



Standard Test Method for Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy¹

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1. Scope

1.1 This test method covers the determination of the aromatic hydrogen content (Procedures A and B) and aromatic carbon content (Procedure C) of hydrocarbon oils using high-resolution nuclear magnetic resonance (NMR) spectrometers. Applicable samples include kerosenes, gas oils, mineral oils, lubricating oils, coal liquids, and other distillates that are completely soluble in chloroform at ambient temperature. For pulse Fourier transform (FT) spectrometers, the detection limit is typically 0.1 mol % aromatic hydrogen atoms and 0.5 mol % aromatic carbon atoms. For continuous wave (CW) spectrometers, which are suitable for measuring aromatic hydrogen contents only, the detection limit is considerably higher and typically 0.5 mol % aromatic hydrogen atoms.

1.2 The reported units are mole percent aromatic hydrogen atoms and mole percent aromatic carbon atoms.

1.3 This test method is not applicable to samples containing more than 1 mass % olefinic or phenolic compounds.

1.4 This test method does not cover the determination of the percentage mass of aromatic compounds in oils since NMR signals from both saturated hydrocarbons and aliphatic substituents on aromatic ring compounds appear in the same chemical shift region. For the determination of mass or volume percent aromatics in hydrocarbon oils, chromatographic, or mass spectrometry methods can be used.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard does not purport to address all of the safety problems, 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.* Specific precautionary statements are given in 7.2 and 7.4.

2. Referenced Documents

2.1 ASTM Standards:

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.01 on Absorption Spectroscopic Methods.

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D 3238 Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method²

D 3701 Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products²

E 386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy³

2.2 *Institute of Petroleum Methods:*

IP Proposed Method BD Aromatic Hydrogen and Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy⁴

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aromatic carbon content*—mole percent aromatic carbon atoms or the percentage of aromatic carbon of the total carbon:

$$\frac{\text{aromatic carbon content}}{\text{aromatic carbon content}} = 100 \times \frac{(\text{aromatic carbon atoms})}{(\text{total carbon atoms})} \quad (1)$$

3.1.1.1 *Discussion*—For example, the aromatic carbon content of toluene is $100 \times (6/7)$ or 85.7 mol % aromatic carbon atoms.

3.1.2 *aromatic hydrogen content*—mole percent aromatic hydrogen atoms or the percentage of aromatic hydrogen of the total hydrogen:

$$\frac{\text{aromatic hydrogen content}}{\text{aromatic hydrogen content}} = 100 \times \frac{(\text{aromatic hydrogen atoms})}{(\text{total hydrogen atoms})} \quad (2)$$

3.1.2.1 *Discussion*—For example, the aromatic hydrogen content of toluene is $100 \times (5/8)$ or 62.5 mol % aromatic hydrogen atoms.

² *Annual Book of ASTM Standards*, Vol 05.02.

³ *Annual Book of ASTM Standards*, Vol 14.01.

⁴ Available from Institute of Petroleum Standards.

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 E 386.

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.

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 CW or pulse FT high-resolution NMR spectrometer. Carbon (^{13}C) 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 both ^1H and ^{13}C NMR spectra.

4.2 The aromatic hydrogen content of the sample is measured by comparing the integral for the aromatic hydrogen band in the ^1H NMR spectrum (5.0 to 10.0 ppm chemical shift region) with the sum of the integrals for both the aliphatic hydrogen band (–0.5 to 5.0 ppm region) and the aromatic hydrogen band (5.0 to 10.0 ppm region).

4.3 The aromatic carbon content of the sample is measured by comparing the integral for the aromatic carbon band in the ^{13}C spectrum (100 to 170 ppm chemical shift region) with the sum of the integrals for both the aliphatic carbon band (–10 to 70 ppm region) and the aromatic carbon band (100 to 170 ppm region).

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

4.5 The integrals of the aliphatic hydrogen band and of the aliphatic carbon band must be corrected for the NMR absorption line due to the internal chemical shift reference tetramethylsilane (0.0 ppm chemical shift in both ^1H and ^{13}C spectra).

5. Significance and Use

5.1 Aromatic content is a key characteristic of hydrocarbon oils and can affect a variety of properties of the oil including its boiling range, viscosity, stability, and compatibility of the oil with polymers.

5.2 Existing methods for estimating aromatic contents use physical measurements, such as refractive index, density, and number average molecular weight (see Test Method D 3238) or infrared absorbance⁵ and often depend on the availability of suitable standards. These NMR procedures do not require standards of known aromatic hydrogen or aromatic carbon contents and are applicable to a wide range of hydrocarbon oils that are completely soluble in chloroform at ambient temperature.

5.3 The aromatic hydrogen and aromatic carbon contents determined by this test method can be used to evaluate changes in aromatic contents of hydrocarbon oils due to changes in processing conditions and to develop processing models in which the aromatic content of the hydrocarbon oil is a key processing indicator.

