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Designation: 436/01

## Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection<sup>1</sup>

This standard is issued under the fixed designation D6379; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### INTRODUCTION

This test method is intended to be technically equivalent to IP 436-01 with an identical title. The ASTM format for test methods has been used, and where possible, equivalent ASTM test methods have replaced the IP or ISO standards.

The test method is intended to be used as one of several possible alternative instrumental test methods that are aimed at quantitative determination of hydrocarbon types in fuels. This does not imply that a correlation necessarily exists between this and any other test method intended to give this information, and it is the responsibility of the user to determine such correlation if necessary.

### 1. Scope\*

1.1 This test method covers a high performance liquid chromatographic test method for the determination of mono-aromatic and di-aromatic hydrocarbon contents in aviation kerosines and petroleum distillates boiling in the range from 50 to 300°C, such as Jet A or Jet A-1 fuels. The total aromatic content is calculated from the sum of the individual aromatic hydrocarbon-types.

NOTE 1—Samples with a final boiling point greater than 300°C that contain tri-aromatic and higher polycyclic aromatic compounds are not determined by this test method and should be analyzed by Test Method D6591 or other suitable equivalent test methods.

1.2 This test method is calibrated for distillates containing from 10 to 25 % m/m mono-aromatic hydrocarbons and from 0 to 7 % m/m di-aromatic hydrocarbons.

1.3 The precision of this test method has been established for kerosine boiling range distillates containing from 10 to 25 % m/m mono-aromatic hydrocarbons and from 0 to 7 % m/m di-aromatic hydrocarbons.

<sup>1</sup>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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In the IP, this test method is under the jurisdiction of the Standardization Committee.

1.4 Compounds containing sulfur, nitrogen, and oxygen are possible interferents. Mono-alkenes do not interfere, but conjugated di- and poly-alkenes, if present, are possible interferents.

1.5 *This standard does not purport to address 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:<sup>2</sup>

- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D6591 Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

<sup>2</sup>For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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

## 2.2 Energy Institute Standards:<sup>3</sup>

**IP 436 Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index**

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *di-aromatic hydrocarbons (DAHs), n*—compounds that have a longer retention time on the specified polar column than the MAHs.

3.1.2 *mono-aromatic hydrocarbons (MAHs), n*—compounds that have a longer retention time on the specified polar column than the non-aromatic hydrocarbons but a shorter retention time than the di-aromatic hydrocarbons.

3.1.3 *non-aromatic hydrocarbons, n*—compounds that have a shorter retention time on the specified polar column than the mono-aromatic hydrocarbons.

3.1.4 *total aromatic hydrocarbons, n*—sum of the MAHs and DAHs.

NOTE 2—The elution characteristics of aromatic and non-aromatic compounds on the specified polar column have not been specifically determined for this test method. Published and unpublished data indicate the major constituents for each hydrocarbon type as follows: (1) Non-aromatic hydrocarbons: acyclic and cyclic alkanes (paraffins and naphthenes), mono-alkenes (if present). (2) MAHs: benzenes, tetralins, indanes, thiophenes, conjugated poly-alkenes. (3) DAHs: naphthalenes, biphenyls, indenenes, fluorenes, acenaphthenes, benzothiophenes.

## 4. Summary of Test Method

4.1 The test portion is diluted 1:1 with the mobile phase, such as heptane, and a fixed volume of this solution injected into a high performance liquid chromatograph fitted with a polar column. This column has little affinity for the non-aromatic hydrocarbons and exhibits a pronounced selectivity for aromatic hydrocarbons. As a result of this selectivity, the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons into distinct bands in accordance with their ring structure, that is, MAHs and DAHs.

4.2 The column is connected to a refractive index detector that detects the components as they elute from the column. The electronic signal from the detector is continually monitored by a data processor. The amplitudes of the signals (peak areas) from the sample aromatics are compared with those obtained from previously-run calibration standards in order to calculate the percent m/m MAHs and DAHs in the sample. The sum of the MAHs and DAHs is reported as the total aromatic content (percent m/m) of the sample.

## 5. Significance and Use

5.1 Accurate quantitative information on aromatic hydrocarbon types can be useful in determining the effects of petroleum processes on production of various finished fuels. This information can also be useful for indicating the quality of fuels and for assessing the relative combustion properties of finished fuels.

