Designation: D7591 – 12 (Reapproved 2017)

Standard Test Method for Determination of Free and Total Glycerin in Biodiesel Blends by Anion Exchange Chromatography[1]

This standard is issued under the fixed designation D7591; 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 and describes an anion exchange chromatography procedure for determining free and total glycerin content of biodiesel (B100) and blends (B0 to B20) with diesel fuel oils defined by Specification D975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D and Specification D6751 (for B100 feedstocks). It is intended for the analysis of biodiesel and blend samples containing between 0.5 mg⁄kg to 50 mg⁄kg glycerin.

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

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.*

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 Oils

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling 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

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:*

3.1.1 *free glycerin, n*—measure of the amount of glycerin remaining in the fuel.

3.1.2 *total glycerin, n*—sum of the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat.

4. Summary of Test Method

4.1 *Free Glycerin*—A small volume of an extract of the blend sample is directly injected into an ion chromatograph consisting of appropriate ion exchange columns and into an electrochemical detector. Glycerin is separated based on its affinity for ion exchange sites of the resin with respect to the resin's affinity for the eluent. An electrochemical detector is employed for detection of glycerin. Glycerin is quantified by peak area based on an external calibration curve, and is reported as µg/g (mg/kg), or may be converted to wt%. Calibration standards are prepared from commercially available glycerin (99+% purity) in an aqueous solution.

4.2 *Total Glycerin*—A small volume extract of a saponified blend sample is directly injected into an ion chromatograph consisting of appropriate ion exchange columns and into an electrochemical detector. Glycerin is separated based on its affinity for ion exchange sites of the resin with respect to the resin's affinity for the eluent. An electrochemical detector is employed for detection of glycerin. Glycerin is quantified by peak area based on an external calibration curve, and is reported as µg/g (mg/kg), or may be converted to wt%.

[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 D02.04.0C on Liquid Chromatography.

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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.

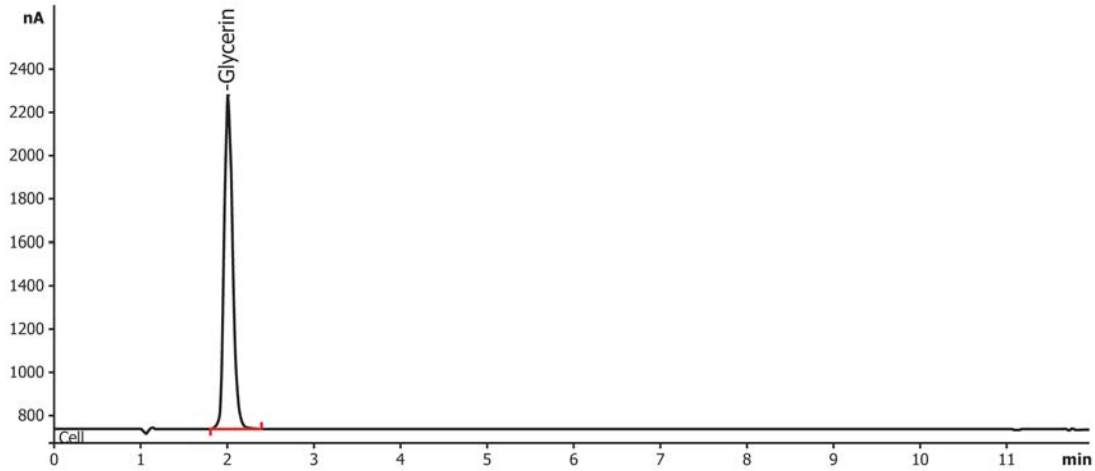

FIG. 1 Typical Chromatogram of a Solution Containing 0.7 mg/kg of Glycerin

Calibration standards are prepared from commercially available glycerin (99+% purity) in an aqueous solution.

5. Significance and Use

5.1 Petroleum-based diesel may be blended with biodiesel. High levels of free glycerin in biodiesel can cause injector deposits ("gel effect"), as well as clogging fuel systems. High levels of unreacted glycerides can cause injector deposits and can adversely affect cold weather operation and filter plugging.

