Standard Test Method for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry[1]

This standard is issued under the fixed designation D2789; 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 the determination by mass spectrometry of the total paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indans or tetralins or both, and naphthalenes in gasoline having an olefin content of less than 3 % by volume and a 95 % distillation point of less than 210 °C (411 °F) as determined in accordance with Test Method D86. Olefins are determined by Test Method D1319, or by Test Method D875.

1.2 It has not been determined whether this test method is applicable to gasoline containing oxygenated compounds (for example, alcohols and ethers).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D875 Method for Calculating of Olefins and Aromatics in Petroleum Distillates from Bromine Number and Acid Absorption (Withdrawn 1984)[3]

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

D2001 Test Method for Depentanization of Gasoline and Naphthas

D2002 Practice for Isolation of Representative Saturates Fraction from Low-Olefinic Petroleum Naphthas (Withdrawn 1998)[3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 The summations of characteristic mass fragments are defined as follows (equations are identical to those in 11.1):

$$\sum 43\ (\text{paraffins}) = \text{total peak height of } m/e^{+}\ 43+57+71+85+99. \tag{1}$$

$$\sum 41\ (\text{monocycloparaffins}) = \text{total peak height of } m/e^{+}\ 41+55+69+83+97. \tag{2}$$

$$\sum 67\ (\text{dicycloparaffins}) = \text{total peak height of } m/e^{+}\ 67+68+81+82+95+96. \tag{3}$$

$$\sum 77\ (\text{alkylbenzenes}) = \text{total peak height of } m/e^{+}\ 77+78+79+91+92+105+106+119+120+133+134+147+148+161+162. \tag{4}$$

$$\sum 103\ (\text{indans and tetralins}) = \text{total peak height of } m/e^{+}\ 103+104+117+118+131+132+145+146+159+160. \tag{5}$$

$$\sum 128\ (\text{naphthalenes}) = \text{total peak height of } m/e^{+}\ 128+141\pm 142+155+156. \tag{6}$$

$$T = \text{total ion intensity} = \sum 41+\sum 43+\sum 67+\sum 77+\sum 103+\sum 128. \tag{7}$$

3.1.2 *carbon number*—by definition, is the average number of carbon atoms in the sample.

3.1.3 *mass number*—with a plus sign as superscript, is defined as the peak height associated with the same mass number.

4. Summary of Test Method

4.1 Samples are analyzed by mass spectrometry, based on the summation of characteristic mass fragments, to determine the concentration of the hydrocarbon types. The average number of carbon atoms of the sample is estimated from

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[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 Spectroscopy.

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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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

spectral data. Calculations are made from calibration data which are dependent upon the average number of carbon atoms of the sample. Results are expressed in liquid volume percent.

5. Significance and Use

5.1 A knowledge of the hydrocarbon composition of gasoline process streams, blending stocks and finished motor fuels is useful in following the effect of changes in plant operating conditions, diagnosing process upsets, blending finished products and in evaluating the relationship between composition and performance properties.

6. Apparatus

6.1 *Mass Spectrometer*—Any mass spectrometer that passes the performance test described in Section 8.

NOTE 1—Calibration and precision data for this method were obtained on Consolidated Electrodynamics Corp. Type 21-101, 21-102, and 21-103 mass spectrometers. These instruments operated with an ion source temperature at or near 250 °C and at a constant magnetic field of about 3100 gauss (G) to 3500 G. Laboratories using either Consolidated Electrodynamics Corp. mass spectrometers that operate with different parameters or instruments other than this design should check the applicability of the calibration data in Table 1. If necessary, individual laboratories should develop their own calibration data using the blends described in Table 2.

6.2 *Sample Inlet System*—Any sample inlet system that allows the introduction of the text mixture (8.2) without loss, contamination, or change of composition.

NOTE 2—Laboratory testing has shown that, unless a special sampling technique or a heated inlet system is used, relatively large errors will occur in the determination of small quantities of indans, tetralins, and naphthalenes.

