Designation: D7806 – 20

Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Ester) and Triglyceride Content in Diesel Fuel Oil Using Mid-Infrared Spectroscopy (FTIR Transmission Method)[1]

This standard is issued under the fixed designation D7806; 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 fatty acid methyl ester (FAME) biodiesel and triglyceride (TAG) concentrations in traditional diesel and renewable diesel fuel blends using a portable mid-infrared spectrometer.

1.2 The method applies to samples with biodiesel concentrations from 3 % to 40 % by volume. Additionally, it applies to samples with biodiesel concentrations from 2 % to 27 % by volume which contain triglycerides concentrations from 1 % to 10 % by volume. Triglycerides from 2 % to 10 % by volume can be determined in samples of diesel having biodiesel concentrations from 3 % to 27 % by volume. FAME and triglyceride can be simultaneously determined outside these stated ranges, but the stated precision estimates do not apply.

1.3 The method is not able to distinguish TAG and FAME if the TAG concentrations is below 0.142× the measured FAME concentrations.

1.4 This procedure is not appropriate for the determination of the concentration of biodiesel in the form of fatty acid ethyl esters (FAEE), see Section 6 for further discussion of possible interferences.

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

1.6 *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.*

1.7 *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

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D1655 Specification for Aviation Turbine Fuels

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, Liquid Fuels, and Lubricants

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

D7418 Practice for Set-Up and Operation of Fourier Transform Infrared (FT-IR) Spectrometers for In-Service Oil Condition Monitoring

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E1655 Practices for Infrared Multivariate Quantitative Analysis

[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.

*A Summary of Changes section appears at the end of this standard

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 composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100 in Specification D6751.

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 percentage by volume of biodiesel fuel in the blend.

3.1.3 *diesel fuel oil, n*—a petroleum-based diesel fuel, as described in Specification D975.

3.1.4 *FAME, n*—a biodiesel composed of long chain fatty acid methyl esters derived from vegetable or animal fats.

3.1.5 *mid-infrared spectroscopy, n*—uses the mid-infrared region of the electromagnetic spectrum, as described in Terminology E131.

3.1.6 *oxygenate-free middle distillate, n*—a petroleum-based fuel meeting the specifications of D975 or E1655, free of compounds containing esters, acids, or ketones.

3.1.7 *renewable diesel fuel, n*—a biomass-based fuel, meeting the specifications in D975.

3.1.8 *triglycerides, TAG, n*—a naturally occurring ester formed from glycerol and three fatty acid groups, which are the main constituents of natural fats and oils, biodiesel feedstocks, fats and/or oils, that have not been transesterified into biodiesel.

3.2 *Acronyms:*

3.2.1 *AU*—absorption unit

3.2.2 *CLS*—classical least squares

3.2.3 *FAEE*—fatty acid ethyl esters

3.2.4 *FAME*—fatty acid methyl esters

3.2.5 *FTIR*—Fourier transform infrared spectrometer

3.2.6 *IR*—infrared

3.2.7 *PL*—path length

3.2.8 *TAG*—triglyceride

4. Summary of Test Method

4.1 This method utilizes a Fourier transform mid infrared spectrometer fitted with a transmission sample cell with a specified path length. A sample of diesel fuel or biodiesel blend is introduced into the sample cell. A beam of infrared light is passed through the sample and the motion of the spectrometer mirrors enables determination of the sample absorption spectrum. Specific regions of the spectrum where FAME and triglycerides show strong absorption are used for the analysis.

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.

5.3 The use of triglycerides in fuels is not approved for transportation applications within any ASTM specification. This test method allows the quantification of triglyceride concentration in biodiesel blends, thus enabling detection of out-of-specification blending.

5.4 This test method is fast, simple to run, inexpensive and requires no sample preparation.

6. Interferences

6.1 The presence of carbonyl containing compounds including carboxylic acids, ketones and aldehydes, as well as fatty acid ethyl esters (FAEE), may result in spectral interference.

