Designation: 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]

1. 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) that exert a vapor pressure between 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), 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) that exert a vapor pressure between 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 °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
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:*

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[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.

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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.

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 °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).

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 °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 5 mL and 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. Measuring chambers exceeding a 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 kPa to 200 kPa (0 psi to 29 psi) with a minimum resolution of 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.

6.1.3 Electronic temperature control shall be used to maintain the measuring chamber at the prescribed temperature within ±0.1 °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 ±0.1 °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,* 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 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), 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.

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)

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 Society[3] 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).

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 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 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 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 and 1 L containers were found to be statistically significant, in addition to having a statistically observable bias being detected between 250 mL and 1 L containers. See Tables 2 and 3, as well as Figs. 1 and 2 for more specific details on precision differences as a function of VP_4 (37.8 °C) and container size, as well as 16.3.3 for specific details on the relative bias between 250 mL and 1 L containers. In general, numerically better repeatability values were determined at VP_4 (37.8 °C) values < 64.3 kPa (9.3 psi) for samples in 1 L containers versus 250 mL containers. Secondly, numerically better reproducibility values were determined at VP_4 (37.8 °C) values < 60.2 kPa (8.7 psi) for samples in 1 L containers versus 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 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.

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

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[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.

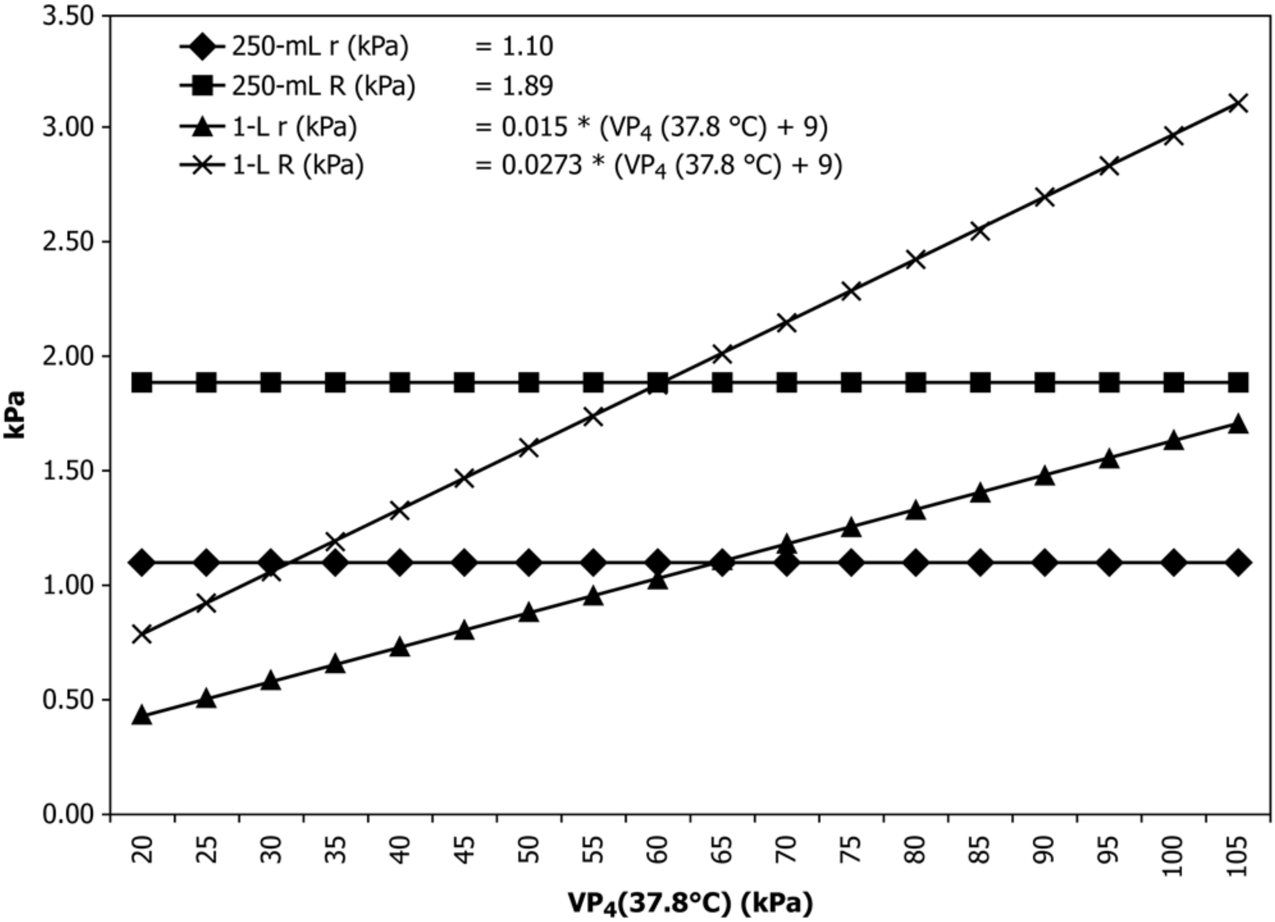

FIG. 1 Plot of VP_4 (37.8 °C) Precision (kPa) by Container Size at Nominal VP_4 (37.8 °C) (kPa) Values Determined

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.

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).

