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Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection[1,2]

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 (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

This test method is intended to be technically equivalent to IP ~~436-01~~436-20 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~~ 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 kerosenes and petroleum distillates boiling in the range from 50 °C 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~~applicable to distillates containing from ~~10 %to 25 % m/m mono-aromatic hydrocarbons and from 0 % to 7 % m/m di-aromatic hydrocarbons.~~0.8 % to 44.0 % by mass mono-aromatic hydrocarbons, 0.23 % to 6.20 % by mass di-aromatic hydrocarbons, and 0.7 % to 50 % by mass total aromatics. Although this method generates results in m/m, results may also be quoted in v/v.

1.3 The precision of this test method has been established for kerosene boiling range distillates containing from ~~10 % to 25 % m/m mono-aromatic hydrocarbons and from 0 % to 7 % m/m di-aromatic hydrocarbons.~~ 0.40 % to 44.0 % by mass mono-aromatic hydrocarbons, 0.02 % to 6.20 % by mass di-aromatic hydrocarbons, and 0.40 % to 50.0 % by mass total aromatics. If results are

[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. The technically equivalent standard as referenced is under the jurisdiction of the Energy Institute Subcommittee SC-G-2.

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~~In the IP, this test method is under the jurisdiction of the Standardization Committee.~~

[2] This test method has been developed through the cooperative effort between ASTM and the Energy Institute, London. ASTM and IP standards were approved by ASTM and EI technical committees as being technically equivalent but that does not imply both standards are identical.

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

quoted in volume, the precision is 0.3 % to 41.4 % by volume mono-aromatics, 0.01 % to 5.00 % by volume di-aromatics, and 0.30 % to 46.3 % by volume total aromatics. As calculated by IP 367-1.

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, 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 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:*[3]

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

2.2 *Energy Institute Standards:*[4]

IP 367–1 (EN ISO 4259 Part 1) Petroleum and related products – Precision of measurement methods and results – Part 1: Determination of precision data in relation to methods of test
IP 436 Test method for determination of automatic 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, indenes, 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~~set of polar columns. These columns have 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.

[3] 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.

[4] Available from Energy Institute, 61 New Cavendish St., London, W1G 7AR, U.K., http://www.energyinst.org.

