



Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)¹

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1. Scope

1.1 This test method covers the determination of the content of fatty acid methyl esters (FAME) biodiesel in diesel fuel oils. It is applicable to concentrations from 1.00 to 20 volume % (see **Note 1**). This procedure is applicable only to FAME. Biodiesel in the form of fatty acid ethyl esters (FAEE) will cause a negative bias.

NOTE 1—Using the proper ATR sample accessory, the range maybe expanded from 1 to 100 volume %, however precision data is not available above 20 volume %.

1.2 The values stated in SI units of measurement are to be regarded as the standard. The values given in parentheses are for information only.

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

2. Referenced Documents

2.1 ASTM Standards:²

- D 975** Specification for Diesel Fuel Oils
- D 976** Test Method for Calculated Cetane Index of Distillate Fuels
- D 1298** Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D 4052** Test Method for Density and Relative Density of Liquids by Digital Density Meter
- D 4057** Practice for Manual Sampling of Petroleum and Petroleum Products

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0F on Absorption Spectroscopic Methods.

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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.

- D 4177** Practice for Automatic Sampling of Petroleum and Petroleum Products
- D 4307** Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D 4737** Test Method for Calculated Cetane Index by Four Variable Equation
- D 5854** Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
- D 6299** Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance
- D 6751** Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
- E 168** Practices for General Techniques of Infrared Quantitative Analysis
- E 1655** Practices for Infrared Multivariate Quantitative Analysis
- E 2056** Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures

3. Terminology

3.1 Definitions:

3.1.1 *biodiesel, n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100. **D 6751**

3.1.2 *biodiesel blend, BXX, n*—a blend of biodiesel fuel with petroleum-based diesel fuel.

3.1.2.1 *Discussion*—In the abbreviation BXX, the XX represents the volume percentage of biodiesel fuel in the blend. **D 6751**

3.1.3 *diesel fuel, n*—petroleum-based middle distillate fuel.

3.1.4 *multivariate calibration, n*—process for creating a model that relates component concentrations or properties to the absorbances of a set of known reference samples at more than one wavelength or frequency. **E 1655**

3.1.4.1 *Discussion*—The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property values for the unknown sample.

3.1.4.2 *Discussion*—The multivariate calibration algorithm employed in this test method is partial least square (PLS) as defined in Practices E 1655.

3.2 Abbreviations:

<i>ATR</i>	= attenuated total reflectance
<i>B_{xx}</i>	= see 3.1.2
<i>FAEE</i>	= fatty acid ethyl esters
<i>FAME</i>	= fatty acid methyl esters
<i>FTIR</i>	= Fourier transform infrared
<i>mid-IR</i>	= mid infrared
<i>PLS</i>	= partial least square
<i>ULSD</i>	= ultra low sulfur diesel

4. Summary of Test Method

4.1 A sample of diesel fuel, biodiesel, or biodiesel blend is introduced into a liquid attenuated total reflectance (ATR) sample cell. A beam of infrared light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the absorption spectrum that correlate highly with biodiesel or interferences are selected for analysis. A multivariate mathematical analysis converts the detector response for the selected areas of the spectrum from an unknown to a concentration of biodiesel.

4.2 This test method uses Fourier transform mid-IR spectrometer with an ATR sample cell. The absorption spectrum shall be used to calculate a partial least square (PLS) calibration algorithm.

5. Significance and Use

5.1 Biodiesel is a fuel commodity primarily used as a value-added blending component with diesel fuel.

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

6. Interferences

6.1 The hydrocarbon composition of diesel fuel has a significant impact on the calibration model. Therefore, for a robust calibration model, it is important that the diesel fuel in the biodiesel fuel blend is represented in the calibration set.

6.2 Proper choice of the apparatus, design of a calibration matrix, utilization of multivariate calibration techniques, and evaluation routines as described in this standard can minimize interferences.

6.3 *Water Vapor Interference*—The calibration and analysis bands in A1.2 lie in regions where significant signals due to water vapor can appear in the infrared spectrum. This shall be accounted for to permit calibration at the low end concentrations.

NOTE 2—Ideally, the spectrometer should be purged with dry air or nitrogen to remove water vapor. The purge should be allowed to stabilize over several hours before analytical work is pursued, due to the rapid changes in the air moisture content within the spectrometer during early stages of the purge. In cases where water vapor prevention or elimination is not possible using a purge, the operator should measure a reference background spectrum for correction of the ratioed spectrum for each sample spectrum measured. This operation is generally automated in today's spectrometer systems and the operator should consult the manu-

TABLE 1 Attenuated Total Reflectance (ATR) Conical Cells Specification

ATR element material	ZnSe
beam condensing optics	conical, non-focusing optics integral to cell body
element configuration	circular cross section with coaxial conical ends
cone half angle	60°
element length	36.83 to 39.37 mm (1.45 to 1.55 in.)
element diameter	3.175 mm (0.125 in.)
angle of incidence at sample interface	53.8°
maximum range of incidence angles	± 1.5°
standard absorbance (1428 cm ⁻¹ band of acetone)	0.38 ± 0.02 AU
material of construction	316 stainless steel
seals	Chemrez or Kalrez o-rings ^A

^A Trademarks of Chemrez, Inc. and Dupont Performance Elastomers L.L.C.

facturer of the spectrometer for specific instructions for implementing automated background correction routines. The spectrometer should be sealed and desiccated to minimize the affect of water vapor variations, and any accessory should be sealed to the spectrometer.

