Designation: D2425 – 04

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 virgin middle distillates 204 to 343°C (400 to 650°F) boiling range, 5 to 95 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 Corp. Type 103 Mass Spectrometers.

1.2 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety problems, 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.* For a specific hazard statement, see 10.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

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

3. Terminology

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

Σ71 (paraffins) = total peak height of m/e^+ 71 + 85.

Σ67 (mono or noncondensed polycycloparaffins, or both) = total peak height of m/e^+ 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97.

Σ123 (condensed dicycloparaffins) = total peak height of m/e^+ 123 + 124 + 137 + 138 + ⋯ etc. up to 249 + 250.

Σ149 (condensed tricycloparaffins) = total peak height of m/e^+ 149 + 150 + 163 + 164 + ⋯ etc. up to 247 + 248.

Σ91 (alkyl benzenes) = total peak height of m/e^+ 91 + 92 + 105 + 106 + ⋯ etc. up to 175 + 176.

Σ103 (indans or tetralins, or both) = total peak height of m/e^+ 103 + 104 + 117 + 118 + ⋯ etc. up to 187 + 188.

Σ115 (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.

Σ141 (naphthalenes) = total peak height of m/e^+ 141 + 142 + 155 + 156 + ⋯ etc. up to 239 + 240.

Σ153 (acenaphthenes or C_nH_{2n-14}, or both) = total peak height of m/e^+ 153 + 154 + 167 + 168 + ⋯ etc. up to 251 + 252.

Σ151 (acenaphthylenes or C_nH_{2n-16}, or both) = total peak height of m/e^+ 151 + 152 + 165 + 166 + ⋯ etc. up to 249 + 250.

Σ177 (tricyclic aromatics) = total peak height of m/e^+ 177 + 178 + 191 + 192 + ⋯ etc. up to 247 + 248.

4. Summary of Test Method

4.1 Samples are separated into saturate and aromatic fractions by Test Method D2549, 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. The average carbon numbers of the hydrocarbon types are estimated from spectral data. Calculations are

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

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.

NOTE 2—Test Method D2549 is presently applicable only to samples having 5 % points of 232°C (450°F) or greater.

5. Significance and Use

5.1 A knowledge of the hydrocarbon composition of process streams and petroleum products boiling within the range of 400 to 650°F (204 to 343°C) 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.

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. Apparatus

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

7.2 *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 to 325°C and to provide an appropriate sampling device.

7.3 *Microburet or Constant-Volume Pipet.*

8. Calibration

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

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

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

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

NOTE 3—The calibration coefficients were obtained for ion source conditions such that the $\Sigma67/\Sigma71$ ratio for *n*-hexadecane was 0.26/1. The cooperative study of this test method indicated an acceptable range for this Σ ratio between 0.2/1 to 0.30/1.

NOTE 4—Users of instruments other than Consolidated Electrodynamics Corp. Type 103 Mass Spectrometers may have to develop their own operating parameters and calibration data.

9. Performance Test

9.1 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 accor-

dance with this method and instructions of the manufacturer to ensure stability before proceeding.

9.2 *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 to 5 min.

10. Mass Spectrometric Procedure

10.1 *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 to 4 Pa (15 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 8.1.1-8.1.3.

11. Calculations

11.1 *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:

$$\Sigma71 = 71 + 85 \tag{1}$$

$$\Sigma67 = 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97 \tag{2}$$

$$\Sigma91 = \Sigma_{N=0}^{N=6}[(91 + 14N) + (92 + 14N)] \tag{3}$$

$$\Sigma103 = \Sigma_{N=0}^{N=6}[(103 + 14N) + (104 + 14N)] \tag{4}$$

$$\Sigma115 = \Sigma_{N=0}^{N=5}[(115 + 14N) + (116 + 14N)] \tag{5}$$

$$\Sigma141 = \Sigma_{N=0}^{N=7}[(141 + 14N) + (142 + 14N)] \tag{6}$$

$$\Sigma153 = \Sigma_{N=0}^{N=7}[(153 + 14N) + (154 + 14N)] \tag{7}$$

$$\Sigma151 = \Sigma_{N=0}^{N=7}[(151 + 14N) + (152 + 14N)] \tag{8}$$

$$\Sigma177 = \Sigma_{N=0}^{N=5}[(177 + 14N) + (178 + 14N)] \tag{9}$$

11.2 Calculate the mole fraction at each carbon number of the alkylbenzenes for $n = 10$ to $n = 18$ as follows:

$$\mu_n = [P_m - P_{m-1}(K_1)]/K_2 \tag{10}$$

where:
μ_n = mole fraction of each alkylbenzene as represented by n which indicates the number of carbons in each molecular species.
m = molecular weight of the alkylbenzene being calculated,
$m - 1$ = molecular weight minus 1,
P = polyisotopic mixture peak at m, $m - 1$,
K_1 = isotopic correction factor (see Table 1), and
K_2 = mole sensitivity for n (see Table 1).

NOTE 5—This step of calculation assumes no mass spectral pattern contributions from other hydrocarbon types to the parent and parent-1 peaks of the alkylbenzenes. Selection of the lowest carbon number 10 is based upon the fact that C_9 alkylbenzenes boil below 204°C (400°F) and their concentration can be considered negligible.

