Designation: D5134 – 21

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.

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 detailed hydrocarbon analysis (DHA) test method covers the determination of hydrocarbon components paraffins, naphthenes, and monoaromatics (PNA) 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 or D6839. The hydrocarbon mixture must have a 98 % point of 250 °C or less as determined by Test Method D3710 or D7096 or equivalent.

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

1.4 This test method may not be completely accurate for PNA above carbon number C7; Test Method D5443 or D6839 may be used to verify or complement the results of this test method for carbon numbers >C7.

1.5 Detailed hydrocarbon components in olefin containing samples may be determined by DHA Test Methods D6729, D6730, or D6733.

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

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in Section 8.

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

---

[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 D02.04.0L on Gas Chromatography Methods.

Current edition approved Dec. 1, 2021. Published December 2021. Originally approved in 1990. Last previous edition approved in 2017 as D5134 – 13 (2017). DOI: 10.1520/D5134-21.

[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.

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

TABLE 1 Typical Retention Characteristics of Naphtha Components

NOTE 1—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
2-Methyl- *4*-Ethylhexane	44.74	41.17	...	832.4

TABLE 1 *Continued*

Compound	Retention Time, min	Adjusted Retention Time, min	Kovats Retention Index @ 35 °C	Linear Retention Index
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.

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 (Withdrawn 2014)[3]
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D5443 Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200 °C by Multi-Dimensional Gas Chromatography
D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, Benzene, and Toluene in Spark Ignition Engine Fuels by Multidimensional Gas Chromatography
D6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography
D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography
D6733 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Metre Capillary High Resolution Gas Chromatography
D7096 Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography
E355 Practice for Gas Chromatography Terms and Relationships
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practices E355 and E594, and Terminology D4175.

---

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

4. Summary of Test Method

4.1 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 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.

4.2 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+}.

5. Significance and Use

5.1 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.

5.2 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.

6. Interferences

6.1 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. Some coelutions of PNA components above C7 may occur and results may not be completely accurate. Test Method D5443 may be used for carbon number distribution above C7 to verify results from this test method.

6.2 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.

7. Apparatus

7.1 *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	$>10^7$

7.2 *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 12.

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

7.3.1 Capacity for at least 250 peaks/analysis.

7.3.2 Normalized area percent calculation with response factors.

7.3.3 Identification of individual components by retention time.

7.3.4 Noise and spike rejection capability.

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

7.3.6 Positive and negative sloping baseline correction.

7.3.7 Peak detection sensitivity for narrow and broad peaks.

7.3.8 Perpendicular drop and tangent skimming as needed.

7.4 *Capillary Column*—This test method utilizes a 50 m (0.2 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 11 for efficiency, resolution, and polarity.

8. Reagents and Materials

8.1 *Carrier Gas,* helium, mol fraction is 99.99 % pure. (**Warning—**Compressed gas under high pressure.)

8.2 *Fuel Gas,* hydrogen, mol fraction is 99.9 % pure. (**Warning—**Extremely flammable gas under pressure.)

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

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

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

8.6 *2-Methylheptane,* mol fraction is 99+ %. (**Warning—**Flammable. Harmful if inhaled.)

8.7 *4-Methylheptane,* mol fraction is 99+ %. (**Warning—**Flammable. Harmful if inhaled.)

8.8 *2-Methylpentane,* mol fraction is 99+ %. (**Warning—**Extremely flammable. Harmful if inhaled.)

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

8.10 *Toluene,* mol fraction is 99+ %. (**Warning—**Flammable. Vapor harmful.)

8.11 *2,3,3-Trimethylpentane,* mol fraction is 99+ %. (**Warning—**Extremely flammable. Harmful if inhaled.)

8.12 *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.

8.13 *Reference Alkylate,* actual refinery production alkylation product used for compound identification as in Fig. 1. (**Warning—**Extremely flammable. Harmful if inhaled.)

8.14 *Reference Virgin Naphtha,* actual refinery production stream used for compound identification as in Fig. 2. (**Warning—**Extremely flammable. Harmful if inhaled.)

8.15 *Reference Reformate,* actual refinery production reformer product ('reformate') for compound identification as in Fig. 3. (**Warning—**Extremely flammable. Harmful if inhaled.)

