Designation: D7941/D7941M – 23

Standard Test Method for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes contaminant determination in 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 (H_2O), oxygen (O_2), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), ammonia (NH_3), and formaldehyde (H_2CO), henceforth referred to as "analyte."

1.2 This test method applies to CRDS analyzers with one or multiple sensor modules (see 6.2 for 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, 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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 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 J2719-2020 (2020) Hydrogen Fuel Quality for Fuel Cell Vehicles[4]

[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 Jan. 15, 2023. Published February 2023. Originally approved in 2014. Last previous edition approved in 2014 as D7941/D7941M – 14. DOI: 10.1520/D7941_D7941M-23.

[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 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.

2.3.7 California Code of Regulations, Title 4, Division 9, Chapter 6, Article 8, Sections 4180-4181 – Hydrogen fuel quality requirements[5]

Environmental Protection Agency 40 CFR: Protection of the Environment, Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit[6]

3. Terminology

3.1 *Definitions:*

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

3.2 *Abbreviations:*

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

3.2.2 *PEM, n*—proton exchange membrane

3.2.3 *SDS, n*—safety data sheet

3.2.4 *slpm, n*—standard liters per minute

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 hydrogen and subsequent measurement using cavity ring-down spectroscopy (CRDS). 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 and ISO 14687 to ensure both fuel cell longevity and optimum efficiency. Contaminant concentrations as low as single-figure ppb(v) 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, the upper limits for the contaminants are specified. Refer to SAE J2719 (see 2.3) for 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 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 properties such as the ortho/para hydrogen spin isomer inversion that can lead to additional hazards in liquid hydrogen usage.

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:*

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 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, an absorption path length 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 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 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

[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.

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.

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 9.

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

7. Hazards

7.1 *High-pressure gases*—**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:*

8.1.1 CRDS analyzer consisting of one or more sensor modules (see 6.2) 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 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 with a specified ultimate vacuum of 10 Torr or less, if a pressurized sample cannot be provided.

8.2 *Materials and Supplies*—Dry inert gas (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:*

9.1.1 Samples in excess of the manufacturer's maximum pressure specifications need to be regulated to a pressure within the allowed range for the CRDS instrument. Consult the manufacturer for required sample pressure conditions.

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, 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 (for example, H_2O), 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 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 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.

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 6.3.6.2) 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(s) and the measurement range(s) specified by the manufacturer for the particular sensor. A CRDS analyzer sensor module shall only be used for the analyte(s) and measurement range(s) for which it was designed.

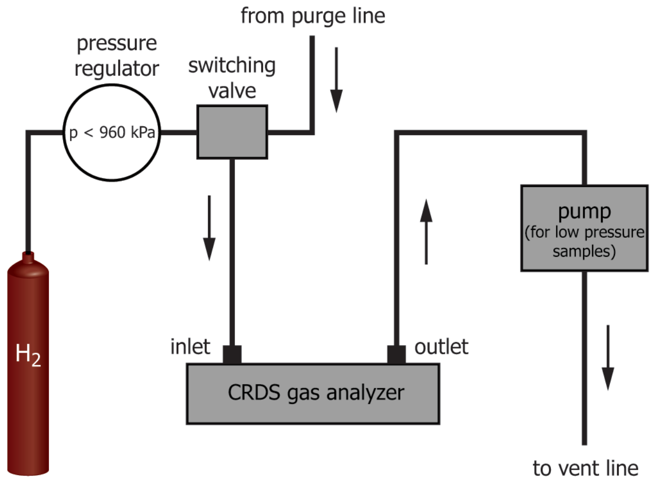

FIG. 1 Typical Sampling Configuration; pump is omitted or bypassed for high pressure samples (>170 kPa) with the appropriate CRDS analyzer

9.6 *Operating Conditions*—In general, exposure to severe weather conditions shall be avoided. The instrument 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 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 SDS 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.

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 a configuration with a manual or automatic means of switching between the sample and an inert purge gas available. The sampling system should be designed to minimize any unswept surfaces when either the sample or purge line is not in use.

10.1.5 An internal 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 used but will act as moisture traps and flow restrictions, resulting in long initial dry-downs and sluggish response. For 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. Using a new metal gasket, 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.] or larger diameter tubing.

