



Designation: D5186 – 22

Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography¹

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 (ϵ) 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 Recom-*

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

2. Referenced Documents

2.1 ASTM Standards:²

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.

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 **D02.04.0C** on Liquid Chromatography.

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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.

*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.³ 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.

³ 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.

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 ± 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 ± 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 μ L to 0.50 μ 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 μ 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.⁴ Other grades may be used,

⁴ 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.