



Designation: D8578 – 24

Standard Test Method for Determination of Biodiesel and Hydrocarbon Types in Middle Distillate and Renewable Diesel Fuels by Supercritical Fluid Chromatography¹

This standard is issued under the fixed designation D8578; 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 quantitation of the total biodiesel, total aromatic hydrocarbons and total polynuclear aromatic hydrocarbons (PAH) in middle distillate and renewable fuels by supercritical fluid chromatography (SFC). The range of total aromatics concentration to which this test method is applicable is from 1.4 % to 52.7 % by mass. The range of polyaromatic hydrocarbon concentrations to which this test method is applicable is from 0.5 % to 21.2 % by mass. The range of biodiesel concentrations to which this test method is applicable is from 1.7 % to 37.2 % by mass.

1.1.1 This test method can be used for the analyses of the hydrocarbons in biodiesel-free fuels. The precision at this time is unknown.

1.1.2 This test method can be used for the analyses of fuels, such as synthetic and renewable fuels that contain less than 1.4 % total aromatics. The precision at this time is unknown.

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

1.3 *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.*

1.4 *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.*

¹ This test method is under the jurisdiction of STEM 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. Referenced Documents

2.1 ASTM Standards:²

- D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D5186 Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
- D6591 Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

3. Terminology

3.1 Definitions:

3.1.1 For the definitions of terms used in this test method, refer to Terminology D4175.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *biodiesel, n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.2.1.1 *Discussion*—Biodiesel is typically produced by a reaction of vegetable oil or animal fat with an alcohol such as

² For referenced STEM standards, visit the STEM website, www.astm.org, or contact STEM Customer Service at www.astm.org/contact. For *Annual Book of STEM Standards* volume information, refer to the standard's Document Summary page on the STEM website.

methanol or ethanol in the presence of a catalyst to yield mono-esters and glycerin. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME).

3.2.2 *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.

4. Summary of Test Method

4.1 A small aliquot of the fuel sample is injected into a packed silica adsorption column and eluted using supercritical carbon dioxide as the mobile phase. The non-aromatics, mono-aromatic, and polynuclear aromatic hydrocarbons in the sample are separated from the biodiesel and detected using a flame ionization detector.

4.2 A six-port switching valve is used to backflush the biodiesel from a short, packed silica adsorption column to the flame ionization detector.

4.3 The detector response to hydrocarbons and biodiesel is recorded throughout the analysis time. The chromatographic areas corresponding to the biodiesel, monoaromatic, polynuclear aromatics, and nonaromatic components are determined and the mass percent content of each of these groups in the fuel is calculated.

5. Significance and Use

5.1 The aromatic hydrocarbon content of motor diesel fuels is a factor that can affect fuel performance, including their cetane number and exhaust emission.

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 The United States Federal Government, in addition to state governments, offers an array of subsidies to reduce emissions caused by the consumption of fossil fuels. Therefore, the production and consumption of biofuels as an alternative fuel to fossil fuels are encouraged. Thus, an appropriate analytical method to determine the content of the biofuels blended with refined fossil fuels is needed. This test method is applicable to materials in the boiling range of middle distillates and higher boiling motor diesel fuels and can be used to determine the total FAME content of the blend as well as the total aromatic content.

5.4 Test Methods **D1319**, **D5186**, and **D6591**, which are used to determine the aromatic hydrocarbon content in middle distillates and higher boiling diesel fuels, report an artificially high aromatic content with fuels containing biodiesel. The higher than actual results are attributed to the biodiesel species coeluting with aromatic species. This test method is based on a group type separation with an additional silica column for

backflushing the biodiesel to the detector to prevent the coelution of the two different group types.

5.5 This test method was developed with the higher boiling point of diesel fuels as the focal point, as it contains the highest number of aromatic rings. If lower boiling point middle distillate fuels are analyzed exclusively, then the chromatographic method can be established with markers similar to the fuels being analyzed.

6. Interferences

6.1 Interferences add to the apparent biodiesel content. Known interferences include polymer additives, oxygenates, and aromatic hydrocarbons larger than four rings.

7. Apparatus

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

NOTE 1—The SFC instruments suitable for Test Method **D6550** are also suitable for this test method.

7.1.1 *Pump*—The SFC instrumentation must include a pump capable of delivering supercritical carbon dioxide to the column at a constant flow by maintaining a constant operating pressure set between 180 bar to 220 bar. The pressure fluctuations of the carbon dioxide delivered by the pump shall not exceed $\pm 0.3\%$ of the operating pressure setpoint.

7.1.2 *Detector*—This test method is limited to the use of the flame ionization detector (FID). The detector must have sufficient sensitivity (see **9.2.2**) to detect 0.01 % by mass toluene in hexadecane under instrument conditions employed in this test method.

7.1.3 *Column Temperature Control*—The chromatograph must be capable of column temperature control to within $\pm 0.5^\circ\text{C}$ (1°F) at the operating temperature setpoint. The setpoint must be at a constant temperature of 40°C .