6.2 The hydrocarbon composition of the diesel fuel has a minor impact on the calibration model. The proper choice of the evaluation routine as described in this standard can minimize interferences from the hydrocarbon composition of the diesel fuel.

6.3 *Water Vapor Interference*—The calibration and analysis bands in used for the calculations in Section 12 lie in regions where significant signals due to water vapor can appear in the infrared spectrum. This shall be accounted for to permit calibration and measurements at the low end concentrations.

NOTE 1—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 effect of water vapor variations, and any accessory should be sealed to the spectrometer.

6.4 *High Lauric Acid Methyl Esters Interference*—Samples with high lauric acid methyl ester (that is, coconut biodiesel) content are known to cause a bias when used in the calibration model. Unless the method is being used to calibrate specifically and exclusively for samples containing high levels of lauric acid methyl esters, feedstocks containing high levels of these compounds should be avoided.

7. Apparatus

7.1 *Mid-IR Spectrometric Analyzer:*

7.1.1 *Fourier Transform Mid-IR Spectrometer (FT-IR)*—The type of apparatus suitable for use in this test method employs an IR source, a liquid transmission cell, a scanning interferometer, a detector, an analog-to-digital converter, a microprocessor, and a method to introduce the sample. The following performance specifications must be met:

spectral resolution	4 cm^{-1}

NOTE 2—The noise of the single beam spectrum at 100 % transmission shall be less than 0.3 % peak-to-peak in the region from 1725 cm^{-1} to 1765 cm^{-1}. The single beam spectrum obtained can be the average of

multiple of FTIR scans but the total collection time shall not exceed 60 seconds.

7.2 *Absorption Cell*—The cell shall be a transmission cell made from non-hygroscopic materials having a significant transmission in the relevant spectral range (1050 cm^{-1} to 1850 cm^{-1}). The nominal path length of the cell shall be 0.10 mm ± 0.015 mm, appropriate to measure the relevant peaks involved in the spectral analysis without going into saturation. The path length should be determined in accordance to Practice D7418.

8. Reagents and Materials

8.1 *Standards for Calibration, Qualification, and Quality Control Check Standards*—Because this method is intended to quantify FAME and triglyceride content in commercial biodiesel blends there are no high purity standard chemical reference materials that are appropriate for development of multivariate calibration models.

8.1.1 B100 (Neat Biodiesel) used for calibration, qualification and quality control standards must be Specification D6751 compliant. If the origin of FAME is known, this type shall be used for calibration. If the type of biodiesel is not known, use soy methyl ester or the FAME most commonly used in the geographical area where the samples are obtained.

8.1.2 The triglycerides shall be food grade oils liquid at room temperature, preferably soy oil or the type of oil most commonly found in the local market, available for purchase commercially. See Annex A2 for further discussion on different biodiesel and triglyceride varieties.

8.1.3 Middle distillate fuel used for calibration, qualification and quality control standards must be Specification D975 compliant, free of biodiesel or biodiesel precursor compounds and should as far as possible be representative of the petroleum base stocks anticipated for blends to be analyzed (that is, crude source, 1D, 2D, blends, winter/summer cuts, etc). See Annex A2 for further discussion on calibration fuels.

9. Sampling and Sample Handling

9.1 *General Requirements:*

9.1.1 Fuel samples to be analyzed by the test method shall be sampled using procedures outlined in Practices D4057 or D4177, where appropriate. Do not use the "Sampling by Water Displacement" procedure.

9.1.2 Protect samples from excessive (<0 °C and >60 °C) temperatures prior to testing.

9.1.3 Until test samples are known to contain <4.0 % by volume TAG, avoid storage of samples in refrigerated conditions (< ≈10 °C).

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

9.2 *Sample Handling During Analysis:*

9.2.1 Equilibrate all samples to the temperature of the laboratory (15 °C to 27 °C) prior to analysis by this test method.

