



Designation: D8276 – 19

Standard Test Method for Hydrocarbon Types in Middle Distillates, including Biodiesel Blends by Gas Chromatography/Mass Spectrometry¹

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

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.

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 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.

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 simultane-

ously. 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 end of these two columns is connected in parallel to the inlet of GC and the other one end of them is connected to the FID and the mass spectrometer, respectively. The column and conditions must provide separation of typical petroleum hydrocarbons in order of increasing boiling point. See Fig. 2 and Fig. 3 for examples of acceptable separation.

6.1.3 *FID*—This test method requires a flame ionization detector (FID). The detector shall have enough sensitivity, linearity, and stability to meet performance requirements.

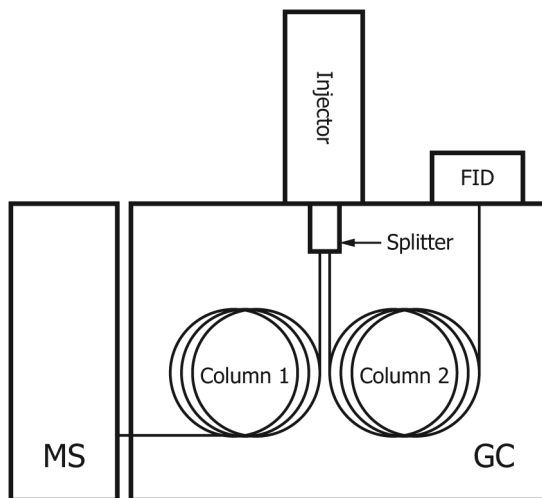


FIG. 1 Schematic Representation of Dual Column GC-MS System

TABLE 1 Recommended Operating Conditions of GC-MS^A

Gas Chromatograph:	
Column	Fused silica WCOT capillary column
Size	30 m × 0.25 mm ID, film thickness 0.25 μm
Stationary phase	Non-polar, such as 100 % dimethyl polysiloxane or 5 % phenyl-methyl polysiloxane
Oven Temperature Program	60 °C for 2 min, then 40 °C /min to 300 °C for 5 min
Inlet	
Temperature	300 °C
Split ratio	30:1
Sample size	1.0 μL
Carrier gas	
Type	Helium
Constant Flow Mode	1 mL/min
Detector	
Type	Flame ionization detector (FID)
Temperature	350 °C
Fuel gas	Hydrogen (~30 mL/min)
Oxidizing gas	Air (~300 mL/min)
Make-up gas	Helium (~25 mL/min)
GC-MS Interface:	
GC-MS interface type	Direct
GC-MS interface temperature	300 °C
Mass Spectrometer:	
Type	Quadrupole
MS data acquisition mode	Full scan
Scan rate (amu/s)	~1500
Mass scan range	m/z 50–300
Ionization voltage	70 eV
MS source temperature	220 °C
Solvent delay	2 min (adjust according to the retention time of solvent in TIC chromatogram)

^A The ILS study was performed under these typical operating conditions given in this table. The operating condition may vary. The length of the WCOT (wall-coated open tubular) column can be 15 m to 30 m; the inner diameter can be 0.15 mm to 0.32 mm. The suitable oven program can be selected to ensure baseline separation of the solvent, sample, and internal standard. See Fig. 2 and Fig. 3 for examples of suitable resolution.

6.1.4 Mass Spectrometry—The mass spectrometer shall be capable of producing electron ionization spectra at 70 eV or higher, and capable of acquiring mass spectra from 50 amu to 300 amu with unit resolution or better. The mass spectrometer shall be capable of being interfaced to a gas chromatograph and capillary column. The interface shall be at a high enough temperature to prevent condensation of components boiling up to 350 °C.

6.1.5 Data Acquisition System—A computerized data acquisition system shall be capable of acquiring of total ion chromatogram (TIC) and FID chromatogram simultaneously during the sample runs. The average mass spectrum for the duration of the chromatographic program shall be obtained for the summation of characteristic mass fragments. And the areas of FID chromatogram shall be integrated manually or automatically.

7. Reagents and Materials

7.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society,

where such specifications are available.³ Other grades may be used, provided it is pure enough to be used without lessening the accuracy of the determination.

7.2 *n*-hexane, reagent grade. (**Warning**—Flammable.)

7.3 *n*-triacontane, reagent grade.

7.4 *Internal Standard Solution*, triacontane dissolved in *n*-hexane solvent to obtain the mass concentrations of 0.001 g/mL to 0.005 g/mL.

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

7.6 *Hydrogen*, 99.9 % pure. (**Warning**—Extremely flammable gas under high pressure.)

7.7 *Air*, compressed, 99.9% pure. (**Warning**—Compressed gas under high pressure that supports combustion.)

7.8 *Quality Control Sample*, used to routinely monitor the stability and performance of the GC-MS system. The quality control (QC) sample is a saturate or an aromatic fraction of middle distillates separated by Test Method D8144. The composition of QC sample shall be similar with that in test sample.

7.9 *Check Standard*, saturate and aromatic fractions separated by Test Method D8144 with known hydrocarbon composition. The accepted reference value (ARV) of this check standard is determined by collaborative experimental work using Test Method D2425 according to the requirement of Practice D6299. If check standards are easily available, they can be also used as QC samples to monitor both stability and accuracy simultaneously.

NOTE 1—Any commercially available check standard with known hydrocarbon composition and uncertainties acceptable for the intended application can also be used.

8. Sampling

8.1 Unless otherwise specified, samples shall be obtained in accordance with Practices D4057, D4177, or other comparable practices. Samples should be stored in sealed containers.

9. Calibration and Preparation of Apparatus

9.1 Prepare the GC-MS system according to manufacturer's instructions and set analysis operating conditions as suggested by Table 1.

9.2 Calibrate and tune the mass spectrometer as following every two weeks or when the overall performance of the mass spectrometry is not satisfied.

9.2.1 Mass calibration for the mass spectrometer is performed using perfluorotributylamine (PFTBA) which contains the masses 69, 131, 219, 414, and 502. An ionization voltage of 70 eV is used.

9.2.2 Tune the spectrometer using the tune file recommended by the manufacturer. Typically, using the masses of 69,

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.