



Designation: ~~D7941/D7941M–14~~ D7941/D7941M – 23

Standard Test Method for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer¹

This standard is issued under the fixed designation D7941/D7941M; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method describes contaminant determination in ~~fuel-cell-grade~~ fuel cell grade hydrogen as specified in relevant ASTM and ISO standards using cavity ring-down spectroscopy (CRDS). This standard test method is for the measurement of one or multiple contaminants including, but not limited to, water (H₂O), oxygen (O₂), methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), ammonia (NH₃), and formaldehyde (H₂CO), henceforth referred to as “analyte.”

1.2 This test method applies to CRDS analyzers with one or multiple sensor modules (see 3.36.2 for definition), ~~each of which is designed for a specific analyte.~~ definition). This test method describes sampling apparatus design, operating procedures, and quality control procedures required to obtain the stated levels of precision and accuracy.

1.3 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other, and values from the two systems shall not be combined.

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, 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](#)

[D5287 Practice for Automatic Sampling of Gaseous Fuels](#)

[D7265 Specification for Hydrogen Thermophysical Property Tables](#)

[D7606 Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases](#)

[D7649E177 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](#)
[Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

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.



~~D7653E691 Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy~~
~~Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method~~

~~2.2 ISO Standards:³~~

~~ISO/DIS 14687-2 Hydrogen fuel—Product specification—Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles~~

~~ISO/DIS 14687-3 Hydrogen fuel—Product Specification—Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances~~

~~ISO 21087 Gas analysis—Analytical methods for hydrogen fuel—Proton exchange membrane (PEM) fuel cell applications for road vehicles~~

~~2.3 U.S.-Specific Standards:~~

~~SAE J2719-2011 (2011) J2719-2020 (2020) Hydrogen Fuel Quality for Fuel Cell Vehicles⁴~~

~~2.3.7 California Code of Regulations, Title 4, Division 9, Chapter 6, Article 8, Sections 4180-4181 – Hydrogen fuel quality requirements⁵~~

~~Environmental Protection Agency 40 CFR: Protection of the Environment, Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit⁶~~

3. Terminology

3.1 Definitions:

~~3.1.1 For definitions of general terms used in this test method, D03 Gaseous Fuels standards, refer to Terminology D4150.~~

3.2 Acronyms: Abbreviations:

~~3.2.1 AIST, n—National Institute of Advanced Industrial Science and Technology~~

~~3.2.1 CRDS, n—cavity ring-down spectroscopy~~

~~3.2.2 IR, PEM, n—infrared proton exchange membrane~~

~~3.2.3 kPa, SDS, n—kilopascals safety data sheet~~

~~3.2.5 LDL, n—lower detection limit~~

~~3.2.6 MSDS, n—material safety data sheet~~

~~3.2.7 NIST, n—National Institute of Standards and Technology~~

~~3.2.8 NPL, n—National Physical Laboratory~~

~~3.2.9 ppb, n—parts per billion v/v~~

~~3.2.10 ppm, n—parts per million v/v~~

~~3.2.11 PTB, n—Physikalisch-Technische Bundesanstalt~~

~~3.2.12 psig, n—pounds per square inch (gauge)~~

~~3.2.4 slpm, n—standard liters per minute~~

~~3.2.14 v/v, n—volume/volume ratio~~

³ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, <http://www.iso.org>.

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

⁵ Available from the California Office of Administrative Law, 300 Capitol Mall, Suite 1250, Sacramento, CA 95814, <http://www.oal.ca.gov/ccr.htm>.

⁶ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20004, <http://www.epa.gov>.

3.2.15 *VCR, n*—~~a type of compression gas fitting~~

3.3 *Additional Definitions*—The “sensor module” consists of the optical system (CRDS mirrors, reference cell, one or more lasers, and other optical components), the detector, and the internal gas handling components (gas lines, filters, and regulators). The complete instrument, including control electronics, can contain a single sensor module or multiple sensor modules.

4. Summary of Test Method

4.1 This test method provides a procedure for the sampling of trace contaminants contained in ~~fuel-cell-grade~~ fuel cell grade hydrogen and subsequent measurement using cavity ring-down spectroscopy (CRDS). ~~Instrument and sampling system configurations for sample pressures ranging from ambient to high pressure (defined as >960 kPa [>125 psig)].~~ Instrument, sampling system configuration and sampling conditions for typical samples of fuel-cell-grade hydrogen are described.