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

10. Calibration of the Apparatus

10.1 Calibrate the instrument 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.

11. Quality Control Checks

11.1 Each day that the instrument is to be used, confirm it is in statistical control by measuring the biodiesel concentration using the procedure outlined in Section 12 on at least one quality control sample of known biodiesel content. The preparation of samples with known biodiesel concentration is described in 11.1.1 and 11.1.2. For details on quality control testing and control charting refer to Practice D6299.

11.1.1 Standard(s) of known biodiesel and triglyceride concentration shall be prepared by mass and converted to volume percent using the measured density as outlined in Section 13.1. At least one standard shall be prepared for each calibration range. Additional standards including 0 % by volume may also be prepared and used for quality control checks.

11.1.2 Standard(s) should be prepared in sufficient volume to allow for a minimum of 30 quality control measurements to be made on one batch of material. Properly package and store the quality control samples to ensure that all analyses of quality control samples from a given lot are performed on essentially identical material.

11.2 If the biodiesel volume percent value estimated for the quality control sample exceeds the action limits described specified in Practice D6299 or equivalent, then the measurement system is out-of-control and cannot be used to measure biodiesel concentrations until the cause of the out-of-control behavior is identified and corrected.

12. Procedure

12.1 Equilibrate all samples to the temperature of the laboratory (15 °C to 27 °C) prior to analysis by this test method.

12.2 *Background Spectrum*—Record a single beam infrared spectrum of dry air or nitrogen.

12.3 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 to the known value for the QC standard(s).

12.4 Rinse the absorption cell according to the manufacturer's instructions. Biodiesel and high concentrations biodiesel blends are difficult to remove from the cell. Flush the cell with sample or use a solvent rinse between measurements to ensure that carry-over between measurements is minimal. Measuring a blank (oxygenate-free middle distillate or jet fuel) after the measurement of the high range quality control sample can be used to verify adequate rinsing.

12.5 Introduce the unknown sample into the sample cell and obtain the digitized absorption spectrum (AS) of the fuel sample over the frequency range from 1050 cm^{-1} to 1850 cm^{-1}.

12.6 Normalize the absorption spectrum to 0.1 mm path length, that is, multiply the spectrum with the factor 0.1/PL, where PL is the path length of the cell in mm. The absorption spectrum after normalization should be used for the subsequent analysis.

12.7 Perform a classical least squares (CLS) (A1.1.8) fit of the spectrum of the unknown sample as described in A1.1.7 and A1.1.8. Determine the respective concentrations using the CLS calibration (A1.1.9).

12.8 Determine the relative contribution of biodiesel and triglycerides.

$$X_i = \frac{c_i}{\sum_i c_i}, i\epsilon \quad \text{FAME and TAG} \tag{1}$$

If $X_{TAG} < 0.14$, set $X_{TAG} = 0$ and $X_{FAME} = 1$.
If $X_{FAME} < 0.14$, set $X_{FAME} = 0$ and $X_{TAG} = 1$.

12.9 Let P be the maximum of the absorption spectrum between 1735 cm^{-1} and 1758 cm^{-1} without any baseline correction.

12.10 If $X_{FAME} > 0$ and $X_{TAG} = 0$, the sample contains only biodiesel.

12.10.1 If P > 1.55 AU, calculate the peak area from 1230 cm^{-1} to 1288 cm^{-1} using the baseline points at 1105 cm^{-1} and 1330 cm^{-1} and use the high range FAME calibration to determine the biodiesel concentration (A1.1.11). Report the triglyceride concentration as zero.

12.10.2 If P ≤ 1.55 AU, calculate the peak area from 1730 cm^{-1} to 1766 cm^{-1} using the baseline points at 1673 cm^{-1} and 1838 cm^{-1} and use the low concentration FAME calibration to determine the biodiesel concentration (A1.1.10). Report the triglyceride concentration as zero.

