

# Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)<sup>1</sup>

This standard is issued under the fixed designation D5191; 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  $(\varepsilon)$  indicates an editorial change since the last revision or reapproval.

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

# 1. Scope\*

1.1 This test method covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid petroleum products, including automotive spark-ignition fuels with or without oxygenates (see Note 1). 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 130 kPa (1.0 psi and 18.6 psi) at 37.8 °C (100 °F) at a vapor-to-liquid ratio of 4:1. Measurements are made on liquid sample sizes in the range from 1 mL to 10 mL. No account is made for dissolved water in the sample.

Note 1—An interlaboratory study was conducted in 2008 involving 11 different laboratories submitting 15 data sets and 15 different samples of ethanol-fuel blends containing 25 volume %, 50 volume %, and 75 volume % ethanol. The results indicated that the repeatability limits of these samples are with in the published repeatability of this test method. on this basis, it can be concluded that D5191 is applicable to ethanol-fuel blends such as Ed75 and Ed85 (Specification D5798) and other ethanol-fuel blends with greater than 10 v% ethanol. See ASTM RR: D02–1694 filed with ASTM for supporting data.  $^2$ 

Note 2—Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the precision and bias statements need not apply.

Note 3—The interlaboratory studies conducted in 1988, 1991, and 2003 to determine the precision statements in Test Method D5191 did not include any crude oil in the sample sets. Test Method D6377, as well as IP 481, have been shown to be suitable for vapor pressure measurements of crude oils.

- 1.1.1 Some gasoline-oxygenate blends may show a haze when cooled to 0 °C to 1 °C. If a haze is observed in 8.5, it shall be indicated in the reporting of results. The precision and bias statements for hazy samples have not been determined (see Note 15).
- 1.2 This test method is suitable for calculation of the dry vapor pressure equivalent (DVPE) of gasoline and gasoline-

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

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oxygenate blends by means of a correlation equation (see Eq 1 in 14.2). The calculated DVPE very closely approximates the dry vapor pressure that would be obtained on the same material when tested by Test Method D4953.

- 1.3 The values stated in SI units are regarded as standard. The inch-pound units given in parentheses are provided for information only.
- 1.4 **WARNING**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website http://www.epa.gov/mercury/faq.htm for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.
- 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 safety warning statements, see 7.2 through 7.8.

### 2. Referenced Documents

2.1 ASTM Standards:<sup>3</sup>

D2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)

D5798 Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical

<sup>&</sup>lt;sup>2</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1694.

<sup>&</sup>lt;sup>3</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



Measurement System Performance

D6377 Test Method for Determination of Vapor Pressure of Crude Oil: VPCR<sub>x</sub> (Expansion Method)

D6378 Test Method for Determination of Vapor Pressure  $(VP_X)$  of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)

D7717 Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis

2.2 IP Standard:

IP 481 Test Method for Determination of the Air Saturated Vapour Pressure (ASVP) of Crude Oil<sup>4</sup>

# 3. Terminology

- 3.1 Definitions:
- 3.1.1 *fuel ethanol (Ed75–Ed85), n*—blend of ethanol and hydrocarbon, of which the ethanol portion is nominally 75 to 85 volume % denatured fuel ethanol.
  - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *absolute vapor pressure*, *n*—the pressure of the airfree sample. It is calculated from the total vapor pressure of the sample by subtracting out the partial pressure of the dissolved air.
- 3.2.2 dry vapor pressure equivalent (DVPE), n—a value calculated by a correlation equation (see 14.2) from the total vapor pressure.
- 3.2.2.1 *Discussion*—The DVPE is expected to be equivalent to the value obtained on the sample by Test Method D4953, Procedure A.
- 3.2.3 total vapor pressure ( $P_{tot}$ ), n—the observed pressure measured in the experiment that is the sum of the partial pressure of the sample and the partial pressure of the dissolved air.
  - 3.3 Abbreviations:
  - 3.3.1 *DVPE*—dry vapor pressure equivalent
  - 3.3.2  $P_{tot}$ —total vapor pressure

# 4. Summary of Test Method

4.1 A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled, evacuated test chamber, or a test chamber with a moveable piston that expands the volume after sample introduction, the internal volume of which is five times that of the total test specimen introduced into the chamber. After introduction into the test chamber, the test specimen is allowed to reach thermal equilibrium at the test temperature, 37.8 °C (100 °F). The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator. Only total pressure measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method, although some instruments can measure the absolute pressure of the sample as well.

