Designation: D2425 – 04 (Reapproved 2009)

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

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 Corporation 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 warning 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:

$\Sigma71$ (paraffins) = total peak height of m/e^+ 71 + 85.

$\Sigma67$ (mono or noncondensed polycycloparaffins, or both) = total peak height of m/e^+ 67 + 68 + 69 + 81 + 82 + 83 + 96 + 97.

$\Sigma123$ (condensed dicycloparaffins) = total peak height of m/e^+ 123 + 124 + 137 + 138 + ⋯ etc. up to 249 + 250.

$\Sigma149$ (condensed tricycloparaffins) = total peak height of m/e^+ 149 + 150 + 163 + 164 + ⋯ etc. up to 247 + 248.

$\Sigma91$ (alkyl benzenes) = total peak height of m/e^+ 91 + 92 + 105 + 106 + ⋯ etc. up to 175 + 176.

$\Sigma103$ (indans or tetralins, or both) = total peak height of m/e^+ 103 + 104 + 117 + 118 + ⋯ etc. up to 187 + 188.

$\Sigma115$ (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.

$\Sigma141$ (naphthalenes) = total peak height of m/e^+ 141 + 142 + 155 + 156 + ⋯ etc. up to 239 + 240.

$\Sigma153$ (acenaphthenes or C_nH_{2n-14}, or both) = total peak height of m/e^+ 153 + 154 + 167 + 168 + ⋯ etc. up to 251 + 252.

$\Sigma151$ (acenaphthylenes or C_nH_{2n-16}, or both) = total peak height of m/e^+ 151 + 152 + 165 + 166 + ⋯ etc. up to 249 + 250.

$\Sigma177$ (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

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 $\Sigma 67/\Sigma 71$ ratio for *n*-hexadecane was 0.26/1. The cooperative study of this test method indicated an acceptable range for this Σ ratio between 0.2/1 to 0.30/1.

NOTE 4—Users of instruments other than Consolidated Electrodynamics Corporation 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:

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

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

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

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

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

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

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

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

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

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:

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

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

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

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:

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

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 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 $\Sigma 177$ 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 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:

$$\Sigma 71 = 71 + 85 \qquad (14)$$

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

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

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

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

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 $\Sigma 91$ 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

TABLE 3 Patterns and Sensitivities for Middle Distillates

Hydrocarbon Type	Paraffins				Noncondensed Cycloparaffins				Condensed Dicycloparaffins			Condensed Tricycloparaffins		
Carbon No...	12	13	14.5	15.5	12	13	14.5	15.5	13	14.5	15.5	13	14.5	15.5
Peaks read:														
$\Sigma71$	100	100	100	100	4	4	6	6	2	1.1	1.5	1	1	2
$\Sigma67$	19	21	23	26	100	100	100	100	160	130	150	175	170	150
$\Sigma123$	...	...	0.1	0.2	1	1	1	3	100	100	100	26	10	20
$\Sigma149$	...	...	...	...	...	...	...	...	0.2	5	8	100	100	100
$\Sigma91$ to 176	0.4	0.4	0.4	0.4	...	...	0.2	3	4	4	5	15	15	20
$\Sigma103$ to 188	...	...	...	...	...	...	...	...	...	...	...	1	...	3
$\Sigma115$ to 186	0.5	...	...	...	1	1	1	1	0.5	...	...	...	...	...
$\Sigma128$ pk	...	...	...	...	...	...	...	...	...	...	...	...	...	...
$\Sigma141$	9	9	10	12	...	...	2	0.3	0.2	...	...	0.1	0.1	0.4
$\Sigma153$	...	...	...	...	1	2	2	2	...	...	...	...	...	...
$\Sigma151$	...	...	...	...	1	5	7	10	...	...	...	...	...	...
$\Sigma177$	...	...	...	...	...	...	2	2	...	...	...	...	...	...
Sensitivity:														
Mole	148	170	192	238	302	347	416	439	220	268	298	220	268	298
Volume	66	70	74	81	145	153	165	170	107	137	117	118	150	127
Mass	87	92	97	104	180	191	204	209	122	156	134	124	158	135

