



Designation: D5443 – 23

Standard Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200 °C by Multi-Dimensional Gas Chromatography¹

This standard is issued under the fixed designation D5443; 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 of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points of 200 °C or less. Hydrocarbons with boiling points greater than 200 °C and less than 270 °C are reported as a single group. Olefins, if present, are hydrogenated and the resultant saturates are included in the paraffin and naphthene distribution. Aromatics boiling at C₉ and above are reported as a single aromatic group.

1.2 This test method is not intended to determine individual components except for benzene and toluene that are the only C₆ and C₇ aromatics, respectively, and cyclopentane that is the only C₅ naphthene. The lower limit of detection for a single hydrocarbon component or group is 0.05 % by mass.

1.3 This test method is applicable to hydrocarbon mixtures including virgin, catalytically converted, thermally converted, alkylated and blended naphtha.

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

1.4.1 The abbreviation for SI unit “coulomb” is “C”.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 8 and Table 1.*

1.6 *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 Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards:*²

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards](#)

[D5134 Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography](#)

[D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, Benzene, and Toluene in Spark Ignition Engine Fuels by Multidimensional Gas Chromatography](#)

[E355 Practice for Gas Chromatography Terms and Relationships](#)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#) and Practice [E355](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *naphthene(s), n—cycloparaffin(s).*

4. Summary of Test Method

4.1 A representative sample is introduced into a gas chromatographic system containing a series of columns and switching valves. As the sample passes through a polar column, the polar aromatic compounds, bi-naphthenes, and high boiling (>200 °C) paraffins and naphthenes are retained. The fraction not retained elutes to a platinum column, that hydrogenates olefins, if present, in this fraction, and then to a molecular sieve column which performs a carbon number separation based on

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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.

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

TABLE 1 Hydrocarbon Test Mixture

Hydrocarbons	Warning
Cyclopentane	(Warning—Extremely Flammable. Harmful if inhaled.)
Pentane	(Warning—Extremely Flammable. Harmful if inhaled.)
Cyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
2,3-Dimethylbutane	(Warning—Extremely Flammable. Harmful if inhaled.)
Hexane	(Warning—Extremely Flammable. Harmful if inhaled.)
1-Hexene	(Warning—Extremely Flammable. Harmful if inhaled.)
Methylcyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
4-Methyl-1-hexene	(Warning—Extremely Flammable. Harmful if inhaled.)
Heptane	(Warning—Flammable. Harmful if inhaled.)
1,cis-2-Dimethylcyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
2,2,4-Trimethylpentane (iso-octane)	(Warning—Flammable. Harmful if inhaled.)
Octane	(Warning—Flammable. Harmful if inhaled.)
1,cis-2,cis-4-Trimethylcyclohexane	(Warning—Flammable. Harmful if inhaled.)
Nonane	(Warning—Flammable. Harmful if inhaled.)
Decane	(Warning—Flammable. Harmful if inhaled.)
Undecane	(Warning—Flammable. Harmful if inhaled.)
Dodecane	(Warning—Flammable. Harmful if inhaled.)
Benzene	(Warning—Extremely Flammable. Harmful if inhaled.)
Methylbenzene (Toluene)	(Warning—Flammable. Harmful if inhaled.)
trans-Decahydronaphthalene (Decalin)	(Warning—Flammable. Harmful if inhaled.)
Tetradecane	(Warning—Harmful if inhaled.)
Ethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2-Dimethylbenzene (o-Xylene)	(Warning—Extremely Flammable. Harmful if inhaled.)
Propylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,4-Trimethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,3-Trimethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,4,5-Tetramethylbenzene	(Warning—Flammable. Harmful if inhaled.)
Pentamethylbenzene	(Warning—Harmful if inhaled.)

molecular structure, that is, naphthenes and paraffins. The fraction remaining on the polar column is further divided into three separate fractions that are then separated on a non-polar column by boiling point. Eluting compounds are detected by a flame ionization detector.

4.2 The mass concentration of each group is determined by the multiplication of detected peak areas by flame ionization detector response factors and normalization to 100 %.

