Designation: D7668 – 14a

Standard Test Method for
Determination of Derived Cetane Number (DCN) of Diesel Fuel Oils—Ignition Delay and Combustion Delay Using a Constant Volume Combustion Chamber Method[1]

1. Scope*

1.1 This test method covers the quantitative determination of the derived cetane number of conventional diesel fuel oils, diesel fuel oils containing cetane number improver additives, and is applicable to products typical of Specification D975, Grades No.1-D and 2-D regular, low and ultra-low-sulfur diesel fuel oils, European standard EN590, and Canadian standards CAN/CGSB-3.517 and CAN/CGSB3.6. The test method may be applied to the quantitative determination of the derived cetane number of biodiesel, blends of diesel fuel oils containing biodiesel material (for example, Specifications D975, D6751, and D7467), and diesel fuel oil blending components.

1.2 This test method utilizes a constant volume combustion chamber with direct fuel injection into heated, compressed synthetic air. A dynamic pressure wave is produced from the combustion of the sample. An equation converts the ignition delay and the combustion delay determined from the dynamic pressure curve to a derived cetane number (DCN).

1.3 This test method covers the ignition delay ranging from 1.9 to 25 ms and combustion delay ranging from 2.5 to 160 ms (30 to 70 DCN). However, the precision stated only covers the range of DCN from 39 to 67.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D613 Test Method for Cetane Number of Diesel Fuel Oil
D975 Specification for Diesel Fuel Oils
D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
D7467 Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)
E456 Terminology Relating to Quality and Statistics

2.2 *EN Standards:*[3]

EN590 Automotive Fuels—Diesel—Requirements and Test Methods

2.3 *Energy Institute Standards:*[4]

IP41 Ignition Quality of Diesel Fuels—Cetane Engine Test Method

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.01.0C on Test Equipment, Procedures, and Instrumentation.

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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 European Committee for Standardization. Central Secretariat: rue de Stassart, 36,B-1050 Brussels, Belgium.

[4] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

***A Summary of Changes section appears at the end of this standard**

2.4 *Canadian Standards:*[5]

CAN/CGSB-3.517 Regular Sulphur Diesel Fuel—Specification

CAN/CGSB 3.6 Automotive Low-Sulphur Diesel Fuel—Specification

2.5 *DIN Standards:*[6]

DIN 73372 Einspritzdüsen Grösse T und U

3. Terminology

3.1 *Definitions:*

3.1.1 *accepted reference value (ARV), n*—a value that serves as an agreed-upon reference for comparison and that is derived as *(1)* a theoretical or established value, based on scientific principles, *(2)* an assigned value, based on experimental work of some national or international organization, such as the U.S. National Institute of Standards and Technology (NIST), or *(3)* a consensus value, based on collaborative experimental work under the auspices of a scientific or engineering group. **E456**

3.1.1.1 *Discussion*—In the context of this method, accepted reference value is understood to apply to the ignition delay and the combustion delay of specific reference materials determined under reproducibility conditions by collaborative experimental work.

3.1.2 *cetane number, n*—a measure of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test. **D4175**

3.1.2.1 *Discussion*—In the context of this test method, cetane number is that defined by Test Method D613/IP41.

3.1.3 *check standard, n*—in QC testing, a material having an accepted reference value used to determine the accuracy of a measurement system.

3.1.3.1 *Discussion*—In the context of this test method, check standard refers to the calibration reference material.

3.1.4 *quality control (QC) sample, n*—for use in quality assurance programs to determine and monitor the precision and stability of a measurement system, a stable and homogeneous material having physical or chemical properties, or both, similar to those of typical samples tested by the analytical measurement system. The material is properly stored to ensure sample integrity, and is available in sufficient quantity for repeated, long term testing. **D6299**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calibration reference material, n*—a pure chemical or a specified mixture of pure chemicals having an assigned ignition delay accepted reference value and an assigned combustion delay accepted reference value.

3.2.2 *chamber wall temperature, n*—temperature, in °C, of the combustion chamber wall.

3.2.3 *charge air, n*—compressed synthetic air at a specified pressure introduced into the combustion chamber at the beginning of each test cycle.

3.2.4 *combustion analyzer, n*—an integrated compression ignition apparatus to measure the ignition and combustion characteristics of diesel fuel oil.

3.2.5 *combustion delay (CD), n*—that period of time, in milliseconds (ms), between the start of fuel injection and mid-point of the combustion pressure curve.

3.2.5.1 *Discussion*—In the context of this test method, the start of fuel injection is interpreted as the rise in the electronic signal that opens the injector and the combustion pressure curve mid-point is interpreted as the part of the pressure curve midway between the chamber static pressure and the maximum pressure generated during the combustion cycle, as measured by a pressure sensor in the combustion chamber. The combustion delay CD measures the time between the injection of the sample and phase of combustion controlled by the diffusive mixing of the air and fuel.

3.2.6 *derived cetane number (DCN), n*—a number calculated using a conversion equation to determine a cetane number.

3.2.6.1 *Discussion*—The conversion equation relates a measured ignition delay or ignition delay and combustion delay from a combustion analyzer, to a cetane number.

3.2.7 *ignition delay (ID), n*—that period of time, in milliseconds (ms), between the start of fuel injection and the start of combustion as determined using the specific combustion analyzer applicable for this test method.

3.2.7.1 *Discussion*—In the context of this test method, start of fuel injection is interpreted as the rise in the electronic signal that opens the injector; combustion is interpreted as the part of the pressure curve generated during the combustion cycle when significant (+0.02 MPa above the chamber static pressure) and sustained increase in rate-of-change in pressure, as measured by a pressure sensor in the combustion chamber.

3.2.8 *injection period, n*—the period of time, in microseconds (µs), that the fuel injector nozzle is open as determined by the length of the electronic signal, in microseconds, that opens the injector.

3.2.9 *operation period, n*—the time, not to exceed 12 h, between successive calibration or QC testing, or both, of the combustion analyzer by a single operator.

