



Designation: D7861 – 14

Standard Test Method for Determination of Fatty Acid Methyl Esters (FAME) in Diesel Fuel by Linear Variable Filter (LVF) Array Based Mid-Infrared Spectroscopy¹

This standard is issued under the fixed designation D7861; 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 determines fatty acid methyl esters (FAME or biodiesel) in diesel fuel oils. FAME can be quantitatively determined from 1.0 % to 30.0 % by volume. This test method uses linear variable filter (LVF) array based mid-infrared spectroscopy for monitoring FAME concentration.

NOTE 1—See Section 6 for a list of interferences that could affect the results produced from this method.

1.2 This test method uses a horizontal attenuated total reflectance (HATR) crystal and a univariate calibration.

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

1.4 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

- D975 Specification for Diesel Fuel Oils
- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D5854 Practice for Mixing and Handling of Liquid Samples 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
- D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
- D7371 Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)
- D7467 Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)
- E168 Practices for General Techniques of Infrared Quantitative Analysis (Withdrawn 2015)³
- E1655 Practices for Infrared Multivariate Quantitative Analysis

3. Terminology

3.1 Definitions:

- 3.1.1 *biodiesel, n*—fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.
- 3.1.2 *biodiesel blend (BXX), n*—blend of biodiesel fuel with diesel fuel oils.
 - 3.1.2.1 *Discussion*—In the abbreviation, BXX, the XX represents the volume percentage of biodiesel fuel in the blend.
- 3.1.3 *diesel fuel, n*—petroleum-based middle distillate fuel.
- 3.1.4 *univariate calibration, n*—a process for creating a calibration model in which a single measured variable, for

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

example, the absorbance at a particular wavelength, is correlated with the concentration or property values for a set of calibration samples.

3.2 Acronyms:

- 3.2.1 *ATR*, *n*—attenuated total reflectance
- 3.2.2 *BXX*, *n*—see 3.1.2
- 3.2.3 *FAEE*, *n*—fatty acid ethyl esters
- 3.2.4 *FAME*, *n*—fatty acid methyl esters
- 3.2.5 *HATR*, *n*—horizontal attenuated total reflectance
- 3.2.6 *LVF*, *n*—linear variable filter

4. Summary of Test Method

4.1 A sample of diesel fuel or biodiesel blend (BXX) is placed onto a HATR sample crystal. Infrared light is imaged through the sample, then through the LVF and finally onto a detector array. The LVF separates the infrared light into specific wavelengths so that the response of the detector array generates an infrared spectrum. Spectral corrections are performed to eliminate interferences caused by diesel and biodiesel variations. A wavelength region of the absorption spectrum that correlates highly with biodiesel is selected for analysis. The area of the selected region is determined. A calibration curve converts the selected area of an unknown sample to a concentration of biodiesel.

4.2 This test method uses a LVF array based mid-infrared spectrometer with an HATR crystal. The absorption spectrum shall be used to calculate a calibration curve.

5. Significance and Use

5.1 Biodiesel is a fuel commodity primarily used as a blending component with diesel fuel. It is important to check the concentration of biodiesel in the diesel fuel in order to make sure it is either not below the minimum allowable limit and or does not exceed the maximum allowable limit.

5.2 This test method is applicable for quality control in the production and distribution of diesel fuel and biodiesel blends.

6. Interferences

6.1 The hydrocarbon composition of diesel fuels can affect the accuracy of the calibration. When possible it is advised that diesel fuels used in calibration be similar to the unknown samples to be analyzed.

6.2 *Undissolved Water and Particulates*—Samples containing undissolved water, particulates, or both will result in erroneous results. If the sample is cloudy or water saturated after it has been equilibrated between 15 °C to 27 °C, filter the sample through a qualitative filter paper until clear prior to their introduction onto the instrument sample crystal.

6.3 The primary spectral interferences are vegetable oils or animal fats, or both. Other means of analysis or separate calibrations may be required if fuel is suspected to be contaminated with vegetable oils or animal fats, or both.

6.4 Due to the inherent variability in LVFs, calibrations cannot be transferred between instruments. Each instrument shall be calibrated separately prior to use.

6.5 This test method is not appropriate for fatty acid ethyl esters (FAEE). FAEEs will cause a negative bias.

7. Apparatus

7.1 Mid-Infrared Spectrometer:

7.1.1 *LVF Array Based Mid-Infrared Spectrometer*—The type of apparatus suitable for use in this test method employs an IR source, a HATR crystal, a LVF paired to a detector array, an A/D converter, a microprocessor, and controller software. Specifications of sub parts of the analyzer listed below will determine the applicability of an instrument to this test method.

7.1.2 The noise level shall be established by acquiring a single beam spectrum of air. The single beam spectrum may be an average of multiple instrument scans but the total collection time shall not exceed 60 s. The noise of the spectrum at 100 % transmission shall be less than 0.3 % in the range of 5.50 μm to 5.90 μm (1818 cm⁻¹ to 1725 cm⁻¹).

7.2 *Detector Array/Linear Variable Filter Specifications*—The infrared detector array shall have at least 128 detection channels. This detector array shall be paired to a LVF with a range that includes the region of 5.4 μm to 6.0 μm. At least ten detector channels shall be within the range of 5.4 μm to 6.0 μm. The filter shall have a resolution of at least 50 cm⁻¹.

