



Designation: D7892 – 22

Standard Test Method for Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry¹

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 test method is used to determine concentrations of total organic halides and total non-methane hydrocarbons (TNMHC) in hydrogen by measurement of individual target halocarbons (Table 1) and hydrocarbons (including formaldehyde, Table 1 and Table 2), respectively.

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

1.3 *Units*—The values stated in SI units are to be regarded as standard.

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, health, and environmental 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 *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 *SAE Standard:*³

SAE J2719 Hydrogen Fuel Quality for Fuel Cell Vehicles

3. Terminology

3.1 *Definitions*—For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.2 *Abbreviations:*

3.2.1 *GC*—gas chromatograph

3.2.2 *m/e*—mass to charge ratio

3.2.3 *MS*—mass spectrometer

3.2.4 *ppb(v)*—parts per billion as a volume

3.2.5 *ppm(v)*—parts per million as a volume

3.2.6 *UHP*—ultra high purity

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

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 ₂ H ₃ Cl ₃	133.4	74	-33	71-55-6	8.876
1,1,2,2-Tetrachloroethane	C ₂ H ₂ Cl ₄	167.9	147	-44	79-34-5	14.627
1,1,2-Trichloroethane	C ₂ H ₃ Cl ₃	133.4	114	-37	79-00-5	11.607
1,2-Dibromoethane	C ₂ H ₄ Br ₂	187.9	132	10	106-93-4	12.555
1,1-Dichloroethane	C ₂ H ₄ Cl ₂	99	57	-97	75-34-3	7.034
1,1-Dichloroethene	C ₂ H ₂ Cl ₂	96.9	32	-122	75-35-4	5.927
1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃	181.5	214	17	120-82-1	19.795
1,2,3,4-tetrachlorohexafluorobutane	C ₄ Cl ₄ F ₆	303.4	134	0 dl; 73 meso	375-45-1	13.008
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	99	84	-35	107-06-2	8.658
1,2-Dichloropropane	C ₃ H ₆ Cl ₂	113	96	-100	78-87-5	10.006
1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	147	181	-17	95-50-1	17.334
1,3-Dichlorobenzene	C ₆ H ₄ Cl ₂	147	173	-24	541-73-1	16.799
1,4-Dichlorobenzene	C ₆ H ₄ Cl ₂	147	174	54	106-46-7	16.881
Benzyl Chloride	C ₇ H ₇ Cl	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 ₃ Br	94.9	4	-94	74-83-9	4.326
Carbon tetrachloride	CCl ₄	153.8	77	-23	56-23-5	9.418
Chlorobenzene	C ₆ H ₅ Cl	112.6	131	-45	108-90-7	13.626
Chloroethane	C ₂ H ₅ Cl	64.5	12	-139	75-00-3	4.52
Chloroform	CHCl ₃	119.4	61	-64	67-66-3	7.987
Chloromethane	CH ₃ Cl	50.5	5	-24	74-87-3	3.504
cis-1,2-dichloroethene	C ₂ H ₂ Cl ₂	97	60	-81	156-59-2	7.728
cis-1,3-Dichloropropene	C ₃ H ₄ Cl ₂	111	104	-85	10061-01-5	10.948
Dibromochloromethane	CHBr ₂ Cl	208.3	119	-22	124-48-1	12.308
Dichlorodifluoromethane	CCl ₂ F ₂	120.9	-30	-158	75-71-8	3.251
Freon113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	C ₂ Cl ₃ F ₃	187.4	48	-35	76-13-1	6.239
Freon114 (1,2-Dichlorotetrafluoroethane)	C ₂ Cl ₂ F ₄	170.9	4	-94	76-14-2	3.641
Hexachlorobutadiene	C ₄ Cl ₆	260.8	210–220	-22 to -19	87-68-3	20.56
Methylene chloride	CH ₂ Cl ₂	84.9	40	-97	75-09-2	6.015
Tetrachloroethene	C ₂ Cl ₄	165.8	121	-19	127-18-4	12.943
trans-1,2-dichloroethene	C ₂ H ₂ Cl ₂	97	48	-81	156-60-5	6.839
trans-1,3-Dichloropropene	C ₃ H ₄ Cl ₂	110	112	-85	10061-02-6	11.401
Trichloroethene	C ₂ HCl ₃	131.4	87	-73	79-01-6	10.177
Trichlorofluoromethane	CCl ₃ F	137.4	23	-111	75-69-4	5.321
Vinyl Chloride	C ₂ H ₂ Cl ₂	62.5	-13	-154	75-01-4	3.8