5. Significance and Use

5.1 Proton exchange membranes (PEM) used in fuel cells are susceptible to contamination from a number of species that can be found in hydrogen. It is critical that these contaminants be measured and verified to be present at or below the amounts stated in SAE J2719, ISO 14687-2 J2719 and ISO 14687-3 14687 to ensure both fuel cell longevity and optimum efficiency. Contaminant concentrations as low as single-figure ~~ppb~~ ppbv for some species can seriously compromise the life span and efficiency of PEM fuel cells. The presence of contaminants in fuel-cell-grade hydrogen can, in some cases, have a permanent adverse impact on fuel cell efficiency and usability. It is critical to monitor the concentration of key contaminants in hydrogen during the production phase through to delivery of the fuel to a fuel cell vehicle or other PEM fuel cell application. In ISO 14687-2 and ISO 14687-3, 14687, the upper limits for the ~~mentioned~~ contaminants are specified. Refer to SAE J2719 and the California Code of Regulations (see 2.3) for ~~example~~ specific national and regional requirements. For hydrogen fuel that is transported and delivered as a cryogenic liquid, there is additional risk of introducing impurities during transport and delivery operations. For instance, moisture can build up over time in liquid transfer lines, critical control components, and long-term storage facilities, which can lead to ~~ice~~ ice ~~up~~ ice ~~buildup~~ within the system and subsequent blockages that pose a safety risk or the introduction of contaminants into the gas stream upon evaporation of the liquid. Users are reminded to consult Practice D7265 for critical thermophysical ~~property~~ properties such as the ortho/para hydrogen spin isomer inversion that can lead to additional hazards in liquid hydrogen usage. ~~In addition to this test method employing CRDS, test methods such as D7649 (carbon dioxide, argon, nitrogen, oxygen and water) and D7653 (IR active species) are used to measure impurities in hydrogen fuel.~~

6. Apparatus

6.1 The analyzers used to measure impurities with reference to the development of this test method are based on CRDS. CRDS is an optical spectroscopic technique that enables measurement of absolute optical extinction by samples that scatter and absorb light. Based upon the optical extinction or “ring-down” rate, a determination of the analyte concentration can be made. See Appendix X1 for a detailed explanation on the principles upon which CRDS is based.

6.2 *Sensor Module*—The sensor module consists of the optical system (CRDS mirrors, reference cell, one or more lasers, and other optical components), the light detector, and the internal gas handling components (gas lines, filters, and regulators). The complete instrument, including control electronics, can contain a single sensor module or multiple sensor modules.

6.3 *Measurement Sequence*—Sequence:

6.3.1 A tunable laser emits a directed beam of light energy through an ultra-high reflectivity mirror into the absorption cell (cavity). The sample gas passes through this cell either ~~via the use of a vacuum pump for samples under 170 kPa [10 psig] or under pressure from sources in excess of 170 kPa [10 psig], regulated to between 170 and 960 kPa [10 and 125 psig].~~ by providing a pressurized gas supply. A vacuum pump is needed at the outlet if sufficient sample pressure to sustain positive flow cannot be provided.

6.3.2 High sensitivity is attained by reflecting the laser light many times through a sample gas contained between two or more highly reflective mirrors; thereby, ~~a~~ an ~~absorption path length as high as~~ absorption path length as of many kilometers through the sample is obtained.

6.3.3 A detector such as a photodiode senses the initial photon flux at the output of the cavity. Once a preset level of light intensity is detected, the light source is shuttered or diverted from the cavity, and the light intensity is measured over time.

6.3.4 On each successive pass through the cell, a small amount of light or ring-down signal emits through ~~the second mirror and one of the mirrors~~, and its intensity is measured by the photodiode detector.

6.3.5 Once the light “rings down,” the detector achieves a point of zero light intensity within a few hundred microseconds and the measurement is complete.

6.3.6 ~~Two measurement sequences are~~ A sequence of two measurements is required to effect a measurement of concentration:

6.3.6.1 *On-peak Measurement*—The laser is tuned to a wavelength at which the analyte absorbs light. The wavelength of choice depends on the analyte, the targeted concentration range, and potential interference from other molecules present in the sample. Suitable wavelengths for certain molecule can commonly be determined by using spectroscopic databases such as HITRAN. The exact wavelength used for each analyte is generally considered a trade secret by the manufacturer.