7.3 *Horizontal Attenuated Total Reflection Crystal*—A horizontal attenuated total reflectance (ATR) crystal, with zinc selenide element mounted on a horizontal plate shall be used. Any number of internal reflections (bounces) may be used, however the absorbance at 1745 cm⁻¹ shall not exceed 1.1 absorbance units for the highest concentration calibration standard used in the calibration range. Therefore, for higher concentration measurements, careful consideration of element length and face angle shall be made to maximize sensitivity without exceeding 1.1 absorbance units at 1745 cm⁻¹.

7.4 Note that other spectrometer configurations can provide adequate results; however, the precision and bias data listed with this test method was collected based on these apparatus specifications. Any modifications can result in precision and or bias that differ from the numbers listed in this test method.

8. Reagents and Materials

8.1 *Purity of Reagents*—Spectroscopic grade (preferred) or reagent grade chemicals shall be used in 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.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.1.1 Hexane, anhydrous [110-54-3] or Heptane [142-82-5] for use as a cell cleaning agent.

⁴ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Annual 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.

8.1.2 B100 used for calibration, qualification, and quality control standards are recommended to be compliant with Specification **D6751** or similar FAME specifications. The biodiesel (B100) shall be FAME. A BQ-9000 certified producer for the biodiesel is recommended to ensure quality of product.⁵

8.1.3 Middle distillate fuel used for calibration, qualification, and quality control standards are recommended to be compliant with Specification **D975** or similar diesel fuel specifications, be free of biodiesel or biodiesel oil precursor, or both. If possible, middle distillate fuel shall be representative of diesel fuels anticipated for blends to be analyzed (crude source, 1D, 2D, blends, winter/summer cuts, low aromatic content, high aromatic content, and so forth).

9. Sampling, Test Specimens, and Test Units

9.1 General Requirements:

9.1.1 Fuel samples to be analyzed by this test method shall be sampled using procedures outlined in Practice **D4057** or **D4177**, where appropriate. Do not use “sampling by water displacement.” FAME is more water-soluble than the hydrocarbon base in a biodiesel blend.

9.1.2 Protect samples from excessive temperatures prior to testing.

9.1.3 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.

9.2 Sample Handling During Analysis:

9.2.1 When analyzing samples using this method, the sample temperature needs to be within the range of 15 °C to 27 °C. Equilibrate all samples to the temperature of the test site (15 °C to 27 °C) prior to analysis by this test method.

9.2.2 After the analysis, if the sample is to be retained, reseal the container before storage.

9.2.3 Avoid using plastic materials for sampling and do not use rubber caps or plastic bottles for storage of the sample.

10. Preparation of Apparatus

10.1 Before use, the instrument needs to be calibrated according to the procedure described in **Annex A1**. This calibration may be performed by the instrument manufacturer prior to delivery of the instrument to the end user. If, after maintenance, the instrument calibration is repeated, the qualification procedure shall also be repeated.

10.2 Before use, the instrument shall be qualified according to the procedure described in **Annex A1**. The qualification need only be carried out when the instrument is initially put into operation, recalibrated, or repaired.

11. Calibration and Standardization

11.1 Information on calibration and qualification of the apparatus can be found in **Annex A1**.

11.2 Confirm the in-statistical-control status of the test method each day it is used by measuring the biodiesel concentration of at least one quality control sample that is

similar in composition and matrix to samples routinely analyzed. For details on quality control sample selection, preparation, testing, and control charting, refer to Practice **D6299**.

11.3 A system that is found to be out of statistical control cannot be used until the root cause(s) of out-of-control is identified and corrected.

11.4 If correction of out-of-control behavior requires repair to the instrument or recalibration of the instrument, the qualification of instrument performance described in **A1.3** shall be performed and the in-statistical control status shall be confirmed.

12. Procedure

12.1 Equilibrate the samples to between 15 °C and 27 °C before analysis.

12.2 Clean the sample crystal of any residual fuel or other contamination according to the manufacturer’s recommendation. Hexane or heptane has been determined to be suitable for cleaning the sample cell. It is recommended that the sample crystal be cleaned at least twice before a baseline spectrum is obtained since a clean baseline spectrum is critical for ensuring correct results.

12.3 Obtain a baseline spectrum in the manner established by the manufacturer of the equipment.

12.4 Prior to the analysis of unknown test samples, establish that the equipment is running properly by collecting the spectrum of the quality control standard(s) and comparing the estimated biodiesel concentration(s) to the known value(s) for the QC standard(s).

12.5 Introduce the unknown fuel sample in the manner established by the manufacturer. Ensure that the entire crystal surface is covered with fuel.

12.6 Obtain the digitized spectral response of the fuel sample in the manner established by the manufacturer of the equipment in a spectral range containing 5.4 μm to 6.0 μm.

12.7 Determine and record the biodiesel concentration according to the calibration curve generated in **Annex A1**.

12.8 Wipe the sample off of the sample crystal and clean thoroughly according to manufacturer’s specification.

12.9 Biodiesel and biodiesel blends containing high concentrations of biodiesel are difficult to remove from the ATR crystal surface. The sample crystal should be cleaned thoroughly between each sample. When in doubt, repeat steps **12.5 – 12.8** and compare the results to ensure adequate cleaning occurred.

13. Report

13.1 Report the following information:

13.1.1 Volume Percent Biodiesel by Test Method D7861, to the nearest 0.1 %.

14. Precision and Bias

14.1 The precision of this test method is based on an interlaboratory study conducted in 2011. A total of twelve

⁵ A current list of BQ9000 producers can be found at the National Biodiesel Accreditation Program’s website <http://www.bq-9000.org/> or by contacting them at 573-635-3893.