6. Interferences

6.1 Interferences can be caused by substances with similar ion chromatographic retention times, especially if they are in high concentration compared to the analyte of interest. Sample dilution can be used to minimize or resolve most interference problems. Also, an excess of unreacted hydroxide (base) during the sample preparation step for total glycerin can cause a pH imbalance on the anion exchange column, resulting in a negative dip in front of the glycerin peak.

6.2 A water dip (system void, negative peak as shown in Fig. 1) can cause interference with some integrators. This dip can be eliminated by dilution with the eluent. The water dip should not be a problem since the glycerin peak is resolved from the void peak.

6.3 Interferences can be caused by contamination of glassware, eluent, reagents, etc. Take care to ensure that contamination is kept at the lowest possible levels. The use of nitrile gloves is highly recommended to prevent contamination during sample preparation.

6.4 There are several known additives based on natural products that might have similar retention times and detector response similar to glycerin. In the case of higher than expected values for biodiesel blends, it is highly recommended that the user needs to verify these higher than expected values for glycerin using a different analytical technique.

6.5 Pre-rinsing of the sample preparation containers with deionized water is mandatory.

7. Apparatus

7.1 *Analytical Balance*—capable of weighing up to 200 g accurately to ±0.0001 g.

7.2 *Desiccator*—containing freshly activated silica gel (or equivalent desiccant) with moisture content indicator.

7.3 *Pipettes or Volumetric Transfer Devices*— 1 mL and 5 mL class A volumetric pipettes or calibrated variable volume automatic pipettes fitted with disposable polypropylene tips.

7.4 *Volumetric Flasks*—25 mL, 50 mL, 100 mL, and 1000 mL class A volumetric flasks.

7.5 *Container*—standard HDPE plastic 100 mL bottle with cap.

7.6 *Ion Chromatograph*—Analytical system with all required accessories including syringes, columns, high-pressure dual piston pump, and detector.

7.6.1 *Injection System*—capable of delivering 5 µL to 25 µL with a precision better than 1 %.

7.6.2 *Pumping System*—capable of delivering mobile phase flows between 0.1 mL/min and 5.0 mL/min with a precision better than 2 %. Due to the corrosive nature of the eluent, a PEEK pump head is recommended.

7.6.3 *Guard Column*—for protection of the analytical column from strongly retained constituents.

7.6.4 *Anion Exchange Column*—capable of producing satisfactory analyte separation.

7.6.5 *Electrochemical Detector*—integrated, temperature controlled to 0.1 °C, capable of measuring at least 0 µA to 200 µA on a linear scale. Detector has a pulsed amperometric detection mode for required sensitivity. Consult with the manufacturer for optimal cell settings.

7.6.6 *Electrochemical Detector Cell*—minimum 3 mm gold working electrode surface with wall jet design, solid state reference and counter electrodes. Ensure a minimal volume in the cell for enhanced sensitivity. A platinum working electrode may also be used.

7.6.7 *Integrator or Chromatography Data System Software*—capable of measuring peak areas and retention times, and performing a baseline correction.

7.6.8 *Sample Digestion System*—capable of heating, and stirring with integrated reflux. Reflux is needed to minimize loss of petroleum diesel in biodiesel blend samples. A chiller is recommended for providing water to the reflux condenser for efficiency and to conserve water resources.

7.7 *Mechanical Wrist Shaker.*

7.8 *Gloves, nitrile.*

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards and eluent solutions. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

8.2 *Water Quality*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II in Specification D1193 or better. For eluent preparation and handling, comply with all ion chromatograph instrument and column vendor requirements (for example, filtering, degassing, etc.).

8.3 *Eluent Stock Solution,* sodium hydroxide (NaOH, 50 % certified, ACS).