7.1.4 *Sample Inlet System*—A liquid sample injection valve is required that is capable of introducing samples with high efficiency such that the performance requirements of Section 9 are met. A sample injection valve with an internal loop size between 0.05 μL to 0.50 μL liquid volume range has been used successfully. The inlet system should be operated at ambient temperature. The sample inlet system must be connected to the chromatographic column so that loss of chromatographic efficiency is avoided.

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

7.1.6 *Columns*—Two columns (one short, one long) of equal inside diameter are required.

7.1.6.1 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 9. Typically, a high-surface-area-silica column, 500 mm long column is used. These columns are packed with particles having an average diameter of 5 μm or less, 600 nm (60 $\text{\AA}$) pores, and a surface area of $\geq 350\text{ m}^2/\text{g}$.

7.1.6.2 A short high-surface-area silica column is used to separate the hydrocarbons in the fuels from the biodiesel. Any liquid or supercritical fluid column can be used providing that it meets the performance requirements of Section 9. Columns that have been used successfully are shown in Table 1.

7.1.7 *Switching Valves*—Two six-way switching valves are configured in accordance with the scheme shown in Fig. 1. This configuration makes available four different valve positions and is used in Test Method D6550. For this test method, the mobile phase must flow through a short silica column and a long analytical silica column connected in series and must be able to direct the flow in the reverse direction through the short silica column. The valve positions are defined as follows:

7.1.7.1 *Position 1*—Silica columns connected in series. Both the long silica column and the short silica column are in the mobile phase flow path. This position is used to load the sample onto the silica columns, separate the diesel from the biodiesel, and to determine the total aromatic and polynuclear aromatic hydrocarbon content.

7.1.7.2 *Position 2*—In this valve position the short silica column is in the flow path of the mobile phase. This position will be used to backflush the biodiesel to the detector.

7.1.8 *Integrator*—Means must be provided for the determination of both individual chromatographic peak areas and the total accumulated area under the chromatogram.

7.1.9 *Sample Filter*—A microfilter with a porosity of 0.20 µm, which is chemically inert to hydrocarbon solvents, shall be used for the removal of microscopic particulate matter from the sample solution. PTFE filter material is recommended.

7.1.10 *Autosampler*, capable of delivering a steady, bubble-free stream of sample to the sample inlet for column introduction.

8. Reagents and Materials

8.1 *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.³

8.2 *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.)

8.3 *Carbon Dioxide (CO₂)*—SFC grade, 99.99 % minimum purity, with less than 0.5 ppm moisture, and supplied pressurized in a cylinder equipped with a dip tube for dispensing liquid CO₂. (**Warning**—Liquid at high pressure. Release of pressure results in the production of extremely cold solid CO₂ and gas, which can dilute available atmospheric oxygen.)

8.4 *Check Standard*—A commercial standard reference material meeting the requirements of subsection 7.2 on Reference Materials in Practice D6299, which, for biodiesel, is gravimetrically prepared, whilst for diesel, it is a commercial grade diesel with ARV determined using an ILS meeting the requirements in D6299, 6.2.2.1 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 of the test method.

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

8.6 Performance Blends:

8.6.1 A quantitative blend consisting of 75 % by mass hexadecane (*n*-C₁₆), 20 % by mass toluene, 3 % by mass tetralin (1,2,3,4-tetrahydronaphthalene), 2 % by mass of naphthalene shall be used to mark the aromatic group types elution and system performance measurements. This performance mix shall be used to determine the column resolution of the long silica column, retention time stability, a relative response factor, asymmetry, and cut times for mono- and poly-aromatic hydrocarbons.

8.6.2 A blend consisting of a diesel containing >20 % by mass PAH content shall be blended with ≥1 % by mass of phenanthrene and ≥50 % by mass of B100. This mixture will be used to measure the column performance of the short silica column.

8.6.3 A switching valve marker material (SVM) blend: a diesel containing >20 % by mass aromatic content shall be blended with ≥1 % by mass of phenanthrene and ≥50 % B100. This mixture will be used to establish a valve actuation time for trapping the biodiesel group onto the short silica column. The chromatogram for this blend is shown in Fig. 2.

8.7 *Calibration Standard Blends*—A nominal blend of purified and distilled FAME components shall be used with diesel fuel or other such fuels in the boiling range of this method that contains no biodiesel for the calibration mixtures. The mixtures are prepared by weight as appropriate to approximate the composition of the fuels being tested. See Section 9 for the preparation of the calibration standard blends.

NOTE 2—Diesel, middle distillates, and other sustainable fuels may be

³ 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.

TABLE 1 Typical Columns

Long Analytical Silica Column		Short Silica Column	
Vendor	Selerity Technologies	Vendor	Selerity Technologies
Packing material	LiChrospher SI 60	Packing material	LiChrospher SI 60
Particle size, µm	5	Particle size, µm	5
Length, mm	500	Length, mm	100 or 50
Internal diameter, mm	1.0	Internal diameter, mm	1.0