6.3 *Manometer*—A manometer suitable for direct reading in the 0 mtorr to 100 mtorr (0 Pa to 13 Pa) range is optional.

NOTE 3—The expression mtorr as used in this procedure replaces the older μ (micron) unit of pressure.

6.4 *Microburet or Constant-Volume Pipet.*

7. Reference Standards

7.1 Samples of the following hydrocarbons will be required: 2-methylpentane, 2,4-dimethylpentane, *n*-octane, methylcyclopentane, methylcyclohexane, *cis*-1,2-dimethylcyclohexane, benzene, toluene, and *p*-xylene (**Warning—**Extremely flammable liquids. Benzene is a

TABLE 1 Calibration Data

	$\sum 43/T$	$\sum 41/T$	$\sum 67/T$	$\sum 77/T$	$\sum 103/T$	$\sum 128/T$	Reference[A]
Paraffins:							
C_6	0.6949	0.3025	0.0019	0.0006	...	...	(1)
C_7	0.7379	0.2583	0.0027	0.0010	...	...	(3)
C_8	0.7592	0.2362	0.0032	0.0014	...	...	(3)
C_9	0.7462	0.2350	0.0052	0.0021	...	0.0113	(12)
C_{10}	0.7772	0.2007	0.0056	0.0014	...	0.0151	(13)
Monocycloparaffins:							
C_6	0.1234	0.8218	0.0460	0.0086	...	...	(1)
C_7	0.0731	0.8213	0.0952	0.0104	...	...	(3)
C_8	0.0737	0.8279	0.0866	0.0117	...	...	(3)
C_9	0.0884	0.8029	0.0942	0.0140	0.0003	0.0003	(12)
C_{10}	0.1471	0.6272	0.2176	0.0080	...	...	(13)
Dicycloparaffins:							
C_8	0.0057	0.1848	0.7843	0.0246	0.0004	...	(4)
C_9	0.0171	0.2270	0.7070	0.0483	0.0005	...	(5)
C_{10}	0.0114	0.2973	0.6582	0.0324	0.0006	...	(6)
Alkylbenzenes:							
C_6	0.0004	0.0004	...	0.9992	...	...	(2)
C_7	0.0146	0.0120	0.0007	0.9726	...	...	(3)
C_8	0.0033	0.0112	0.0007	0.9488	0.0359	...	(3)
C_9	0.0061	0.0218	0.0020	0.9103	0.0598	...	(12)
C_{10}	0.0095	0.0350	0.0025	0.8656	0.0839	0.0034	(13)
Indans and tetralins:							
C_9	0.0144	0.0101	0.0002	0.1600	0.8154	...	(7)
C_{10}	0.0062	0.0123	0.0044	0.2314	0.7236	0.0222	(8)
C_{11}	0.0231	0.0199	0.0017	0.1619	0.7456	0.0477	(9)
Naphthalenes:							
C_{10}	0.0121	0.0037	0.0008	0.0581	0.0065	0.9188	(10)
C_{11}	0.0702	0.0140	0.0011	0.0172	0.0018	0.8957	(11)

[A] References to source of calibration data:
(1) National cooperative by letter of Nov. 22, 1965.
(2) Local task group cooperative by meeting of March 1966.
(3) National cooperative by letter of Aug. 6, 1962.
(4) API No. 448, 100 %, bicyclo-(3.3.0)-octane.
(5) Shell data, 100 %, for 1-methyl-cis-(3.3.0)-bicyclooctane.
(6) API No. 412, 100 %, trans-decalin.
(7) Unweighted API No. 413 and No. 1214 spectra of indan.
(8) API No. 1103, 13 %; API No. 1104, 13 %; API No. 941, 37 %; API No. 539, 37 %.
(9) Unweighted averages of API Nos. 1216, 1106, 1107, 1108, 1109.
(10) Unweighted average of local task group (3 laboratories) data.
(11) Unweighted average of API No. 990 and No. 991.
(12) National cooperative by letter of Oct. 11, 1967.
(13) Proposed Method of Test for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry; Appendix VII D2-1958.

