



Designation: D7171 – 20

Standard Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy¹

This standard is issued under the fixed designation D7171; 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 covers the determination of the hydrogen content of middle distillate petroleum products using a low-resolution pulsed nuclear magnetic resonance (NMR) spectrometer. The boiling range of distillates covered by the test method is 150 °C to 390 °C. While this test method may be applicable to middle distillates outside this boiling range, in such cases the precision statements may not apply. The test method is generally based on Test Methods D3701 and D4808, with a major difference being the use of a pulsed NMR spectrometer instead of a continuous wave NMR spectrometer.

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

1.2.1 The preferred units are mass %.

1.3 *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.*

1.4 *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

D3701 Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic

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 D02.03 on Elemental Analysis.

Current edition approved May 1, 2020. Published June 2020. Originally approved in 2005. Last previous edition approved in 2016 as D7171 – 16. DOI: 10.1520/D7171-20.

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.

Resonance Spectrometry

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4808 Test Methods for Hydrogen Content of Light Distillates, Middle Distillates, Gas Oils, and Residua by Low-Resolution Nuclear Magnetic Resonance Spectroscopy

D5291 Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

2.2 *Other Documents:*

MIL-DTL-5624 Turbine Fuel, Aviation, Grades JP-4 and JP-5³

MIL-DTL-83133 Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37)

MIL-DTL-16884 Fuel, Naval Distillate

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration, n*—the determination of the values of the significant parameters by comparison with values indicated by a set of calibration standards.

3.1.2 *calibration curve (or calibration line), n*—the graphical or mathematical representation of a relationship between the assigned (known) values of calibration standards and the measured responses from the measurement system.

3.1.3 *calibration standard, n*—a standard having an assigned (known) value (reference value) for use in calibrating a measurement instrument or system. This standard is not used to determine the accuracy of the measurement instrument or system (see *check standard*).

³ Available online at the ASSIST Quick Search website <http://quicksearch.dla.mil>.

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

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

3.1.4.1 *Discussion*—This standard is not used to calibrate the measurement instrument or system (see *calibration standard*).

3.1.5 *low resolution nuclear magnetic resonance (NMR) spectroscopy, n*—a form of NMR spectroscopy using a simple NMR analyzer that employs a low magnetic field and consequently low NMR frequency. An example is proton NMR below 60 MHz. Resolution is expressed as time at half height of signal and is typically 1 millisecond (ms) or less.

3.1.6 *nuclear magnetic resonance (NMR) spectroscopy, n*—that form of spectroscopy concerned with radio-frequency-induced transitions between magnetic energy levels of atomic nuclei.

3.1.7 *radio frequency, n*—the range of frequencies of electromagnetic radiation between 3 kHz and 300 GHz.

3.1.8 *recycle delay, n*—NMR spectrometer parameter setting for the time delay that allows magnetization recovery.

3.1.9 *relaxation time constant (T_1), n*—a numerical value which is a measure of magnetization relaxation time following an excitation pulse of an NMR spectrometer.

4. Summary of Test Method

4.1 A test specimen is analyzed in a pulsed NMR spectrometer calibrated with reference standard materials. The analyzer records in a nondestructive fashion the total NMR signal, which arises from the absolute amount of hydrogen atoms in the reference standards and test sample. The absolute hydrogen signal intensity reported by the pulsed NMR instrument for the standard and test specimens is normalized by the corresponding sample mass. The resulting signal-per-gram ratios are used as a means of comparing theoretical hydrogen contents of the standards with that of the sample. The result is expressed as the hydrogen content (on a mass % basis) of the sample.

4.2 To ensure an accurate measure of the absolute hydrogen content of the reference standards and sample, it is necessary to ensure that the measured hydrogen signal intensity is always directly proportional to the absolute hydrogen content of the standards and sample.

4.3 Undercounting of the reference standard with respect to the sample is avoided by a number of strategies, including accurate filling into the linear response region of the sample compartment so that the mass recorded for the sample represents the true amount measured by NMR, and use of a recycle delay considerably greater than the longest relaxation time constant (T_1) for the sample.