10.2.2 Careful consideration should be given when venting the H_2 sample gas. Hydrogen is an asphyxiate and fire hazard. Consult local regulations for venting hydrogen. If the sample contains high concentrations of contaminants or dangerous substances, take appropriate safety measures. Consult the 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 slpm to 1.0 slpm, remove the sample outlet cap from the sensor module. Using a new metal gasket, 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 do not require user calibration with respect to the absorption measurement or the instrument's zero. Calibration standards are used during manufacturing to establish calibration and traceability. CRDS analyzers are based on fundamental physical principles and should not require periodic 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, consisting of two or more highly reflective mirrors. The optical losses in the cavity reduce the amount of light with each pass which defines a "ring-down time." When target molecules are present in the gas flowing through the cavity, they absorb 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*—A commonly available CRDS instrument contains a spectroscopic reference cell that automatically recenters the laser frequency during measurements to coincide with the analyte's peak absorption frequency. The reference cell 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 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. Running a tune-Tau Zero cycle at least every month is recommended to ensure accurate contaminant 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*—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.

11.5 *Avoidance of Interferences*—When multiple analytes are present in the sample, biased readings can occur due to spectral interference. Before installation, the analyzer shall be tested for common interferences to ensure correct concentration readings.

11.5.1 *Non-interfering Species*—In any CRDS instrument, nitrogen, hydrogen, oxygen, and noble gases do not interfere with the measurement regardless of their concentration. Interference testing for these species is therefore not required.

11.5.2 *Samples and Analytes for Interference Testing*—CO_2, H_2O and CH_4 can potentially interfere with the measurement of other analytes. For interference testing, separate sample gas mixtures of 200 ppm(v) of CO_2 in H_2, 500 ppm(v) of H_2O in H_2 (100 times the maximum concentration in SAE J2719), and 1000 ppm(v) CH_4 in H_2 (10 times the maximum concentration in SAE J2719) shall be prepared and analyzed. The gas mixtures shall contain as little as possible of the analyzer's target analyte(s), but no more than allowed by SAE J2719 (see Table 1). Interference tests are to be performed for each analyte measured by the CRDS instrument, either simultaneously or separately. Every analyte shall be tested for interference with all prepared sample gas mixtures, unless one of them is the target analyte itself (for example, if CO_2 is the analyte, interference testing for CO_2 is obviously not applicable).

11.5.3 *Negative Readings*—If the CRDS instrument has any setting that–if enabled–would prevent the analyzer from showing negative concentration readings, this feature has to be disabled for the interference tests.

11.5.4 *Settling and Measurement Times*—After connecting each sample gas, allow for sufficient time to achieve stable readings (typically 5 min to 10 min). Longer settling and measurement times may be required for "sticky" molecules such as H_2O.

11.5.5 *Determination of Maximum Interference Bias*—To determine the maximum bias due to interference for analyte *i*, follow these steps for each analyte:

11.5.5.1 Calculate the mean concentration reading C_{ij} of analyte *i* when run with sample *j* (with *j* being one of the three sample gas mixtures of CO_2, H_2O, or CH_4, described in 11.5.2).

11.5.5.2 Calculate $POS_i = \sum_j C_{ij}$ for all $C_{ij}>0$

and

$NEG_i = \sum_j |C_{ij}|$ for all $C_{ij}<0$.

11.5.5.3 The maximum bias B^i_{max} is then determined by

$$B^i_{\max} = N^{-1} \times \max\{POS_i, NEG_i\} \quad (1)$$

where:

N = 100 for CO_2 and H_2O, N = 10 for CH_4.

11.5.6 *Insignificant Interference*—If B^i_{max} is smaller than the analyzer's 3σ detection limit for analyte *i*, the interference bias is regarded as insignificant.

TABLE 1 Specifications

NOTE 1—Repeatability measured with different instruments with separate, dedicated sensor modules for each analyte. Typical response time to obtain results below is two to three min.

