INTERNATIONAL

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Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry[1]

This standard is issued under the fixed designation D2425; 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.

1. Scope*

1.1 This test method covers an analytical scheme using the mass spectrometer to determine the hydrocarbon types present in conventional and synthesized hydrocarbons that have a boiling range of 160 °C to 343 °C (320 °F to 650 °F), 5 % to 95 % by volume as determined by Test Method D86. Samples with average carbon number value of paraffins between C_{12} and C_{16} and containing paraffins from C_{10} and C_{18} can be analyzed. Eleven hydrocarbon types are determined. These include: paraffins, noncondensed cycloparaffins, condensed dicycloparaffins, condensed tricycloparaffins, alkylbenzenes, indans or tetralins, or both, C_nH_{2n-10} (indenes, etc.), naphthalenes, C_nH_{2n-14} (acenaphthenes, etc.), C_nH_{2n-16} (acenaphthylenes, etc.), and tricyclic aromatics.

NOTE 1—This test method was developed on Consolidated Electrodynamics Corporation Type 103 Mass Spectrometers. Operating parameters for users with a Quadrupole Mass Spectrometer are provided.

1.2 This test method is intended for use with full boiling range products that contain no significant olefin content.

Biodiesel (FAME components) could interfere with the separation of the sample and the characteristic mass fragments of FAME compounds are not defined in the procedure.

Hydrocarbons containing tertiary carbon fragments, sometimes found in synthetic aviation fuels, will interfere with the characteristic mass fragments of paraffins and result in a false, elevated cycloparaffin content.

NOTE 2—"No significant olefin content" for this method means <2.0 % by volume by Test Method D1319.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.4 *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.* For a specific warning statement, see 11.1.

1.5 *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:*[2]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D2549 Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, 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

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to many common gas chromatographic procedures and terms. Detailed definitions of these can be found in Practice E355 and Terminology D4175.

3.2 *Definitions of Terms Specific to This Standard:*

[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 D02.04.0M on Mass Spectrometry.

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[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.

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

3.2.1 *conventional hydrocarbons, n*—hydrocarbons derived from the following conventional sources: crude oil, natural gas liquid condensates, heavy oil, shale oil, and oil sands.

3.2.2 *synthesized hydrocarbons, n*—hydrocarbons derived from alternative sources such as coal, natural gas, biomass, and hydrogenated fats and oils by processes such as gasification, Fischer-Tropsch synthesis, and hydroprocessing.

4. Summary of Test Method

4.1 Samples are separated into saturate and aromatic fractions by liquid chromatography, and each fraction is analyzed by mass spectrometry. The analysis is based on the summation of characteristic mass fragments to determine the concentration of hydrocarbon types.

4.2 The summation of characteristic mass fragments are defined as follows:

$\sum 71$ (paraffins) = total peak height of m/e^+ 71 + 85.

$\sum 67$ (mono or noncondensed polycycloparaffins, or both) = total peak height of m/e^+ 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97.

$\sum 123$ (condensed dicycloparaffins) = total peak height of m/e^+ 123 + 124 + 137 + 138 + ··· etc. up to 249 + 250.

$\sum 149$ (condensed tricycloparaffins) = total peak height of m/e^+ 149 + 150 + 163 + 164 + ··· etc. up to 247 + 248.

$\sum 91$ (alkyl benzenes) = total peak height of m/e^+ 91 + 92 + 105 + 106 + ··· etc. up to 175 + 176.

$\sum 103$ (indans or tetralins, or both) = total peak height of m/e^+ 103 + 104 + 117 + 118 + ··· etc. up to 187 + 188.

$\sum 115$ (indenes or C_nH_{2n-10}, or both) = total peak height of m/e^+ 115 + 116 + 129 + 130 + ··· etc. up to 185 + 186.

128 (naphthalene) = total peak height of m/e^+ 128.

$\sum 141$ (naphthalenes) = total peak height of m/e^+ 141 + 142 + 155 + 156 + ··· etc. up to 239 + 240.

$\sum 153$ (acenaphthenes or C_nH_{2n-14}, or both) = total peak height of m/e^+ 153 + 154 + 167 + 168 + ··· etc. up to 251 + 252.

$\sum 151$ (acenaphthylenes or C_nH_{2n-16}, or both) = total peak height of m/e^+ 151 + 152 + 165 + 166 + ··· etc. up to 249 + 250.

$\sum 177$ (tricyclic aromatics) = total peak height of m/e^+ 177 + 178 + 191 + 192 + ··· etc. up to 247 + 248.

4.3 The average carbon numbers of the hydrocarbon types are estimated from spectral data. Calculations are made from calibration data dependent upon the average carbon number of the hydrocarbon types. The results of each fraction are mathematically combined according to their mass fractions as determined by the separation procedure. Results are expressed in mass percent.

5. Significance and Use

5.1 A knowledge of the hydrocarbon composition of process streams and petroleum products boiling within the range of 160 °C to 343 °C (320 °F to 650 °F) is useful in following the effect of changes in process variables, diagnosing the source of plant upsets, and in evaluating the effect of changes in composition on product performance properties.

5.2 A test method to determine total cycloparafins and low level aromatic content is necessary to meet specifications for aviation turbine fuel containing synthesized hydrocarbons.

6. Interferences

6.1 Nonhydrocarbon types, such as sulfur and nitrogen-containing compounds, are not included in the matrices for this test method. If these nonhydrocarbon types are present to any large extent, (for example, mass percent sulfur >0.25) they will interfere with the spectral peaks used for the hydrocarbon-type calculation.

7. Sample Separation

7.1 Sample is to be separated into saturate and aromatic fractions. Liquid chromatography procedures based on Test Methods D2549, D1319, and D6379 have been used.