6.4 *Fatty Acid Ethyl Esters (FAEE) Interference*—The presence of FAEE in the composition of the biodiesel will result in an overall lower concentration measurement of biodiesel content. Outlier statistical results may be a useful tool for determining high concentration FAEE content (see ASTM Research Report RR: D02-1624³).

6.5 *Undissolved Water*—Samples containing undissolved water will result in erroneous results. Filter cloudy or water saturated samples through a dry filter paper until clear prior to their introduction into the instrument sample cell.

7. Apparatus

7.1 Mid-IR Spectrometric Analyzer:

7.1.1 *Fourier Transform Mid-IR Spectrometer*—The type of apparatus suitable for use in this test method employs an IR source, a liquid attenuated total internal reflection cell, a scanning interferometer, a detector, an A-D converter, a micro-processor, and a method to introduce the sample. The following performance specifications shall be met:

Scan Range	4000 to 650 cm ⁻¹
Resolution	4 cm ⁻¹

7.1.2 The noise level shall be established by acquiring a single beam spectrum using air or nitrogen. The single beam spectrum obtained can be the average of multiple of FTIR scans but the total collection time shall not exceed 60 seconds. If interference from water vapor or carbon dioxide is a problem, the instrument shall be purged with dry air or nitrogen. The noise of the spectrum at 100 % transmission shall be less than 0.3 % in the region from 1765 to 1725 cm⁻¹.

7.2 *Absorption Cell*, multi-bounce (multi-reflections) attenuated total reflectance cell. It shall meet one of the following requirements:

7.2.1 *Conical Attenuated Total Reflectance (ATR) Cell*, having similar specifications defined in Table 1. This cell is suitable for the low, medium, and high concentration ranges.

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1624.

7.2.2 *Horizontal Attenuated Total Reflectance (ATR) Cell*, with ZnSe element ATR mounted on a horizontal plate. The absorbance at 1745 cm⁻¹ shall not exceed 1.2 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 1.2 absorbance units at 1745 cm⁻¹.

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 *B100 (Neat Biodiesel)*—Used for calibration, qualification, and quality control standards shall be compliant with Specification **D 6751**. The B100 shall be fatty acid methyl esters. Soy methyl ester (SME) was used in calibration standards for developing the precision of this test method. Esters derived from other feedstocks, for example animal fats, canola oil, jatropha oil, palm oil, rapeseed oil, and yellow grease may be used. Standards made with yellow grease methyl esters should not represent more than 50 % of the number of the calibration standards. A BQ-9000 certified producer for the biodiesel is recommended to ensure quality of product. See **Annex A2** for further discussion.

8.1.2 *Middle Distillate Fuel*—Used for calibration, qualification, and quality control standards shall be compliant with Specification **D 975**, free of biodiesel or biodiesel oil precursor, or both. As far as possible, middle distillate fuel shall be representative of petroleum base stocks anticipated for blends to be analyzed (crude source, 1D, 2D, blends, winter/summer cuts, low aromatic content, high aromatic content, and the like). See **Annex A2** for calibration set.

8.1.3 *Diesel Cetane Check Fuel—Low (DCCF-Low)*.⁵ (See **A2.2** for alternative material.)

8.1.4 *Diesel Cetane Check Fuel—High (DCCF-High)*.

8.1.5 *Diesel Cetane Check Fuel—Ultra High (DCCF-Ultra High)*.

8.1.6 *Acetone [67-64-1]*—Reagent grade.

8.1.7 *Toluene [108-88-3]*—Reagent grade.

8.1.8 *Methanol [67-56-1]*—Reagent grade.

8.1.9 *Triple Solvent*—A mixture of equal parts by volume of toluene, acetone, and methanol.

9. Sampling and Sample Handling

9.1 General Requirements:

9.1.1 Fuel samples to be analyzed by this test method shall be sampled using procedures outlined in Practice **D 4057** or Practice **D 4177**, 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 the FTIR, the sample temperature needs to be within the range of 15 to 27°C. Equilibrate all samples to the temperature of the laboratory (15 to 27°C) prior to analysis by this test method.

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

10. Calibration and Qualification of the Apparatus

10.1 Before use, the instrument needs to be calibrated according to the procedure described in **Annex A1**. This calibration can 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 is also repeated.

10.2 Before use, the instrument is 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. Quality Control Checks

11.1 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 **D 6299**.

11.2 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.

11.3 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 before the system is used to measure the biodiesel content of samples.

12. Procedure

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

12.2 Clean the sample cell of any residual fuel according to the manufacturer’s instructions. Remove the fuel by flushing the cell with sufficient solvent or the subsequent sample to ensure complete washing. For difficult to remove substances like B100, precede flushing with triple solvent. Evaporate the residual solvent with either dry air or nitrogen.

⁴ *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.

⁵ The sole source of supply of the material known to the committee at this time is Chevron Phillips Chemical Company LLC, 10001 Six Pines Drive, The Woodlands, TX 77380. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.