



Standard Test Method for Oxidation Stability of Biodiesel (B100) and Blends of Biodiesel with Middle Distillate Petroleum Fuel (Accelerated Method)¹

This standard is issued under the fixed designation D7462; 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 a measurement of the oxidation stability of biodiesel (B100) and blends of biodiesel with middle distillate petroleum fuels under specified oxidizing conditions at 95°C. Specifically, the oxidation stability is assessed by the formation and measurement of insoluble degradation materials.

NOTE 1—Biodiesel B100, composed of alkyl esters, can have good solubility for some products of oxidative degradation. Thus some B100 samples could undergo significant degradation, but show little or no sediment formation. By contrast, many petroleum diesel fuels have relatively poor solubility for products of oxidative degradation, so Bxx blends, such as B20, could show higher sediment levels. Refer to [Appendix X1](#) for a suggested paraffinic dilution procedure to evaluate oxidative degradation of B100 for degradation materials that are soluble in B100, but insoluble in iso-octane.

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.*

2. Referenced Documents

2.1 ASTM Standards:²

[D381 Test Method for Gum Content in Fuels by Jet Evaporation](#)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability and Cleanliness of Liquid Fuels.

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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.

[D943 Test Method for Oxidation Characteristics of Inhibited Mineral Oils](#)

[D1193 Specification for Reagent Water](#)

[D2274 Test Method for Oxidation Stability of Distillate Fuel Oil \(Accelerated Method\)](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D4625 Test Method for Middle Distillate Fuel Storage Stability at 43°C \(110°F\)](#)

3. Terminology

3.1 Definitions:

3.1.1 *adherent insolubles (formerly adherent gum), n*—material that is produced in the course of stressing distillate fuel under the conditions of this test and which adheres to the glassware after fuel has been flushed from the system.

3.1.2 *filterable insolubles, n*—material that is produced in the course of stressing the sample fuel under the conditions of this test and can be removed from the fuel by filtration. This includes both material suspended in the fuel and material easily removed from the oxidation cell and oxygen delivery tube with hydrocarbon solvent.

3.1.3 *total insolubles, n*—sum of the adherent and filterable insolubles.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *zero time, n*—time the first of a batch of oxidation cells is placed in the heating bath.

3.2.1.1 *Discussion*—This is the time taken as the start of the 16 h of residence in the heating bath.

4. Summary of Test Method

4.1 A 350-mL volume of filtered sample is aged at 95°C for 16 h while oxygen is bubbled through the sample at a rate of 3 L/h. After aging, the sample is cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity. The interior of the oxidation cell is also washed with

hydrocarbon solvent to remove any filterable insolubles and liquid that can be removed by the solvent. These washings are also filtered and included as filterable insolubles.

4.2 Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent. The trisolvent is evaporated to obtain the quantity of adherent insolubles.

4.3 The sum of the filterable and adherent insolubles, expressed as milligrams per 100 mL, is reported as total insolubles.

5. Significance and Use

5.1 This test method provides a measurement of the oxidation stability of biodiesel and biodiesel blends.

5.2 The test method may not provide a prediction of the quantity of insolubles that will form in field storage over any given period of time. The amount of insolubles formed in such field storage is subject to the specific storage conditions, which are too variable for this test method to predict accurately.

5.3 This test method yields results more rapidly than Test Method D4625, the 43°C bottle test. However, as a result of the significantly elevated temperature and the pure oxygen atmosphere, the nature and amount of insolubles may deviate to a greater extent than Test Method D4625 from those formed in field storage.

6. Interferences

6.1 Oxidation is a major chemical process causing adherent and filterable insolubles to form. Any substances, such as copper or chromium, that catalyze oxidation reactions will cause more rapid or greater quantities of insoluble material, or both, to form. Since the apparatus used in this test can also be used in Test Method D943, where coils of copper and steel are used, it is important that any residues that could contain these metals be eliminated from the apparatus by thorough cleaning prior to use. Similarly, to preclude the presence of chromium ions, as well as to protect laboratory personnel from potential harm, chromic acid shall not be used for cleaning glassware in the practice of this test method.

