



Designation: D5304 – 20

# Standard Test Method for Assessing Middle Distillate Fuel Storage Stability by Oxygen Overpressure<sup>1</sup>

This standard is issued under the fixed designation D5304; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

## 1. Scope\*

1.1 This test method covers a procedure for assessing the potential storage stability of middle distillate fuels such as Grade No. 1D and Grade No. 2D diesel fuels, in accordance with Specification D975.

1.2 This test method is applicable to either freshly refined fuels or fuels already in storage.

1.3 This test method is suitable for fuels containing stabilizer additives as well as fuels containing no such additives. However, fuels additized with dispersant additives, including dispersant-containing stability additives, may be ranked inaccurately using this test method compared to fuels that are not additized with dispersant additives.

1.4 Appendix X1 provides information on other suggested test times and temperatures for which this test method may be used.

1.5 The values stated in SI units are to be regarded as 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.* For specific warning statements, see 4.1, 6.2, 6.3, and 7.4.

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.*

<sup>1</sup> 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 D02.14 on Stability, Cleanliness and Compatibility of Liquid Fuels.

Current edition approved Sept. 1, 2020. Published September 2020. Originally approved in 1992. Last previous edition approved in 2015 as D5304 – 15. DOI: 10.1520/D5304-20.

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)

D975 Specification for Diesel Fuel

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

E1 Specification for ASTM Liquid-in-Glass Thermometers

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, see Terminology D4175.

3.1.2 *membrane filter, n*—a porous article of closely controlled pore size through which a liquid is passed to separate matter in suspension.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *oxygen overpressure, n*—partial pressures of oxygen higher than that of air at atmospheric pressure.

3.2.2 *potential storage stability, n*—the tendency of a fuel to form insolubles under the conditions of this test method.

3.2.3 *reactor, n*—any vessel capable of sustaining pressures and temperatures above ambient, sometimes designated pressure vessel.

3.2.4 *weighing assembly, n*—a set of two filters and two aluminum weighing dishes used to determine total insolubles for each sample or blank.

<sup>2</sup> 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

#### 4. Summary of Test Method

4.1 A 100 mL aliquot of filtered fuel is placed in a borosilicate glass container. The container is placed in a pressure vessel which has been preheated to 90 °C. The pressure vessel is pressurized with oxygen to 800 kPa (absolute) (100 psig) for the duration of the test. The pressure vessel is placed in a forced air oven at 90 °C for 16 h. (**Warning**—Observe all normal precautions while using oxygen under pressure and at high temperatures in the presence of combustible liquids. Appropriate shielding should be used for any containers under pressure. Pressurize and depressurize the containers *slowly* using appropriate personnel shielding. Never attempt to open the pressure vessel while it is pressurized. All fuel and solvent handling should be done in an appropriate fume hood only.) After aging and cooling, the total amount of fuel insoluble products is determined gravimetrically and corrected according to blank determinations.

#### 5. Significance and Use

5.1 The results of this test method are useful in ranking a specific fuel sample against other specific fuel samples or standards when tested under identical conditions. Specific fuel samples containing dispersant additives, such as dispersant-containing stability additives, have shown inaccurate ranking against fuel samples that do not contain dispersant additives using this test method.<sup>3</sup> This test method is not meant to relate a specific fuel to specific field handling and storage conditions. The formation of insolubles is affected by the material present in the storage container and by the ambient conditions. Since this test method is conducted in glass under standardized conditions, the results from different fuels can be compared on a common basis.

#### 6. Apparatus

6.1 *Sample or Blank Container*, a brown borosilicate glass bottle capable of holding 100 mL of sample but with total volume less than 200 mL, or a Test Method **D525** glass insert. A top closure of aluminum foil, perforated with small holes for breathing, will be required if there is more than one sample per pressure vessel.

6.2 *Pressure Vessel(s) (Reactor(s))*, designed for safe operating pressures of 800 kPa (100 psig) in oxygen service (**Warning**—See 4.1.) equipped with a pressure gauge. (**Warning**—The pressure for the procedure in this test method is 800 kPa (absolute) (100 psig). Many pressure gauges are calibrated in kPa (gauge). For such gauges, the test pressure would be 700 kPa (gauge). Maximum gauge gradations should be 20 kPa (5 psig)). The gauge should be calibrated against standards, and capable of holding the four sample containers. Pressure vessels having internal volumes from 250 mL to 8000 mL have been used and found to be suitable. If 250 mL vessels such as Test Method **D525** oxidation vessels are used, four will be required. The larger volume pressure vessels can

accommodate multiple sample or blank containers). The pressure vessel(s) (reactor(s)) must be obtained only from commercial sources.

