Designation: D7892 – 15

Standard Test Method for Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D7892; 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 The gas chromatography/mass spectrometry (GC/MS) procedure described in this method is used to determine concentrations of total organic halides and total non-methane hydrocarbons (TNMHC) by measurement of individual target halocarbons (Table 1) and hydrocarbons (including formaldehyde, Table 1 and Table 2), respectively. Measurement of these substances is required for application of SAE J2719 to hydrogen fuel quality where this fuel is intended for use in fuel cell vehicles. SAE 2719 states hydrogen fuel is expected to contain less than 0.05 µmole/mole total halogenates (including organic halides), 2 µmole/mole total non-methane hydrocarbons (C1 Basis, 3.2.16) and 0.01 µmole/mole formaldehyde.

1.2 Based upon the GC/MS/full scan analysis of a 400 mL hydrogen sample, the reporting limit (RL) is 0.001 µmole/mole for each target compound listed in Table 1 and Table 2, with the exception of 0.002 µmole/mole for ethane and 0.002 µmole/mole for ethene.

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

1.4 The values stated in SI units are to be regarded as 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]

D4150 Terminology Relating to Gaseous Fuels

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

2.2 *Other Standards:*[3]

SAE J2719 Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles

3. Terminology

3.1 *Definitions*—For definitions of terms use in this test method, refer to Terminology D4150.

3.2 *Definitions:*

3.2.1 *absolute pressure*—pressure measured with reference to absolute zero pressure usually expressed as kPa, mm Hg, bar or psi.

3.2.2 *constituent*—component (or compound) found within a hydrogen fuel mixture.

3.2.3 *contaminant*—contaminant as defined in this application is an impurity that adversely affects the components within a fuel cell system or hydrogen storage system.

3.2.4 *cryogen*—a refrigerant is used to obtain very low temperatures. The cryogen used in this method is liquid nitrogen (bp -196 °C).

3.2.5 *dynamic calibration*—Calibration of an analytical system uses gaseous calibration standard generated by diluting a known concentration of compressed gaseous standard with a diluent gas.

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

[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 SAE International (SAE), 400 Commonwealth Dr., Warrendale, PA 15096, http://www.sae.org.

TABLE 1 Organic Halides

Target Compounds	Formulas	MW	BP°C	MP°C	CAS No.	Retention Time (min)
1,1,1-Trichloroethane	$C_2H_3Cl_3$	133.4	74	-33	71-55-6	8.876
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	167.9	147	-44	79-34-5	14.627
1,1,2-Trichloroethane	$C_2H_3Cl_3$	133.4	114	-37	79-00-5	11.607
1,2-Dibromoethane	$C_2H_4Br_2$	187.9	132	10	106-93-4	12.555
1,1-Dichloroethane	$C_2H_4Cl_2$	99	57	-97	75-34-3	7.034
1,1-Dichloroethene	$C_2H_2Cl_2$	96.9	32	-122	75-35-4	5.927
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	181.5	214	17	120-82-1	19.795
1,2,3,4-tetrachlorohexafluorobutane	$C_4Cl_4F_6$	303.4	134	0 dl; 73 meso	375-45-1	13.008
1,2-Dichloroethane	$C_2H_4Cl_2$	99	84	-35	107-06-2	8.658
1,2-Dichloropropane	$C_3H_6Cl_2$	113	96	-100	78-87-5	10.006
1,2-Dichlorobenzene	$C_6H_4Cl_2$	147	181	-17	95-50-1	17.334
1,3-Dichlorobenzene	$C_6H_4Cl_2$	147	173	-24	541-73-1	16.799
1,4-Dichlorobenzene	$C_6H_4Cl_2$	147	174	54	106-46-7	16.881
Benzyl Chloride	C_7H_7Cl	126.6	179	-39	100-44-7	16.769
Bromodichloromethane	$CHBrCl_2$	162	90	-57	75-27-4	10.189
Bromoform	$CHBr_3$	252.7	149	8	75-25-2	14.303
Bromomethane	CH_3Br	94.9	4	-94	74-83-9	4.326
Carbon tetrachloride	CCl_4	153.8	77	-23	56-23-5	9.418
Chlorobenzene	C_6H_5Cl	112.6	131	-45	108-90-7	13.626
Chloroethane	C_2H_5Cl	64.5	12	-139	75-00-3	4.52
Chloroform	$CHCl_3$	119.4	61	-64	67-66-3	7.987
Chloromethane	CH_3Cl	50.5	5	-24	74-87-3	3.504
cis-1,2-dichloroethene	$C_2H_2Cl_2$	97	60	-81	156-59-2	7.728
cis-1,3-Dichloropropene	$C_3H_4Cl_2$	111	104	-85	10061-01-5	10.948
Dibromochloromethane	$CHBr_2Cl$	208.3	119	-22	124-48-1	12.308
Dichlorodifluoromethane	CCl_2F_2	120.9	-30	-158	75-71-8	3.251
Freon113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	$C_2Cl_3F_3$	187.4	48	-35	76-13-1	6.239
Freon114 (1,2-Dichlorotetrafluoroethane)	$C_2Cl_2F_4$	170.9	4	-94	76-14-2	3.641
Hexachlorobutadiene	C_4Cl_6	260.8	210–220	-22 to -19	87-68-3	20.56
Methylene chloride	CH_2Cl_2	84.9	40	-97	75-09-2	6.015
Tetrachloroethene	C_2Cl_4	165.8	121	-19	127-18-4	12.943
trans-1,2-dichloroethene	$C_2H_2Cl_2$	97	48	-81	156-60-5	6.839
trans-1,3-Dichloropropene	$C_3H_4Cl_2$	110	112	-85	10061-02-6	11.401
Trichloroethene	C_2HCl_3	131.4	87	-73	79-01-6	10.177
Trichlorofluoromethane	CCl_3F	137.4	23	-111	75-69-4	5.321
Vinyl Chloride	$C_2H_2Cl_2$	62.5	-13	-154	75-01-4	3.8