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

TABLE 2 Relationship Between Average Carbon Numbers of Alkylbenzenes, Paraffins, and Cycloparaffins

Alkylbenzenes	Paraffin and Cycloparaffin
Average Carbon No.	Average Carbon No.
10	11
11	12
12	13
13	15(14.5)
14	16(15.5)

11.3 Find the average carbon number of the alkylbenzenes, A, in the aromatic fraction as follows:

$$A = (\Sigma_{n=10}^{n=18} n \times \mu_n)/(\Sigma_{n=10}^{n=18} \mu_n) \quad (11)$$

11.4 Calculate the mole fraction at each carbon number of the naphthalenes for $n = 11$ to $n = 18$ as follows:

$$x_n = [P_m - P_{m-1}(L_1)]/L_2 \quad (12)$$

where:
x_n = mole fraction of each naphthalene as represented by n which indicates the number of carbons in each molecular species,
m = molecular weight of the naphthalenes being calculated,
$m - 1$ = molecular weight minus 1,
P = polyisotopic mixture peak at m, $m - 1$,
L_1 = isotopic correction factor (see Table 1), and
L_2 = mole sensitivity for n (see Table 1).

NOTE 6—This step of calculation assumes no mass spectral pattern contributions to the parent and parent-1 peaks of the naphthalenes. The concentration of naphthalene itself at a molecular weight of 128 shall be determined separately from the polyisotopic peak at m/e^+ 128 in the matrix calculation. The average carbon number for the naphthalenes shall be calculated from carbon number 11 (molecular weight 142) to 18 (molecular weight 240).

11.5 Find the average carbon number of the naphthalenes, B, in the aromatic fraction as follows:

$$B = (\Sigma_{n=11}^{n=18} n x_n)/(\Sigma_{n=11}^{n=18} x_n) \quad (13)$$

11.6 Selection of pattern and sensitivity data for matrix carbon number of the types present. The average carbon number of the paraffins and cycloparaffins ($\Sigma71$ and $\Sigma67$, respectively) are related to the calculated average carbon of the alkylbenzenes (11.3), as shown in Table 2. Both $\Sigma71$ and $\Sigma67$ are included in the aromatic fraction matrix to check on possible overlap in the separation. The other types present, represented by Σ's 103, 115, 153, and 151, are usually relatively low in concentration so that their parent ions are affected by other types present. The calculation of their average

carbon number is not straight forward. Therefore, their average carbon numbers are estimated by inspection of the aromatic spectrum. Generally, their average carbon numbers may be taken to be equivalent to that of the naphthalenes, or to the closest whole number thereof, as calculated in 11.5. The average carbon number of tricyclic aromatics $\Sigma177$ has to be at least C_{14} and in full boiling range middle distillates C_{14} may be used to represent the $\Sigma177$ types carbon number. From the calculated and estimated average carbon numbers of the hydrocarbon types, a matrix for the aromatic fraction is set up using the calibration data given in Table 3. A sample matrix for the aromatic fraction is shown in Table 4. The matrix calculations consist in solving a set of simultaneous linear equations. The pattern coefficients are listed in Table 3. The constants are the Σ values determined from the mass spectrum. Second approximation solutions are of sufficient accuracy. If many analyses are performed using the same type of a matrix, the matrix may be inverted for simpler, more rapid desk calculation. Matrices may also be programmed for automatic computer operations. The results of matrix calculations are converted to mass fractions by dividing by mass sensitivity. The mass fractions are normalized to the mass percent of the aromatic fraction, as determined by the separation procedure.

11.7 *Saturate Fraction*—Read peak at heights from the record of the mass spectrum corresponding to m/e^+ ratios of 67 to 69, 71, 81 to 83, 85, 91, 92, 96, 97, 105, 106, 119, 120, 123, 124, 133, 134, 137, 138, 147 to 152, 161 to 166, 175 to 180, 191 to 194, 205 to 208, 219 to 222, 233 to 236, 247 to 250. Find:

$$\Sigma71 = 71 + 85 \quad (14)$$

$$\Sigma67 = 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97 \quad (15)$$

$$\Sigma123 = \Sigma_{N=0}^{N=9} [(123 + 14N) + (124 + 14N)] \quad (16)$$

$$\Sigma149 = \Sigma_{N=0}^{N=7} [(149 + 14N) + (150 + 14N)] \quad (17)$$

$$\Sigma91 = \Sigma_{N=0}^{N=6} [(91 + 14N) + (92 + 14N)] \quad (18)$$

11.8 Selection of the pattern and sensitivity data for matrix calculation is dependent upon the average carbon number of the types present. The average carbon number of the paraffins and cycloparaffin types (Σ's 71, 69, 123, and 149), are related to the calculated average carbon number of the alkylbenzenes of the aromatic fraction (11.3), as shown in Table 2. The $\Sigma91$ is included in the saturate fraction as a check on the efficiency of the separation procedure. The pattern and sensitivity data for the $\Sigma91$ are based on the calculated or estimated average carbon number from the mass spectra of the aromatic fraction (see 11.3). From the determined average carbon numbers of the hydrocarbon types, a matrix for the saturate fraction is set up