Designation: D7649 − 10 (Reapproved 2017)

Standard Test Method for Determination of Trace Carbon Dioxide, Argon, Nitrogen, Oxygen and Water in Hydrogen Fuel by Jet Pulse Injection and Gas Chromatography/Mass Spectrometer Analysis[1]

This standard is issued under the fixed designation D7649; 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 carbon dioxide, argon, nitrogen, oxygen and water in high pressure fuel cell grade hydrogen by gas chromatograph/mass spectrometer (GC/MS) with injection of sample at the same pressure as sample without pressure reduction, which is called "Jet Pulse Injection". The procedures described in this method were designed to measure carbon dioxide at 0.5micromole per mole (ppmv), Argon 1 ppmv, nitrogen 5 ppmv and oxygen 2 ppmv and water 4 ppmv.

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

1.3 The mention of trade names in standard does not constitute endorsement or recommendation for use. Other manufacturers of equipment or equipment models can be used.

1.4 *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.*

1.5 *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 *Other Standards:*

SAE TIR J2719 Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles April 2008[2]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *absolute pressure*—pressure measured with reference to absolute zero pressure, usually expressed as kPa, mm Hg, bar or psi. All the pressures mentioned in this method are absolute pressure.

3.1.2 *constituent*—A 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 by reacting with its components. An adverse effect can be reversible or irreversible.

3.1.4 *dynamic calibration*—calibration of an analytical system using calibration gas standard generated by diluting known concentration compressed gas standards with hydrogen, as used in this method for carbon dioxide, argon, nitrogen and oxygen (7.3 and 7.4).

3.1.5 *extracted ion chromatogram (EIC)*—a GC/MS chromatogram where a selected ion is plotted to determine the compound(s) of interest.

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

3.1.7 *hydrogen fuel*—hydrogen to be tested without compositional change due to sample introduction, etc.

3.1.8 *jet pulse injection*—high pressure hydrogen fuel sample is introduced instantaneously at the same pressure into GC/MS.

3.1.9 *relative humidity*—ratio of actual pressure of existing water vapor to maximum possible pressure of water vapor in the atmosphere at the same temperature, expressed as a percentage.

3.1.10 *response factor (RF)*—-the amount in volume (μL) of an analyte divided by the EIC area of the analyte.

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, as used in this method for water concentration in hydrogen.

3.2 *Acronyms:*

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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.

Current edition approved April 1, 2017. Published April 2017. Originally approved in 2010. Last previous edition approved in 2010 as D7649-10. DOI: 10.1520/D7649–10R17.

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

3.2.1 *FCV*—fuel cell vehicle.

3.2.2 *PEMFC*—proton exchange membrane fuel cell.

4. Summary of Test Method

4.1 The simultaneous analysis of carbon dioxide, argon, nitrogen, oxygen and water at 0.5 – 5 ppmv (micromole per mole) in hydrogen fuel samples from fueling stations is challenging due to high hydrogen fuel sample pressure and possible contaminations from ambient air.

4.2 In this method, a small stainless steel loop is initially pressurized with high pressure hydrogen standard or sample without any pressure regulation or restriction ("Sample Loop Pressurization", Fig. 1). The hydrogen in the loop is then released entirely as a "jet pulse" into a T-union which splits sample into a 0.25 µm ID 30 m long capillary column and an electronic flow controller (EFC) used to vent excess hydrogen to the atmosphere ("Jet Pulse Injection", Fig. 2). Less than 1% of hydrogen enters the capillary column with the remaining sample venting to atmosphere through EFC. As demonstrated in Appendix X1, the hydrogen volume "jet pulse injected" into the capillary column is a constant volume and independent of the sample loop pressure when the sample loop pressure is over 90 psi. Therefore, the constant hydrogen volume from standards or samples is GC/MS analyzed in regardless of standard or sample pressures.

4.3 Jet pulse injected volume into the capillary column is approximate 100 µL (In Appendix X1, this volume is calculated to be 115µL under the analytical conditions described in Appendix X1). When a 2-mL of sample loop is pressurized to 200 psi, the hydrogen in the loop is (200 psi/14.7psi) × 2 mL or 27 mL. Hence, 99.5% of the hydrogen sample vents to atmosphere. This type of "Jet Pulse Injection" has been found acceptable for the analysis of high pressure hydrogen fuel sample since the hydrogen volume injected is independent of the pressures of hydrogen standards or samples. Consequently it is unnecessary to regulate standards and hydrogen samples to the same pressure. In addition to possible trace leaks or air trapped inside, regulators are not recommended as moisture on the regulator surface can be released into the sample resulting in a high moisture determination.

