C1 basis is an analytical technique where all of the hydrocarbons are assumed to have the same response as methane. Sensitivity from 0.1 part per million (ppm(v), µmole/mole) up to 1000 parts per million (ppm(v), µmole/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 an 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 total hydrocarbons "as methane," because all hydrocarbon species are quantified the same as methane 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 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

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 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 J2719 Hydrogen Quality Guideline for Fuel Cell Vehicles

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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[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.

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

3.1.1 *C1 Hydrocarbon, n*—a hydrocarbon carbon content expressed in terms of methane.

3.1.2 *C2 Hydrocarbon, n*—a hydrocarbon carbon content expressed in terms of ethane.

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

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

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

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

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

3.1.9 *static 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 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 ± 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 methane. Therefore, if the THC result is 1 ppm(v) and the hydrocarbon was methane (CH_4) there would be 1 µmole of methane/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 total hydrocarbons (measured as methane) 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 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 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 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 (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 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.

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

7.1 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 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 standard mixtures of methane in hydrogen traceable to NIST or another national metrology institute. Recommended methane concentrations used in this test method are listed in Table 1. Accuracy of the standard must be 1% or better. (**Warning—**Extremely flammable gas under high pressure.)

TABLE 1 Zero Span Gas Used for Calibration

ZERO	SPAN
Hydrogen—99.999%; <0.1 ppm(v) THC	10± 2 ppm(v) Methane Balance Hydrogen

7.4 Other 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) 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

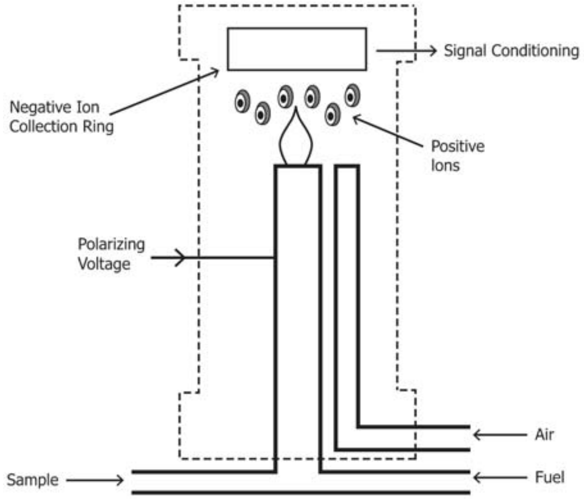

FIG. 1 Typical FID Burner Diagram

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 shall be calibrated each day that it is used with zero gas (hydrogen, 99.999 % min purity, < 0.1 ppm(v) THC) and span gas certified standards. Most instruments make it 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) CH_4 balance H_2 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 recorded. It is suggested that the concentrations used be 20%, 50%, and 90% of the maximum range that will be used. A linear regression analysis is performed using the result of each concentration level. Linearity is confirmed when the R-squared value is calculated and the result is 0.9999 or greater. Linearity should always be established at the time the instrument is first installed and prior to first use, and within 375 days of the last verification.

10.2 Compare calculated results to the certified value for a standard at or near the midpoint of the calibration range (4 to 6 ppm(v) CH_4 in H_2), before adopting the calibration. Results should agree within 2% or better of the certified value.

10.3 *Quality Assurance*—It is recommended to use a control chart to record the response of the certified standard each time the instrument is operated for the analysis of a sample. This can be accomplished during the calibration procedure (see 11.2.7). After the calibration has been completed on the instrument, document the response for the midpoint calibration standard (see 11.2.5). After a representative set of data has been recorded, the data can be plotted as a Shewart control chart to determine instrument trends. The standard three sigma (3 σ) control limits can be set as acceptance criteria for the performance of this instrument.

10.3.1 Results are reported with respect to a lower detectable limit of the analysis being performed with the instrument. A lower detectable limit of 0.1 ppm(v) has been established for this method using the student's *t*-test value for seven samples. Control charts aid in the maintaining of reproducible detection limits.

10.3.2 For this method, a standard of 0.47 ppm(v) of CH_4, balance H_2 was analyzed seven times, along with corresponding blanks of zero gas (hydrogen, 99.999% min purity, < 0.1 ppm(v) THC). The mean and standard deviation of the resulting data was computed. The Method Detection Limit (MDL) was determined using a student's *t* value of 99 % confidence level and calculations as described in EPA 40 CFR Part 136 Appendix B. A final method detection limit (MDL) of 0.06 ppm(v) was determined for this analyzer.

TABLE 2

0.47 ppm(v) std.	ppm(v) Readings	ppm(v) Readings-Zero	ppm(v) Readings-Final
Run 1	0.48	0.019	0.46
Run 2	0.50	0.013	0.49
Run 3	0.47	0.16	0.45
Run 4	0.51	0.034	0.47
Run 5	0.51	0.049	0.46
Run 6	0.53	0.027	0.50
Run 7	0.46	0.011	0.45
Avg	0.49	0.024	0.47
Std Dev - s	0.026	0.013	0.019
MDL = *t* × *s*	*t* = 3.14		MDL = 0.06 ppm(v)
t = student *t* value for seven samples			

11. Procedure

11.1 *Sampling*—Sampling at the sample source shall always be done in a manner that ensures safety and that a representative sample is being analyzed. Lack of precision and accuracy in using this method can most often be attributed to improper sampling procedures. (See Test Method D7606.)

