



Designation: D8305 – 19

Standard Test Method for The Determination of Total Aromatic Hydrocarbons and Total Polynuclear Aromatic Hydrocarbons in Aviation Turbine Fuels and other Kerosene Range Fuels by Supercritical Fluid Chromatography¹

This standard is issued under the fixed designation D8305; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the determination of the concentration of total aromatics, and total polynuclear aromatic hydrocarbons in aviation turbine fuels and other kerosenes by supercritical fluid chromatography within the working range as listed below:

Prop. (mass %)	Method Working Range ^A	Valid Test Result Range ^B
PolyArom	0.3017 to 3.443	0.144 to 3.893
Tot Arom	0.2863 to 24.6256	0.004 to 25.375

^A Method working range:

high expected concentration limit, estimated using highest ILS sample mean
low expected concentration limit, estimated using lowest ILS sample mean

^B Valid test result range: due to testing variation, results within this range inclusively are considered valid for reporting and for applying the precision (R and r) functions as per Practice D6300.

1.2 This test method may also be used for the analyses of jet fuels, such as Synthetic Paraffinic Kerosenes (SPK) that contain not less than 0.29 % total aromatics by Test Method D2425.

1.3 This test method includes correlations to test methods Test Method D1319 for total aromatics and to Test Method D1840 for total naphthalenes content.

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*

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.

Current edition approved Dec. 1, 2019. Published February 2020. DOI: 10.1520/D8305-19.

Development of International Standards, Guides and Recommendations 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

D1655 Specification for Aviation Turbine Fuels

D1840 Test Method for Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry

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

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6379 Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum 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

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

D7566 Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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.

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, in which the rings are fused together such as naphthalene, acenaphthene, and alkylated derivatives of these hydrocarbons; may also include biphenyls.

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.

3.1.8 *total aromatic hydrocarbons, n*—hydrocarbon compounds containing one or more aromatic rings; this group includes benzene, alkyl-substituted benzenes, indans, tetralins, alkyl-substituted indans, alkyl-substituted tetralins, naphthalene, acenaphthenes, alkylated naphthenes, biphenyl and three aromatic rings fused together; it is the sum of the mononuclear and polynuclear hydrocarbons.

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. Mononuclear and polynuclear aromatics in the sample are separated from nonaromatic hydrocarbons 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 percent 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 aviation turbine fuels is a factor that can affect their density, elastomer compatibility, system durability and exhaust emissions. The aromatic hydrocarbon content and the polynuclear aromatic hydrocarbon such as naphthalene content of aviation turbine fuels affect their combustion characteristics and smoke-forming tendencies. These properties are controlled by maximum aromatics and naphthalene content specifications for refined aviation turbine fuels (see Specification D1655) and by both minimum and maximum aromatic content, and maximum

naphthalene content, for semi synthetic aviation turbine fuels (see Specification D7566).

5.2 The Federal Aviation Administration regulates the aromatic content of aviation fuels, thus requiring an appropriate analytical determination to ensure compliance with the regulations. Producers of aviation fuels will require similar determinations for process and quality control. This test method can be used to make such determinations.

6. Apparatus Requirements

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 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.

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 0.01 % 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 $\pm 0.5\text{ }^{\circ}\text{C}$ ($1\text{ }^{\circ}\text{F}$) at the operating temperature setpoint. The setpoint must be at a constant temperature between $35\text{ }^{\circ}\text{C}$ and $45\text{ }^{\circ}\text{C}$.

6.1.4 *Sample Inlet System*—A liquid sample injection valve is required that is capable of introducing samples with an internal loop size between $0.05\text{ }\mu\text{L}$ to $0.50\text{ }\mu\text{L}$ liquid volume range. The inlet system should be operated between $25\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. 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 shall 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 individual chromatographic peak areas and the total accumulated area under the chromatogram.

6.1.8 *Sample Filter*—A microfilter of a porosity of $0.20\text{ }\mu\text{m}$, which is chemically-inert to hydrocarbon solvents, shall be used for the removal of microscopic particulate matter from the sample solution

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.³ 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 (CO₂)*—Supercritical fluid chromatographic grade, 99.99 % minimum purity, supplied pressurized in a cylinder equipped with a dip tube for removal of liquid CO₂. (**Warning**—Liquid at high pressure. Release of pressure results in production of extremely cold solid CO₂ and gas, which can dilute available atmospheric oxygen.)

7.4 *Check Standard*—A commercial standard reference material, which has accepted reference values, in accordance within 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*-C₁₆), 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, 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. If the performance characteristics in terms of retention and resolution, specified in 8.2, are not achieved, modify the temperature and pressure to achieve compliance while staying within the permissible ranges as defined in 6.1 of this test method.

8.2 System Performance:

8.2.1 *Resolution*—Analyze the performance mixture prepared in 7.6. Calculate resolution between the nonaromatics and monoaromatics (RES_{NM}), and, resolution between the

monoaromatics and polynuclear aromatics (RES_{MP}) in accordance with Eq 1 and 2 respectively. RES_{NM} must be ≥ 10 ; RES_{MP} must be ≥ 4 .

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

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

where:

- t_1 = time for the *n*-C₁₆ 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*-C₁₆ 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.

8.2.1.1 *Asymmetry*—Analyze the performance mixture prepared in 7.6. The asymmetry of the hexadecane peak shall be less than 1.5 when calculated in accordance to the following equation (see Fig. 1):

$$T = W_{0.05} / 2f \quad (3)$$

where:

- T = peak asymmetry or tailing factor,
- $W_{0.05}$ = the distance from the leading edge to the tailing edge, measured at a point 5 % of the peak height from the baseline, and
- f = the distance from the peak maximum to the leading edge of the peak at the position of 5 % peak.

8.2.2 *Detector Sensitivity*—Measure the signal to noise ratio (S/N) for 0.01 % by weight of toluene in hexadecane. The peak height of toluene shall be five times the baseline noise where the baseline noise is calculated by 8.2.2.1.

8.2.2.1 To measure the baseline noise, allow the signal to record for a minimum of 10 min with no less than 300 readings. Calculate the standard deviation ($\sigma_{baseline}$) of the readings. Baseline noise in 8.2.2 = $6 \sigma_{baseline}$.

8.2.3 *Retention Time Repeatability*—For *n*-C₁₆ and toluene peaks, the absolute value of the difference in retention time between duplicate runs shall not exceed 0.5 % of the average retention time for the two runs.

8.2.4 *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:

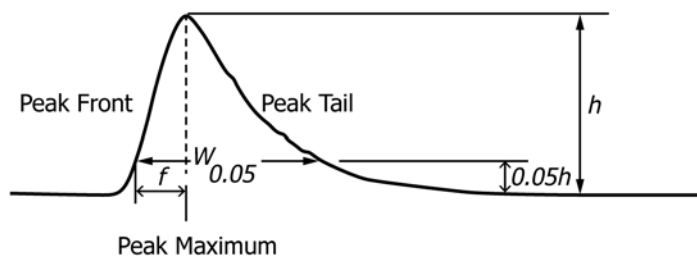


FIG. 1 Peak Asymmetry

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.