8.3.1 *Eluent Preparation,* 0.10 *M* NaOH. Weigh 8.00 g ± 0.02 g of 50 % NaOH in reagent water in a 1 L volumetric flask and dilute to volume with degassed reagent water. The eluent solution used may be different if other systems or analytical columns are used. Other volumes of stock solution may be prepared using appropriate ratios of reagents. Ready to use reagents may be used. Consult with the instrument manufacturer for guidance and use. Do not store sodium hydroxide solutions in glass.

8.4 *Potassium Hydroxide Solution for Total Glycerin,* 1.0 *M* KOH. Weigh out 56.1 g of ACS grade potassium hydroxide pellets. Dissolve the pellets in approximately 250 mL DI water in a 1 L volumetric flask. Use caution when handling the flask due to the heat produced during the dissolution of the potassium hydroxide. Dilute to the mark with DI water. Prepared ready to use 1.0 *M* potassium hydroxide solutions made with acceptable purity materials may also be used. Keep containers tightly closed when not in use to minimize carbonate formation from atmospheric carbon dioxide.

9. Preparation of Standard Solutions

9.1 Stock and working solutions.

[3] *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 *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.

TABLE 1 Preparation of Glycerin Standards in Water

Glycerin Standard, mg/kg	Water (final weight), g	Glycerin Stock Solution, g
50	100	5.0
20	100	2.0
10	100	1.0
5	100	0.5
1	100	0.1
0.5	100	0.05

9.1.1 *Glycerin Stock Solution, 1000 mg/L*—Accurately weigh 1 g of 99.5+ % glycerin to the nearest tenth of a milligram (0.0001 g) and transfer to a 1 L volumetric flask. Dilute to the mark with water. Shake or swirl to mix the standard for homogeneity. Other volumes of stock solution may be prepared using the appropriate ratio of reagents.

9.2 *Working Standards*—Prepare glycerin working standards according to Table 1.

9.2.1 Alternatively, commercial stock calibration solutions can be used, provided that the solutions are traceable to primary stock solutions or certified reference materials, and are free from other analytes.

10. Calibration

10.1 Set up the ion chromatograph according to the manufacturer's instructions. No specific parameters are given here since different manufacturer's equipment might require changes in eluent, flow conditions, and instrument settings to perform the separation and obtain the results. Calibrate the ion chromatograph with at least five concentration levels of glycerin, starting near but above the minimum detection limit, and covering the expected working range of samples subsequently to be analyzed. Select concentrations of calibrant solutions used that bracket the expected range for the samples to be analyzed. Use one or more mid-range standards to verify the linearity of the calibration plot.

10.1.1 Typical ion chromatographic conditions:

Flow: 1.0 mL/min

Sample loop: 10 µL

Other analytical conditions may be used per the manufacturer's instructions.

NOTE 1—The sample loop volume will vary based on the column capacity, sensitivity, and other factors. Refer to ion chromatography equipment manuals and column information for instrument/column-specific details.

10.1.2 Establish analytical curves with only one detector scale setting. This will prevent a change of slope affecting the analytical curve.

10.2 Verify the analytical calibration plot daily or whenever samples are to be run, prior to the analysis of samples to verify the system resolution, calibration, and sensitivity as part of the quality verification process (see Section 14).

10.3 Repeat calibration after any change of the ion chromatography eluent solution from 8.3, to reestablish ion retention times and resolution. Use a check standard to verify calibration, retention times, and resolution after any change in the IC eluent solution from 8.3. Recalibrate if needed.