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

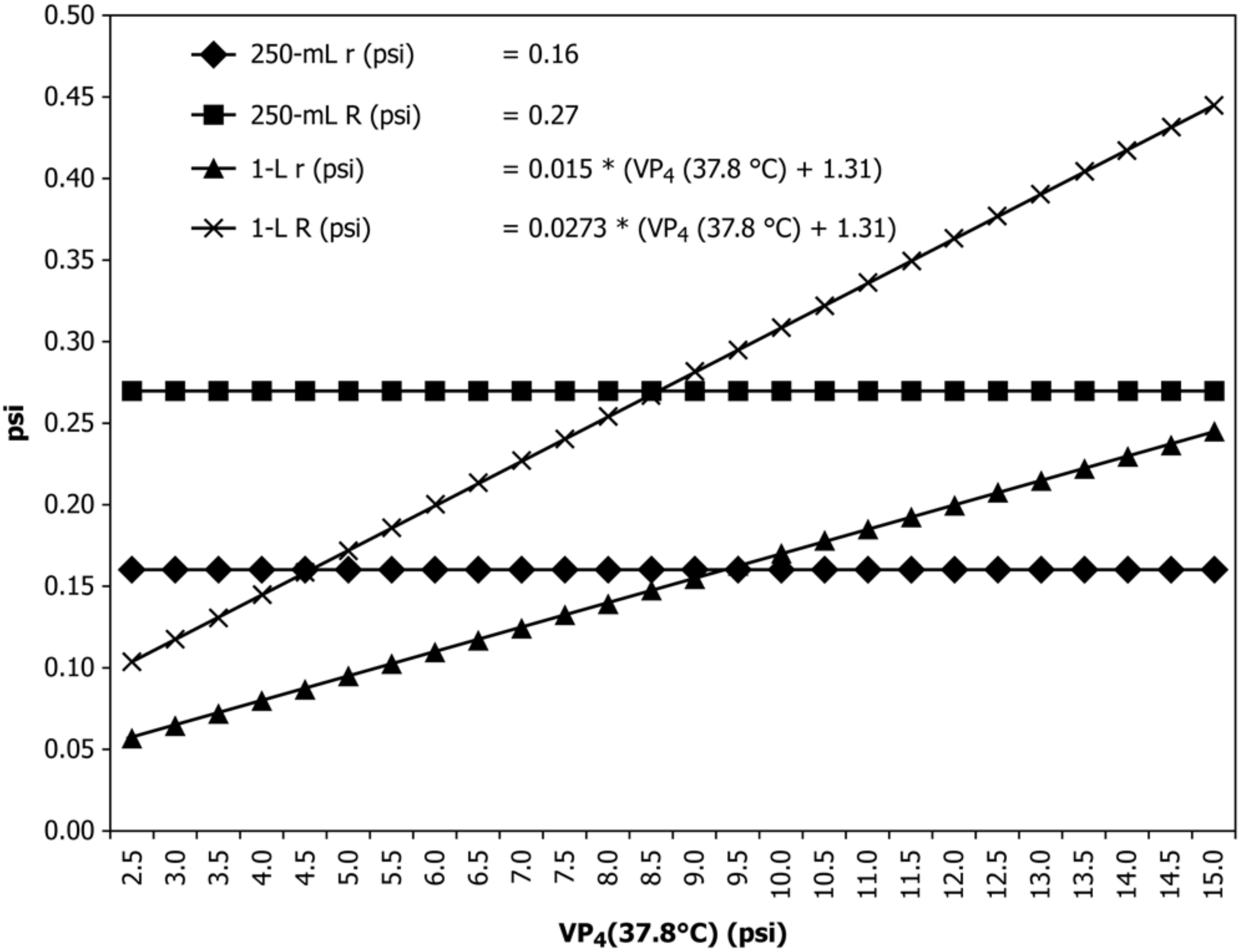

FIG. 2 Plot of VP_4 (37.8 °C) Precision (psi) by Container Size at Nominal VP_4 (37.8 °C) (psi) Values Determined

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:*

10.1.1 Check the calibration of the transducer as indicated from the verification of instrument performance (see Section 11) and quality control checks (see Section 12). The calibration of the transducer is checked using two reference points: zero pressure (<0.1 kPa) and the ambient barometric pressure.

NOTE 11—Calibration frequency of the pressure transducer may vary with instrument type and frequency of use. A calibration check of the pressure transducer at least once every six months is recommended.

10.1.2 Connect a McLeod gauge or a calibrated electronic vacuum measuring device to the vacuum source in line with the measuring chamber (see Note 12). Apply vacuum to the measuring chamber. When the vacuum measuring device registers a pressure less than 0.1 kPa (0.8 mm Hg), adjust the transducer control to zero or to the actual reading on the vacuum measuring device as dictated by the instrument design or manufacturer's instructions.

NOTE 12—Refer to Annex A6.3 on Vacuum Sensors in Test Method D2892 for further details concerning the calibration of electronic vacuum measuring devices and proper maintenance of McLeod gauges.

10.1.3 Open the measuring chamber of the apparatus to atmospheric pressure and observe the corresponding pressure value of the transducer. Ensure that the apparatus is set to display the TP_X and not a calculated or corrected value. Compare this pressure value with the pressure obtained from a mercury barometer, or equivalent, as the pressure reference standard. The pressure measuring device shall measure the local station pressure at the same elevation as the apparatus in the laboratory at the time of pressure comparison.

NOTE 13—Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings. These shall not be used for calibration of the apparatus.

10.1.4 Repeat 10.1.2 and 10.1.3 until the zero and barometric pressures read correctly without further adjustments.

10.2 *Temperature Sensor*—Verify the calibration of the platinum resistance thermometer used to monitor the measuring chamber temperature at least every six months against a nationally traceable thermometer, such as one that is traceable to National Institute of Standards and Technology (NIST) or to national authorities in the country in which the equipment is used.

11. Verification of Instrument Performance

11.1 After calibration, verify the instrument performance as an independent check against the instrument calibration each day the instrument is in use. For pure compounds (see 7.1) and blends that are prepared from pure compounds, multiple test specimens may be taken from the same container over time, provided spent test specimens are not reused, in whole or in part. Table 1 provides the accepted reference value (ARV) and uncertainty limits (at least 95 % confidence interval) of reference fluids tested in the 2003 ILS (see 16.1), which is based on the vapor pressure (VP_4 (37.8 °C)) value measured. This information, combined with the tolerance value recommended by instrument manufacturers, was used to establish the acceptable testing range for the reference fuels to verify instrument performance.

NOTE 14—In the 2003 ILS (see 16.1), a study was conducted to determine the effect that the percent capacity of material in the 250 mL reference fluid containers had on precision and bias through replicate testing from the same bottle. The data indicated that there was no statistically observable effect on precision and bias for 3 of the 4 reference fluids. For materials with DVPE values >100 kPa, such as pentane, the precision appears to worsen with diminishing liquid volume in the bottle. It is recommended that if pentane is used, that the % capacity in the container be ≥50 %.

NOTE 15—In the 2007 ILS (see 16.1) using aviation turbine fuel, 2,2 dimethylbutane was tested producing results comparable to the 2003 ILS (see 16.1). A mean of 68.6 kPa with a standard deviation of 0.3 kPa was determined. In the 2007 ILS (see 16.1) with aviation turbine fuels, 99.95 % toluene was tested with a mean of 7.7 kPa and standard deviation of 0.2 kPa.

