



Designation: D8383 – 21

Standard Test Method for Methyl Hydrogen Content of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy¹

This standard is issued under the fixed designation D8383; 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 total methyl hydrogen content of unadditized base stock (lubricating oils) hydrocarbon oils that are completely soluble in chloroform at ambient temperature using high-resolution nuclear magnetic resonance (NMR) spectrometers.

1.2 The reported units are mol percent methyl hydrogen atoms. For pulse Fourier transform (FT) spectrometers, the detection limit is typically 0.1 % mol hydrogen atoms. The interim precision is applicable in the range 20.5 % to 38.7 % mol methyl hydrogen.

1.3 This method is applicable to samples containing <0.1 % mol olefinic hydrogens.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 7.2 and 7.3.

1.6 *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

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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 D02.04.0F on Absorption Spectroscopic Methods.

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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.

D5292 Test Method for Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy (Withdrawn 2018)³

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, Liquid Fuels, and Lubricants

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy (Withdrawn 2015)³

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *methyl hydrogen, n*—H-NMR signal in the spectral region of 0.1 ppm to the valley at approximately 1 ppm as a percentage of total hydrogens.

3.1.1.1 *Discussion*—NMR spectrometers meeting vendor specifications for signal to noise ratio and resolution are acceptable as defined in 6.1.

3.2 Definitions of chemical shift (reported in parts per million (ppm)), internal reference, spectral width, and other NMR terminology used in this test method can be found in Practice E386 or any suitable vendor recommended method to convert to ppm.

3.3 Chloroform-d refers to chloroform solvent in which hydrogen is replaced by deuterium, the heavier isotope of hydrogen. Chloroform-d is available from a variety of chemical and isotope suppliers (Test Method D5292).

4. Summary of Test Method

4.1 Hydrogen (¹H) nuclear magnetic resonance (NMR) spectra are obtained on solutions of the sample in chloroform-d, using a pulse FT high-resolution NMR spectrometer. Tetramethylsilane is preferred as an internal reference in these solvents for assigning the 0.0 parts per million (ppm) chemical shift position in the ¹H spectra.

³ The last approved version of this historical standard is referenced on www.astm.org.

4.2 The methyl hydrogen content of the sample is measured by comparing the total integral for the ¹H NMR spectrum of the 0.1 ppm to about 1 ppm chemical shift region with the integral from 0.1 ppm to about 8 ppm. Integration is for all the signal peaks greater than 0.1 %, excluding the solvent peaks.

4.3 The integral of the hydrogen content must be corrected for the NMR absorption line due to residual chloroform (7.25 ppm chemical shift) in the predominantly chloroform-d solvent.

5. Significance and Use

5.1 Methyl hydrogen content is a key characteristic of hydrocarbon lubricating oils and can affect a variety of properties of the oil including its boiling range, viscosity, low temperature flow, and oxidation stability.

5.2 The NMR procedure does not require calibration standards of known methyl hydrogen content and is applicable to a wide range of hydrocarbon lubricating oils that are completely soluble in chloroform at ambient temperature.

6. Apparatus

6.1 *High-Resolution Nuclear Magnetic Resonance Spectrometer*—A high-resolution pulse Fourier transform (FT) NMR spectrometer capable of being operated according to the conditions in Table 1 and of producing peaks having widths less than the frequency ranges of the majority of chemical shifts and coupling constants for the measured nucleus and yielding the required values on the specified quality control standard may be used. Precision was developed using 400 MHz and 500 MHz spectrometers.

6.2 *NMR Tubes*—Usually a 5 mm outside diameter tube compatible with the configuration pulse FT spectrometer.

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 shall 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

⁴ACS 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.

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use.

7.2 *Chloroform-d*—For ¹H NMR, chloroform-d must contain less than 0.2 % by volume residual chloroform. Care must be taken not to contaminate the solvent with water and other extraneous materials. (**Warning**—Health hazard. Highly toxic. Cancer suspect agent. Can be fatal when swallowed and harmful when inhaled. Can produce toxic vapors when burned.)

7.3 *Tetramethylsilane*, American Chemical Society (ACS) reagent internal chemical shift reference for ¹H and ¹³C NMR spectra. (**Warning**—Flammable liquid.)

