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:*

---

[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.

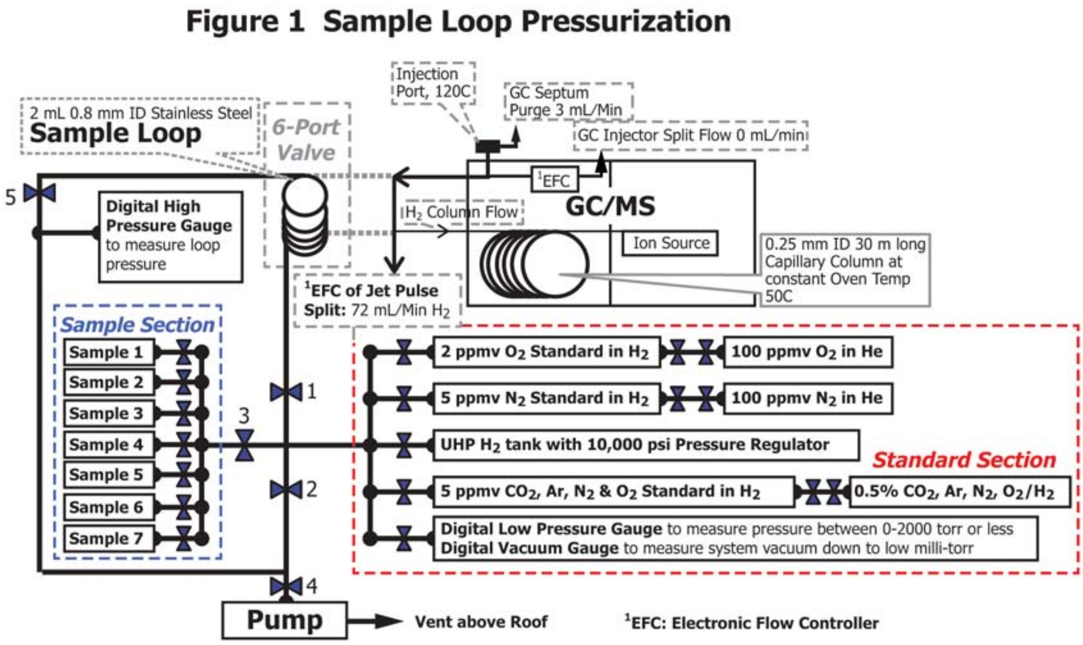

FIG. 1 Sample Loop Pressurization

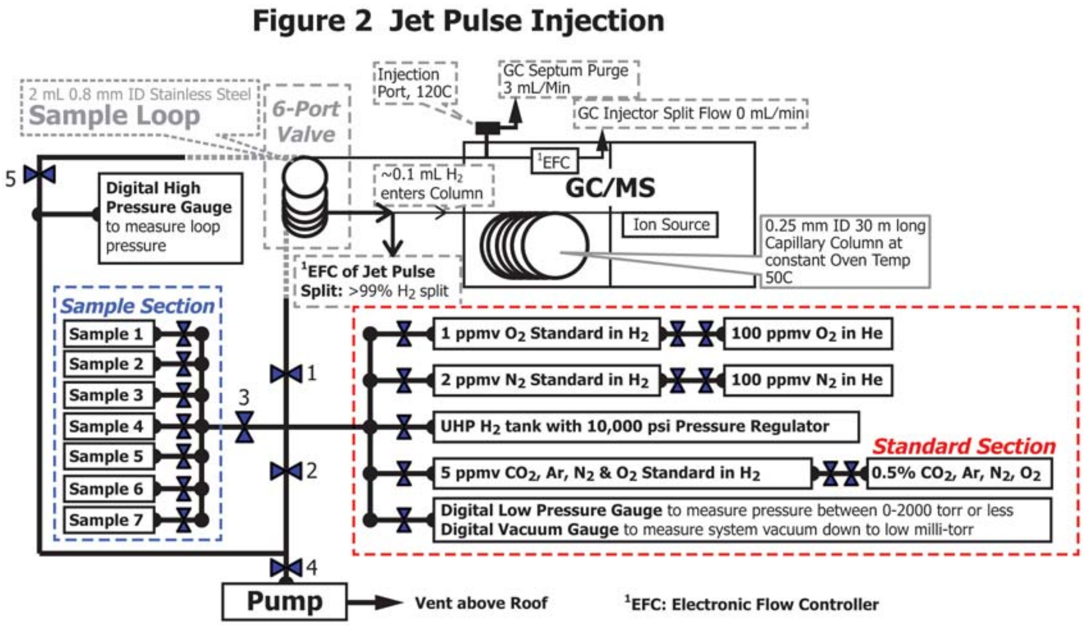

FIG. 2 Jet Pulsed Injection

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

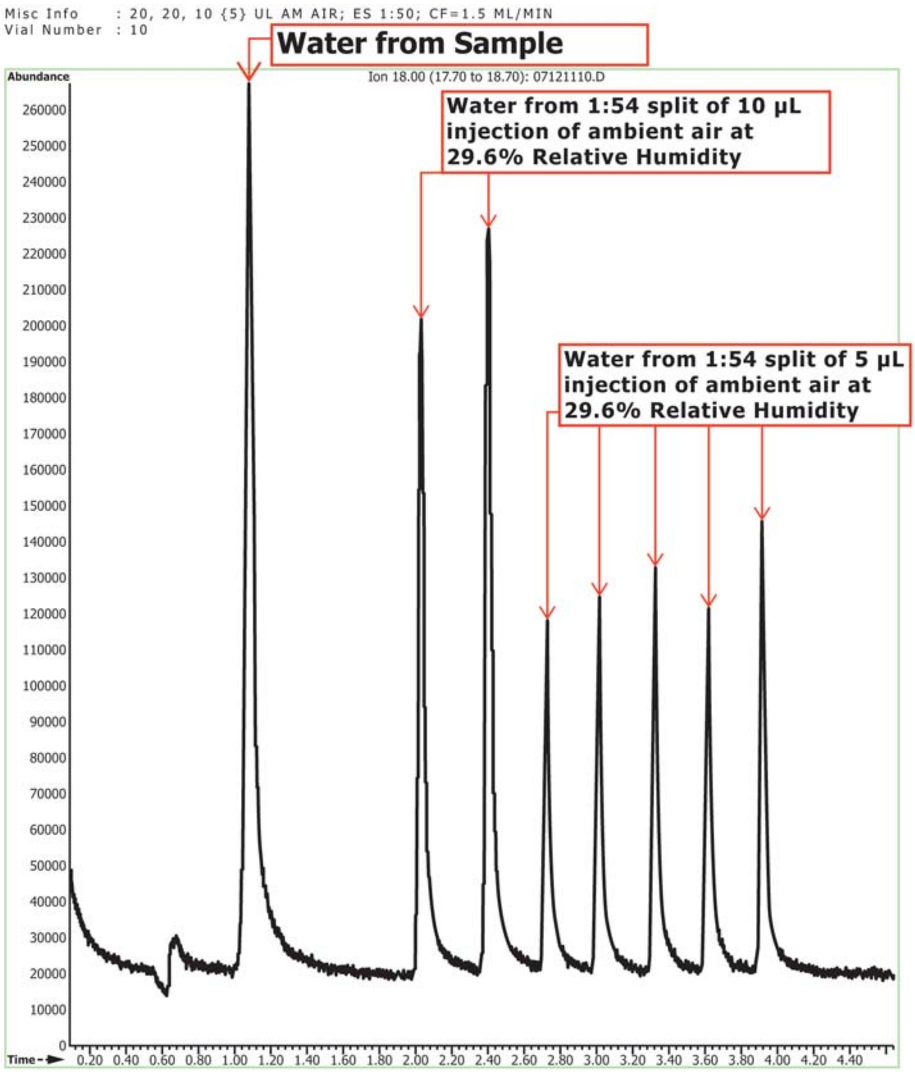

FIG. 3 m/e18 Extracted Ion Chromatogram of Sample Analysis with Co-Injection of Ambient Air

connected to the inlet system before beginning an analytic sequence to minimize the potential for air or moisture contamination due to addition or replacement of standard or sample containers.

6.4.3 *Vacuum Pump*—an oil vacuum pump that can pump down to 50 mtorr or less.

6.4.4 *Sample Loop*—stainless steel tubing with 1⁄16 in. OD and 2 mL inside volume. Both ends of the sample loop are connected to a six port valve (6.4.1).

6.4.5 *Jet Pulse Split*—a T-union connects the following three portions.

6.4.5.1 Six port valve (6.4.1)

6.4.5.2 Inlet of GC column (6.4.2)

6.4.5.3 Inlet of an electronic flow controller (EFC) with its outlet to ambient air. The flow rate of this EFC is always electronically set at 150mL/min to vent most of the GC injector split flow (72mL/min) during "Sample Loop Pressurization" (Fig. 1) and released hydrogen from pressurized sample loop in "Jet Pulse Injection" (Fig. 2).

6.4.6 *Digital Vacuum Gauge*—capable of measuring absolute pressure at vacuum range 0 to 12,000 milli-torr (mtorr or 10^{-3} torr). For the vacuum range from 0 to 1000 mtorr, the accuracy is ± 10% or± 10 mtorr, whichever is larger.

6.4.7 *Digital Pressure Gauges*—Two types of digital pressure gauges are required. A pressure gauge 0 to 1000 psig is used to measure sample and standard final pressure. Another digital pressure gauge in the low and narrow pressure range, such as 0 to 2000 torr, is used to measure the pressure of pure gases in initial standard preparation.