11.2 Values obtained within the acceptable testing range intervals in Table 1 indicate that the instrument is performing at the level deemed acceptable by this standard. If values outside the acceptable testing range intervals are obtained, verify the quality of the pure compound(s) and re-check the calibration of the instrument (see Section 10).

NOTE 16—A reference fluid consisting of a 44.0/56.0 (m/m) blend of pentane/toluene was included in the 2003 ILS (see 16.1), but results indicated that the data was not normally distributed.

12. Quality Control Checks

12.1 After having verified that the instrument is performing properly, use a quality control (QC) sample that is representative of the fuel(s) routinely tested by the laboratory to confirm that the instrument is in statistical control following the guidelines given in Practice D6299.

12.2 Record the VP_4 (37.8 °C) value and compare this to the decision criteria for statistical control. If the result is found to be outside the decision criteria for statistical control, initiate an investigation for root causes.

12.3 Store the QC sample in an environment suitable for long term storage without sample degradation. See Appendix X4 for guidelines and suggestions for preparing, storing, and isolating QC samples for use in the test.

13. Procedure

13.1 Set the sample introduction temperature of the measuring chamber between 20 °C and 37.8 °C.

13.2 Set the vapor-liquid ratio to the desired value X:1 (for test results related to Test Method D5191, set the vapor-liquid ratio to 4:1).

13.3 Connect an aliquot of sample either in a syringe, pressurized sample container, or tubing immersed in the sample to the inlet of the apparatus. Make provisions to avoid loss of high volatiles in the sample. The overall volume of the sample shall exceed the volume of three rinsing cycles plus the final test volume. Follow the manufacturer's instructions for introducing the test specimen into the measuring chamber.

13.4 Perform the three rinsing cycles (see 9.3) immediately after connecting the sample.

13.5 Introduce the test specimen into the measuring chamber by a stroke of the piston. The volume of the specimen shall be such that after the expansion to the final volume the programmed vapor-liquid ratio is achieved.

13.6 Close the inlet valve, and make the first expansion by a stroke of the piston.

13.7 Allow the temperature of the measuring chamber to increase to within 0.1°C of the desired test temperature. Monitor the TP_X at least once per second for at least 1 min. When all readings taken within 20 s agree within 0.3 kPa, record this resulting total pressure as $TP_{X,1}$.

13.8 Make the second expansion, and monitor the TP_X at least once per second for at least 1 min. When all readings taken within 20 s agree within 0.3 kPa, record this resulting total pressure as $TP_{X,2}$.

13.9 Repeat 13.8 for the third expansion, and record the resulting total pressures as $TP_{X,3}$.

13.10 *Check for Sample Separation*—After introducing the test specimen into the instrument for analysis, check the remaining sample for sample separation (see 8.4). This condition does not apply when the sample is aviation turbine fuel.

14. Calculation

14.1 Calculate the partial pressure of the air, PPA_t, at the test temperature t, using the following equation:

$$PPA_t = \frac{(TP_{X,1} - TP_{X,3})(TP_{X,2} - TP_{X,3})}{\frac{V_3 - V_1}{V_2 - V_1}(TP_{X,1} - TP_{X,2}) - (TP_{X,1} - TP_{X,3})} \qquad (2)$$

where:

$TP_{X,\,1}$ = total pressure after first expansion,
$TP_{X,2}$ = total pressure after second expansion,
$TP_{X,3}$ = total pressure after third and final expansion,
V_1 = volume after the first expansion,
V_2 = volume after the second expansion, and
V_3 = final volume after the third expansion.

14.2 Calculate the vapor pressure $VP_{X,t}$ at test temperature t, using the following equation:

$$VP_{X,t} = TP_{X,3} - PPA_t \qquad (3)$$

where:

PPA_t = partial pressure of the air at temperature t.

14.3 See Appendix X1 for the derivation of the equations.

15. Report

15.1 Report the results to the nearest 0.1 kPa (0.02 psi), along with the volume container size (250 mL or 1 L for gasoline and gasoline-oxygenate blends; for aviation turbine fuel, 100 mL) in which the result was obtained, and specify the test temperature and vapor-liquid ratio.

$$VP_X\,(Tm°\mathrm{C}) = \#\#.\#\ \mathrm{kPa\ or}\ \#\#.\#\#\ \mathrm{psi} \qquad (4)$$

$$Pair(Tm°\mathrm{C}) = \#\#.\#\ \mathrm{kPa\ or}\ \#\#.\#\#\ \mathrm{psi} \qquad (5)$$

where:

X = vapor-liquid ratio,
$Pair$ = partial pressure of the dissolved air, and
Tm = measuring temperature.

15.2 If a haze was observed in 8.4, state on the report document that the test sample was hazy. Examples of acceptable reporting statements are a result of xx.xH or the statement "Sample Hazy - Yes."

16. Precision and Bias

16.1 *Precision*—The precision of this test method for gasoline and gasoline-oxygenate blends was developed in a 2003 interlaboratory cooperative test program[5] using Practice D6300

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1619.

TABLE 2 Repeatability (gasoline and gasoline-oxygenate blends)

Container Size	Repeatability (r)
250 mL	1.10 kPa (0.16 psi)
1 L	$0.015\,(X+B)$

where:
$X = VP_4$ (37.8 °C) kPa (psi), and
$B = 9$ kPa (1.31 psi).

and involving 12 laboratories, 2 types of instruments, and 20 types of hydrocarbon and hydrocarbon-oxygenate blends. See X3.2 and X3.4 for additional information concerning the number and nature of the sample types and instruments evaluated. The precision of this test method for aviation turbine fuels was developed in a 2007 interlaboratory cooperative test program[6] using Practice D6300 and involving 7 laboratories, 2 types of instruments, 11 samples of aviation turbine fuel (Jet A, A1, C, JP4, TS-1), and toluene.

16.1.1 *Repeatability (Gasoline and Gasoline-Oxygenate Blends)*—The difference between duplicate test results obtained by the same or potentially different operators with the same apparatus in the laboratory using identical test specimens withdrawn from separate 250 mL or 1 L containers under constant operating conditions would, in the long run, in the normal and correct operation of the test method, exceed the constant value associated with 250 mL containers or the value calculated for 1 L containers as per the equation in Table 2 only in one case in twenty across the nominal VP_4 (37.8 °C) range of 17.0 kPa to 106.0 kPa (2.5 psi to 15.4 psi).