6.2 Ultraviolet light exposure has been found to increase the amount of total insolubles. Therefore, the fuel being tested shall be shielded from direct exposure to ultraviolet light (sunlight or fluorescent). Conduct all sampling, measuring, filtration, and weighing away from direct sunlight and in as dark an area as would be compatible with other laboratory operations. Storage before stress, the stress period and cool-down after stressing shall be in the dark.

7. Apparatus

7.1 *Oxidation Cell*, of borosilicate glass, as shown in Fig. 1, shall consist of a test tube, condenser, and oxygen delivery tube. This cell is identical to that used in Test Method D2274.

7.2 *Heating Bath/Block*, shall be capable of maintaining a uniform temperature at $95 \pm 1^\circ\text{C}$. It shall be large enough to hold the desired number of oxidation cells immersed to a depth of approximately 350 mm. Further, the construction must

permit shielding the fuel samples in the oxidation cells from light while they are undergoing oxidation.³

7.3 *Flow Meters*, shall have a capability of measuring 3 ± 0.3 L/h of oxygen. One flow meter shall be provided for each oxidation cell.

7.4 *Filter Drying Oven*, shall be capable of safely evaporating the solvent at $90 \pm 2^\circ\text{C}$ for the drying of filter materials.

7.5 *Glassware Drying Oven*, shall be capable of drying glassware at $105 \pm 5^\circ\text{C}$.

7.6 *Filter Assembly*, see Fig. 2, shall be capable of holding the filters described in 7.7.

7.7 *Filter Media*, 47-mm diameter glass fiber membrane filters with a nominal pore size of 0.7 μm .

7.8 *Evaporating Beaker*, borosilicate glass beaker, of 100 to 200-mL capacity.

7.9 *Hot Plate or Heating Block*, capable of heating a liquid in the evaporating vessel (7.8) to 135°C .

7.10 ALL equipment should be calibrated according to the manufacturer's instructions on a periodic basis to ensure consistency of results.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type III of Specification D1193.

8.3 *2,2,4-trimethylpentane (isooctane)*, 99.75 % purity pre-filtered through a filter medium of the type specified in 7.7.

8.4 *Oxygen*, 99.5 % purity or better. When the oxygen is delivered through a plant system of piping, a filter shall be provided adjacent to the constant temperature bath to prevent the introduction of line debris or moisture into the oxidation cells; a pressure regulator adequate to maintain a constant flow of gas through the apparatus shall also be used. A tank of oxygen of the specified purity can be used provided it is equipped with a two-stage pressure regulator.

8.5 *Trisolvent*, a mixture of equal volumes of acetone, methanol, and toluene. See 8.1. It has been found that commercial grades of acetone, if used in the trisolvent, can have impurities that cause an apparently greater level of adherent insolubles to be measured. It is particularly important that technical, commercial, practical, or industrial grades (however they are designated by the particular manufacturer)

³ This apparatus is available from suppliers of specialty petroleum testing equipment.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *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.