Contaminant/Analyte	SAE J2719 Detection Limit [ppb(v)]	Tested 3σ detection limit [ppb(v)]	Tested repeatability [ppb(v)] at mean concentration level [ppb(v)]
Water (H_2O)[A]	5000	LR: 0.08 HR: 4.2	LR: 0.10 at 0.44 HR: 5.2 at 15 and 20 at 996
Methane (CH_4)	100 000	0.68	0.48 at 0.40
Carbon Monoxide (CO)	200	41	26 at 21
Carbon Dioxide (CO_2)	2000	161	92 at 81
Formaldehyde (H_2CO)	200	6.1	5.5 at 5.5
Ammonia (NH_3)	100	0.86	0.97 at 1.52
Oxygen (O_2)	5000	0.12	0.042 at 0.34

[A] HR (high range) and LR (low range) models use different absorption lines.

11.5.7 *Significant Interference*—If B^i_{max} is larger than the analyzer's 3σ detection limit for analyte i, the interference bias is regarded as significant; however, the measured signal may be a real reading from residual analyte *i* in the sample gas mixture. In this case, a spectroscopic analysis can distinguish a real reading from an interference. Please contact the instrument manufacturer for guidance regarding this analysis. If the measured reading is indeed an interference, the instrument or the measurement procedure for analyte *i* has to be modified appropriately. After implementation of these modifications, analyte *i* shall be re-tested for interference.

12. Conditioning

12.1 When the start-up procedure described in Section 9 has been completed, as a final step, the system should be purged with an inert gas for at least 15 min with a flow rate of 0.5 slpm to 1.0 slpm or until such time as the measured analyte concentration has stabilized. The time required to reach a steady analyte concentration may be longer (shorter) with a lower (higher) flow rate.

13. Procedure

13.1 CRDS provides a continuous measurement of an analyte concentration in a given matrix gas. Measuring the analyte concentration in each sample is a matter of switching between the purge gas and sample gas and allowing the measurement reading to stabilize. To obtain correct concentration readings, the appropriate gas matrix must be selected in the instrument software, in this case "Hydrogen." Incorrect matrix gas selection may result in false concentration readings.

14. Calculation or Interpretation of Results

14.1 As described in Section 11, a CRDS instrument provides a direct, absolute reading of an analyte concentration in a given gas sample for a specified concentration range. No further interpretation is required. Measurement data may be accessed via download of a file stored within the instrument or collected in real-time via analog or digital output.

14.2 If it was determined that a specific molecule has significant interference on the results for a target analyte (see 11.5), results require correction to account for the presence/concentration of the interfering molecule.

15. Report

15.1 Report sampling date and time, sampling duration, any corrections made due to interference and additional comments as necessary. Combine with the relevant file containing the analyte concentration data.

16. Detection Limits, Precision, Bias, and Linearity

16.1 *Test Configurations for Different Analytes*—A commonly available CRDS analyzer sensor module is generally configured according to Fig. 2. The sensor module possesses the same general configuration for every analyte in Table 1; however, laser wavelength and optical coatings are specific to each analyte. The sensor module can be configured as an integrated single-channel analyzer (sensor plus electronics) or as a multi-channel instrument with multiple sensor modules sharing one control unit. The test sample is a mixture of the analyte in H_2, typically, from a certified gas cylinder (±2 % accuracy). For H_2O, a moisture generator is used to generate a known concentration of H_2O.

16.2 *Detection Limits*—The detection limits for all molecules listed in Table 1 are based on the required detection limit stated in SAE J2719. The CRDS numbers are determined by experiment using the specific configuration following the ASTM definition (i.e. dedicated sensor module per analyte). The detection limit is specified as three times the standard deviation (3σ) of the measured analyte concentration using a gas sample that contains no or extremely small amounts of the analyte.

16.3 *Linearity*—Due to the fundamental principles on which CRDS is based, a typical instrument exhibits a linearity coefficient of >0.995 over at least four orders of magnitude of concentration. Fig. 3 shows test data of a typical instrument for trace O_2 detection with different intrusion levels (step-up and step-down pyramid) in the lower part of the dynamic range. The correlation between nominal and measured concentration is 0.995 with a linearity coefficient (R^2) of 0.9995 for the step-up intrusion and 1.011 with an R^2 of 0.9999 for the step-down intrusion.