6.3.6.2 *Off-peak Measurement*—The laser is tuned to a wavelength at which the analyte does not absorb light. The wavelength of choice depends on the analyte, the targeted concentration range, and potential interference from other molecules present in the sample. As before, suitable wavelengths can be determined by consulting spectroscopic databases such as HITRAN. The exact wavelength used for the off-peak measurement of each analyte is considered a trade secret by the manufacturer, but it is generally in close proximity to the on-peak wavelength. In a gas of consistent analyte concentration, an off-peak measurement is required only occasionally; however, it is recommended that an off-peak measurement is performed at least once per month. In samples with rapidly changing gas composition or analyte concentrations, an off-peak measurement may be performed as frequently as every few minutes. ~~The frequency of off-peak measurement does not affect the accuracy of the final measurement.~~

6.3.7 The on-peak and off-peak measurements are used to calculate the concentration of the analyte in the sample gas as per a variation of the Beer-Lambert Law relating the extinction of light to the absorbance of the material through which the light is travelling.

6.4 Details concerning specific instrument configurations for a range of sample pressures can be found in Section 99.

6.5 A full description of the CRDS technique can be found in Appendix X1.

7. Hazards

7.1 ~~High-pressure gases~~ *High-pressure gases*—~~st/0f08d785-cedf-4052-9729-2861fe46a4b6/astm-d7941-d7941m-23~~
Warning—**WARNING**—Improper handling of compressed gas cylinders containing air, hydrogen, or inert gases such as nitrogen or helium can result in explosion. Rapid release of hydrogen or inert gases can result in asphyxiation. Hydrogen is a potential fire hazard. Compressed air supports combustion.

7.2 Hydrogen

7.2.1 Potential fire and explosion hazard.

7.2.2 Purge with inert gas before oxygen service.

8. Equipment, Materials, and Supplies

8.1 *Equipment*—Equipment:

8.1.1 CRDS analyzer consisting of laser source(s), sample cavity, photodiode detector, reference gas cell, and internal gas handling components (gas lines, particle filters, and regulators to maintain a constant pressure), which constitute each sensor module, as one or more sensor modules (see 6.2 well as) and control electronics.

8.1.2 Electrical and fiber optic cables to connect the control electronics and the laser source with each sensor module, if the sensing sensor modules are provided as separate units.

8.1.3 Gas sample lines made from appropriate material (stainless steel recommended) with a diameter of at least 6 mm [0.25 in.] from the sample extraction point to the analyzer inlet and the analyzer outlet to the vent or vacuum pump.

8.1.4 A vacuum pump for low pressure samples (see with a specified ultimate vacuum 9.1.1) which can reach a pressure of approximately 1 Torr or less of 10 Torr or less, if a pressurized sample cannot be provided.

8.2 *Materials and Supplies*—Dry inert gas (e.g. (for example, nitrogen or clean dry air) as purge gas for installation of the analyzer.

9. Sampling, Test Specimens, and Test Units

9.1 *Sampling—Sampling:*

9.1.1 For those CRDS instruments that can accept sample pressures from ambient up to 960 kPa [125 psig], a vacuum pump is required for sample pressures below 170 kPa [10 psig]. The analyzer may be used in the absence of a vacuum pump for sample pressures between 170 and 960 kPa [10 and 125 psig]. Samples in excess of 960 kPa [125 psig] shall be regulated down the manufacturer’s maximum pressure specifications need to be regulated to a pressure acceptable for the CRDS instrument before introduction to the inlet. Exceeding the maximum allowable pressure may damage the within the allowed range for the CRDS instrument. Consult the manufacturer for required sample pressure conditions. CRDS analyzers configured exclusively for use at pressures above 170 kPa [10 psig] cannot be used for lower pressure samples even with addition of a vacuum pump.

9.1.2 Commonly available CRDS instruments contain appropriate particle filtration inside the internal gas handling components; further filtration is generally not required unless specified by the manufacturer for special analytes and sample conditions.

9.1.3 To connect gas lines to the instrument, VCR vacuum coupling radiation (VCR) fittings are recommended. When making connections, always use a new gasket (nickel or stainless steel gaskets are recommended).

9.1.4 For the measurement of most common analytes (e.g. (for example, H₂O), sample lines and wetted components shall be of stainless steel construction, ideally with electro-polished surface finish, free from particulate and other contamination such as oils and other hydrocarbons. Certain analytes may require alternative materials or surface treatments, or both, to optimize sampling conditions. Contact an appropriate vendor for further advice.

9.1.5 Switching valves shall be constructed with a stainless steel diaphragm type and with the surface area of valves and other wetted components kept to a minimum, avoiding any dead volume. Surface treatments for the wetted surfaces when available to minimize the absorption of impurities. impurities should be used. Contact an appropriate vendor for further advice. Sample line length should be minimized and “dead-legs” avoided, preventing diffusion of contamination from unswept surfaces. Refer to Practices D5287 and D7606 for further sampling guidance.

