Standard Test Method for
Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D5134; 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.

ε^1 NOTE—Updated sole source of supply footnotes editorially in May 2008.

INTRODUCTION

Despite the many advances in capillary gas chromatography instrumentation and the remarkable resolution achievable, it has proven difficult to standardize a test method for the analysis of a mixture as complex as petroleum naphtha. Because of the proliferation of numerous, similar columns and the endless choices of phase thickness, column internal diameter, length, etc., as well as instrument operating parameters, many laboratories use similar *but not identical* methods for the capillary GC analysis of petroleum naphthas. Even minute differences in column polarity or column oven temperature, for example, can change resolution or elution order of components and make their identification an individual interpretive process rather than the desirable, objective application of standard retention data. To avoid this, stringent column specifications and temperature and flow conditions have been adopted in this test method to ensure consistent elution order and resolution and reproducible retention times. Strict adherence to the specified conditions is essential to the successful application of this test method.

1. Scope

1.1 This test method covers the determination of hydrocarbon components of petroleum naphthas as enumerated in Table 1. Components eluting after *n*-nonane (bp 150.8°C) are determined as a single group.

1.2 This test method is applicable to olefin-free (<2 % olefins by liquid volume) liquid hydrocarbon mixtures including virgin naphthas, reformates, and alkylates. Olefin content can be determined by Test Method D1319. The hydrocarbon mixture must have a 98 % point of 250°C or less as determined by Test Method D3710.

1.3 Components that are present at the 0.05 mass % level or greater can be determined.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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.* Specific warning statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
D3710 Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 A representative sample of the naphtha is introduced into a gas chromatograph equipped with a methyl silicone bonded phase fused silica capillary column. Helium carrier gas transports the vaporized sample through the column in which the components are separated. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved May 1, 2008. Published September 2008. Originally approved in 1990. Last previous edition approved in 2003 as D5134–98(2003). DOI: 10.1520/D5134-98R08E01.

[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.

TABLE 1 Typical Retention Characteristics of Naphtha Components

NOTE—The abbreviations *N* and *P* refer to unidentified naphthenes and paraffins respectively.

Compound	Retention Time, min	Adjusted Retention Time, min	Kovats Retention Index @ 35°C	Linear Retention Index
Methane	3.57	0.00	100.0	...
Ethane	3.65	0.08	200.0	...
Propane	3.84	0.27	300.0	...
Isobutane	4.14	0.57	367.3	...
n-Butane	4.39	0.82	400.0	...
2,2-Dimethylpropane	4.53	0.96	415.5	...
Isopentane	5.33	1.76	475.0	...
n-Pentane	5.84	2.27	500.0	...
2,2-Dimethylbutane	6.81	3.24	536.2	...
Cyclopentane	7.83	4.26	564.1	...
2,3-Dimethylbutane	7.89	4.32	565.5	...
2-Methylpentane	8.06	4.49	569.5	...
3-Methylpentane	8.72	5.15	583.4	...
n-Hexane	9.63	6.06	600.0	...
2,2-Dimethylpentane	11.22	7.65	624.2	...
Methylcyclopentane	11.39	7.82	626.5	...
2,4-Dimethylpentane	11.68	8.11	630.3	...
2,2,3-Trimethylbutane	12.09	8.52	635.4	...
Benzene	13.29	9.72	649.1	...
3,3-dimethylpentane	13.84	10.27	654.8	...
Cyclohexane	14.19	10.62	658.3	...
2-Methylhexane	15.20	11.63	667.8	...
2,3-Dimethylpentane	15.35	11.78	669.1	...
1,1-Dimethylcyclopentane	15.61	12.04	671.4	...
3-Methylhexane	16.18	12.61	676.2	...
cis-1,3-Dimethylcyclopentane	16.88	13.31	681.8	...
trans-1,3-Dimethylcyclopentane	17.22	13.65	684.4	...
3-Ethylpentane	17.44	13.87	686.1	...
trans-1,2-Dimethylcyclopentane	17.57	14.00	687.0	...
2,2,4-Trimethylpentane	17.80	14.23	688.7	...
n-Heptane	19.43	15.86	700.0	...
Methylcyclohexane + *cis-1,2*-Dimethylcyclopentane	22.53	18.96	718.6[A]	...
1,1,3-Trimethylcyclopentane + *2,2*-Dimethylhexane	23.05	19.48	721.4[A]	...
Ethylcyclopentane	24.59	21.02	729.3[A]	...
2,5-Dimethylhexane + *2,2,3*-Trimethylpentane	25.12	21.55	731.9[A]	...
2,4-Dimethylhexane	25.47	21.90	733.5[A]	...
1,trans-2,cis-4-Trimethylcyclopentane	26.43	22.86	738.0[A]	...
3,3-Dimethylhexane	26.79	23.22	739.6[A]	...
1,trans-2,cis-3-Trimethylcyclopentane	28.01	24.44	744.9[A]	...
2,3,4-Trimethylpentane	28.70	25.13	747.8[A]	...
Toluene + *2,3,3*-Trimethylpentane	29.49	25.92	751.1[A]	730.2[B]
1,1,2-Trimethylcyclopentane	31.21	27.64	...	741.7[B]
2,3-Dimethylhexane	31.49	27.92	...	743.6[B]
2-Methyl-3-ethylpentane	31.69	28.12	...	744.9[A]
2-Methylheptane	33.06	29.49	...	754.1[B]
4-Methylheptane + *3*-Methyl-*3*-ethylpentane	33.34	29.77	...	756.0[B]
3,4-Dimethylhexane	33.49	29.92	...	757.0[B]
1,cis-2,trans-4-Trimethylcyclopentane + *1,cis-2,cis-4*-Trimethylcyclopentane	33.73	30.16	...	758.6[B]
cis-1,3-Dimethylcyclohexane	34.45	30.88	...	763.4[B]
3-Methylheptane + *1,cis-2,trans-3*-Trimethylcyclopentane	34.64	31.07	...	764.7[B]
3-Ethylhexane + *trans-1,4*-Dimethylcyclohexane	34.83	31.26	...	766.0[B]
1,1-Dimethylcyclohexane	35.81	32.24	...	772.5[B]
2,2,5-Trimethylhexane + *trans-1,3*-Ethylmethylcyclopentane	36.75	33.18	...	778.8[B]
cis-1,3-Ethylmethylcyclopentane	37.14	33.57	...	781.4[B]
trans-1,2-Ethylmethylcyclopentane	37.39	33.82	...	783.1[B]
2,2,4-Trimethylhexane + 1,1-Ethylmethylcyclopentane	37.68	34.11	...	785.1[B]
trans-1,2-Dimethylcylohexane	38.14	34.57	...	788.1[B]
1,cis-2,cis-3-Trimethylcyclopentane	39.21	35.64	...	795.3[B]
trans-1,3-Dimethylcyclohexane + *cis-1,4*-Dimethylcyclohexane	39.54	35.97	...	797.5
n-Octane	39.91	36.34	...	800.0
Isopropylcyclopentane + *2,4,4*-Trimethylhexane	40.76	37.19	...	805.7
Unidentified C9-Naphthene	40.88	37.31	...	806.5
Unidentified C8-Naphthene	41.52	37.95	...	810.8
Unidentified C9-Naphthene	41.88	38.31	...	813.2
cis-1,2-Ethylmethylcyclopentane + *2,3,5*-Trimethylhexane	42.55	38.98	...	817.7
2,2-Dimethylheptane	43.20	39.63	...	822.0
cis-1,2-Dimethylcyclohexane	43.43	39.86	...	823.6
2,2,3-Trimethylhexane + 9N	43.76	40.19	...	825.8
2,4-Dimethylheptane	43.88	40.31	...	826.6
4,4-Dimethylheptane + *9N*	44.09	40.52	...	828.0
Ethylcyclohexane + *n*-Propylcyclopentane	44.36	40.79	...	829.8