4.3 This test method provides limited identification of individual hydrocarbon components. Test Method **D5134** may be used to obtain speciation of a number of individual compounds. For samples containing olefins, Test Method **D6839** provides carbon number distributions of hydrocarbon types (PIONA).

5. Significance and Use

5.1 A knowledge of the composition of hydrocarbon refinery streams is useful for process control and quality assurance.

5.2 Aromatics in gasoline are soon to be limited by federal mandate. This test method can be used to provide such information.

6. Interferences

6.1 Chemicals of a non-hydrocarbon composition may elute within the hydrocarbon groups, depending on their polarity, boiling point, and molecular size. Included in this group are ethers (for example, methyl-tertiary butyl ether) and alcohols (for example, ethanol).

7. Apparatus

7.1 *Chromatograph*—A gas chromatograph capable of isothermal operation at $130\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$. The gas chromatograph must contain the following:

7.1.1 A heated flash vaporization sample inlet system capable of operation in a splitless mode.

7.1.2 Associated gas controls with adequate precision to provide reproducible flows and pressures.

7.1.3 A flame ionization detection system optimized for use with packed columns and capable of the following:

Isothermal temperature operation	150 °C to 170 °C
Sensitivity	>0.015 C/g
Minimum detectability	5×10^{-12} g carbon/s
Linearity	> 10^7

Some instruments will produce a non-linear response for benzene, above approximately 5.5 % by mass, and for toluene above approximately 15 % by mass. The linearity of these components above these concentrations must be verified with appropriate blends. Where non-linearity has been shown to exist, samples, that contain no higher than C_{13} , can be analyzed if the sample is diluted with $n-C_{15}$ and the instrument is equipped with a prefractionating column. The sample may also be diluted with a component that is not present in the sample and this component will then not be included in the normalized report.

7.2 *Sample Introduction System*—Manual or automatic liquid sample system operated in a splitless mode. Although this test method is intended primarily for use with syringe sample injection, automatic sampling valves have also been found satisfactory. Devices capable of a reproducible injection volume of 0.1 μL to 0.5 μL are suitable. The sample introduction system must be capable of heating the sample to a temperature that ensures total sample vaporization. A temperature range of 120 °C to 180 °C has been found suitable.

7.3 *Electronic Data Acquisition System*—The data acquisition and integration device used for detection and integration must meet or exceed the following specifications:

- 7.3.1 Capacity for at least 75 peaks for each analysis,
- 7.3.2 Normalized area percent calculation,
- 7.3.3 Noise and spike rejection capability,
- 7.3.4 Sampling rates for fast (<2 s) peaks,
- 7.3.5 Peak width detection for narrow and broad peaks, and
- 7.3.6 Perpendicular drop and tangent skimming as required.

7.4 *Independent Temperature Control*—This test method requires the temperature control of five columns, column switching valves and sample lines. The columns consist of polar, non-polar, Tenax³, platinum, and molecular sieve columns. The specifications for these columns are listed in **Table 2**. The polar column, non-polar column, column switching valves, and sample lines require isothermal operation at a temperature equivalent to the temperature of the gas chromatograph oven. These components may be located in the gas chromatograph oven. The Tenax column, platinum column, and molecular sieve column require operation at temperatures

³ Tenax is a registered trademark of AKZO, Velperweg 76, P.O. Box 9300, 6800 SB Arnhem, The Netherlands.

TABLE 2 Typical Column Specifications

Specification	Column Type				
	Polar	Non-Polar	Tenax ³	Molsieve	Platinum
Column length, m	3	4	0.16 to 0.18	1.8	0.002 to 0.06
Column inside diameter, mm	2.0 to 2.1	1.8 to 2.0	2.5	1.6 to 2.0	1.6
Liquid phase	OV-275 ^A	OV-101 ^A
Percent liquid phase	30	4–5
Support material	Chromasorb ^B	Chromasorb ^B
	PAW	WAW
Packing material	Tenax ³	Molecular sieve 13X ^{C, D}	...
Mesh size	60/80	80/100	80/100

^A OV-101 and OV-275 are registered trademarks of Ohio Valley Specialty Chemical Co., 115 Industry Rd., Marietta, OH 45750.

^B Chromasorb is a registered trademark of World Minerals, Corp., Santa Barbara, CA.