6.4.8 *Pressure Regulator*—A 10,000 psi pressure regulator is used to reduce UHP hydrogen pressure to approximate 400 psi for calibration standard preparation. It is also used to pressurize the inlet system during method blank analysis, and during inlet system flushing.

7. Reference Standards

7.1 Typical reference standards are listed in Fig. 1. Two standards prepared in helium containing 100 ppmv O_2 and 100 ppmv N_2, are commercial available. Remaining standards listed in Fig. 1 are prepared as per below.

7.2 *0.5% CO_2, Ar, N_2 and O_2 in hydrogen*—An evacuated 1-L cylinder is connected to four pressure-regulated compressed gas cylinders containing reagent or UHP grade CO_2, Ar, N_2 and O_2. The system is evacuated to less than 500 mtorr with all the regulators opened and the main cylinder valves closed. With the system isolated from vacuum pump, the 1-L cylinder valve is opened and 100 torr of each target compound from the compressed gas cylinders is expanded into the system and 1-L cylinder. The 1-L cylinder is then pressured using UHP hydrogen to 390 psi, or $390/14.7 \times 760 = 2.02 \times 10^4$ torr. The concentration of each target compound is 100 torr/(2.02×10^4 torr) = 0.5 %. This standard can be used as a co-injection standard (9.3.3) and further diluted to prepare a 5 ppmv standard (7.3). The UHP hydrogen used for preparation of both 0.5% (7.2) and 5 ppmv standards (7.3) are free from CO_2, Ar, N_2 and O_2 by this test method.

7.3 *5ppmv CO_2, Ar, N_2 and O_2 in hydrogen:*

7.3.1 Close all the valves in Fig. 1 except leave Valves 2, 4 and both valves of the cylinder labeled with "5 ppmv CO_2, Ar, N_2& O_2 Standard in H_2" open. Evacuate the "Standard Section" in Fig. 1 to less than 100 mtorr.

7.3.2 Close Valve 2 and pressurize the "Standard Section" in Fig. 1 to above 100 psi by UHP hydrogen.

7.3.3 Open Valve 2 and pump the "Standard Section" in Fig. 1 to less than 100 mtorr and then close it.

7.3.4 Close the valve of the standard cylinder close to the 0.5% standard and open the valve of the cylinder containing the 0.5% CO_2, Ar, N_2 and O_2 in hydrogen for about 10 s and then close it.

7.3.5 Open the valve of the standard cylinder close to the 0.5% standard for 5 s and close it. Measure the pressure by the digital pressure gauge in Fig. 1.

7.3.6 Pressurize the "Standard Section" in Fig. 1 to less than 400 psi with UHP H_2 with 10,000 psi pressure regulator and close the other valve of the standard cylinder.

7.3.7 The concentration of the standard is calculated as following. If the pressure in 7.3.5 is 20 torr and final pressure 385 psi (7.3.6), the concentration is (20 torr × (0.50/100)/(385/14.7×760) = 5.0 ppmv.

7.3.8 Low concentration standards other than 5 ppmv can be prepared and used as calibration standards.

7.4 *Detection Limit Standards of Oxygen and Nitrogen*— ~2 ppmv O_2 and ~5 ppmv N_2 in hydrogen. The preparation of these two standards from commercially available 100 ppmv O_2 and N_2 in helium, respectively, is in the same as that for 5ppmv CO_2, Ar, N_2 and O_2 in hydrogen (7.3). The detection limit standards are analyzed in each analytical sequence to validate acceptable detection of oxygen and nitrogen at the detection limit.

8. Preparation of Apparatus

8.1 *GC/MS*—Place in service in accordance to the manufacturer's instructions. Perform daily mass calibration using FC-43. As stated in 6.1, each of the peak intensities of m/e 18, 28, 29, and 32 should be less than 10% of m/e 69 in the mass spectrum of FC-43 used for mass calibration. In order to achieve this condition, the GC column flow rate of GC/MS system should be set at a high flow rate, such as, 2mL/min, while the system is in standby mode to remove any air in the carrier gas line. In addition, when any air may be introduced into the carrier gas system, such as when changing the hydrogen carrier gas tank, the GC total split flow rate is set at 100mL/min for an hour to rapidly remove air in the carrier gas line.

9. Procedure

9.1 The detailed procedures used to perform jet pulse injection followed by GC/MS analysis are listed below. The procedures are split into two sections – sample loop pressurization (Fig. 1) and jet pulse injection/GC/MS analysis (Fig. 2).

9.2 *Sample Loop Pressurization (Fig. 1):*

9.2.1 With all the valves closed in Fig. 1, Valves 2, 3 and 4 are opened and pumped down including both standard and sample sections to less than 100 mtorr. If this pressure cannot be lowered to at least 100 mtorr, perform a leak check.