12.11 If $X_{FAME} = 0$ and $X_{TAG} > 0$, the sample contains only triglycerides.

12.11.1 If P > 1.55 AU, report the concentration determined by the CLS calibration, c_{TAG} (A1.1.9). Report the biodiesel concentration as zero.

12.11.2 If P ≤ 1.55 AU, calculate the peak area from 1730 cm^{-1} to 1766 cm^{-1} using the baseline points at 1673 cm^{-1} and 1838 cm^{-1} and use the low concentration TAG calibration to determine the triglyceride concentration (A1.1.10). Report the biodiesel concentration as zero.

12.12 If $X_{FAME} > 0$ and $X_{TAG} > 0$, the sample contains a mixture of biodiesel and triglycerides.

12.12.1 If P > 1.55 AU, report the biodiesel and triglyceride concentrations determined by the CLS calibration, c_{TAG} and c_{FAME} (A1.1.9).

12.12.2 If P ≤ 1.55 AU, calculate the peak area from 1730 cm^{-1} to 1766 cm^{-1}, using the baseline points at 1673 cm^{-1} and 1838 cm^{-1} and use the low concentration FAME calibration to determine the sum of triglyceride and biodiesel concentrations, C (A1.1.10). Calculate the biodiesel and triglyceride concentrations as $C \cdot X_{FAME}$ and $C \cdot X_{TAG}$ respectively.

13. Calculation

13.1 *Conversion to Volume Percent of Biodiesel*—To convert the calibration and qualification standards to volume percent use Eq 2:

$$V_b = M_b(D_f / D_b) \tag{2}$$

where:

V_b = biodiesel volume percent,
M_b = biodiesel mass percent,
D_f = relative density at 15.56 °C of the calibration or qualification standard being tested as determined by Practice D1298 or Test Method D4052, and
D_b = B100 biodiesel blend stock relative density at 15.56 °C of the calibration or qualification standard being tested as determined by Practice D1298 or Test Method D4052.

13.2 *Conversion to Volume Percent of Triglyceride*—To convert the calibration and qualification standards to volume percent, use Eq 3:

$$V_t = M_t(D_f / D_t) \tag{3}$$

where:

V_t = triglyceride volume percent,
M_t = triglyceride mass percent,
D_f = density at 15.56 °C of the calibration or qualification standard being tested as determined by Practice D1298 or Test Method D4052, and
D_t = triglyceride density at 15.56 °C of the calibration or qualification standard being tested as determined by Practice D1298 or Test Method D4052.

13.3 This test method is most accurate when the biodiesel used in the calibration is derived from the same source as the biodiesel in the samples being analyzed. If the biodiesel used in the calibration is derived from a different source than the biodiesel in the sample being analyzed, adjusting the factory calibration with an additional 2-point calibration is allowed.

14. Report

14.1 Report volume percent biodiesel and volume percent triglycerides by Test Method D7806, to the nearest 0.1 % by volume for concentrations below 10 % by volume. For higher concentrations, report to the nearest 0.1 % by volume.

15. Precision and Bias

15.1 The precision of this test method, which was determined by statistical examination of the results from a 16 lab by 22 sample interlaboratory study, is as follows:

15.2 *Repeatability (r):*

15.2.1 An interlaboratory study[3] was carried out to estimate the repeatability of the method. The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test samples would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty, where X = the average of two test results.

15.2.1.1 FAME in Diesel / No TAG measured:

$$r = 1.43E\text{-}02 * X^{1.332} \quad \text{Vol. \%} \tag{4}$$

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2002. Contact ASTM Customer Service at service@astm.org.

15.2.1.2 FAME in Diesel / TAG measured from 2 % to 10 % by volume:

$$r = 4.58E\text{-}02 * X^{1.179} \quad \text{Vol. \%} \tag{5}$$

15.2.1.3 TAG in Diesel / biodiesel measured from 3 % to 27 % by volume:

$$r = 4.20E\text{-}02 * X^{1.421} \quad \text{Vol. \%} \tag{6}$$

15.3 *Reproducibility (R):*

15.3.1 An interlaboratory study[3] was carried out to estimate the reproducibility of the method. The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where x = the average of the two test results.