3.3 *Abbreviations:*

3.3.1 *ARV*—accepted reference value

3.3.2 *CD*—combustion delay

3.3.3 *CN*—cetane number

3.3.4 *DCN*—derived cetane number

3.3.5 *ID*—ignition delay

3.3.6 *QC*—quality control

4. Summary of Test Method

4.1 A small specimen of sample is injected into a heated, temperature-controlled, constant volume chamber, which has previously been charged with compressed air of a specified quality. Each injection produces a compression ignition combustion cycle detected using a pressure sensor. The ignition delay and combustion delay are measured from the rise of the electronic signal that activates the injector solenoid to two

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[5] Available from the Canadian General Standards Board, Sales Centre, Gatineau, Canada, K1A1G6. www.ongc-cgsb.ca.

[6] Available from Beuth Verlag GmbH (DIN-- DIN Deutsches Institut fur Normung e.V.), Burggrafenstrasse 6, 10787, Berlin, Germany, http://www.en.din.de.

specific points along the combustion pressure wave produced by the combustion cycle. A complete sequence comprises 5 preliminary injection cycles and 15 subsequent injection cycles used for the sample analysis. The ID and CD measurements for the last 15 injection cycles are statistically reviewed and the outlying ID's and CD's are eliminated using Peirce's Criterion.[7] The remaining ID's and CD's are averaged to produce the two independent results. An equation converts the average ID result and the average CD result into a DCN.

5. Significance and Use

5.1 The ID and CD values and the DCN value determined by this test method provides a measure of the ignition characteristics of diesel fuel oil used in compression ignition engines.

5.2 This test can be used by engine manufacturers, petroleum refiners and marketers, and in commerce as a specification aid to relate or match fuels and engines.

5.3 The relationship of diesel fuel oil DCN determinations to the performance of full-scale, variable-speed, variable-load diesel engines is not completely understood.

5.4 This test can be applied to non-conventional diesel fuels.

5.5 This test determines ignition characteristics and requires a sample of approximately 370 mL and a test time of approximately 30 min using a fit-for-use instrument.

6. Interferences

6.1 **Warning—**Minimize exposure of sample fuels, calibration reference materials, QC samples, and check standards to sunlight or fluorescent lamp UV emissions to minimize induced chemical reactions that can affect the delay measurements.[8]

6.1.1 Exposure of these fuels and materials to UV wavelengths shorter than 550 nm for a short period of time can significantly affect ignition delay measurements.

NOTE 1—The formation of peroxide and radicals can affect ignition delay measurement. These formations are minimized when the sample or material is stored in the dark in a cold room at a temperature of less than 10°C and covered by a blanket of nitrogen.

7. Apparatus

7.1 *General*—This test method uses an integrated automated analytical measurement system[9] comprised of:

7.1.1 *Combustion Chamber*—A cylindrical chamber having a volume of 0.473 ± 005 L, with external heating elements, heat shield, and electrically actuated intake and exhaust valves. There is an opening at one end of the chamber to accommodate insertion of the fuel injection nozzle assembly and there are openings at the other end of the chamber to insert air, remove exhaust, and attach a pressure sensor.

7.1.2 *Fuel Injection System*—A high pressure sample, generated using a hydraulic pump and pressure multiplier, is delivered to a commercial electronic diesel fuel injector. A sample reservoir supplies the pressure multiplier with sample to ensure proper and repeatable injection of calibration, QC material, and test specimens into the combustion chamber. The system includes:

7.1.2.1 *Fuel Sample Reservoir*—A metal reservoir having a nominal volume of 200 mL.

7.1.2.2 *Hydraulic Pump*—Capable of producing fuel pressures up to 19 MPa.

7.1.2.3 *Pressure Multiplier*—10:1 ratio.

7.1.2.4 *Fuel Injector*—A solenoid-based common rail diesel fuel injector from Bosch with the part number 0445110181 (Annex A6).

7.1.2.5 *Safety Burst Disk*—Relieves the high pressure if the sample pressure exceeds 180 MPa. The burst disk is attached to the high pressure sample system manifold block opposite the injector.

7.1.2.6 *Flush Valve*—High pressure air actuated valve used to exchange samples.

7.1.3 *Coolant System*—A closed loop circulating coolant system to control the temperature of the combustion injector nozzle and dynamic pressure sensor. The system includes an auxiliary heat exchanger with built-in circulating pump and flow control valves.

7.1.4 *Instrument Sensors*—Sensors used to measure and either indicate the value of a variable or transmit the condition for control or data acquisition purposes such as:

7.1.4.1 *Combustion Chamber Static Pressure Sensor*—A calibrated sensor installed to correct the temperature offset of dynamic pressure sensor.

7.1.4.2 *Combustion Chamber Dynamic Pressure Sensor*—A calibrated sensor installed to measure the pressure within the combustion chamber.

7.1.4.3 *Sample Pressure Sensor*—A calibrated sensor installed to measure the pressure of the sample injected into the combustion chamber.

7.1.4.4 *Nitrogen Pressure Sensor*—A sensor installed to measure the inlet pressure from the nitrogen regulator.

7.1.4.5 *Combustion Chamber Inner Wall Temperature Sensor*—Type K thermocouple with a stainless steel sheath.

7.1.4.6 *Injector Nozzle Cooling Jacket Temperature Sensor*—Type K thermocouple with stainless steel sheath, inserted in the injector nozzle coolant passage.

7.1.5 *Computerized Control, Data Acquisition, Data Analysis and Reporting System*—A microprocessor controlled system with a keyboard for manual entry of operating instructions, an LCD monitor for visual observation of all testing functions, and a printer for printed copy output of test results. The computer-based system provides automated control of the relevant combustion analyzer and subsystem component functions and collects and processes all relevant signals from the temperature and pressure sensors.

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[7] Ross, Stephen, "Peirce's Criterion for the Elimination of Suspect Experimental Data," *Journal of Engineering Technology*, Fall 2003.

[8] Supporting data, "Sunlight and Air Exposure Effects on Octane Number or Cetane Number of Petroleum Product Samples," have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1502.

[9] The sole source of supply of the analyzer described in this method known to the committee at this time is PAC LP, 8824 Fallbrook Drive, Houston, TX 77064. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

7.2 *Instrument Schematic*—A schematic of the instrument is reproduced in Annex A4.

7.3 *Compressed Gas Pressure Regulators:*

7.3.1 *Charge Air Regulator*—A two-stage regulator capable of controlling the downstream pressure to a minimum pressure of 2.2 MPa.

7.3.2 *Nitrogen Regulator*—A two-stage regulator capable of controlling the downstream pressure to a minimum pressure of 0.7 MPa.