4.2 The measured total vapor pressure is converted to a dry vapor pressure equivalent (DVPE) by use of a correlation equation (see Eq 1 in 14.2).

# 5. Significance and Use

- 5.1 Vapor pressure is a very important physical property of volatile liquids.
- 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 This test method is more precise than Test Method D4953, uses a small sample size (1 mL to 10 mL), and requires about 7 min to complete the test.

# 6. Apparatus

- 6.1 Vapor Pressure Apparatus—The type of apparatus suitable for use in this test method employs a small volume test chamber incorporating a transducer for pressure measurements and associated equipment for thermostatically controlling the chamber temperature and for evacuating the test chamber prior to sample introduction or expanding the volume after sample introduction by a moveable piston.
- 6.1.1 The test chamber shall be designed to contain between 5 and 50 mL of liquid and vapor and be capable of maintaining a vapor-to-liquid ratio between 3.95 to 1.00 and 4.05 to 1.00.

Note 4—The test chamber employed by the instruments used in generating the precision and bias statements were constructed of stainless steel, aluminum, or brass.

Note 5—Test chambers exceeding a 15 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 177 kPa (0 psi to 25.7 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of  $\pm 0.8$  kPa ( $\pm 0.12$  psi). The pressure measurement system shall include associated electronics and readout devices to display the resulting pressure reading.
- 6.1.3 A thermostatically controlled heater shall be used to maintain the test chamber at 37.8 °C  $\pm$  0.1 °C (100 °F  $\pm$  0.2 °F) for the duration of the vapor pressure measurement.
- 6.1.4 A platinum resistance thermometer shall be used for measuring the temperature of the test chamber with a resolution of 0.1  $^{\circ}$ C (0.2  $^{\circ}$ F) and an accuracy of 0.1  $^{\circ}$ C (0.2  $^{\circ}$ F).
- 6.1.5 The vapor pressure apparatus shall have provisions for introduction of the test specimen into an evacuated test chamber, or into a test chamber by a moveable piston, and for the cleaning or purging of the chamber following or preceding the test.
- 6.2 *Vacuum Pump*, capable of reducing the pressure in the test chamber to less than 0.01 kPa (0.001 psi) absolute.
- 6.3 Syringe, (optional, depending on sample introduction mechanism employed with each instrument) gas-tight, 1 mL to 20 mL capacity with a  $\pm 1$  % or better accuracy and a  $\pm 1$  % or better precision. If a syringe is used to measure the sample volume, the capacity of the syringe should not exceed two times the volume of the test specimen being dispensed.

 $<sup>^{\</sup>rm 4}$  Available from the Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K.

TABLE 1 Accepted Reference Value (ARV) and Acceptable Testing Range for Reference Fluids Analyzed in the 2003 ILSA

Reference Fluid	ARV [P <sub>tot</sub> ] ± Uncertainty, (kPa)	Recommended Instrument Manufacturer Tolerance, (kPa)	Acceptable Testing Range for Reference Fuel [P <sub>tot</sub> ], (kPa)	
Pentane	112.8 ± 0.2	± 1.0	112.8 ± 1.2 (111.6 to 114.0)	
2,2 Dimethylbutane	$74.1 \pm 0.2$	± 1.0	74.1 ± 1.2 (72.9 to 75.3)	
2,3 Dimethylbutane	57.1 ± 0.2	± 1.0	57.1 ± 1.2 (55.9 to 58.3)	
	ARV [P <sub>tot</sub> ] ± Uncertainty,	Recommended Instrument	Acceptable Testing Range for	
Reference Fluid	(psi)	Manufacturer Tolerance,	Reference Fuel [Ptot],	
	(psi)	(psi)	(psi)	
Pentane	16.36 ± 0.03	± 0.14	16.36 ± 0.17 (16.19 to 16.53)	
2,2 Dimethylbutane	$10.75 \pm 0.03$	± 0.14	10.75 ± 0.17 (10.58 to 10.92)	
2,3 Dimethylbutane	$8.28 \pm 0.03$	± 0.14	8.28 ± 0.17 (8.11 to 8.45)	

<sup>&</sup>lt;sup>A</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1619.