16.1.2 *Repeatability (Aviation Turbine Fuel)*—The difference between duplicate test results obtained by the same or potentially different operators with the same apparatus in the laboratory using identical test specimens withdrawn from separate 100 mL containers under constant operating conditions would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 in one case in twenty.

16.1.3 *Reproducibility (Gasoline and Gasoline-Oxygenate Blends)*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material withdrawn from separate 250 mL or 1 L containers would, in the long run, in the normal and correct operation of the test method, exceed the constant value associated with 250 mL containers or the value calculated for 1 L containers as per the equation in Table 4 only in one case in twenty across the nominal VP_4 (37.8 °C) range of 17.0 kPa to 106.0 kPa (2.5 psi to 15.4 psi).

16.1.4 *Reproducibility (Aviation Turbine Fuel)*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material withdrawn from separate 100 mL containers under constant operating conditions would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 5 in one case in twenty.

TABLE 3 Repeatability (aviation turbine fuel)

Temperature, °C	Repeatability (kPa)	Effective Range (kPa)
25	0.6	0.1–11.0
37.8	$0.06(Y+4)$	0.3–17.0
50	$0.035(Y+15)$	0.5–26.0
100	1.70	5.4–107.5

where:
$Y = VP_4$ kPa

TABLE 4 Reproducibility (gasoline and gasoline-oxygenate blends)

Container Size	Reproducibility (R)
250 mL	1.89 kPa (0.27 psi)
1 L	$0.0273\,(X+B)$

where:
$X = VP_4$ (37.8 °C) kPa (psi), and
$B = 9$ kPa (1.31 psi).

TABLE 5 Reproducibility (aviation turbine fuel)

Temperature, °C	Reproducibility (R) kPa	Effective Range (kPa)
25	1.0	0.1–11.0
37.8	$0.11(Y+4)$	0.3–17.0
50	$0.065(Y+15)$	0.5–26.0
100	2.2	5.4–107.5

where:
$Y = VP_4$ kPa

16.1.5 See Table 6 and Figs. 1 and 2 for a summary of the precision values on gasoline and gasoline-oxygenate blends determined for nominal VP_4 (37.8 °C) values determined in kPa (psi) from Tables 2 and 4.

16.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

16.3 *Relative Bias to Test Method D5191*—The degree of expected agreement between VP_4 (37.8 °C) results by this test method using 1 L containers and DVPE results by Test Method D5191 using 1 L containers has been assessed in accordance with Practice D6708. The degree of agreement can be further improved using bias correction schemes considered in Practice D6708. Sample specific biases were observed, but they can be included in the calculation of between method reproducibility as a random effect. See Eq 6 for predicting DVPE results determined by Test Method D5191 using 1 L containers, based on VP_4 (37.8 °C) results obtained by this method using 1 L containers. This condition does not apply when the sample is aviation turbine fuel.

$$Predicted\ DVPE_{1-L\ container} = VP_4\left(37.8\ °C\right)_{1-L\ container} - Relative\ Bias \tag{6}$$

where:

$VP_4\ (37.8\ °C)_{1\text{-}L\ container}$ = VP_4 (37.8 °C) result determined by this method using a 1 L container, and
Relative Bias = 1.005 kPa (0.15 psi).

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1651.

TABLE 6 Repeatability and Reproducibility Values for Nominal VP_4 (37.8 °C) Values Determined by the Method

VP_4 (37.8 °C)	250 mL Containers		1 L Containers		VP_4 (37.8 °C)	250 mL Containers		1 L Containers	
(kPa)	r (kPa)	R (kPa)	r (kPa)	R (kPa)	(psi)	r (psi)	R (psi)	r (psi)	R (psi)
20	1.10	1.89	0.44	0.79	2.50	0.16	0.27	0.06	0.10
25	1.10	1.89	0.51	0.93	3.00	0.16	0.27	0.06	0.12
30	1.10	1.89	0.59	1.06	3.50	0.16	0.27	0.07	0.13
35	1.10	1.89	0.66	1.20	4.00	0.16	0.27	0.08	0.14
40	1.10	1.89	0.74	1.34	4.50	0.16	0.27	0.09	0.16
45	1.10	1.89	0.81	1.47	5.00	0.16	0.27	0.09	0.17
50	1.10	1.89	0.89	1.61	5.50	0.16	0.27	0.10	0.19
55	1.10	1.89	0.96	1.75	6.00	0.16	0.27	0.11	0.20
60	1.10	1.89	1.04	1.88	6.50	0.16	0.27	0.12	0.21
65	1.10	1.89	1.11	2.02	7.00	0.16	0.27	0.12	0.23
70	1.10	1.89	1.19	2.16	7.50	0.16	0.27	0.13	0.24
75	1.10	1.89	1.26	2.29	8.00	0.16	0.27	0.14	0.25
80	1.10	1.89	1.34	2.43	8.50	0.16	0.27	0.15	0.27
85	1.10	1.89	1.41	2.57	9.00	0.16	0.27	0.15	0.28
90	1.10	1.89	1.49	2.70	9.50	0.16	0.27	0.16	0.30
95	1.10	1.89	1.56	2.84	10.00	0.16	0.27	0.17	0.31
100	1.10	1.89	1.64	2.98	10.50	0.16	0.27	0.18	0.32
105	1.10	1.89	1.71	3.11	11.00	0.16	0.27	0.18	0.34
					11.50	0.16	0.27	0.19	0.35
					12.00	0.16	0.27	0.20	0.36
					12.50	0.16	0.27	0.21	0.38
					13.00	0.16	0.27	0.21	0.39
					13.50	0.16	0.27	0.22	0.40
					14.00	0.16	0.27	0.23	0.42
					14.50	0.16	0.27	0.24	0.43
					15.00	0.16	0.27	0.24	0.45

TABLE 7 Calculated Cross-Method Reproducibility Values between Predicted $DVPE_{1\text{-}L\ Container}$ Values by Eq 6 and Test Method D5191 at Nominal DVPE Levels