Hydrocarbon Type	Alkylbenzenes				Indans or Tetralins, or Both				Indenes or C_nH_{2n-10}, or Both			Naphthalenes		
Carbon No...	11	12	13	14	10	11	12	13	10	13	10	11	12	13
Peaks read:														
$\Sigma71$	0.3	0.3	0.4	0.5	0.2	0.4	0.4	1	0.3	1.7	0.5	5.2	1.5	2
$\Sigma67$	0.7	0.7	2	3	0.6	1	1	2	0.3	6.0	0.8	1.2	1.5	2
$\Sigma123$	0.1	0.1	0.2	0.3	...	0.1	1	2	0.4	4.8	0.5	0.5	7.8	4
$\Sigma149$	1.3	1	1.5	2	...	0.1	0.2	0.3	...	0.9	...	0.1	0.7	0.5
$\Sigma91$ to 176	100	100	100	100	15 to 34[A,B]	18	17	15	0.6	6.2	0.1	0.9	1	1
$\Sigma103$ to 188	9	10	10	9	100	100	100	100	1.5	20.3	0.6	0.1	0.1	0.1
$\Sigma115$ to 186	4.4	4.5	5	5	20 to 12[A,B]	28	25	25	100	100	11.4	23	19	18
$\Sigma128$ pk	0.7	1	1	1	3	5.4	7	...	15	13	100	0.7	5.6	5.6
$\Sigma141$	...	...	...	...	...	1.0	2.5	...	...	28	...	100	100	100
$\Sigma153$	...	...	...	...	...	...	...	...	...	6.1	...	...	8	10
$\Sigma151$	...	...	...	...	...	...	...	...	...	4.5	...	...	7	7
$\Sigma177$	...	...	...	...	...	...	...	...	...	0.6	...	...	...	...
Sensitivity:														
Mole	450	450	450	450	380	420	420	420	410	372	236	360	380	380
Volume	265	242	222	206	280	276	250	227	307	198	211	259	248	226
Mass	304	278	256	237	288	288	263	241	315	200	184	254	244	224

Hydrocarbon Type	Acenaphthenes or C_nH_{2n}-14, or Both		Acenaphthylenes or C_nH_{2n}-16		Tricyclic Aromatics	Characteristic Mass Groupings	
Carbon No...	12	13	12	13	14	Peaks Read	Hydrocarbon Types
Peaks read:							
$\Sigma71$	1	1	1	1	0.6	$\Sigma71$ = 71, 85	paraffins
$\Sigma67$	0.3	2	1	5	0.7	$\Sigma67$ = 67, 68, 69, 81, 82, 83, 96, 97	cycloparaffins, mono or noncondensed cycloparaffins
$\Sigma91$ to 176	0.1	5	1	3	18		
$\Sigma103$ to 188	...	3	0.2	3	1.5	$\Sigma123$ = 123, 134, 137, 138 up to 249, 250	condensed dicycloparaffins
$\Sigma115$ to 186	0.8	0.8	0.3	2.7	1.0	$\Sigma149$ = 149, 150, 163, 164 up to 247, 248	condensed tricycloparaffins
$\Sigma128$ pk	1	0.7	0.2	0.1	0.8	$\Sigma91$ = 91, 92, 105, 106 up to 175, 176	alkylbenzenes
$\Sigma141$	8	10	1	...	0.3	$\Sigma103$ = 103, 104, 117, 118, up to 187, 188	indan or tetrains, or both
$\Sigma153$	100	100	17	15	3.5	$\Sigma115$ = 115, 116, 129, 130 up to 185, 186	C_nH_{2n-10}(indenes, etc.)
$\Sigma151$	27	20	100	100	30	$\Sigma128$ = poly 128 pk	naphthalene
$\Sigma177$	...	4	...	15	100	$\Sigma141$ = 141, 142, 155, 156 up to 239, 240	naphthalenes
Sensitivity:							
Mole	330	330	340	340	365	$\Sigma153$ = 153, 154, 167, 168 up to 251, 252	C_nH_{2n-14}(acenaphthenes, etc.)
Volume	218	198	199	187	211	$\Sigma151$ = 151, 152, 165, 166 up to 249, 250	C_nH_{2n-16}(acenaphthylenes, etc.)
Mass	214	196	224	205	205	$\Sigma177$ = 177, 178, 191, 192 up to 247, 248	tricyclic aromatics

[A] = methyl indans.

[B] tetralins.