5. Significance and Use

5.1 Hydrogen content represents a fundamental quality of a petroleum distillate that has been correlated with many of the performance characteristics of that product. Combustion properties of gas turbine fuels are related primarily to hydrogen content. As hydrogen content of these fuels decreases, soot deposits, exhaust smoke, and thermal radiation increase. Soot deposits and thermal radiation can increase to the point that

combustor liner burnout will occur. Hydrogen content is a procurement requirement of the following military fuels: JP-5 specified in MIL-DTL-5624, JP-8 specified in MIL-DTL-83133, and Naval Distillate Fuel specified in MIL-DTL-16884.

5.2 This test method provides a simple and precise alternative to existing test methods (D3701, D4808, and D5291) for determining the hydrogen content of petroleum distillate products.

6. Apparatus

6.1 Nuclear Magnetic Resonance Spectrometer:

6.1.1 This test method requires a low-resolution pulsed instrument capable of measuring a nuclear magnetic resonance signal due to hydrogen atoms in the sample in a linear fashion over the filling volume of interest. The instrument includes the following:

6.1.1.1 Permanent magnet to provide the necessary static magnetic field for the NMR test,

6.1.1.2 Sample compartment containing a radio frequency (RF) coil for excitation and detection, and

6.1.1.3 Electronic unit to control and monitor the resonance condition involving magnet temperature control and field offset coils.

6.1.2 The test method also requires that the instrument have the ability to equilibrate samples within the probe at a constant temperature (that is, 35 °C or 40 °C).

6.2 *Conditioning Block*—Block of aluminum alloy drilled with holes of sufficient size to accommodate the nominal 18 mm diameter test cells to a depth of at least 42 mm and with a centrally positioned well to house a temperature-sensing device, such as a thermometer or thermocouple.

6.3 *Conditioning Apparatus*—Bath or other temperature control device (into which the conditioning block is inserted) for controlling block temperature to 35 °C ± 0.2 °C or 40 °C ± 0.2 °C.

6.4 *Test Cell*—Glass tube (with a flat or round bottom) with an outside diameter of 17.6 mm to 18.1 mm and an inside diameter of 15.2 mm to 16.4 mm. Any tube length that permits easy insertion into and removal from the NMR sample chamber may be used.

6.5 *Polytetrafluorethylene (PTFE) Plug*—Device made of PTFE used to tightly fit and close the test cells. An example of one type of PTFE plug design is shown in Fig. 1.

6.6 *Insertion Rod*—Straight, rigid rod with a threaded end (to screw into the PTFE plug) for inserting and removing the PTFE plugs from the test cells. Any diameter and length rod that facilitates easy plug insertion and removal may be used.

6.7 *Analytical Balance*—Top loading pan-type balance, capable of weighing the test cells in an upright position to an accuracy of 0.001 g or better.

6.8 *Volume Transferring Device*—Capable of accurately and repeatedly delivering a fixed volume of material within ±1 % or better, for use in preparing test specimens and standards for analysis. A 10 mL capacity serological pipet with 0.1 mL marked subdivisions has been found suitable to use.

TABLE 1 Hydrogen Content of Reference Standards

Compound	Mass % Hydrogen
dodecane	15.386
pentadecane	15.185
2-nonanone	12.756
ethyl caprate	12.077
octyl acetate	11.703
ethyl heptanoate	11.466
3-cyclohexanepropionic acid	10.324
cyclohexyl acetate	9.924
diethyl malonate	7.552
2-phenylethyl acetate	7.367

7.3 *Quality Control (QC) Samples*, preferably are portions of one or more petroleum distillate materials that are stable and representative of the samples of interest. These QC samples can be used to monitor the precision and stability of the testing process as described in Section 15.

8. Hazards

8.1 Wear appropriate personal protective equipment when working with the materials in Section 7. Transfer all reagents in a fume hood and immediately seal containers tightly. Avoid prolonged or repeated exposure to materials.

9. Sampling

9.1 Take a homogeneous sample in accordance with Practice D4057. Mix the sample prior to taking a representative aliquot as the test specimen.