8. Reagents and Materials

8.1 *Calibration Reference Material:*

8.1.1 40:60 mixture by weight of hexadecane and 2,2,4,4,6,8,8-heptamethylnonane, respectively, measured with an accuracy of 0.01 percent of:

8.1.1.1 *Hexadecane*—With a minimum purity of 99.0 volume percent. (**Warning—**Combustible. Vapor harmful.)

8.1.1.2 *2,2,4,4,6,8,8-Heptamethylnonane*—With a minimum purity of 98.0 volume percent. (**Warning—**Combustible. Vapor harmful.)

8.1.1.3 For peroxide-free material, the assigned ID_{ARV} is 2.96 ms and the assigned CD_{ARV} is 4.90 ms.

NOTE 2—Hydrocarbons can form peroxides and other free radically formed contaminants that can influence the ID and CD. Experience has found some 40:60 blends of hexadecane and 2,2,4,4,6,8,8-heptamethylnonane meeting the purity specification can contain peroxides and other free radically form contaminants. Typically, the peroxides and other free radically formed contaminants can be removed from the 40:60 mixture of hexadecane and 2,2,4,4,6,8,8-heptamethylnonane by subjecting the blend to activated 4Å molecular sieves.

8.1.2 *Methylcyclohexane (MCH)*—With a minimum purity of 99.0 volume percent. The assigned ID_{ARV} for this material is 11.00 ms and the assigned CD_{ARV} for this material is 17.00 ms. (**Warning—**Flammable. Vapor harmful. Vapor may cause flash fire.)

NOTE 3—Hydrocarbons can form peroxides and other free radically formed contaminants that can influence the ID and CD. Experience has found some MCH meeting the purity specification but which does not meet the ID_{ARV} or CD_{ARV}. It is recommended that new material be qualified prior to use.

8.2 *Check Standard:*

8.2.1 *Calibration Reference Material*—40:60 mixture by weight of hexadecane and 2,2,4,4,6,8,8-heptamethylnonane (see 8.1). (**Warning—**Combustible. Vapor harmful.)

8.2.2 *Quality Control Sample*—A stable and homogeneous diesel fuel oil having physical and chemical properties similar to those of typical sample fuels routinely tested (**Warning—** Combustible. Vapor harmful.)

8.3 *Charge Air*—A compressed synthetic air mixture containing 20.0 ± 0.5 volume percent oxygen with the balance nitrogen, less than 0.003 volume percent hydrocarbons, and less than 0.025 volume percent water. It is suggested that a quality control test be performed after an air cylinder has been changed (**Warning—** Compressed gas under high pressure that supports combustion.)

8.4 *Compressed Nitrogen*—Compressed nitrogen having a minimum purity of 99.9 volume percent (**Warning—** Asphyxiant. Compressed gas under high pressure.)

8.5 *Coolant System Fluid*—A 50:50 volume mixture of water and commercial ethylene glycol-based antifreeze (**Warning—**Poison. Maybe harmful or fatal if inhaled or swallowed.)

8.5.1 *Antifreeze*—A commercial automotive cooling system ethylene glycol-based solution.

8.5.2 *Water*—A distilled or reagent-grade, conforming to Specification D1193, Type IV.

8.6 *Heptane*—(*n*-Heptane) with a minimum purity of 99.5 volume percent. (**Warning—**Flammable. Vapor harmful. Vapor may cause flash fire.)

9. Sampling and Test Specimen Preparation

9.1 *Sampling:*

9.1.1 Collect diesel fuel oil samples in accordance with Practices D4057 or D4177. (**Warning—** Collect and store diesel fuel oil samples in a suitable container such as a dark brown glass bottle, a metal can, or a minimally reactive plastic container to minimize exposure to UV emissions.)

9.1.2 Refer to Practice D5854 for appropriate information relating to the mixing and handling of diesel fuel oil samples.

9.2 *Test Specimen Preparation:*

9.2.1 *Sample Fuel Temperature*—Condition the diesel fuel oil sample before opening the storage container, so that it is at room temperature, typically 18 to 32°C.

9.2.1.1 Fuel temperature should be raised at least 14°C above the fuel's cloud point. Fuel sample should be homogeneous before testing.

NOTE 4—Give consideration to the fuel composition related to sample temperature to avoid the loss of lower boiling components that may affect the DCN value.

9.2.2 Collect the specimen in a dark brown bottle, metal can or nonreactive plastic container.

10. Basic Apparatus Settings and Standard Operating Conditions

10.1 Operation of the combustion analyzer, associated equipment, instrumentation, and computer system requires setting a series of testing variables to prescribed specifications. Some of these settings are established by component specifications, others are operating conditions that are monitored or controlled by the computer software or by operator adjustment.

10.2 *Settings Based on Component Specifications:*

10.2.1 *Combustion Chamber Leakage Rate*—Shall be less then 0.75 kPa/s, as measured during the automated check of the sealing integrity of the combustion chamber.

NOTE 5—The computer system initiates an automatic diagnostic procedure consisting of zero-adjustment of the chamber dynamic pressure sensor and a chamber sealing integrity check.

10.3 *Standard Operating Conditions:*

10.3.1 *Chamber Static Pressure*—The average Chamber Static Pressure for the 15 combustion cycles is required to be within 2.00 ± 0.02 MPa.

10.3.2 *Chamber Wall Temperature,* 560 to 640°C.

10.3.2.1 The Chamber wall temperature is initially set by the manufacturer. The temperature set-point is monitored and controlled by the computer. Adjustment of the controller set-point is required, in accordance with the calibration procedure.

10.3.2.2 The average wall temperature for the 15 combustion cycles is required to be within ±0.2°C of the set point temperature.

10.3.3 *Injector Nozzle Coolant Jacket Temperature*—Set the coolant reservoir temperature to achieve an injector nozzle coolant passage temperature of 50 ± 2°C. This is determined and recorded by the computer. A temperature outside the range given during a 15 combustion cycle measurement indicates a possible malfunctioning of the cooling system.

10.3.4 *Injection Pressure*—Set by the manufacture to 100 MPa. An individual injection does not occur unless the high pressure sample sensor measures 100 ± 1.5 MPa. If the sample pressure is outside the tolerance limit the hydraulic pressure is adjusted and the injection process is re-initiated. If an appropriate sample pressure is not found after 5 adjustments of the hydraulic pressure the test is aborted and the user is warned of the fault.