TABLE 1 *Continued*

Compound	Retention Time, min	Adjusted Retention Time, min	Kovats Retention Index @ 35°C	Linear Retention Index
2-Methyl-*4*-Ethylhexane	44.74	41.17	...	832.4
2,6-Dimethylheptane + *9N*	44.95	41.38	...	833.8
1,1,3-Trimethylcyclohexane	45.21	41.64	...	835.5
Unidentified *C9*-Naphthene	45.56	41.99	...	837.8
2,5-Dimethylheptane + *9P*	45.92	42.35	...	840.3
3,5-Dimethylheptane + *3,3*-Dimethylheptane + *N*	46.09	42.52	...	841.4
Unidentified *C9*-Naphthene	46.31	42.74	...	842.9
Unidentified *C9*-Naphthene	46.55	42.98	...	844.5
Ethyl Benzene	47.15	43.58	...	848.5
Unidentified *C9*-Naphthene	47.37	43.80	...	850.0
Unidentified Naphthene + *2,3,4*-Trimethylhexane	47.53	43.96	...	851.0
Unidentified Naphthenes	47.78	44.21	...	852.7
Unidentified Naphthene + Paraffin	48.13	44.56	...	855.1
m-Xylene	48.49	44.92	...	857.5
p-Xylene	48.63	45.06	...	858.4
2,3-Dimethylheptane	48.93	45.36	...	860.4
3,4-Dimethylheptane[C] + N	49.10	45.53	...	861.6
3,4-Dimethylheptane[C]	49.29	45.72	...	862.8
Unidentified Naphthene	49.41	45.84	...	863.6
4-Ethylheptane + *N*	49.65	46.08	...	865.2
4-Methyloctane	50.10	46.53	...	868.3
2-Methyloctane	50.26	46.69	...	869.3
Unidentified Naphthene	50.41	46.84	...	870.3
Unidentified Naphthene	50.73	47.16	...	872.5
3-Ethylheptane + *N*	50.96	47.39	...	874.0
3-Methyloctane	51.15	47.58	...	875.3
Unidentified Naphthene	51.35	47.78	...	876.6
o-Xylene + *1,1,2*-Trimethylcyclohexane	51.54	47.97	...	877.9
Unidentified Naphthene + *2,4,6*-Trimethylheptane	51.74	48.17	...	879.2
Unidentified Naphthene	52.12	48.55	...	881.8
Unidentified Paraffin	52.24	48.67	...	882.6
Unidentified Naphthenes	52.56	48.99	...	884.7
Unidentified Naphthene	52.85	49.28	...	886.7
Unidentified Naphthene + Paraffin	53.06	49.49	...	888.1
Unidentified Naphthene	53.26	49.69	...	889.4
Unidentified Naphthene	53.46	49.89	...	890.8
Unidentified Naphthene	54.02	50.45	...	894.5
Unidentified Naphthene	54.40	50.83	...	897.1
n-Nonane	54.84	51.27	...	900.0
Unidentified Naphthene	54.98	51.41	...	900.9

[A] Extrapolated from n-C_6 and n-C_7. See A1.1.3.

[B] Extrapolated from n-C_8 and n-C_9. See A1.2.3.

[C] Stereoisomers.

system or integrating computer. Each eluting peak is identified by comparing its retention index to a table of retention indices and by visual matching with a standard chromatogram. The table of retention indices has been established by running reference compounds under identical conditions or by gas chromatographic—mass spectrometric (GC/MS) analysis of reference samples under the same conditions, or both.

3.2 The mass concentration of each component is determined by area normalization with response factors. Peaks eluting after *n*-nonane are summed and reported as C_{10+}.

4. Significance and Use

4.1 A knowledge of the hydrocarbon components comprising a petroleum naphtha, reformate, or alkylate is useful in valuation of crude oils, in alkylation and reforming process control, in product quality assessment, and for regulatory purposes. Detailed hydrocarbon composition is also used as input in the mathematical modeling of refinery processes.

4.2 Separation of naphtha components by the procedure described in this test method can result in some peaks that represent coeluting compounds. This test method cannot attribute relative concentrations to the coelutants. In the absence of supporting information, use of the results of this test method for purposes which require such attribution is not recommended.

5. Interferences

5.1 If present, olefinic hydrocarbons with boiling points less than 150°C will be separated and detected along with the saturates and aromatics. Some of the olefins will coelute with saturates or aromatics and give erroneously high concentrations for those components.

5.2 Alcohols, ethers, and other organic compounds of similar volatility can also interfere by coeluting with saturate or aromatic hydrocarbons thereby causing erroneously high values to be determined.