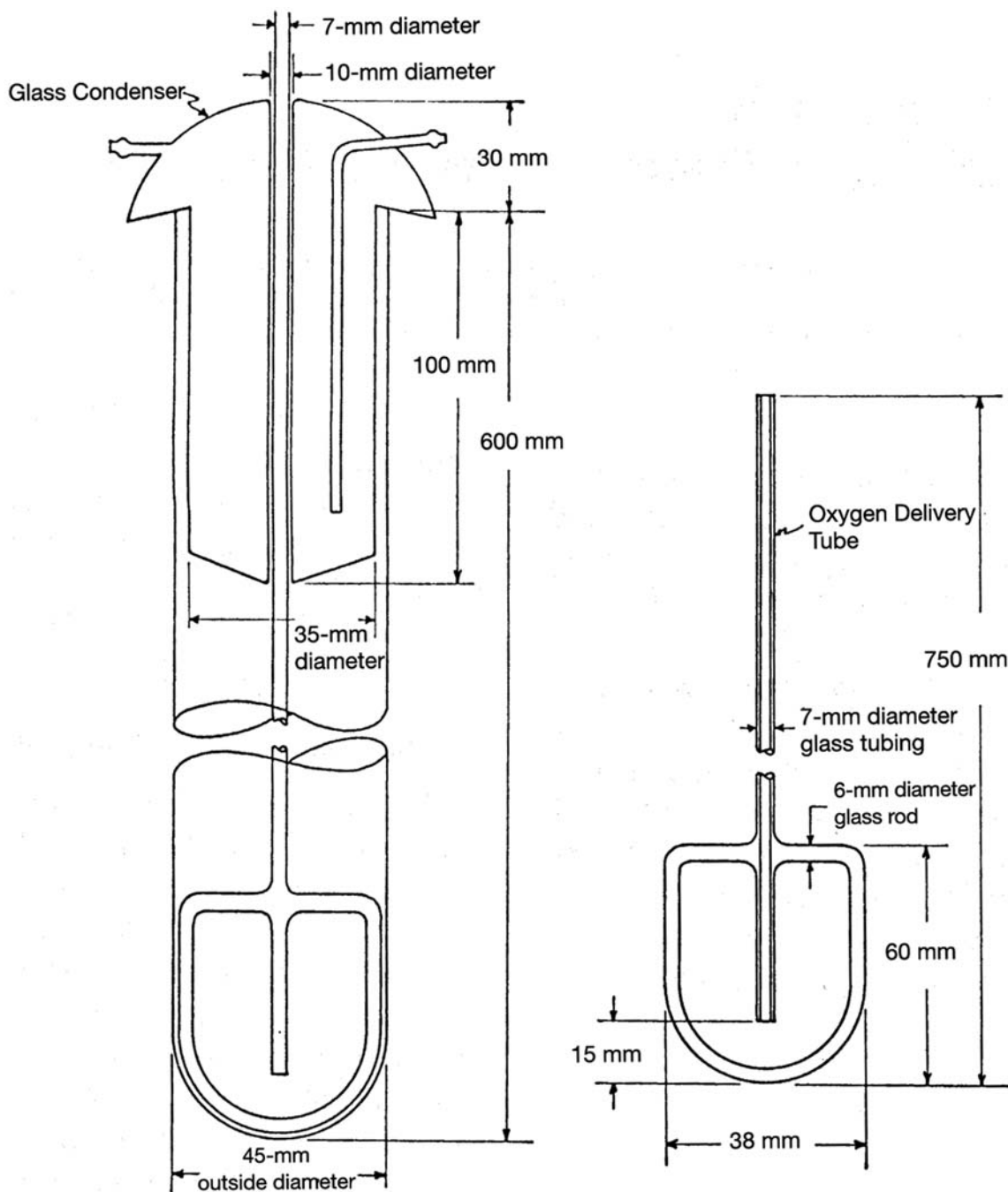


FIG. 1 Oxidation Cell

are not to be used, as their use may lead to apparently increased levels of adherent insolubles. (**Warning**—Fire hazard; toxic.)

9. Samples and Sampling

9.1 When obtaining samples for the laboratory, follow Practices D4057 or D4177, or other standard practice capable of providing representative samples.

9.2 Analyze fuel samples as soon as possible after receipt. When a fuel cannot be tested within one day, blanket it with an inert gas such as oxygen-free nitrogen, argon, or helium. It is preferable to store the sample at a temperature of 5 to 10°C.

9.3 *Test Samples*—Reduction of the laboratory sample to test sample size (about 400 mL for each determination) depends upon the size of sample received by the laboratory. If the laboratory sample is stored in a tank, drum, or 19-L or larger can, use the pertinent procedures of Practice D4057. Thoroughly mix smaller laboratory samples by shaking, rolling, or other techniques before taking an aliquot portion by pouring, pipetting, or other means. Clean any tube, thief, pipette, beaker, or other substance that is to contact the laboratory sample with trisolvant and dry it prior to use. Prior to mixing thoroughly and taking an aliquot, allow samples that