10.3.5 *Injection Period*—Set by the instrument using the computer controlled calibration process. The injection period is limited to the range from 2000 to 2700 µs.

11. Calibration and Quality Control Testing

11.1 *Calibration*—Calibrate the combustion analyzer: *(1)* after it is installed and commissioned, *(2)* after replacement of critical parts or components of combustion chamber assembly, fuel injection system, or instrument sensors, *(3)* after calibration of the chamber static pressure, or chamber dynamic pressure sensors, or *(4)* whenever check standard or QC sample determinations are not in statistical control, and the assignable causes for QC non-compliance have been suitably addressed.

11.2 *Pre-calibration Procedure:*

11.2.1 Open the valve at the source of the charge air supply and adjust the pressure regulator as needed to provide the specification pressure. Open the valve at the source of the nitrogen supply and adjust the pressure regulator as needed to provide the specification pressure. Turn on the circulation coolant system.

11.2.2 Position the combustion analyzer power switch to ON and warm-up the combustion analyzer. After the chamber wall temperature has stabilized a chamber leakage test will be performed to determine the chamber leakage rate. If the leakage test fails, a warning is issued.

11.2.3 Clean the sample system (see Annex A2).

11.3 *Hexadecane/Heptamethylnonane Calibration Procedure*—The calibration reference material is tested to affirm that the combustion chamber wall temperature and the sample injection period settings produce ignition delay measurements for this material that are within specification limits.

11.3.1 To ensure homogeneity the calibration reference material CRM) must be above 20°C. Agitate the calibration reference material before use.

11.3.2 Remove the sample reservoir cap and wash the stem and threads and the sample reservoir with approximately 50 mL of the calibration reference material. Reinstall the sample reservoir cap.

11.3.3 Flush the entire aliquot of the calibration reference material through the fuel injection system by pressing the Flush button. Refer to the instruction manual of the manufacturer.

11.3.4 Charge the instrument with the calibration reference material (at least 160 mL) and wipe the stem and threads of the sample reservoir cap with a clean dry towel and secure the sample reservoir cap to the sample reservoir.

11.3.5 Perform the automatic calibration procedure.

11.3.5.1 If the average ID value or the average CD value is outside the acceptance limits, the combustion chamber inner surface temperature controller set-point is adjusted by the computer to cause a change in the combustion chamber wall temperature or the sample injection period is adjusted by the computer to inject the appropriate quantity of sample into the combustion chamber, or both. The automatic calibration procedure performed by the processor controlling the instrument is summarized in Annex A5.

NOTE 6—ID increases when the combustion chamber inner surface temperature decreases and vice versa. CD decreases when a larger sample volume is injected into the combustion chamber and vice versa.

11.3.5.2 If the temperature controller set-point adjustment from the previous setting exceeds ±4°C or the injection period adjustment from the previous setting exceeds ±100 µs, a system malfunction is suspected and diagnostic procedures to determine and remedy the problem are recommended. Refer to the instruction manual of the manufacturer.

11.3.6 The combustion analyzer calibration is complete when the calibration reference material average delays are within the specified acceptance limits of 2.96 ± 0.16 ms for ID and 4.90 ± 0.08 ms for CD.

11.3.7 Without flushing, refill the sample reservoir with the calibration reference material (CRM) and perform a single determination of the calibration reference material. The result must satisfy the acceptance limits of 2.96 ± 0.16 ms for ID and 4.90 ± 0.08 ms for CD. If the single determination exceeds the acceptance limits for either ID or CD, perform the calibration procedure again.

11.4 *Methylcyclohexane Calibration Procedure*—Perform two consecutive ignition delay and combustion delay measurements using methylcyclohexane. Perform the second determination by refilling the sample reservoir without flushing.

11.4.1 To pass the calibration test, each single result of the ID and CD measurements must be within 11.00 ± 1.30 ms and 17.00 ± 1.40 ms, respectively.

11.4.2 To pass the calibration test, the averaged result of the ID and CD measurements must be within 11.00 ± 1.10 ms and 17.00 ± 1.20 ms, respectively.

11.4.3 If any of the single results or the average results is outside the respective limits, system performance is unacceptable and it is recommended that diagnostic procedures be used to determine and remedy the problem before performing a new calibration. Refer to the instruction manual of the manufacturer.

11.4.4 The combustion analyzer calibration is complete when both the hexadecane/heptamethylnonane and methylcyclohexane datasets are acceptable.

11.5 *Quality Control (QC Testing)*—Conduct a regular statistical quality assurance (quality control) program in accordance with the techniques of Practice D6299 or equivalent.

11.5.1 This test method requires a quality control testing at the beginning of each operating period using a single determination for ID and CD for the check standard and the DCN for at least one QC sample.

11.5.2 The QC sample is a typical diesel fuel oil having an ignition delay that represents the primary range of use for the combustion analyzer.

11.5.2.1 If the combustion analyzer is used for testing fuel having a very wide range of ignition delays, it may be useful to have a second QC sample of a different DCN.

11.5.3 Conduct a QC test whenever there is a change from one charge air cylinder to another.

NOTE 7—The oxygen content of the new charge air cylinder may differ from that of the previous source and can have a significant effect on the delay measurements.

11.5.4 *Check Standard*—Perform a single measurement of the hexadecane/heptamethylnonane calibration reference material.

11.5.4.1 This determination is acceptable if it satisfies the limits protocol specified in Practice D6299 or equivalent.

11.5.4.2 Prior to having established ID and CD tolerances for the calibration reference material in accordance with Practice D6299 or equivalent, use the warning limits of ±0.13 ms and ±0.07 ms for ID and CD, respectively, and action limits of ±0.18 ms and ±0.10 ms for ID and CD, respectively, based on the single determination for the calibration reference material, as per 11.1.[10]

11.5.5 *QC Sample*—Perform a single measurement of the quality control sample.

11.5.5.1 This determination is acceptable if it satisfies the limits protocol specified in Practice D6299 or equivalent.

11.5.6 The combustion analyzer is deemed fit for use when both the check standard result and the quality control standard result are acceptable. If any of the measurement results are not acceptable, conduct a calibration before performing additional sample measurements.