17. Precision and Bias

17.1 The precision of this test method is based on an interlaboratory study of ASTM D7941, Standard Test Method

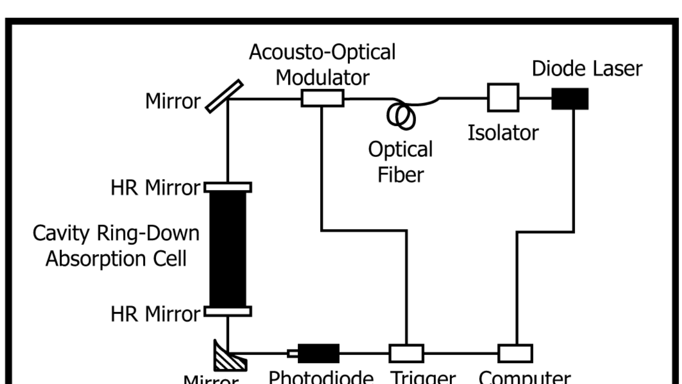

FIG. 2 Typical CRDS Configuration

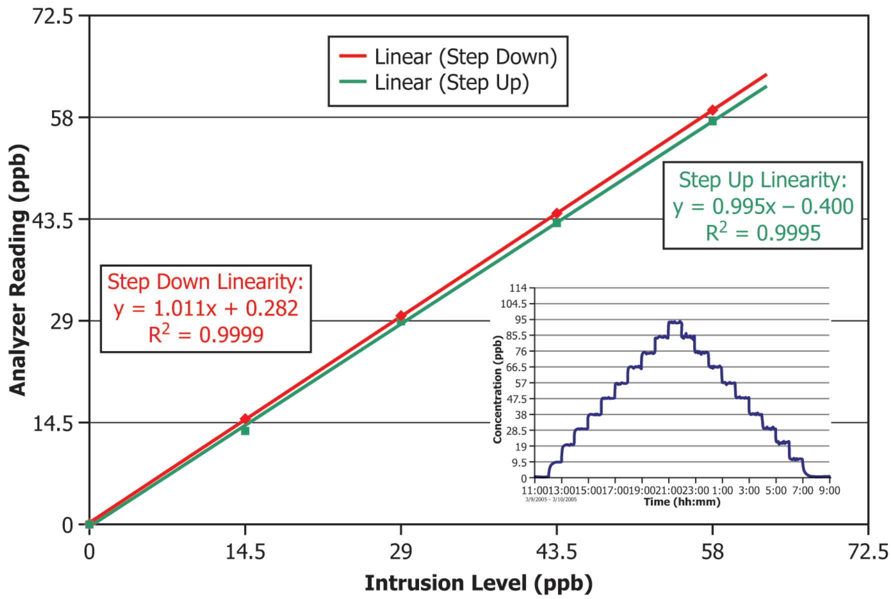

FIG. 3 Pyramid Step Intrusion of Different Analyte Levels (O_2) Using a Typical CRDS Trace Analyzer

for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer, conducted in 2021. Five laboratories tested one sample gas containing CO_2, CO and CH_4 in hydrogen. Every "test result" represents an individual determination, and all participants were instructed to report three replicate test results for each material. Practice E691 was followed for the design of study and analysis of the data; the details are given in ASTM Research Report No. D03-2000.[7]

17.1.1 *Repeatability Limit (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the determined values only in one case in 20.

17.1.1.1 Repeatability limit can be interpreted as the maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

17.1.1.2 Repeatability limits are listed in Tables 2-4 below.

17.1.2 *Reproducibility Limit (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

17.1.2.1 Reproducibility limit can be interpreted as the maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

17.1.2.2 Reproducibility limits are listed in Tables 2-4 below.

17.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

17.1.4 Any judgment in accordance with statement 17.1.1 and 17.1.2 would normally have an approximate 95 % probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories reporting replicate results essentially guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the repeatability limit as a general guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

17.2 *Bias*—At the time of the study, no accepted reference material suitable for determining the bias for this test method was included for testing, therefore no statement on bias is being made.

17.3 The precision statement was determined through statistical examination of 27 results, from 5 laboratories, on 1 material.