11.2 *Calibration:*

11.2.1 Open the zero and span gas cylinder valves. Connect the zero gas to the analyzer inlet and adjust the flow to the manufacturer's specification.

11.2.2 Adjust the zero control so that the display reads 0.0.

11.2.3 Connect the span gas to the analyzer inlet and adjust the span control to the concentration of the span standard.

11.2.4 Repeat steps 11.2.2 and 11.2.3, alternating between zero and span, until the displays reaches the exact values of the standards without further adjustment. If after three adjustments, the display does not reach the value of the span standard (within 5 %), stop and proceed to optimize the FID according to the manufacturer's instructions.

11.2.5 Connect a gas cylinder of methane in hydrogen with a known certified value at or near the midpoint of the calibration range to the analyzer inlet. Adjust the flow of the standard to the same flow that was used for the zero and span gases. Wait for the reading to stabilize and record the ppm(v) concentration of the standard provided by the analyzer display. Results should agree with the certified value within 5 % or better. Repeat steps 11.2.1 through 11.2.4 if results exceed 5 %.

11.2.6 An adjustment to either zero or span necessitates a check of the opposite end of the scale. Close the zero and span gas cylinder valves.

11.2.7 If a control chart is to be used for quality assurance as recommended in 10.3, document the midpoint calibration value obtained in 11.2.5 in the control chart for this instrument along with the calibration gas cylinder serial number, standard concentration, accuracy value, date, time, and initials. Other acceptable ways to monitor the performance of the test method may be used.

11.3 *Sample Analysis:*

11.3.1 Connect a regulator to the sample vessel, and connect the sample from the regulator to the analyzer inlet via appropriate sample line connections. Ensure the sample pressure regulator does not exceed the maximum inlet pressure recommended by the instrument manufacturer. The sample pressure and flow rate must be the same as what was used to calibrate the instrument and they should never exceed the manufacturer's specification.

11.3.2 Wait for the reading to stabilize and record the ppm/v concentration of the display.

11.4 *Shutdown:*

11.4.1 Close main valve from sample vessel and allow regulator to return to atmospheric pressure. Disconnect sample connection to analyzer.

11.4.2 Close the fuel and air cylinder valves.

11.4.3 Check that the zero and span standard cylinder valves have been closed.

11.4.4 Shut down instrument in accordance with manufacturer's procedures.

12. Calculations

12.1 A direct readout of the instrument display can be used if the instrument is calibrated where the zero and span gain are set so that the displayed percent of full scale is the same as the ppm(v) concentration in the standards. This obviates the need for mathematical calculation and expedites THC analysis.

13. Report

13.1 Report the concentration of the total hydrocarbon content as the ppm(v) concentration of the readout display. The number of significant digits retained for the quantitative value of the total hydrocarbon content shall be such that accuracy is neither sacrificed or exaggerated. The expressed numerical value of the total hydrocarbon content should not be presumed to be more accurate than the corresponding certified value of the methane in the calibration standard.

14. Precision and Bias

NOTE 1—Statements of precision and bias for this method will be provided as a result of interlaboratory testing which will be performed within 5 years.

14.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials.

14.1.1 *Repeatability:* 1% full scale for successive identical samples. Repeatability data to be added within 5 years of method approval.

14.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials.

14.2.1 The reproducibility of this test method for measuring impurities present in H_2 fuel gas, is being determined and will be available within five years of the publication of this standard, based upon the results of interlaboratory testing.

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

14.4 *Precision*—The estimate of the repeatability for impurities present in H_2 fuel gas is based upon the standard deviation of 7 successive test results multiplied by a factor of 2.77. That represents the 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 resulting in the following:

Impurity Component	Estimated Repeatability at Average (ppm(v))
Total Hydrocarbon as CH_4	0.05 at 0.47 ppm(v)

15. Keywords

15.1 flame ionization detector (FID); total carbon analysis (TCA); total hydrocarbon (THC)

BIBLIOGRAPHY

ASTM Standards [2]

(1) D1945 Test Method for Analysis of Natural Gas by Gas Chromatography

(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) F307 Practice for Sampling Pressurized Gas for Gas Analysis

(6) F1398 Test Method for Determination of Total Hydrocarbon Contribution by Gas Distribution System Components

EPA Standard[3]

(7) EPA Method 25.3 Determination of Low Concentration Non-Methane, Non-Ethane Organic Compound Emissions from Clean Fueled Combustion Sources, South Coast Air Quality Management District

IEC Standard [5]

(8) IEC 60079-29-2 Selection, Installation, Use and Maintenance of Detectors for Flammable Gases and Oxygen

ISO Standards [6]

(9) ISO TS 14687-2 Hydrogen Fuel- Product Specification- Part 2: Proton Exchange Membrane (PEM) Fuel Cell Applications for Road Vehicles.

(10) ISO/TR 15916 Basic Consideration for Safety of Hydrogen Systems

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[5] Available from International Electrotechnical Commission (IEC), 3 rue de Varembé, Case postale 131, CH-1211, Geneva 20, Switzerland, http://www.iec.ch.

[6] 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.

(11) ISO/TR 26142 Hydrogen Detection Apparatus

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