Designation: D7806 – 12

Standard Test Method for Determination of the Fatty Acid Methyl Ester (FAME) Content of a Blend of Biodiesel and Petroleum-Based Diesel Fuel Oil Using Mid-Infrared Spectroscopy[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 the content of biodiesel (fatty acid methyl esters—FAME) in diesel fuel oils. It is applicable to concentrations from 1 to 30 volume %. This procedure is applicable only to FAME. This test method is not appropriate for the determination of the concentration of biodiesel that is in the form of fatty acid ethyl esters (FAEE).

1.2 The values stated in SI units 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]

D975 Specification for Diesel Fuel Oils

D1298 Test Method for Density, Relative Density (Specific Gravity), 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

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

E131 Terminology Relating to Molecular Spectroscopy

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 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.

4. Summary of Test Method

4.1 A sample of diesel fuel or biodiesel blend is introduced into a liquid sample cell having a specified path length. 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. Mathematical analysis

[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.

converts the detector response for the selected areas or peaks of the spectrum of an unknown to a concentration of biodiesel.

4.2 This test method can utilize two different types of spectrometers.

4.2.1 A Fourier Transform Mid-IR Spectrometer fitted with a transmission sample cell can be used. The absorbance spectrum is baseline corrected to eliminate linear and constant background from the spectrum. Linear regression calibration is calculated without considering the influence of interferences.

4.2.2 A filter-based Mid-IR spectrometer fitted with a transmission cell can be used. The absorbance values at specified wavenumbers are used to develop a multiple linear regression calibration.

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 fast and simple to run.

5.3 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 primary spectral interferences are vegetable oils, or animal fats, or both.

6.2 The hydrocarbon composition of the 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.

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

6.4 This procedure is applicable only to FAME. The concentration of fatty acid ethyl esters (FAEE) cannot be determined using this test method.

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 (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 deuterated triglycine sulfate detector, an analog-to-digital converter, a microprocessor, and a method to introduce the sample. The following performance specifications must be met:

scan range	4000 to 650 cm^{-1}
spectral resolution	4 cm^{-1}
digital resolution	1 cm^{-1}

NOTE 1—To obtain a digital resolution of 1 cm^{-1} for a spectrum recorded at 4 cm^{-1} requires that the interferogram be zero filled prior to Fourier transformation. Consult the FT-IR manufacturer's instructions for the appropriate zero fill parameter settings to achieve this digital resolution.

7.1.1.1 The noise level shall be established by taking and ratioing two successive single beam spectra of dry air. The single beam spectra obtained can be the average of multiple of FTIR scans. The noise of the spectrum at 100 % transmission shall be less than 0.3 % peak-to-peak in the region from 1765 to 1725 cm^{-1}.

7.1.2 *Filter-based Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method minimally employs an IR source, an infrared transmission cell, wavelength discriminating filters, a chopper wheel, a lithium tantalate detector, an analog-to-digital converter, a microprocessor, and a method to introduce the sample. The frequencies and bandwidths of the filters are specified in Table 1.

7.2 *Transmission Cell*—The cell shall be a transmission cell made from materials having a significant transmission in the appropriate IR wavelength region. The nominal path length of the cell shall be 0.10 (± 0.01) mm, appropriate to measure the peak regions (as defined in Table 1) of samples in scope without going into saturation. If path length information from the manufacturer is not available, use cyclohexane as a path length check sample (see A1.2).

8. Reagents and Materials

8.1 *Standards for Calibration, Qualification, and Quality Control Check Standards*—As this test method is intended to quantify FAME 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. The B100 shall be a methyl fatty acid ester derived from soy. The B100 used to generate the precision of this test method was derived from soy. See Annex A2 for further discussion.

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

8.1.3 *Diesel Cetane Check Fuel*—Low (DCCF-Low).[3]

[3] The sole source of supply of the apparatus known to the committee at this time is Chevron Phillips Chemical Company LP, 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.