- 6.4 *Iced Water Bath, Refrigerator, or Air Bath,* for chilling the samples and syringe to temperatures between 0 °C to 1 °C (32°F to 34 °F).
- 6.5 *Pressure Measuring Device*, capable of measuring local station pressure with an accuracy of 0.20 kPa (0.03 psi), or better, at the same elevation relative to sea level as the apparatus in the laboratory.
- 6.5.1 When a mercury barometer is not used as the pressure measuring device, the calibration of the pressure measuring device employed shall be periodically checked (with traceability to a nationally recognized standard) to ensure that the device remains within the required accuracy specified in 6.5.
- 6.6 McLeod Vacuum Gage 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 Hg to 5 mm Hg). The calibration of the electronic vacuum measuring device shall be regularly verified in accordance with the annex section on Vacuum Sensors (A6.3) of Test Method D2892.

### 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 on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>5</sup> 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 sections 7.2, 7.3, 7.4, 7.7, and 7.8 (blended by mass with pentane) are suggested for verification of instrument performance (see Section 11), based on the reference fuels analyzed in the 2003 interlaboratory study (ILS)<sup>6</sup> (see Table 1) and 2014 interlaboratory study (ILS)<sup>7</sup>(see

Table 2). Such reference fuels are not to be used for instrument calibration. Table 1 and Table 2 identify the accepted reference value (ARV) and uncertainty limits, as well as the acceptable testing range for each of the reference fuels listed.

Note 6—Verification fluids reported by 28 of the 29 D5191 data set participants in the 2003 ILS<sup>6</sup> included the following (with number of data sets identified in parenthesis): 2,2-dimethylbutane (18), cyclopentane (5), pentane (2), 2,3-dimethylbutane (1), 3-methylpentane (1), and methanol (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

- 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 samples and test specimens in accordance with Practice D4057, except do not use the "Sampling by Water Displacement" section for fuels containing oxygenates. Use either 250 mL or 1 L (1 qt) sized containers filled between 70 % and 80 % with sample. For best testing precision (reproducibility), it is recommended that 1 L sized containers be used.

Note 7—The current precision statements were derived from the 2003 ILS $^6$  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 ullage requirement if it is recognized that the precision can be affected. The differences in precision results obtained from 250 mL and 1 L containers were found to be statistically

<sup>&</sup>lt;sup>5</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see Annual Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>&</sup>lt;sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1619. Contact ASTM Customer Service at service@astm.org.

<sup>&</sup>lt;sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1805. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Accepted Reference Value (ARV) and Acceptable Tolerance Range for Reference Fluids Analyzed in the 2014 ILSA

Reference Fluid	ARV [P <sub>tot</sub> ] ± Expanded Uncertainty, (kPa)	Reference Fluid Standard Deviation (kPa) Determined in ILS	Acceptable Tolerance Range for Single Result on Reference Fluid [P <sub>tot</sub> ], (kPa)
Cyclopentane	72.97 ± 0.21	0.58	72.97 ± 1.95 (71.02 to 74.92)
22.0/78.0 (m/m) Blend of Pentane/Toluene	$46.45 \pm 0.13$	0.36	46.45 ± 1.21 (45.24 to 47.66)
44.0/56.0 (m/m) Blend of Pentane/Toluene	$68.78 \pm 0.23$	0.63	68.78 ± 2.10 (66.68 to 70.88)
68.5/31.5 (m/m) Blend of Pentane/Toluene	88.58 ± 0.21	0.58	88.58 ± 1.95 (86.63 to 90.53)
Reference Fluid	ARV [P <sub>tot</sub> ] ± Expanded Uncertainty, (psi)	Reference Fluid Standard Deviation (psi) Determined in ILS	Acceptable Tolerance Range for Single Result on Reference Fluid [P <sub>tot</sub> ], (psi)
Cyclopentane	$10.58 \pm 0.03$	0.08	10.58 ± 0.28 (10.30 to 10.86)
22.0/78.0 (m/m) Blend of Pentane/Toluene	$6.74 \pm 0.02$	0.05	6.74 ± 0.18 (6.56 to 6.92)
44.0/56.0 (m/m) Blend of Pentane/Toluene	$9.98 \pm 0.03$	0.09	$9.98 \pm 0.30$ (9.68 to 10.28)
68.5/31.5 (m/m) Blend of Pentane/Toluene	12.85 ± 0.03	0.08	12.85 ± 0.28 (12.57 to 13.13)

A Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1805.

significant, whereas there was no statistically observable bias detected between 250 mL and 1 L containers. See tables in Section 16, as well as Figs. 1 and 2 for more specific details on precision differences as a function of DVPE value and container size. In general, numerically better repeatability values were determined at DVPE values < 85 kPa (12.3 psi) for samples in 1 L containers versus 250 mL containers. Secondly, numerically better reproducibility values were determined for samples in 1 L containers versus 250 mL containers for the entire DVPE range covered in 16.1.2.

8.1.3 To determine conformance with specifications, or regulations, or both, it may be necessary to prepare laboratory hand blends of gasoline blendstocks and denatured fuel ethanol for testing purposes, including vapor pressure. If necessary, then, a hand blend sample, prepared carefully in accordance with a procedure such as that described in Practice D7717, shall be considered suitable for the performance of this test. This hand blend, once prepared, shall then be considered equivalent to the 'sample or samples,' referred to in 8.1.4 through 8.5 of this Sampling section, as well as in subsequent sections of this test method.

8.1.4 Perform the vapor pressure determination on the first test specimen withdrawn from a sample container. Do not use the remaining sample in the container for a second vapor pressure determination. If a second determination is necessary, obtain a new sample.

Note 8—The effect of taking more than one test specimen from the same sample container was evaluated as part of the 2003 ILS.<sup>6</sup> 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<sup>6</sup> using the first test specimen withdrawn from 250 mL and 1 L clear glass containers.

- 8.1.5 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate ice bath or refrigerator.
- 8.1.6 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.
- 8.2 Sampling Handling Temperature—Place the sample container and contents in an ice bath or refrigerator to the  $0\,^{\circ}\text{C}$  to  $1\,^{\circ}\text{C}$  (32  $^{\circ}\text{F}$  to 34  $^{\circ}\text{F}$ ) range prior to opening the sample container. Allow sufficient time to reach this temperature.

Note 9—One way to verify the sample temperature is by direct measurement of the temperature of a similar liquid in a similar container placed in the cooling bath or refrigerator at the same time as the sample. Alternatively, temperature-monitoring studies conducted by laboratories

have determined the minimum amount of time necessary to achieve the required temperature requirements stated in 8.2, based upon typical sample receipt temperatures and cooling capacities of the instrumentation employed by the laboratory on samples included in such studies. The results of such studies have subsequently been applied to additional samples submitted for analysis. Typical minimum time durations reported by laboratories have ranged between approximately 30 min and 45 min, however, laboratories choosing this option need to determine the minimum cooling time required for their specific operation by conducting their own temperature-monitoring study.

- 8.3 Verification of Sample Container Filling—With the sample at a temperature of 0 °C to 1 °C, take the container from the cooling bath or refrigerator, and wipe dry with absorbent material. If the container is not transparent, unseal it and using a suitable gage, confirm that the sample volume equals 70 % to 80 % of the container capacity (see Note 10). If the sample is contained in a transparent glass container, verify that the container is 70 % to 80 % full by suitable means (see Note 10).
- 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 necessary, and return the sample container to the cooling bath or refrigerator.

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. For transparent containers, using a marked ruler or by comparing the sample container to a like container which has the 70 % and 80 % levels clearly marked, has been found suitable.

- 8.4 Air Saturation of the Sample in the Sample Container:
- 8.4.1 Transparent Containers Only—Since 8.3 does not require that the sample container be opened to verify the sample capacity, it is necessary to unseal the cap momentarily before resealing it, so that samples in transparent containers are treated the same as samples in non-transparent containers.

