



Designation: D6591 – 06



Designation: 548/06

Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection¹

This standard is issued under the fixed designation D6591; 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.

INTRODUCTION

This test method has the same title as IP 548-06 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, tri+-aromatic, and polycyclic aromatic 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 corresponding 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, D6379 or other suitable equivalent test methods.

1.2 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) tri+-aromatic hydrocarbons, 0 to 26 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons.

1.3 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.

1.4 By convention, this standard defines the aromatic hydrocarbon types on the basis of their elution characteristics from the specified liquid chromatography column relative to model aromatic compounds. Quantification is by external calibration using a single aromatic compound, which may or may not be representative of the aromatics in the sample, for each aromatic hydrocarbon type. Alternative techniques and methods may classify and quantify individual aromatic hydrocarbon types differently.

1.5 Fatty Acid Methyl Esters (FAME), if present, interfere with tri+-aromatic hydrocarbons. If this method is used for diesel containing FAME, the amount of tri+-aromatics will be over estimated.

1.6 *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
D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0C on Liquid Chromatography.

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*A Summary of Changes section appears at the end of this standard.

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5186 Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography

D6379 Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

2.2 IP Standard:³

IP 548 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 majority of mono-aromatic hydrocarbons, but a shorter retention time than the majority of tri+-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 majority of non-aromatic hydrocarbons but a shorter retention time than the majority of 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 majority of mono-aromatic hydrocarbons.

3.1.4 *polycyclic aromatic hydrocarbons (POLY-AHs)*, *n*—in this test method, sum of the di-aromatic hydrocarbons and tri+-aromatic hydrocarbons.

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

3.1.6 *tri+-aromatic hydrocarbons (T+AHs)*, *n*—in this test method, compounds that have a longer retention time on the specified polar column than the majority of DAHs.

3.1.6.1 *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) T+AHs:

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 T+AHs. At a predetermined time, after the elution of the DAHs, the column is backflushed to elute the T+AHs 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 measured calibration standards in order to calculate percent m/m MAHs, DAHs, and T+AHs in the sample. The sum of the percentages by mass of DAHs and T+AHs is reported as the percent m/m POLY-AH. The sum of MAHs, DAHs, and T+AHs 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 **D1319**, 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 **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. Test Method **D5186**, currently specified by CARB, is also applicable to the determination of both total aromatics and polynuclear aromatic hydrocarbons in diesel fuel. Test Method **D5186**, however, specifies the use of supercritical fluid chromatography equipment that may not be readily available.

NOTE 2—Test Method **D5186** was previously specified by CARB as an alternative to Test Method **D1319**.

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 %

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 Available from Institute of Petroleum, 61 New Cavendish St., London, WIM 8AR, UK.