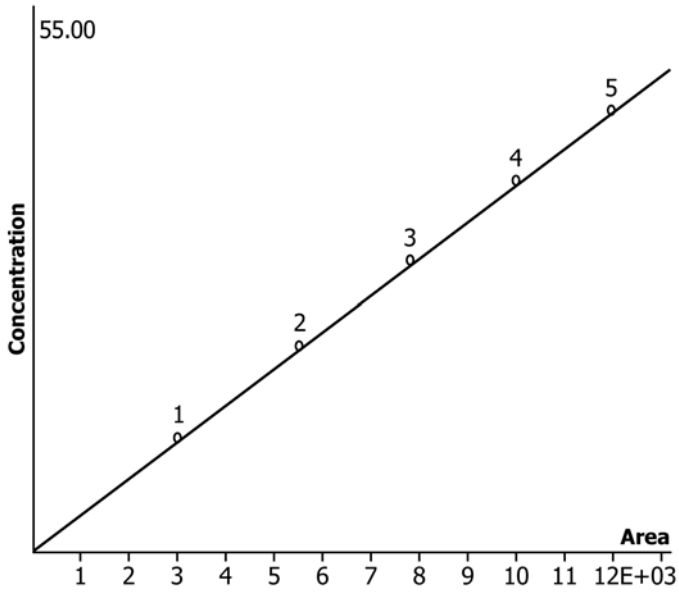

FIG. 2 Typical Glycerin Calibration Plot

10.4 *Measurement of the Calibration Standards*—Inject 10 µL of each calibration solution from 9.2 into the ion chromatograph, and measure the areas of the peaks corresponding to glycerin. Generally, one injection per sample is sufficient. Refer to Section 14 for quality control discussion.

10.5 Construct the glycerin calibration plots by plotting the peak areas against the glycerin concentrations. Use linear regression to determine the best straight-line calibration. A linear least squares correlation coefficient of 0.99 or greater is required (see Fig. 2). The response factor for glycerin, Rf, is the slope of the calibration plot straight line, in mg/kg/(area count).

10.5.1 If the plot of the peak area values against the ion concentrations is not linear (the correlation factor should be at least 0.99), the procedure should be checked for errors, and if necessary, the calibration should be repeated starting from Section 9.

11. Procedure

11.1 *For Free Glycerin in Biodiesel and its Blends:*

11.1.1 Obtain samples in accordance with Practice D4057 or Practice D4177. Mix the samples thoroughly to ensure homogeneity. A representative portion shall be taken for analysis. Ensure that the sample containers do not contain any residual glycerin. Use clean containers that have been rinsed with Type II reagent water and dried prior to use.

11.1.2 Thoroughly mix the samples in their containers immediately prior to withdrawal of a test sample.

11.1.3 Accurately weigh 5 g of sample to the nearest 0.001 g into a 100 mL container with a cap, and record the weight.

11.1.4 Add 50 g of deionized water to the container (with previously weighed sample), and record the weight to the nearest 0.001 g. Close the container, and shake for 5 min on a mechanical wrist shaker.

11.1.5 After shaking the sample, let it settle until the oil and aqueous phases are separated.

11.1.6 Set up the ion chromatograph in accordance with the manufacturer's instructions.

11.1.7 Equilibrate the system by pumping eluent for 15 min to 30 min or until a stable baseline is obtained.

11.1.8 Start the ion chromatographic run in accordance with the manufacturer's instructions.

11.1.9 Directly inject 10 µL of the aqueous extract into the ion chromatograph, and measure the area of the peak corresponding to glycerin.

11.1.9.1 For most samples, a single injection is sufficient. However for every tenth sample, perform two injections and calculate the mean of the peak areas corresponding to glycerin. The two area measurements shall be within 20 % of each other. If the areas are different by more than 20 %, do not continue running samples, until at least 20 % area repeatability can be achieved.

11.1.10 If the glycerin concentration exceeds that of the highest calibration solution, dilute the sample solution with water as appropriate, and repeat the sample measurement. Take into account the dilution factor in the calculation of glycerin content in the sample. Calculate the dilution factor as described in 12.1.

11.2 *For Total Glycerin in Biodiesel and its Blends:*

11.2.1 Obtain samples in accordance with Practice D4057 or Practice D4177. Mix the samples well to ensure homogeneity. A representative portion shall be taken for analysis. Ensure that sample containers do not contain any residual glycerin. Use clean containers that have been rinsed with Type II reagent water and dried prior to use.