6. Apparatus

6.1 *Instrumentation*—A gas chromatograph capable of column oven temperature programming from 35°C to 200°C in 1°C/min increments is required. A heated flash vaporizing injector designed to provide a linear sample split injection (for example, 200:1) is also required for proper sample introduction. The associated carrier gas controls must be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. A hydrogen flame ionization detector designed for optimum response with capillary columns (with the required gas controls and electronics) must meet or exceed the following specifications:

Operating temperature	100°C to 300°C
Sensitivity	>0.015 C/g
Minimum detectability	5×10^{-12} g carbon/second
Linearity	$>10^7$

6.2 *Sample Introduction System*—Manual or automatic liquid syringe sample injection to the splitting injector may be employed. Devices capable of 0.2 µL to 1.0 µL injections are suitable. It should be noted that inadequate splitter design or poor injection technique, or both, can result in sample fractionation. Operating conditions which preclude fractionation should be determined in accordance with Section 11.

6.3 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantitation of these analyses must meet or exceed these minimum requirements:

6.3.1 Capacity for at least 250 peaks/analysis.

6.3.2 Normalized area percent calculation with response factors.

6.3.3 Identification of individual components by retention time.

6.3.4 Noise and spike rejection capability.

6.3.5 Sampling rates for fast (<1 s) peaks.

6.3.6 Positive and negative sloping baseline correction.

6.3.7 Peak detection sensitivity for narrow and broad peaks.

6.3.8 Perpendicular drop and tangent skimming as needed.

6.4 *Capillary Column*—This test method utilizes a 50-m (0.21-mm inside diameter) fused silica capillary column with bonded (cross-linked) methyl silicone phase and a film thickness (d_f) of 0.5 µm. Other columns with these nominal dimensions may be suitable. However, all columns must meet the criteria set out in Section 10 for efficiency, resolution, and polarity.

7. Reagents and Materials

7.1 *Carrier Gas*, helium, 99.99 % pure. (**Warning**—Compressed gas under high pressure.)

7.2 *Fuel Gas*, hydrogen, 99.9 % pure. (**Warning**—Extremely flammable gas under pressure.)

7.3 *Make-up Gas*, helium or nitrogen, 99.99 % pure. (**Warning**—Compressed gases under higher pressure.)

7.4 *n-Heptane*, 99+ mol %. (**Warning**—Flammable. Harmful if inhaled.)

7.5 *Methane*—(**Warning**—Extremely flammable gas.)

7.6 *2-Methylheptane*, 99+ mol %. (**Warning**—Flammable. Harmful if inhaled.)

7.7 *4-Methylheptane*, 99+ mol %. (**Warning**—Flammable. Harmful if inhaled.)

7.8 *2-Methylpentane*, 99+ mol %. (**Warning**—Extremely flammable. Harmful if inhaled.)

7.9 *n-Octane*, 99+ mol %. (**Warning**—Flammable. Harmful if inhaled.)

7.10 *Toluene*, 99+ mol %. (**Warning**—Flammable. Vapor harmful.)

7.11 *2,3,3-Trimethylpentane*, 99+ mol %. (**Warning**—Extremely flammable. Harmful if inhaled.)

7.12 *Column Evaluation Mixture*, a qualitative synthetic mixture of pure liquid hydrocarbons with the following approximate composition: 0.5 % toluene, 1 % *n*-heptane, 1 % 2,3,3-trimethylpentane, 1 % 2-methylheptane, 1 % 4-methylheptane, 1 % *n*-octane in 2-methylpentane solvent.

7.13 *Reference Alkylate,*[3] actual refinery alkylation product used to prepare Fig. 1. (**Warning**—Extremely flammable. Harmful if inhaled.)

7.14 *Reference Naphtha,*[3] actual refinery stream used to prepare Fig. 2. (**Warning**—Extremely flammable. Harmful if inhaled.)

7.15 *Reference Reformate,*[3] actual refinery reformer product used to prepare Fig. 3. (**Warning**—Extremely flammable. Harmful if inhaled.)

8. Sampling

8.1 Hydrocarbon liquids (including naphthas) with Reid vapor pressures of 110 kPa (16 psi) or less may be sampled either into a floating piston cylinder or into an open container.

8.1.1 *Cylinder Sampling*—Refer to Test Method D3700 for instructions on transferring a representative sample of a hydrocarbon fluid from a source into a floating piston cylinder. Add inert gas to the ballast side of the floating piston cylinder to achieve a pressure of 350 kPa (45 psi) above the vapor pressure of the sample.

8.1.2 *Open Container Sampling*—Refer to Practice D4057 for instructions on manual sampling from bulk storage into open containers. Stopper container immediately after drawing sample.

8.2 Preserve the sample by cooling to approximately 4°C and by maintaining that temperature until immediately prior to analysis.

8.3 Transfer an aliquot of the cooled sample into a precooled septum vial, then seal appropriately. Obtain the test specimen for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

9. Preparation of Apparatus

9.1 Install and condition column as per manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. If leaks are found, tighten or replace fittings before proceeding.

9.2 Calibrate the gas chromatograph column oven temperature sensors using an independent, electronic temperature measuring device such as a thermocouple or platinum resistance temperature detector.

9.2.1 Place the independent temperature measuring probe in the oven in the region occupied by the column. Do not allow sensor to touch the walls of the oven.

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[3] The sole source of supply of these qualitative reference samples known to the committee at this time is Supelco, Inc., Bellefonte, PA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