DVPE (kPa)	R_{xy} (kPa)	DVPE (psi)	R_{xy} (psi)
20	1.47	2.50	0.21
25	1.54	3.00	0.21
30	1.63	3.50	0.22
35	1.71	4.00	0.23
40	1.80	4.50	0.24
45	1.89	5.00	0.25
50	1.98	5.50	0.26
55	2.08	6.00	0.26
60	2.17	6.50	0.27
65	2.27	7.00	0.28
70	2.37	7.50	0.29
75	2.47	8.00	0.30
80	2.57	8.50	0.31
85	2.67	9.00	0.32
90	2.77	9.50	0.33
95	2.87	10.00	0.34
100	2.97	10.50	0.35
		11.00	0.36
		11.50	0.37
		12.00	0.38
		12.50	0.39
		13.00	0.40
		13.50	0.41
		14.00	0.42
		14.50	0.43

TABLE 8 Calculated Cross-Method Reproducibility Values between Predicted $DVPE_{1\text{-}L\ Container}$ Values by Eq 7 and Test Method D5191 at Nominal DVPE Levels

DVPE (kPa)	R_{xy} (kPa)	DVPE (psi)	R_{xy} (psi)
20	2.05	2.50	0.29
25	2.07	3.00	0.29
30	2.10	3.50	0.30
35	2.12	4.00	0.30
40	2.15	4.50	0.30
45	2.18	5.00	0.31
50	2.20	5.50	0.31
55	2.23	6.00	0.31
60	2.26	6.50	0.31
65	2.29	7.00	0.32
70	2.32	7.50	0.32
75	2.35	8.00	0.32
80	2.37	8.50	0.32
85	2.40	9.00	0.33
90	2.43	9.50	0.33
95	2.46	10.00	0.33
100	2.49	10.50	0.34
		11.00	0.34
		11.50	0.34
		12.00	0.34
		12.50	0.35
		13.00	0.35
		13.50	0.35
		14.00	0.36
		14.50	0.36

16.3.1 The degree of expected agreement between VP_4 (37.8 °C) results by this test method using 250 mL containers and DVPE results by Test Method D5191 using 1 L containers has also been assessed in accordance with Practice D6708. The degree of agreement can be further improved using bias correction schemes considered in Practice D6708. Sample specific biases were observed, but they can be included in the calculation of between method reproducibility as a random effect. See Eq 7 for predicting DVPE results determined by Test Method D5191 using 1 L containers, based on VP_4 (37.8 °C) results obtained by this method using 250 mL containers.

$$Predicted\ DVPE_{1-L\ container} = VP_4\left(37.8\ °C\right)_{250-mL\ container} - Relative\ Bias \quad (7)$$

where:

VP_4 (37.8 °C)$_{250\text{-}mL\ container}$ = VP_4 (37.8 °C) result determined by this method using a 250 mL container, and

Relative Bias = 0.751 kPa (0.11 psi).

16.3.2 Based on the results from the 2003 interlaboratory study, the difference between any single predicted DVPE result using Eq 6 or Eq 7 and this test method, versus any single DVPE result, obtained using a 1 L container in Test Method D5191, over the long-term and correct operation of both test methods, for any sample meeting the scope of both test methods, is estimated to exceed the values in Tables 7 and 8 no more than one case in twenty.

NOTE 17—For average values between those listed linearly, interpolate between the cross-method reproducibility values in Tables 7 and 8. See Appendix X5 for more details and explanation on cross-method reproducibility values. In addition, Figs. X5.1 and X5.2 provide graphical representations of the information in Tables 7 and 8.

16.3.3 *Relative Bias (250 mL containers versus 1 L containers)*—The degree of expected agreement between VP_4 (37.8 °C) results obtained by this test method using 250 mL containers versus 1 L containers has been assessed in accordance with Practice D6708. The degree of agreement between the two container sizes can be improved using the following bias correction formula as shown in Eq 8 and 9. No sample specific biases were observed in the D6708 analysis.

$$Predicted\ VP_4\ (37.8\ °C)_{1-L\ container}\ (kPa) = VP_4\ (37.8\ °C)_{250-mL\ container}\ (kPa) + 0.137 \quad (8)$$

$$Predicted\ VP_4\ (37.8\ °C)_{1-L\ container}\ (psi) = VP_4\ (37.8\ °C)_{250-mL\ container}\ (psi) + 0.02 \quad (9)$$

NOTE 18—The precision and bias statements may not be applicable to gasolines observed to be hazy in 8.4.

NOTE 19—Different correlation formulas have been developed for Test Method D5191 (for gasoline and gasoline-oxygenate blends) by various agencies to correlate either to Test Method D4953, Procedure B, or to Test Method D323. The relative bias for the VP_X calculated by these different formulas are as follows:

Correlation formula for Test Method D4953, Procedure B, used by the EPA.
EPA: DVPE = (0.956 Ptot) − 2.39 in kPa
DVPE = (0.956 Ptot) − 0.347 in psi

Relative bias = 0.137 kPa (0.02 psi)

Correlation formula for Test Method D323, used by CARB
CARB: RVPE = (0.972 Ptot) − 4.93 in kPa
RVPE = (0.972 Ptot) − 0.715 in psi

Relative bias = 1.575 kPa (0.23 psi)

17. Keywords

17.1 aviation turbine fuel; dry vapor pressure; gasoline; gasoline and gasoline-oxygenate blends; hydrocarbon-oxygenate blends; mini method; petroleum products; vapor pressure; variable volume method

APPENDIXES

(Nonmandatory Information)

X1. DERIVATION OF EQUATIONS USED TO CALCULATE VP_X

X1.1 Theory

X1.1.1 The measured TP_X of the air containing liquid is the sum of the VP_X of the liquid and the PPA in the liquid.

X1.1.2 *Derivation of Equation*—The derivation is based on the assumption that the VP_X of the liquid is constant within the accuracy of the measurement for all three vapor-liquid ratios.

X1.1.2.1 The TP_X after the three expansions may be expressed by the following equations:

$$TP_{X,1} = VP_X + PPA_{V,1} \quad \text{or} \quad PPA_{V,1} = TP_{X,1} - VP_X \quad (X1.1)$$

$$TP_{X,2} = VP_X + PPA_{V,2} \quad \text{or} \quad PPA_{V,2} = TP_{X,2} - VP_X \quad (X1.2)$$

$$TP_{X,3} = VP_X + PPA_{V,3} \quad \text{or} \quad PPA_{V,3} = TP_{X,3} - VP_X \quad (X1.3)$$

X1.1.2.2 The free volume V_A for the air in the sample can be defined as follows:

$$V_A = (k/100)\ V_L \quad (X1.4)$$

where:

k = solubility of air in the sample in %, and
V_L = sample volume.