TABLE 2 Compositions of Calibration Mixtures

Component (Volume Percent)	Paraffins	Cyclo-paraffins	Cyclo-Alkyl-benzenes
C_6 Blends			
n-Hexane	46	...	...
2-Methylpentane	28	...	...
3-Methylpentane	20	...	...
2-2-Dimethylbutane	1	...	...
2,3-Dimethylbutane	5	...	...
Cyclohexane	...	46	...
Methylcyclopentane	...	54	...
Benzene	...	...	100
C_7 Blends			
n-Heptane	45	...	...
2-Methylhexane	23	...	...
3-Methylhexane	16	...	...
2,2-Dimethylpentane	4	...	...
2,3-Dimethylpentane	6	...	...
2,4-Dimethylpentane	5	...	...
3,3-Dimethylpentane	1	...	...
Methylcyclohexane	...	57	...
Ethylcyclopentane	...	9	...
1,1-Dimethylcyclopentane	...	4	...
1,*t*-2-Dimethylcyclopentane	...	14	...
1,*t*-3-Dimethylcyclopentane	...	16	...
Toluene	...	...	100
C_8 Blends			
n-Octane	39	...	...
2-Methylheptane	19	...	...
3-Methylheptane	16	...	...
4-Methylheptane	8	...	...
3-Ethylhexane	3	...	...
2,3-Dimethylhexane	4	...	...
2,4-Dimethylhexane	5	...	...
2,5-Dimethylhexane	6	...	...
Ethylcyclohexane	...	20	...
1,*t*-2-Dimethylcyclohexane	...	18	...
1,*c*-3-Dimethylcyclohexane	...	25	...
1,*t*-4-Dimethylcyclohexane	...	11	...
1-Methyl-*c*-2-ethylcyclopentane	...	7	...
1,1,3-Trimethylcyclopentane	...	5	...
1,*t*-2,*c*-3-Trimethylcyclopentane	...	9	...
1,*t*-2,*c*-4-Trimethylcyclopentane	...	5	...
Ethylbenzene	...	...	10
p-Xylene	...	...	23
m-Xylene	...	...	46
o-Xylene	...	...	21

Component (Volume Percent)	Paraffins	Cyclo-paraffins	Alkyl-benzenes
C_9 Blends			
n-Nonane	33	...	...
2-Methyloctane	20	...	...
3-Methyloctane	16	...	...
4-Methyloctane	8	...	...
3-Ethylheptane	3	...	...
2,6-Dimethylheptane	12	...	...
2,2-Dimethylheptane	2	...	...
3,3-Diethylpentane	1	...	...
2,2,5-Trimethylhexane	2	...	...
2,2,5-Trimethylhexane	1	...	...
2,4-Dimethyl-3-ethylpentane	1	...	...
2,2,3,3-Tetramethylpentane	1	...	...
n-Propylcyclohexane	...	1	...
Isopropylcyclohexane	...	2	...
1-Methyl-*c*-2-ethylcyclohexane	...	3	...
1-Methyl-*t*-2-ethylcyclohexane	...	4	...
1-Methyl-*c*-3-ethylcyclohexane	...	8	...
1-Methyl-*t*-3-ethylcyclohexane	...	8	...
1-Methyl-*c*-4-ethylcyclohexane	...	4	...
1-Methyl-*t*-4-ethylcyclohexane	...	5	...
1,*c*-2, *c*-3-trimethylcyclohexane	...	2	...
1,*t*-2, *t*-3-trimethylcyclohexane	...	3	...
1,*t*-2,*c*-3-trimethylcyclohexane	...	3	...
1,*t*-2,*c*-4-trimethylcyclohexane	...	15	...
1,*t*-2,*t*-4-trimethylcyclohexane	...	15	...
1,*c*-3,*c*-5-trimethylcyclohexane	...	5	...
1,*c*-3,*t*-5-trimethylcyclohexane	...	5	...
n-Butylcyclopentane	...	1	...
1,*c*-2-Diethylcyclopentane	...	12	...
1,*t*-2,*c*-3,*t*-4-tetramethylcyclopentane	...	4	...
n-Propylbenzene	...	...	3
Isopropylbenzene	...	...	1
1-Methyl-2-ethylbenzene	...	...	8
1-Methyl-3-ethylbenzene	...	...	19
1-Methyl-4-ethylbenzene	...	...	11
1,2,3-Trimethylbenzene	...	...	10
1,2,4-Trimethylbenzene	...	...	36
1,3,5-Trimethylbenzene	...	...	12