11.2.2 Thoroughly mix the samples in their containers immediately prior to withdrawal of a test specimen.

11.2.3 Accurately weigh 2.5 g of sample to the nearest tenth of a gram into a suitable size glass reflux vessel and record the mass to the nearest 0.001 g.

11.2.4 Pipette 20.0 mL of 1.0 *M* KOH solution into the glass reflux vessel (with previously weighed sample). Carefully place a stir bar into the vessel. Close the container and place it on the reflux apparatus carousel.

11.2.5 When using a chiller, turn the chiller on for reflux. Set the chiller temperature between 5 °C to 10 °C to provide efficient cooling for reflux of the sample. When using tap water for cooling the reflux, turn on the water.

11.2.6 Similarly prepare multiple samples for digestion. Follow the manufacturer's instructions and precautions for the apparatus.

11.2.7 Turn the stirrer on and heat the sample at 95 °C for 60 min.

11.2.8 After digestion, remove the refluxed sample to a rack for cooling.

11.2.9 Carefully draw the aqueous phase of the sample into a previously tared 100 mL container (for example, an HDPE bottle).

11.2.10 Rinse the wall of the reflux vessel with deionized water and transfer it to give a final weight of 50 g. Record the weight (Vf) to the nearest ±0.001 g.

NOTE 2—It is recommended to perform several small rinses rather than one larger rinse.

11.2.11 Mix well. Transfer a portion of the prepared sample into an auto sampler vial. Analyze the samples in accordance with steps 11.1.6 to 11.1.10.

NOTE 3—Extraction efficiency can be verified using commercially available glycerides samples. Also, commercially available soy-based material and an animal-based material that can be used for verification. When this procedure is run for the first time and then periodically thereafter, it is important to verify that the extraction efficiency is 100 % ± 10 %.

NOTE 4—With variation in feed stocks (vegetable source versus animal based source) of Biodiesel it may be necessary to increase KOH concentration from 1 *M* to 2 *M*.

11.2.12 To check the extraction efficiency, prepare the glyceride standard using steps 11.2.1 to 11.2.11 in triplicate. Substitute the weighing step 11.2.3, with the following procedure. Weigh an amount of glyceride standard to make a stock glyceride standard such that when 2.5 g are diluted to a total weight of 50 g, the glycerin (not glyceride) content will be about a 30 ppm (mg/kg). For prediluted standards, use the entire vial. If weighing a neat standard, then the minimum weight used to make the stock glyceride standard should be at least 1 gram on a scale with at least 1 mg precision. A suitable solvent for most standards is ethyl acetate. Dilute to the total weight intended for the stock standard, Ws, with the solvent and record Ws to the nearest mg. Proceed with step 11.2.3 by weighing the 2.5 g using the stock glyceride standard into the glass reflux vessel and recording the weight to the nearest milligram. Check the calibration curve by running a calibration standard that has a lower concentration of glycerin than that expected from the glycerin standard. Run the three glyceride standards to be used to check the extraction efficiency per the IC procedure listed in 11.1.6 through 11.1.10. Follow this run with a calibration standard having a concentration higher than that of the glyceride standard to confirm the calibration curve accuracy. Once the calibration curve accuracy has been verified, then compare the peak areas obtained in the runs from the three glyceride standards, A1, A2, and A3. The difference between the lowest (A1) and the highest (A3) area counts should be less than 10% of the area counts obtained for the standard whose area count (A2) is between the high and low glyceride standard area counts. If all of the above criteria are met, then the extraction efficiency is the average of the concentrations of the total glycerin calculated in accordance with 12.1 and 12.2 divided by the expected glycerin concentration. The expected glycerin concentration is calculated by using the following formulas:

$$Cg = Wgly*92.09/(Mgly*Ws) \quad (1)$$

$$Cge = Ws*Cg/Vf \quad (2)$$

$$Ca = (C1+C2+C3)/3 \quad (3)$$

$$Eeff = Ca/Cge*100\% \quad (4)$$

where:

Cg = concentration of glycerin in the stock solution,
Wgly = weight of the glyceride standard, in grams,
Mgly = molecular weight of the glyceride standard,
Ws = total weight of the stock solution,
Cge = expected concentration of the glycerin based on the published value of the standard,
Vf = weight of the final solution, in grams,
Ca = average from the triplicate glyceride standard runs,
C1, C2, C3 = concentrations calculated for each the three glyceride standard runs from steps 12.1 and 12.2, and
Eeff = extraction efficiency.