9.2.2 Open Valves 1 and 5 and close Valves 2 and 4, followed with pressurization of the sample loop with UHP hydrogen to 300 – 400 psi.

9.2.3 Open Valve 4 only to pump down the entire system to less than 10 torr and then open Valve 2 to less than 1 torr. Simultaneously, measure the flow rate from EFC of the jet pulse split (6.4.5); this should be close to 72 mL/min.

9.2.4 Close both Valves 2 and 4 and pressurize the entire system with standard or sample and measure the loop pressure using a digital high pressure gauge as depicted in Fig. 1. For safety reason, it is recommended that the loop pressure not be over 500 psi. For the method blank analysis using UHP hydrogen, the loop should be pressurized to approximate 400 psi.

9.3 *Jet Pulse Injection/GC/MS Analysis (Fig. 2):*

9.3.1 Switch the six port valve to "Jet Pulse Injection" (Fig. 2) and simultaneously start GC/MS acquisition.

9.3.2 Measure the GC injector split flow rate, which should be 0 mL/min since most injector split flow vents out from the jet pulse split (6.4.5). Measure the GC septum purge flow, which should be approximate 3 mL/min.

9.3.3 After 1.5 minutes from the start of GC/MS acquisition, the 0.5% CO_2, Ar, N_2 and O2 in hydrogen (6.2), 1% CO_2 in nitrogen or ambient air is co-injected three times and 18 seconds apart. The volume and time interval of co-injections can be varied, for example, those in Table X1.1 of Appendix X1. The reasons for co-injection are listed under "Co-Injection" of Appendix X1. Each GC/MS analysis is completed in less than 5 minutes.

9.3.4 A typical analytic sequence is shown in Table 1. As shown in this table, except for the method blank, each standard or sample is analyzed consecutively three times. The three analyses of each standard or sample should generate the same extracted ion chromatogram (EIC) areas of target compounds within analytical error, as described in Appendix X1; this demonstrates that the jet pulse injected the same volume of each hydrogen standard or sample. The EIC of target compounds are m/e44 for CO_2, 40 Ar, 29 N_2, 32 O_2 and 18 H_2O.

TABLE 1 Analytical Sequence[A]

#	Analytical Sequence[B]	Co-Injection
1	UHP Hydrogen – This analysis must be repeated if any target compound is over the detection limits	10, 10 & 10µL 0.5% CO2, Ar, N_2 and O_2 in H_2 (7.2)
2	Detection Limit Standard of O_2- 2 ppmv O_2 in H_2	10, 10 & 10µL 0.5% CO_2, Ar, N2 and O_2 in H_2 (7.2)
3	Detection Limit Standard of O_2- 2 ppmv O_2 in H_2	5, 5 & 5µL commercially available standard, such as, 1% CO_2 in N_2; it is used to compare the RF of CO_2 from 0.5% CO_2, Ar, N_2 and O_2 in H_2 (7.2) and also used to demonstrate the syringe used is free from water before injection of ambient air in next analysis, water must not be detected at this co-injection.
4	Detection Limit Standard of O_2- 2 ppmv O_2 in H_2	10, 5 & 2µL Ambient Air. The 2µL injection of ambient air is detection limit standard.
5	Detection Limit Standards of N_2- 5 ppmv N_2 in H_2	10, 10 & 10µL 0.5% CO_2, Ar, N_2 and O_2 in H_2 (7.2)
6	Detection Limit Standards of N_2- 5 ppmv N_2 in H_2	5, 5 & 5µL 1% CO_2 in N_2; water must not be detected at this co-injection before injection of ambient air in next analysis.
7	Detection Limit Standards of N_2- 5 ppmv N_2 in H_2	10, 5 & 2µL Ambient Air. The 2µL injection of ambient air is detection limit standard.
8	5 ppmv CO_2, Ar, N_2 and O_2 in hydrogen (7.3)	10, 10 & 10µL 0.5% CO_2, Ar, N_2 and O_2 in H_2 (7.2)
9	5 ppmv CO_2, Ar, N_2 and O_2 in hydrogen (7.3)	5, 5 & 5µL 1% CO_2 in N_2; water must not be detected at this co-injection before injection of ambient air in next analysis
10	5 ppmv CO_2, Ar, N_2 and O_2 in hydrogen (7.3)	10, 5 & 2µL Ambient Air. The 2µL injection of ambient air is detection limit standard
11	UHP Hydrogen – This analysis must be repeated if any target compound is over detection limits	10, 10 & 10µL 0.5% CO_2, Ar, N_2 and O_2 in H_2 (7.2)
12	Sample #1	10, 10 & 10µL 0.5% CO_2, Ar, N_2 and O_2 in H_2 (7.2)
13	Sample #1	5, 5 & 5µL 1% CO_2 in N_2; water must not be detected at this co-injection before injection of ambient air in the next analysis
14	Sample #1	10, 5 & 2µL Ambient Air. The 2µL injection of ambient air is detection limit standard.
• • • The additional samples are analyzed as Sample #1.		