TABLE 2 Non-Halogenated Non-Methane Hydrocarbons

Target Compounds	Formula	MW	BP°C	MP°C	CAS No.	Retention Time (min)
1,2,4-Trimethylbenzene	C_9H_{12}	120.20	169	-44	95-63-6	16.557
1,3,5-Trimethylbenzene	C_9H_{12}	120.20	165	-45	108-67-8	16.045
1,3-Butadiene	C_4H_6	54.09	-4	-109	106-99-0	3.985
1,4-Dioxane	$C_4H_8O_2$	88.11	101	12	123-91-1	10.601
2-Butanone	C_4H_8O	72.11	80	-86	78-93-3	7.516
2-Hexanone	$C_6H_{12}O$	100.16	128	-56	591-78-6	12.325
4-Ethyltoluene	C_9H_{12}	120.19	162	-62	622-96-8	15.969
4-Methyl-2-Pentanone	$C_6H_{12}O$	100.16	117–118	-85	108-10-1	11.154
Acetone	C_3H_6O	58.08	56–57	-95 to -93	67-64-1	5.356
Ethene	C_2H_4	28.05	-104	-169	9002-88-4	2.771
Benzene	C_6H_6	78.11	80	6	71-43-2	9.294
Cyclohexane	C_6H_{12}	84.16	81	6	110-82-7	9.529
Ethane	C_2H_6	30.07	-89	-183	74-84-0	2.82
Ethanol	C_2H_6O	46.07	78	-114	64-17-5	5.556
Ethyl Acetate	$C_4H_8O_2$	88.11	77	-84	141-78-6	7.958
Ethylbenzene	C_8H_{10}	106.17	136	-95	100-41-4	13.962
Formaldehyde	CH_2O	30.03	-19	-92	50-00-0	3.025
Heptane	C_7H_{16}	100.2	98–99	-91 to -90	142-82-5	10.342
Hexane	C_6H_{14}	86.18	68–69	-96 to -94	110-54-3	7.875
Isopropyl Alcohol	C_3H_8O	60.1	83	-89	67-63-0	6.38
Methyl tert-Butyl Ether	$C_5H_{12}O$	88.15	55	-109	1634-04-4	7.199
Propane	C_3H_8	44.1	-42	-188	74-98-6	3.173
Propene	C_3H_6	42.08	-48	-185	115-07-1	3.137
Styrene	C_8H_8	104.16	145	-31	100-42-5	14.503
Tetrahydrofuran	C_4H_8O	72.11	66	-108	109-99-9	8.529
Toluene	C_7H_8	92.15	111	-95	108-88-3	11.866
Vinyl acetate	$C_4H_6O_2$	86.09	73	-93	108-05-4	7.134
Xylenes, m&p-	C_8H_{10}	106.17	139(m) 138(p)	-48(m) 13(p)	108-38-3(m) 106-42-3(p)	14.132
Xylenes, o-	C_8H_{10}	106.16	144	-24	95-47-6	14.638

3.2.7 *hydrogen fuel*—hydrogen sampled at a vehicle fueling nozzle, without change of composition by drying, sampling, etc.

3.2.8 *internal standard*—material added to samples in a known amount to serve as a reference measurement.

3.2.9 *internal standard calibration*—calibration performed using internal standards to compensate for variation of GC/MS sensitivity. In this test method, 0.005 µmole/mole each of 1,4-difluorobenzene, and D5-chlorobenzene are added during a GC/MS/full scan analysis for the target compounds listed in Table 1 and Table 2.