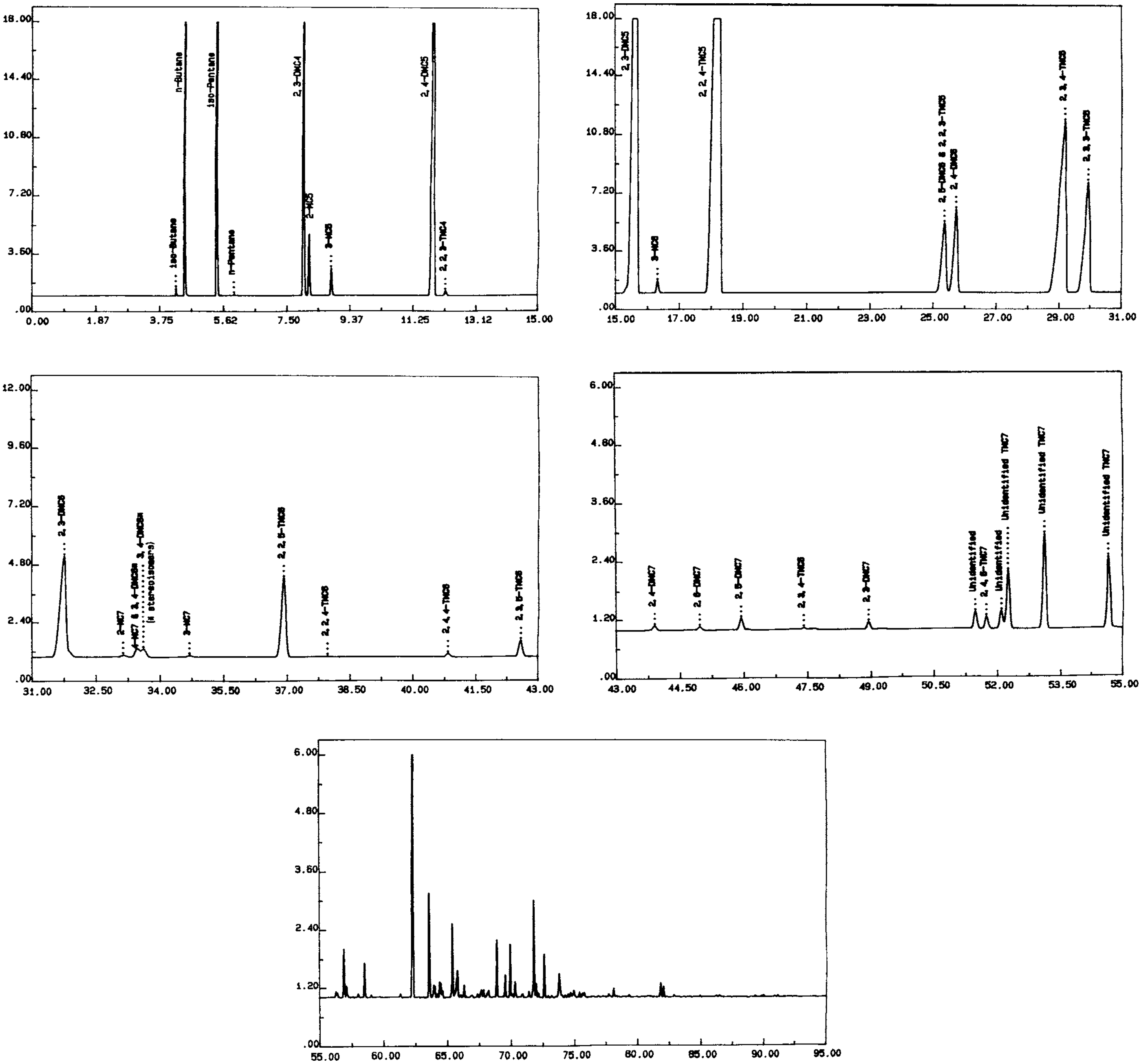

FIG. 1 Reference Alkylate Chromatogram

9.2.2 Set the oven temperature to 35°C and allow oven to equilibrate for at least 15 min, then observe the temperature reading.

9.2.3 If the reading of the independent temperature sensor is more than 0.5°C different from 35°C, follow manufacturer's instructions to adjust calibration of GC oven temperature.

NOTE 1—Differences of as little as 1°C can change the resolution of two closely eluting peaks (of dissimilar hydrocarbon types) enough to affect integration and quantitation while 2 to 3°C may cause those same peaks to be unresolved or even reverse their elution order.

9.3 Adjust the operating conditions of the gas chromatograph to conform to the list in Table 2. Turn on the detector, ignite flame, and allow the system to equilibrate.

9.4 Set carrier gas flow rate such that the retention time of toluene at 35°C is 29.6 ± 0.2 min.

9.4.1 As a matter of practicality, it may be easier to first set an *approximately* correct flow rate, using methane gas injections. To do this, adjust the carrier gas flow (or column head pressure) until the retention time of methane on the 50-m column is 3.6 min.

