



Designation: ~~D6378~~—~~10~~ **D6378 – 10** (Reapproved 2016)

Standard Test Method for Determination of Vapor Pressure (VP_x) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)¹

This standard is issued under the fixed designation D6378; 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^{*}Scope

1.1 This test method covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in vacuum by volatile, liquid petroleum products, hydrocarbons, and hydrocarbon-oxygenate mixtures. This test method is suitable for testing samples with boiling points above 0°C (32°F) 0°C (32°F) that exert a vapor pressure between ~~7 and 150 kPa (1.0 and 21 psi)~~ at 37.8°C (100°F) 7 kPa and 150 kPa (1.0 psi and 21 psi) at 37.8°C (100°F) at a vapor-to-liquid ratio of 4:1. The liquid sample volume size required for analysis is dependent upon the vapor-to-liquid ratio chosen (see **Note 1**) and the measuring chamber volume capacity of the instrument (see **6.1.1** and **Note 3**).

NOTE 1—The test method is suitable for the determination of the vapor pressure of volatile, liquid petroleum products at temperatures from 0°C to 100°C at vapor to liquid ratios of 4:1 to 1:1 ($X = 4$ to 1) and pressures up to ~~500 kPa (70 psi)~~, 500 kPa (70 psi), but the precision statement (see Section 16) may not be applicable.

1.2 This test method also covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in vacuum by aviation turbine fuels. This test method is suitable for testing aviation turbine fuel samples with boiling points above 0°C (32°F) 0°C (32°F) that exert a vapor pressure between ~~0 and 110 kPa (0 and 15.5 psi)~~ 0 kPa and 110 kPa (0 psi and 15.5 psi) at a vapor-to-liquid ratio of 4:1, in the temperature range from ~~25 to 100~~ 25°C to 100°C (77°F to 212°F); 25°C to 100°C (77°F to 212°F).

1.3 The vapor pressure (VP_x) determined by this test method at a vapor-liquid ratio of 4:1 ($X = 4$) of gasoline and gasoline-oxygenate blends at 37.8°C can be correlated to the dry vapor pressure equivalent (DVPE) value determined by Test Method **D5191** (see **16.3**). This condition does not apply when the sample is aviation turbine fuel.

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

1.5 *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 **7.2 – 7.8**.

2. Referenced Documents

2.1 ASTM Standards:²

- [D323 Test Method for Vapor Pressure of Petroleum Products \(Reid Method\)](#)
- [D2892 Test Method for Distillation of Crude Petroleum \(15-Theoretical Plate Column\)](#)
- [D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)
- [D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)
- [D4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends \(Dry Method\)](#)
- [D5191 Test Method for Vapor Pressure of Petroleum Products \(Mini Method\)](#)
- [D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement](#)
- [D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products](#)
- [D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)

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 **D02.08** on Volatility.

Current edition approved Oct. 1, 2010/Oct. 1, 2016. Published November 2010/November 2016. Originally approved in 1999. Last previous edition approved in 2008/2010 as ~~D6378~~D6378 – 10 – 08. DOI: ~~10.1520/D6378-10~~10.1520/D6378-10R16.

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.

***A Summary of Changes section appears at the end of this standard**

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *dry vapor pressure equivalent (DVPE)*—a value calculated by a correlation equation from the total pressure (Test Method **D5191**), which is equivalent to the value obtained on the sample by Test Method **D4953**, Procedure A.

3.1.2 *partial pressure from dissolved air (PPA), n*—the pressure exerted in vacuum from dissolved air that escapes from the liquid phase into the vapor phase.

3.1.3 *Reid vapor pressure equivalent (RVPE)*—a value calculated by a correlation equation from the TP_X , which is equivalent to the value obtained on the sample by Test Method **D323**.

3.1.4 *total pressure (TP_X), n*—the pressure exerted in vacuum by air- and gas-containing petroleum products, components and feedstocks, and other liquids, in the absence of undissolved water at a vapor-liquid ratio of X:1.