TABLE 2 CO_2 Contaminant Concentration in ppb(v)

Material	Number of Laboratories	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	n	$\bar{x}$	S_r	S_R	r	R
Hydrogen Fuel	3	2243.067	39.867	95.514	111.629	267.438

[A] The average of the laboratories' calculated averages.

TABLE 3 CO Contaminant Concentration in ppb(v)

Material	Number of Laboratories n	Average[A] $\bar{x}$	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
Hydrogen Fuel	2	279.850	24.802	54.945	69.445	153.845

[A] The average of the laboratories' calculated averages.

TABLE 4 CH_4 Contaminant Concentration in ppb(v)

Material	Number of Laboratories n	Average[A] $\bar{x}$	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
Hydrogen Fuel	4	1035.5583	1.8648	16.9288	5.2216	47.4006

[A] The average of the laboratories' calculated averages.

18. Validation and Quality Assurance/Control Procedures

18.1 *Validation:*

18.1.1 *Validation Procedure using a Certified Cylinder*—Although CRDS instruments are accurate upon manufacture, improper installation of the gas sampling system may result in precise but inaccurate measurements. Upon installation of a new system, the CRDS readings shall be validated using a cylinder standard, certified to ±2 % accuracy and containing concentrations in the range of 1 ppm(v) to 10 ppm(v) for every monitored analyte. To ensure long-term integrity of the measurement results, the validation procedure may be repeated periodically. Validation is recommended at least once per year.

18.1.2 *Tampering with the Calibration and Suspicious Readings*—If at any point analyzer measurements appear suspect or it appears the instrument's calibration settings have been tampered with, a point-of-use purifier for the analyte to be measured can be used (see 18.1.3). Alternatively, a Cavity Peak Scan (see 18.1.4) can be performed to validate the accuracy of the instrument's measurements without having to use a certified cylinder standard or a purifier.

18.1.3 *Employing a Point-of-Use Purifier*—If readings on the analyzer appear to be suspiciously high, a point-of-use purifier for the target analyte can be installed directly at the inlet of the analyzer. If the readings remain high after installation, the analyzer may be malfunctioning. A Cavity Peak Scan may be performed as an additional method of verification.

18.1.4 *Cavity Peak Scan Procedure*—Instead of only measuring on the peak of the absorption line of the analyte at a fixed laser temperature, the temperature can be varied in small increments (typically 0.02 °C increments within –3 °C to +1 °C around the normal operating temperature) to provide a scan of the entire absorption line. One manufacturer of CRDS instruments provides this procedure as automated program. The results of the scan along with the instrument's displayed reading are usually sent to the manufacturer who can verify that the Cavity Peak Scan results match the displayed reading.

18.2 *Instrument Failure*—A typical CRDS analyzer contains critical components which cause the instrument to not produce data or to deliver inaccurate readings when they are compromised. Proper operation of these components is ensured via the following procedures:

18.2.1 *Laser Source*—In case of a failure of the laser source, there will be no light available for the measurement system. The CRDS instrument monitors the light intensity from the diode. If laser light is not detected, the instrument will cease to measure and alert the user of the laser failure.

18.2.2 *Mirror Reflectivity*—Mechanical shock, extreme temperatures, particulate matter or other contamination can change the reflectivity of the cavity mirrors. The instrument provides a regular "tune" cycle (see 11.3) to adjust for changes in mirror reflectivity. When analyzing clean and analytically consistent samples such as most hydrogen fuel samples, the "tune" cycle should be run once a month. When analyzing potentially dirty sample or samples with variable sample gas compositions, mechanical instability, or rapidly changing temperature, a "tune" is recommended more frequently. A change in mirror reflectivity may affect the noise performance of the instrument (sensitivity and precision); however, measurement accuracy is generally not affected.

18.2.3 *Electronic Components*—Any failure in electronic components will result in the instrument being non-functional.