[A] Percentage relative humidity and atmospheric pressure are measured during each analysis for water concentration calculation by Eq and Eq .

[B] The co-injection starts after 1.5 minutes from the beginning of GC/MS acquisition. Three consecutive co-injections are injected at 18 seconds apart. However, different volumes and numbers of co-injections at different time intervals can be used, such as the example in Table X1.1 in Appendix X1.

TABLE 2 Example of GC/MS Operating Parameters

Gas Chromatograph	
Column:	30m 0.25mm ID 0.2µm DB-5 fused silica column
Carrier Gas;	Ultrahigh purity hydrogen
Column Flow Rate:	1.5 cm^3/min
Septum Purge Flow Rate:	3mL/min
Loop Split Flow Rate:	72cm^3/min
Isothermal Column Temperature:	50°C
Injector Temperature:	220°C
Mass Spectrometer	
Repetitively scan from m/e 15 to 50 at one second or fewer intervals.	

In general, the variation of EIC areas of 5 ppmv CO_2, Ar, N_2 and O_2 in hydrogen (7.3) in three consecutive analyses in the analytical sequence (Table 1) are less than 10% RSD for CO_2 and Ar. For N_2 and O_2, the %RSD should be less than 30% due to the baseline noise of GC/MS analysis.

10. Calculation

10.1 The concentrations of carbon dioxide, argon, nitrogen and oxygen in hydrogen sample can be calculated from the EIC areas of carbon dioxide at m/e44, argon m/e40, nitrogen m/e29, and oxygen m/e32 using Eq . See Fig. 4.

10.2 The jet pulse injected volume described in 9.3.4 can be calculated from the RF of co-injection (Eq) and the EIC area of jet pulse injected 5 ppmv standard (7.2), as shown in Eq . The split ratio is the ratio of sum of the flow rates of the jet pulse split, GC injector split and injector septum purge over the column flow rate. In general, it is close to 50. Since air contains 0.934% of argon, the RF of argon can be also calculated from ambient air co-injection.

10.3 The concentration of water in hydrogen cannot be calculated from Eq since a water standard at low ppmv in hydrogen cannot be prepared or purchased commercially. However, the relative humidity of ambient air can be precisely measured by humidity meter; therefore, a known amount of water in co-injected ambient air of a known volume can be used as a calibration standard for water. The percentage of water in ambient air is relative humidity times the saturated water vapor pressure in mm Hg divided by atmospheric pressure in mm Hg. At 25°C, the atmosphere is saturated with water vapor when the partial pressure of water is 23.756 torr. The RF of water at 25C is calculated in Eq and water concentration in a hydrogen sample according to Eq . Examples for all calculations, except Eq , in Section 10 are contained in Appendix X1. The 2µL ambient air injection is

$$\textit{Sample Concentration} = \frac{\textbf{Average EIC Area of Jet Pulse Injected Sample}}{\textbf{Average EIC Area of Jet Pulse Injected Standard}} \times \textit{Standard Concentration} \cdots (1)$$

$$\textit{Response Factor (RF)} = \frac{\textbf{Volume (μL) of Co Injected Standard} \times \textbf{Concentration of Standard}}{\textbf{Split Ratio} \times \textbf{Peak Area of EIC Area}} \cdots (2)$$

$$\textit{Jet Pulse Injected Volume (μL)} = \frac{\textbf{EIC Area of Jet Pulse Injected 5 ppmv Standard (7.3)} \times \textbf{RF}}{\frac{5}{1,000,000}\ \textbf{(Concentration of 5 ppmv Standard)}} \cdots (3)$$

$$RF\ of\ H_2O = \frac{\textbf{Co Injected Air Volume (μL)} \times \frac{\textbf{23.756 torr}}{\textbf{atmospheric pressure in torr}} \times \textbf{Relative Humidity}}{\textbf{Split Ratio} \times \textbf{Area of } \frac{m}{e}\ \textbf{18 of } H_2O\ \textbf{in coinjected air}} \cdots (4)$$

$$H_2O\ Conc.\ (ppmv)\ in\ sample = \frac{\textbf{Average } \frac{m}{e}\ \textbf{18 Area of Jet Pulse Injected } \mathbf{H_2}\ \textbf{Sample} \times RF\ of\ H_2O}{\textbf{Jet Pulse Injected Hydrogen Volume in μL as calculated in (3)}} \times 1,000,000 \cdots (5)$$

$$\textit{Detection Limit of water} = \frac{2\ \mu L \times 0.25 \times 23.756\ torr}{50 \times 100\ \mu L \times 760\ torr} \times 1,000,000 = 3.1\ ppmv \cdots (6)$$

FIG. 4 Equations

used to determine the detection limit of water. The jet injected volume is in general 100μL under the conditions in Fig. 1. If the relative humidity is 25%, atmospheric pressure 760 torr and split ratio (10.2) 50, the detection limit of water is 3.1ppmv, as shown in Eq .