10. Preparation of Test Specimens and Standards

10.1 Fig. 1 is an example of a PTFE plug. Dimensions may be varied to best seal the chosen test cell. Drill and thread the plug hole to mate the insertion rod thread. All test cells and PTFE plugs used shall be well cleaned and dry. Weigh a clean empty test cell and PTFE plug (W_1) on an analytical balance to the nearest 0.001 g. Use of a jig for supporting the test cell on the balance pan is recommended for flat bottom test cells and required for round bottom test cells. For round bottom test cells, a paper clip dispenser (with hole in top) works well for this function. Transfer a fixed volume (in accordance with the tolerances specified in 6.8) of a reference standard or test specimen into the test cell to a fill height of nominally 32 mm (representing a nominal 6 mL volume). The choice of fill height is not critical, but fill height shall be the same for all standards and samples to ensure good results. Use the same test cell source (that is, manufacturer and part number) for all standards and test specimens. This will ensure uniformity of fluid height in the NMR sample compartment, an important parameter in the test method. Take care to not introduce the fluid down the side of the test cell. Seal the reference standard container immediately after the material transfer to minimize moisture pickup. Using the insertion rod with a PTFE plug attached, push the PTFE plug into the test cell until it is just above the liquid surface (that is, nominal 1 cm), keeping the tube upright. Gently twisting the plug as it is inserted will aid the escape of air from the test cell and normally ensure that the lip of the plug is turned up around the entire circumference. Unscrew the insertion rod carefully without disturbing the plug. Weigh the filled, sealed test cell (W_2) on the analytical

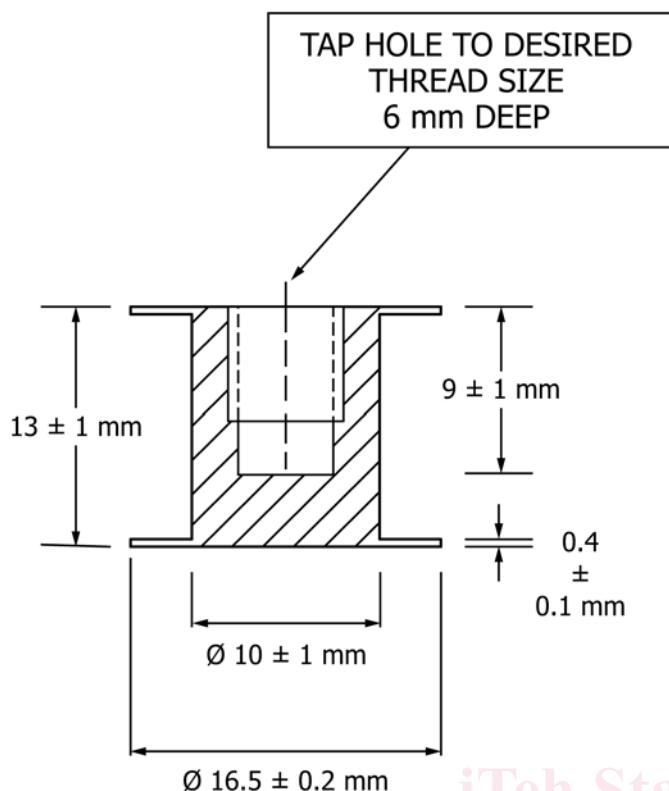


FIG. 1 Example of a PTFE Plug (not to scale)

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *List of Available Calibration, Reference, or Check Standards* (see Table 1). (**Warning**—Irritant. Combustible. Avoid breathing vapor. Avoid contact with eyes, skin, and clothing.) applies to all of the following:

- 7.2.1 3-cyclohexanepropionic acid, 99 % minimum purity.
- 7.2.2 cyclohexyl acetate, 99 % minimum purity.
- 7.2.3 diethyl malonate, 99 % minimum purity.
- 7.2.4 dodecane, 99 % minimum purity.
- 7.2.5 ethyl caprate, 99 % minimum purity.
- 7.2.6 ethyl heptanoate, 99 % minimum purity.
- 7.2.7 2-nonanone, 99 % minimum purity.
- 7.2.8 octyl acetate, 99 % minimum purity.
- 7.2.9 pentadecane, 99 % minimum purity.
- 7.2.10 2-phenylethyl acetate, 99 % minimum purity.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

balance to the nearest 0.001 g. Determine the sample mass from the difference ($W_2 - W_1$) of the two weighings.

10.2 Repeat 10.1 for all standards and test specimens.

11. Preparation of Apparatus

11.1 Place the conditioning block in the conditioning apparatus. Select a testing temperature of 35 °C or 40 °C based on the NMR instrument manufacturer's recommendation for the sample type to be tested. Adjust the conditioning apparatus setting to the selected 35 °C ± 0.2 °C or 40 °C ± 0.2 °C reading on a calibrated thermocouple or thermometer placed in a test cell filled with a test fluid and placed in the conditioning block/apparatus. Allow at least 30 min for temperature equilibrium after a setting adjustment. After adjustment, measure the aluminum block temperature at the thermometer/thermocouple well in the block, and control the conditioning apparatus at this block temperature.

