



Standard Test Method for Water Tolerance (Phase Separation) of Gasoline-Alcohol Blends¹

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1. Scope

1.1 This test method covers the ability of gasoline-alcohol blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be stored or exposed in use.

1.2 This test method is intended to measure the temperature at which a gasoline-alcohol blend separates into two distinct phases in accordance with the criteria defined in this test method. Samples that form a haze are considered not to have phase separated.

1.3 This test method is applicable to gasoline-alcohol blends for use as fuels in spark-ignition engines that contain saturated C₁ to C₄ alcohols only. The test method does not apply to fuels that contain an alcohol as the primary component, such as M85 or Ed85, or to gasoline-ether blends.

1.4 The values stated in SI units are the standard, except when other units are specified by federal regulation. Values given in parenthesis are provided for informational purposes.

1.5 This standard may involve hazardous materials, operations, and equipment. *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 the 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:

- D 2500 Test Method for Cloud Point of Petroleum Products²
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³
- D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination³
- D 4814 Specification for Automotive Spark-Ignition Engine Fuel⁴
- D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurement⁴

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A on Gasoline and Oxygenated Fuels.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 05.03.

E 1 Specification for ASTM Thermometers⁵

3. Terminology

3.1 Definitions:

3.1.1 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

3.1.2 *gasoline-alcohol blend, n*—a fuel consisting primarily of gasoline, along with a substantial amount (more than 0.35 mass % oxygen or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more alcohols.

3.1.3 *phase separation, n*—the formation of two layers, a lower aqueous constituent and an upper hydrocarbon constituent, separated by either a common boundary or a layer of emulsion.

3.1.3.1 *Discussion*—Test specimens having droplets clinging to the sides of the container or collected on its bottom, that are visible to the unaided eye, are considered to be phase separated.

4. Summary of Test Method

4.1 The sample of fuel is cooled at a controlled rate to its lowest expected storage or use temperature and is periodically observed for phase separation. The apparatus of Test Method D 2500 or a dry ice-isopropyl alcohol bath may be used. A maximum cooling rate of 2°C (4°F)/min is specified because phase separation in gasoline-alcohol blends can have a relatively long but unpredictable induction period.

5. Significance and Use

5.1 Gasoline-alcohol blends have a very limited ability to retain water in solution or in a stable suspension, and if the amount of water in the blend exceeds this limit, the fuel will separate into a lower aqueous phase and an upper hydrocarbon phase. The most important factor governing the ability of a specific fuel to retain water without such separation is its temperature. This test method is intended to determine the maximum temperature at which the fuel will separate. The 10th percentile 6-h minimum temperatures or 10°C (50°F), whichever is lower, for the time of year and geographic area of the United States in which the fuel may be stored or used are

⁵ *Annual Book of ASTM Standards*, Vol 14.03.

tabulated in Table 13 of Specification D 4814. The temperatures represent the maximum temperatures above which the fuel must not separate into two distinct phases.

5.2 Since the aqueous phase can be highly corrosive to many metals and the spark-ignition engine cannot operate on such a fuel that has phase separated, such separation is very undesirable.

5.3 Blends containing low-molecular weight alcohols are generally hygroscopic and can eventually absorb enough moisture from ambient air to cause separation. The problem of phase separation can usually be avoided if the fuels are sufficiently water-free initially and care is taken during distribution to prevent contact with water. To help ensure this, gasoline-alcohol blends shall be tested to the lowest temperatures that they expect to encounter, dependent on the time and geographic location of intended use, as tabulated in Table 13 of Specification D 4814.

6. Apparatus (see Fig. 1)

6.1 *Test Container*—The test container must be made of clear, cylindrical glass, with a flat bottom, that has a 33.2 to 34.8-mm outside diameter, a 30 to 32.4-mm inside diameter, a wall thickness no greater than 1.6 mm, and a height between 115 to 125 mm. The jar shall be marked with a line to indicate the test specimen height 54 ± 3 mm above the inside bottom. The specification conforms to the test jar identified in Test Method D 2500.

6.2 *Thermometer*—ASTM thermometer 6C (range -80 to $+20^{\circ}\text{C}$, with 1°C graduations, 76-mm immersion) meeting the requirements in Specification E 1. A thermometer mounted to pass through the stopper must be provided for each test container.

6.3 *Viton Rubber Stopper*—A stopper of appropriate dimensions to snugly fit the test container, bored centrally for the test thermometer. Other suitable types of rubber stoppers may be substituted for the Viton rubber stoppers.

6.4 *Jacket*, made of metal or glass, watertight, cylindrical, flat bottom, about 115 mm in depth, with an inside diameter of 44.2 to 45.8 mm. It must be supported free of excessive

vibration and supported firmly in a vertical position in the cooling bath specified in 6.7 so that no more than 25 mm projects out of the cooling medium.

6.5 *Disk*, made of cork or felt, 6 mm in thickness, to fit loosely on the inside bottom of the jacket.