9.1.6 *Sampling Setup*—A schematic of the sampling setup is shown in Fig. 1.

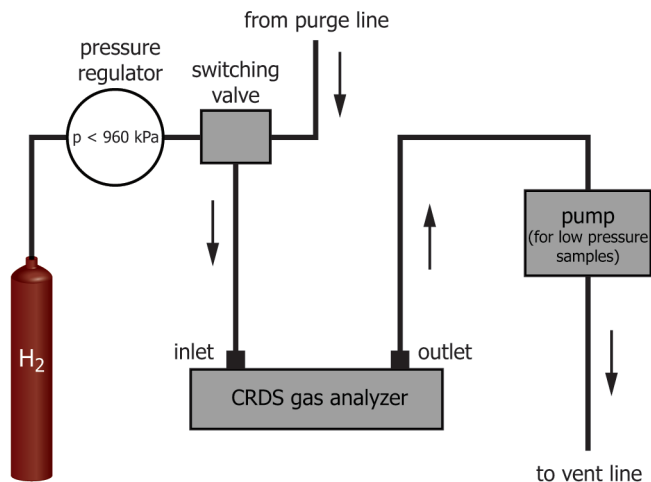


FIG. 1 Typical Sampling Configuration; pump is omitted or bypassed for high pressure samples (>170 kPa) with the appropriate CRDS analyzer



9.2 *Test Specimens*—Test specimens may be samples of fuel-cell-grade hydrogen ranging from ambient to high pressure with an instrument hardware and software configuration defined accordingly. Additional pressure regulation will be required for samples exceeding the maximum allowed pressure (see 9.1.1). Refer to Practice D7606 for guidance on this matter.

9.3 *Method Blank*—A CRDS instrument uses a spectroscopic zero (see 6.2.6.26.3.6.2) to determine the measurement zero or baseline. A blank sample is therefore not required.

9.4 *Test Units*—The test unit considered for the preparation of this test method is a commonly available CRDS instrument. The configuration of the internal sampling system will vary depending on the available sample pressure.

9.5 *Instrument and Analytes*—The general setup of the CRDS instrument is independent of the analyte to be measured; however, some components of the sensor module such as the laser source and the cavity mirrors are specific to the ~~analyte~~analyte(s) and the measurement ~~range~~range(s) specified by the manufacturer for the particular sensor. A CRDS analyzer sensor module shall only be used for the ~~analyte~~analyte(s) and measurement ~~range~~range(s) for which it was designed.

9.6 *Operating Conditions*—In general, exposure to severe weather conditions shall be avoided. The instrument ~~is able to~~can tolerate typical ambient fluctuations of pressure and moderate changes in temperature (within operating limits). A typical operating temperature range is between ~~10°C and 40°C~~10 °C and 40 °C with non-condensing humidity conditions. Refer to the manufacturer specification for operating conditions of a specific CRDS analyzer.

10. Preparation of Apparatus

NOTE 1—In addition to the procedure outlined in this section, consult Practice D7606 for guidance on sampling high pressure hydrogen. In general, this procedure does not vary for different analytes; however, if the sample contains high concentrations of a dangerous substance, appropriate safety precautions must be taken. Consult the analyte's MSD/SSDS for guidance.

10.1 *Connecting the sample to the inlet:*

10.1.1 The manual or factory should be consulted for appropriate sample lines and fittings, which may vary depending on analyte. Sample lines shall be free of particulate or other contamination. /D7941M-23

10.1.2 The manual or factory should be consulted for recommended fittings, welds, and regulators.

10.1.3 Use the shortest possible connection from sample source to the analyzer inlet.

10.1.4 To avoid contamination from ambient air, purge sample line(s) before connecting to the sensor module. It is advisable to have ~~an arrangement whereby~~a configuration with a manual or automatic means of switching between the sample and an inert purge gas is available. The sampling system should be designed so as to minimize any unswept surfaces when either the sample or purge line is not in use.

10.1.5 An internal ~~particle~~particulate filter is used and is intended to trap larger particles that may be introduced into the flow system during hookup. External particle filters may be ~~connected~~used but will act as moisture traps and flow restrictions, resulting in long initial dry-downs and sluggish response. For ~~this particular instrument,~~most instruments, a 2 µm particle size filter is recommended.

10.1.6 *During and after installation*—The sample gas inlet pressure shall be maintained within the instrument's specifications (see 9.1.1).