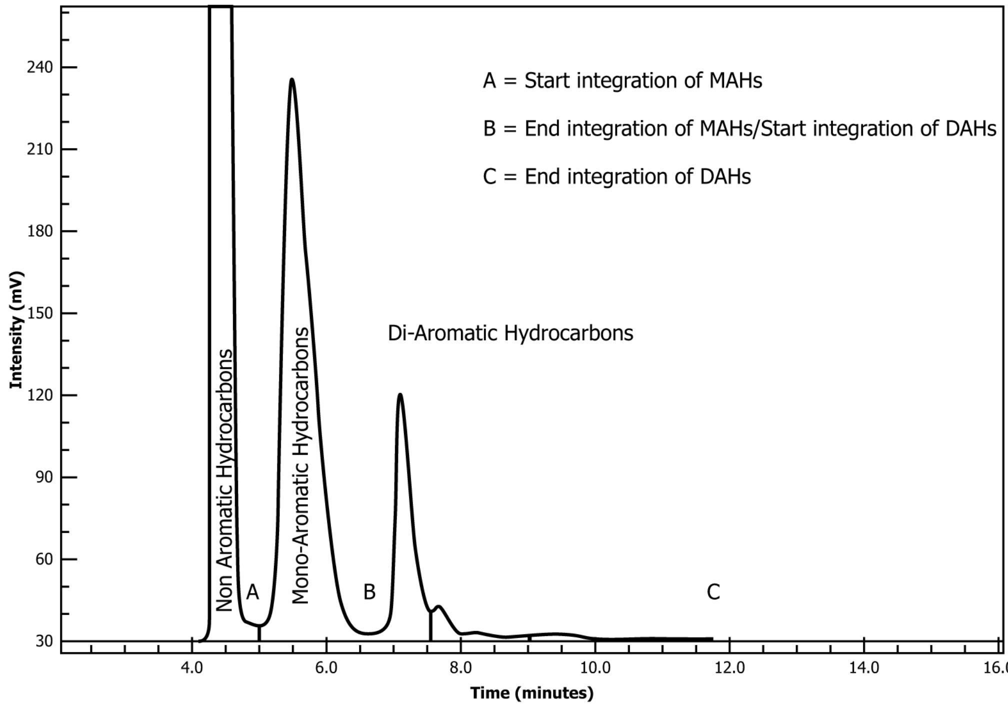

FIG. 1 Example Chromatogram of an Aviation Fuel Showing Integration Points and Aromatic Hydrocarbon Type Groups

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. Although this method generates results in m/m, results can also be quoted in percent v/v either by calibrating in v/v or by converting m/m to v/v by using the densities of the sample and standards.

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 mL⁄min 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 µL~~5 µL (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 µL~~5 µL (typically in the range from 3 µL to 20 µL) 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 µm 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 is ~~suitable, provided it meets~~ suitable. The column(s) used shall satisfy the resolution requirements laid down in 9.4.3. Column lengths from 150 mm to 300 mm with an internal diameter from 4 mm to 5 mm and packed with 3 µm or 5 µm particle size stationary phase have been found to be satisfactory. The use of a guard column (for example, 30 mm by 4.6 mm internal diameter) packed with silica or amino-bonded silica is recommended but not essential. It has been found that the use of a 2-column set provides the required separation and resolution for this method. Those used for the Inter-Laboratory study to generate the precision statements were SphereClone 5 µm NH2 (250 mm by 4.6 mm) coupled with the Zorbax SB-CN 5 µm (150 mm by 4.6 mm). Other columns are known to work when the separation (9.4.1) and resolution (9.4.3) criteria are met or exceeded prior to use. When joining two columns together, minimize the dead-volume between the columns.

6.5 *HPLC Column Oven*—Any suitable HPLC column oven (block heating or air circulating) capable of maintaining a constant temperature (±1 °C) within the range from 20 °C 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 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,~~ A, of 10 mL and 100 mL capacity.

6.9 *Analytical Balance,* accurate to ±0.0001 g.

7. Reagents

7.1 *Cyclohexane,* ≥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,* ~~≥98 %~~ ≥97 % 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 ≥98 % purity are commercially available from all major suppliers.

7.4 *o-Xylene (1,2-Dimethylbenzene),* ≥98 % pure.

7.5 *1-phenyldodecane ≥97 %.*

7.6 *hexamethylbenzene ≥97 %.*

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 mL/min ± 0.2 mL/min and ensure that the reference cell of the refractive index detector is full of mobile phase (see 6.6). 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 this can be accomplished with a makeup flow set at one tenth of the analytical flow.

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

9.3 Prepare a system resolution standard (SRS) by weighing ~~cyclohexane (1.0 g ± 0.1 g),~~ to the nearest 0.0001 g cyclohexane (1.0 g), *o*-xylene (0.5 g ± 0.05 g), and 1-methylnaphthalene (0.05 g ± 0.005 g) hexamethylbenzene (0.1 g) and 1-phenyldodecane (0.5 g) (each ±10 %) into a 100 mL volumetric flask and making up to the mark with heptane.

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

9.4 When operating conditions are steady, as indicated by a stable horizontal baseline, inject ~~10 µL~~5 µL of the SRS (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 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 ~~three~~ components of the ~~SRS.~~SRS and that they appear in the order, Cyclohexane, 1-phenyldodecane, 1,2-dimethylbenzene, hexamethylbenzene, 1-methylnaphthalene.