6.6 *Gasket*—A ring form, about 5 mm in thickness, to fit snugly around the test container and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test container and hard enough to hold its shape. Its purpose is to prevent the test container from touching the jacket.

6.7 *Cooling Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertically, capable of reducing the test specimen temperature to -42°C (-44°F) for the test analysis, similar to that specified in 6.7 of Test Method D 2500. The required bath temperatures may be maintained by refrigeration, if available, otherwise by suitable freezing mixtures, such as a dry ice-isopropyl alcohol bath.

6.8 *Pipettes* (optional), disposable or volumetric, for rinsing and transferring test specimens into the test container.

7. Reagents and Materials

7.1 *Acetone*—Technical grade acetone is suitable for use in the cooling baths, provided it does not leave a residue on drying.

NOTE 1—**Warning:** Extremely flammable.

7.2 *Carbon Dioxide (Solid) or Dry Ice*—A commercial grade of dry ice is suitable for use in the cooling baths.

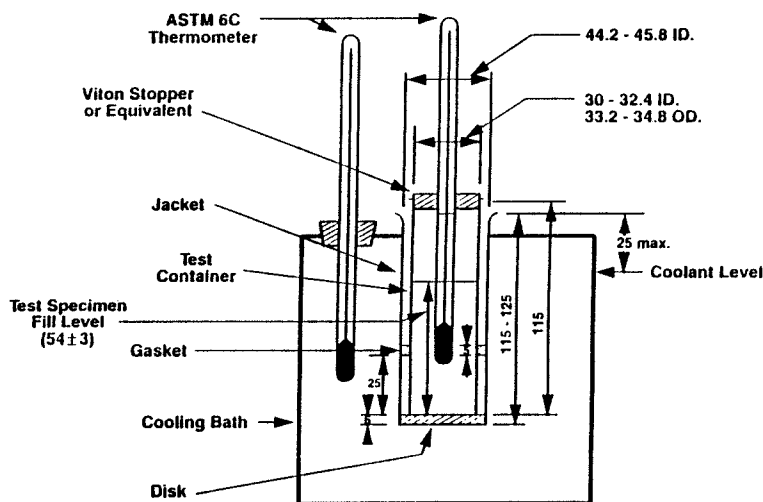
NOTE 2—**Warning:** Extremely cold (-78.5°C). Avoid direct contact with the skin.

7.3 *Isopropyl Alcohol (2-propanol)*—A commercial grade of dry isopropyl alcohol is suitable for use in the cooling baths.

NOTE 3—**Warning:** Flammable.

7.4 *Methyl Alcohol*—A commercial or technical grade of dry methyl alcohol is suitable for use in the cooling baths.

NOTE 4—**Warning:** Flammable. Vapor harmful. Toxic.



NOTE 1—Dimensions are in millimetres (not to scale).

FIG. 1 Position of Thermometer in Fuel Sample

8. Sampling and Handling

8.1 Draw samples in accordance with the instructions in Practice D 4057. Draw samples into 1 L (1 qt) clear glass containers. Fill container 70 to 80 % with sample to allow the user of the test method an opportunity to visually inspect the sample for cleanliness, free water, or impurities before proceeding with the test. In the event a sample is to be taken from a retail type dispenser prior to analysis, use the nozzle sampling procedure described in Practice D 5842 in place of the instructions in Practice D 4057.

NOTE 5—Paragraph 6.4.2 of Practice D 4306 does not recommend the use of borosilicate glass bottles for water separation testing of aviation fuels, but rather recommends the use of epoxy-lined cans. Gasoline-alcohol sample matrices are quite different than aviation fuels and therefore Practice D 4306 is not applicable or appropriate. The use of clear glass containers does not compromise the sample integrity of gasoline-alcohol blend samples for analyses and allows visual inspection of samples that would not be possible if epoxy-lined cans were used.

8.2 Samples shall not be chilled during storage so as to prevent possible phase separation prior to testing, that may be irreversible upon warming. Store samples at ambient temperature.

8.3 Because gasoline-alcohol blends are hygroscopic, as well as volatile, minimize contact with the atmosphere by keeping the sample containers tightly closed except when transferring the sample.

9. Procedure

9.1 Shake the sample to redissolve any water that may have settled out during storage.

9.2 Carry out steps 9.3-9.5 as promptly as possible to minimize vaporization losses and absorption of water from the atmosphere.

9.3 Rinse out the test container with a portion of the sample to be tested by either pouring a small portion directly from the sample container or by using a 5-mL pipette. If using the 5-mL pipette, draw the specimen from approximately the center of the sample container to minimize the chance of atmospheric moisture coming in contact with the specimen taken. Drain the specimen used to rinse the test container.