poison, carcinogen, and is harmful or fatal if swallowed.). Only reagent grade chemicals conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[4] National Institute of Standards and Technology (NIST) standard hydrocarbon samples, or other hydrocarbons of equal purity should be used.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8. Performance Test

8.1 *Calibration for Test Mixture*—Calibrate the instrument in accordance with the manufacturer's instructions for the compounds listed in 7.1, using the same manipulative technique as described in 10.2. Express the calibration data in units of peak height per unit of liquid volume (V) at constant sensitivity. Determine $\sum 41/V$, $\sum 43/V$, and $\sum 77/V$ for each of the reference standards and calculate a weighted average value for each hydrocarbon group type in accordance with the composition of the test mixture as described in 8.2. Construct an inverse from the averaged coefficients.

NOTE 4—The volume, V, ordinarily is expressed as microlitres.

NOTE 5—A desk calculator frequently is used for the calculation of 8.1 and in such cases small inverse terms can be undesirable. If necessary, it is permissible to divide all averaged coefficients by some suitable constant prior to inversion in order to obtain larger values in the inverse.

8.2 *Test Mixture*—Prepare the synthetic mixture by weight from reference standards[4] to obtain a final composition approximating the following but accurately known within ± 0.07 %:

Reference Standard	Liquid Volume Percent in Mixture	Approximate Weight in Grams to Give 5 mL of Mixture
2-Methylpentane	7.2	0.237
2,4-Dimethylpentane	9.4	0.318
n-Octane	16.6	0.587
Methylcyclopentane	7.1	0.267
Methylcyclohexane	10.0	0.387
cis-1,2-Dimethylcyclohexane	15.5	0.620
Benzene	7.7	0.341
Toluene	10.0	0.436
p-Xylene	16.5	0.714
	100.0	3.907

Record the mass spectrum of the test mixture from m/e^+ 32 to 120 using the manipulative technique as described in 10.2. Compute $\sum 41/V$, $\sum 43/V$, and $\sum 77/V$ from the spectrum of the test mixture and calculate the composition using these values and the inverse of 8.1. The calculated composition should agree with known concentrations within the following limits:

	Percent
Total paraffins	±0.8
Total cycloparaffins	±1.3
Total aromatics	±0.7

If the test mixture cannot be analyzed successfully, consideration should be given to interference, stability, sensitivity, resolution, sample handling, or ability of the analyst.

8.3 *Background*—After pumping out the test mixture specified in 10.2, scan the mass spectrum from m/e^+40 to 100. Background peaks at 43 and 91 should be less than 0.1 % of the corresponding peaks in the mixture spectrum. If both tests of performance are met, it may be presumed that the instrument is satisfactory for sample analysis.

9. Sample Preparation

9.1 Dependentanize the sample in accordance with Test Method D2001.

9.2 Determine the olefin content of the dependentanized sample in accordance with Test Methods D1319 or D875.

10. Procedure

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, check its operation according to the manufacturer's instructions to ensure stability before proceeding. Then make the performance test (Section 8).

10.2 *Obtaining the Mass Spectrum*—Using a microburet[5] or a constant-volume pipet, introduce sufficient sample through the inlet system to give a pressure of 20 to 60 mtorr (2.7 to 8.0 Pa). Record the amount of sample introduced and the final pressure after expansion into the inlet system when a microburet and manometer are used. Recharge the sample until pressure readings that differ by 1 % or less are obtained. Attaining this pressure check means that a given microburet is being used at constant volume. When the pressure check is obtained, admit the sample to the mass spectrometer and record the mass spectrum of the sample from m/e^+ 32 to 186.