9.4.2 Ensure that the data system can accurately measure the peak area of 1-methylnaphthalene.

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

9.4.3 Ensure ~~that~~ the ~~resolution~~resolutions between cyclohexane and ~~o~~phenyldodecane~~-xylene~~ is not less than ~~five.~~3 and between hexamethylbenzene and 1-methylnaphthalene is not less than 5 before proceeding.

9.4.3.1 ~~*Column Resolution*—~~ Calculate the ~~resolution~~ Resolutions, R1, between cyclohexane and ~~o~~1,2-dimethylbenzene and~~-xylene as follows:~~ R2, between hexamethylbenzene and 1-methyl naphthalene using the following equation:

TABLE 1 Concentration Standards

		Calibration Standard			
		A	B	C	D
Cyclohexane	g/100 mL	5.0	2.0	0.5	0.1
o-xylene	g/100 mL	15.0	5.0	1.0	0.1
1-Methylnaphthalene	g/100 mL	5.0	1.0	0.2	0.05

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

$$\text{Resolution1} = \frac{2 \times (t_2 - t_1)}{1.699 \times (y_2 + y_1)} \quad (1)$$

$$\text{Resolution2} = \frac{2 \times (t_4 - t_3)}{1.699 \times (y_4 - y_3)} \quad (2)$$

where:

t_1 = retention time of cyclohexane peak in seconds,
~~t_2 = retention time of o-xylene peak in seconds,~~
t_2 = retention time of the phenyldodecane peak, in seconds,
~~y_1 = half-height peak width of cyclohexane in seconds, and~~
y_1 = width at half-height of the cyclohexane peak, in seconds,
~~y_2 = half-height peak width of o-xylene in seconds.~~
y_2 = width at half-height of the phenyldodecane peak, in seconds,
t_3 = retention time of the hexamethylbenzene peak, in seconds,
t_4 = retention time of the 1-methylnaphthalene peak, in seconds,
y_3 = width at half-height of the hexamethylbenzene peak, in seconds, and
y_4 = width at half-height of the 1-methylnaphthalene peak, in seconds.

If the resolution is less than ~~five,~~ listed in 9.4.3, check to see that all system components are functioning correctly and that the chromatographic dead volume has been minimized. Adjust the flow rate to see if this improves the resolution, and make sure that the mobile phase is of sufficiently high quality. Finally, regenerate or replace the column.

9.5 Repeat 9.4, and ensure that the repeatabilities for peak area measurements of *o*-xylene and 1-methylnaphthalene are within ~~the precision of this test method.~~ 2 %.

NOTE 13—If peak area repeatabilities are poor, check to see that the injection system is working optimally and that the baseline is stable (minimal drift) and noise-free.

10. Procedure

10.1 *Calibration:*

10.1.1 Prepare four calibration standards (A, B, C, and D), in accordance with the concentrations given in Table 1, by weighing, to the nearest 0.0001 g, the appropriate materials into 100 mL volumetric flasks and making up to the mark with heptane.

NOTE 14—The recommended concentrations in Table 1 will cover most petroleum materials distilling in the kerosene boiling range. Other standard concentrations may be used provided they meet the requirements of the test method (that is, linearity, detector sensitivity, and column resolution).

NOTE 15—The calibration standard solutions should be stored in tightly stoppered bottles (for example, 100 mL volumetric flasks) in a dark place between 5 °C and 25 °C. Under these conditions, the solutions are viable for at least six months.

10.1.2 When operating conditions are steady (see 9.4), inject ~~10 µL~~ 5 µL of Calibration Standard A. Record the chromatogram, and measure the peak areas for each aromatic standard. Ensure that baseline separation is obtained between all three components.

10.1.3 Repeat 10.1.2 using Calibration Standards B, C, and D.

10.1.4 Plot percent m/v (g/100 mL) concentration (on the y axis) against area counts (on the x axis) for each aromatic standard, that is, *o*-xylene and 1-methylnaphthalene. Calibration plots should be linear with a correlation coefficient greater than 0.999 and an intercept of less than ±0.01. A computer or data system may be used to interpret these calibrations.