TABLE 1 Filter Frequencies and Bandwidths

Center Wave Number (±0.15 % of wave number)	Bandwidth (in wavelength units) (full width at half height)
1745 cm^{-1}	1 % of λc
1605 cm^{-1}	1 % of λc
1159 cm^{-1}	1 % of λc
915 cm^{-1}	1 % of λc
769 cm^{-1}	1 % of λc
698 cm^{-1}	1 % of λc

8.1.4 *Diesel Cetane Check Fuel*—High (DCCF-High).[3]

8.1.5 *n-Hexane [110-54-3]*—Reagent grade. (**Warning—** Flammable.)

8.1.6 *Hexadecane [544-76-3]*—With a minimum purity of 99.0 volume percent.

8.1.7 *Acetone [67-64-1]*—Reagent grade. (**Warning—** Flammable.)

8.1.8 *Toluene [108-88-3]*—Reagent grade. (**Warning—** Flammable.)

8.1.9 *Cyclohexane [110-82-7]*—Reagent grade. (**Warning—**Flammable.)

8.1.10 *Methanol [67-56-1]*—Reagent grade. (**Warning—** Flammable.)

8.1.11 *Triple Solvent*—A mixture of equal parts by volume of toluene, acetone, and methanol. (**Warning—**Flammable.)

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 temperatures prior to testing.

9.1.3 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 typical 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 saved, reseal the container before storing.

10. Calibration and Qualification of the Apparatus

10.1 Calibrate the instrument 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. Perform this qualification procedure anytime the instrument is calibrated.

10.2 Perform this qualification procedure when an instrument is initially put into operation, when it is recalibrated, or when it is repaired. The qualification procedure is described in Annex A1.

11. Quality Control Checks

11.1 Each day it is to be used, confirm that the instrument 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 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 concentration shall be prepared by mass according to A1.1.1 and converted to volume % using the measured density as outlined in Section 13. At least one standard shall be prepared for each calibration range. For example, 2 volume % may be used for the low calibration range, 20 volume % for high calibration range. Additional standards including 0 volume percent 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 % 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 estimate biodiesel concentrations until the cause of the out-of-control behavior 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 A1.4 shall be performed before the system is used to measure biodiesel content on samples.

12. Procedure

12.1 *FTIR Procedure:*

12.1.1 If the FTIR instrument is used, remove the fuel by flushing the cell and inlet-outlet lines with sufficient solvent, described in 8.1.11. Evaporate the residual solvent with dry air.

12.1.2 *Background Spectrum*—Record a single beam infrared spectrum of dry air. This spectrum can be used as a background spectrum for 6 h.

12.1.3 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). Introduce enough standard to the cell to ensure that the cell is washed by a volume of at least three times the dead volume of the sample introduction system.

12.1.4 Equilibrate the unknown fuel sample to the typical temperature of the laboratory (15 to 27°C) before analysis.

12.1.5 Introduce enough of the fuel sample to the cell to ensure the cell is washed by a volume of at least three times the dead volume of the sample introduction system.

12.1.6 Obtain the digitized spectral response of the fuel sample over the frequency region from 4000 to 650 cm^{-1}.

12.1.7 Measure the absorption spectrum and note the maximum absorption value of the peak in the region 1765 to 1720 cm^{-1}.

12.1.8 Biodiesel and high concentrations of biodiesel in biodiesel blends are difficult to remove from the cell surface. Flush several times with sample or use a solvent rinse between samples. When in doubt, repeat steps 12.1.6 through 12.1.8 and compare result to ensure adequate rinsing occurred.

12.1.9 For FTIR instruments using a baseline correction step and a linear regression calibration, determine the biodiesel concentration using the calibration models developed in A1.3 by following the steps outlined as follows.

12.1.9.1 If the absorption value (determined in 12.1.8) is smaller or equal to 1.0, calculate the baseline corrected absorption spectrum. The baseline is defined through the absorption values at the wavenumber 1708 and 1785 cm^{-1}.

Calculate the area from the wavenumber 1713 to 1784 cm^{-1}. Estimate the biodiesel concentration by applying the low concentration linear regression calibration (see A1.3.3.1).

