



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

This standard is issued under the fixed designation D 5304; 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 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 D 975.

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.

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

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 4.1, 6.2, 6.3, 7.4, 10.1, and 10.2.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)<sup>2</sup>

D 975 Specification for Diesel Fuel Oils<sup>2</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination<sup>3</sup>

D 4625 Test Method for Distillate Fuel Storage Stability at 43°C (110°F)<sup>3</sup>

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

E 1 Specification for ASTM Thermometers<sup>4</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *membrane filter, n*—a thin medium of closely controlled pore size through which a liquid is passed and on which particulate matter in suspension is retained.

3.1.2 *oxygen overpressure*—partial pressures of oxygen higher than that of air at atmospheric pressure.

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

3.1.4 *reactor*—any vessel capable of sustaining pressures and temperatures above ambient, sometimes designated pressure vessel or bomb.

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

## 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

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.03.

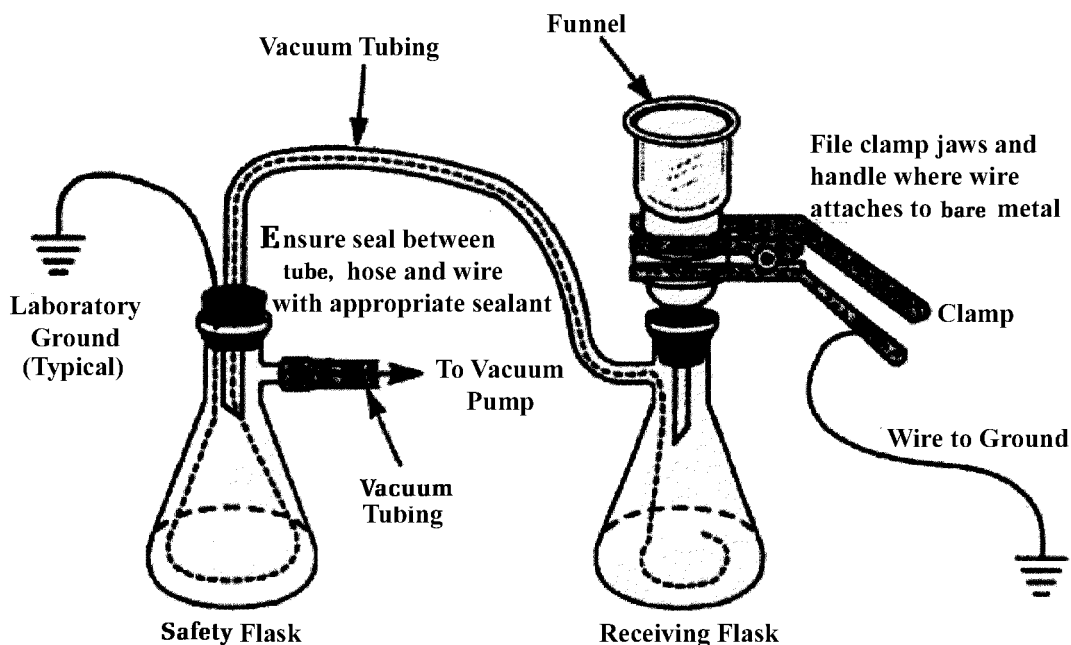


FIG. 1 Schematic of Filtration System

standards with or without stabilizer additives when tested under identical conditions. 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 D 525 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))*<sup>5</sup>, designed for safe operating pressures of 800 kPa (100 psig) in oxygen service (**Warning**—See 4.1), equipped with a pressure gage (**Warning**—The pressure for the procedure in this test method is 800 kPa (absolute) (100 psig). Many pressure gages are calibrated in kPa (gage). For such gages, the test pressure would be 700 kPa (gage). Maximum gage gradations should be 20 kPa (5 psig)). The gage should be calibrated against standards, and capable of holding the four sample containers (**Warning**—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 D 525 oxidation bombs

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  $90 \pm 1^\circ\text{C}$  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. (**Warning**—Static (non-forced air) ovens and unstirred liquid medium baths, such as the Test Method D 525 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  $110 \pm 5^\circ\text{C}$ . 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 – 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.