NOTE 16—It should only be necessary to calibrate the refractive index detector on a daily basis.

NOTE 17—It is recommended that a reference kerosene or one of the four calibration standards be run after every five samples to check the stability of the system.

~~NOTE 18—To determine % (V/V) aromatic hydrocarbon types, establish % (V/V) calibration plots (mL/100 mL versus peak area) in place of % (m/V) calibration plots (g/100 mL versus peak area). Divide the % (m/V) concentrations of *o*-xylene and 1-methylnaphthalene by their respective densities at 20°C to convert to % (V/V) (mL/100 mL). See also Note 19 and Note 22.~~

10.1.5 To determine % (v/v) aromatic hydrocarbon types, establish % (v/v) calibration plots (mL/100 mL versus peak area) in place of % (m/v) calibration plots (g/100 mL versus peak area). Divide the % (m/v) concentrations of *o*-xylene and 1-methylnaphthalene by their respective densities at 20 °C to convert to % (v/v) (mL/100 mL). See also 10.2.5 and 11.1.1.

10.2 *Analysis of Samples:*

10.2.1 Weigh, to the nearest 0.001 g, between 4.9 g and 5.1 g of test portion into a 10 mL volumetric flask, and make up to the mark with heptane. Shake thoroughly to mix. Allow solution to stand for 10 min and filter (see 6.3), if necessary, to remove insoluble material.

10.2.1.1 For products in which the concentration of one or more aromatic hydrocarbon types fall outside the calibration range, prepare a more concentrated (for example, 10 g/10 mL) or more dilute (2 g/10 mL) test portion solution as appropriate.

~~NOTE 19—To determine % (V/V) aromatic hydrocarbon types, prepare a V/V dilution of the test portion by either *(1)* accurately pipetting 5 mL of test portion into a 10 mL volumetric flask and making up to the mark with heptane, or *(2)* dividing the test portion weight by its density determined using Test Method D4052 to convert to a volume. See also Note 18 and Note 22.~~

10.2.2 When operating conditions are steady (see 9.4) and identical to those used for obtaining the calibration data (see 10.1), inject ~~10 µL~~5 µL of the test portion solution (see 10.2.1) and start data collection.

10.2.3 With reference to Fig. 1, devise a suitable method to find and identify correctly the MAHs and DAHs. Fig. 1 shows a typical chromatogram for an aviation fuel.

10.2.4 Draw a baseline from just before the beginning of the non-aromatics peak to a point on the chromatogram where the baseline is stable and flat and all components have eluted. Drop vertical lines from valley to baseline at the appropriate points (see Fig. 1), and measure peak areas for MAHs and DAHs.

NOTE 18—If the chromatographic data have been processed automatically, visually check to see that the integration parameters have correctly identified and integrated the peaks.

10.2.5 To determine % (v/v) aromatic hydrocarbon types, prepare a v/v dilution of the test portion by either *(1)* accurately pipetting 5 mL of test portion into a 10 mL volumetric flask and making up to the mark with heptane, or *(2)* dividing the test portion weight by its density determined using Test Method D4052 to convert to a volume. See also 10.1.5 and 11.1.1.

11. Calculation

11.1 *Percent m/m Aromatic Hydrocarbon Type Contents*—Calculate the percent m/m contents for MAHs and DAHs using the following equation:

$$\text{\% m/m MAHs or DAHs} = \frac{[(A \times S) + I] \times V}{M} \quad (3)$$

where:

A = MAH or DAH peak area for the sample,
S = slope of MAH or DAH calibration plot (% m/v versus peak area),
I = intercept of MAH or DAH % m/v calibration plot,
M = mass (g) of test portion taken (see 10.2.1), and
V = total volume (mL) of test portion solution (see 10.2.1).