## 6. Apparatus

6.1 *High Performance Liquid Chromatograph (HPLC)*—Any high performance liquid chromatograph capable of pumping the mobile phase at flow rates between 0.5 and 1.5 mL/min with a precision better than 0.5 % and a pulsation of <1 % full scale deflection under the test conditions described in Section 9. See Fig. 1.

6.2 *Sample Injection System*—The sample injection system shall be capable of injecting 10  $\mu$ L (nominal) of sample solution with a repeatability better than 2 %.

6.2.1 An equal and constant volume of the calibration and sample solutions shall be injected into the chromatograph. Both manual and automatic sample injection systems (using either complete or partial filling of the sample loop) will, when used correctly, meet the repeatability requirements laid down in 6.2. When using the partial loop filling mode, it is recommended that the injection volume should be less than half the total loop volume. For complete filling of the loop, best results are obtained by overfilling the loop at least six times.

6.2.2 Sample injection volumes other than 10  $\mu$ L (typically in the range from 3 to 20  $\mu$ L) may be used provided they meet the requirements laid down for injection repeatability (see 6.2), refractive index sensitivity and linearity (see 9.4 and 10.1), and column resolution (see 9.4)

6.3 *Sample Filter (Optional)*—A microfilter of porosity 0.45  $\mu$ m or less, which is chemically-inert towards hydrocarbon solvents, is recommended for the removal of particulate matter from the sample solutions.

6.4 *Column System*—Any stainless steel HPLC column(s) packed with an approved amino-bonded (or polar amino/cyano-bonded) silica stationary phase<sup>4</sup> is suitable, provided it meets the resolution requirements laid down in 9.4.3. Column lengths from 150 to 300 mm with an internal diameter from 4 to 5 mm and packed with 3 or 5  $\mu$ m particle size stationary phase have been found to be satisfactory. The use of a guard column (for example, 30 by 4.6-mm internal diameter) packed with silica or amino-bonded silica is recommended but not essential.

6.5 *HPLC Column Oven*—Any suitable HPLC column oven (block heating or air circulating) capable of maintaining a constant temperature ( $\pm 1^\circ\text{C}$ ) within the range from 20 to 40°C.

NOTE 3—The refractive index detector is sensitive to both sudden and gradual changes in the temperature of the eluent. All necessary precautions should be taken to establish constant temperature conditions throughout the liquid chromatograph system.

NOTE 4—Alternative forms of temperature control, for example, temperature-controlled laboratories, are permitted.

6.6 *Refractive Index Detector*—Any refractive index detector may be used provided it is capable of being operated over the refractive index range from 1.3 to 1.6, meets the sensitivity requirement specified in 9.4.2, gives a linear response over the calibration range, and has a suitable output signal for the data system. If the refractive index detector has a facility for

<sup>3</sup> Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K.

<sup>4</sup> Stationary phases known to give suitable results include Spherisorb 3NH<sub>2</sub>, Spherisorb 5NH<sub>2</sub>, Partisil 5 PAC, and Partisphere 5 PAC.

