Designation: D 5186 – 99

An American National Standard

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 D 5186; 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, 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:*

D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption[2]
D 1655 Specification for Aviation Turbine Fuels[2]
D 2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry[2]

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.

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 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 D 1655).

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

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 D 1319, 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 D 2425 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 D 1319 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 D 1319 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 D 2425.

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.

TABLE 2 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

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) 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 to 0.50-µL liquid volume range. The inlet system should be operated at between 25 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. 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

TABLE 1 Typical Operating Conditions

Parameter	A	B	C	D
Column Vendor	Chromegasphere	Suprex	YMC	Hewlett-Packard
Packing	SI 60	Petro-Pak S™	SI 60	HP-Hydrocarbon
Length (mm)	250	250	500	250
ID (mm)	2	2	1	4.6
Particle size, mm	5	5	10	5
Temperature, °C	30	40	30	28
CO_2 pressure, atm	115	125	115	197^A
Flow rate, mL/min^B	40	37	33	20
Injection, µL	0.1	0.1	0.06	0.5
FID, temperature, °C	350	385	350	350
Air, mL/min	300	800	280	400
H_2, mL/min	50	80	33	50
Air makeup, mL/min	15	n/a	n/a	n/a
Analysis time, min	15–20	15	24	5

^{A}Post-column (downstream) pressure regulation.

^{B}Decompressed, gaseous CO_2 flow, measured at column exit.

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[3] Data obtained in a comparison study of Test Methods D 1319 and D 5186 are filed at ASTM Headquarters with Research Report RR: D02-1276.

[4] Results are filed at ASTM Headquarters. Request Research Report: D02-1388.