<sup>5</sup> Pressure vessels available from the following sources have been found to be satisfactory for use with this test method: Koehler Instrument Company, Inc., 1595 Sycamore Ave., Bohemia, NY 11716-1796; Parr Instrument Company, 211 53rd Street, Moline, IL 61265; and Stanhope-Seta Limited, Park Close, Englefield Green Egham, Surrey TW20 Oxd, England.

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 to 25 min to evaporate.

6.10 *Thermometer*, conforming to the requirements prescribed in Specification E 1. 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 such specifications are available.<sup>6</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 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 D 4057 or D 4177. 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 D 4306.

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 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 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). (**Warning**—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  $\pm$  10 kPa (100  $\pm$  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  $\pm$  1°C for 16 h  $\pm$  15 min using the thermometer specified in 6.10.

<sup>6</sup> *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.

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 ± 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 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 to 115°C for at least 4 h. Remove from the oven and allow approximately 1 h to cool to ambient temperature (25 ± 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:

$$TI = B - C - D \tag{1}$$

**TABLE 1 Precision Data for Various Levels of Stability**

Average Value mg/100 mL	Repeatability mg/100 mL	Reproducibility mg/100 mL
1.0	0.2	0.6
2.0	0.4	1.1
3.0	0.6	1.7
4.0	0.8	2.2
5.0	1.1	2.8
6.0	1.3	3.4
7.0	1.5	3.9

$$D = (E - F) / 2 \tag{2}$$

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 (±) 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 (±) 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>7</sup>**

13.1 *Precision*—The precision of this test method (see Table 1) 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 would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$\text{Repeatability} = 0.21 x \tag{3}$$

where:

x = the average of two results in mg/100 mL.

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

$$\text{Reproducibility} = 0.56 x \tag{4}$$

where:

x = the average of two results in mg/100 mL.

NOTE 3—The interlaboratory testing involved 18 sets of data and 6 samples. Intercomparison data using Test Method D 4625 for all six fuels was generated at two of the laboratories. The precision statement is applicable for all conditions and apparatus in this test method except Appendix X1.

13.2 *Bias*—The nature of this test and the parameters being measured are such that a true bias statement cannot be written.

**14. Keywords**

14.1 distillate fuels; fuel insolubles; oxidative stability; oxygen overpressure; stability; storage stability

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1297.



**APPENDIX**
**(Nonmandatory Information)**
**X1. SUGGESTED EXPERIMENTAL CONDITIONS FOR USE OF THIS STORAGE STABILITY TEST FOR RESEARCH PURPOSES**
**X1.1 Scope**

X1.1.1 This appendix provides information on conditions of pressure, temperature, and test duration under which approximately the same amount of insolubles will be formed.

X1.1.2 This appendix relates levels of insolubles formed under the oxygen overpressure conditions of one month of storage at 40°C under 800 kPa (absolute) (100 psig) of oxygen pressure to equivalent times of storage at 20°C and at 40°C under atmospheric (101 kPa absolute) (14.7 psi absolute) air pressure.

X1.1.3 Table X1.1 of this appendix suggests temperatures and test durations under 800 kPa (absolute) (100 psig) of oxygen pressure that yield approximately the same amounts of insolubles as would be obtained after bottle storage for 40 months at 20°C under atmospheric air pressure.

**X1.2 Equivalent Test Conditions**

X1.2.1 At 40°C, the use of oxygen at 800 kPa (absolute) (100 psig) in place of an air atmosphere at atmospheric

**TABLE X1.1 Combinations of Temperature and Test Duration Under 800 kPa (Absolute) (100 psig) Oxygen That Yield Approximately the Same Amount of Insolubles as 20°C Storage for 40 Months Under Atmospheric Air Pressure**

Temperature, °C	Test Duration
40	32 days
60	8 days
80	48 h
90	24 h
100	16 h

pressure (101 kPa absolute) (14.7 psi absolute) increases insoluble formation about tenfold with most middle distillate fuels. Because a one month storage under atmospheric air at 40°C yields approximately the same amount of insolubles as four months of atmospheric air storage at 20°C, a one month storage at 40°C under 800 kPa (absolute) (100 psig) oxygen pressure is found to yield approximately the same amount of insolubles as 40 months of storage at 20°C under atmospheric air pressure.

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