X1.1.2.3 Applying the gas law equation for the three different volumes and using the term V_A for the free air volume, the following relationship can be defined:

$$(V_1 + V_A)PPA_{X,1} = (V_2 + V_A)PPA_{X,2} = (V_3 + V_A)PPA_{X,3} \quad (X1.5)$$

X1.1.2.4 Using Eq X1.1-X1.3, the two following equations are derived:

$$(V_1 + V_A)(TP_{X,1} - VP_X) = (V_2 + V_A)(TP_{X,2} - VP_X) \quad (X1.6)$$

$$(V_1 + V_A)(TP_{X,1} - VP_X) = (V_3 + V_A)(TP_{X,3} - VP_X) \quad (X1.7)$$

X1.1.2.5 Solving the Eq X1.6 and X1.7, the formula for the PPA in the final volume can be derived:

$$PPA_{X,3} = \frac{(TP_{X,1} - TP_{X,3})(TP_{X,2} - TP_{X,3})}{\dfrac{V_3 - V_1}{V_2 - V_1}(TP_{X,1} - TP_{X,2}) - (TP_{X,1} - TP_{X,3})} \quad (X1.8)$$

where:

$TP_{X,1}$ = total pressure after first expansion,
$TP_{X,2}$ = total pressure after second expansion,
$TP_{X,3}$ = total pressure after third and final expansion,
V_1 = vapor volume after the first expansion,
V_2 = vapor volume after the second expansion, and
V_3 = final vapor volume after the third expansion.

X1.1.2.6 The air corrected vapor pressure is calculated by:

$$VP_X = TP_{X,3} - PPA_{X,3} \quad (X1.9)$$

X2. AIR CORRECTION AT A TEMPERATURE OTHER THAN THE TEST TEMPERATURE

X2.1 The vapor pressure VP_X can be determined at a temperature t_1 that is different from the test temperature t according to the following procedure:

X2.1.1 After determination of $TP_{X,3}$ at temperature t, regulate the temperature of the measuring chamber to the temperature t_1 ± 0.1°C.

X2.1.2 Monitor the TP_X at least once per second for at least 1 min. When all readings taken within 20 s agree within 0.3 kPa, record this resulting total pressure as $TP_{X,t1}$.

X2.1.3 The partial pressure of the air at the temperature t_1, PPA_{t1} , can be determined using the following equation derived from the gas laws as follows:

$$PPA_{t1} = PPA_t\left(273.2+t_1\right)/\left(273.2+t\right) \tag{X2.1}$$

where:

PPA_t = partial pressure of the air at test temperature t,
t_1 = current temperature of the measuring chamber, in °C, and
t = previous test temperature during the gas determination procedure, in °C.

X2.1.4 Calculate the air corrected vapor pressure $VP_{X,t1}$ at temperature t_1, using the following equation:

$$VP_{X,t1} = TP_{X,t1} - PPA_{t1} \tag{X2.2}$$

where:

$TP_{X,t1}$ = total pressure at temperature t_1, and
PPA_{t1} = partial pressure of the air at temperature t.

X3. INFORMATION RELATING TO THE 2003 INTERLABORATORY STUDY (ILS)[5] INVOLVING ANALYSES BY TEST METHODS D5191 AND D6378

X3.1 ILS Objectives Pertaining to Test Method D6378

X3.1.1 Determine the repeatability ("r") and reproducibility ("R") of Test Method D6378.

X3.1.2 Compare precision statements of Test Method D5191 versus Test Method D6378.

X3.1.3 Determine if the use of 250 mL containers influences vapor pressure results as compared to results obtained with 1-L containers.

X3.1.4 Determine if multiple determinations from one container are acceptable.

X3.1.5 Investigate the possibility to use blends whose vapor pressure can be tailored by concentration as a verification fluid.

X3.1.6 Determine relative bias of Test Method D6378 to Test Method D5191.

X3.1.7 Determine if the contribution of dissolved air is correctly measured in D6378 for different levels of dissolved gas.

X3.1.8 Compare results of D6378 to theoretical Peng-Robinson Equation of State (PR EOS) results for reference samples.

X3.2 Samples

X3.2.1 Participants in the study analyzed randomly ordered sample sets comprised of blind duplicates and replicates from the same container of 20 types of hydrocarbons and hydrocarbon-oxygenate blends contained in 250 mL and 1 L clear glass containers (that is, 20 samples × 2 duplicates × 2 bottle sizes × 2 replicates/bottle = 160 analyses/data set). The twenty sample types included 6 conventional gasolines (with and without ethanol added), 5 reformulated gasolines (RFG) containing either MTBE or ethanol, 6 CARB gasolines (2 without oxygenates, 2 with MTBE, and 2 with ethanol), 1 avgas, 1 JP4, and 1 condensate. The total vapor pressure of the samples ranged from approximately 22 kPa to 110 kPa (3.2 psi to 16.0 psi).

X3.3 Reference Fuels

X3.3.1 Participants in the study analyzed 4 coded reference fuels (44.0 % / 56.0 % (m/m) blend of pentane/toluene, pentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) in quadruplicate, following a specific protocol provided to the laboratories, which included a study to evaluate how results may be affected as the % capacity of material in the container varies. The reference fuels were contained in 250 mL clear, glass containers.

X3.4 Test Method D6378 Instrument Types and Data Sets Evaluated

X3.4.1 A total of 12 data sets were received from 10 laboratories that analyzed samples by D6378, using one or more of the following two instrument types (with the number of data sets submitted by vendor or model, or both, given in parentheses): Grabner VPS (8), and Grabner VPS Online (4).

X4. GUIDELINES AND SUGGESTIONS FOR PREPARING, STORING, AND ISOLATING QC SAMPLES FOR USE IN THIS TEST

X4.1 A suggested approach for preparing samples for quality control (QC) purpose using a volatile liquid petroleum product such as gasoline, is to obtain a homogeneous bulk supply (for example, ≥20 L) of the material in a suitably sized and sealed container filled to 70 % to 80 % capacity that is representative of the sample types that are to be measured for the intended period of time (for example, select a summer grade gasoline or winter grade gasoline depending on the vapor pressure season). Since analysis by D6378 does not require pre-chilling of the sample to 0 °C to 1 °C as required in D5191, this bulk supply may be kept at ambient conditions or in a refrigerated location, such as in a "cold room." Portions of the bulk supply may be transferred into smaller 250 mL or 1 L containers filled to 70 % to 80 % capacity and stored until needed for analysis or transferred from the bulk supply container just prior to analysis.