12. Procedure

12.1 *Operating Procedure:*

12.1.1 With the combustion analyzer in shutdown mode, start a new operating period as follows:

12.1.1.1 Open the valve at the source of the charge air supply and adjust the pressure regulator as needed to provide the specification pressure. Open the valve at the source of the nitrogen supply and adjust the pressure regulator as needed to provide the specification pressure. Turn on the circulation coolant system.

12.1.1.2 Position the combustion analyzer power switch to ON and warm-up the combustion analyzer. After the chamber wall temperature has stabilized a chamber leakage test will be automatically performed by the instrument to determine the chamber leakage rate. If the leakage test fails, a warning is issued.

12.2 *Test Procedure:*

12.2.1 Remove the sample reservoir cap and wash the stem and threads and the sample reservoir with approximately 50 mL of the test specimen. Reinstall the sample reservoir cap.

12.2.2 Flush the entire test specimen through the fuel injection system by pressing the Flush button. Refer to the instruction manual of the manufacturer.

12.2.3 Fill the sample reservoir past the upper level sensor with the test specimen (at least 160 mL). Wipe the stem and threads of the reservoir cap with a clean, dry towel. Reinstall the sample reservoir cap.

12.2.4 Flush the entire test specimen through the fuel injection system by pressing the Flush button.

12.2.5 Remove the sample reservoir cap and refill the sample reservoir past the upper level sensor with the test specimen (at least 160 mL). Wipe the stem and threads of the reservoir cap with a clean, dry towel. Reinstall the sample reservoir cap.

12.2.6 Initiate an automatic ID and CD determination procedure using the appropriate computer commands. At the end of the test, a test output summary is automatically displayed on the computer screen. The user can optionally print the result with the printer, store the result in memory and export the result to an external memory device.

12.2.7 The delay results are obtained by averaging the ID and CD measurements of the last 15 cycles to get an average ID and an average CD. If either of the ID and CD pairs are identified as a statistical outlier according to Peirce's Criterion[7] that pair of ID and CD measurements are removed from the 15 measurements and are not included in calculating the average value. The outlying delays, if any, are noted in the result record. A maximum of three outlier pairs of ID and CD measurements for a specific injection are allowed.

12.2.8 Flush the remaining test specimen from the sample reservoir through the sample injection system by pressing the Flush button.

12.2.9 The fuel system is now prepared for the next specimen determination (see 12.2) or unit shut down (see 12.3).

12.3 *Unit Shutdown:*

12.3.1 Confirm that the entire specimen has been discharged from the fuel injection system and that the sample reservoir is empty.

12.3.2 Close the valve at the source of the charge air supply and nitrogen supply. Use the applicable computer command to shut down the combustion analyzer. Do not turn off the circulation coolant system until 1.5 h has elapsed or until prompted to do so by the appropriate message on the LCD.

NOTE 8—The shutdown procedure decompresses the combustion chamber and switches off the heating element to allow the combustion chamber to cool down. If the instrument shutdown procedure is not followed the circulation coolant system must continue to operate for at least 1.5 h after the main power to the instrument has been removed.

12.3.3 After 1.5 h or after the appearance of appropriate prompt on the LCD position the combustion analyzer power switch to OFF.

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[10] Supporting data (the results of the 2010 Intralaboratory Ruggedness Test Program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1704.

13. Calculation

13.1 The DCN result is obtained by converting the average ID and CD result from 12.2.7 to DCN using the multivariate equation:

$$DCN = 13.028 + (-5.3378/ID) + (300.18/CD) + (-1267.90/CD^2) + (3415.32/CD^3) \quad (1)$$

14. Report

14.1 Report the following information:

14.1.1 A reference to this standard,

14.1.2 The sample identification,

14.1.3 The date of the test,

14.1.4 The average ID result and the average CD result to the nearest hundredth (0.01 ms),

14.1.5 The DCN result to the nearest tenth (0.1),

14.1.6 The test's average chamber wall temperature to the nearest tenth °C,

14.1.7 The test's injection period, and

14.1.8 The number of outlier data pairs eliminated for the calculation of the average ID and the average CD.

14.1.9 If the calibration reference material was obtained pre-blended from an external source, report "external source;" if it was blended at the testing facility from reagents in 8.1.1 and 8.2.1, report "internal source."

15. Precision and Bias

15.1 *Precision*—The precision statements were derived from a 2013 interlaboratory cooperative test program using statistical analysis procedures described in Practice D6300. Participants analyzed 20 sample sets comprised of 13 distillate fuels, 2 blends of biodiesel in distillate fuel (B2-B7 and B20), 4 B-100 biodiesels (Soy, Canola, Tallow and a 30/70 blend of soy and rapeseed, respectively) and 1 aviation turbine fuel. The DCN range was 39 to 67. The blended calibration reference material (CRM) described in 8.1.1 was provided to the ILS participants performing D7668. Six unique blending sites were used to blend seven different batches of the CRM. Each blending site acquired their own hexadecane and 2,2,4,4,6,8,8-heptamethylnonane. Sixteen laboratories participated using the D7668 method and eleven laboratories participated using the D613 method. Information on the type of samples and their average cetane number are in the research report.[11]

NOTE 9—The precision of test results obtained using CRM blended by the test operator has not been determined.

15.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus, under constant operating conditions, on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 1 in only one case in twenty.

15.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in normal and correct operation of this test method, exceed the values in Table 1 only in one case in twenty.

15.1.3 Examples of precision are shown in Table 2 for information.

15.2 *Bias*—The ID and CD determined using this test method have no bias because ID and CD are defined only in terms of this test method.

15.3 *Relative Bias*—The degree of expected agreement between DCN results by this test method and CN results by Test Method D613 has been assessed in accordance with Practice D6708 using the interlaboratory study conducted between November 2012 and February 2013.

15.3.1 No bias-correction considered in Practice D6708 can further improve the agreement between results from Test Method D7668 and Test Method D613, for material types and property ranges studied. Sample-specific bias, as defined in Practice D6708, was observed for some samples.

