



Designation: D5186 – 22

# Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography<sup>1</sup>

This standard is issued under the fixed designation D5186; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the determination of the total amounts of monoaromatic and polynuclear aromatic hydrocarbon compounds in motor diesel fuels and blend stocks by supercritical fluid chromatography (SFC). The range of aromatics concentration to which this test method is applicable is from 1 % to 75 % by mass. The range of polynuclear aromatic hydrocarbon concentrations to which this test method is applicable is from 0.5 % to 50 % by mass.

1.2 This test method includes relative bias for Test Method D5186 versus Test Method D1319 and Test Method D6591 versus Test Method D5186 for diesel fuels. The applicable ranges of the correlation ranges are presented in the Relative Bias section. The correlations are applicable only in the stated ranges and only to diesel fuels.

1.3 This test method and correlations were developed for diesel samples not containing biodiesel; the presence of biodiesel will interfere with the results. The correlation equations are only applicable between these concentration ranges and to diesel fuels that do not contain biodiesel.

1.4 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

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.*

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.*

<sup>1</sup> 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 D02.04.0C on Liquid Chromatography.

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*mentations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

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

D6591 Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

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

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *critical pressure, n*—that pressure needed to condense a gas at the critical temperature.

3.1.2 *critical temperature, n*—the highest temperature at which a gaseous fluid may be converted to a liquid by means of compression.

3.1.3 *mononuclear aromatic hydrocarbons, n*—hydrocarbon compounds containing exactly one aromatic ring. This group includes benzene, alkyl-substituted benzenes, indans, tetralins, alkyl-substituted indans, and alkyl-substituted tetralins.

3.1.4 *polynuclear aromatic hydrocarbons, n*—all hydrocarbon compounds containing two or more aromatic rings. These rings may be fused as in naphthalene and phenanthrene, or separate as in biphenyl.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

3.1.5 *restrictor, n*—a device, attached to the outlet of a chromatographic column, to restrict the mobile phase flow such that the mobile phase is maintained in the supercritical state throughout the chromatographic column.

3.1.6 *supercritical fluid, n*—a fluid maintained in a thermodynamic state above its critical temperature and critical pressure.

3.1.7 *supercritical fluid chromatography, n*—a class of chromatography that employs supercritical fluids as mobile phases.

## 4. Summary of Test Method

4.1 A small aliquot of the fuel sample is injected onto a packed silica adsorption column and eluted using supercritical carbon dioxide mobile phase. Monoaromatics and polynuclear aromatics in the sample are separated from nonaromatics and detected using a flame ionization detector.

4.2 The detector response to hydrocarbons is recorded throughout the analysis time. The chromatographic areas corresponding to the monoaromatic, polynuclear aromatic, and nonaromatic components are determined and the % by mass content of each of these groups in the fuel is calculated by area normalization.

## 5. Significance and Use

5.1 The aromatic hydrocarbon content of motor diesel fuels is a factor that can affect their cetane number and exhaust emissions.

5.2 The United States Environmental Protection Agency (USEPA) regulates the aromatic content of diesel fuels. California Air Resources Board (CARB) regulations place limits on the total aromatics content and polynuclear aromatic hydrocarbon content of motor diesel fuel, thus requiring an appropriate analytical determination to ensure compliance with the regulations. Producers of diesel fuels will require similar determinations for process and quality control. This test method can be used to make such determinations.

5.3 This test method is applicable to materials in the boiling range of motor diesel fuels and is unaffected by fuel coloration. Test Method **D1319**, which has been mandated by the USEPA for the determination of aromatics in motor diesel fuel, excludes materials with final boiling points greater than 315 °C (600 °F) from its scope. Test Method **D2425** is applicable to the determination of both total aromatics and polynuclear aromatic hydrocarbons in diesel fuel, but is much more costly and time consuming to perform.

5.4 Results obtained by this test method have been shown to be statistically more precise than those obtained from Test Method **D1319** for typical diesel fuels, and this test method has a shorter analysis time.<sup>3</sup> Results from this test method for total polynuclear aromatic hydrocarbons are also expected to be at least as precise as those of Test Method **D2425**.

<sup>3</sup> Supporting data (obtained in a comparison study of Test Methods **D1319** and **D5186**) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1276. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).