15.3.1.1 FAME in Diesel / No TAG measured:

$$R = 0.151 * X^{0.817} \quad \text{Vol. \%} \tag{7}$$

15.3.1.2 FAME in Diesel / TAG measured from 2 % to 10 % by volume:

$$R = 9.04E\text{-}02 * X^{1.179} \quad \text{Vol. \%} \tag{8}$$

15.3.1.3 TAG in Diesel / biodiesel measured from 3 % to 27 % by volume

$$R = 0.140 * X^{1.421} \quad \text{Vol. \%} \tag{9}$$

15.4 *Bias*—Because no suitable reference materials were included in the interlaboratory test program, no statement of bias is being made.

NOTE 3—The research report RR:D02-2002 contains a comparison between prepared concentrations and the stable means for FAME and triglycerides.

15.5 Examples of the above precision estimates are shown in Table 1.

TABLE 1 Precision Estimate Examples for FAME in Diesel / no TAG Detected, FAME in Diesel / TAG Detected, and TAG / FAME Detected for Different Concentrations

C (% Vol)	FAME / no TAG Detected		FAME / TAG Detected		TAG / FAME Detected	
	r	R	r	R	r	R
2			0.10	0.20	0.11	0.37
3	0.06	0.37	0.17	0.33	0.20	0.67
5	0.12	0.56	0.31	0.60	0.41	1.38
7	0.19	0.74	0.45	0.90	0.67	2.22
10	0.31	0.99	0.69	1.36		
15	0.53	1.38	1.12	2.20		
20	0.78	1.75	1.57	3.09		
25	1.04	2.10	2.04	4.02		
30	1.33	2.44				
40	1.95	3.08				

16. Keywords

16.1 biodiesel; biodiesel blend; biodiesel (FAME); FAME; infrared spectroscopy; triglyceride

ANNEXES

(Mandatory Information)

A1. CALIBRATION – PROCEDURE A

A1.1 *Calibration Matrix*—Calibration standards shall be prepared in accordance with Practice D4307 or appropriately scaled for larger blends and Practice D5854, where appropriate. Whenever possible, use blend components known to be fully compliant with Specification D975 (for base petroleum diesel components) and Specification D6751 (for B100 biodiesel components). See Annex A2 for selecting blend components.

A1.1.1 Equilibrate all samples to the temperature of the laboratory (15 °C to 27 °C) prior to preparation of samples and analysis.

A1.1.2 Measure the density for each of the components to be mixed and of the calibration standards according to either Test Method D1298 or Test Method D4052.

A1.1.3 For each of the calibration standards, convert the mass percent to volume percent according to the Eq 2 and Eq 3 presented in 13.1. If the densities of the calibration standards cannot be measured, it is acceptable to convert to volume percent using the densities of the individual components measured using Test Method D1298 or Test Method D4052.

A1.1.4 Calibrations for biodiesel and triglycerides are done individually. The calibration steps outlined in sections A1.1.9 to A1.1.13 must thus be made for both substances. To obtain the best precision and accuracy of calibration using the linear regression model, prepare two calibration sets for each compound as described in Table A1.1. Set A contains samples with concentrations between 0 % and 7 % by volume (approximately corresponding to an absorption spanning 0 AU to

TABLE A1.1 Recommended Instrument Calibration Sets A and B

Sample	Concentration (vol %)	Matrix	Set A	Set B
1	0.00	Middle Distillate	X	
2	1.00	Middle Distillate	X	
3	3.00	Middle Distillate	X	
4	5.00	Middle Distillate	X	
5	7.00	Middle Distillate	X	X
6	9.00	Middle Distillate		X
7	12.00	Middle Distillate		X
8	15.00	Middle Distillate		X
9	20.00	Middle Distillate		X
10	30.00	Middle Distillate		X
11	40.00	Middle Distillate		X