Designation: D8276 – 19 (Reapproved 2024)

Standard Test Method for Hydrocarbon Types in Middle Distillates, including Biodiesel Blends by Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D8276; 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 an analytical scheme using the gas chromatography/mass spectrometry (GC-MS) to determine the hydrocarbon types present in middle distillates 170 °C to 365 °C boiling range, 5 % to 95 % by volume as determined by Test Method D86, including biodiesel blends with up to 20 % by volume of fatty acid methyl ester (FAME). The detailed hydrocarbon composition, total aromatic hydrocarbon and polycyclic aromatic hydrocarbon contents can be determined. The hydrocarbon types include: paraffins, noncondensed cycloparaffins, condensed dicycloparaffins, condensed tricycloparaffins, alkylbenzenes, indans or tetralins, or both, C_nH_{2n-10} (indenes, etc.), naphthalenes, C_nH_{2n-14} (acenaphthenes, etc.), C_nH_{2n-16} (acenaphthylenes, etc.), and tricyclic aromatics. The content of FAME in biodiesel blends can also be determined by GC.

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

1.3 *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.*

1.4 *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]

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

D2425 Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

D8144 Test Method for Separation and Determination of Aromatics, Nonaromatics, and FAME Fractions in Middle Distillates by Solid-Phase Extraction and Gas Chromatography

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 The detailed definitions of the summation of characteristic mass fragments can be found in Test Method D2425.

3.1.2 *dual column GC-MS system, n*—a gas chromatography/mass spectrometry system equipped with a hydrogen flame ionization detector (FID). Samples introduced by the sample introduction system are split into two capillary columns in parallel, in which one column connected to the FID and the other one connected to the mass spectrometer.

3.1.3 *polycyclic aromatic hydrocarbons, n*—sum of the concentrations of naphthalenes, C_nH_{2n-14} (acenaphthenes, etc.), C_nH_{2n-16} (acenaphthylenes, etc.) and tricyclic aromatics.

[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 Spectrometry.

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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.

3.1.4 *total aromatic hydrocarbons, n*—sum of the concentrations of alkylbenzenes, indans, tetralins, C_nH_{2n-10} (indenes, etc.) and polycyclic aromatics.

4. Summary of Test Method

4.1 Samples are separated into saturate, aromatic, and/or FAME fractions by Test Method D8144. Aliquots of internal standards are added to these fractions and all of these fractions are analyzed by the dual column GC-MS system. The contents of the saturates, aromatic, and/or FAME fractions are calculated based on the FID peak areas according to Test Method D8144 and the detailed hydrocarbon composition analysis can be determined by the summation of characteristic mass fragments in the saturate and aromatic fractions. Calculations are performed as the procedures described in Test Method D2425 and the concentration of hydrocarbon types in each fraction are mathematically combined according to their mass percents. The contents of total aromatics and polycyclic aromatics can be calculated by summing up the concentrations of corresponding hydrocarbon types. The content of FAME in biodiesel blends can be determined by GC-FID. Results are expressed in mass percent.

5. Significance and Use

5.1 A knowledge of the hydrocarbon composition of the middle distillates, including the biodiesel blends is useful in following the effect of changes in process variables, diagnosing the source of plant upsets, and in evaluating the effect of changes in composition on product performance properties. The total aromatics content and polycyclic aromatics content are also important to evaluate the quality of diesel fuels/biodiesel blends. It requires an appropriate analytical method to make such determinations for diesel fuel/biodiesel blends production process and quality control.

5.2 This test method provides a comprehensive analytical strategy for the determination of the total aromatics contents, polycyclic aromatics contents and the detail hydrocarbon composition of diesel fuel/biodiesel blends to ensure compliance with certain specifications or regulations.

5.3 Test Method D2425 is applicable to the determination of the detailed hydrocarbon composition in middle distillates, however, the pre-separation procedure of elution chromatography is time-consuming and not eco-friendly. By combining with the separation procedures described in Test Method D8144, the dual column GC-MS system proposed in this method can determine the total aromatic hydrocarbon contents, polycyclic aromatic hydrocarbon contents and detailed hydrocarbon composition of diesel fuel/biodiesel blends simultaneously. The content of FAME in biodiesel blends can also be determined by GC. It is demonstrated to be time-saving and eco-friendly for the quality control of diesel fuel and biodiesel blends.

6. Apparatus

6.1 *Dual Column GC-MS System*—The dual column GC-MS system shall be equipped with sample introduction system, capillary column, column temperature programmer, FID, mass spectrometer, and data acquisition system. Samples are introduced into the dual column GC-MS system and split into two capillary columns in parallel, then analyzed by the FID and mass spectrometer, respectively. The schematic representation of dual column GC-MS system is shown in Fig. 1. Recommended GC-MS operating conditions are given in Table 1. The GC-MS system and operating conditions shall ensure baseline separation of the solvent, sample and internal standard as shown in Fig. 2 and Fig. 3. Any other GC-MS system and operating conditions capable of yielding equivalent results may be used.

6.1.1 *Sample Introduction System*—Manual or recommended automated liquid syringe injection into a splitting inlet may be employed. An inlet adaptor and two-hole ferrule are required for connecting two capillary columns in parallel to the inlet of GC. The sample amount reaching the column (combination of injection volume and split ratio) should meet the requirement of separation efficiency of column and linear response calibration range.

6.1.2 *Capillary Column*—Two identical non-polar silica capillary columns are recommended in this test method. One

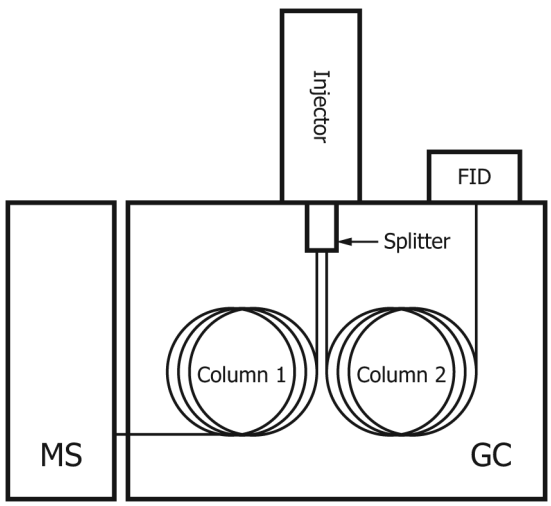

FIG. 1 Schematic Representation of Dual Column GC-MS System