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Standard Test Method for Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy[1]

This standard is issued under the fixed designation D5292; 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 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 standard. No other units of measurement are included in this 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 7.3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3238 Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method

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

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

2.2 *Energy Institute Methods:*

IP Proposed Method BD Aromatic Hydrogen and Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy[3]

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:

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

$$(\text{aromatic carbon atoms})/(\text{total carbon atoms})$$

3.1.1.1 *Discussion*—For example, the aromatic carbon content of toluene is 100 × (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:

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

$$(\text{aromatic hydrogen atoms})/(\text{total hydrogen atoms})$$

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0F 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.

[3] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K.

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

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.

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 (^{1}H) 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 ^{1}H 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 ^{1}H 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 ^{1}H 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 D3238) or infrared absorbance[4] 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.

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

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 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 ^{1}H 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 D3701 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.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use.

[4] 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.

[5] "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 ^{1}H and ^{13}C 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

7.2 *Chloroform-d*—For ^{1} H 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. 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 ^{1}H and ^{13}C NMR spectra. (**Warning—**Flammable liquid.)

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

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. 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 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. 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 ^{1}H or ^{13}C 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.