18.3 *Gas Sampling System*—The gas flow must be maintained within the required specifications for both flow and pressure (see 9.1.1) for instrument functionality and accurate analyte measurement. If a pressurized sample is used, regulators are to be set appropriately to ensure sufficient pressure to achieve positive flow through the analyzer without overpressurizing the instrument. For pressures requiring a vacuum pump, proper operation of the pump must be ensured. While not required, monitoring the flow through the instrument using a calibrated mass flow meter at the sample outlet (or behind the vacuum pump for low pressure samples) is recommended.

19. Keywords

19.1 absorption; absorption spectroscopy; Beer-Lambert law; infrared absorption; infrared analysis; infrared (IR) absorption; laser; laser-based spectroscopy; near-infrared; NIR; PEM fuel cell; optical technique; tunable diode laser; quantum cascade laser; cavity-enhanced spectroscopy; cavity ring-down spectroscopy; vehicle fuel

APPENDIX

(Nonmandatory Information)

X1. CAVITY RING-DOWN SPECTROSCOPY (CRDS)

X1.1 General Principle

X1.1.1 CRDS is a form of optical absorption spectroscopy. It works by attuning the wavelength of laser light to the unique molecular fingerprint of an analyte. The light and sample are contained in an optical cavity containing highly reflective mirrors (typically R >99.99 %) affixed to opposite ends of the cell. By rapidly shutting off the laser firing into the cavity, the light intensity built up inside the cavity will decay due to the residual transmission of the mirrors and the absorption of the analyte. By comparing this decay time with a reference measurement performed at a wavelength where the analyte does not absorb, the absorption characteristics of the analyte can be measured.

X1.2 Relation to the Beer-Lambert Law

X1.2.1 The Beer-Lambert Law relates the extinction of light to the absorption properties of a sample in the following way:

$$I(l) = I_0 \exp(-\alpha l) \quad (X1.1)$$

where

I = intensity of the light after a path length through the sample
l = path length
I_0 = original light intensity
α = absorption coefficient of the sample

In CRDS, the light intensity I_0 is built up inside a cavity with a fixed length L; therefore, the decaying intensity can also be regarded as a time-dependent decay, hence

$$I(t) = I_0 \exp(-t/\tau) \quad (X1.2)$$

where τ is the characteristic "ring-down time" of the CRDS system, which is given by

$$\tau = \frac{1}{c} \times \frac{L}{1 - R + \alpha L} \quad (X1.3)$$

Here, we assume for simplicity that the refractive index of the sample is ≈1 and that there are no losses other than the analyte absorption and mirror losses.

X1.3 On- and Off-peak Measurement

X1.3.1 To measure the absorption of a specific analyte, the ring-down time both on the peak of the absorption and at a "zero" wavelength, where the analyte does not absorb, is compared. Typically, a tunable laser is used to change between on- and off-peak wavelengths. The on-peak measurement is given by Eq X1.4. Off-peak, the ring-down time τ_0 is only determined by the mirror losses, hence:

$$\tau_0 = \frac{1}{c} \times \frac{L}{1 - R} \quad (X1.4)$$

X1.4 Determination of Analyte Concentration

X1.4.1 By comparing the on-peak ring-down time τ with the off-peak ring-down time τ_0, the number density of the analyte N_X is determined via

$$N_x = \frac{1}{\sigma_x c} \times \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \quad (X1.5)$$

Here, σ_x is the known absorption cross-section of the analyte at the chosen on-peak wavelength, typically obtained from a spectroscopic reference database (see X1.8.1). From the number density, the relative concentration can be calculated using the ideal gas law.

X1.5 Advantage of CRDS

X1.5.1 *Insensitivity to Intensity Noise*—It is notable that Eq X1.3-X1.5, which are used to determine the analyte concentration, do not contain the light intensities I or I_0 in contrast to classic absorption spectroscopy. This means, that CRDS is insensitive to laser intensity fluctuations, thus eliminating one typical noise source.

X1.5.2 *Sensitivity Enchancement*—With the mirror reflectivity R typically being very close to unity, the denominator in Eq X1.3 and X1.4 becomes very small, causing a massive effective increase in the interaction length. In a CRDS system, this enhancement leads to an effective absorption path length of many kilometers.

X1.6 Typical CRDS Setup

X1.6.1 The key components in Fig. 2 are as follows:

X1.6.2 *Diode Laser*—Emits coherent light. Although diode lasers are typically used, any tunable laser source with sufficient quality may be coupled into the cavity.