4.4 A mass spectrometer provides sensitive and selective detection towards carbon dioxide, argon, nitrogen, oxygen and water.

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 performance. The following are the reported effects (SAE TIR J2719) of the compounds determined by this test method.

5.2 *Carbon Dioxide (CO_2),* acts largely as a diluent, however in the fuel cell environment CO_2 can be transformed into CO.

5.3 *Water (H_2O),* is an inert impurity, as it does not affect the function of a fuel cell stack; however, it provides a transport mechanism for water-soluble contaminants, such as Na^+ or K^+. In addition, it may form ice on valve internal surface at cold weather or react exothermally with metal hydride used as hydrogen fuel storage.

5.4 *Inert Gases (N_2 and Ar),* do not normally react with a fuel cell components or fuel cell system and are considered diluents. Diluents can decrease fuel cell stack performance.

5.5 *Oxygen (O_2),* in low concentrations is considered an inert impurity, as it does not adversely affect the function of a fuel cell stack; however, it is a safety concern for vehicle on board fuel storage as it can react violently with hydrogen to generate water and heat.

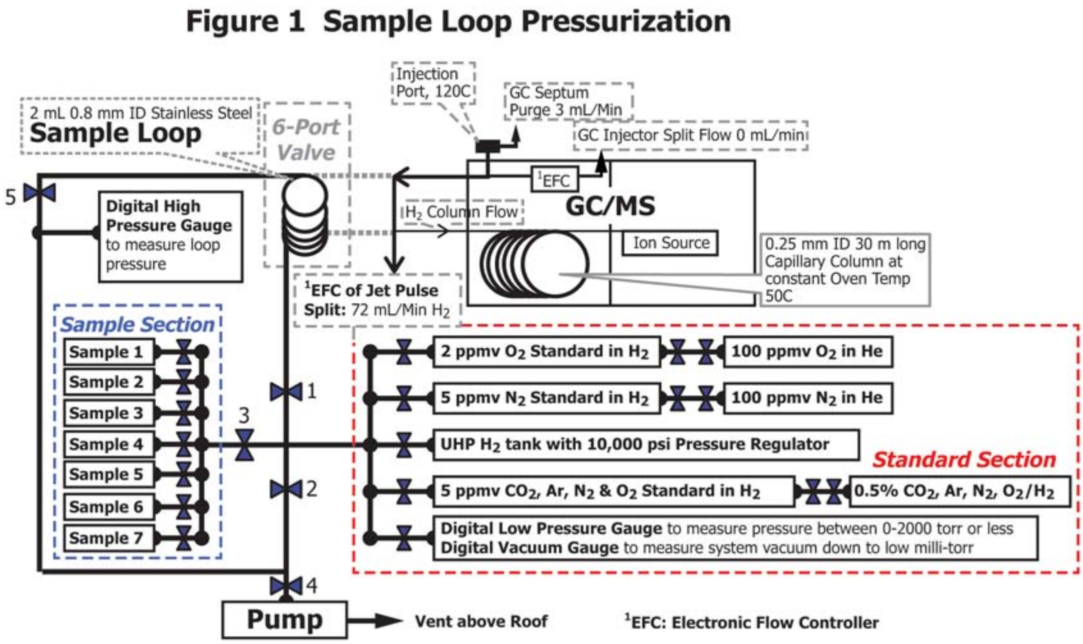

FIG. 1 Sample Loop Pressurization

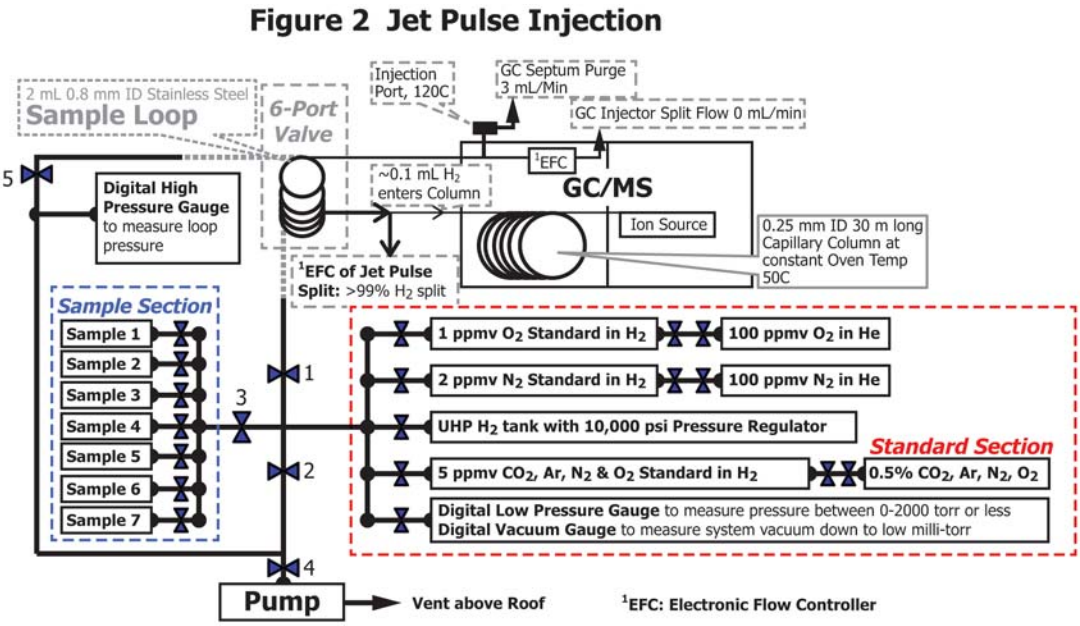

FIG. 2 Jet Pulsed Injection

6. Apparatus

6.1 *Mass Spectrometer (MS)*—The MS can perform mass calibration with a scanning range from m/e 15 to 650. The background peak intensities of water, nitrogen, argon, oxygen and carbon dioxide in the mass spectrum of FC-43 (perfluorotributylamine), used for mass calibration, should be less than 10% of m/e 69 to demonstrate a background acceptable for the determination of these analytes before beginning sample analysis. All analytes determined according to this method have a molecular mass less than 44 amu; therefore, the mass scanning range of m/e 15 to 50 is typically used.

6.2 *Data System*—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:

6.2.1 Graphic presentation of the total ion chromatogram (TIC) and extracted ion chromatogram (EIC).

6.2.2 Digital display of chromatographic peak areas.

6.2.3 Identification of peaks by retention time and mass spectra.

6.2.4 Calculation and use of response factors.

6.2.5 External standard calculation and data presentation.

6.3 *Gas chromatography (GC)*—Chromatographic system capable of obtaining retention time repeatability of 0.05 min (3 s) throughout the analysis.