NOTE 1—Alkylate, virgin naphtha, and reformer production refinery reference samples may be available from several vendors; alternatively, in-house production materials or equivalent that matches closely the fingerprints in the chromatograms (Figs. 1-3) may be used.

9. Sampling

9.1 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. Samples taken into piston samplers may be sampled into a GC

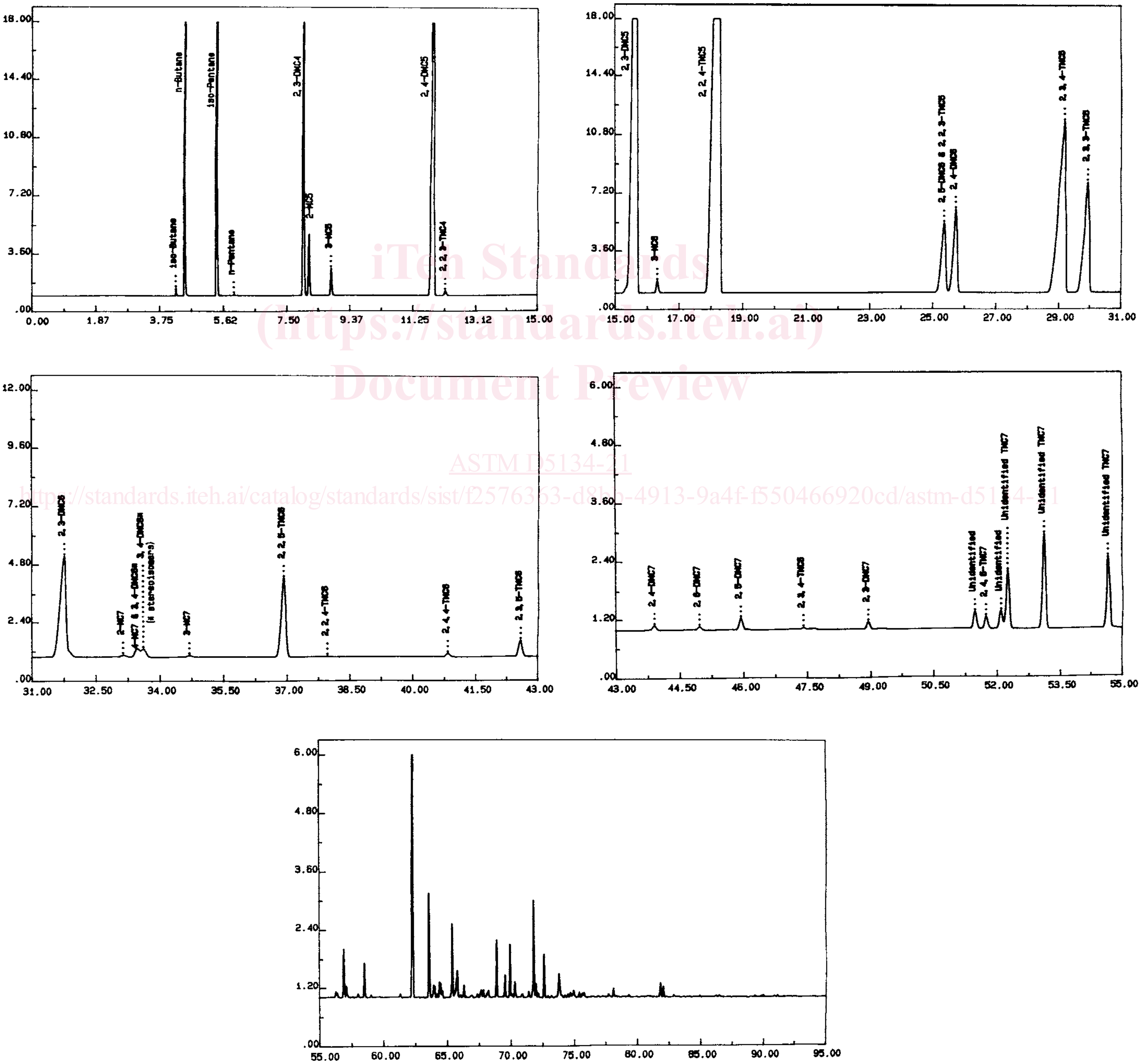