## 6. Apparatus

6.1 *Supercritical Fluid Chromatograph (SFC)*—Any SFC instrumentation can be used that has the following capabilities and meets the performance requirements in Section 8.

6.1.1 *Pump*—The SFC instrumentation must include a pump capable of delivering supercritical carbon dioxide to the column without pressure fluctuations and at constant flow. The pump is typically a single-stroke-type (syringe) pump or a highly dampened reciprocating pump with pressure fluctuations not exceeding  $\pm 0.3$  % of the operating pressure.

6.1.2 *Detector*—This test method is limited to the use of the flame ionization detector (FID). The detector must have sufficient sensitivity to detect 0.1 % by mass toluene in hexadecane under instrument conditions employed in this test method.

6.1.3 *Column Temperature Control*—The chromatograph must be capable of column temperature control of at least  $\pm 0.5$  °C (1 °F) at the operating temperature.

6.1.4 *Sample Inlet System*—A liquid sample injection valve is required, capable of reproducibly introducing samples in the 0.05  $\mu$ L to 0.50  $\mu$ L liquid volume range. The inlet system should be operated at between 25 °C and 30 °C. The sample inlet system must be connected to the chromatographic column so that loss of chromatographic efficiency is avoided.

6.1.5 *Post-column Restrictor*—A device capable of maintaining mobile phase supercritical conditions within the column and up to the detector inlet must be connected to the end of the column.

6.1.6 *Column*—Any liquid or supercritical fluid chromatographic column may be used that provides separation of nonaromatic, monoaromatic, and polynuclear aromatic hydrocarbons and meets the performance requirements of Section 8.

6.1.7 *Integrator*—Means must be provided for the determination of both discrete chromatographic peak areas and the accumulated area under the chromatogram. This can be done by means of a computer or electronic integrator. The computer or integrator must have the capability of correcting for baseline shifts during the run.

6.1.8 *Sample Filter*—A microfilter of a porosity of 0.20  $\mu$ m, which is chemically-inert to hydrocarbon solvents, may be used for the removal of microscopic particulate matter from the sample solution that potentially may harm the injection valve and affect system performance.

## 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.<sup>4</sup> Other grades may be used,

<sup>4</sup> *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.

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 *Air*—Zero grade (hydrocarbon-free) is used as the FID oxidant. (**Warning**—Air is usually supplied as a compressed gas under high pressure and supports combustion.)

7.3 *Carbon Dioxide (CO<sub>2</sub>)*—Supercritical fluid chromatographic grade, 99.99 % minimum purity, supplied pressurized in a cylinder equipped with a dip tube for removal of liquid CO<sub>2</sub>. (**Warning**—Liquid at high pressure. Release of pressure results in production of extremely cold solid CO<sub>2</sub> and gas, which can dilute available atmospheric oxygen.)

7.4 *Check Standard*—A commercial standard reference material, which has accepted reference values, in accordance with Section 6 on Reference Materials in Practice D6299. Alternatively, samples subjected to round robin may be used as check standards. It is important that the standard deviation of the values of the laboratory exchange program not be statistically greater than the reproducibility for the test method.

7.5 *Hydrogen*—Hydrogen of high quality (hydrocarbon-free) is used as the fuel for the flame ionization detector. (**Warning**—Hydrogen is usually supplied under high pressure and is extremely flammable.)

7.6 *Performance Mixture*—A quantitative mixture of approximately 75 % by mass hexadecane (*n*-C<sub>16</sub>), 20 % by mass toluene, 3 % by mass tetralin (1,2,3,4-tetrahydronaphthalene), and 2 % by mass naphthalene is used for performance checks.

7.7 *Quality Control Sample*—A homogeneous material having similar physical and chemical properties to the samples to be analyzed. The choice of such material should be guided by Section 6 on Reference Materials in Practice D6299. Examples of such material can be motor diesel fuel or other typical samples containing aromatics and polynuclear aromatics similar to the samples to be analyzed.

## 8. Preparation of Apparatus

8.1 Install the SFC instrumentation in accordance with the manufacturer's instructions. System operating conditions will depend upon the column used and optimization of performance. If the performance characteristics in terms of retention and resolution, specified in 8.2, are not achieved, modify the temperature, pressure, or mobile phase flow rate to achieve compliance. A column of low activity may be reactivated by solvent rinsing using established liquid chromatography activation techniques.

