Designation: D 5292 – 99

An American National Standard

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 D 5292; 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 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:*

D 3238 Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method[2]

D 3701 Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[2]

E 386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy[3]

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 Spectroscopy[4]

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:

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

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:

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

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

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.04.0Fon Absorption Spectroscopic Methods.

Current edition approved Nov. 10, 1999. Published December 1999. Originally published as D 5292 – 92. Last previous edition D 5292 – 93.

[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 (^{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 D 3238) or infrared absorbance[5] 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 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.

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

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 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 ^{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.

[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 Pharamacopeia."

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

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 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 ^{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.

9.6 *Procedure A—^{1}H NMR Measurements Using a Continuous Wave (CW) NMR Spectrometer:*

9.6.1 Pipette a homogeneous sample of the hydrocarbon oil into an NMR sample tube compatible with the configuration of the CW 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 50 % 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 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 CW^{1}H NMR spectrum. If tetramethylsilane has been used as an internal standard, assign this absorption a chemical shift value of 0.0 ppm.

9.6.4 Integrate the NMR spectrum over two chemical shift regions, from 5.0 to 10.0 ppm (Region A) and from − 0.5 to 5.0 ppm (Region B). See Appendix X1 for recommendations on the integration procedure.

9.6.5 Subtract the portion of integral contributed by the NMR absorption line of residual chloroform solvent (7.25 ppm in the^{1}H NMR spectrum) from the total integral value for Region A. If a residual chloroform absorption line is not apparent, make no correction to the Region A integral value.

9.6.6 If tetramethylsilane was used as an internal chemical shift reference, subtract the portion of integral contributed by the NMR absorption line of TMS (0.0 ppm in the^{1}H NMR spectrum) from the total integral value for Region B.

9.6.7 Calculate the aromatic hydrogen content using the corrected integral values for Regions A and B and the instructions in 10.1 and 10.2.

9.7 *Procedure B—^{1}H NMR Measurements Using a Pulse Fourier Transform (FT) NMR Spectrometer:*

9.7.1 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 or 10 mm outside diameter capped NMR tube.

9.7.2 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 value. Check to ensure that the final solution is homogeneous and free of undissolved particles.

9.7.3 Using the instrumental conditions indicated in Table 2, acquire and plot the pulse FT^{1}H NMR spectrum. If tetramethylsilane has been used as an internal standard, assign this absorption a chemical shift value of 0.0 ppm.

9.7.4 Fig. 1 shows an acceptable pulse FT ^{1}H NMR spectrum of a gas oil test sample dissolved in chloroform-d.

9.7.5 Integrate the NMR spectrum over two chemical shift regions, from 5.0 to 10.0 ppm (Region A) and from −0.5 to 5.0 ppm (Region B). See Appendix X1 for recommendations on the integration procedure.

9.7.6 Subtract the portion of integral contributed by the NMR absorption line of residual chloroform solvent (7.25 ppm in the ^{1} H NMR spectrum) from the total integral value for Region A. If a residual chloroform absorption line is not apparent or if carbon tetrachloride was used as solvent, make no correction to the Region A integral value.

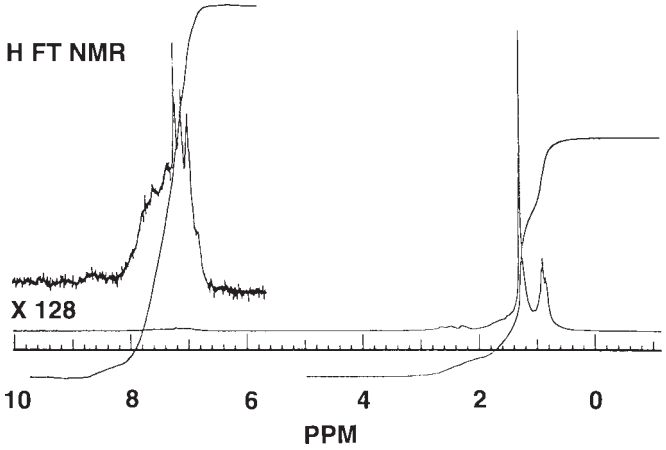

FIG. 1 80 MHz^1 H NMR Spectrum of a Gas Oil

9.7.7 If tetramethylsilane was used as an internal chemical shift reference, subtract the portion of integral contributed by the NMR absorption line of TMS (0.0 ppm in the^{1}H NMR spectrum) from the total integral value for Region B.