3.2.10 *poisoning*—process by which the catalysts inside a PEMFC are made inoperative due to the activity of contaminants that can bind to or chemically alter the catalyst used in a fuel cell.

3.2.11 *reporting limit, RL*—the lowest level of an analyte that an individual laboratory can confidently report for a particular matrix.

3.2.12 *qualitative accuracy*—the ability of an analytical system to correctly identify compounds.

3.2.13 *quantitative accuracy*—the ability of an analytical system to correctly measure the concentration of an identified compound.

3.2.14 *static calibration*—calibration of an analytical system using standards in a form, matrix, state, or manner different from samples to be analyzed.

3.2.15 *surrogate*—a pure analyte, which is extremely unlikely to be found in a sample that is added to a sample aliquot in a known amount. It is measured using the same procedure(s) used to measure the target compounds in the sample. The purpose of a surrogate analyte is to monitor the method performance with each sample.

3.2.15.1 *Discussion*—In this method, 0.005 µmole/mole each of bromochloromethane and 4-bromofluorobenzene are added to every sample or standard during analysis. The surrogate recoveries are expected to be within 70 % and 130 %.

3.2.16 *total non-methane hydrocarbons (C_1 basis)*—the concentration of total non-methane hydrocarbons (C_1 basis) is defined by the following formula:

$$\text{Total non-methane hydrocarbons } (C_1 \text{ basis}) = \Sigma_{i=1}^{all} (\text{concentration of found non-methane hydrocarbon}_i) \times \text{its carbon numbers}_i \quad (1)$$

3.3 *Acronyms:*

3.3.1 *EIC*—extracted ion chromatogram

3.3.2 *FCV*—fuel cell vehicle

3.3.3 *GC*—gas chromatograph

3.3.4 *IS*—internal standard

3.3.5 *ISO*—International Organization for Standardization

3.3.6 *m/e*—mass to charge ratio

3.3.7 *MS*—mass spectrometer

3.3.8 *NIST*—National Institute of Standards and Technology

3.3.9 *NTC*—non-target compound

3.3.10 *ppb(v) ($\mu L/m^3$)*—parts per billion as a volume/volume ratio

3.3.11 *ppm(v) (µL/L)*—parts per million as a volume/volume ratio

3.3.12 *PEMFC*—proton exchange membrane fuel cell

3.3.13 *RL*—reporting limits

3.3.14 *SIM*—selected ion monitoring

3.3.15 *TC*—target compounds

3.3.16 *TIC*—total ion current

3.3.17 *UHP*—ultra high purity (99.999%)

3.3.18 *UOM*—unit of measure

3.3.19 *US EPA or EPA*—The United States of America Environmental Protection Agency

4. Summary of Test Method

4.1 The target compounds in Table 1 and Table 2, which may be contained in a 400 mL hydrogen sample, are cryogenically frozen or concentrated onto a glass bead trap at -150 °C. The target compounds are slowly desorbed by warming to 10 °C and transferred to a Tenax trap cooled to -60 °C using desorption flow rate of 10 mL/min. This process leaves water in the glass bead trap and dehydrates the sample. The Tenax trap is then desorbed by heating to 180 °C and the target compounds cyro-focused at -170 °C at the entrance to a GC column (see 6.5). The cyro-focusing section is then rapidly heated up to 80 °C to release the cryo-focused target compounds, which are eventually eluted from the column and analyzed using a mass spectrometer scanning from m/e 23 to 100 for initial 4.5 min and from m/e 34 to 550 the remaining analytical time. The retention times of the target compounds are listed in Table 1 and Table 2 under the chromatographic conditions in 6.5.

5. Significance and Use

5.1 Low operating temperature fuel cells such as PEMFCs require high purity hydrogen for optimal performance and longevity. Organic halides and formaldehyde can react with catalyst in PEMs and non-methane hydrocarbons degrade PEM stack performance.

6. Apparatus

6.1 *Sample Concentration System*—The sample concentration system and GC/MS system described in this test method (4) are commercially available.

6.2 *Data Acquisition*—A computer or other data recorder, loaded with appropriate software for data acquisition, reduction and reporting, possessing the following capabilities is required.

6.2.1 Graphic presentation of the chromatogram.

6.2.2 Digital display of chromatographic peak areas.

6.2.3 Identification of peaks by retention time or relative retention time.

6.2.4 Calculation using of response factors.

6.2.5 Internal standard calculation and data presentation.

6.3 Hydrogen Fuel Sample Container – Any sample container with working pressures up to 12.4 MPa (1800 psi) can be