11.2 Set the NMR instrument recycle delay to 20 s. Set the test specimen chamber temperature to 35 °C ± 0.1 °C or 40 °C ± 0.1 °C (consistent with selected conditioning temperature). Set all other NMR instrument parameters in accordance with the manufacturer's instructions. Ensure that the NMR spectrometer has been on for the minimum warm-up time recommended by the manufacturer and that the sample chamber temperature has equilibrated to 35 °C ± 0.1 °C or 40 °C ± 0.1 °C. Keep the room temperature below 28 °C to permit good thermal equilibrium of equipment.

11.3 The magnetic environment around the NMR spectrometer shall be kept constant during the calibration and testing. The position of substantial ferromagnetic metal objects, such as gas cylinders or metal chairs, cabinets, and doors, within 1 m of the spectrometer shall not be changed. Metal cabinet doors and drawers near (under) the spectrometer shall not be opened or closed during the analysis.

12. Procedure

12.1 Place the filled, weighed test cells in the conditioning block/apparatus. The test cells shall remain in the conditioning block/apparatus for a minimum of 20 min to reach thermal equilibrium.

12.2 Reference standards which may be used for this test method and their theoretical % hydrogen concentrations are shown in Table 1. These reference standards may be used as either calibration standards or check standards. Select calibration standards from Table 1 consistent with the instrument manufacturer's instructions for the calibration line. Use at least two pure compounds (99 % purity or better) bracketing the region of interest for establishing the calibration line. If more than two reference standards are used for calibration, the regression coefficient shall be ≥ 0.98 .

12.3 Select a conditioned test cell containing a reference standard. Quickly wipe its exterior surfaces with a lint-free cloth and carefully insert it into the NMR instrument sample chamber. The test cell should be positioned so that the material to be analyzed is in the optimum measurement region of the NMR sample chamber. Allow at least 10 s for the test cell assembly to reach thermal equilibrium in the instrument.

Follow the instrument manufacturer's instructions for establishing the calibration line. Remove the test cell from the instrument. Similarly, run the other calibration standards to complete the calibration.

12.4 Insert a conditioned test cell (in the same manner described in 12.3) containing a check standard into the sample chamber. The check standard is a material of known % hydrogen, but not one of the materials used as a calibration standard. In Table 1, 2-nonanone is a good check standard since its hydrogen content is the closest in Table 1 to that of a number of middle distillate products. Allow at least 10 s for thermal equilibrium, and run the check standard in accordance with the instrument manufacturer's instructions for analyzing test specimens. The % hydrogen value determined shall agree within 1.5 % relative of the known value before proceeding with testing of petroleum distillate samples. If the check standard is not within 1.5 % relative of the known value, recalibration of the NMR instrument is required. The check standard shall be run prior to each new batch of distillate test specimens and at least once on each day of analysis.

12.5 Insert a conditioned test cell (as described in 12.3) containing a middle distillate test specimen into the sample chamber. Allow at least 10 s for the middle distillate test cell to reach thermal equilibrium. Follow the instrument manufacturer's instructions for analyzing the test specimen. Similarly, run other test specimens. Similarly, analyze the check standard after completing the batch of middle distillate test specimens. If the result is not within 1.5 % relative of the known concentration, recalibrate the instrument and reanalyze all test specimens run since the last acceptable check standard analysis.

13. Calculation

13.1 Pulsed NMR instruments have software routines that calculate the % hydrogen based on the calibration entries, the instrument response, and the sample mass entries as appropriate for the instrument manufacturer's programs.

14. Report

14.1 Report the mass % hydrogen content of the middle distillate test specimen to the nearest 0.01 mass % hydrogen.

15. Quality Control (QC)

15.1 As per the frequency indicated in 12.4, confirm the accuracy of the instrument by analyzing a check standard (see 3.1.4).

15.1.1 Determined values for the check standards shall be within 1.5 % relative of the known values before proceeding with sample analyses. Investigate and take appropriate corrective actions when results determined for the check standard fall outside the allowed range (see 12.5).

15.2 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 7.3).

15.2.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.