3.1.5 *vapor pressure (VP_X), n*—the total pressure minus the PPA in the liquid at a vapor-liquid ratio of X:1.

$$VP_X = TP_X - PPA \quad (1)$$

4. Summary of Test Method

4.1 Employing a measuring chamber with a built-in piston, a sample of known volume is drawn into the temperature controlled chamber at $20 \pm 20^\circ\text{C}$ or higher. After sealing the chamber, the temperature of the chamber is increased to a specified value simultaneously with the first expansion. Two further expansions are performed to a final volume of (X+1) times that of the test specimen. After each expansion, the TP_X is determined. The PPA and the solubility of air in the specimen are calculated from the three resulting pressures. The (VP_X) is calculated by subtracting the PPA in the liquid from TP_X .

NOTE 2—For liquids containing very low levels of high vapor pressure contaminants, which behave like a gas, this test method of determination of the PPA and gases may lead to wrong results since the partial pressure of the contaminants will be included in the PPA. This effect is shown when the value of the PPA and gases exceeds the average maximum limit of 7 kPa (1 psi) (1 psi).

5. Significance and Use

5.1 Vapor pressure is a very important physical property of volatile liquids for shipping and storage.

5.2 The vapor pressure of gasoline and gasoline-oxygenate blends is regulated by various government agencies.

5.3 Specifications for volatile petroleum products generally include vapor pressure limits to ensure products of suitable volatility performance.

5.4 In this test method, an air saturation procedure prior to the measurement is not required, thus eliminating losses of high volatile compounds during this step. This test method is faster and minimizes potential errors from improper air saturation. This test method permits VP_X determinations in the field.

5.5 This test method can be applied in online applications in which an air saturation procedure prior to the measurement cannot be performed.

6. Apparatus

6.1 The apparatus suitable for this test method employs a small volume, cylindrically shaped measuring chamber with associated equipment to control the chamber temperature within the range from 0°C to $100 \pm 100^\circ\text{C}$. The measuring chamber shall contain a movable piston with a maximum dead volume of less than 1 % of the total volume at the lowest position to allow sample introduction into the measuring chamber and expansion to the desired vapor-liquid ratio. A static pressure transducer shall be incorporated in the piston. The measuring chamber shall contain an inlet/outlet valve combination for sample introduction and expulsion. The piston and the valve combination shall be at the same temperature as the measuring chamber to avoid any condensation or excessive evaporation.

6.1.1 The measuring chamber shall be designed to contain between ~~55 mL~~ and ~~15 mL~~ 15 mL of liquid and vapor and be capable of maintaining a vapor-liquid ratio of 4:1 to 1:1. The accuracy of the adjusted vapor-liquid ratio shall be within 0.05.

NOTE 3—The measuring chamber employed by the instruments used in generating the precision and bias statements were constructed of nickel plated aluminum and stainless steel with a total volume of ~~5 mL~~ 5 mL. Measuring chambers exceeding a ~~5 mL~~ 5 mL capacity can be used, but the precision and bias statements (see Section 16) are not known to apply.

6.1.2 The pressure transducer shall have a minimum operational range from ~~0 to 200 kPa (0 to 29 psi)~~ 0 kPa to 200 kPa (0 psi to 29 psi) with a minimum resolution of ~~0.1 kPa (0.01 psi)~~ 0.1 kPa (0.01 psi) and a minimum accuracy of ± 0.2 kPa (± 0.03 psi). The pressure measurement system shall include associated electronics and readout devices to display the resulting pressure reading.

TABLE 1 Accepted Reference Value (ARV) and Acceptable Testing Range for Reference Fluids (Note 16)

Reference Fluid	ARV [VP ₄ (37.8°C)] ± Uncertainty, (kPa)	Recommended Instrument Manufacturer Tolerance, (kPa)	Acceptable Testing Range for Reference Fuel [VP ₄ (37.8°C)], (kPa)
Pentane	107.9 ± 0.2	±1.0	107.9 ± 1.2 (106.7 to 109.1)
2,2 Dimethylbutane	68.8 ± 0.2	±1.0	68.8 ± 1.2 (67.6 to 70.0)
2,3 Dimethylbutane	51.7 ± 0.2	±1.0	51.7 ± 1.2 (50.5 to 52.9)