12.1.9.2 If the absorption value (determined in 12.1.7) is greater than 1.0, calculate the baseline corrected absorption spectrum. The baseline is defined through the absorption values at the wavenumber 1126 and 1225 cm^{-1}. Calculate the area from the wavenumber 1126 to 1220 cm^{-1}. Estimate the biodiesel concentration by applying the high concentration linear regression calibration (see A1.3.3.2).

12.2 *Filter-Based Mid-IR Instruments:*

12.2.1 Equilibrate the unknown fuel sample to the typical temperature of the laboratory (15 to 27°C) before analysis.

12.2.2 Introduce enough of the fuel sample to the cell to ensure the cell is washed by a volume of at least three times the dead volume of the sample introduction system.

12.2.3 For the filter-based Mid-IR test apparatus determine the biodiesel concentration using the calibration models developed in A1.4 by following the steps outlined as follows.

12.2.3.1 Estimate the FAME concentration using the universal equation developed in A1.4.2.

12.2.3.2 If the estimated FAME concentration is ≤6.0 volume percent use the low concentration equation developed in A1.4.3 to determine the FAME concentration.

12.2.3.3 If the estimated FAME concentration is >6.0 volume percent but ≤30.0 volume percent use the high concentration equation developed in A1.4.4 determine the FAME concentration.

12.2.3.4 The precision of the analysis may cause the result obtained from the narrow range calibration to not correspond to the result obtained from the universal calibration at the interface between the narrow calibrations (6.00 volume percent). If the result from the universal calibration and the result from the indicated narrow calibration agree to within the cross method reproducibility then the result using the narrow calibration is the accepted result. If the two results do not agree then check the instrument performance using a check standard.

13. Calculation

13.1 *Conversion to Volume % of Biodiesel*—To convert the calibration and qualification standards to volume % use Eq 1:

$$V_b = M_b(D_f/D_b) \quad (1)$$

where:

V_b = biodiesel volume %,
M_b = biodiesel mass %,
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 *Calculation of the Peak Area*—To calculate the peak area use Eq 2:

$$A_{v_1-v_2} = \sum_{i=v_1}^{v_2-1} \frac{x_i + x_{i+1}}{2} \quad (2)$$

where:

$A_{v_1-v_2}$ = area of the absorption spectrum in the range from v_1 to v_2,
v = wave number in cm^{-1},
x_i = absorbance at wave number i, and
i = enumeration index.

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, the result of the analysis may be corrected using a multiplicative factor corresponding to (MWunk/Dunk)*(Dcal/MWcal) where MW and D are the molecular weight and density of the calibration and unknown biodiesel.

14. Report

14.1 Report the following information:

14.1.1 Volume % biodiesel by Test Method D7806, to the nearest 0.1 %.

15. Precision and Bias

15.1 The precision of this test method, which was determined by statistical examination of intralaboratory results, is as follows:

NOTE 2—For the FTIR ruggedness study, the data was obtained by testing 8 samples in duplicate on 3 different apparatus in 1 laboratory using 4 operators. The FAME was blended into 2 different diesel fuels to produce concentrations in the samples ranging from 2 volume percent to 21 volume percent. The FAME in the sample was sourced from either soy or rapeseed triglycerides. For the filter instrument ruggedness study, the data was obtained by testing 30 samples in duplicate on a single apparatus in 1 laboratory using 1 operator. The FAME was blended into 2 different diesel fuels to produce concentrations in the samples ranging from 0 volume percent to 27 volume percent. The FAME in the sample was sourced from soy triglycerides.

15.2 *Repeatability:*

15.2.1 *For FTIR Instruments Using Linear Regression*—For biodiesel concentrations between 2 and 22 volume %, 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:

$$X \pm 0.3 \text{ volume \%}$$

where X is the biodiesel concentration determined. A full interlaboratory study will be completed within a five year period to estimate the repeatability.

