



# Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 2425; 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.

## 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 D 86. 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 Electro-dynamics 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:

- D 86 Test Method for Distillation of Petroleum Products<sup>2</sup>
- D 2549 Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography<sup>2</sup>

## 3. Terminology

### 3.1 Descriptions of Terms Specific to This Standard;

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analyses.

Current edition approved April 10, 1999. Published June 1999. Originally published as D 2425 – 65 T. Last previous edition D 2425 – 93.

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

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

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

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

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

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

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

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

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

3.9 128 (naphthalene) = total peak height of  $m/e^+ 128$ .

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

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

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

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

## 4. Summary of Test Method

4.1 Samples are separated into saturate and aromatic fractions by Test Method D 2549, 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 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 D 2549, 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 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  $\mu$ A are used.

NOTE 3—The calibration coefficients were obtained for ion source conditions such that the  $\Sigma 67/\Sigma 71$  ratio for *n*-hexadecane was 0.26/1. The cooperative study of this test method indicated an acceptable range for this  $\Sigma$  ratio between 0.2/1 to 0.30/1.

NOTE 4—Users of instruments other than Consolidated Electroynamics 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 accordance 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**—See Note 5.) 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.

NOTE 5—**Warning:** Hydrocarbon samples of this boiling range are combustible.

## 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:

$$\Sigma 71 = 71 + 85, \quad (1)$$

$$\Sigma 67 = 67 + 68 + 81 + 82 + 83 + 96 + 97, \quad (2)$$

$$\Sigma 91 = \sum_{N=0}^{N=6} [(91 + 14N) + (92 + 14N)], \quad (3)$$

$$\Sigma 103 = \sum_{N=0}^{N=6}, \quad (4)$$

$$\Sigma 115 = \sum_{N=0}^{N=5}, \quad (5)$$

$$\Sigma 141 = \sum_{N=0}^{N=7}, \quad (6)$$

$$\Sigma 153 = \sum_{N=0}^{N=7}, \quad (7)$$

$$\Sigma 151 = \sum_{N=0}^{N=7}, \quad (8)$$

$$\Sigma 177 = \sum_{N=0}^{N=5} [(177 + 14N) + (178 + 14N)]. \quad (9)$$

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

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

where:

$\mu_n$  = 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 6—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.

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

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

**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

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 7—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:

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

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 ( $\Sigma 71$  and  $\Sigma 67$ , respectively) are related to the calculated average carbon of the alkylbenzenes (11.3), as shown in Table 2. Both  $\Sigma 71$  and  $\Sigma 67$  are included in the aromatic fraction matrix to check on possible overlap in the separation. The other types present, represented by  $\Sigma$ '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

**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)

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  $\Sigma 177$  has to be at least  $C_{14}$  and in full boiling range middle distillates  $C_{14}$  may be used to represent the  $\Sigma 177$  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  $\Sigma$  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:

$$\Sigma 71 = 71 + 85, \quad (14)$$

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

$$\Sigma 123 = \sum_{N=0}^{N=9}, \quad (16)$$

$$\Sigma 149 = \sum_{N=0}^{N=7}, \quad (17)$$

$$\Sigma 91 = \sum_{N=0}^{N=6} [(91 + 14N) + (92 + 14N)]. \quad (18)$$

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 ( $\Sigma$ '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  $\Sigma 91$  is included in the saturate fraction as a check on the efficiency of the separation procedure. The pattern and sensitivity data for the  $\Sigma 91$  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 using the calibration data given in Table 3. A sample matrix for the saturate fraction is shown in Table 5. The matrix calculations of the saturate fraction consists in solving a set of