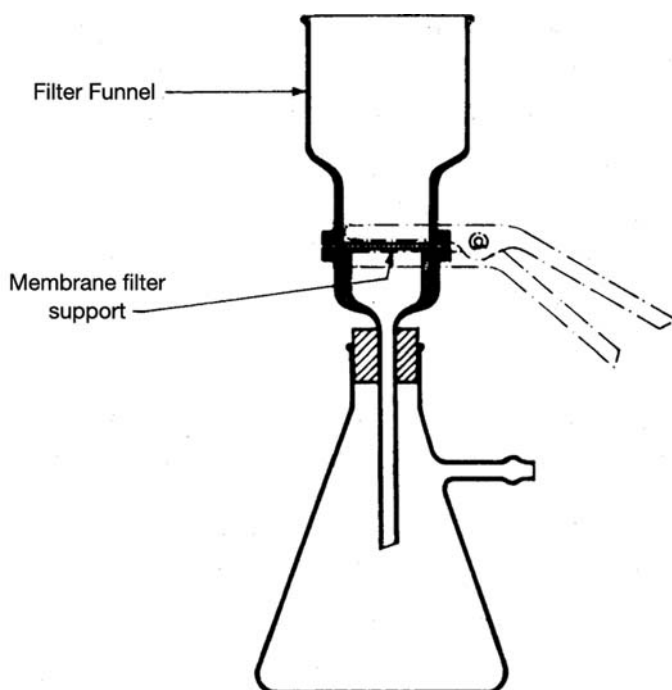


FIG. 2 Apparatus for Determining Filterable Insolubles

have been stored at reduced temperatures to warm to room temperature or heat above the cloud point for sampling.

10. Preparation of Apparatus

10.1 *Preparation of Glassware Other Than Oxidation Cells*—Rinse all glassware thoroughly with trisolvant followed by water, then wash with a mildly alkaline or neutral laboratory detergent. Rinse three times with deionized or distilled water. Dry the glassware in an oven or rinse it with acetone and air-dry it to remove water.

10.2 *Preparation of Oxidation Cells and Accessories*—After completion of 10.1, soak the oxidation cells and accessories in laboratory detergent in water. Allow the glassware to soak at least two hours. Wash, drain, and then rinse the glassware five times with tap water followed by three rinses with distilled or deionized water. Rinse with acetone; drain and allow the oxidation cell and oxygen delivery tube to dry.

10.3 *Preparation of Evaporating Beakers*—Dry the cleaned beakers (10.1) for 1 h in an oven at $105 \pm 5^\circ\text{C}$. Place the beakers near the balance being careful to prevent contamination of the beakers from airborne particles or other contaminants. Allow the beakers to cool for 1 h. Weigh beakers to the nearest 0.1 mg.

11. Procedure

11.1 *Preparing the Sample*—Place one filter (described in 7.7) on the filter support and clamp the filter funnel to the support as shown in Fig. 2. Apply suction (approximately 80 kPa). Pour 400 mL of the fuel through the filter (see 7.7) into a clean (10.1) 500-mL glass suction flask. Repeat preparation for each sample to be run. After filtration is complete, discard the filter media. Never use the same filters for a second increment of fuel, because any material deposited on the filters

by a previous increment of fuel can result in a greater removal of solids from the next increment.

11.2 Assembling the Oxidation Apparatus:

11.2.1 Place a clean oxygen delivery tube into a clean oxidation cell (Section 10) and pour 350 ± 5 mL of the filtered fuel into the cell. As soon thereafter as possible, but in no case greater than 1 h after measuring the sample, immerse the test cell in the 95°C heating bath. During any interim period store the cells in the dark. Keep the level of sample in the oxidation cell below the level of the liquid medium in the heating bath.

11.2.2 Place a condenser over the oxygen delivery tube and oxidation cell; connect the condenser to the cooling water. Connect the oxygen delivery tube to the oxygen supply through the flow meter and adjust the oxygen flow to 3 ± 0.3 L/h. Make sure samples are protected from light. When the number of test cells is less than the capacity of the heating bath, fill the empty positions with dummy oxidation cells containing 350 mL of a stable petroleum liquid with physical properties similar to those of the fuel being tested.

11.2.3 Record the time the first oxidation cell is placed in the bath as zero time.

11.3 Cool the Sample:

11.3.1 After 16 ± 0.25 h from zero time, remove the samples from the heating bath in the same sequence as they were placed therein. Cover the opening of each cell with a piece of aluminum foil or plastic to prevent entrance of dirt, dust, or moisture. Record the time the first cell is removed.