6.3 *Heater*, capable of maintaining the test temperature at 90 °C ± 1 °C for the duration of the test. Ensure heater temperature uniformity. Heater shall be capable of holding the pressure vessel(s) (reactor(s)) described in 6.2. Static (non-forced air) ovens and unstirred liquid medium baths, such as the Test Method **D525** water bath, are unsuitable. Use of these heaters will give erroneous results due to nonuniformity of temperature.) The reactor should be placed in an oven so that the entire reactor is uniformly receiving heat. (**Warning**—Use of an explosion-proof oven is required.)

6.4 *Drying Oven*, forced air operated at 110 °C ± 5 °C. Static ovens or vacuum ovens are not suitable.

6.5 *Water Aspirator or Vacuum Pump*, as a source of vacuum.

6.6 *Aluminum Dish* (disposable), capable of holding 47 mm diameter filters and 30 mL of adherent insolubles solvent.

6.7 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

6.8 *Filtration System*—Arrange the following components as shown in Fig. 1.

6.8.1 *Funnel and Funnel Base*, with filter support for a 47 mm diameter membrane and a locking ring or spring action clip.

6.8.2 *Ground/Bond Wire*, 0.912 mm to 2.59 mm (No. 10 through No. 19) bare-stranded, flexible, stainless steel, or copper installed in the flasks and grounded as shown in Fig. 1.

6.8.3 *Receiving Flask*, 1.5 L or larger borosilicate glass vacuum filter flask, which the filtration apparatus fits into, equipped with a sidearm to connect to the safety flask.

6.8.4 *Safety Flask*, 1.5 L or larger borosilicate glass vacuum filter flask equipped with a sidearm to connect the vacuum system. A fuel and solvent resistant rubber hose through which the grounding wire passes shall connect the sidearm of the receiving flask to the tube passing through the rubber stopper in the top of the safety flask.

6.9 *Hot Plate*, capable of operating at low heat so that 10 mL of toluene placed in the aluminum dish described in 6.6 will require 10 min to 25 min to evaporate.

6.10 *Thermometer*, conforming to the requirements prescribed in Specification **E1**. Temperature measuring devices such as ASTM 61C (IP No. 63C), liquid-in-glass thermometers, thermocouples, or platinum resistance thermometers that provide equivalent or better accuracy and precision may be used.

6.11 *Forceps*, approximately 12 cm long, flat-bladed, with non-serrated, non-pointed tips.

#### 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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

<sup>3</sup> Williams, S., "Engineering Investigation of 2004/05 East Coast F-76 Rapid Fuel Degradation," NAVAIRSYSCOM REPORT 4451/06-006, August 14, 2006.