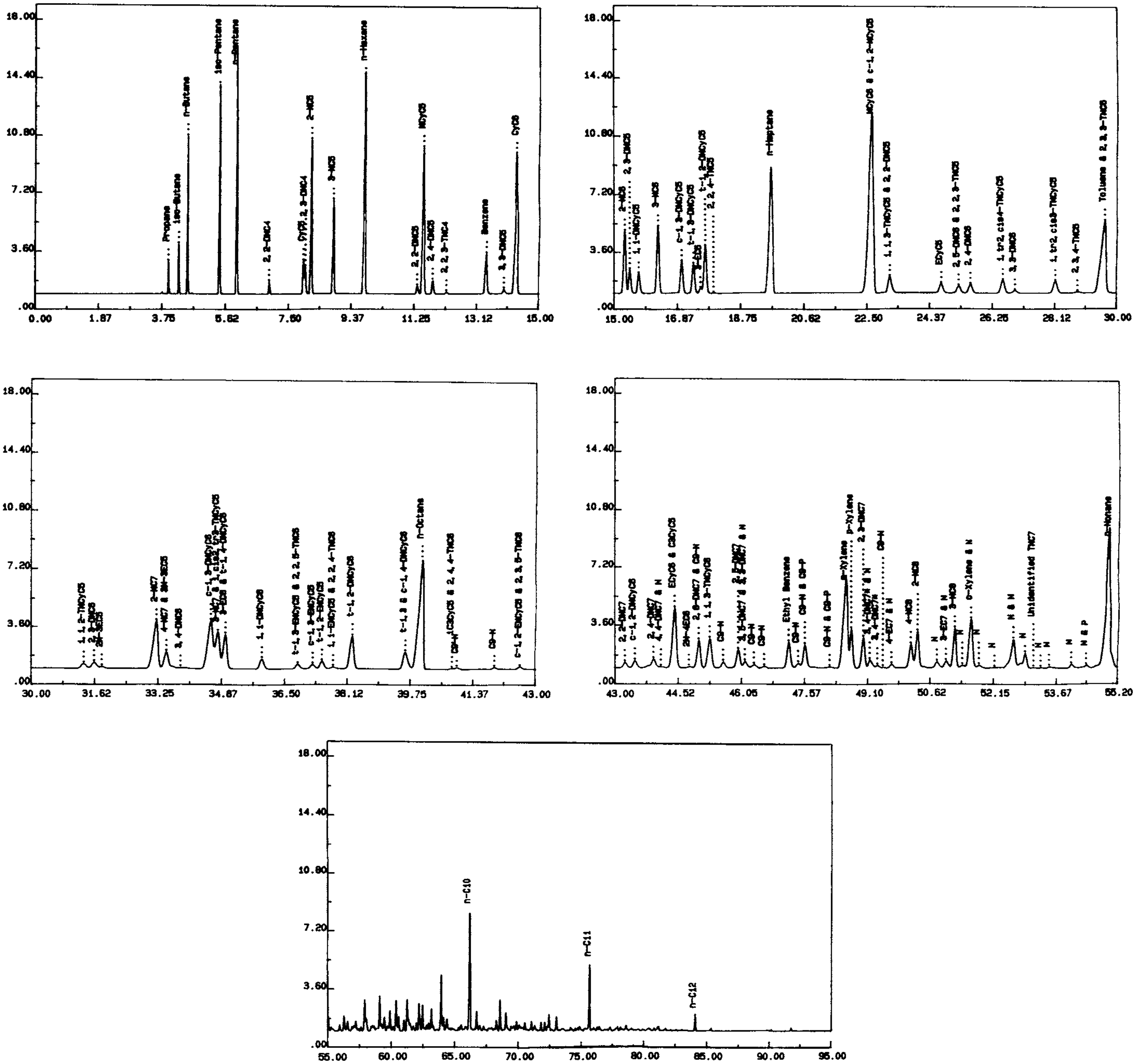

FIG. 2 Reference Naphtha Chromatogram

9.4.2 Make final adjustments to flow rate so that toluene is retained for the specified 29.6 ± 0.2 min. As this specification is critical to achieving reproducibility of retention times among different laboratories, care must be taken that the toluene does not overload the column and cause skewed peaks with resultant shifts in peak apex position. Injection of a 1 % toluene solution should preclude this possibility.

10. Column Evaluation

10.1 In order to establish that a column will perform the required separation, certain specifications must be met with respect to efficiency, resolution, and polarity. Determine the following data for new columns. Check older columns on a periodic basis to ensure that column deterioration has not occurred. A column which does not meet these specifications is unsuitable for use.

10.2 Set oven temperature parameters for isothermal operation. Under isothermal conditions at 35°C, inject ~25 µL of methane and record the retention time. Also at 35°C, analyze the column evaluation mixture described in 7.12. Record the retention times and the peak widths at half height of each of the components.

10.2.1 Calculate efficiency of the column using Eq 1. The number of theoretical plates (n) must be greater than 225 000.

$$n = 5.545\ (t_R/W_h)^2 \tag{1}$$

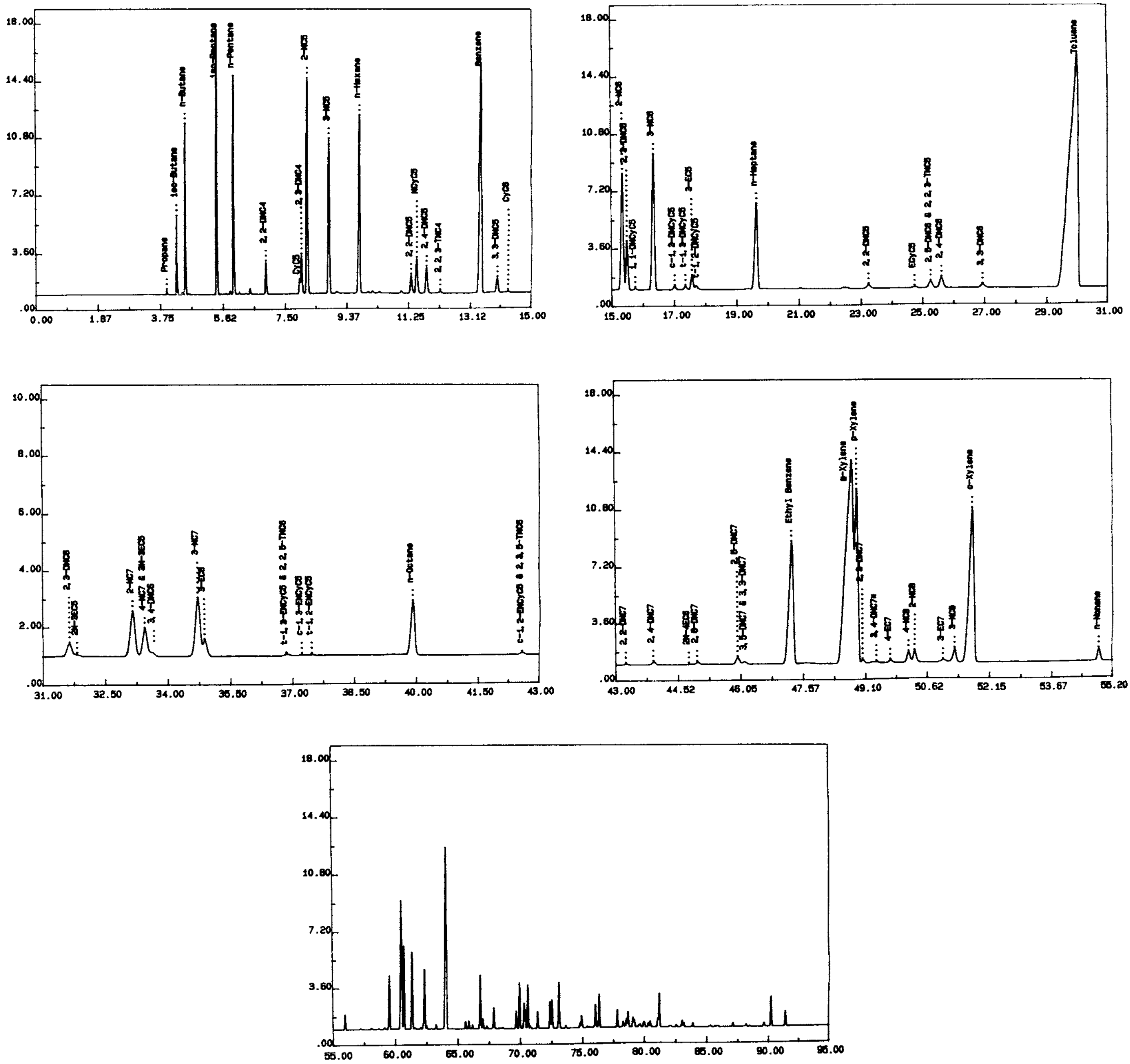

FIG. 3 Reference Reformate Chromatogram

where:

n = number of theoretical plates,
t_R = retention time of *n*-octane, and
W_h = peak width of *n*-octane at half height (in same unit as retention time).