Document Preview

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 ₉ H ₁₂	120.20	169	-44	95-63-6	16.557
1,3,5-Trimethylbenzene	C ₉ H ₁₂	120.20	165	-45	108-67-8	16.045
1,3-Butadiene	C ₄ H ₆	54.09	-4	-109	106-99-0	3.985
1,4-Dioxane	C ₄ H ₈ O ₂	88.11	101	12	123-91-1	10.601
2-Butanone	C ₄ H ₈ O	72.11	80	-86	78-93-3	7.516
2-Hexanone	C ₆ H ₁₂ O	100.16	128	-56	591-78-6	12.325
4-Ethyltoluene	C ₉ H ₁₂	120.19	162	-62	622-96-8	15.969
4-Methyl-2-Pentanone	C ₆ H ₁₂ O	100.16	117–118	-85	108-10-1	11.154
Acetone	C ₃ H ₆ O	58.08	56–57	-95 to -93	67-64-1	5.356
Ethene	C ₂ H ₄	28.05	-104	-169	9002-88-4	2.771
Benzene	C ₆ H ₆	78.11	80	6	71-43-2	9.294
Cyclohexane	C ₆ H ₁₂	84.16	81	6	110-82-7	9.529
Ethane	C ₂ H ₆	30.07	-89	-183	74-84-0	2.82
Ethanol	C ₂ H ₆ O	46.07	78	-114	64-17-5	5.556
Ethyl Acetate	C ₄ H ₈ O ₂	88.11	77	-84	141-78-6	7.958
Ethylbenzene	C ₈ H ₁₀	106.17	136	-95	100-41-4	13.962
Formaldehyde	CH ₂ O	30.03	-19	-92	50-00-0	3.025
Heptane	C ₇ H ₁₆	100.2	98–99	-91 to -90	142-82-5	10.342
Hexane	C ₆ H ₁₄	86.18	68–69	-96 to -94	110-54-3	7.875
Isopropyl Alcohol	C ₃ H ₈ O	60.1	83	-89	67-63-0	6.38
Methyl tert-Butyl Ether	C ₅ H ₁₂ O	88.15	55	-109	1634-04-4	7.199
Propane	C ₃ H ₈	44.1	-42	-188	74-98-6	3.173
Propene	C ₃ H ₆	42.08	-48	-185	115-07-1	3.137
Styrene	C ₈ H ₈	104.16	145	-31	100-42-5	14.503
Tetrahydrofuran	C ₄ H ₈ O	72.11	66	-108	109-99-9	8.529
Toluene	C ₇ H ₈	92.15	111	-95	108-88-3	11.866
Vinyl acetate	C ₄ H ₆ O ₂	86.09	73	-93	108-05-4	7.134
Xylenes, m&p-	C ₈ H ₁₀	106.17	139(m) 138(p)	-48(m) 13(p)	108-38-3(m) 106-42-3(p)	14.132
Xylenes, o-	C ₈ H ₁₀	106.16	144	-24	95-47-6	14.638

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 used. A sample container fitting the requirements of Practice D7606 with internal surface coated with silicon has been used in the application of this method. The sample container should demonstrate the absence of each organic halide or hydrocarbon at less than the reporting limit before it is used for sample collection.

6.4 *Carrier Gas Control*—Constant flow control of carrier gas is critical for optimal and consistent analytical performance. Control is achieved by use of two-stage pressure regulators, fixed flow restrictors, mass flow controller, or electronic pressure controllers.

6.5 *Chromatographic Column and Conditions*—A 60 m, 0.32 mm ID, 3 μ m dimethylpolysiloxane stationary phase or similar fused silica column is used with a flow rate of 1 mL/min. An initial column temperature of 35 °C (1.5 min) followed by ramping to 110 °C at 9 °C/min then to 210 °C (4 min) at 11 °C/min has been successfully used in performance of this test method.