11. Precision and Bias

11.1 *Precision*—The estimate of the repeatability for impurities present in H_2 fuel gas, is based upon the standard deviation of 14 successive test results multiplied by a factor of 2.77 which represent that 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 result in the following:

Target Constituents	Estimated Repeatability at Average (ppmv)
Carbon Dioxide	0.51 at 2.7
Argon	0.53 at 2.6
Nitrogen	2.2 at 2.6
Oxygen	2.0 at 2.7
Water	1.6 at 5.1

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

12. Keywords

12.1 jet pulse injection; high pressure hydrogen; gas chromtography/mass spectrometer detection

APPENDIX

(Nonmandatory Information)

X1. JET PULSE INJECTION

X1.1 Summary

X1.1.1 To demonstrate that "Jet Pulse Injection" as depicted in Fig. 2 injects a constant volume of hydrogen into a GC/MS independent of hydrogen pressure, an experiment is performed to analyze a diluted calibration standard in hydrogen repetitively by jet pulse injection/GC/MS. The hydrogen pressure of the diluted calibration drops gradually during the entire experiment. The EIC areas of the target compounds are measured for each analysis. The results indicate that the EIC areas remain constant within the analytic error independent of hydrogen pressure drop. This leads to the conclusion that the hydrogen volume injected by jet pulse injection is constant independent of hydrogen pressure of this diluted calibration standard.

X1.2 Experimental

X1.2.1 A diluted calibration standard, Standard-J in Table X1.1, in a one liter steel containerwas analyzed consecutively by jet pulse injection/GC/MS from the Standard-J initial pressure 210 to 78 psi, as listed in Table X1.1. As shown in this table, the analytical sequence of 1st to 4th Analysis of Standard J was repeated a total of 6 times with total 24 analyses. Before this sequence of analyses of Standard-J, UHP hydrogen was

TABLE X1.1 Analysis of Standard-J by Jet Pulse Injection/GC/MS

Analytical Number	Jet Pulse Injection	Associated Co-Injection	Pressure (psi) of Standard-J
Method Blank	UHP H_2 (304 psi)		
1st Analysis	Standard-J	100, 100, 50, 50, 20, 20, 20 µL of 0.5% CO2, Ar, O2 and 2.0% N2 in H2	210
2nd Analysis	Standard-J	20, 20, 10, 10, 10, 10, 10 µL of Concentrated Standard 2 -1.0% CO2 in N2	201
3rd Analysis	Standard-J	20, 20, 10, 10, 10, 10, 10 µL of Ambient Air	193
4th Analysis	Standard-J	No Co-Injection	185

The analytical sequence from 1st to 4th Analysis is repeated additional six times with the pressure of Standard-J decreases consecutively as following. The number after analysis is the number of 1st to 4th Analysis being repeated.

177 psi,1stAnalysis - 2	170 psi, 2nd Analysis - 2	163 psi, 3rd Analysis - 2	155 psi, 4th Analysis - 2
149 psi, 1st Analysis - 3	142 psi, 2nd Analysis - 3	136 psi, 3rd Analysis - 3	131 psi, 4th Analysis - 3
125 psi, 1st Analysis - 4	120 psi, 2nd Analysis - 4	115 psi, 3rd Analysis - 4	110 psi, 4th Analysis - 4
106 psi, 1st Analysis - 5	101 psi, 2nd Analysis - 5	97 psi, 3rd Analysis - 5	93 psi, 4th Analysis - 5
89 psi, 1st Analysis - 6	85 psi, , 2nd Analysis - 6	82 psi, 3rd Analysis - 6	78 psi, 4th Analysis - 6

Standard-J contains 7.7 ppmv CO_2 , 7.7 ppmvAr, 7.7 ppmv O2 and 31.8 ppmv N_2 in H_2; Standard-J is prepared from the dilution through pressurization of the 0.5% CO_2, Ar, O_2 and 2.0% N_2 in H_2 listed above as co-injection standard.

analyzed by the jet pulse injection/GC/MS to demonstrate no target compounds were detected above detection limits.

X1.3 Co-Injection

X1.3.1 As shown in Table X1.1, each analysis is co-injected, after 1.3 minutes from the beginning of jet pulse injection, with a series of volumes of concentrated calibration standards or ambient air at approximate 12 seconds apart through the GC injector in Fig. X1.1. However, every four analysis in the sequence does not have a co-injection. The reasons for co-injection are listed below.