X4.2 An alternative approach is to test retained samples prior to disposal as a technique to estimate site precision by comparing results obtained on the initial sample analysis with the results obtained on retained samples containing the same material. This approach may be advantageous for laboratories that may not have access to bulk supplies of a given sample, but are required to keep retain samples of samples they initially test for a specific amount of time before discarding. The suggestion is to test the retain sample that is about to be discarded (that is, the retain sample has reached its required retention period) and plot the differences between the results from the original certification analysis and the retain results (calculated by $\text{Measurement}_{\text{initial}} - \text{Measurement}_{\text{final}}$) using individual (I-chart), moving range (MR), and optional exponentially weighted moving average (EWMA) control charts as indicated in Practice D6299. Separate control charts should be maintained for product grades that are significantly different in vapor pressures (for example, winter grade gasoline versus summer grade gasoline).

X4.2.1 The mean of the I-chart of differences is expected to be zero; an out-of-control signal (individual chart or EWMA) represents a potential signal for either a shift in the test method as practiced by the site or a change in the retain sample relative to the original. Both root causes are of high operational significance to the site. This approach has the additional benefit of continuously monitoring the integrity of the retain system in addition to evaluating the site's test method precision.

X5. INFORMATION ON CROSS-METHOD REPRODUCIBILITY VALUES BETWEEN PREDICTED $\text{DVPE}_{\text{1-L container}}$ VALUES DETERMINED BY Eq 6 AND Eq 7 AND TEST METHOD D5191

X5.1 *Cross-method Reproducibility (R_{XY})*—As defined in Practice D6708, cross-method reproducibility is a quantitative expression of the random error associated with the difference between two results obtained by different operators using different apparatus and applying the two methods X and Y, respectively, each obtaining a single result on an identical test sample, when the methods have been assessed and an appropriate bias-correction has been applied. It is defined as the 95 % confidence limit for the difference between two such single and independent results. For method X results, this will be Predicted $\text{DVPE}_{\text{1-L container}}$ results (Eq 6) and for method Y results, this will be D5191 DVPE results obtained using 1 L containers.

X5.1.1 Based on the 2003 ILS,[5] an evaluation of cross-method reproducibility between predicted $\text{DVPE}_{\text{1 L container}}$ using Eq 6 of this test method and Test Method D5191 using 1 L containers was performed. Eq X5.1 provides the formula for calculating the cross-method reproducibility between these two methods based on this criteria.

$$Cross - method\ reproducibility\ (R_{xy}),\ \text{kPa (psi)} = \sqrt{(0.57R_x^2 + 0.53R_y^2)} \tag{X5.1}$$

where:

R_x = Test Method D6378 Reproducibility Value, kPa (psi), based on VP_4 (37.8 °C)$_{\text{1 L container}}$ input, and

R_y = Test Method D5191 Reproducibility Value, kPa (psi), based on DVPE input using 1 L containers.

NOTE X5.1—In order to calculate the cross-method reproducibility (R_{xy}) for a given DVPE level, one needs to rearrange Eq 6 in terms of VP_4 (37.8 °C) such that VP_4 (37.8 °C) = Predicted DVPE + Relative Bias. By doing so, if one were to calculate R_x in terms of kPa, then the R_x equation can be rewritten as: R_x (kPa) = 0.0273*(Predicted DVPE (kPa) + Relative Bias (kPa) + 9 kPa) = 0.0273*(Predicted DVPE (kPa) + 10.005 kPa). Similarly, if calculating R_x in terms of psi, then the R_x equation can be rewritten as: R_x (psi) = 0.0273*(Predicted DVPE (psi) + 1.46 psi).

X5.1.2 Similar to the information in X5.1.1, an evaluation of the cross-method reproducibility between predicted $\text{DVPE}_{\text{1 L container}}$ using Eq 7 of this method involving VP_4 (37.8 °C)$_{\text{250 mL container}}$ inputs and Test Method D5191 using 1 L containers was performed. Eq X5.2 provides the formula for calculating the cross-method reproducibility between these two methods based on this criteria.

$$Cross - method\ reproducibility\ (R_{xy}),\ \text{kPa (psi)} = \sqrt{(0.65R_x^2 + 0.56R_y^2)} \tag{X5.2}$$

where:

R_x = Test Method D6378 Reproducibility Value, kPa (psi), for 250 mL containers, and

R_y = Test Method D5191 Reproducibility Value, kPa (psi), based on DVPE input using 1 L containers.