6.6 *Sample Container Cleaning System*—For simultaneous cleaning of several sample containers, the following is recommended.

6.6.1 *Vacuum Pump*—capable of evacuating sample vessel(s) to an absolute pressure of less than 0.05 mmHg.

6.6.2 *Vacuum Gauge*—capable of measuring vacuum down to an absolute pressure of 0.01 mmHg or less.

6.6.3 *Isothermal Oven*—used to heat containers to 80 °C during cleaning.

7. Compressed Gas Standards

7.1 *Compressed Gas Standards*:

7.1.1 The gaseous calibration standards for target compounds listed in Table 1 and Table 2, internal calibration standards, and surrogates used in this method are commercially available at concentration of 1 ppm(v).

7.1.2 Alternative approaches for generation of calibration standards, internal standards and surrogates are acceptable as

long as accuracy and stability can be verified and satisfy application requirements.

7.2 *Carrier Gas*—UHP hydrogen is used; however, other UHP gases, such as helium, can also be used provided application requirements are met. No target compounds in Table 1 and Table 2 are present at greater than reporting limits in the carrier gas.

7.3 *Sample Transferring Gas for Sample Concentration*—UHP hydrogen is used; however, other UHP gases, such as helium, can also be used provided application requirements are met. See 10.3.

7.4 *Liquid Nitrogen*—Required for cryogenic cooling.

8. Equipment Preparation

8.1 *GC/MS and Sample Concentration System*—Placed into service in accordance to the manufacturer's instructions with performance of daily GC/MS mass calibration using perfluorotributylamine (FC-43).

8.2 *Liquid Nitrogen Dewar*—A 160 to 230 L liquid nitrogen Dewar with a head pressure of 0.15 MPa (22 psi) is used for cryogenic cooling.

9. Hazards

9.1 *Warning*—Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.

10. Laboratory Procedures

10.1 *Sampling Procedures*—See Practice D7606.

10.2 *Sample Receipt*—Examine the overall condition of each sample container; perform leak checks and record observations in a dedicated logbook. Each container should possess an attached sample identification tag that includes the weight of hydrogen sampled, pressure of hydrogen in the container, the sampling place, date and time of sample collection.

10.3 *Sample Concentration and Analysis*—The four steps of sample concentration are described below.

10.3.1 *Concentration Using a Glass Bead Trap*—Flow 20 mL of the standard containing 100 ppb(v) of each internal standard and surrogate at a flow rate of 100 mL/min through a glass bead trap cooled to -150 °C. Then, pass 400 mL of a hydrogen sample (10.3.1.1) or known volume of gaseous calibration standards, at the same flow rate, through the glass bead trap at -150 °C. The flow rate and sample volume passing through the trap is established using an electronic flow controller at the flow outlet end of the trap. This process will trap all the target compounds, internal standards, surrogates, and trace water contained in the hydrogen sample or in gaseous calibration standards. However, if the hydrogen sample contains the non-hydrogen constituents with their concentrations

higher than the highest concentration of the initial calibration (10.4), less volume of the hydrogen samples should be used such that the highest compound concentration is within initial calibration range (10.4). In this case, the reporting limits will be adjusted by multiplying the reporting limits by a dilution factor, which is 400 mL over the hydrogen volume (mL) analyzed.

10.3.1.1 *Method to Flow Hydrogen Sample from Hydrogen Fuel Sample Container*—The hydrogen samples after sampling in accordance with Practice D7606 are generally around 6.9 MPa (1000 psi). To take a 400 to 500 mL high pressure hydrogen sample directly, as described in 10.3.1, may be challenging. One method to reduce the hydrogen pressure before sample concentration to a more easily handled value is to attach a short electropolished stainless steel (SS) tubing to the sample container valve. The other end of the short SS tubing is connected through an inlet valve to the inlet line of the sample concentration system, as shown in Fig. 1. The short SS tubing must be evacuated using a vacuum pump before sample concentration. The hydrogen sample introduction process is accomplished by pressurizing the short SS tubing while the inlet valve is closed. Then, upon closing the sample container valve, the inlet valve is opened, thus expanding the high pressure hydrogen into the sample concentration system through the inlet line; thereby, achieving a lower sample introduction pressure. The process is repeated several times until enough volume of sample taken using an electronic flow controller (10.3.1), which is not only controlling and measuring the sample flow, but also integrating the total flow so that the volume of the sample can be measured in real time.

