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Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography[1]

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~~ Scope*

1.1 This test method covers the determination of the total amounts of monoaromatic and polynuclear aromatic hydrocarbon compounds in motor diesel fuels, aviation turbine 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 mass %. The range of polynuclear aromatic hydrocarbon concentrations to which this test method is applicable is from 0.5 to 50 mass %.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
D1655 Specification for Aviation Turbine Fuels
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

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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*—~~hydro~~hydrocarbon~~carbon~~ 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.

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.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum ~~Products~~ 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**

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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 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. The aromatic hydrocarbon content and the naphthalenes content of aviation turbine fuels affect their combustion characteristics and smoke-forming tendencies. These properties represent specifications for aviation turbine fuels (see Specification D1655).

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)~~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] Cooperative study data[4] have found this test method to be more precise than the published precision of Test Method D1319 when applied to aviation turbine fuels and diesel fuels. 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.

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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.

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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 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)~~±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~~0.05 µL to ~~0.50 µL~~0.50 µL liquid volume range. The inlet system should be operated at between ~~25~~25 °C and ~~30°C.~~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. ~~Some columns and conditions that have been used successfully are shown in Table 1.~~

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.

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

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[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.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1388.

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 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_2)*— Supercritical fluid chromatographic grade, 99.99 % minimum purity, supplied pressurized in a cylinder equipped with a dip tube for removal of liquid CO_2. (**Warning—**Liquid at high pressure. Release of pressure results in production of extremely cold solid CO_2 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 in 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 mass % hexadecane (n-C_{16}), 20 mass % toluene, 3 mass % tetralin (1,2,3,4-tetrahydronaphthalene), and 2 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, aviation turbine 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. ~~Conditions listed in Table 1 have been used successfully.~~ 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.

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NOTE 1—This temperature can be increased (up to ~~40°C)~~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:

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

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

where:

t_1 = time for the n-C_{16} 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_{16} 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_{16} 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:

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[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.