15.2.2 *For Filter Instruments Using Linear Regression*—For biodiesel concentrations between 0 and 28 volume %, 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:

$$X \pm 0.34 \text{ volume \%}$$

where X is the biodiesel concentration determined. A full interlaboratory study will be completed within a five year period to estimate the repeatability.

15.3 *Reproducibility:*

15.3.1 *For FTIR Instruments Using Linear Regression*—A full interlaboratory study will be completed within a five year period to estimate the reproducibility.

15.3.2 *For Filter Instruments Using Linear Regression*—A full interlaboratory study will be completed within a five year period to estimate the reproducibility.

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

16. Keywords

16.1 biodiesel; biodiesel blend; infrared spectroscopy

ANNEXES

(Mandatory Information)

A1. CALIBRATION AND QUALIFICATION OF THE APPARATUS

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 *Calibration Matrices for Filter and FTIR Instruments using a Transmission Cell*—To obtain the best precision and accuracy of calibration using the linear regression model, prepare two biodiesel calibration sets as set forth in Table A1.1. The first set (Set A) contains samples with biodiesel concentrations between 0 and 7 volume %. The second set (Set B) contains samples with biodiesel concentrations from 7 to 30 volume %.

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 % biodiesel to volume % biodiesel according to the Eq 1 presented in 13.1. If the densities of the calibration standards can not be measured, it is acceptable to convert to volume % using the densities of the individual components measured using Test Method D1298 or Test Method D4052.

A1.2 *Transmission Cell Path Length Detection*—For FTIR instruments use cyclohexane to determine the sample cell path length. Determine the maximum absorption of the peak at 862 cm^{-1} using the abscissa as the baseline. The range of the absorption maximum of that peak shall be 1.33 ± 0.10. Calculate the path length:

$$P = h/10.22 - 0.03 \quad \text{(A1.1)}$$

where:

P = sample cell path length [mm], and
h = maximum absorbance of the peak at 862 cm^{-1}.

A1.3 FTIR Instrument Calibration

A1.3.1 Equilibrate all samples to the typical temperature of the laboratory (15 to 27°C) prior to analysis. Fill the sample cell with the calibration standards in accordance with Practices E168 or in accordance with the manufacturer's instructions.

A1.3.2 Using the FTIR spectrometer, acquire the digitized spectral data over the frequency region from 4000 to 650 cm^{-1} for each of the calibration standards. The infrared spectrum is the negative logarithm of the ratio of the single beam infrared spectrum obtained with a sample and the single beam infrared spectrum with dry air. The same single beam spectrum of dry air (or nitrogen) can be used for 6 h then has to be reacquired.

A1.3.3 Two separate regression calibrations will be developed. Subscript the calibration constants with the cell path length used to the nearest 0.001 mm. Calibration can be transferred to sample cells of the same type. In case the sample cell is being exchanged, determine the path length of the new cell according to A1.2. Multiply the regressed coefficients (slope and ordinate intercept of the regression lines developed in A1.3.3.1 and A1.3.3.2) with the factor obtained by calculating the ratio of the path length of the old cell by the path length of the new cell and subscript again the new constants with the new sample cell path length.

A1.3.3.1 Develop the low concentration linear regression calibration using spectra obtained from the samples in calibration Set A detailed in Table A1.1. For the FTIR spectroscopic data calculate the "two point"-baseline corrected absorption spectrum from 1708 to 1785 cm^{-1}. Then calculate the area from 1713 to 1784 cm^{-1}. Use a linear least squares regression in calculating the calibration constants.

A1.3.3.2 Develop the high concentration linear regression calibration using spectra obtained from the samples in calibration Set B detailed in Table A1.1. For the FTIR spectroscopic data calculate the "two point"-baseline corrected absorption spectrum from 1126 to 1225 cm^{-1}, then calculate the area from 1126 to 1220 cm^{-1}. Use a linear least squares regression in calculating the calibration constants.