9.7.8 Calculate the aromatic hydrogen content using the corrected integral values for Regions A and B and the instructions in 10.1 and 10.2.

9.8 *Procedure C—^{13}C NMR Measurements Using a Pulse Fourier Transform (FT) NMR Spectrometer:*

9.8.1 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 or 10 mm outside diameter capped NMR tube.

9.8.2 If a relaxation reagent is used, weigh 10 mg of chromium 2,4-pentanedionate per 1 mL of final solution volume directly into the tube or vial containing the hydrocarbon oil.

NOTE 1—A relaxation reagent is recommended but is not required for this procedure (see X1.4.3). If relaxation reagent is not used, however, the" sequence delay time" (see Practice E 386) instrumental setting must be increased to a significantly longer time than that used when relaxation reagent is present. Failure to use the longer "sequence delay time" as indicated in Table 2 will generate erroneous results.

9.8.3 Add chloroform-d to the NMR sample tube to generate a final solution consisting of up to 50 % v/v for petroleum distillates in solvent and up to 30 % v/v for coal liquids in solvent. The concentrations of sample oil in solvent should be optimized for the spectrometer in use but can be as high as the indicated values. Check to ensure that the final solution is homogeneous and free of undissolved particles.

9.8.4 Using the instrumental conditions indicated in Table 2, acquire and plot the pulse FT^{13}C NMR spectrum. If tetramethylsilane has been used as an internal standard, assign this absorption a chemical shift value of 0.0 ppm.

9.8.5 Fig. 2 shows an acceptable pulse FT ^{13}C NMR spectrum of a gas oil test sample dissolved in chloroform-d containing relaxation reagent.

9.8.6 Integrate the NMR spectrum over two chemical shift regions, from 100 to 170 ppm (Region A) and from −10 to 70

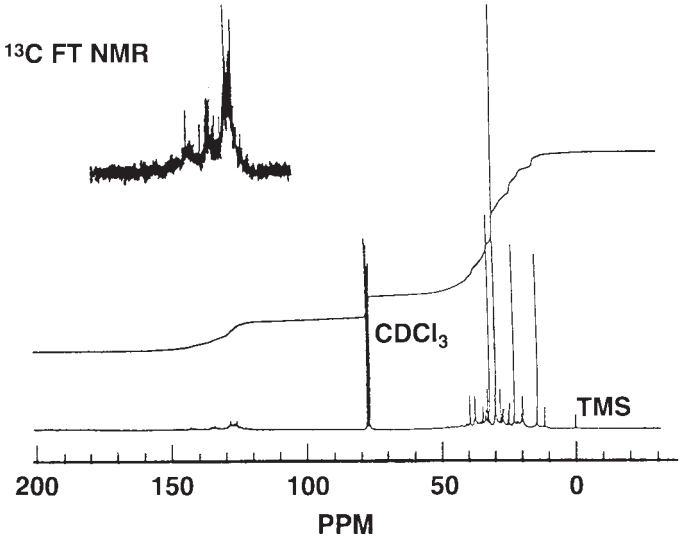

FIG. 2 100 MHz^{13} C NMR Spectrum of a Gas Oil

ppm (Region B). See Appendix X1 for recommendations on the integration procedure.

9.8.7 If tetramethylsilane has been used as an internal chemical shift reference, subtract the portion of integral contributed by the NMR absorption line of TMS (0.0 ppm in the ^{13}C NMR spectrum) from the total integral value for Region B.

9.8.8 Calculate the aromatic carbon content using the corrected integral values for Regions A and B and the instructions in 10.1 and 10.3.