11.3.2 Place the oxidation cells in a dark, ventilated site at room temperature until the fuel attains room temperature but for no longer than 4 h.

11.4 Determining Filterable Insolubles:

11.4.1 For each sample to be filtered, use a single, pre-weighed, glass fiber filter. In addition, for each set of samples to be analyzed at one time, use a single glass fiber filter as a moisture blank or control.

NOTE 2—The stacked filter method used in test methods such as Test Method D2274 has been found to introduce errors when testing biodiesel.

11.4.2 Assemble the filter apparatus as illustrated in Fig. 2 using a single, pre-weighed, glass fiber filter. Apply vacuum and pour the cooled sample through the filter.

NOTE 3—If the filtration of the sample cannot be completed within 25 min as a result of severe filter plugging, filter the remaining fuel through a second, pre-weighed filter.

11.4.3 Remove the filtered sample from the filtration flask and retain it for additional analysis, if desired. Reassemble the filter apparatus to complete the rinsing procedures.

11.4.4 On completion of filtration, completely rinse the oxidation cell with three separate 50 ± 5 mL volumes of isooctane from a squeeze bottle or vessel capable of directing a fine stream of isooctane. *The necessity to thoroughly rinse the oxidation cells cannot be overemphasized. It is essential that all biodiesel residues be removed from the glass surfaces.* Pass all rinsings through the filter assembly.

11.4.5 After rinsing of the oxidation cell is complete, wash down the sides of the funnel with an additional 50 ± 5 mL of isooctane directed as a fine stream. The stream of isooctane

should be directed in a manner that, where possible, would push particles to the middle of the filter pad.

11.4.6 After filtration is complete, disconnect the top part of the filter assembly and wash down the rim of the filter media and adjacent parts of the filter assembly with a further 50 ± 5 mL of isooctane. Be certain the area of the filters previously under the filtration funnel is adequately rinsed to eliminate any presence of residual distillate fuel. *The necessity to thoroughly rinse the filter membrane cannot be overemphasized. It is essential that all biodiesel residues be removed from the filter.* Discontinue the vacuum and disconnect the filter assembly. Discard the solvent rinsings.

11.4.7 Dry the filters at 90°C for 30 min, cool them for 30 min, and weigh them to the nearest 0.1 mg.

11.5 Determining Adherent Insolubles:

11.5.1 After the final rinsing of the oxidation cell and the oxygen delivery tube with isooctane, dissolve adherent insolubles from the surfaces of these pieces using three equal rinses, totaling 75 ± 5 mL, of trisolvent.

11.5.2 Examine the oxidation cell and the oxygen delivery tube for evidence of stain or color indicating incomplete removal. If such stain or color is noted, rinse with a fourth 25-mL volume of trisolvent.

11.5.3 Evaporate the trisolvent from the rinsings in either of two ways:

11.5.3.1 For each sample, collect the trisolvent rinsings in a tared evaporating beaker. Place the beaker and contents in the heating block or on a hot plate and evaporate the trisolvent at 135°C under a hood. When all the solvent has evaporated, place the tared beaker in a desiccator without desiccant to cool for 1 h. When dry and cool, weigh the beaker to the nearest 0.1 mg.

11.5.3.2 Optionally, collect the rinsings in one or two 100-mL beakers of the type specified for Test Method **D381** and evaporate the trisolvent at 160°C by the Test Method **D381** air-jet method.

11.5.4 Run an adherent insolubles blank by evaporating a volume of trisolvent equal to that used in the test and correct for the presence of impurities in the solvent.

12. Calculation

12.1 Calculate the filterable insolubles mass (F) in milligrams per 100 mL. Subtract the tare mass of the blank (W_3) and sample (W_1) filters from their final masses (W_2), (W_4) respectively. Subtract the corrected mass of the blank from the corrected mass of the sample and divide by 3.5.

$$F = \frac{(W_2 - W_1) - (W_4 - W_3)}{3.5} \quad (1)$$

where:

W_1 = tare mass of the sample filter, mg,

W_2 = final mass of the sample filter, mg,

W_3 = tare mass of the blank filter, mg, and

W_4 = final mass of the blank filter, mg.