10.2.2 Calculate resolution (R) between 2-methylheptane and 4-methylheptane using Eq 2. R must be at least 1.35.

$$R = \frac{2(t_{R(A)} - t_{R(B)})}{1.699\,(W_{h(A)} + W_{h(B)})} \tag{2}$$

TABLE 2 Operating Conditions

Column Temperature Program	
Initial temperature:	35°C ± 0.5°C
Pre-injection equilibration time:	5 min
Initial hold time:	30 min
Program rate:	2°C/min
Final temperature:	200°C
Final hold time:	10 min
Injector	
Temperature:	200°C
Split ratio:	200:1
Sample size:	0.2 to 1.0 µL
Detector	
Type:	flame ionization
Temperature:	250°C
Fuel gas:	hydrogen (~30 mL/min)
Oxidizing gas:	air (~250 mL/min)
Make-up gas:	nitrogen (~30 mL/min)
Carrier Gas	
Type:	helium
Average linear velocity:	~23 cm/s @35°C (see 9.4)

where:

R = resolution,

$t_{R(A)}$ = retention time of *4*-methylheptane,

$t_{R(B)}$ = retention time of *2*-methylheptane,

$W_{h(A)}$ = peak width at half-height of *4*-methylheptane, and

$W_{h(B)}$ = peak width at half-height of *2*-methylheptane

10.2.3 Determine relative polarity of the column using the difference in Kovats Retention Indices (see Annex A1) of toluene and *2,3,3*-trimethylpentane. The relative polarity of the column $I_{(2.3,3\text{-TMP})}$- $I_{(\text{Toluene})}$ must be 0.4 ± 0.4 at 35°C.

NOTE 2—This specification is critical. Seemingly slight differences in the polarity have a significant effect on the relative order of elution of components, thus making peak identifications difficult.

10.2.3.1 Kovats Retention Index is given by:

$$I_A = 700 + 100 \left[\frac{\log t'_{R(A)} - \log t'_{R(C7)}}{\log t'_{R(C8)} - \log t'_{R(C7)}} \right] \tag{3}$$

where:

I_A = retention index of component eluting between $n - C_7$ and $n - C_8$,

$t'_{R(A)}$ = adjusted retention time of component,

$t'_{R(C7)}$ = adjusted retention time of *n*-heptane, and

$t'_{R(C8)}$ = adjusted retention time of *n*-octane.

10.2.3.2 *Adjusted retention time* of a peak is determined by subtracting the retention time of an unretained substance (methane) from the retention time of the peak.

10.2.3.3 If *2,3,3*-trimethylpentane and toluene are not resolved, run separate mixtures, each containing only one of these compounds along with *n*-C_7 and *n*-C_8 in *2*-methylpentane solvent.

11. Split Injection Linearity

11.1 The choice of split ratio used is dependent upon the split linearity characteristics of the particular injector and the sample capacity of the column. Overloading of the column may cause loss of resolution for some components and, since overloaded peaks are skewed, variance in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, watch for any skewed peaks that may indicate overload. Note the component size and where possible, avoid conditions leading to this problem during actual analyses.

11.2 Splitting injector linearity should be established to determine proper quantitative parameters and limits. Use a standard mixture of known weight percentages of 10 to 20 pure (99 + %) hydrocarbons, covering the boiling range of this test method. To prevent losses due to volatility, do not use any compounds lighter than *n*-hexane.

11.3 Inject and integrate this standard under the following conditions, using the operating conditions listed in Table 2. Split ratio may be determined by direct flow measurements or by calculation as shown in Annex A2. Faster temperature programming may be used as long as the components are eluted as discrete peaks.

Injection Temperature: 200°C.	Split: 100:1	Sample: 0.2, 0.5, 1.0 µL
	Split: 200:1	Sample: 0.2, 0.5, 1.0 µL
Injection Temperature: 250°C.	Split: 100:1	Sample: 0.2, 0.5, 1.0 µL
	Split: 200:1	Sample: 0.2, 0.5, 1.0 µL

11.4 Calculate the concentration of each compound in the mixture by area normalization with response factors. Use a response factor of 1.00 for all compounds except benzene (0.90) and toluene (0.95). Determine the relative error of the calculated concentrations from the known concentrations.

$$\%\ \text{relative error} = \frac{100 \times (\text{calculated concentration} - \text{known concentration})}{\text{known concentration}} \tag{4}$$

11.5 Use only those combinations of conditions from 11.3 which result in 3 % or less relative error. This is the splitter linearity range.

12. Procedure for Gas Chromatographic Analysis of Sample

12.1 Set the instrument operating variables to within the limits specified in Table 2. If necessary, change split ratio, sample size, or injection port temperature, or combination thereof, to ensure splitter linearity as determined in Section 11.

12.2 Verify that the isothermal retention time of toluene (at 35°C) is 29.6 ± 0.2 min as discussed in 9.4.

12.3 Set the recorder or integration device, or both, for accurate presentation of the data. Set up instrument sensitivity such that any component of at least 0.05 % mass will be detected, integrated, and reported.

12.4 Inject 0.2 to 1.0 µL of sample into the injection port and start the analysis. Sample size must be consistent with the splitter linearity range as determined in Section 11. Obtain a chromatogram and peak integration report.

NOTE 3—Petroleum naphtha samples may contain appreciable quantities of highly volatile components. Samples should be chilled in their original container to 4°C (39°F) before opening for subsampling or transfer (see Section 8).