^C Sodium form of molecular sieve 13X.

^D May also contain a mix of molecular sieves 13X and 5A to separate normal and iso-paraffins.

other than the gas chromatograph oven temperature. These columns may be temperature controlled by any means that will meet the specifications in [Table 2](#).

7.4.1 Ability to control the temperature of the Tenax column within a range from 60 °C to 280 °C, with a tolerance of ± 5 °C at any point. The time required to heat this column between any two points must be no more than 1 min. The time required to cool this column between any two points must be no more than 5 min,

7.4.2 Ability to control the temperature of the molecular sieve column within a range from 100 °C and 490 °C, with a tolerance of ± 10 °C at any point. The time required to heat this column between any two points must be no more than 10 min. The time required to cool this column from 450 °C to 100 °C must be no more than 15 min, and

7.4.3 Ability to control the platinum column within a temperature range of 170 °C and 350 °C. During routine analysis, this column is operated within a temperature range of 170 °C to 220 °C.

NOTE 1—Newer analyzers may have updated hardware and/or separation columns types and traps dimensions. Precision using using newer hardware configurations or conditions have not been studied by ASTM. The precision listed in this method was obtained with hardware described in this test method.

8. Materials

8.1 *Carrier Gases*—For carrier gases, it is recommended to install commercial active oxygen scrubbers and water dryers, such as molecular sieves, ahead of the instrument to protect the system’s chromatographic columns. Follow supplier instructions in the use of such gas purifiers and replace as necessary.

8.1.1 *Hydrogen*, 99.995 % by mol minimum purity, <0.1 $\mu\text{L/L}$ H₂O. (**Warning**—Extremely flammable gas under high pressure.)

8.1.2 *Helium*, 99.995 % by mol minimum purity, <0.1 $\mu\text{L/L}$ H₂O. (**Warning**—Compressed gas under high pressure.)

8.2 Detector Gases:

8.2.1 *Hydrogen*, 99.99 % by mol minimum purity. (**Warning**—Extremely flammable gas under high pressure.)

8.2.2 *Air*, less than 10 $\mu\text{L/L}$ each of total hydrocarbons and water. (**Warning**—Compressed gas under high pressure.)

8.3 *Valve Actuation Gas*—This test method permits the use of any type of valve switching or valve actuation. When pneumatic valves are used, air of any grade that will result in

no water condensation or will not introduce oil or other contaminants in the switching valves may be used. Air from a piston operated compressor equipped with a water and oil separator has been found suitable. Column switching valves that do not require air to operate do not have this air requirement.

8.4 *Columns*—Five columns, as described in [Table 2](#). These column specifications are to be considered as guidelines and have been found to be acceptable. Other materials or combinations of materials may also provide acceptable performance. The suitability of each column is determined by test criteria as defined in [Section 9](#).

NOTE 2—It is not the intention of this test method to include detailed column preparation steps. Columns may be prepared in any way that follows accepted safety practices and results in columns that will meet the performance requirements of [Section 10](#).

8.5 *Valves*—This test method uses valves for column switching and flow switching. Any commercially available valves may be used that are intended for, or adapted for use in gas chromatography that meet the following specifications:

8.5.1 The column switching valves are generally installed in the gas chromatograph oven. These valves must be capable of continuous operation at the operating temperature of the GC oven.

8.5.2 Materials used in the construction of the valves must be unreactive to hydrocarbons present in the sample under analysis conditions. Stainless steel, PFA, and vespel materials have been found suitable.

8.5.3 Valves must be sized such that they offer little restriction to carrier gas flow under the analysis conditions defined in this test method.

8.5.4 Care must be taken to prevent the introduction of any form of foreign material or contaminant into the valve that may adversely affect its performance.

8.6 *Hydrocarbon Test Mixture*—A quantitative synthetic mixture of pure hydrocarbons, an example of which is identified in [Table 1](#), is used to tune the instrument analysis conditions and establish that the instrument is performing within specifications. Individual hydrocarbon components, in addition to those listed in [Table 1](#), may be used to aid in the analysis. The concentration level of each component in the hydrocarbon test mixture is not critical as long as the concentration is accurately known. Percentage ranges from 1.0 % to