11. Calculation

11.1 *Peaks*—Read peak heights from the record of the mass spectrum of the sample corresponding to m/e^+ ratios of 41, 43, 55, 57, 67, 68, 69, 71, 77, 78, 79, 81, 82, 83, 84, 85, 86, 91, 92, 95, 96, 97, 98, 99, 100, 103, 104, 105, 106, 112, 113, 114, 117, 118, 119, 120, 126, 127, 128, 131, 132, 133, 134, 140, 141, 142, 145, 146, 147, 148, 154, 155, 156, 159, 160, 161, 162, 168, 169, 170.

11.1.1 Calculate the following combined peak heights by adding together the indicated peaks:

$$\sum 43 = m/e^+\ 43+57+71+85+99. \tag{8}$$

$$\sum 41 = m/e^+\ 41+55+69+83+97. \tag{9}$$

$$\sum 67 = m/e^+\ 67+68+81+82+95+96. \tag{10}$$

$$\sum 77 = m/e^+\ 77+78+79+91+92+105+106+119+120+133+134+147+148+161+162. \tag{11}$$

$$\sum 103 = m/e^+\ 103+104+117+118+131+132+145+146+159+160. \tag{12}$$

$$\sum 128 = m/e^+\ 128+141 \pm 142+155+156. \tag{13}$$

$$T = \text{total ion intensity} = \sum 41+\sum 43+\sum 67+\sum 77+\sum 103+\sum 128. \tag{14}$$

11.2 *Carbon Number Calculated from Spectral Data:*

11.2.1 *Calculation of Alkylbenzene Apparent Carbon Number:*

11.2.1.1 Calculate monoisotopic peaks at 92, 106, 120, 134, 148, and 162:

$$\text{Mono } 92 = 92^+ - 0.0769\,(91^+) \tag{15}$$

$$\text{Mono } 106 = 106^+ - 0.0880\,(105^+) \tag{16}$$

$$\text{Mono } 120 = 120^+ - 0.0991\,(119^+) \tag{17}$$

$$\text{Mono } 134 = 134^+ - 0.1102\,(133^+) \tag{18}$$

$$\text{Mono } 148 = 148^+ - 0.1212\,(147^+) \tag{19}$$

$$\text{Mono } 162 = 162^+ - 0.1323\,(161^+) \tag{20}$$

11.2.1.2 Convert the poly 78 mixture and the monoisotopic peaks to a molar basis by multiplying each by the following factors:

Poly 78 × 1.0	Mono 134 × 2.7
Mono 92 × 1.7	Mono 148 × 2.8
Mono 106 × 2.2	Mono 162 × 2.9
Mono 120 × 2.4	

11.2.1.3 Normalize the products of the preceding step to obtain the relative mole fractions of the C_6 to C_{12} alkylbenzenes. An apparent carbon number can then be calculated by

[5] Satisfactory microburets are described in the following sources: Taylor, R. C., and Young, W. S., "Application to Spectrometer Calibration and to Preparation of Known Mixtures," *Analytical Chemistry*, ANCHA, Vol 17, 1945, p. 811; and Purdy, K. M., and Harris, R. J., *Ibid,* Vol 22, 1950, p. 1337.

totaling the products of each mole fraction and the corresponding number of carbon atoms per molecule. This carbon number is assumed to apply to all akylbenzenes, indans, tetralins, and naphthalenes.

11.2.2 *Calculation of Paraffin Apparent Carbon Number* (Note 5):