Reference Fluid	ARV [VP ₄ (37.8 °C)] ± Uncertainty, (psi)	Recommended Instrument Manufacturer Tolerance, (psi)	Acceptable Testing Range for Reference Fuel [VP ₄ (37.8°C)], (psi)
Pentane	15.65 ± 0.03	±0.14	15.65 ± 0.17 (15.48 to 15.82)
2,2 Dimethylbutane	9.98 ± 0.03	±0.14	9.98 ± 0.17 (9.81 to 10.15)
2,3 Dimethylbutane	7.50 ± 0.03	±0.14	7.50 ± 0.17 (7.33 to 7.67)

6.1.3 Electronic temperature control shall be used to maintain the measuring chamber at the prescribed temperature within $\pm 0.1^\circ\text{C} \pm 0.1^\circ\text{C}$ for the duration of the vapor pressure measurement.

6.1.4 A platinum resistance thermometer shall be used for measuring the temperature of the measuring chamber. The minimum temperature range of the measuring device shall be from 0°C to 100°C with a resolution of 0.1°C and an accuracy of $\pm 0.1^\circ\text{C} \pm 0.1^\circ\text{C}$.

6.1.5 The vapor pressure apparatus shall have provisions for rinsing the measuring chamber with a solvent of low vapor pressure or with the next sample to be tested.

6.2 *Vacuum Pump for Calibration*, *Calibration*, capable of reducing the pressure in the measuring chamber to less than 0.01 kPa (0.001 psi) absolute.

6.3 *McLeod Vacuum Gauge or Calibrated Electronic Vacuum Measuring Device for Calibration*, to cover at least the range from 0.01 to 0.67 kPa (0.1 to 5 mm Hg) (0.01 kPa to 0.67 kPa (0.1 mm to 5 mm Hg)). The calibration of the electronic vacuum measuring device shall be regularly verified in accordance with Annex A6.3 on Vacuum Sensors in Test Method D2892.

6.4 *Pressure Measuring Device for Calibration*, capable of measuring local station pressure with an accuracy and a resolution of 0.1 kPa (1 mm Hg) (0.1 kPa (1 mm Hg)), or better, at the same elevation relative to sea level as the apparatus in the laboratory.

NOTE 4—This test method does not give full details of instruments suitable for carrying out this test. Details on the installation, operation, and maintenance of each instrument may be found in the manufacturer's manual.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use chemicals of at least 99 % purity for verification of instrument performance (see Section 11). Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society³ where such specifications are available. Lower purities can be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

7.1.1 The chemicals in 7.3, 7.4, and 7.7 are suggested for verification of instrument performance (see Section 11), based on the reference fuels analyzed in the 2003 interlaboratory study (ILS) (see 16.1, Table 1, and Note 16). Such reference fuels are not to be used for instrument calibration. Table 1 identifies the accepted reference value (ARV) and uncertainty limits, as well as the acceptable testing range for each of the reference fuels listed.

NOTE 5—Verification fluids reported by 12 of the D6378 data set participants in the 2003 ILS (see 16.1) included the following (with number of data sets identified in parentheses): 2,2-dimethylbutane (11), and 2,3-dimethylbutane (1).

7.2 *Cyclopentane*, (**Warning**—Cyclopentane is flammable and a health hazard).

7.3 *2,2-Dimethylbutane*, (**Warning**—2,2-dimethylbutane is flammable and a health hazard).

7.4 *2,3-Dimethylbutane*, (**Warning**—2,3-dimethylbutane is flammable and a health hazard).

7.5 *Methanol*, (**Warning**—Methanol is flammable and a health hazard).

7.6 *2-Methylpentane*, (**Warning**—2-methylpentane is flammable and a health hazard).

7.7 *Pentane*, (**Warning**—Pentane is flammable and a health hazard).

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.

