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An American National Standard



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

This standard is issued under the fixed designation D 6591; 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 has the same title as IP 391-95 and is intended to be technically equivalent. 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, di-aromatic, and polyaromatic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range from 150 to 400°C. The total aromatic content in % m/m is calculated from the sum of the individual aromatic hydrocarbon types.

NOTE 1—Aviation fuels and petroleum distillates with a boiling point range from 50 to 300°C are not determined by this test method and should be analyzed by Test Method, D 6379 or other suitable equivalent test methods.

1.2 This test method is calibrated for distillates containing from 4 to 40 % (m/m) mono-aromatic hydrocarbons, 0 to 20 % (m/m) di-aromatic hydrocarbons, 0 to 6 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons.

1.3 The precision of this test method has been established for diesel fuels and their blending components, containing

from 4 to 40 % (m/m) mono-aromatic hydrocarbons, 0 to 20 % (m/m) di-aromatic hydrocarbons, 0 to 6 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons.

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 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<sup>2</sup>
- D 2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry<sup>2</sup>
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

D 5186 Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography<sup>3</sup>

D 6379 Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates – High Performance Liquid Chromatography Method With Refractive Index Detection<sup>4</sup>

## 2.2 IP Standard:<sup>5</sup>

IP 391 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 of Terms Specific to This Standard:

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

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

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

3.1.4 *polycyclic aromatic hydrocarbons (PAHs), n*—in this test method, compounds that have longer retention times on the specified polar column than the majority of DAHs.

3.1.5 *total aromatic hydrocarbons, n*—in this test method, sum of the MAHs, DAHs, and PAHs.

3.1.5.1 *Discussion*—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, and conjugated poly-alkenes, (3) DAHs: naphthalenes, biphenyls, indenenes, fluorenes, acenaphthenes, and benzothiophenes and dibenzothiophenes, (4) PAHs: phenanthrenes, pyrenes, fluoranthenes, chrysenes, triphenylenes, and benzantracenes.

## 4. Summary of Test Method

4.1 A known mass of sample is diluted in the mobile phase, and a fixed volume of this solution is injected into a high performance liquid chromatograph, fitted with a polar column. This column has little affinity for the non-aromatic hydrocarbons while exhibiting 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, DAHs, and PAHs. At a predetermined time,

after the elution of the DAHs, the column is backflushed to elute the PAHs as a single sharp band.

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 percent m/m MAHs, DAHs, and PAHs in the sample. The sum of MAHs, DAHs, and PAHs is reported as the total aromatic content (percent m/m) of the sample.

## 5. Significance and Use

5.1 The aromatic hydrocarbon content of motor diesel fuel is a factor that can affect exhaust emissions and fuel combustion characteristics, as measured by cetane number.

5.2 The United States Environmental Protection Agency (US EPA) 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.

5.3 This test method is applicable to materials in the same boiling range as motor diesel fuels and is unaffected by fuel coloration. Test Method D 1319, which has been mandated by the US EPA 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. Test Method D 5186, currently specified by CARB, is also applicable to the determination of both total aromatics and polynuclear aromatic hydrocarbons in diesel fuel. Test Method D 5186, however, specifies the use of supercritical fluid chromatography equipment that may not be readily available.

NOTE 2—Test Method D 5186 was previously specified by CARB as an alternative to Test Method D 1319.

## 6. Apparatus

6.1 *High Performance Liquid Chromatograph (HPLC)*—Any HPLC 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.

6.2 *Sample Injection System*, capable of injecting 10 µL (nominal) of sample solution with a repeatability >1 %.

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 µL (typically in the range from 3 to 20 µL) may be used, provided they meet

<sup>4</sup> Annual Book of ASTM Standards, Vol 05.04.

<sup>5</sup> Available from Institute of Petroleum, 61 New Cavendish St., London, WIM 8AR, UK.

the requirements laid down for injection repeatability (see 6.2), refractive index sensitivity and linearity (see 9.4.2 and 10.1.5), and column resolution (see 9.4.3).

6.3 *Sample Filter*, if required (see 10.2.1)—A microfilter of porosity 0.45  $\mu\text{m}$  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>6</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  $\mu\text{m}$  particle size stationary phase have been found to be satisfactory. The use of a guard column (for example, 30 x 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 *Backflush Valve*—Any manual or automatic (air or electrically actuated) flow-switching valve designed for use in HPLC systems that is capable of operating at pressures up to  $2 \times 10^4$  kPa.

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

6.8 *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.

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

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

## 7. Reagents

7.1 *Cyclohexane*, > 99 % pure.

NOTE 5—Cyclohexane may contain benzene as an impurity.

<sup>6</sup> Stationary phases known to give suitable results include Spherisorb 3  $\text{NH}_2$ , Spherisorb 5  $\text{NH}_2$ , Partisil 5 PAC, and Partisphere 5 PAC.

7.2 *Heptane*, HPLC Grade. For use as HPLC mobile phase. (**WARNING**—Heptane is 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 *o-Xylene (1,2-Dimethylbenzene)*,  $\geq 98$  % pure.

7.4 *1-Methylnaphthalene*,  $\geq 98$  % pure.

7.5 *Phenanthrene*,  $\geq 98$  % pure.

7.6 *Dibenzothiophene*,  $\geq 95$  % pure.

7.7 *9-Methylanthracene*,  $\geq 95$  % 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.

## 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 D 4057 or D 4177, or a similar standard.

## 9. Apparatus Preparation

9.1 Set up the chromatograph, injection system, column, backflush valve, column oven, refractive index detector, and computing integrator in accordance with the appropriate equipment manuals. Install the HPLC column and backflush valve in the column oven. Insert the backflush valve so that the detector is always connected independently of the direction of flow through the column (see Fig. 1). The sample injection valve shall be maintained at the same temperature as the sample solution; in most cases this will be at room temperature.

