Designation: D8396 – 22

Standard Test Method for Group Types Quantification of Hydrocarbons in Hydrocarbon Liquids with a Boiling Point between 36 °C and 343 °C by Flow Modulated GCxGC – FID[1]

This standard is issued under the fixed designation D8396; 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 quantitative determination of total n-paraffins, total i-paraffins, total naphthenes (cycloparaffins), total one ring (1R) and total two ring plus (2R+) aromatic hydrocarbons in hydrocarbon liquids having a boiling point between 36 °C and 343 °C by GCxGC (flow modulated comprehensive two-dimensional gas chromatography). The method has been applied to aviation turbine fuels and is applicable to other low olefinic fuels in the stated boiling point range.

1.2 This test method has an interim precision. An expanded full interlaboratory study is to be completed in <5 years. The test method working concentration ranges in mass percent for which the interim precision has been determined are as follows:

Hydrocarbon Type	Lower limit (mass percent)	Upper limit (mass percent)
Total i-paraffins	22.0	24.3
Total n-paraffins	19.0	21.9
Total naphthenes (cycloparaffins)	34.3	36.7
Total one ring aromatics	18.7	21.8
Total two ring plus aromatics	0.5	1.9

1.3 This test method is applicable to other group type concentration ranges, to other hydrocarbon types such as selected individual components, for example, benzene, toluene, or n-paraffins by carbon number, or to other hydrocarbon streams; however, precision has not been determined at this time. A future ILS will include a variety of sample types and extend the reporting.

1.4 This test method is not intended to determine unsaturated hydrocarbons, such as olefins, content which may interfere with the cycloparaffins; this test method is applicable to samples with < 1% by mass total olefins as determined by D1319.

1.5 This test method is not intended to determine FAME (fatty acid methyl esters). For such applications, Test Method D7797, IP 585, or equivalent test methods are available.

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 test method does not mandate or describe a specific software package for data processing and display. Any commercially available GCxGC software used for data processing and display shall meet the requirements for the calculation of the results. Appendix X1 provides some guidelines.

1.8 *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.*

1.9 *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:*

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

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre

[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.

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Capillary (with Precolumn) High-Resolution Gas Chromatography
D7797 Test Method for Determination of the Fatty Acid Methyl Esters Content of Aviation Turbine Fuel Using Flow Analysis by Fourier Transform Infrared Spectroscopy—Rapid Screening Method
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 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 *comprehensive two-dimensional gas chromatography (GCxGC), n*—an analytical technique which utilizes two different columns with two distinct orthogonal polarity stationary phases that separate target components.

3.2.1.1 *Discussion*—The effluent from the first-dimension column is collected, focused, and injected into the second-dimension column via a flow modulator. The effluent from the second-dimension is then directed into an FID. Using the two columns of different polarity allows the separation of the specified compounds into compound classes and several individual compounds.

3.2.2 *first-dimension column, n—in this test method*, a polar column used to separate components based on differences in polarity of the compounds being separated.

3.2.3 *flow modulator, n*—GCxGC system in which the interface device operates by a flow switching mechanism.

3.2.4 *GCxGC orthogonality, n*—two chromatographic dimensions that employ different separation mechanisms to determine elution times for the purpose of component identification and in which each dimension can be treated as statistically independent; in this test method, orthogonality is achieved by using two column phases that are different in polarity, such as a polar and non-polar column, to attain the required resolution of the components.

3.2.5 *hydrocarbon liquids, n—in this test method*, fuels or process streams primarily composed of hydrogen and carbon, with a boiling point in the range of approximately 36 °C to 343 °C and containing <1 % by volume total olefins, such as aviation fuels and kerosenes.

3.2.5.1 *Discussion*—Applicable fuels and processed streams may contain compounds of oxygen, nitrogen, or sulfur, or combinations thereof; however, these compounds, if present, usually are spread over a wide range of boiling point and in very low concentrations (for example, mg/kg) that cannot be detected and do not interfere with this test method. More specialized techniques may be required for their detection.

3.2.6 *injection time, n*—the time that the valve is switched to the second-dimension column.

3.2.7 *modulation, n*—the process of continuously collecting and reinjecting per modulation period onto the second-dimension column each fraction eluting from the first-dimension column.

3.2.8 *modulation delay, n*—the time between the start of the analysis and the first modulation.

3.2.9 *modulation period, n*—the duration of a complete cycle of modulation, i.e., the time between two successive injections into the second column.

3.2.10 *modulator, n*—interface device between the two columns in a comprehensive two-dimensional separation system that accumulates eluate of the first column for a brief period, typically on the order of seconds, for fast reinjection into the second column.

3.2.11 *monitor column, n*—a column allowing recording the chromatogram from the first-dimension column.

3.2.12 *peak or blob, n*—a graphical representation in the two-dimensional chromatogram of a component eluting from the GCxGC system; it is the sum of all the individual modulated cycles for that component.

3.2.13 *second-dimension column or secondary column, n—in this test method*, a non-polar “boiling point” column used to acquire the second-dimension separation data based upon differences in boiling point of the components.

3.2.14 *separation space, n*—the plane region within the two-dimensional GCxGC plot in which compounds are, or may be, distributed.

3.2.15 *template, n*—a graphical object applied to a two-dimensional GCxGC image that is used to identify the boundaries between different hydrocarbon types.

3.2.16 *wrap-around, n*—the occurrence or appearance of second dimension peaks in consecutive modulation cycles, caused by second-dimension retention times that exceed the modulation period.

4. Summary of Test Method

4.1 A representative sample is injected into a gas chromatograph that is equipped with a two-stage flow modulator system, first-dimension and second-dimension capillary GC columns, and a flame ionization detector (FID). The flow modulator serves as an interface between the two GC columns. The first-dimension column in the series is a high-resolution capillary GC column coated with a polar stationary phase. The second-dimension GC column is a non-polar capillary. The modulator repetitively accumulates and re-injects fractions eluting off the first-dimension column onto the second-dimension column, which is connected to the FID. The outcome is a series of high-speed two-dimensional chromatograms from the second-dimension column from which peak data are collected, and then transformed into two-dimensional output by GCxGC software.

NOTE 1—This test method uses flow modulation and intermediate precision is based on such modulation. Precision and bias compared to other modulators, such as thermal modulation, has not been determined. Such other modulations may be tested in a future ILS to determine bias and precision.