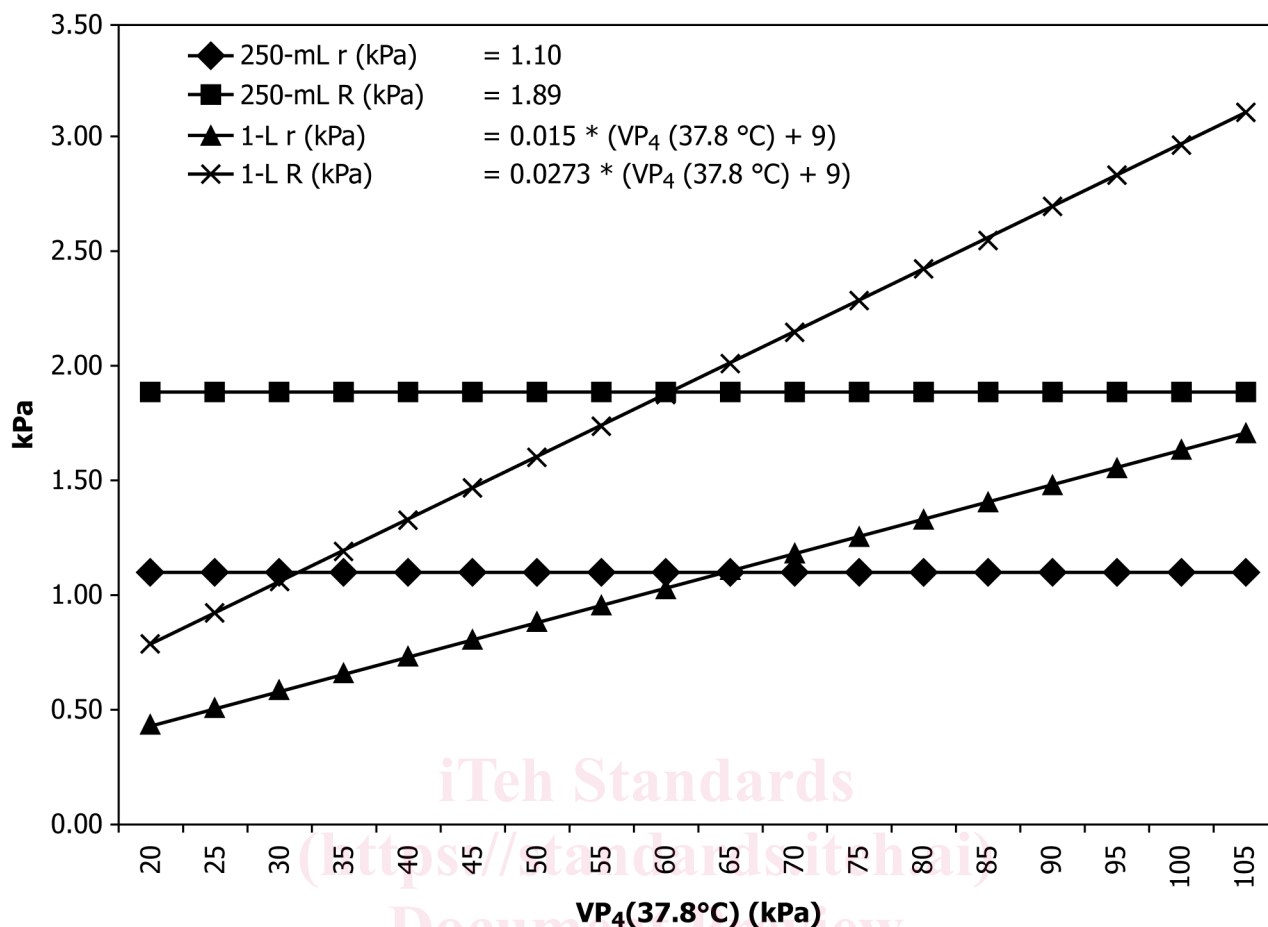


FIG. 1 Plot of VP₄(37.8°C) Precision (kPa) by Container Size at Nominal VP₄(37.8°C) (kPa) Values Determined

7.8 Toluene, (Warning—Toluene is flammable and a health hazard).

8. Sampling and Sample Introduction

8.1 General Requirements:

8.1.1 The extreme sensitivity of vapor pressure measurements to losses through evaporation and the resulting changes in composition is such as to require the utmost precaution and the most meticulous care in the drawing and handling of samples.

8.1.2 Obtain a sample and test specimen in accordance with Practice D4057, D4177, D5842, or D5854 when appropriate, except do not use the Sampling by Water Displacement section for fuels containing oxygenates. Use either a 250-mL (250 mL) or 1-L (1 qt) sized container filled between 70% and 80% with sample. See Note 6 on effect of sample size on testing precision.