10. Calculation

10.1 Calculate the aromatic hydrogen or aromatic carbon content as follows:

$$\textit{aromatic hydrogen or aromatic carbon content} = [A/(A + B)] \times 100\ \% \quad (3)$$

where:

A = integral value of the aromatic portion of the spectrum, and

B = integral value of the aliphatic portion of the spectrum.

10.2 For the aromatic hydrogen content: A is the corrected integral value for Region A (from 5.0 to 10.0 ppm) and B is the corrected integral value for Region B (from − 0.5 to 5.0 ppm). The result is expressed as mole percent aromatic hydrogen atoms or % H(Ar).

10.3 For the aromatic carbon content: A is the integral value for Region A (from 100 to 170 ppm) and B is the corrected integral value for Region B (from − 10 to 70 ppm). The result is expressed as mole percent aromatic carbon atoms or % C(Ar).

11. Report

11.1 Report the mole percent aromatic hydrogen atoms or the mole percent aromatic carbon atoms to one decimal place.

12. Precision and Bias [7]

12.1 The precision of this test method is dependent on the aromatic content of the sample.

12.2 *Precision*—The precision of this test method as determined by the statistical examination of inter-laboratory test results in the range 1 to 78 (aromatic hydrogen content) and 8 to 93 (aromatic carbon content) is as follows:

12.2.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions or identical test material would, in the long run, in the normal and correct operation of this test method, exceed the following values only in one case in twenty:

(Aromatic Hydrogen) Content (% H(Ar))	(Aromatic Carbon) Content (% C(Ar))
0.32 $X^{1/2}$	0.59 $X^{1/3}$

Where X is the aromatic content determined from the NMR measurement.

12.2.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test materials would, in the long run, exceed the following values only in one case in twenty:

(Aromatic Hydrogen) Content (% H(Ar))	(Aromatic Carbon) Content (% C(Ar))
0.49 $X^{1/2}$	1.37 $X^{1/3}$

Where X is the aromatic content determined from the NMR measurement.

NOTE 2—Precision limits are based on a round-robin test program carried out in 1985 and 1986 by the Institute of Petroleum (see IP Method BD) and ASTM Committee D02.04F. Twelve cooperator laboratories tested five oils, namely a lubricating oil, a gas oil, two aromatic distillates, and an anthracene oil, whose aromatic hydrogen and carbon contents varied as described in 13.2.

12.2.3 *Bias*—For pure hydrocarbons consisting of a single compound or a known mixture of known aromatic compounds where the aromatic hydrogen or carbon content 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 hydrocarbon oil composed of an unknown mixture of many aromatic compounds, the bias cannot be determined on such materials.

13. Keywords

13.1 aromatic carbon content; aromatic hydrogen content; continuous wave; Fourier transform; hydrocarbon oils; NMR; nuclear magnetic resonance spectroscopy

[7] The results of the cooperative test program, from which these values have been derived, are filed at ASTM Headquarters.

APPENDIX

(Nonmandatory Information)

X1. GENERAL OPERATING GUIDELINES FOR HIGH-RESOLUTION NMR SPECTROSCOPY

X1.1 The following guidelines are to be used in conjunction with the spectrometer manufacturer's instructions for optimum performance of the NMR spectrometer supplemented by the information contained in Practice E 386.

X1.2 *Practices for Obtaining Acceptable High-Resolution NMR Spectra:*

X1.2.1 The homogeneity of the instrument's magnetic field must be optimized so that the best possible spectral resolution and signal to noise ratio are obtained. The tuning of the detector must also be optimized according to the manufacturer's instructions.

X1.2.2 The solution concentration should remain constant from sample to sample for both ^{1}H and ^{13}C NMR measurements. In order to ensure an accurate integration in a CW spectrum, the solution concentration must be such that a sufficiently good signal to noise ratio is obtained on the smallest band to be measured. Signal averaging in pulse FT NMR should continue until a similar condition is reached. Recommended signal to noise ratios for CW and pulse FT NMR techniques are indicated in Table 1 and Table 2.

X1.3 *NMR Chemical Shift References for NMR Spectra:*

X1.3.1 The preferred internal reference compound for ^{1}H NMR spectra is tetramethylsilane (TMS). The ^{1}H chemical shift position for the single ^{1}H NMR absorption line observed for this compound is defined as 0.0 ppm.