6.3.1 *Interface with MS*—A heated interface connecting the GC column to the MS ion source.

6.3.2 *GC Column*—A 0.25mm ID 30m 0.25 µm film thickness DB-5 column has been successfully used to perform this analysis. Other capillary columns may be used provided chromatographic peaks do not significantly tail. One end of the GC column is connected to the Jet Pulse Split (6.4.5) and the other end is connected to the ion source inlet of a mass spectrometer.

6.3.3 *Carrier Gas*—Ultra high purity hydrogen is used as carrier gas. Use of helium carrier gas results in unacceptable broadening of the water chromatographic peak. An example of water peaks is shown in Fig. 3.

6.3.4 *GC Injector*—An injector port with a glass insert and a septum is connected through a 1⁄16 in. OD stainless steel tubing to a jet pulse split (6.4.5) in the inlet system (6.4). The injector temperature is set to at 220°C to ensure that all water vapor in injected ambient air are not condensed in the injector. The GC column and total split flow rate are electronically set at 1.5 and 75 mL/min, respectively. The GC total split flow includes a GC septum purge flow of 3mL/min (Fig. 1 and Fig. 2) and GC injector split flow of 72mL/min.

6.4 *Inlet System*—A system introduces high pressure samples or standards into GC/MS for analysis. The sample or standard enter the inlet system through "Sample Loop Pressurization" (Fig. 1) and then leave the inlet system to GC/MS through "Jet Pulse Injection" (Fig. 2). While the inlet system is in "Sample Loop Pressurization", the sample loop (6.4.4) is pressurized directly with hydrogen samples or calibration standards without pressure regulation or flow restriction. Afterwards, a six-port sample valve (6.4.1) switches the inlet system to "Jet Pulse Injection", in which pressurized hydrogen in the sample loop is released instantaneously onto the GC column (6.3.2) and jet pulse split (6.4.5). Since the sample pressure is high, all parts of the inlet system must be capable of working at pressures of 1500 psi or higher.

6.4.1 *Six Ports Valve*—This valve is used to switch from "Sample Loop Pressurization" (Fig. 1) to "Jet Pulse Injection" (Fig. 2).

6.4.2 *Samples and Calibration Standards*—All calibration standards and samples are prepared or collected in 1800 psi pressure rated containers with a DOT 3A1800 label (United Stated Department of Transportation mandated label) affixed to the outside surface. All calibration standards and samples are