7.4 *Pristane 2,6,10,14-Tetramethylpentadecane*, ≥98 % mass purity. (**Warning**—Flammable liquid.)

8. Sampling

8.1 It is assumed that a representative sample acquired by a procedure of Practice D4057 or equivalent has been received in the laboratory. If the test is not to be conducted immediately upon receipt of the sample, store in a cool place until needed.

8.2 A minimum of approximately 10 mL of sample is required for this test method. This should allow duplicate determinations, if desired.

8.3 All samples must be homogeneous prior to subsampling. If any suspended particles present are attributable to foreign matter such as rust, filter a portion of the sample to be tested through a small plug of glass wool, contained in a clean small funnel, into a clean and dry vial, or NMR sample tube containing chloroform-d.

8.4 If the sample contains waxy materials, heat the sample in the container to approximately 60 °C and mix with a high-shear mixer prior to sampling. It may be necessary to transfer a portion of the sample to an NMR tube containing chloroform-d by means of a pipet which has been heated to approximately 60 °C to maintain the homogeneity of the sample.

8.5 For a valid test result, samples must be completely soluble in chloroform-d. Check to ensure that the final solution is homogeneous and free of undissolved particles.

9. Procedure

9.1 The procedure is described in this section for determining the hydrogen methyl content of lubricating hydrocarbons.

TABLE 1 Typical Sample and Instrument Conditions for Pulse Fourier Transform Measurements of ¹H NMR Spectra Used to Obtain Precision

Solvent	Chloroform-d
Sample concentration	Must be optimized for the instrument in use but may be as high as 5 % v/v
Sample temperature	Instrument ambient
Internal lock	Deuterium (when chloroform-d is used for ¹ H NMR)
Sample spinning rate	As recommended by manufacturer, typically 10 Hz to 20 Hz
Pulse flip angle	Approximately 45°
Sequence delay time	¹ H NMR 15 s
Memory size for acquisition	Choose to give a minimum digitizing rate of 0.5 Hz/point for ¹ H. Use a minimum acquisition time of 3 s to 4 s.
Spectral width	At least 15 ppm in frequency and centered, as close as possible, to the 5 ppm chemical shift value
Signal to noise levels	A minimum of 20:1 for the maximum height of the smaller integrated band
Chemical shift reference:	Preferably tetramethylsilane (0.0 ppm) at no greater than 1 % volume concentration

9.2 The procedure selected by the analyst will depend on the available NMR instrumentation.

9.3 **Appendix X1** and **Practice E386** should be used in conjunction with the NMR spectrometer manufacturer's instructions in order to ensure optimum performance of the NMR instrument in the application of these procedures.

9.4 If tetramethylsilane is used as an internal chemical shift standard, prepare a 1 % v/v TMS in solvent solution by adding tetramethylsilane to chloroform-d solvent.

9.5 If it is inconvenient to prepare the test solution directly in the NMR sample tube as suggested in the following procedures, the test solution can be prepared in a small vial and transferred into the NMR sample tube after solvent addition and sample dissolution. Care should be exercised to ensure that the final solution concentrations are not different from those indicated in the procedures and that no contamination occurs during the transfer process.

9.6 *Procedure—¹H NMR Measurements using a Pulse Fourier Transform (FT) NMR Spectrometer:*

9.6.1 Pipette a homogeneous sample of the hydrocarbon oil into an NMR sample tube compatible with the configuration of the pulse FT spectrometer, usually a 5 mm outside diameter capped NMR tube.

9.6.2 Add chloroform-d to the NMR sample tube to generate a final solution consisting of up to 5 % v/v hydrocarbon oil

in solvent. The concentration of hydrocarbon oil in solvent should be optimized for the spectrometer in use but can be as high as the indicated 5 % v/v value. Check to ensure that the final solution is homogeneous and free of undissolved particles.

9.6.3 Using the instrumental conditions indicated in **Table 1**, acquire and plot the pulse FT ¹H NMR spectrum. Assign to the internal standard tetramethylsilane absorption a chemical shift value of 0.0 ppm.

9.6.4 **Fig. 1** shows an acceptable pulse FT ¹H NMR spectrum and integration of a lubricating oil sample dissolved in chloroform-d.