X1.3.2 The preferred internal reference compound for ^{13}C NMR spectra is tetramethylsilane (TMS). The ^{13}C chemical shift position for the single ^{13}C NMR absorption line observed for this compound is defined as 0.0 ppm.

X1.4 *Quantitative Measurements by High-Resolution NMR Spectroscopy:*

X1.4.1 Quantitative CW spectra can be obtained provided the signals are not saturated by the application of the radiofrequency (r-f) field at too high a power level. Consult the spectrometer manufacturer's instructions for recommended r-f field settings.

X1.4.2 Quantitative FT spectra which are acquired by collecting the signal response following short r-f pulses require the consideration of a number of parameters. The duration and the spacing of the r-f pulses must be selected to ensure that the sample's ^{1}H and ^{13}C nuclei return to an equilibrium condition between pulses. Since this return to equilibrium occurs rapidly in ^{1}H NMR (usually between 1 to 5 s) and a good signal to noise ratio can usually be obtained in a short time of data acquisition, quantitative results can be obtained in ^{1}H NMR without placing major constraints on instrument time.

X1.4.3 The corresponding relaxation times for ^{13}C NMR are much longer (usually between 2 to 20 s) and, coupled with its decreased sensitivity compared to ^{1} H NMR, a considerable time of data acquisition can be required to obtain quantitative ^{13}C NMR results. Adding a suitable paramagnetic relaxation reagent, such as chromium (III) 2,4-pentanedionate, to the sample is recommended as a means to reduce the relaxation times of all the carbon-13 nuclei and, in so doing, shorten the time required between r-f irradiation pulses. The relaxation reagent does not change the number of scans that must be averaged to achieve an acceptable signal to noise ratio, however.

X1.4.4 Carbon-13 NMR spectra are acquired under conditions such that the spin-spin coupling interaction between hydrogen and carbon nuclei is removed or decoupled. Under certain hydrogen decoupling conditions, however, energy transfer from hydrogen to carbon nuclei may result in an enhancement in the carbon signal intensity known as the nuclear Overhauser enhancement (nOe) (see Practice E 386). The magnitude of this effect is broadly dependent on the number of hydrogen atoms bonded to a particular carbon, the chemical environment of the specific carbon, and the magnetic field strength. In order to suppress this phenomenon and avoid distorted integral data, gated decoupling must be used in which the hydrogen decoupler is only switched on during acquisition of the ^{13}C signals. Gated decoupling should be used in conjunction with the relaxation reagent indicated in X1.3.3 to minimize the nOe effect on the ^{13} C NMR integral data.

X1.4.5 The NMR spectrum obtained after Fourier transformation on a pulse FT spectrometer should have a computer-limited spectral resolution sufficient to accurately define the aromatic and aliphatic absorption bands.

X1.4.6 The NMR spectrum must also have a reasonably flat baseline over the entire spectral region so that the areas under these absorption bands can be accurately integrated. Two techniques are available to obtain flat baselines: optimization of the pulse FT data acquisition conditions (receiver dead time, filter band width, etc.) and computer-assisted baseline correction of the NMR spectrum after Fourier transformation. The first technique is preferable although often unachievable in practice. The second technique should be applied with caution as it can cause distortions in the spectrum and in the integral. Consult the spectrometer manufacturer's instructions for recommended baseline correction procedures.

X1.4.7 It is absolutely essential that the spectrum, whether collected on a pulse FT or CW spectrometer, be phased correctly before the integrals are measured. Consult the instrument manufacturer's instructions for proper and improper spectrum phasing. Power spectrum or absolute value spectrum options must not be used.

X1.4.8 In order to obtain accurate integral data, analog integral traces must be horizontal both before and after the peak or band being integrated.

X1.4.9 Vertical expansion of the analog integral traces must be as large as possible. If using manual measuring methods,

maximize the integral trace by vertical expansion and check again that the integral trace is horizontal both before and after the peak or band being integrated.