11.2.2.1 Calculate monoisotopic peaks at 86, 100, 114, 128, 142, 156, 170:

$$\text{Mono } 86 = 86^{+} - 0.0668\,(85^{+}) + 0.0026\,(84^{+}) - 0.014\,(\text{mono } 92^{+}) - 0.008\,(\text{mono } 106^{+}) - 0.008\,(\text{mono } 120^{+}) \quad (21)$$

$$\text{Mono } 100 = 100^{+} - 0.0779\,(99^{+}) + 0.0034\,(98^{+}) - Hg\,(\text{Note } 7) \quad (22)$$

$$\text{Mono } 114 = 114^{+} - 0.0890\,(113^{+}) + 0.0044\,(112^{+}) \quad (23)$$

$$\text{Mono } 128 = 128^{+} - 0.1001\,(127^{+}) + 0.0055\,(126^{+}) \quad (24)$$

$$\text{Mono } 142 = 142^{+} - 0.113\,(141^{+}) + 0.0068\,(140^{+}) \quad (25)$$

$$\text{Mono } 156 = 156^{+} - 0.1224\,(155^{+}) + 0.0081\,(154^{+}) \quad (26)$$

$$\text{Mono } 170 = 170^{+} - 0.1335\,(169^{+}) + 0.0096\,(168^{+}) \quad (27)$$

11.2.2.2 Place these peaks on a molar basis by multiplying each peak by empirical factors as follows (Note 7):

Mono 86 × 1.0
Mono 100 × 0.92
Mono 114 × 1.4
Mono 128 × 1.8
Mono 142 × 1.9
Mono 156 × 2.0
Mono 170 × 2.1

11.2.2.3 Normalize the products of the preceding step to obtain the relative mole fractions of the C_6 to C_{12} paraffins. Calculate an apparent carbon number by totaling the products of each mole fraction and the corresponding number of carbon atoms per molecule. This carbon number is assumed to apply to all paraffins and cycloparaffins.

NOTE 6—Small amounts of naphthalenes, which have intense ions at 128, 141, and 142, may introduce errors into the results of this calculation. Large errors will be detected by a bimodal distribution of the individual paraffinic peaks. A relatively large 141 peak could also be indicative of naphthalenes. If naphthalenes appear to be present it is suggested that the paraffin carbon number be calculated from the mass spectrum of the saturate portion of the sample which may be easily obtained by Test Methods D2002. If the saturates cannot be obtained the paraffin carbon number should be assumed to be 0.5 number less than that of the aromatics.

11.2.2.4 The term Hg refers to a background correction that must be applied if mercury peaks are present in the spectrometer. This correction must be determined for each instrument under conditions that simulate a sample run.

NOTE 7—The factors in 11.2.1 and 11.2.2 which are used to convert parent monoisotopic peaks of alkylbenzenes and paraffins to a molar basis are average values of data that were obtained in three laboratories. These data were obtained by making direct pressure sensitivity measurements of the appropriate blends described in Table 2 and extrapolation of these results for the carbon number range from 10 through 12. This same procedure can be utilized by an individual laboratory if desired.

11.3 *Calculation of Compound Types*—Using the proper inverse from Table 3 according to the carbon number of the sample, calculate the liquid volume percent of each hydrocarbon type. This selection may vary for the same sample depending upon the carbon number of the paraffins and aromatics. For example, if the paraffin carbon number is 7.0 and that of the alkylbenzenes is 8.0, the carbon number 7 inverse would be used to calculate the volume fraction of paraffins and cycloparaffins, whereas the carbon number 8 inverse would be used to calculate the aromatics. Volume fractions must then be normalized.