NOTE 1—This temperature can be increased (up to 40 °C) if the resolution between the monoaromatics and polynuclear aromatics is not satisfactory. Lower temperatures are suggested to improve resolution between nonaromatics and monoaromatics.

### 8.2 System Performance:

8.2.1 *Resolution*—Analyze the performance mixture prepared in 7.6. The resolution between the nonaromatics and monoaromatics ( $R_{NM}$ ) must be at least four and resolution between the monoaromatics and polynuclear aromatics ( $R_{MD}$ ) must be at least two when calculated in accordance with the following equations:

$$R_{NM} = \frac{2 \times (t_2 - t_1)}{1.699 \times (y_2 + y_1)} \quad (1)$$

$$R_{MD} = \frac{2 \times (t_4 - t_3)}{1.699 \times (y_4 + y_3)} \quad (2)$$

where:

- $t_1$  = time for the *n*-C<sub>16</sub> peak apex, s,
- $t_2$  = time for the toluene peak apex, s,
- $t_3$  = time for the tetralin peak apex, s,
- $t_4$  = time for the naphthalene peak apex, s,
- $y_1$  = peak width at half height of *n*-C<sub>16</sub> peak, s,
- $y_2$  = peak width at half height of toluene, s,
- $y_3$  = peak width at half height of tetralin, s, and
- $y_4$  = peak width at half height of naphthalene, s.

8.2.2 *Retention Time Reproducibility*—Repeated injections of the performance mixture must show a retention time repeatability (maximum difference between duplicate runs) of not more than 0.5 % for *n*-C<sub>16</sub> and toluene peaks.

8.2.3 *Detector Accuracy Test*—This test method assumes that the FID response approximates the theoretical unit carbon response. To verify this assumption, analyze the performance mixture and calculate the response factors, relative to hexadecane ( $RRF_i$ ), for each of the components in the performance mix, using the following equations:

$$RF_i = \frac{A_i}{M_i} \quad (3)$$

$$RRF_i = \frac{RF_i}{RF_{C16}} \quad (4)$$

where:

- $A_i$  = Component *i* in performance mix, % by area,
- $M_i$  = Component *i* in performance mix, known % by mass,
- $RF_i$  = response factor of Component *i*,
- $RF_{C16}$  = response factor of hexadecane in performance mix, and
- $RRF_i$  = relative response factor of Component *i*.

These values can then be compared to the theoretical response factor for each component in the performance mix as calculated by the following equation:

$$RRF_{theo} = \left( \frac{12.01 \times n}{MW} \right) \times \left( \frac{226.4}{12.01 \times 16} \right) \quad (5)$$

where:

- 12.01 = atomic mass of carbon,
- n* = number of carbon atoms in component molecule,
- MW* = molecular mass of component,
- 226.4 = molecular mass of hexadecane, and
- 16 = number of carbon atoms in hexadecane molecule.

The measured  $RRF$  for each component in the test mixture must be within  $\pm 10$  % of the theoretical value as calculated with Eq 5 or summarized in Table 1. If this is not attained, it will be necessary to vary the injection volume, restrictor position, or detector gas flows, or combination thereof, until agreement is attained.

### 8.2.4 Detector Linearity Check:

8.2.4.1 The following procedure has been found to be useful for verifying detector linearity. It is recommended that the

TABLE 1 Theoretical Response Factors

Component	Carbon Number	Molecular Mass	$RRF_{theo}$
Toluene	7	92.13	1.075
Tetralin	10	132.2	1.070
Naphthalene	10	128.2	1.104

range of aromatics covers at least the samples to be analyzed. However, the size of the hexadecane ( $n\text{-C}_{16}$ ) diluent peak tends to exceed the linear range of the FID. Should this occur, the detector accuracy test (see 8.2.3) provides one indication of linear performance.

8.2.4.2 Select a motor diesel or aviation turbine fuel that has an aromatics content equal to or greater than the maximum concentration to be analyzed. Accurately prepare two weighed blends of this fuel in  $n\text{-C}_{16}$ . The mass dilutions should nominally contain fuel and  $n\text{-C}_{16}$  in proportions of 1:1 and 1:3.