13. Calculation

13.1 Identify each peak by visually matching it with its counterpart in the appropriate standard chromatogram, Fig. 1,

Fig. 2, or Fig. 3. Make allowances for differences in relative peak sizes with different samples. Peaks eluting after *n*-nonane are not identified individually.

NOTE 4—To aid the analyst in setting up this test method and identifying peaks in the chromatograms, *qualitative* reference samples of the alkylate, naphtha, and reformate actually used to generate Fig. 1, Fig. 2, and Fig. 3 are available. Each can be analyzed and its chromatogram compared directly with the corresponding figure to assist in peak assignments.

13.2 Each peak can also be identified by matching its retention index with that of the compounds listed in Table 1. Equations for calculating retention indices are given in Annex A1. Retention indices of compounds eluted during the initial isothermal portion of the analysis must be calculated using the Kovats equation. Retention indices of all other components must be calculated using the equation for linear indices. Differences from the values in the table must be allowed for due to slight differences in columns, temperature, and flow. As noted in 11.1, retention times and therefore retention indices also vary as a result of column overload.

13.3 If a computing integrator is used for automatic identification, examine the report to ensure peaks are properly identified.

NOTE 5—Careful review of peak identifications is extremely important. Failure to do so may result in serious errors.

13.4 Sum the areas of all peaks eluting after *n*-nonane. This group will be treated as a single component, C_{10+}.

13.5 Calculate the mass percent of each component (including C_{10+}) according to the following equation:

$$\text{Mass \% component } i = \frac{A_i \times B_i}{\Sigma\,(A_i \times B_i)} \times 100 \qquad (5)$$

where:

A_i = area of peak representing component *i,* and

B_i = relative mass response factor for component *i*. Use a response factor of 1.00 for all components except benzene (0.90) and toluene (0.95).

NOTE 6—Relative mass response factors determined using quantitative calibration standards may be substituted for the assigned factors in 13.5. However, the reproducibility of the test method (Table 3) is based on data calculated using the assigned factors. Differences in interlaboratory results on the same sample may exceed the published reproducibility values as a result of using empirically determined response factors.

14. Report

14.1 Report the mass percent and identity of each component through *n*-nonane to the nearest 0.01 %.

14.2 Report the mass percent of C_{10+} to the nearest 0.01 %.

14.3 Report the total mass percent of all unidentified components through *n*-nonane.

15. Precision and Bias [4]

15.1 *Precision*—The precision of any individual measurement resulting from the application of this test method depends on several factors including the volatility of the component, its concentration, and the degree to which it is resolved from other closely eluting components. As it is not practical to determine the precision of measurement for every component (or group of components) separated by this test method, Table 3 presents the repeatability and reproducibility values for selected, representative components.

TABLE 3 Repeatability and Reproducibility for Selected Naphtha Components

Component Name	Repeatability	Reproducibility
Isobutane	$0.071(x)^{0.85}$	$0.13(x)^{0.85}$
n-Butane	$0.091(x)^{0.85}$	$0.17(x)^{0.85}$
Isopentane	$0.072(x)^{0.67}$	$0.17(x)^{0.67}$
n-Pentane	$0.051(x)^{0.67}$	$0.14(x)^{0.67}$
Cyclopentane^A	$0.026(x)^{0.50}$	$0.087(x)^{0.50}$
2,3-Dimethylbutane^A	$0.027(x)^{0.67}$	$0.12(x)^{0.67}$
3-Methylpentane	$0.015(x)$	$0.034(x)$
Methylcyclopentane	$0.016(x)$	$0.038(x)$
Benzene	$0.037(x)^{0.67}$	$0.092(x)^{0.67}$
2,3-Dimethylpentane^A	$0.014(x)$	$0.051(x)$
3-EthylPentane^A	$0.019(x)$	$0.094(x)$
n-Heptane	$0.012(x)^{0.50}$	$0.030(x)^{0.50}$
trans-1,2-Dimethylcyclopentane^A	$0.016(x)$	$0.053(x)$
Methylcyclohexane	$0.065(x)^{0.50}$	$0.16(x)^{0.50}$
Toluene	$0.015(x)$	$0.031(x)$
2,5-Dimethylhexane	$0.012(x)$	$0.030(x)$
2-Methylheptane	$0.037(x)^{0.50}$	$0.094(x)^{0.50}$
n-Octane	$0.010(x)$	$0.070(x)$
trans-1,2-Dimethylcyclohexane	$0.010(x)$	$0.024(x)$
1,1-Dimethylcyclohexane	0.0095 %	0.023 %
p-Xylene^A	$0.018(x)$	$0.15(x)$
2,2-Dimethylheptane	0.0050 %	0.0099 %
4-Methyloctane^A	$0.029(x)^{0.50}$	$0.073(x)^{0.50}$
n-Nonane^A	$0.017(x)$	$0.050(x)$

^{A} Component that is incompletely resolved, (*x*) refers to the mass percent component found.

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the repeatability values shown in Table 3 only in one case in twenty.

15.1.2 *Reproducibility*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 3 only in one case in twenty.

15.2 *Bias*—Bias in the measurements resulting from the application of this test method cannot be determined since there is no accepted reference material suitable for determining bias.

16. Keywords

16.1 alkylate; capillary gas chromatography; hydrocarbon composition; petroleum naphtha; reformate

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1265.

ANNEXES

(Mandatory Information)

A1. KOVATS AND LINEAR RETENTION INDICES

A1.1 The logarithmic *Kovats Retention Index*[5] is a gas chromatographic parameter characteristic of a solute's relative retention on a specified liquid phase at a specified (isothermal) temperature. It is a very useful tool in the qualitative identification of chromatographic peaks.

A1.1.1 Based on the observation that under isothermal conditions the adjusted retention times of members of a homologous series increase logarithmically with increasing carbon number, the Kovats Retention Index is a number indicating (on a logarithmic scale) the retention of a compound relative to the series of *n*-alkanes. (Adjusted retention time is the actual retention time minus the retention time of an unretained component such as methane.)