8.1.2.1 When the sample is aviation turbine fuel, use of 100-mL (100 mL) size containers are suitable when they are filled to a minimum of 80%.

NOTE 6—The current precision statements for gasoline and gasoline-oxygenate blends were derived from the 2003 ILS (see 16.1) using samples in 250-mL (250 mL) and 1-L (1 qt) clear glass containers. However, samples in containers of other sizes as prescribed in Practice D4057 may be used, with the same filling requirement, but the precision can be affected. The differences in precision results obtained from 250-mL (250 mL) and 1-L (1 qt) containers were found to be statistically significant, in addition to having a statistically observable bias being detected between 250-mL (250 mL) and 1-L (1 qt) containers. See Tables 2 and 3, as well as Figs. 1 and 2 for more specific details on precision differences as a function of VP₄(37.8°C) (37.8 °C) and container size, as well as 16.3.3 for specific details on the relative bias between 250-mL (250 mL) and 1-L (1 qt) containers. In general, numerically better repeatability values were determined at VP₄(37.8°C) (37.8 °C) values < 64.3 kPa (9.3 psi) for samples in 1-L (1 qt) containers versus 250-mL (250 mL) containers. Secondly, numerically better reproducibility values were determined at VP₄(37.8°C) (37.8 °C) values < 60.2 kPa (8.7 psi) for samples in 1-L (1 qt) containers versus 250-mL (250 mL) containers.

NOTE 7—The current precision statements for aviation turbine fuels were derived from the 2007 ILS (see 16.1) using samples in 100-mL (100 mL) containers. However, samples in containers of other sizes as prescribed in Practice D4057 may be used, with the same filling requirement, but the precision has not been determined.

8.1.3 Perform the VP_x determination, including the rinsing (see 9.3), on the first test specimen withdrawn from a sample container. Do not use the remaining sample in the container for a second VP_x determination. If a second determination is necessary, obtain a new sample. This condition does not apply when the sample is aviation turbine fuel.