TABLE 1 Repeatability (r) and Reproducibility (R) for Derived Cetane Number (DCN), Ignition Delay (ID), and Combustion Delay (CD)

	r	R	Applicable Range
DCN	0.0198 (DCN – 21)	0.0463 (DCN – 21)	39.4 – 66.8 DCN
ID	$0.003035\ ID^{2.5}$	$0.00986\ ID^{2.5}$	2.47 – 4.09 mS
CD	$0.00281\ CD^2$	$0.00644\ CD^2$	3.71 – 6.74 mS

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[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1771. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability and Reproducibility Values for Information

ID (ms)	Repeatability	Reproducibility
2.50	0.03	0.10
3.00	0.05	0.15
3.25	0.06	0.19
3.50	0.07	0.23
4.00	0.10	0.32
CD (ms)		
3.90	0.04	0.10
4.50	0.06	0.13
5.25	0.08	0.18
6.00	0.10	0.23
6.75	0.13	0.29
DCN		
40.0	0.38	0.88
45.0	0.48	1.11
50.0	0.57	1.34
55.0	0.67	1.57
60.0	0.77	1.81
65.0	0.87	2.04

15.3.2 Differences between results from Test Method D7668 and Test Method D613, for the sample types and property ranges studied, are expected to exceed the following Between Methods Reproducibility (R_{xy}), as defined in Practice D6708, about 5 % of the time.

$$\text{Between Methods Reproducibility}(R_{xy}) = (0.82 \quad R_x^2 + 0.82 \quad R_y^2)^{0.5} \tag{2}$$

where:

R_{D613} = the range 37.7 to 65.1 CN.
R_{D7668} = the range 39.4 to 66.8 DCN.

15.3.3 Values for R_{xy} are presented in Table 3.

NOTE 10—As a consequence of sample-specific biases, R_{xy} may exceed the reproducibility for Test Method D7668 (R_x), or the reproducibility for Test Method D613 (R_y), or both. Users intending to use Test Method D7668 as a predictor of Test Method D613, or vice versa, are advised to assess the required degree of prediction agreement relative to the estimated R_{xy} to determine the fitness-for-use of the prediction.

16. Keywords

16.1 cetane number; derived cetane number; diesel performance; ignition characteristic; ignition delay

TABLE 3 Between Method Reproducibility (R_{xy})

(DCN +CN_{D613})/2	R_{xy}
40	2.66
45	3.26
50	3.86
55	4.47
60	5.07
65	5.67

ANNEXES

(Mandatory Information)

A1. HAZARDS INFORMATION

INTRODUCTION

In the performance of the standard test method there are hazards to personnel. These are indicated in the text. For more detailed information regarding the hazards, refer to the appropriate Material Safety Data Sheet (MSDS) for each of the applicable substances to establish risks, proper handling, and safety precautions.

A1.1 **Warning—**Combustible. Vapor Harmful.

A1.1.1 *Applicable Substances:*

A1.1.1.1 Diesel fuel oil.

A1.1.1.2 Quality control sample.

A1.2 **Warning—**Flammable.

A1.2.1 *Applicable Substances:*

A1.2.1.1 Hexadecane.

A1.2.1.2 2,2,4,4,6,8,8-Heptamethylnonane.

A1.2.1.3 Methylcyclohexane.

A1.2.1.4 *n*-Heptane.

A1.3 **Warning—**Poison. Maybe Harmful or Fatal if Inhaled or Swallowed.

A1.3.1 *Applicable Substance:*

A1.3.1.1 Ethylene glycol antifreeze.

A1.4 **Warning—**Compressed gas under high pressure that supports combustion.

A1.4.1 *Applicable Substance:*

A1.4.1.1 Compressed synthetic air.

A1.5 **Warning—**Asphyxiant. Compressed gas under high pressure.

A1.5.1 *Applicable Substance:*

A1.5.1.1 Compressed nitrogen.

A1.6 **Warning—**Hot surfaces. Vapors May Cause Flash Fire.

A1.6.1 *Applicable Substances:*

A1.6.1.1 Protective cage enclosing the combustion chamber,

A1.6.1.2 Exposed areas of the combustion chamber around the injector and dynamic pressure sensor, A1.6.1.3 Exposed areas of the combustion chamber,

A1.6.1.4 Near the combustion chamber, and

A1.6.1.5 Inside the combustion chamber protective cage.

A2. PRECALIBRATION SAMPLE SYSTEM CLEANING PROCEDURE

A2.1 Clean the sample reservoir, the sample reservoir cap, and the sample system.

A2.1.1 Wash the sample reservoir cap stem and threads, sample reservoir funnel, the inside walls of the sample reservoir and the protruding level sensor housings with approximately 50 mL of anhydrous *n*-heptane (purity > 99.5%) and flush the solvent from the sample reservoir.

A2.1.2 Replace the sample reservoir cap and flush the solvent completely from the sample reservoir allowing the flush cycle to run its full course.

A2.1.3 Remove the sample reservoir cap and wipe the stem and threads of the sample reservoir cap with a clean dry towel. Repeat steps A2.1.1 and A2.1.3.

A2.1.4 Leave off the sample reservoir cap and allow the solvent to evaporate. Using dry, oil-free compressed air to assist with evaporation of the solvent is permissible.

A3. CALCULATION OF ID AND CD

A3.1 Figure A3.1 demonstrates the process for calculating the ID and the CD used by this method to calculate the DCN result.

A3.1.1 The timing of the ignition delay starts with the leading edge of the electronic pulse sent to the solenoid of the common rail injector.

A3.1.2 ID is defined as the elapsed time, in milliseconds, between the leading edge of the electronic pulse sent to the solenoid of the common rail injector and the time at which a pressure of 0.02 MPa above the static chamber pressure is determined from the recorded combustion pressure curve.

A3.1.3 CD is defined as the elapsed time, in milliseconds, between the leading edge of the electronic pulse sent to the solenoid of the common rail injector and the time at which a pressure that represents the midpoint of the net pressure increase of combustion pressure curve.