TABLE A1.1 Instrument Calibration Sets A and B

Sample	Biodiesel [vol %]	Matrix	Set A	Set B
1	0.00	Hexadecane	X	
2	0.25	Hexadecane	X	
3	0.50	Hexadecane	X	
4	1.00	Hexadecane	X	
5	1.50	Hexadecane	X	
6	2.00	Hexadecane	X	
7	2.50	Hexadecane	X	
8	3.00	Hexadecane	X	
9	4.00	Hexadecane	X	
10	5.00	Hexadecane	X	
11	6.00	Hexadecane	X	X
12	9.00	Hexadecane		X
13	10.00	Hexadecane		X
14	15.00	Hexadecane		X
15	20.00	Hexadecane		X
16	21.00	Hexadecane		X
17	25.00	Hexadecane		X
18	27.50	Hexadecane		X
19	30.00	Hexadecane		X
20	0.00	DCCF-Low	X	
21	0.25	DCCF-Low	X	
22	0.50	DCCF-Low	X	
23	1.00	DCCF-Low	X	
24	1.50	DCCF-Low	X	
25	2.00	DCCF-Low	X	
26	2.50	DCCF-Low	X	
27	3.00	DCCF-Low	X	
28	4.00	DCCF-Low	X	
29	5.00	DCCF-Low	X	
30	6.00	DCCF-Low	X	X
31	9.00	DCCF-Low		X
32	10.00	DCCF-Low		X
33	12.00	DCCF-Low		X
34	15.00	DCCF-Low		X
35	18.00	DCCF-Low		X
36	19.00	DCCF-Low		X
37	20.00	DCCF-Low		X
38	21.00	DCCF-Low		X
39	25.00	DCCF-Low		X
40	27.50	DCCF-Low		X
41	30.00	DCCF-Low		X
42	0.00	DCCF-High	X	
43	0.25	DCCF-High	X	
44	0.50	DCCF-High	X	
45	1.00	DCCF-High	X	
46	1.50	DCCF-High	X	
47	2.00	DCCF-High	X	
48	2.50	DCCF-High	X	
49	3.00	DCCF-High	X	
50	4.00	DCCF-High	X	
51	5.00	DCCF-High	X	
52	6.00	DCCF-High	X	X
53	9.00	DCCF-High		X
54	10.00	DCCF-High		X
55	12.00	DCCF-High		X
56	15.00	DCCF-High		X
57	18.00	DCCF-High		X
58	19.00	DCCF-High		X
59	20.00	DCCF-High		X
60	21.00	DCCF-High		X
61	25.00	DCCF-High		X
62	27.50	DCCF-High		X
63	30.00	DCCF-High		X

A1.4 Filter Instrument Calibration

A1.4.1 Using the filter spectrometer acquire the absorbance values at the frequencies specified in Table 1.

A1.4.2 Derive a universal prediction equation to for filter-based instruments by applying the multiple linear regression to determine the calibration coefficients derived from the calibration data acquired in A1.3.3 and the concentration data from Set A and Set B described in Table A1.1.

$$C_{UP} = C_1 \cdot A_1 + C_2 \cdot A_2 + \ldots + I_{UP}$$

(The final form of the equation will be determined during the calibration process)

where:

C_{UP} = the FAME concentration in volume percent predicted using the universal prediction,
C_x = the correlation coefficient determined from the multiple linear regression analysis of the calibration samples,
A_x = the absorbance of the sample measured at filter x, and
I_{UP} = the intercept resulting from the multiple linear regression analysis.

A1.4.2.1 The universal prediction equation is used to estimate the concentration of FAME in the sample so the appropriate concentration range-based calibration equation can be applied.

A1.4.3 Derive a low concentration prediction equation by applying the multiple linear regression to determine the calibration coefficients derived from the calibration data acquired in A1.3.3 and the concentration data from Set A described in Table A1.1.

$$C_L = D_1 \cdot A_1 + D_2 \cdot A_2 + \ldots + I_L$$

(The final form of the equation will be determined during the calibration process)

where:

C_L = the FAME concentration in volume percent,
D_x = the correlation coefficient determined from the multiple linear regression of the calibration samples,
A_x = the absorbance of the sample measured at filter x, and
I_L = the intercept resulting from the multiple linear regression analysis.