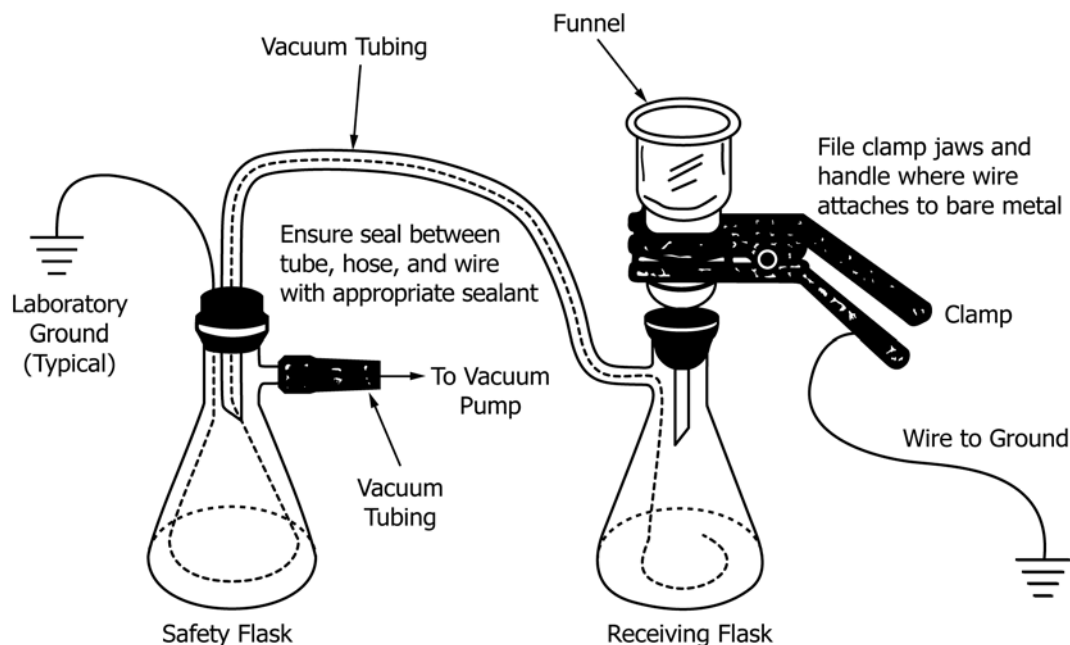


FIG. 1 Schematic of Filtration System

such specifications are available.<sup>4</sup> 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 or precision of the determination.

7.2 *Nylon Membrane Filters*, plain, 47 mm diameter, pore size 0.8  $\mu\text{m}$ .

7.3 *Hydrocarbon Solvent*—Hexanes, heptane, isooctane, or petroleum ether with residue upon evaporation of less than 0.001 % and boiling range between 35 °C and 100 °C are satisfactory. Filter before use with the filter specified in 7.2.

7.4 *Oxygen*—Use 99.5 % minimum oxygen from cylinders with two stage regulators capable of delivering up to 1600 kPa (200 psig). The secondary regulator should be calibrated against standards to deliver 800 kPa  $\pm$  10 kPa (100 psig  $\pm$  1 psig). (**Warning**—Oxygen at elevated temperature and pressure is capable of causing explosion or fire.)

7.5 *Adherent Insolubles Solvent (TAM)*—An equal volume mixture of toluene, acetone, and methanol (TAM). Filter before use with the filter specified in 7.2.

## 8. Sampling

8.1 *Field Sampling*—Field sampling should be in accordance with Practices D4057 or D4177. Bulk fuel to be sampled must be above its cloud point and thoroughly mixed prior to aliquot sampling. For field sampling and shipping, use only epoxy-lined steel cans that have been cleaned according to Practice D4306.

<sup>4</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar 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.

8.2 *Laboratory Subsampling*—Fuel to be sampled must be above its cloud point and thoroughly mixed prior to aliquot sampling. Use clean amber or clean borosilicate glass containers for laboratory handling. Fuel in clear bottles must be protected from light, for example, by wrapping in aluminum foil.

## 9. Preparation of Apparatus

9.1 Rinse the sample containers thoroughly with the TAM solvent followed by water. Then wash with a mildly alkaline or neutral pH laboratory detergent. Rinse with deionized or distilled water. Let bottles stand overnight with distilled water in them. Dry in a drying oven at 105 °C to 115 °C. Ensure the sample bottles are cleaned thoroughly. Leave no soap residue on the inside of the bottles (Note 1).

NOTE 1—Even a slight soap residue left on the walls of the bottle could alter sediment results.

9.2 Soak the aluminum weighing dishes in fresh, clean TAM solvent for several minutes followed by drying in a drying oven at 105 °C to 115 °C. Even new aluminum dishes must be cleaned with TAM solvent and dried before the initial weighing. Two hours after removal from the oven, firmly nest one dish inside of another for each sample replicate and for each blank replicate to be run. This is both the adherent insolubles evaporation assembly and, in combination with two unweighed nylon membrane filters, the weighing assembly for each test sample or blank.

9.3 Using forceps, place two dry filters in the aluminum weighing dish assembly from 9.2 and weigh the entire assembly of two filters and two aluminum dishes to the nearest 0.1 mg. A separate two filter plus two weighing dish assembly (the so-called weighing assembly) is required for each sample

and blank replicate. Weigh the filter and weighing dish assembly three times about one-half hour apart and take the average reading. This allows for changes in weight due to temperature and humidity.

9.4 Place the pressure vessel(s) specified in 6.2 in a heater specified in 6.3 to preheat to test temperature.

## 10. Procedure

10.1 Place two unweighed nylon membrane filters in a filter funnel. Prefilter, under vacuum (see 6.5), 220 mL of fuel to be tested. Transfer 100 mL of the filtered fuel to each of two glass sample containers (see 6.1). Place these sample containers plus two blank sample containers in the pre-heated pressure vessel(s) (see 9.4). If more than one fuel is to be tested simultaneously, additional glass sample containers are required. However, only a single pair of blank containers is required. Close the pressure vessel(s) after inspecting the vessel seals and replacing if necessary.