X1.3.1.1 Instrumentation sensitivity variation through the entire analytical sequence can be monitored through the response factor (RF, Eq) variation of the target compounds in the co-injection.

X1.3.1.2 The volume of hydrogen from Standard-J injected through jet pulse injection is unknown; however, the volume injected through jet pulse injection can be measured by comparison of the extracted ion chromatogram (EIC) areas of each target compound from jet pulse injection and its response factor (RF) from the co-injection, as shown in (Eq).

X1.3.1.3 The RF of water can be calculated from co-injected ambient air, as shown in Eq (Fig. 4). The water concentration in the jet pulse injected hydrogen sample can be calculated (Eq) from the RF of water and the jet pulse injected volume (Eq). For each analysis, the extracted ion chromatogram (EIC) areas of carbon dioxide at m/e44, argon m/e40, nitrogen m/e29, oxygen m/e32 and water m/e18 are obtained for Standard-J and seven co-injections. We use $[M+1]^+$ m/e29 for quantitation of nitrogen, instead of its molecular ion m/e28, since m/e29 is the base peak while hydrogen is used as carrier gas. The ion m/e29 is N_2H^+ and formed in the following ion-molecule or chemical ionization reaction. See Fig. X1.2.

Carbon dioxide and argon, but not oxygen, also have similar ion-molecular reaction as nitrogen. However, unlike nitrogen, their molecular ions are base peaks. Carbon dioxide has both m/e 44 and 45 in the ratio of 2:1, argon m/e 40 and 41 1:0.8, however, nitrogen m/e 28 and 29 0.7:1.

X1.3.1.4 In this entire analytical process, Standard-J is repetitively jet pulse injected into the GC/MS, which leads to a Standard-J pressure decrease consecutively from 210 to 78 psi. If the jet pulse injection method injects the same volume of the Standard-J into GC/MS each time in spite of pressure drop, the EIC areas of the target compounds should be the same within instrumentation variation.

X1.3.1.5 The instrumentation variation is measured as the percent relative standard deviation of the co-injections response factor (RF), which is the ratio of the volume of the target compound co-injected onto GC column over the EIC area of the target compound. Since the co-injection into the GC injector is split, the volume of the target compound injected is (volume injected through GC injector × Concentration of the target compound/split ratio). The split ratio is the ratio of the sum of the flow rates of the jet pulse split, GC injector split and injector septum purge over the column flow rate, which is 75/1.5 or 50 for the case in Fig. X1.1. An example to calculate RF of CO_2 using Eq (10.2) is shown below for 10µL co-injection of 0.49% CO_2, Ar, N_2, and O_2 in H_2.

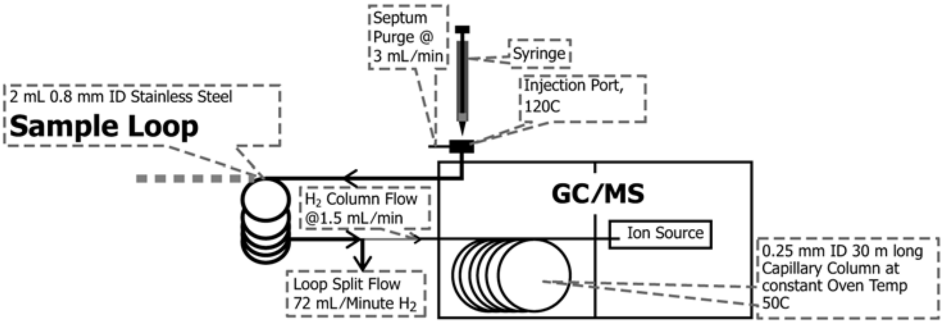

FIG. X1.1 Co-Injection

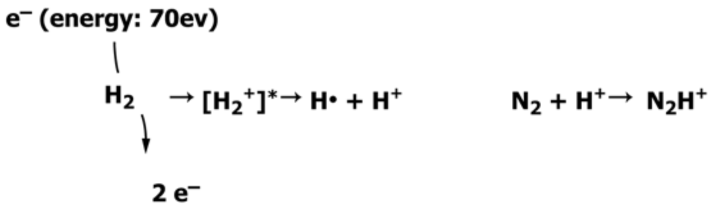

FIG. X1.2

$$RF = \frac{10\mu L \times \frac{0.49}{100}(concentration)}{50\,(Split\ Ratio) \times \frac{m}{e}\,44\,Area}$$

X1.3.1.6 The EIC areas of carbon dioxide, argon, nitrogen and oxygen in Standard-J analyzed by jet pulse injection in the entire analytical process are summarized for in Table X1.2. The %RSD of EIC areas for carbon dioxide of Standard-J are 6.8 %, which are practically identical to the corresponding %RSD of co-injection RFs, 7.3 %, within experimental errors. This means that the volumes of carbon dioxide of Standard-J jet pulse injected into GC/MS throughout the entire analytical process are identical. The same argument can apply to argon, since %RSD of argon from jet pulse injected Standard-J, 7.1%, is almost identical to that of co-injection, 8.7%. The only way to get constant jet pulse injected volume of both carbon dioxide and argon in Standard-J is through constant hydrogen volume of Standard-J injected by jet pulse injection throughout the entire analytical process. The nitrogen and oxygen have higher %RSD for both Standard-J and co-injection, probably due to nitrogen and oxygen always present in the GC/MS background.