TABLE 3 Inverse Matrices Based on Liquid Volume Sensitivity

	$\sum 43/T$	$\sum 41/T$	$\sum 67/T$	$\sum 77/T$	$\sum 103/T$	$\sum 128/T$
Paraffins	+0.009016	−0.001368	+0.000257	−0.000003	...	...
Monocycloparaffins	−0.004471	+0.010285	−0.002391	−0.000002	...	...
Dicycloparaffins	+0.000100	−0.000258	+0.004325	+0.000000	...	...
Alkylbenzenes	+0.000017	−0.000048	−0.000149	+0.005117	...	...
Carbon No. 7						
Paraffins	+0.007241	−0.000655	+0.000105	−0.000100	−0.000100	...
Monocycloparaffins	−0.002542	+0.007283	−0.001695	−0.000051	−0.000035	...
Dicycloparaffins	+0.000167	−0.000523	+0.004387	+0.000001	+0.000003	...
Alkylbenzenes	+0.000010	−0.000044	−0.000134	+0.004576	−0.000897	...
Indans and tetralins	+0.000000	+0.000000	−0.000002	+0.000000	+0.005424	...
Carbon No. 8						
Paraffins	+0.006449	−0.000584	+0.000090	−0.000011	−0.000105	−0.000082
Monocycloparaffins	−0.001902	+0.006132	−0.001428	−0.000063	−0.000029	+0.000006
Dicycloparaffins	+0.000128	−0.000469	+0.004375	+0.000001	+0.000003	−0.000004
Alkylbenzenes	+0.000007	−0.000049	−0.000125	+0.004375	−0.000857	−0.000271
Indans and tetralins	−0.000000	+0.000002	+0.000004	−0.000207	+0.005465	−0.000026
Naphthalenes	+0.000000	+0.000000	+0.000000	+0.000000	+0.000000	+0.005757
Carbon No. 9						
Paraffins	+0.006043	−0.000673	+0.000071	−0.000018	−0.000095	−0.000075
Monocycloparaffins	−0.001933	+0.006183	−0.001929	−0.000130	−0.000017	+0.000011
Dicycloparaffins	+0.000212	−0.000822	+0.006809	+0.000003	+0.000004	−0.000006
Alkylbenzenes	+0.000007	−0.000040	−0.000261	+0.004015	−0.000787	−0.000248
Indans and tetralins	+0.000001	+0.000002	+0.000020	−0.000361	+0.005496	−0.000016
Naphthalenes	−0.000090	+0.000008	−0.000000	+0.000000	+0.000001	+0.005759
Carbon No. 10						
Paraffins	+0.005766	−0.001562	+0.000606	+0.000001	−0.000025	−0.000070
Monocycloparaffins	−0.001897	+0.007443	−0.003315	−0.000270	−0.000004	+0.000015
Dicycloparaffins	+0.000666	−0.002792	+0.007592	+0.000087	−0.000032	−0.000009
Alkylbenzenes	−0.000006	+0.000021	−0.000201	+0.003903	−0.001240	−0.000238
Indans and tetralins	+0.000002	−0.000001	+0.000029	−0.000709	+0.007315	−0.000007
Naphthalenes	−0.000120	+0.000033	−0.000012	−0.000006	−0.000174	+0.005761

11.3.1 When an integral carbon number is not obtained two inverses should be applied and the results weighted. For example, if the paraffin carbon number is 7.4, both the carbon number 7 and carbon number 8 inverses should be applied for the paraffins and cycloparaffins. The volume fraction to be used would then be the value obtained from the carbon number 7 inverse plus 0.4 of the difference between the values obtained from the carbon number 7 and carbon number 8 inverses.

NOTE 8—Although calculation of the composition of the sample by interpolation between the results of two adjacent carbon number inverses gives good results, the availability of computers suggests the use of an even better procedure which is not practical when hand calculators are used. It should be possible in calculating each sample to select matrix elements by interpolation between adjacent carbon numbers in a table of calibration data and to calculate sample composition from the resulting matrix either by computing an inverse or by use of an iterative procedure.

11.4 *Olefin Content of Sample:*

11.4.1 If the bromine number is used, calculate the liquid volume percent olefins in accordance with Test Method D875. If the fluorescent indicator adsorption Test Method D1319 is used, the liquid volume percent olefins is obtained.

11.4.2 For samples containing less than 3 % olefins, subtract the liquid volume percent olefins from the monocycloparaffin results obtained from the inverse.

11.5 Calculate the analysis on the original basis, including the volume of olefins and the pentanes and lighter hydrocarbons removed, if any, as separate results.

12. Calibration Data

12.1 Compositions of synthetic hydrocarbon mixtures are shown in Table 2. These mixtures were analyzed by cooperative programs and the results, as presented in Table 1, are the basis for the inverses in Table 3. Sensitivities and liquid volume factors which were applied to the calibration data in Table 1 are described in Table 4.