FIG. 1 Reference Alkylate Chromatogram

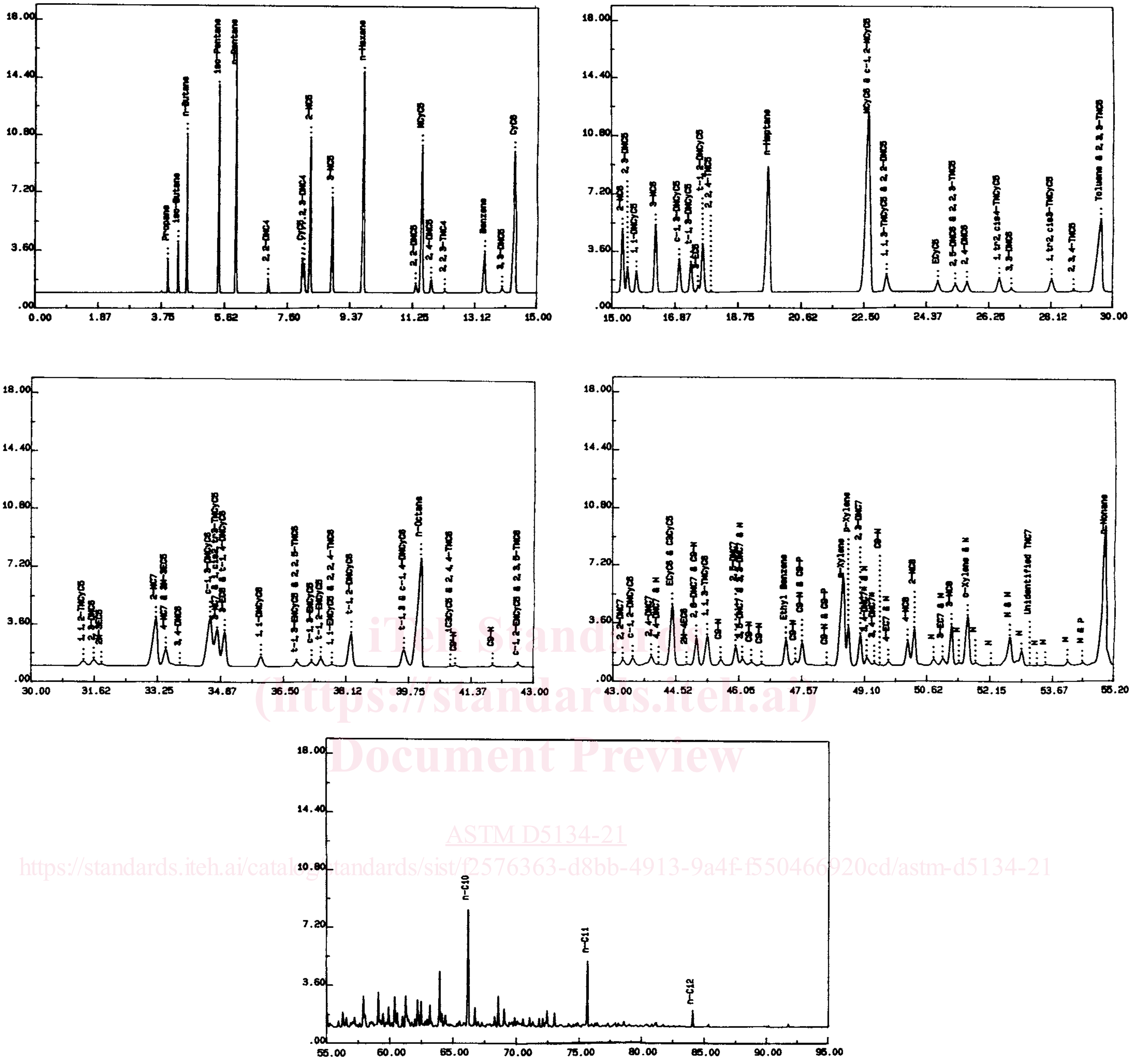

FIG. 2 Reference Virgin Naphtha Chromatogram

vial or equivalent provided that upon chilling and transfer does not lead to significant losses of light components.

NOTE 2—Although possible, this test method has not been evaluated for injection of pressurized samples that require high pressure liquid injection valves.

9.1.1 *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.