A1.4.3.1 The low calibration equation is used to predict the FAME concentration for samples that have a FAME concentration of ≤6.0 volume percent as determined using the universal prediction equation.

A1.4.4 Derive a high concentration prediction equation by applying the multiple linear regression to determine the calibration coefficients derived from the calibration data acquired in A1.3.3 and the concentration data from Set B described in Table A1.1.

$$C_H = E_1 \cdot A_1 + E_2 \cdot A_2 + \ldots + I_H$$

(The final form of the equation will be determined during the calibration process)

where:

C_H = the FAME concentration in volume percent,
E_x = the correlation coefficient determined from the multiple linear regression of the calibration samples,
A_x = the absorbance of the sample measured at filter x, and
I_H = the intercept resulting from the multiple linear regression analysis.

A1.4.4.1 The high calibration equation is used to predict the FAME concentration for samples that have a FAME concentration of >6.0 volume percent and ≤30 volume percent as determined using the universal prediction equation.

A1.5 *Qualification of the Filter Instrument Performance*—Once a calibration(s) has been established, the individual calibrated instrument must be qualified to ensure that the instrument accurately and precisely measures biodiesel in the presence of typical compression-ignition engine fuel compounds that, in typical concentrations, present spectral interferences. This qualification need only be carried out when the instrument is initially put into operation, is recalibrated, or repaired.

A1.5.1 *Preparation of Qualification Samples*—Prepare multicomponent qualification standards of the biodiesel by mass according to Practices D4307 (or appropriately scaled for larger blends), or D5854, where appropriate. These standards shall be similar to, but not the same as, the mixtures established for the calibration set used in developing the calibration. Prepare the qualification samples so as to vary the concentrations of biodiesel and of the interfering components over a range that spans at least 95 % of that for the calibration standards. The numbers of required standards are suggested by Practices E1655 and, in general, will be three times the number of independent variables in the calibration equation.

A1.5.2 *Acquisition of Qualification Data*—For each of the qualification standards, measure the biodiesel concentration, expressed in volume %, according to the procedure established in Section 12. The adequacy of the instrument performance is determined following the procedures similar to those described in Practice E2056.

A1.5.3 The standard error of qualification (SEQ) is calculated as follows:

$$SEQ = \sqrt{\sum_{i=1}^{q} (\hat{y}_i - y_i)^2 / q} \qquad \text{(A1.2)}$$

where:

q = number of surrogate qualification mixtures,
y_i = component concentration for the ith qualification sample, and
$\hat{y}_i$ = estimate of the concentration of the ith qualification sample

A1.5.3.1 An F value is calculated by dividing SEQ by PSEQ (the pooled standard error of qualification for the round robin instruments). The F value is compared to a critical F value with q degrees of freedom in the numerator and DOF(PSEQ) degrees of freedom in the denominator. Values of PSEQ and DOF(PSEQ) for the two instrument types are given in Table A1.2, and the critical F values in Table A1.3.

A1.5.3.2 If the F value is less than or equal to the critical F value from the table, then the instrument is qualified to perform the test.

A1.5.3.3 If the F value is greater than the critical F value from the table, then the instrument is not qualified to perform the test.

TABLE A1.2 Pooled Standard Error of Qualification for the Filter Instrument

	Filter based-IR Calibration D7806
PSEQ	
DOF(PSEQ)	