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 the reference cell of the refractive index detector is full of mobile phase. 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 the reference cell is full of solvent. The best way to accomplish this is either (1) to 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) to continuously make up for solvent evaporation by supplying a steady flow through the reference cell. The make-up flow is optimized so that reference and analytical cell miss-match due to drying-out, temperature, or pressure gradients are minimized. Typically, this can be accomplished with a make-up flow set at one tenth of the analytical flow.

NOTE 9—The flow rate may be adjusted (typically within the range from 0.8 to 1.2 mL/min) to an optimum value in order to meet the resolution requirements specified in 9.4.3.

9.3 Prepare a system performance standard (SPS) by weighing cyclohexane ( $1.0 \pm 0.1$  g), *o*-xylene ( $0.5 \pm 0.05$  g),

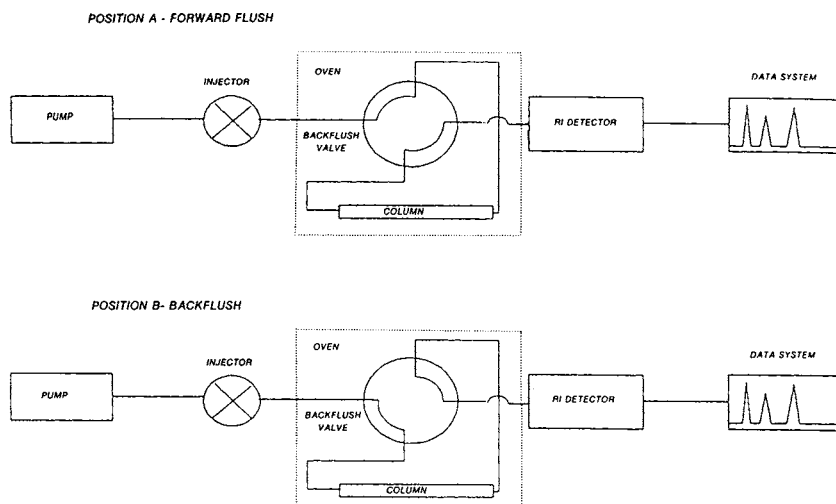


FIG. 1 Diagrammatic Representation of Liquid Chromatograph

dibenzothiophene ( $0.05 \pm 0.005$  g) and 9-methylanthracene ( $0.05 \pm 0.005$  g) into a 100 mL volumetric flask and making up to the mark with heptane. Ensure that the dibenzothiophene and 9-methylanthracene are dissolved in the *o*-xylene-cyclohexane mixture (for example, by using an ultrasonic bath) before adding heptane.

NOTE 10—The SPS may be kept for up to one year if stored in a tightly stoppered bottle in a dark place between 5 and 25°C.

9.4 When operating conditions are steady, as indicated by a stable horizontal baseline, inject 10 $\mu$ L of the SPS (see 9.3) and record the chromatogram, using the data system.

NOTE 11—Baseline drift over the period of the HPLC analysis run should be less than 0.5 % of the peak height for cyclohexane. A baseline drift greater than this indicates problems with the temperature control of the column/refractive index detector or polar material eluting from the column, or both. A period of up to 1 h may be required before the liquid chromatograph reaches steady state conditions.

9.4.1 Ensure that baseline separation is obtained between all four components of the SPS (see Fig. 2).

9.4.2 Ensure that the data system can accurately measure the peak areas of dibenzothiophene and 9-methylanthracene.

NOTE 12—The S/N (signal to noise) ratio for dibenzothiophene and 9-methylanthracene should be 3:1 or greater.

9.4.3 Ensure that the resolution between cyclohexane and *o*-xylene is not less than five.

9.4.3.1 *Column Resolution*—Calculate the resolution between cyclohexane and *o*-xylene as follows:

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

where:

- $t_1$  = retention time of cyclohexane peak in seconds,
- $t_2$  = retention time of *o*-xylene peak in seconds,

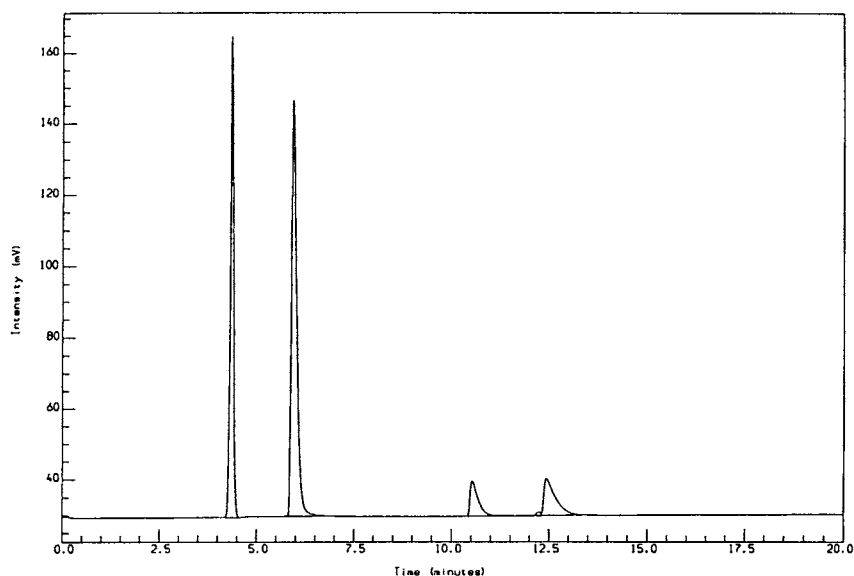


FIG. 2 Chromatogram of System Calibration Standard