9.4 Using a pipette, draw a sufficient quantity of test specimen from approximately the center of the sample container and dispense a volume into the rinsed test container so that the bottom of the test specimen meniscus is at the marked line. Alternatively, pour a test specimen directly from the sample container so that the bottom of the test specimen meniscus is at the line. If the test specimen has phase separated, as defined in 3.1.3 or 3.1.3.1, terminate the test and obtain a new sample for analysis.

9.5 Insert a thermometer through a centrally bored Viton rubber, or equivalent material stopper, as specified in 6.3. Seal the test container that holds the test specimen by snugly fitting the stopper into the test container opening. Position the thermometer at approximately the center of the fuel sample (see Fig. 1).

NOTE 6—**Caution:** Avoid forcing the thermometer through the stopper to minimize the potential for injury.

9.6 Place a gasket around the test container, approximately

25 mm from the bottom, and place a disk on the bottom of the jacket in the cooling bath. Place the disk and jacket into the cooling medium a minimum of 10 min before the test container is inserted.

9.7 Depending upon the time of year and geographic location at which the fuel may be used, set-up the appropriate number of cooling baths with the temperatures kept between the ranges shown in Table 1.

9.8 Insert the test container in the jacket of Bath 1. The sample is not to be swirled or shaken while in the jacket. Take the first temperature reading at 14°C (57°F).

9.9 At 2°C (4°F) intervals, remove the test container from the jacket in the cooling bath and shake vigorously for 5 to 10 s. Wipe the exterior of the test container with a towel moistened with isopropyl alcohol to remove any condensation, and observe the condition of the test specimen for no more than 5 s against a light colored, illuminated background. Monitor the cooling rate while in the jacket, so as to not exceed 2°C (4°F)/min.

NOTE 7—It is likely that the test specimen will get hazy prior to actual phase separation. Although the observation of a hazy test specimen is not a criterion for failure, the temperature at which the haze forms may be of importance to the user of the test method.

9.10 If the test specimen has not phase separated and has not reached the test temperature identified in Table 13 of Specification D 4814, return the test container to the jacket. If the test specimen has phase separated, record the temperature and go to 9.17. If the test specimen has not phase separated and has reached the maximum test temperature above which the fuel must not phase separate, in accordance with Table 13 of Specification D 4814, for the time of year and location for intended use, go to 10.1. If the user of the test method is interested in determining the actual phase separation temperature of the test specimen, even though it meets the seasonal and geographical requirement of Table 13 in Specification D 4814, the option exists for continuing the test.

9.11 When the test specimen temperature reaches + 10°C (50°F) and has not phase separated or reached its intended test temperature, transfer the test container to Bath 2, maintained at a temperature between - 18 and -15°C (0 and 5°F).

9.12 Repeat steps 9.9 and 9.10 for the test specimen in Bath 2 until the test specimen reaches a temperature of -8°C (18°F).

9.13 When the test specimen temperature reaches -8°C (18°F) and has not phase separated or reached its intended test temperature, transfer the test container to Bath 3, maintained at a temperature between - 35 and -32°C (-31 and -26°F).

9.14 Repeat steps 9.9 and 9.10 for the test specimen in Bath 3 until the test specimen reaches a temperature of -24°C (-11°F).

9.15 When the test specimen temperature reaches -24°C (-11°F) and has not phase separated or reached its intended test

TABLE 1 Bath and Test Specimen Temperature Ranges

| Bath | Bath Temperature Setting, °C (°F) | | Test Specimen Temperature Range, °C (°F) | |
|------|-----------------------------------|--------------|--|--------------|
| 1 | -1 to +2 | (30 to 36) | >10 | (>50) |
| 2 | -18 to -15 | (0 to 5) | +10 to -8 | (14 to 18) |
| 3 | -35 to -32 | (-31 to -26) | -8 to -24 | (18 to -11) |
| 4 | -52 to -49 | (-62 to -56) | -24 to -42 | (-11 to -44) |

temperature, transfer the test container to Bath 4, maintained at a temperature between -52 and -49°C (-62 and -56°F).

9.16 Repeat steps 9.9 and 9.10 for the test specimen in Bath 4 until the test specimen reaches a temperature of -42°C (-44°F).

9.17 Allow the test specimen to warm at ambient temperature. Shake the sample vigorously after each temperature rise of 2°C (4°F), and observe. Record a *warming* phase recombination temperature. Average the temperature results obtained upon *cooling* and *warming* to determine the phase separation temperature.

10. Report

10.1 Report the averaged phase separation temperature determined in 9.17 or a *Pass* from 9.10.

10.2 A *Pass* result indicates that the test specimen did not phase separate upon cooling to the temperature specified in Table 13 of Specification D 4814 for the given time of year and geographic location for the intended use or storage of the fuel.

11. Precision and Bias

11.1 The precision and bias of this test method will be determined in an interlaboratory study within five years of adopting this test method.

12. Keywords

12.1 alcohols; automotive spark-ignition engine fuel; ethanol; gasoline-alcohol blends; methanol; phase separation; propanol; water tolerance

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