NOTE 5—For prediluted standards, Wgly = concentration of the standard * volume (not weight) of the standard used before it is diluted to make the glyceride stock standard solution. Wgly must be converted to grams. For standards listed as µg/mg, convert to grams by dividing Wgly by 1 000 000. For standards listed as mg/g, convert to grams by dividing Wgly by 1000.

12. Calculation

12.1 Calculate the dilution factor:

$$dF = Vf/Vi \quad (5)$$

where:

dF = dilution factor,
Vi = weight of the initial sample, in grams, and
Vf = weight of the final solution, in grams.

12.2 The individual concentrations of free and total glycerin in the biodiesel blend samples, in mg/kg (µg/g) are calculated as shown in Eq 4.

$$C = A \times Rf \times dF \quad (6)$$

where:

C = concentration of glycerin in the biodiesel sample, in mg/kg,
A = anion peak area, from the ion chromatogram in 10.4, in counts,
Rf = calibration plot response factor from 10.5, in mg/kg/counts, and

TABLE 2 Free Glycerin Range for Blend—Reference Table

Example concentration, mass%	B100		B11 to B20		B7 to B10		B1 to B6	
	r	R	r	R	r	R	r	R
0.005	0.00027	0.00037	0.0004	0.0011	0.0002	0.0036	0.0007	0.0010
0.0100	0.00048	0.0006	0.00081	0.0022	0.00017	0.0029	0.0019	0.0027
0.0200	0.00083	0.0011	0.00161	0.0045	0.00014	0.0024	0.0025	0.0057
0.0300	0.00115	0.0015	0.00242	0.0067	0.00012	0.0021	0.0047	0.0105
0.0400	0.00145	0.0019	0.00322	0.0090	0.00011	0.0019	0.0064	0.0162
0.0500	0.00173	0.0023	0.00403	0.0112	0.00011	0.0018	0.0067	0.0226

dF = dilution factor (final weight of prepared sample divided by initial weight of sample).

12.3 Bound glycerin in biodiesel blends is calculated as follows:

$$\textit{Bound Glycerin} = \textit{Total Glycerin}\ (\textit{from}\ 11.2) - \textit{Free Glycerin}\ (\textit{from}\ 11.1) \quad (7)$$

12.4 The results in mg/kg shall be converted to percent by mass by dividing by 10 000.

13. Report

13.1 Report the free glycerin content results to nearest 0.01 % by mass (100 mg⁄kg) for B100 and to the nearest 0.001 % by mass (10 mg⁄kg) for blends. Specify that these results were obtained using ASTM Test Method D7591.

13.2 Report the total glycerin content results to nearest 0.01 % by mass (100 mg⁄kg) for B100 and to the nearest 0.001 % by mass (10 mg⁄kg) for blends. Specify that these results were obtained using ASTM Test Method D7591.

14. Quality Control

14.1 Confirm the performance of the instrument or the test procedure by analyzing one or more quality check sample(s) after each calibration and on at least each day of use thereafter. For example, a good check sample could be a single representative glycerin standard (see X1.5) that is analyzed repetitively by procedures in 11.1.1 through 11.2.10. These results are plotted in control charts to check the system for statistical stability, as in X1.3.

14.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix Appendix X1 may be used as the QC/QA system.

15. Precision and Bias[4]

15.1 The precision of this test method is based on an interlaboratory study conducted in 2009. Eleven laboratories participated in this study. Each of the labs was asked to report replicate test results for eleven different diesel and biodiesel blends. Every "test result" reported represents a single determination or measurement. Practice E691 was followed for the design and analysis of the data; the details are given in Research Report RR:D02-1737.