NOTE 3—Test Method D2549 is presently applicable only to samples having 5 % points of 232 °C (450 °F) or greater. Guidance on using Test Methods D1319 and D6379 is provided in the Annexes.

PROCEDURE A—MAGNETIC SECTOR SPECTROMETER

8. Apparatus

8.1 *Mass Spectrometer*—The suitability of the mass spectrometer to be used with this method of analysis shall be proven by performance tests described herein.

8.2 *Sample Inlet System*—Any inlet system permitting the introduction of the sample without loss, contamination, or change in composition. To fulfill these requirements it will be necessary to maintain the system at an elevated temperature in the range of 125 °C to 325 °C and to provide an appropriate sampling device.

8.3 *Microburet or Constant-Volume Pipet.*

9. Calibration

9.1 Calibration coefficients are attached which can be used directly provided:

9.1.1 Repeller settings are adjusted to maximize the m/e^+ 226 ion of *n*-hexadecane.

9.1.2 A magnetic field is used that will permit scanning from m/e^+ 40 to 292.

9.1.3 An ionization voltage of 70 eV and ionizing currents in the range 10 µA to 70 µA are used.

NOTE 4—The calibration coefficients were obtained for ion source conditions such that the ∑67/∑71 ratio for *n*-hexadecane was 0.26/1. The cooperative study of this test method indicated an acceptable range for this ∑ ratio between 0.2/1 to 0.30/1.

10. Performance Test

10.1 Generally, mass spectrometers are in continuous operation and should require no additional preparation before analyzing samples. If the spectrometer has been turned on only recently, it will be necessary to check its operation in accordance with this method and instructions of the manufacturer to ensure stability before proceeding.

10.2 *Mass Spectral Background*—Samples in the carbon number range C_{10} to C_{18} should pump out so that less than 0.1 % of the two largest peaks remain. For example, background peaks from a saturate fraction at m/e^+ 69 and 71 should be reduced to less than 0.1 % of the corresponding peaks in the mixture spectrum after a normal pump out time of 2 min to 5 min.

11. Mass Spectrometric Procedure

11.1 *Obtaining the Mass Spectrum for Each Chromatographic Fraction*—Using a microburet or constant-volume pipet, introduce sufficient sample through the inlet sample to give a pressure of 2 Pa to 4 Pa (15 mtorr to 30 mtorr) in the inlet reservoir. (**Warning—**Hydrocarbon samples of this boiling range are combustible.) Record the mass spectrum of the sample from m/e^+ 40 to 292 using the instrument conditions outlined in 9.1.1 – 9.1.3.

PROCEDURE B—QUADRUPOLE SPECTROMETER

12. Apparatus

12.1 *Mass Spectrometer*—Mass spectrometers provided with a quadrupole as ion separator and use electron impact at 70 ev have been used.

12.2 *Sample Inlet System*—Any inlet system permitting the introduction of the sample without loss, contamination, or change in composition. Separation of components is not required.

12.2.1 For sample fractions that do not contain solvents:

12.2.1.1 The inlet to introduce the sample into the detector can be an all glass inlet system (also known as AGIS) connected to the GC inlet and interfaced with the mass spectrometer with uncoated tubing. The inlet system is installed in a gas chromatograph and heated at 300 °C, isothermal.

12.2.1.2 Gas chromatography using a boiling point column.

12.2.2 For sample fractions that contain solvents, gas chromatography using a boiling point column should be used to isolate the solvent.

NOTE 5—Appendix X2 provides additional information on chromatography options for samples with or without solvents.

12.2.3 Split ratio should be adjusted to prevent detector overload.

13. Calibration

13.1 Mass calibration is performed using PerFluoroTriButylAmine (PFTBA) which contains the masses 69, 131, 219, 414, and 502. An ionization voltage of 70 ev is used.

13.2 Tune the spectrometer using the tune file recommended by the manufacturer. Typically, the masses of 69, 219, 502 are used for tuning with 219 being the ion for repeller maximum. Ensure that none of the masses are saturated.

13.3 It is possible to check the tuning by introducing n-hexadecane and verifying that the sum of the ∑67/∑71 = 0.2 – 0.3. Verify that the sum elements are those shown in 15.1, Eq 1 and Eq 2.

14. Mass Spectrometric Procedure

14.1 *Obtaining the Mass Spectrum for Each Chromatographic Fraction*—Using an automated sampling system or manual injection, inject an appropriate amount of each sample fraction. Record the mass spectrum of the sample from m/e^+ 50 to 300.

15. Calculations and Report

NOTE 6—A guideline for the calculations is available in Appendix X1.

15.1 *Aromatic Fraction*—Read peak heights from the record mass spectrum corresponding to m/e^+ ratios of 67 to 69, 71, 81 to 83, 85, 91, 92, 96, 97, 103 to 106, 115 to 120, 128 to 134, 141 to 148, 151 to 162, 165 to 198, 203 to 212, 217 to 226, 231 to 240, 245, 246, 247 to 252.
Find:

$$\sum 71 = 71 + 85 \quad (1)$$

$$\sum 67 = 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97 \quad (2)$$

TABLE 1 Parent Ion Isotope Factors and Mole Sensitivities

Carbon No.	*m/e*	Isotope Factor, K_1	Mole Sensitivity, K_2
Alkylbenzenes			
10	134	0.1101	85
11	148	0.1212	63
12	162	0.1323	60
13	176	0.1434	57
14	190	0.1545	54
15	204	0.1656	51
16	218	0.1767	48
17	232	0.1878	45
18	246	0.1989	42
		L_1	L_2
Naphthalenes			
11	142	0.1201	194
12	156	0.1314	166
13	170	0.1425	150
14	184	0.1536	150
15	198	0.1647	150
16	212	0.1758	150
17	226	0.1871	150
18	240	0.1982	150