X1.3.1.7 However, the same argument can be applied to nitrogen and oxygen. From these experimental results, one can conclude that the hydrogen volumes injected by jet pulse injection is constant and independent of the hydrogen pressure for hydrogen pressure over 90 psi. However, Standard-J does not contain water or moisture since moisture is easily absorbed onto surfaces, including the internal surface of the standard container. For the same reason, commercial moisture standards are not available in ppmv concentrations. However, the relative humidity of ambient air can be precisely measured by humidity meter; therefore, ambient air can be used as a calibration standard for moisture. The percentage of water in ambient air is the percentage of humidity measured times the saturated water vapor pressure in mm Hg divided by atmospheric pressure in mm Hg. At 25°C, the atmosphere is saturated with water vapor when the partial pressure of water is 23.756 torr. The RF of water is calculated in Eq and water concentration in hydrogen sample Eq .

X1.3.1.8 As shown in Eq , the jet pulse injected hydrogen volume must be calculated (Eq) to obtain the water concentration in samples. An example of calculation of the jet pulse injected volume by Eq is given for the analytical data in Table X1.2. The average area of m/e 44 of jet pulse injected standard J and average RF of co-injected CO_2 are 15803 and 5.6 × 10^{-8}, respectively, as shown in Table X1.2. For standard J containing 7.7 ppmv CO_2, the jet pulse injected volume is calculated based on CO_2 as below.

$$Jet\ Pulsed\ Injected\ Volume = \frac{15803\ area\ unit \times 5.6 \times 10^{-3}\frac{\mu L}{area\ unit}}{\frac{7.7}{1,000,000}} = 115\mu L$$

X1.3.1.9 As the same token, the jet pulse injected volume calculated using m/e40 of Ar is (5640 × 1.7 × 10^{-7})/(7.7/1000000) = 124 µL. The difference between both jet pulse injected volumes is 7.5%. However, the jet pulse injected volumes calculated based on nitrogen and oxygen are 102 and 88 µL, respectively. Since its large %RSD for both average areas through jet pulse injection, these two jet pulse injected volumes are only for reference. In general, we use the jet pulse injected volume calculated using CO_2 since its EIC noise is smallest.

TABLE X1.2 Extracted Ion Chromatogram (EIC) Areas of Standard-J

Pressure range	Carbon Dioxide, 7.7 ppmv			Argon, 7.7 ppmv			Nitrogen, 31.8 ppmv×			Oxygen, 7.7 ppmv×			Water
	Average m/e 44 Area of Standard-J	%RSD of m/e 44 Area of Standard-J	Average and %RSD of RFs of CO_2 in Co-Injection	Average m/e 40 Area of Standard-J	%RSD of m/e 40 Area of Standard-J	Average and %RSD of RFs of Ar in Co-Injection	Average m/e 29 Area of Standard-J	%RSD of m/e 29 Area of Standard-J	Average and %RSD of RFs of N_2 in Co-Injection	Average m/e 32 Area of Standard-J	%RSD of m/e 32 Area of Standard-J	Average and %RSD of RFs of O_2 in Co-Injection	Average and %RSD of RFs of H_2O in Co-Injection
210 → 78 psi	15803	6.8 %	5.6 × 10^{-8} 7.3 %	5640	7.1 %	1.7 × 10^{-7} 8.7 %	17145	12 %	1.9 × 10^{-7} 20 %	2504	28 %	2.7 × 10^{-7} 22 %	1.5 × 10^{-8} 12%

ADDITIONAL READING

ASTM Standards:[3]

(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) D4626 Test Method for Analysis of Natural Gas by Gas Chromatography
(5) D4626 Test Method for Analysis of Natural Gas by Gas Chromatography
(6) F307 Practice for Sampling Pressurized Gas for Gas Analysis

Other Standards:[4]

(7) California Code of Regulations, Title 4, Division 9, Chapter 6, Article 8 , Sections 4180 – 4181

ISO Standards:[5]

(8) ISO/TR 15916 : 2004 Basic consideration for safety of hydrogen systems
(9) ISO 26142 Hydrogen detection apparatus
(10) ISO TS 14687-2 Hydrogen fuel — Product Specification — Part 2: Proton exchange membrane fuel cell (PEMFC) applications for road vehicles

---

[3] 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.

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

[5] 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.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/