10.2 Set the oxygen cylinder secondary regulator to deliver 800 kPa (absolute) (100 psig). Connect the pressure vessel to an oxygen cylinder via the preset regulator and pressurize *slowly* to about 800 kPa (100 psig). (**Warning**—See 4.1.) Release the pressure *slowly*, repeat the pressurization and release the pressure *slowly*. The third and final time, pressurize to 800 kPa  $\pm$  10 kPa (100 psig  $\pm$  1 psig) as preset on the secondary regulator. (**Warning**—See 6.2.)

10.3 Close the pressure vessel isolation valve and maintain temperature at 90 °C  $\pm$  1 °C for 16 h  $\pm$  15 min using the thermometer specified in 6.10.

10.4 At the end of the aging period, measure and record the pressure. The test is invalid if the pressure has dropped more than 20 kPa (absolute) (2 psig) and must be repeated after replacing the pressure vessel seals. *Slowly* release the pressure to atmospheric, then open the reactor.

10.5 Remove the sample containers from the pressure vessel(s) and allow the containers to cool slowly to ambient (25 °C  $\pm$  5 °C) in the dark for a minimum of 1 h. Do not expose the samples to light prior to filtration.

10.6 Place the two filters from a preweighed weighing assembly from 9.3 in a filter assembly and apply suction. Completely filter the contents of a sample container. After the sample container is empty and the filter is dry, (1) relieve the vacuum, (2) thoroughly rinse the inside of the sample container with at least 25 mL of filtered hydrocarbon solvent (see 7.3), and pour into filter holder, and (3) pull solvent through filter with vacuum. Repeat steps (1) through (3). Wash down filter holder with filtered hydrocarbon solvent from a rinse bottle and pull through filter.

10.7 Wash down the inside of the funnel and the outside of the joint between the funnel and the filter base with filtered hydrocarbon solvent.

10.8 With the vacuum applied, carefully separate the funnel from the filter base. Wash the periphery of the membrane filter by directing a gentle stream of filtered hydrocarbon fluid from the edge to the center, exercising care not to wash any of the particulate from the surface of the membrane filter.

10.9 Maintain vacuum after the final washing for 10 s to 15 s to remove excess filtered hydrocarbon solvent from the membrane filter.

10.10 Carefully rinse the sample container with two consecutive 15 mL portions of TAM solvent. Be sure to contact the entire inner surface of the sample container with solvent. Pour both solvent rinses into the upper dish of the nested aluminum weighing dish assembly (see 9.2) from which the filters were taken in 10.6 (see 9.3).

10.11 Place the nested aluminum dishes on a hot plate and slowly evaporate the TAM just to dryness. Follow this same procedure with each of the blank correction containers.

10.12 Put the two test filters in the upper dish of the nested aluminum dish assembly from which they were taken in 10.6. Place these weighing assemblies in the drying oven at 105 °C to 115 °C for at least 30 min. Remove from the oven and allow approximately 1 h to cool to ambient temperature (25 °C  $\pm$  5 °C). Weigh each of the weighing assemblies to the nearest 0.1 mg.

## 11. Calculation

11.1 Calculate the total insolubles in mg/100 mL as follows:

$$TI = B - C - D \quad (1)$$

$$D = (E - F)/2 \quad (2)$$

where:

*TI* = total insolubles of an individual sample,

*B* = mass of an individual sample weighing assembly after filtering of aged sample, mg,

*C* = mass in mg of an individual sample weighing assembly before filtering of aged sample, mg,

*D* = blank correction for an individual sample. Blanks (*D*) can gain or lose weight. Remember to correct for either by ensuring the calculations reflect the sign ( $\pm$ ) correctly.

*E* = the sum of the two blank weighing assemblies after filtering, and

*F* = the sum of the two blank weighing assemblies before filtering.

NOTE 2—Blanks (*D*) can gain or lose weight. Remember to correct for either by ensuring the calculations reflect the sign ( $\pm$ ) correctly.

## 12. Report

12.1 Report the total insolubles to the nearest 0.1 mg/100 mL for each sample replicate.

## 13. Precision and Bias<sup>5</sup>

13.1 *Precision*—The precision of this test method, as determined by the statistical examination of interlaboratory test results, is as follows:

13.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1598.