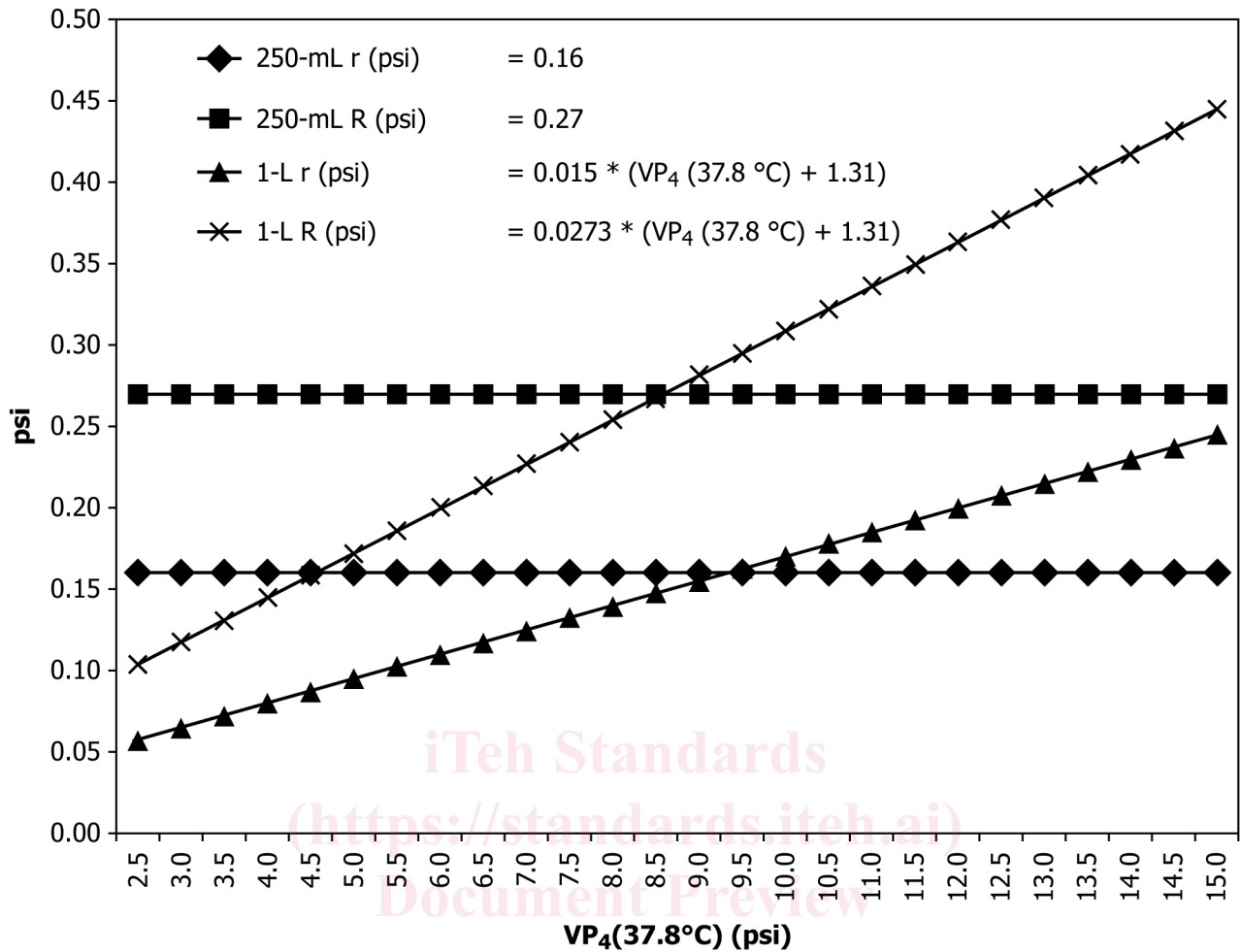


FIG. 2 Plot of VP₄(37.8°C) (37.8 °C) Precision (psi) by Container Size at Nominal VP₄(37.8°C) (37.8 °C) (psi) Values Determined

NOTE 8—For gasoline and gasoline-oxygenate blends, the effect of taking more than one test specimen from the same sample container was evaluated as part of the 2003 ILS (see 16.1). A precision effect was observed between the first and second replicates taken from both the 1-L and 250-mL containers evaluated. The current precision statements were derived from the 2003 ILS (see 16.1) using the first test specimen withdrawn from 250-mL and 1-L clear glass containers.

NOTE 9—For aviation turbine fuels the effect of taking more than one test specimen from the same sample container was evaluated as part of the 2007 ILS (see 16.1). No precision effect was observed between the first and second replicates taken from the 100-mL containers evaluated.

8.1.4 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate ice bath or refrigerator.

8.1.5 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.

8.2 *Sampling Handling*—This test method does not require pre-chilling of the sample and air saturation at ambient barometric pressure in order to limit the variability in the dissolved gas content of the sample prior to measurement. This test method measures the total sample vapor pressure at three V/L ratios (triple expansion) in order to estimate the partial pressure of dissolved gas and hydrocarbon partial pressure using ideal gas calculations. This has been shown to be acceptable up to at least 5 bar (about 5 atmospheres) of gas saturation.

8.2.1 Samples may be introduced to the instrument over a wide variation of temperatures and pressures, provided the test specimen remains as a single phase (that is, no separated liquid or gaseous phase). Experiments with temperatures between -10 °C to +50 °C and ambient pressures up to 300 kPa have been found suitable with certain gasoline samples.⁴

8.2.2 For gasoline and gasoline-oxygenate blends, the precision statement is based on sample introduction at ambient temperature and pressure from either 250-mL or 1-L clear, glass sample bottles. For aviation turbine fuels, the precision is based on sample introduction at ambient temperature and pressure from 100-mL containers. Precision may be affected with sample introduction under different conditions, but such information has not been determined.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1609.

8.2.3 Sample pre-chilling or air saturation, or both, are not required, but sample chilling, air saturation, or degassing, or a combination thereof, is acceptable, as it will have no significant effect on the result. This allows vapor pressure and distillation tests to be conducted on the same sample.