12.2 The inverses in Table 3 were calculated as follows:

12.2.1 For a given carbon number and for a specific hydrocarbon class the set of values $\sum 43/T$, $\sum 41/T$, and so forth, were divided by the largest number in the set. These new values and their hydrocarbon classes were listed in proper order to form an array or matrix.

12.2.2 All elements in this new array which were representative of one hydrocarbon class were multiplied by the corresponding pressure sensitivity for that class and carbon number.

12.2.3 The matrix as obtained in 12.2.2 was inverted.

12.2.4 The inverse terms for a given hydrocarbon class and carbon number were multiplied by the corresponding liquid volume factor. Finally, all new terms were divided by 100.

13. Precision and Bias

13.1 The precision of this test method as obtained by statistical examination of interlaboratory test results on samples having the composition given in Table 5 is as follows:

13.1.1 *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 in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 5 only in one case in twenty.

13.1.2 *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 5 only in one case in twenty.

NOTE 9—If samples are analyzed that differ appreciably in composition from those used for the interlaboratory study, this precision statement may not apply.

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

14. Keywords

14.1 alkylbenzenes; dicycloparaffins; gasoline; hydrocarbon types; indans; mass spectrometry; monocycloparaffins; naphthalenes; paraffins

TABLE 4 Pressure Sensitivities and Liquid Volume Factors[A]

	Paraffins	Monocycloparaffins	Dicycloparaffins	Alkylbenzenes	Indans or Tetralins	Naphthalenes	Reference[B]
Sensitivity:							
C_6	156.5	117.2	313.0	174.7	...	...	(1)
C_7	210.5	188.8	313.0	233.4	227.1	...	(1)
C_8	261.0	252.0	313.0	283.3	227.1	228.4	(1)
C_9	308.4	280.6	240.0	349.3	227.1	228.4	(1)
C_{10}	353.0	299.8	248.6	404.0	192.3	228.4	(2)
Liquid volume factor:							
C_6	131.8	111.1	133.5	89.4	...	...	(3)
C_7	147.6	129.5	133.5	106.8	123.2	...	(3)
C_8	163.6	146.5	133.5	123.0	123.2	131.5	(3)
C_9	179.8	161.1	157.2	138.4	123.2	131.5	(3)
C_{10}	189.4	175.2	157.8	152.8	136.3	131.5	(4)

[A] The terms sensitivities and liquid volume factors are proportional to total ion yield per unit pressure and liquid volume per unit pressure, respectively. The sensitivities are expressed as relative to the *n*-butane sensitivity of 100.0 for m/e^+ 43.

[B] References:

(1) Sensitivity data were determined by Mobil Oil with a micromanometer and were transmitted by cooperative letter of July 28, 1967.

(2) Sensitivity data were extrapolated from Mobil Oil C_6 through C_9 sensitivities except for the DCP and I/T classes. These were calculated from API Spectra No. 412 and No. 539, respectively.

(3) Liquid volume factors were calculated by Mobil Oil and were transmitted by cooperative letter of July 28, 1967.

(4) Liquid volume factors were calculated by Sinclair Oil.

TABLE 5 Precision Data for Cooperative Samples

Type	Naphtha					Reformate				
	Volume Percent	σ_r	σ_R	r	R	Volume Percent	σ_r	σ_R	r	R
Paraffins	52.6	0.3	1.7	1.0	5.3	34.2	0.4	1.7	1.3	5.3
Monocycloparaffins	34.6	0.2	1.8	0.7	5.6	4.0	0.1	0.6	0.3	1.8
Dicycloparaffins	5.2	0.1	0.5	0.4	1.7	0.1	0.0	0.1	0.0	0.2
Alkylbenzenes	6.3	0.1	0.4	0.4	1.4	56.6	0.2	2.1	0.6	6.8
Indans and tetralins	0.9	0.1	0.1	0.1	0.4	2.2	0.1	0.5	0.3	1.6
Naphthalenes	0.3	0.0	0.1	0.1	0.4	3.0	0.1	0.8	0.3	2.6

σ_r = repeatability standard deviation.
σ_R = reproducibility standard deviation.
r = repeatability.
R = reproducibility.