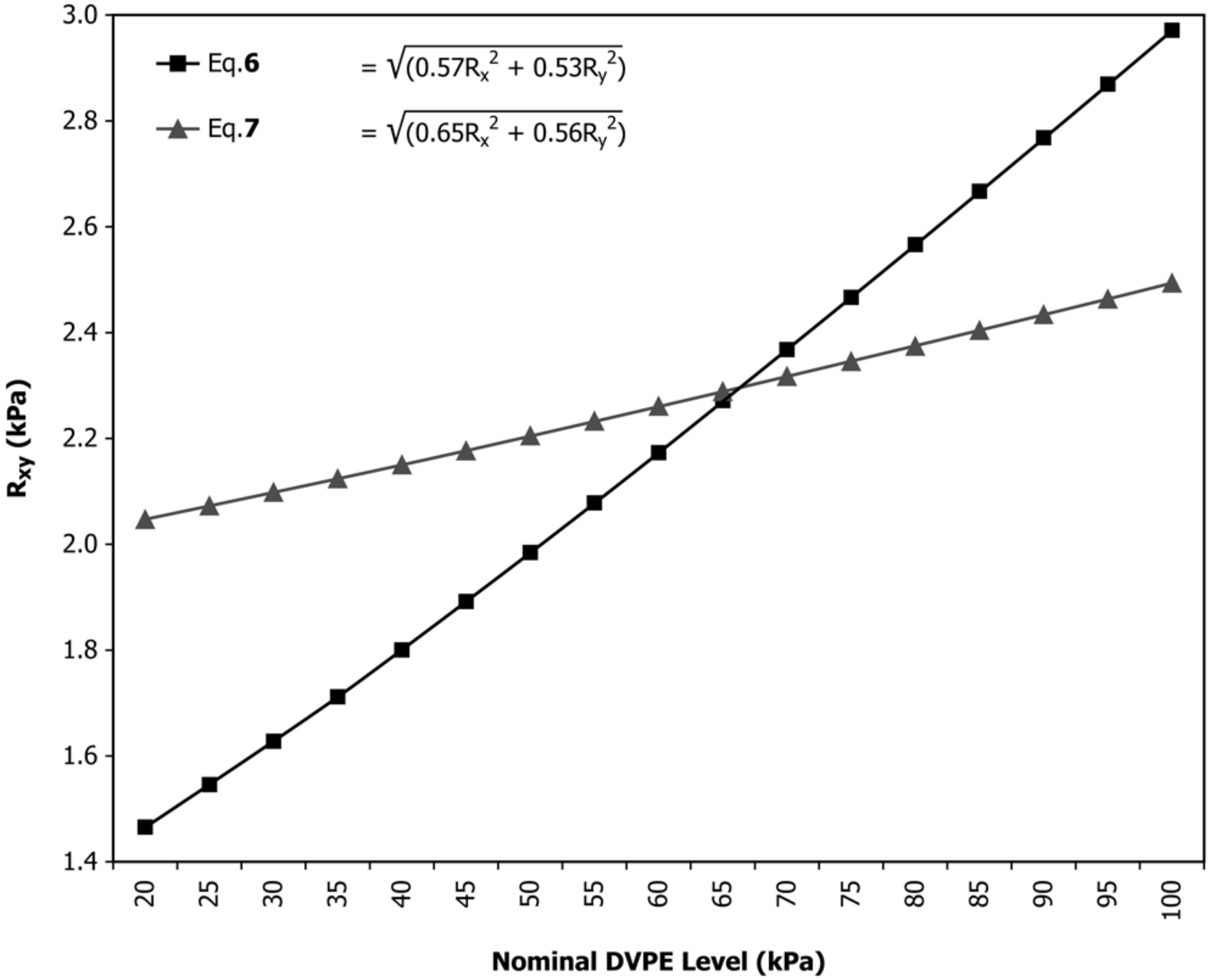

FIG. X5.1 Cross-Method Reproducibility (R_{xy}) Values (kPa) Between Predicted DVPE$_{1\ L\ container}$ Values Determined by Eq 6 and Eq 7 and Test Method D5191 at Nominal DVPE Levels (kPa)

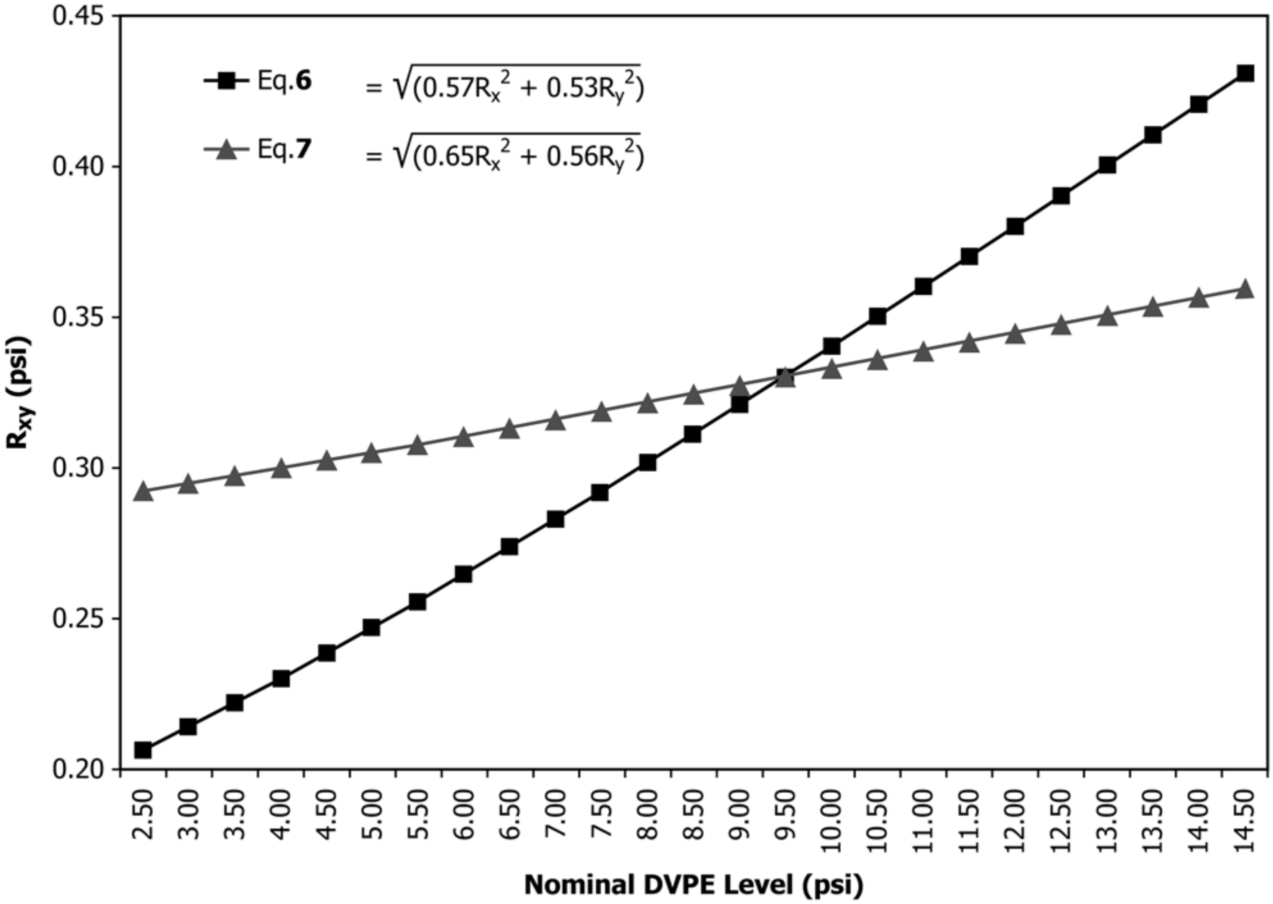

FIG. X5.2 Cross-Method Reproducibility (R_{xy}) Values (psi) Between Predicted DVPE$_{1\ L\ container}$ Values Determined by Eq 6 and Eq 7 and Test Method D5191 at Nominal DVPE Levels (psi)

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