A1.1.2 The equation used to calculate the Kovats Retention Index I_{iso} of a compound A is given by Eq A1.1:

$$I_{iso} = 100 \times N + 100 \times \left(\frac{\log t'_{R(A)} - \log t'_{R(N)}}{\log t'_{R(N+1)} - \log t'_{R(N)}} \right) \quad \text{(A1.1)}$$

where $t'_{R(N)}$ and $t'_{R(N+1)}$ *are the adjusted retention times of* *n*-alkanes of carbon number N *and* $N+1$ that are respectively smaller and larger than $t'_{R(A)}$, *the adjusted retention time of a compound A.*

A1.1.3 Over a limited range and with some loss in accuracy, Kovats Retention Indices can be calculated by extrapolation rather than interpolation. In such case N and $N+1$ would be defined as the carbon numbers of consecutive *n*-alkanes, both eluting immediately before (or after) compound A. The equation otherwise remains unchanged.

A1.1.4 By definition the Kovats Retention Indices of *n*-alkanes are $100 \times N$ (for example, for *n*-hexane, I = 600 and for *n*-heptane, I = 700).

A1.1.5 Kovats Retention Indices are calculated from adjusted retention times obtained from a strictly isothermal analysis or from the initial isothermal temperature hold portion (if used) of a programmed temperature analysis. One may *not* utilize data from isothermal portions of an analysis which follow temperature changes incurred during a run.

A1.1.6 These indices are independent of other operating parameters. Kovats Retention Indices calculated from retention times determined on any suitable chromatographic system can be compared directly with those from any other suitable system as long as the liquid phase and the temperature are the same. Published compilations are an excellent source of indices for identification purposes.

A1.2 The *Linear Retention lndex*[6] is an extension of the Kovats concept to programmed temperature gas chromatography. The Linear Retention Index of a solute is dependent not only on the liquid phase but on other operating parameters as well. It is a useful indicator of relative retention of solutes on chromatographic systems operating under identical or nearly identical conditions.

A1.2.1 Based on the approximation that under programmed temperature conditions the actual retention times of members of a homologous series increase linearly with increasing carbon number, the Linear Retention Index is a number indicating (on a linear scale) the retention of a compound relative to the series of *n*-alkanes.

A1.2.2 The equation used to calculate the Linear Retention Index (I_{prog}) of a compound A is given by Eq A1.2:

$$I_{prog} = 100 \times N + 100 \times \left(\frac{t_{R(A)} - t_{R(N)}}{t_{R(N+1)} - t_{R(N)}} \right) \quad \text{(A1.2)}$$

where t_R is the actual retention time and the subscripts, *A, N,* and $N+1$ are defined as in A1.1.2 above.

A1.2.3 Over a limited range and with some loss in accuracy, Linear Retention Indices can be calculated by extrapolation rather than interpolation. In such cases, N and $N+1$ would be defined as the carbon numbers of consecutive *n*-alkanes, both eluting immediately after (or before) compound A. The equation otherwise remains unchanged.

A1.2.4 By definition, the Linear Retention Indices of *n*-alkanes are $100 \times N$ (for example, for *n*-octane, I = 800 and for *n*-nonane, I = 900).

A1.2.5 The usual application of the Linear Retention Index system is to linear programmed temperature analyses without isothermal plateaus (even at the beginning of the run). However, since the indices are generally limited to analyses with essentially identical operating conditions anyway, some analysts have used the Linear Retention Index system to reduce data from procedures utilizing complex temperature profiles. Such indices are not theoretically defensible, but nevertheless are useful indicators of relative retention especially for standard test methods.

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[5] Kovats, E., *Advances in Chromatography,* Vol 1, 1964.

[6] Van den Dool and Dratz, *Journal of Chromatography* , Vol 11, 1963, p. 463.

A2. MEASUREMENT AND CALCULATION OF FLOW PARAMETERS

A2.1 Column flow rate can be measured directly on some instruments at the flame ionization detector jet using a soap film flow-meter. This is the preferred way as long as all other gas flows can be turned off during the measurement.

A2.2 Column flow rate can also be calculated from column dimensions and flow parameters using the following series of equations:

A2.2.1 *Column Hold-up Time (s)*:

$$t_m = \text{retention time of methane} \qquad \text{(A2.1)}$$

A2.2.2 *Average Linear Gas Velocity (cm/s)*:

$$\bar{\mu} = L/t_m \qquad \text{(A2.2)}$$

when L is the column length, cm.

A2.2.3 *Gas Compressibility Correction Factor*:

$$j = \frac{3}{2} \times \frac{(p^2 - 1)}{(p^3 - 1)} \qquad \text{(A2.3)}$$

where p is the ratio of column inlet to column outlet absolute pressure.

A2.2.4 *Column Outlet Linear Velocity (cm/s)*:

$$\mu_o = \bar{\mu}/j \qquad \text{(A2.4)}$$

A2.2.5 *Column Cross-Sectional Area (cm^2)*:

$$A_c = \frac{\pi\,(d_i)^2}{4} \qquad \text{(A2.5)}$$

where d_i is the internal diameter of the column, cm.

A2.2.6 *Column Carrier Gas Flow Rate (cm^3/min)*:

$$F_c = \mu_o \times A_c \times 60 \qquad \text{(A2.6)}$$

A2.3 *Injection Split Ratio:*

$$\text{Split ratio} = \frac{F_c + F_v}{Fc} \qquad \text{(A2.7)}$$

where F_v is the directly measured flow rate through the splitter vent.

A2.4 *Example*—Given a 50-m column of 0.21-mm inside diameter, inlet pressure of 220 kPa (gage), outlet pressure of 101 kPa (absolute), retention time of methane of 3.62 min, and flow out the splitter vent of 200 cm ^{3}/min, calculate column flow rate and split ratio as follows:

$$t_m = 3.62\ \text{min} = 217\ \text{s} \qquad \text{(A2.8)}$$

$$\bar{\mu} = (5000)/(217) = 23.0\ \text{cm/s}$$

$$P = \frac{(220\ \text{kPa} + 101\ \text{kPa})}{101\ \text{kPa}} = 3.18$$

$$j = 3/2 \times [(3.18^2 - 1)/(3.18^3 - 1)] = 0.438$$

$$\mu_o = 23.0/0.438 = 52.5\ \text{cm/s}$$

$$A_c = \frac{\pi \times (0.021)^2}{4} = 0.000346\ \text{cm}^2$$

$$F_c = 52.5 \times 0.000346 \times 60 = 1.09\ \text{cm}^3\text{/min}$$

Split ratio = (200 + 1.09)/1.09 = 184:1