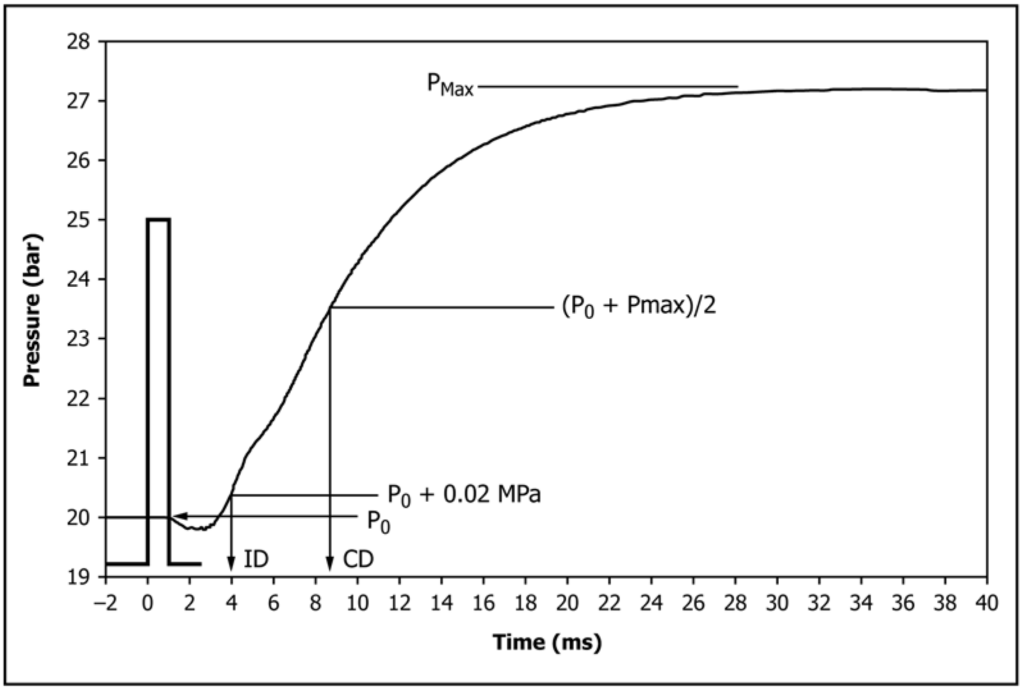


FIG. A3.1 Electronic Signal That Activates the Common Rail Injector Solenoid and the Electronic Signal Produced by the Dynamic Pressure Sensor During a Combustion Cycle

A4. INSTRUMENT SCHEMATIC

A4.1 Figure A4.1 is a schematic of the instrument used in this method.

A4.2 *Combustion Chamber*—A stainless steel vessel manufactured from three pieces. The top piece accepts the common rail injector (N1) and provides for a coolant passage to cool the common rail injector. A type K thermocouple (T1) is used to monitor cooling fluid temperature and used to set the bath temperature for the closed loop circulating coolant system. Fitted to the bottom of the combustion chamber is the dynamic pressure sensor (P2) used to record the combustion pressure curve. The dynamic pressure sensor is also cooled using the circulated cooling fluid. The combustion chamber wall is heated using a clamp shell heater (H1). The wall temperature of the combustion chamber is measured using a type K thermocouple (T2). A thermal fuse is fitted to the back of the clamp shell heater to prevent overheating of the combustion chamber.

A4.3 *Fuel Injection System*:

A4.3.1 The sample vessel is the fuel sample reservoir and is fitted with two level sensors (L1, L2). The upper level sensor (L1) warns the user when the sample vessel is getting full. When triggered, the lower level sensor (L2) stops the analysis process preventing air from being introduced into the high pressure sample loop. A removable PTFE (polytetrafluoroethlyene) filter with a 5 µm pore size is placed down stream from the sample vessel to filter particulate matter from the sample. The fuel sample is forced through the sample fuel injection system using low pressure nitrogen gas above the sample in the sample reservoir.

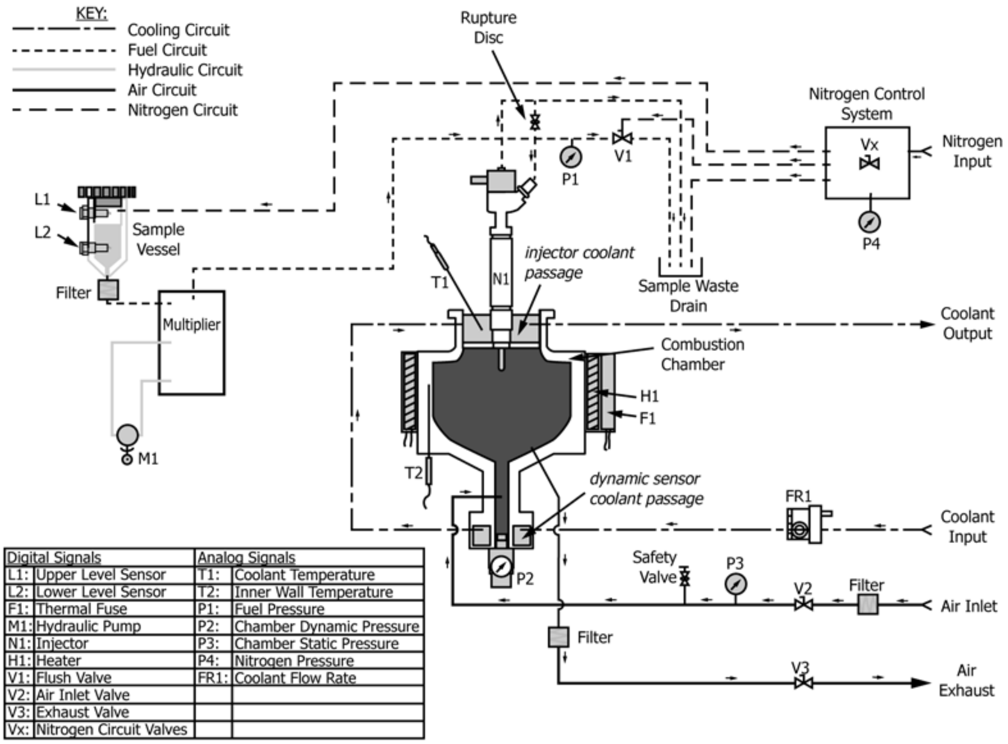
A4.3.2 The sample is pushed into the high pressure multiplier (Multiplier) through a one-way valve by the head pressure of nitrogen in the sealed sample vessel. The pressure multiplier is controlled by the hydraulic pump and the pressure control circuit (M1). The pressure multiplier produces a sample pressure that is 10× the pressure generated by the hydraulic pump.