8.2.4 Degassing and some hydrocarbon loss occurs during the air saturation step when the sample is supersaturated with dissolved gas relative to ambient barometric pressure. Hydrocarbon loss increases as saturation gas pressure increases. Sealed sample systems are recommended for gas saturations greater than about 2 bar gas pressure (about 2 atmospheres or 30 psia).

8.2.5 For bottle samples, insert the sample introduction tube as close to the sample bottle bottom as practical.

8.2.6 Pressurized samples from a sealed sample system, pressurized floating pressure cylinders or equivalent may be used within the pressure and temperature limits specified by the manufacturer for the instrument being used. Excessive extremes of pressure and temperature may result in precision different than that measured under the conditions of ambient pressure and temperature used to prepare the precision statement. The temperature and pressure of the sample system should be controlled so that only a single phase liquid is in the sealed sample system during sample introduction.

8.2.6.1 Excessive cooling of samples that contain alcohols could result in phase separation (see 8.4), extraction of alcohol, and a lower vapor pressure value being determined, unless the sample remains well mixed during sample introduction (that is, introduction of a test specimen is representative of the composition once heated to test temperature). This can be prevented by not cooling samples containing alcohols, prior to the vapor pressure determination.

8.2.6.2 Excessive cooling of samples may result in formation of ice or hydrates that may impair proper operation of the sample system.

8.2.6.3 Excessive heating of samples may result in vapor formation, resulting in a higher or lower measured vapor pressure, depending if vapor or remaining liquid phase is introduced, respectively.

8.3 *Verification of Sample Container Filling*—If the sample is contained in a transparent container, verify that the container is 70 to 80 % full by suitable means, such as by using a marked ruler or by comparing it to a like container that has the 70 % and 80 % levels clearly marked. If the container is not transparent, unseal it and, using a suitable gauge, confirm that the sample volume equals 70 to 80 % of the container capacity (see Note 10). When the sample is aviation turbine fuel, verify that the container is at least 80 % full prior to removal of the first specimen.

NOTE 10—For non-transparent containers, one way to confirm that the sample volume equals 70 to 80 % of the container capacity is to use a dipstick that has been pre-marked to indicate the 70 % and 80 % container capacities. The dipstick should be of such material that it shows wetting after being immersed and withdrawn from the sample. To confirm the sample volume, insert the dipstick into the sample container so that it touches the bottom of the container at a perpendicular angle before removing the dipstick.

8.3.1 Discard the sample if the container is filled to less than 70 %, by volume, of the container capacity.

8.3.2 If the container is more than 80 % by volume full, pour out enough sample to bring the container contents within the 70 % to 80 % by volume range. Do not return any sample to the container once it has been withdrawn.

8.3.3 Reseal the container, if opened.

8.4 *Verification of Single Phase Sample*—After drawing the test specimens and transferring them into the instrument for analysis, check the remaining sample for phase separation. If the sample is contained in a transparent container, this observation can be made prior to sample transfer. If the sample is contained in a non-transparent container, shake the sample thoroughly and immediately pour a portion of the remaining sample into a glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into distinct phases. If the sample separates into two distinct phases with a discernible common boundary, then discard the test and the sample. If the sample has a hazy appearance, but does not have two distinct phases, then phase separation has not occurred. The test is valid, but the precision and bias in Section 16 may not apply (see 15.2). This verification procedure does not apply when the sample is aviation turbine fuel.

9. Preparation of Apparatus

9.1 Prepare the instrument for operation in accordance with the manufacturer's instructions.

9.2 Rinse the measuring chamber, if necessary, with a solvent. Acetone has a sufficiently low vapor pressure and can be used successfully. Rinsing is performed by drawing the solvent into the chamber by the piston and expelling the solvent into the waste container.

9.3 To avoid contamination of the test specimen with the previous sample or the solvent, rinse the measuring chamber a minimum of three times with the sample to be tested. Fill the measuring chamber with sample to at least half the total volume of the chamber for each rinse. This rinsing procedure shall always be carried out immediately before the measuring procedure (see 13.4).

9.4 If a syringe is used for introduction of the test specimen, ensure the syringe is at the same temperature conditions as the sample. Avoid water contamination of the syringe reservoir by suitably sealing the syringe during the cooling process.

10. Calibration

10.1 *Pressure Transducer:*