8.2.4.3 Analyze the fuel and two blends by the procedure in Section 9. Determine the measured % by mass aromatics present in the neat fuel and each blend as described in Section 10.

8.2.4.4 Calculate the expected concentration of aromatics in the two blends using the following equation:

$$B = A \times \frac{D}{C+D} \quad (6)$$

where:

- A = aromatics in the original fuel, % by mass,
- B = expected aromatics in the diluted fuel, % by mass,
- C = mass of hexadecane in the dilution, and
- D = mass of original diesel fuel in the dilution.

8.2.4.5 Compare the measured results obtained for % by mass aromatics in the two dilutions with their corresponding expected aromatics results. These values should agree to within the repeatability limits stated in 13.1.1. If agreement is not obtained, it may be necessary to adjust restrictor position or FID gas flows, clean the FID, or decrease the injection volume.

## 9. Procedure

9.1 Using the same conditions as determined and used in Section 8, analyze the samples. Record the chromatographic data, stopping only when the sample has been completely eluted from the column. This is observed, at the end of the run, by the detector signal returning to baseline and remaining there. This will generally occur after the elution of the tricyclic aromatics.

NOTE 2—It is recommended to filter the sample prior to analysis to remove any micro-particles that may affect the performance of the instrument.

9.2 Integrate the total chromatographic area from the beginning of the first peak to the return to baseline at the end of the chromatogram (see Fig. 1).

9.2.1 The chromatogram consists of one peak for the nonaromatics and one or more peaks for the aromatics.

9.2.1.1 Assign the area corresponding to the first peak (terminating at the bottom of the lowest valley between the retention times of hexadecane and toluene from the analysis of the performance mix) to the nonaromatics.

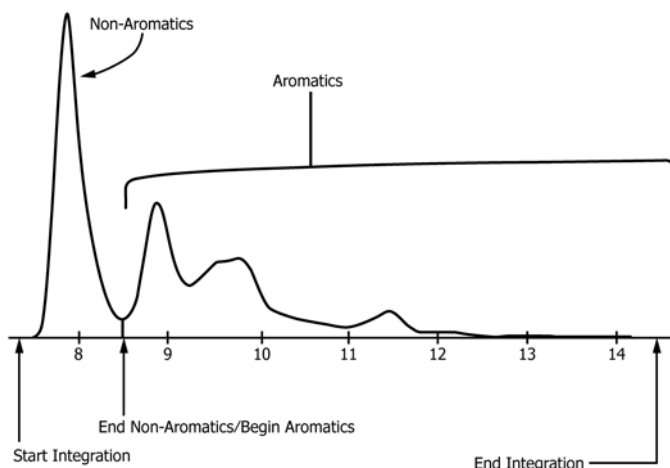


FIG. 1 Typical Chromatogram

9.2.1.2 All of the integrated area eluting after the bottom of this valley but prior to the time corresponding to the start (not the apex) of the naphthalene peak (determined in the analysis of the performance mixture) is assigned to the monoaromatics. Use area summing to determine the total area of this region in the chromatogram.

9.2.1.3 All of the integrated area occurring after the start time of the naphthalene peak through the final return to baseline is assigned to the polynuclear aromatic hydrocarbons. Use area summing to determine the total area of this region in the chromatogram.

## 10. Calculation

10.1 Determine the % by mass for monoaromatics, polynuclear aromatic hydrocarbons, and total aromatics content as follows:

$$M \% = 100 \times \frac{AM}{AN+AM+AP} \quad (7)$$

$$P \% = 100 \times \frac{AP}{AN+AM+AP} \quad (8)$$

$$A \% = M \% + P \% \quad (9)$$

where:

- M % = monoaromatics in sample, % by mass,
- P % = polynuclear aromatic hydrocarbons in sample, % by mass,
- A % = total aromatics in sample, % by mass,
- AM = area of monoaromatics in sample,
- AN = area of nonaromatics in sample, and
- AP = area of polynuclear aromatic hydrocarbons in sample.

## 11. Determination of Accuracy and Precision

11.1 Routinely assess the precision and accuracy of the analytical system as follows:

11.1.1 Accuracy—Analyze a check standard monthly as described in Section 9. The results obtained for total aromatics and polynuclear aromatics shall agree within the accepted reference values. Alternatively, exchange samples circulated as part of an interlaboratory program can be used as described in