15.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "r" value for that material; "r" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

Free Glycerin in Biodiesel and Biodiesel Blends

For B100	Repeatability = 0.19E-01 * X ^ 0.8 mass%
For B1 to B6 blends	Repeatability = 1.8960 * X ^ 1.5 mass%
For B7 to B10 blends	Repeatability = 4.289E-06 * X ^ -0.3 mass%
For B10 to B20 blends	Repeatability = 8.863E-02X mass%

Total Glycerin in Biodiesel and Biodiesel Blends

For B100	Repeatability = 0.117 * X ^ 1.4 mass%
For B1 to B6 blends	Repeatability = 5.079E-02X mass%
For B7 to B10 blends	Repeatability = 0.2798 * X ^ 1.5 mass%
For B10 to B20 blends	Repeatability = 1.243 * X ^ 1.3 mass%

15.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "R" value for that material; "R" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

Free Glycerin in Biodiesel and Biodiesel Blends

For B100	Reproducibility = 0.2537 * X ^ 0.8 mass%
For B1 to B6 blends	Reproducibility = 2.9337 * X ^ 1.5 mass%
For B7 to B10 blends	Reproducibility = 9.373E-06 * X ^ -0.3 mass%
For B10 to B20 blends	Reproducibility = 2.645E-02X mass%

Total Glycerin in Biodiesel and Biodiesel Blends

For B100	Reproducibility = 0.8274 * X ^ 1.4 mass%
For B1 to B6 blends	Reproducibility = 9.856E-02X mass%
For B7 to B10 blends	Reproducibility = 0.7850 * X ^ 1.5 mass%
For B10 to B20 blends	Reproducibility = 2.422 * X ^ 1.3 mass%

NOTE 6—Repeatability and reproducibility for petroleum diesel (used as blank) cannot be calculated as all the results are represented as less than detection limit (zeros).

NOTE 7—Higher than B20 blends is not tested at this time. It will be user's responsibility to establish appropriate reproducibility and repeatability statements.

15.1.3 Use Table 2 as reference for free glycerin range for blend. Use Table 3 as reference for total glycerin range for blend.

15.1.4 The terms *repeatability limit* and *reproducibility limit* are used as specified in Practice E177.

15.1.5 Any judgment in accordance with statements in 15.1.1 and 15.1.2 would have an approximate 95 % probability of being correct.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1737. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Total Glycerin Range for Blend—Reference Table

Example concentration, mass%	B100		B11 to B20		B7 to B10		B1 to B6	
	r	R	r	R	r	R	r	R
0.025	0.0031	0.0047	0.0007	0.0018	0.0011	0.0031	0.0013	0.0025
0.050	0.0062	0.0110	0.0015	0.0037	0.0031	0.0077	0.0025	0.0049
0.100	0.0123	0.0250	0.0029	0.0073	0.0088	0.0217	0.0051	0.0099
0.200	0.0242	0.0460	0.0058	0.0146	0.0232	0.0523	0.0102	0.0197
0.240	0.0289	0.0593	0.0070	0.0176	0.0305	0.0688	0.0122	0.0237

15.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

15.3 The precision statement was determined through statistical examination of 345 results, from eight laboratories, on a total of eleven different petroleum blends.

15.3.1 To judge the equivalency of two test results, it is recommended to choose the petroleum blend closest in characteristics to the test blend.

16. Keywords

16.1 biodiesel blends; free glycerin; glycerin; ion chromatography; total glycerin

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method should determine the average value and control limits of the QC sample (see Practice D6299, Practice D6792, and MNL 7[5]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D6299, Practice D6792, and MNL 7[5]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and homogeneous and stable under the anticipated storage conditions. See Practice D6299, Practice D6792, and MNL 7[5] for further guidance on QC and control charting techniques.

[5] MNL 7, *Manual on Presentation of Data and Control Chart Analysis*, ASTM International, W. Conshohocken.