10.3.2 *Desorption of the Target Compounds from the Glass Bead Trap to the Tenax Trap*—Desorb the target compounds on the glass bead trap at a temperature of 10 °C onto a Tenax trap which is maintained at -60 °C with an UHP hydrogen flow at 10 mL/min. This process leaves water in the glass bead trap and dehydrates the samples or standards. The dehydration of the samples or standards is important for the analysis of formaldehyde since formaldehyde may not be detected by this method without this dehydration step. The reason is probably due to that formaldehyde is in equilibrium with methanediol, which is more predominating in the presence of water. This dehydration step is capable of removing the excess water from the hydrogen samples containing moisture so that formaldehyde at low concentration in these hydrogen samples can be detected.

10.3.3 *Cryo-focusing*—The organic compounds contained on the Tenax trap are desorbed at 180 °C for 2 min and cyro-focused onto a 0.53 mm ID cryo-focusing column at -170 °C.

10.3.4 *Desorption of Cryo-focusing Column*—The target compounds on the cryo-focusing column are rapidly desorbed at 80 °C and released into an analytical capillary column (see 6.5).

10.3.5 The GC/MS acquisition starts simultaneously upon desorption of the cryo-focusing column. Within the initial 4.5 min, the mass spectrometer scans from m/e 23 to 100 to provide a determination of ethene, ethane, propene, propane, and formaldehyde. The scan is then changed to m/e 34-550 to identify and quantify the remaining compounds listed in Table 1 and Table 2.

10.4 *Initial Calibration*—The initial calibration is the sequential analyses of three to five calibration standards at different concentrations from the lowest concentration at the reporting limits to the highest concentration ten or twenty times of the reporting limits. The acceptance criteria for initial calibrations are listed below.

10.4.1 All target compounds in the analysis of the standard at reporting limit must be detected at or above 3 times signal-to-noise level.

10.4.2 The relative standard deviation (%RSD) of the response factors (RF, 10.1) of each compound in the initial calibration should be less than 30 % to demonstrate the linearity of each compound over initial calibration concentration range. The method blank (10.7) and samples can be analyzed after initial calibration within 24 h from the start of the first initial calibration analysis.

10.5 *Continuous Calibration*—The reporting limit standard is firstly analyzed each day and all the target compounds must be detected at or above 3 times signal-to-noise level before this analysis can be employed as continuous calibration. An example of the GC/MS full scan chromatogram of all the compounds in Table 1 and Table 2 at the reporting limits is shown in Fig. 2. Fig. 3 is the extracted ion chromatograms of formaldehyde at 1 ppb(v) by GC/MS in full scan. The method blank (10.7) and samples can be analyzed afterwards within 24 hours from the start of the continuous calibration. For target compounds found in samples above the reporting limits, the difference of its average initial calibration RF from its daily continuous calibration RF are expected to be less than 30 %.

10.6 *Method Detection Limit Demonstration*—Refer to 4 CFR 136, appendix B (2.2.6).

10.7 *Method Blank Analysis*—A 400 mL UHP hydrogen is analyzed prior to sample analysis to demonstrate that no target compounds in Table 1 and Table 2 are present at greater than reporting limits in the blank.

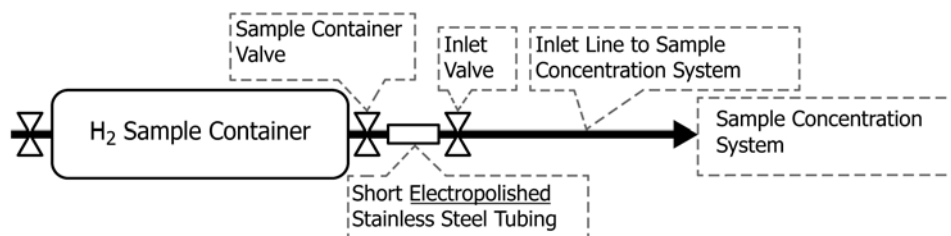


FIG. 1 Flow Hydrogen Sample from a High Pressure Sample