9.6.4.1 **Table 2** summarizes the integration regions required for the calculation of mol percent methyl protons.

9.6.5 **Fig. 2** shows the spectrum and integration of the methyl hydrogens in the pristane reference material.

9.6.5.1 Integrate the NMR spectrum over two chemical shift regions, from 0.1 ppm to the lowest point valley at approximately 1 ppm and from 0.1 ppm to 3 ppm. See **Appendix X1** for recommendations on the integration procedure.

9.6.5.2 Integrate the NMR spectrum over the olefinic H range from 3 ppm to 6 ppm.

9.6.5.3 Integrate the NMR spectrum over the aromatic H range from 6 ppm to 8 ppm.

9.6.6 Subtract the portion of integral contributed by the NMR absorption line of residual chloroform solvent (7.25 ppm

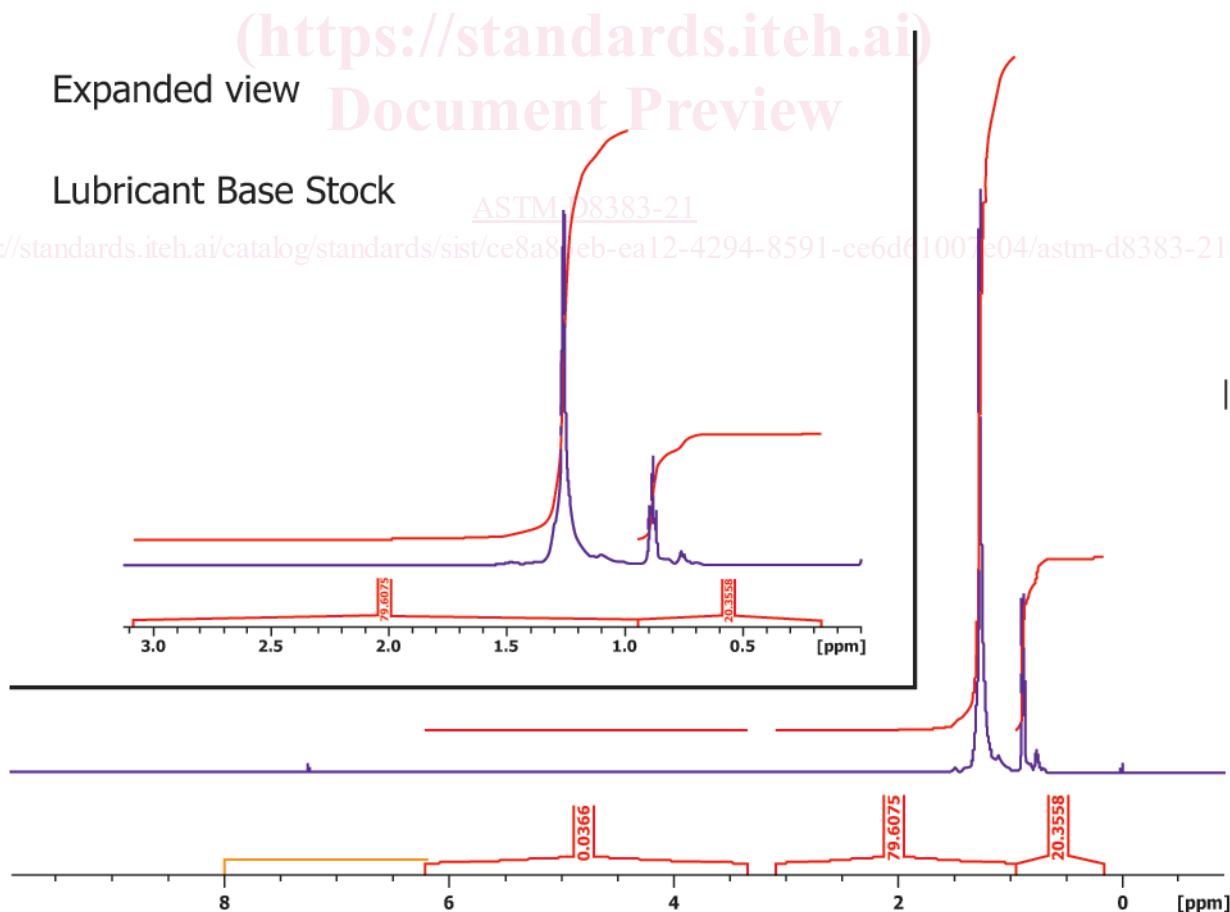


FIG. 1 500 MHz ¹H NMR Spectrum of a Lubricant Base Stock showing the Proper Integration for the Methyl Hydrogens in the Region of 0.1 ppm to the Lowest Point Valley at Approximately 1.0 ppm