12.2 Calculate the adherent insolubles mass (A) in milligrams per 100 mL. Subtract the tare mass of the blank (W_7) and sample (W_5) beakers from their final masses (W_8), (W_6), respectively. Subtract the corrected mass of the blank from the corrected mass of the sample and divide by 3.5.

$$A = \frac{(W_6 - W_5) - (W_8 - W_7)}{3.5} \quad (2)$$

where:

W_5 = tare mass of the sample beaker, mg,

W_6 = final mass of the sample beaker, mg,

W_7 = tare mass of the blank beaker, mg, and

W_8 = final mass of the blank beaker, mg.

12.3 Calculate the total insolubles mass (T) in milligrams per 100 mL as the sum of the filterable insolubles (F) and the adherent insolubles (A).

$$T = F + A \quad (3)$$

T = total insolubles, mg/100 mL,

F = filterable insolubles, mg/100 mL, and

A = adherent insolubles, mg/100 mL.

13. Report

13.1 Report total insolubles in mg/100 mL, to the nearest 0.1 mg/100 mL.

13.2 A report of filterable insolubles (F), and the adherent insolubles (A) is optional. Report units in milligrams per 100 mL.

14. Precision and Bias

14.1 *Precision*—No interlaboratory study has yet been conducted for this test method. However, data from two laboratories have shown that the precision of this test method for measuring oxidation stability of biodiesel and biodiesel blends is essentially as given in Test Method **D2274**. It is planned to conduct an interlaboratory study before the five-year reapproval of this test method.

14.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for this test method no statement on bias is being made.

15. Keywords

15.1 adherent insolubles; biodiesel fuel; filterable insolubles; oxidation stability

APPENDIX
(Nonmandatory Information)
X1. ISOCTANE INSOLUBLES (OPTIONAL ADDITIONAL PROCEDURE FOR AGED SAMPLE)
X1.1 Introduction

X1.1.1 This optional, additional sample workup is a measure of the soluble polymers that precipitate when the aged B100 is mixed with a non-polar solvent, isooctane. This procedure is typically only performed on B100, not on biodiesel blends.

X1.2 Procedure

X1.2.1 Oven dry and weigh a pair of glass fiber filters (one sample and one blank) as in Section 11.

X1.2.2 Using a glass container of appropriate size, mix 100 mL of aged sample (see Section 11.4.3) with 400 mL of filtered isooctane. Shake the mixture for 10 s to thoroughly mix the sample and the solvent. Allow the mixture to stand for 10-15 min.

X1.2.3 Assemble the filtration apparatus using only the sample filter from X1.2.1.

X1.2.4 Apply the vacuum to the filtration apparatus and pour the sample/solvent mixture through the filter. Filter the entire mixture.

X1.2.5 Rinse the glass container and the filter funnel with sufficient filtered isooctane to remove all visible signs of B100 residue. This step may require several hundred milliliters of solvent; but, at a minimum, use three 25-mL portions of solvent to rinse the glass container. Use a wash bottle with

solvent to rinse the inside surfaces of the filter funnel. Pour all rinsings through the filter.

X1.2.6 Remove the filter funnel and carefully rinse any residue from the bottom of the funnel onto the filter. Then carefully rinse the filter thoroughly to remove the last traces of biodiesel.

X1.2.7 Turn off the vacuum and remove the sample filter.

X1.2.8 Dry the sample and blank filters in the oven, allow them to cool, and reweigh them as in Section 11.

X1.3 Calculation

X1.3.1 Calculate the isooctane insolubles (I) in milligrams per 100 mL. Subtract the tare mass of the blank (W_{11}) and sample (W_9) filters from their final masses (W_{10}), (W_{12}) respectively. Subtract the corrected mass of the blank from the corrected mass of the sample and divide by 3.5.

$$I = (W_{10} - W_9) - (W_{12} - W_{11}) \quad (X1.1)$$

W_9 = tare mass of the sample filter, mg,
 W_{10} = final mass of the sample filter, mg,
 W_{11} = tare mass of the blank filter, mg, and
 W_{12} = final mass of the blank filter, mg.

X1.4 Report

X1.4.1 Report the isooctane insolubles (I) in mg/100 mL.

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