X1.6.3 *Isolator*—Prevents light feedback from interfering with the laser.

X1.6.4 *Acousto-optic modulator (AOM)*—Shuttering device for the light source. The use of an AOM is exemplary; it may be replaced with an alternate device performing the same function, which is to rapidly shut off the light beam. Electrically shuttering off the light source is also an alternate implementation.

X1.6.5 *CRDS absorption cell*—With highly reflective mirrors, creates measurement cavity.

X1.6.6 *Photodiode*—Detects and measures the light intensity, as it leaves the absorption cell.

X1.6.7 *Trigger*—Works in concert with the photo-diode and sends signal to the AOM or alternate shut-off device to start the ring-down decay.

X1.7 Ring-down/Exponential Decay

X1.7.1 In Fig. X1.1, the concept of ring-down decay within the cavity after the laser source is shuttered is shown. As the laser light bounces back and forth between the ultra-high reflective mirrors, the analyte species absorbs the light energy until it is completely extinct. Measuring the light emitted through the end mirror reveals the exponential decay of the intracavity intensity.

X1.8 Key Points and Principles

X1.8.1 The spectroscopic characteristics (line strength and pressure broadening coefficient) of the analyte are fundamental physical properties and are permanently programmed into the instrument by factory calibration using NIST traceable reference standards. Any modifications implemented into the analyzer are based on acceptance by recognized authorities, including the U.S. National Institute of Standards and Technology (NIST), the National Physical Laboratory (NPL) in the United Kingdom, the National Institute of Advanced Industrial Science and Technology (AIST) in Japan.

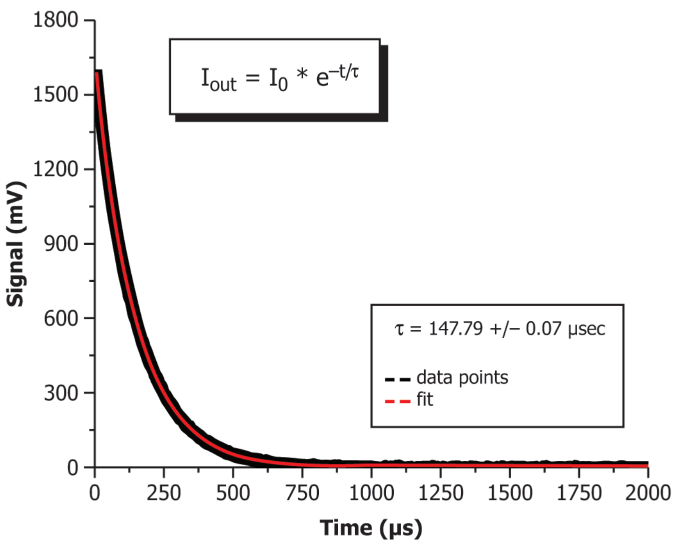

FIG. X1.1 Ring-Down Decay within the Cavity after the Laser Source is Shuttered

X1.8.2 The laser is selected to operate at the wavelength required for the target analyte. One common method to ensure that long-term wavelength stability is an internal spectroscopic verification standard, such as a reference cell, which contains a small amount of the target analyte, and can be an automatic feedback process to maintain the correct laser wavelength.

X1.8.3 Periodic determination of τ_0 ensures that any changes to the mirror losses are cancelled out. Factory prequalification of each unit assures the system is operating within specification. It is recommended that a τ_0 measurement (called "tune") is performed at least monthly, either manually or on an automated schedule. Additional "tune" cycles are recommended when changing sample gases, after the instrument was turned off, and when the analyzer is moved to a different location.

X1.8.4 The matrix gas hydrogen is transparent throughout the wavelength range of the used tunable lasers and around the absorption peaks of the analytes in particular. The gas matrices (including H_2) in the library of a CRDS analyzer have been tested to ensure they do not absorb light at the same wavelength as the target analyte. The correct matrix (here H_2) has to be selected from the library to allow for the correct calculation of the concentration using the right pressure broadening coefficient, which is pre-programmed into the instrument's gas matrix database.