TABLE 4 Aromatic Concentration Matrix

Hydrocarbon Type	Paraffins	Cycloparaffins	Alkylben-zenes	Indans and Tetralins	Indenes	Naphthalene	Naphthalenes	Acenaph-thenes C_nH_{2n-14}	Acenaph-thylenes C_nH_{2n-16}	Tricyclic Aromatics
Carbon No.	15.5	15.5	14	13	13	10	13	13	13	14
Peaks read:										
$\Sigma 71$	100	6	0.5	1	1.7	0.5	2	1	1	0.6
$\Sigma 67$	26	100	3	2	6	0.8	2	2	5	0.7
$\Sigma 91$	0.4	3	100	15	6.2	0.1	1	5	3	18
$\Sigma 103$	...	2	9	100	20.3	0.6	0.1	3	3	1.5
$\Sigma 115$	...	1	5	25	100	11.4	18	0.8	2.7	1
$\Sigma 128$ pk	...	...	1	3	13	100	5.6	0.7	0.1	0.8
$\Sigma 141$	12	0.3	...	...	28	...	100	10	...	0.3
$\Sigma 153$	...	2	...	...	6.1	...	10	100	15	3.5
$\Sigma 151$	...	10	...	...	4.5	...	7	20	100	30
$\Sigma 177$	...	2	...	...	0.6	...	...	4	15	100
Sensitivity:										
Mole	238	439	450	420	372	236	380	330	340	365
Volume	81	170	206	227	198	211	226	198	187	211
Weight	105	209	237	241	200	184	224	196	205	205

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 simultaneous linear equations. The results of the matrix calculations (second approximation solutions are sufficient) are converted to mass fractions by dividing by mass sensitivity. The mass fractions are normalized to the mass percent of the saturate fraction as determined by the separation procedure.

12. Precision and Bias

12.1 The precision of this test method as obtained by statistical examination of interlaboratory test results on samples having the composition given in Table 6 is as follows:

12.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would be in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 7 only in one case in twenty.

12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 7 only in one case in twenty.

TABLE 6 Composition of Samples Tested[A]

Component	Mean, Mass, %	σ_r[B]	σ_R[C]
Sample No. 7[D]:			
Paraffins	44.25	0.16	1.30
Monocycloparaffin	22.04	0.34	1.70
Dicyloparaffin	8.54	0.23	1.42
Tricycloparaffin	2.84	0.11	0.64
Alkylbenzene	0.33	0.04	0.10
Sample No. 8[E]:			
Paraffins	0.07	0.14	0.14
Cycloparaffin	0.75	0.15	0.25
Alkylbenzene	5.10	0.10	0.44
Indan and/or tetralin	3.65	0.09	0.14
$C_nH2n-10$	2.05	0.08	0.20
Naphthalenes	5.15	0.08	0.29
$C_nH2n-14$	2.50	0.04	0.28
$C_nH2n-16$	1.65	0.10	0.18
$C_nH2n-18$	1.05	0.04	0.14

[A] Twelve laboratories cooperated and each sample was run twice.
[B] σ_r = repeatability standard deviation.
[C] σ_R = reproducibility standard deviation.
[D] Sample No. 7 = saturate fraction of a virgin middle distillate (78.0 wt % of total).
[E] Sample No. 8 = aromatic fraction of a virgin middle distillate (22.0 wt % of total).

NOTE 7—If samples are analyzed that differ appreciably in composition from those used for the interlaboratory study, this precision statement may not apply.

NOTE 8—The precision for this test method was not obtained in accordance with D02-1007.

TABLE 5 Saturate Concentration Matrix

Hydrocarbon Type	Paraffins	Monocyclo-paraffins	Dicyclo-paraffins	Tricyclo-paraffins	Alkyl-benzenes
Carbon No.	15.5	15.5	15.5	15.5	14
$\Sigma 71$	100	6	1.5	2	0.5
$\Sigma 67$	26	100	150	150	3
$\Sigma 123$	0.2	3	100	20	0.3
$\Sigma 149$	...	...	8	100	2
$\Sigma 91$	0.4	3	5	20	100
Sensitivity:					
Mole	238	439	298	298	450
Volume	81	170	117	127	206
Weight	105	209	134	135	237

TABLE 7 Precision of Test Method

Compound	Concentration Mass, %	Repeatability	Reproducibility
Saturate Fraction:			
Paraffins	40 to 50	0.5	4.0
Monocycloparaffins	18 to 25	1.1	5.2
Dicycloparaffins	6 to 12	0.7	4.4
Tricycloparaffins	1 to 5	0.3	2.0
Alkylbenzenes	0 to 3	0.2	0.3
Aromatic Fraction:			
Paraffins	0 to 2	0.4	0.6
Cycloparaffins	0 to 2	0.5	0.9
Alkylbenzenes	3 to 8	0.3	1.4
Indan and/or tetralins	2 to 5	0.3	0.5
$C_nH2n-10$	0 to 4	0.3	0.7
Naphthalenes	3 to 8	0.3	1.0
$C_nH2n-14$	0 to 3	0.1	0.9
$C_nH2n-16$	0 to 3	0.3	0.7
$C_nH2n-18$	0 to 3	0.1	0.4

12.2 *Bias*—Bias cannot be determined because there is no acceptable reference material suitable for determining the bias for this test method.

13. Keywords

13.1 hydrocarbon types; mass spectrometry; middle distillates