10.1.7 Assuming appropriate inlet pressure conditions (see 9.1.1), remove the sample inlet cap and connect the sample line to an inert purge gas source or a switching valve that connects to both the purge and sample gas. Use two wrenches to hold the fitting in place while tightening. Tighten the VCR fitting with a new metal gasket and purge at least 15 minutes before connecting to the sensor module.

10.1.8 Assuming appropriate inlet pressure conditions (see 9.1.1) and sufficient purge (see 10.1.7), remove the purge line from

the instrument and connect the sample line to the sensor module. ~~With~~ Using a new metal gasket, immediately connect the sample line to the sensor module sample inlet and tighten the VCR fitting. If a switching valve is used, switch from the purge to the sample gas.

10.1.9 Save the sample inlet cap for future use.

10.2 *Connecting to the sample outlet:*

10.2.1 It is generally recommended that the instrument be vented to atmospheric pressure. It can also be vented to a vacuum pump. The vent line shall consist of ~~6-mm [0.25-in.]~~ 6 mm [0.25 in.] or larger diameter tubing.

10.2.2 Careful consideration should be given when venting the H₂ sample gas. Hydrogen is an asphyxiate and fire hazard. ~~Also, consult~~ Consult local regulations for venting hydrogen. If the sample contains high concentrations of contaminants ~~or~~ dangerous substances, take appropriate safety measures. Consult the ~~MSDS~~ SDS for proper venting of the sample gas.

10.2.3 If the vent line is connected to a vacuum pump, ensure the pump line is closed before switching on the pump. Ensure that the vacuum pump is certified for use with hydrogen gas.

10.2.4 Assuming appropriate inlet pressure conditions (see 9.1.1), with a flow of ~~0.5 to 1.0 slpm,~~ 0.5 slpm to 1.0 slpm, remove the sample outlet cap from the sensor module. ~~With~~ Using a new metal gasket, immediately connect the vent line to the sample outlet and tighten the VCR fitting.

10.2.5 Open the line to atmosphere or a vacuum pump and allow 15 min to purge the sample lines.

10.2.6 Save the sample outlet cap for future use.

11. Calibration and Standardization

11.1 *Calibration*—CRDS analyzers are essentially “self-calibrating” ~~do not require user calibration~~ with respect to the absorption measurement. ~~Although calibration measurement or the instrument’s zero.~~ Calibration standards are used during manufacturing for the purpose of traceability, to establish calibration and traceability. CRDS analyzers are based on fundamental physical principles and ~~should not require periodic recalibration.~~ recalibration; however, a known gas standard may be required for verification (see 18.1.1) in some applications. CRDS analyzers measure the time (typically in microseconds) for light to decay (“ring down”) inside an optical cavity, typically consisting of two or more highly reflective mirrors. The optical losses in the cavity reduce the amount of light with each pass, allowing for the measurement of pass which defines a “ring-down time.” When a number of target molecules are present in the gas flowing through the cavity, they absorb light, therefore shortening the light shortens this ring-down time. A full description of CRDS can be found in Appendix X1. In practice, the two critical parameters that shall be controlled are the laser frequencies that correspond to a zero point (Tau Zero) and a point of peak or maximum absorption (Tau Peak). These are controlled as follows:

11.2 *Reference cell*—Cell—A commonly available CRDS instrument contains a spectroscopic reference cell that automatically ~~re-centers~~ re-centers the laser frequency during measurements to coincide with the analyte’s peak absorption frequency. The reference cell itself is a small, permanently sealed container of the target analyte. A very small percentage of the laser light is sent to the reference cell, which continuously verifies that the laser remains at the correct wavelength, which does not change with wavelength without change due to changes in ambient temperature or pressure.

11.3 *Tune*—The tune-Tau Zero mode is used to determine the off-peak ring-down time of the system. This measurement is used in calculating the final concentration and is run in the same sample gas and under the same sample conditions as the analyte measurement itself. ~~measurement.~~ Running a tune-Tau Zero cycle at least every month is recommended to ensure accurate contaminant ~~concentration.~~ concentration measurements. This may be done manually via the appropriate menu, or the process can be automated to a designated schedule. For one typical manufacturer, the tune-Tau Zero cycle runs for approximately two minutes during which time the instrument is not delivering measurement data.

11.4 *Laser optimization*—Optimization—Over time, the laser may drift off the analyte’s absorption peak. The software adjusts the laser current to keep the laser “on peak.” Laser optimization is recommended at least once per year to ensure the unit is operating optimally.