Designation: D7371 – 14 (Reapproved 2022)

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]

This standard is issued under the fixed designation D7371; 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 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 % by 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 may be expanded from 1 % to 100 % by volume, however precision data is not available above 20 % by 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, 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]

D975 Specification for Diesel Fuel

D976 Test Method for Calculated Cetane Index of Distillate Fuels

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

D4737 Test Method for Calculated Cetane Index by Four Variable Equation

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

D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

D7467 Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)

E168 Practices for General Techniques of Infrared Quantitative Analysis

E1655 Practices for Infrared Multivariate Quantitative Analysis

E2056 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. **D6751**

3.1.2 *biodiesel blend, BXX, n*—a blend of biodiesel fuel with petroleum-based diesel fuel. **D7467**

3.1.2.1 *Discussion*—In the abbreviation BXX, the XX represents the volume percentage of biodiesel fuel in the blend. **D6751**

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

[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 D02.04.0F 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.

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. **E1655**

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 E1655.

3.2 *Abbreviations:*

3.2.1 *ATR*—attenuated total reflectance

3.2.2 *Bxx*—see 3.1.2

3.2.3 *FAEE*—fatty acid ethyl esters

3.2.4 *FAME*—fatty acid methyl esters

3.2.5 *FTIR*—Fourier transform infrared

3.2.6 *mid-IR*—mid infrared

3.2.7 *PLS*—partial least square

3.2.8 *ULSD*—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 blendstock 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 manufacturer 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 (for additional FAEE information, see research report referenced in Section 15).

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 microprocessor, and a method to introduce the sample. The following performance specifications shall be met:

Scan Range	4000 cm^{-1} 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 cm^{-1} 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.

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}.