TABLE 2 Regions of the H-NMR Spectra to Integrate

Integration Region (ppm)	Hydrogen Types
0.1 to lowest point valley at approximately 1	Methyl hydrogens
0.1 to 3	Total non-aromatic hydrogens
3 to 6	Olefinic hydrogens
6 to 8	Aromatic hydrogens
7.25	Chloroform (solvent) hydrogens for blank subtraction

in the ^1H NMR spectrum) from the total integral value. If a residual chloroform absorption line is not apparent or if carbon tetrachloride was used as solvent, make no correction to the integral value.

9.6.7 For the tetramethylsilane internal chemical shift reference, subtract the portion of integral contributed by the NMR absorption line of TMS (0.0 ppm in the ^1H NMR spectrum) from the total integral value.

9.6.8 Calculate the methyl hydrogen content using the corrected integral values and the instructions in 11.1.

10. Quality Control

10.1 *Reference Material*—Analyze the 2,6,10,14-Tetramethylpentadecane (pristane) reference material when first setting-up of test method or performing major instrument maintenance and with each batch of samples (Fig. 2). The value obtained shall be in the range of 44.9 % mol \pm 0.5 % mol methyl hydrogens. In addition, an independent unadditized lubricating base oil certified control standard as specified in Practice D6299 is strongly recommended. Monitor the performance of the reference material(s) and control standards using SQC charting in accordance with Practice D6299.

11. Calculation

11.1 Calculate the total hydrogen content integral:

Total hydrogen content integral = TH = (integral between 0.1 ppm and 3 ppm) + (integral between 3 ppm and 6 ppm) + (integral between 6 ppm and 8 ppm)

11.1.1 Integrals between 3 ppm and 6 ppm or between 6 ppm and 8 ppm that are less than 0.1 % mol of the total hydrogens are counted as zero to eliminate noise from the spectra.

11.2 Calculate the total methyl hydrogen content as follows:

Total mol percent methyl hydrogen content = $100 \times$ [integral between 0.1 ppm to the lowest point valley near 1 ppm / TH].

12. Report

12.1 Report the total mol percent methyl hydrogen atoms to one decimal place.

13. Precision and Bias

13.1 *Repeatability*:

13.1.1 *Interim repeatability* ($r_{interim}$)—The repeatability standard deviation and associated repeatability limits from a single operator for different average property values has been determined as per Practice D6300 and are listed in Table 3.

TABLE 3 Interim Repeatability

Average mol percent methyl hydrogens	20.530	29.594	38.671
std dev	0.299	0.263	0.100
$r_{interim}$	0.902	0.794	0.300

where: $r_{interim}$ is the value that the difference between two independent 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 exceed about 5 % of the time in the normal and correct operation of the test method.

13.1.1.1 Table 4 represents the raw data used to calculate the interim repeatability in Table 3.

13.2 *Reproducibility*—Not available at this time. An inter-laboratory study of this test method is planned and a complete precision statement is expected to be available on or before 2026.

13.3 *Bias*—For pure hydrocarbons consisting of a single compound where the hydrogen is either known from the compound molecular structure or can be calculated from the known concentrations of different molecular structures, no bias of the NMR method with respect to the known or calculated value is observed. Since there is no accepted reference method suitable for measuring bias on a lubricating hydrocarbon oil composed of an unknown mixture of many methyl hydrogen containing compounds, the bias cannot be determined on such materials.

14. Keywords

14.1 continuous wave; Fourier transform; hydrocarbon oils; lubricant base stocks; methyl hydrogen content; NMR; nuclear magnetic resonance spectroscopy