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

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

9.3 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.

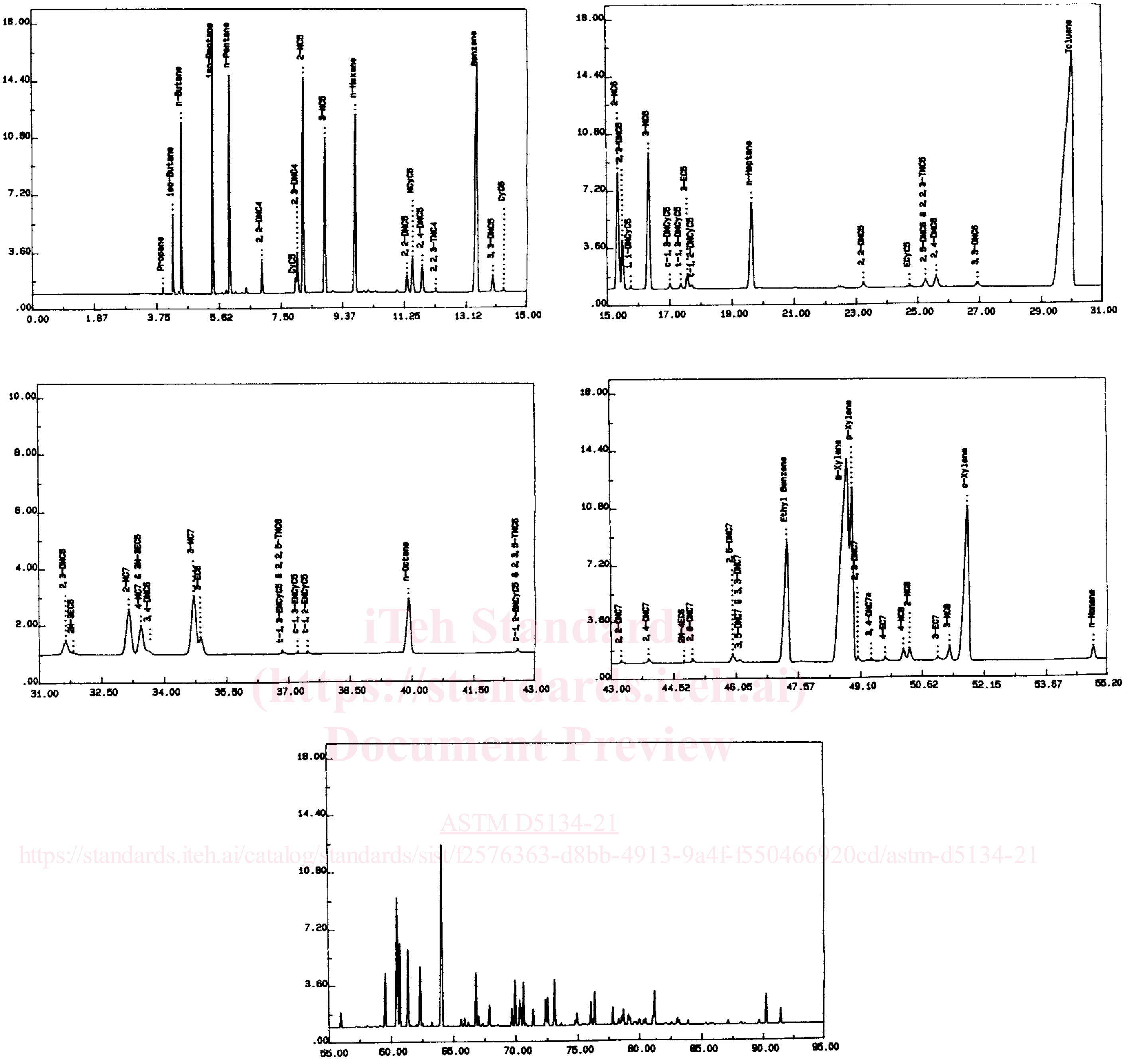

FIG. 3 Reference Reformer Product (Reformate) Chromatogram

10. Preparation of Apparatus

10.1 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.

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

10.2.1 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.

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

10.2.3 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 3—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 °C to 3 °C may cause those same peaks to be unresolved or even reverse their elution order.

10.3 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.