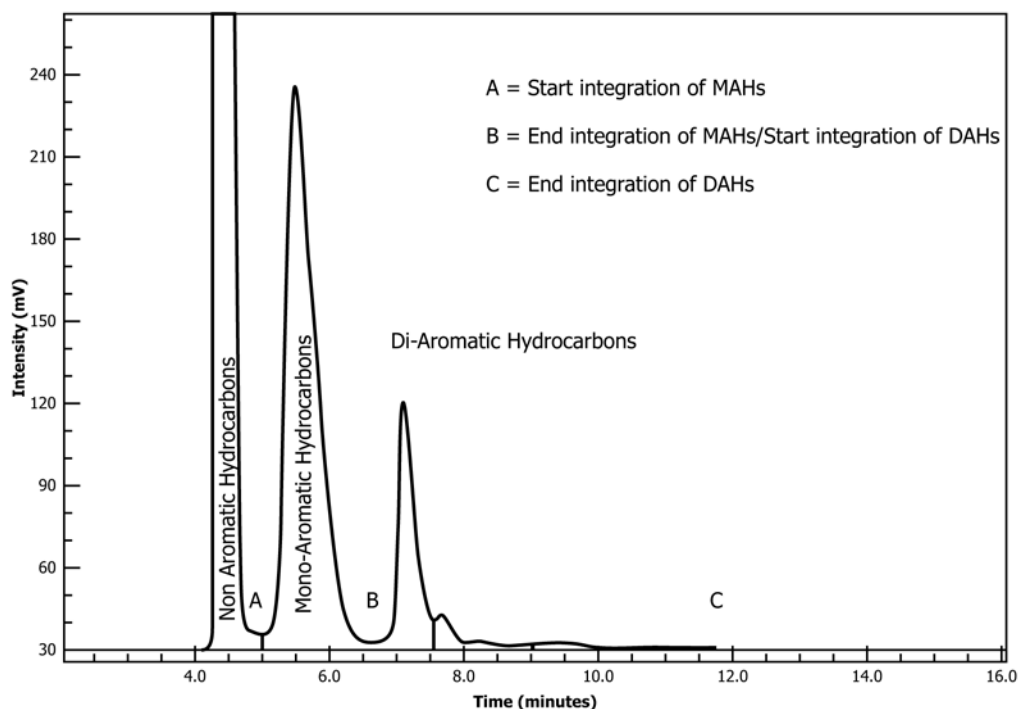


FIG. 1 Example Chromatogram of an Aviation Fuel Showing Integration Points and Aromatic Hydrocarbon Type Groups

independent temperature control, it is recommended that this is set at the same temperature as the column oven.

6.7 *Computer or Computing Integrator*—Any data system can be used provided it is compatible with the refractive index detector, has a minimum sampling rate of 1 Hz, and is capable of peak area and retention time measurement. The data system should also have minimum facilities for post-analysis data processing, such as baseline correction and reintegration. The ability to perform automatic peak detection and identification and to calculate sample concentrations from peak area measurements is recommended but not essential.

6.8 *Volumetric Flasks*, Grade B, or better, of 10 mL and 100 mL capacity.

6.9 *Analytical Balance*, accurate to  $\pm 0.0001$  g.

## 7. Reagents

7.1 *Cyclohexane*,  $\geq 99$  % pure.

NOTE 5—Cyclohexane may contain benzene as an impurity.

7.2 *Heptane*, HPLC Grade. For use as HPLC mobile phase. (**Warning**—Hydrocarbon solvents are highly flammable and may cause irritation by inhalation, ingestion, or skin contact.)

NOTE 6—It is recommended practice to degas the HPLC mobile phase before use.

7.3 *1-Methylnaphthalene*,  $\geq 98$  % pure. (**Warning**—Gloves should be worn when handling aromatic compounds (for example, disposable vinyl gloves).)

NOTE 7—Purity is determined by gas chromatography with flame ionization detection. The highest purity standards available should be used. Standards of  $\geq 98$  % purity are commercially available from all major suppliers.

7.4 *o-Xylene (1,2-Dimethylbenzene)*,  $\geq 98$  % pure.

## 8. Sampling

8.1 The laboratory fuel sample from which an aliquot is being drawn for the purposes of this test method shall be representative of the lot of fuel. The laboratory sample should be obtained by following Practice D4057 or D4177, or a similar standard.

## 9. Apparatus Preparation

9.1 Set up the chromatograph, injection system, column and column oven, refractive index detector, and computing integrator in accordance with the appropriate equipment manuals. The HPLC column shall be installed in the column oven.

NOTE 8—The column oven is optional if alternative arrangements are made to maintain a constant temperature environment, for example, a temperature-controlled laboratory (see 6.5).

9.2 Adjust the flow rate of the mobile phase to a constant  $1.0 \pm 0.2$  mL/min and ensure that the reference cell of the refractive index detector is full of mobile phase (see 6.6.1). Allow the temperature of the column oven (and refractive index detector if equipped with temperature control) to stabilize.

9.2.1 To minimize drift, it is essential to make sure that the reference cell is full of solvent. The best way to accomplish this is either to (1) flush the mobile phase through the reference cell (then isolate the reference cell to prevent evaporation of the solvent) immediately prior to analysis, or (2) continuously make up for solvent evaporation by supplying a steady flow through the reference cell. The makeup flow is optimized so that reference and analytical cell mismatch due to drying-out, temperature, or pressure gradients are minimized. Typically