A4.3.3 The high pressure fuel sample generated by the Multiplier enters the high pressure sample manifold. Attached to the high pressure manifold is the common rail fuel injector (N1), the sample pressure sensor (P1) and the air operated high pressure flush valve (V1), and the high pressure safety burst disk (Rupture Disk). The sample pressure sensor measures the pressure of the sample before the sample is injected into the combustion chamber. If the measured sample pressure is not within the tolerance limits, the solenoid on the common rail injector will not be energized and the sample will not be injected into the combustion chamber. If the sample fuel pressure exceeds the safety margin of the high pressure system, the rupture disk will break and the sample pressure will be relieved into the waste bottle. Opening the flush valve (V1) allows the sample to be flushed from the sample vessel and the sample lines to the sample waste bottle.

A4.4 The nitrogen Control System is a series of solenoid valves that are used to pressurize and vent the nitrogen to the sample vessel and the air operated flush valve (V1).

A4.5 *Coolant System*—A closed loop circulating coolant system filled with a 50:50 volume percent mixture of glycol-based antifreeze and water. The temperature output from the thermocouple T1 is used to adjust the bath temperature of the chiller such that T1 reports a temperate of 50 ± 2°C. The flow sensor (FR1) is a safety device to ensure that coolant is flowing through the cooling spaces in the combustion chamber. The combustion chamber clamp shell heater is de-energized if the flow sensor does not detect flow.

A4.6 *Charge Air Circuit*—The synthetic air used to charge the combustion chamber is first filtered to protect the air inlet solenoid valve (V2). The combustion chamber static pressure sensor (P3) is used to correct for the temperature offset of the dynamic pressure sensor (P2). The Safety Valve ensures the pressure inside the combustion chamber does not exceed 5 MPa. The filter placed in front of the exhaust solenoid valve (V3) prevents particulate matter generated during the combustion from fouling exhaust valve.



Digital Signals		Analog Signals	
L1:	Upper Level Sensor	T1:	Coolant Temperature
L2:	Lower Level Sensor	T2:	Inner Wall Temperature
F1:	Thermal Fuse	P1:	Fuel Pressure
M1:	Hydraulic Pump	P2:	Chamber Dynamic Pressure
N1:	Injector	P3:	Chamber Static Pressure
H1:	Heater	P4:	Nitrogen Pressure
V1:	Flush Valve	FR1:	Coolant Flow Rate
V2:	Air Inlet Valve		
V3:	Exhaust Valve		
Vx:	Nitrogen Circuit Valves		

FIG. A4.1 Instrument Schematic

A5. AUTOMATIC CALIBRATION PROCEDURE

INTRODUCTION

This annex summarized the adjustments to the combustion chamber wall temperature setpoint and the injection period made by the processor controlling the instrument during the calibration procedure.

A5.1 After cleaning and filling the sample vessel with the hexadecane/heptamethylnonane calibration reference material, the calibration procedure is initiated by pressing the appropriate softkey.

A5.2 The sample is loaded into the high pressure sample loop and injections of the sample into the combustion chamber begin.

A5.3 Using a moving average, ID and CD are tested for stability.

A5.4 Once ID and CD are determined to be stable the ID's and CD's from the last 15 injections are averaged to calculate an average ID and an average CD using Pierce's Criterion to identify outlying ID and CD pairs.

A5.5 The average ID is compared to the target ID value of 2.96 ± 0.16 ms and the average CD is compared to the target CD value of 4.90 ± 0.08 ms. If the ID and CD meet their respective target values within the acceptance tolerance intervals, the calibration procedure is terminated.

A5.6 If ID or CD, or both, exceed their respective tolerance interval, the magnitude and sign of the difference between the average value and the target value causes the combustion wall temperature setpoint or the injection period, or both, respectively, to be adjusted on a sliding scale and in a particular direction.

A5.7 If an adjustment is made, the chamber wall temperature is allowed to stabilized, and an additional 15 sample injections are acquired to calculate average ID and average CD values.

A5.8 If the ID and CD meet their respective target value within the acceptance tolerance interval the calibration procedure is terminated. See A5.5.

A5.9 If the average ID is outside the tolerance limit, the magnitude and sign of the difference between the average value for ID and the ID target value causes the combustion wall temperature setpoint to be adjusted on a sliding scale and in a particular direction, respectively.

A5.10 After the chamber wall temperature has stabilized, an additional 15 sample injections are made to calculate average ID and CD values.

A5.11 Steps A5.9 and A5.10 are repeated until the average value for ID falls within the tolerance limit for the ID target value.

A5.12 If the average CD value is outside the tolerance limit, but the average ID is within the tolerance limit, the magnitude and sign of the difference between the average value for CD and the CD target value causes the injection period to be adjusted on a sliding scale and in a particular direction, respectively. See A5.5.

A5.13 After the chamber wall temperature has stabilized, an additional 15 sample injections are acquired and the average ID and CD are calculated.

A5.14 Steps A5.12 and A5.13 are repeated until the average value for CD falls within the tolerance limit for the CD target value. See A5.5.

A5.15 The iterative calibration procedure continues until the average ID and average CD value are within their respective target value acceptance interval for a set of 15 injections.

A6. COMMON RAIL INJECTOR CHARACTERIZATION

A6.1 The common rail injector is manufactured by Bosch and has the part number 0445110181.

A6.2 The total number of jets is six.

A6.3 Jet orifice diameter: 0.17 mm.

A6.4 The flow volumes are measured using hexadecane. The values are the average volume per injection from four injectors.

TABLE A6.1 Injection Volume

Injection Pulse Width (µs)	Injection Volume (µL)
2000	101
2250	113
2500	125
2750	138

SUMMARY OF CHANGES

Subcommittee D02.01.0C has identified the location of selected changes to this standard since the last issue (D7668 – 14) that may impact the use of this standard. (Approved May 1, 2014.)

(1) Added new subsection 14.1.9.

Committee D02 has identified the location of selected changes to this standard since the last issue (D7668 – 12a) that may impact the use of this standard. (February 1, 2014)

(1) Updated Precision and Bias (Section 15).
(2) Revised 1.1, 1.3, 8.1.1, 8.1.1.3, 8.1.2, 8.2.1, 10.3.2, 10.3.5, 11.3.6, 11.3.7, 11.4, 11.4.1, 11.4.2, 11.5.4.1, 13.1, A5.5, Table A6.1.

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