6. Apparatus

6.1 *High-Resolution Nuclear Magnetic Resonance Spectrometer*—A high-resolution continuous wave (CW) or pulse Fourier transform (FT) NMR spectrometer capable of being operated according to the conditions in Table 1 and Table

TABLE 1 Sample and Instrument Conditions for Continuous Wave (CW) Measurements of ^1H NMR Spectra

| | |
|--------------------------|--|
| Solvent | Chloroform-d |
| Sample concentration | Up to 50 % v/v for distillable oils |
| Sample temperature | Instrument ambient |
| Internal lock | None |
| Sample spinning rate | As recommended by manufacturer, typically 20 Hz |
| r-f Power level | As recommended by instrument manufacturer |
| Signal to noise level | A minimum of 5:1 for the maximum height of the smaller integrated absorption band |
| Chemical shift reference | Preferably tetramethylsilane (0.0 ppm) at no greater than 1 vol % concentration |
| Integration | Integrate over the range – 0.5 to 5.0 ppm for the aliphatic band and 5.0 to 10.0 ppm for the aromatic band |

2 and of producing peaks having widths less than the frequency ranges of the majority of chemical shifts and coupling constants for the measured nucleus.

6.1.1 ^1H NMR spectra can be obtained using either CW or pulse FT techniques but ^{13}C measurements require signal averaging and, therefore, currently require the pulse FT technique. Low resolution NMR spectrometers and procedures are not discussed in this test method (see Test Method D 3701 for an example of the use of low resolution NMR).

6.2 *Tube Tubes*—Usually a 5 or 10 mm outside diameter tube compatible with the configuration of the CW or 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.⁶ Other grades may be 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 vol % residual chloroform. Care must be taken not to contaminate the solvent with water and other extraneous materials. (**Warning:** Health hazard. Highly toxic.

⁵ Brandes, G., "The Structural Groups of Petroleum Fractions. I. Structural Group Analysis With the Help of Infrared Spectroscopy," *Brennstoff-Chemie* Vol 37, 1956, p. 263.

⁶ "Reagent Chemicals, American Chemical Society Specification." American Chemical Society, Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

TABLE 2 Sample and Instrument Conditions for Pulse Fourier Transform Measurements of ¹H and ¹³C NMR Spectra

| | |
|--|---|
| Solvent: | |
| ¹ H NMR | Chloroform-d |
| ¹³ C NMR | Chloroform-d |
| Sample concentration: | |
| ¹ H NMR | Must be optimized for the instrument in use but may be as high as 5 % v/v |
| ¹³ C NMR | Up to 50 % v/v for petroleum distillates and 30 % v/v for coal liquids |
| Relaxation agent | |
| | Chromium (III) 2,4-pentanedionate recommended for ¹³ C NMR solutions only. Where used, a 20 mM solution (about 10 mg per mL) |
| Sample temperature | |
| Instrument ambient | |
| Internal lock | |
| Deuterium (when chloroform-d is used for ¹ H NMR) | |
| Sample spinning rate | |
| As recommended by manufacturer, typically 20 Hz | |
| ¹ H Decoupling | |
| Only for ¹³ C NMR. Broadband over the whole of the ¹ H frequency range, gated on during ¹³ C data acquisition only with a decoupler rise time less than 2 m/s | |
| Pulse flip angle | |
| Approximately 30° | |
| Sequence delay time: | |
| | ¹ H NMR > 10 s |
| | ¹³ C NMR > 3 s with and > 60 s without relaxation agent |
| Memory size for acquisition: | |
| Choose to give a minimum digitizing rate of 0.5 Hz/point for ¹ H and 1.2 Hz/point for ¹³ C NMR. If necessary, increase memory size and zero fill | |
| Spectral width: | |
| ¹ H NMR | At least 15 ppm in frequency and centered, as close as possible, to the 5 ppm chemical shift value |
| ¹³ C NMR | At least 250 ppm in frequency and centered, as close as possible, to the 100 ppm chemical shift value |
| Filter bandwidth | |
| Set to be equal to or greater than the spectral width and as permitted by the instrument's filter hardware | |
| Exponential line broadening | |
| Set at least equal to the digitizing rate | |
| Signal to noise levels: | |
| ¹ H NMR | A minimum of 20:1 for the maximum height of the smaller integrated band |
| ¹³ C NMR | A minimum of 60:1 for the maximum height of the chloroform-d resonance appearing between 75 and 80 ppm on the chemical shift scale |
| Chemical shift reference: | |
| ¹ H NMR | Preferably tetramethylsilane (0.0 ppm) at no greater than 1 vol % concentration |
| ¹³ C NMR | Preferably tetramethylsilane (0.0 ppm) at no greater than 1 vol % concentration. If this reference is not used, the central peak of chloroform-d is set to 77.0 ppm |
| Integration: | |
| ¹ H NMR | Integrate over the range – 0.5 to 5.0 ppm for the aliphatic band and 5.0 to 10.0 ppm for the aromatic band |
| ¹³ C NMR | Integrate over the range – 10 to 70 ppm for the aliphatic band and 100 to 170 ppm for the aromatic band |

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 *Chromium (III) 2,4-Pentanedionate*, relaxation reagent for ¹³C NMR spectra, typically 97 % grade.

8. Sampling

8.1 It is assumed that a representative sample acquired by a procedure of Practice D 4057 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. Procedures

9.1 Three different procedures are described in this section for determining the aromatic hydrogen content, (see 9.6) Procedures A and B (see 9.7), and the aromatic carbon content of hydrocarbon oils, Procedure C (see 9.8).

9.2 The procedure selected by the analyst will depend on the available NMR instrumentation and on whether an aromatic hydrogen or aromatic carbon content is of greater value in evaluating the characteristics of the hydrocarbon oil.

9.3 Appendix X1 and Practice E 386 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. Since TMS is very volatile, this solution should be refrigerated or replaced if the characteristic absorption due to TMS is no longer evident in the ¹H or ¹³C NMR spectrum.

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.