TABLE A1.3 Critical F Value

Denominator, Degrees of Freedom	7	8	9	10	12	14	16	18	20	25	30	40	50	100
7	3.79	3.73	3.68	3.64	3.57	3.53	3.49	3.47	3.44	3.40	3.38	3.34	3.32	3.27
8	3.50	3.44	3.39	3.35	3.28	3.24	3.20	3.17	3.15	3.11	3.08	3.04	3.02	2.97
9	3.29	3.23	3.18	3.14	3.07	3.03	2.99	2.96	2.94	2.89	2.86	2.83	2.80	2.76
10	3.14	3.07	3.02	2.98	2.91	2.86	2.83	2.80	2.77	2.73	2.70	2.66	2.64	2.59
11	3.01	2.95	2.90	2.85	2.79	2.74	2.70	2.67	2.65	2.60	2.57	2.53	2.51	2.46
12	2.91	2.85	2.80	2.75	2.69	2.64	2.60	2.57	2.54	2.50	2.47	2.43	2.40	2.35
13	2.83	2.77	2.71	2.67	2.60	2.55	2.51	2.48	2.46	2.41	2.38	2.34	2.31	2.26
14	2.76	2.70	2.65	2.60	2.53	2.48	2.44	2.41	2.39	2.34	2.31	2.27	2.24	2.19
15	2.71	2.64	2.59	2.54	2.48	2.42	2.38	2.35	2.33	2.28	2.25	2.20	2.18	2.12
16	2.66	2.59	2.54	2.49	2.42	2.37	2.33	2.30	2.28	2.23	2.19	2.15	2.12	2.07
17	2.61	2.55	2.49	2.45	2.38	2.33	2.29	2.26	2.23	2.18	2.15	2.10	2.08	2.02
18	2.58	2.51	2.46	2.41	2.34	2.29	2.25	2.22	2.19	2.14	2.11	2.06	2.04	1.98
19	2.54	2.48	2.42	2.38	2.31	2.26	2.21	2.18	2.16	2.11	2.07	2.03	2.00	1.94
20	2.51	2.45	2.39	2.35	2.28	2.22	2.18	2.15	2.12	2.07	2.04	1.99	1.97	1.91
25	2.40	2.34	2.28	2.24	2.16	2.11	2.07	2.04	2.01	1.96	1.92	1.87	1.84	1.78
30	2.33	2.27	2.21	2.16	2.09	2.04	1.99	1.96	1.93	1.88	1.84	1.79	1.76	1.70
35	2.29	2.22	2.16	2.11	2.04	1.99	1.94	1.91	1.88	1.82	1.79	1.74	1.70	1.63
40	2.25	2.18	2.12	2.08	2.00	1.95	1.90	1.87	1.84	1.78	1.74	1.69	1.66	1.59
45	2.22	2.15	2.10	2.05	1.97	1.92	1.87	1.84	1.81	1.75	1.71	1.66	1.63	1.55
50	2.20	2.13	2.07	2.03	1.95	1.89	1.85	1.81	1.78	1.73	1.69	1.63	1.60	1.52
60	2.17	2.10	2.04	1.99	1.92	1.86	1.82	1.78	1.75	1.69	1.65	1.59	1.56	1.48
70	2.14	2.07	2.02	1.97	1.89	1.84	1.79	1.75	1.72	1.66	1.62	1.57	1.53	1.45
80	2.13	2.06	2.00	1.95	1.88	1.82	1.77	1.73	1.70	1.64	1.60	1.54	1.51	1.43
90	2.11	2.04	1.99	1.94	1.86	1.80	1.76	1.72	1.69	1.63	1.59	1.53	1.49	1.41

A2. SELECTION OF BIODIESEL AND DIESEL FUEL FOR CALIBRATION AND VALIDATION SAMPLES

A2.1 B100 Biodiesel for Calibration Set

A2.1.1 Experience has shown biodiesel made from these various base stock materials have very similar absorbance in the spectral region used in this test method. However, B100 shall meet Specification D6751. If the B100 is obtained from a biodiesel producer, it is recommended the provider be BQ-9000 certified to ensure the quality of the product. NIST is another source for certified soy-based B100.

A2.2 Diesel Fuel for Calibration Set

A2.2.1 Middle distillate fuel used for calibration, qualification and quality control standards shall be Specification D975 compliant, free of biodiesel or biodiesel oil precursor, or both. Low, High and Ultra-High diesel cetane check fuels from Chevron Phillips Chemical Company LP are the preferred source of diesel fuel for making the calibration, qualification and quality control sets.