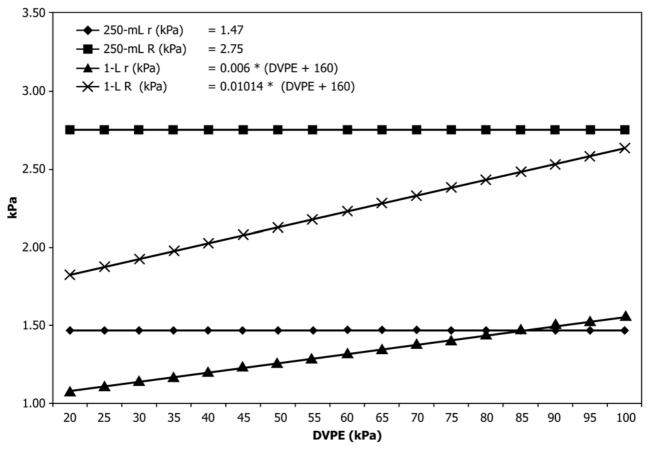


FIG. 1 Plot of DVPE Precision (kPa) by Container Size at Nominal DVPE (kPa) Values Determined

8.4.2 With the sample again at a temperature of 0 °C to 1 °C, take the container from the cooling bath or refrigerator, wipe it dry with an absorbent material, remove the cap momentarily, taking care that no water enters, reseal and shake vigorously. Return it to the cooling bath or refrigerator for a minimum of 2 min.

8.4.3 Repeat 8.4.2 twice more. Return the sample to the cooling bath or refrigerator until the beginning of the procedure.

8.5 Verification of Single Phase Samples—After drawing a test specimen and introducing it 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, mix the sample thoroughly and immediately pour a portion of the remaining sample into a clear glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into two distinct phases. The hazy appearance shall not be considered grounds for rejection of the fuel. If a second phase is observed, discard the test and the sample. Hazy samples may be analyzed (see Section 15).

# 9. Preparation of Apparatus

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

9.2 If a vacuum pump is used for evacuation, prior to sample introduction, visually determine from the instrument display that the test chamber pressure is stable and does not exceed 0.1 kPa (0.01 psi). When the pressure is not stable or exceeds this value, check that the chamber is clean of volatile materials remaining in the chamber from a previous sample or check the calibration of the transducer.

9.3 If a syringe is used for introduction of the sample specimen, chill the syringe to between 0 °C and 1.0 °C (32 °F to 34 °F) such as in a refrigerator or ice bath before drawing in the sample specimen. Water contamination of the syringe reservoir during this cooling procedure shall be avoided. One way to achieve this is by sealing the outlet of the syringe during the cooling process.

# 10. Calibration

10.1 Pressure Transducer:

10.1.1 Perform a calibration check 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.

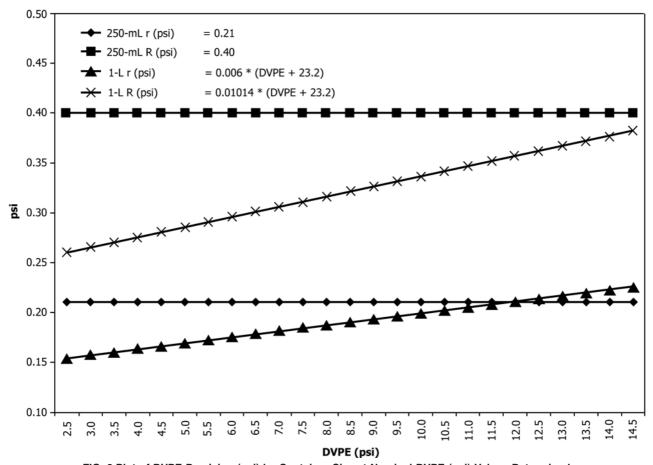


FIG. 2 Plot of DVPE Precision (psi) by Container Size at Nominal DVPE (psi) Values Determined

10.1.2 Connect a McLeod gage or a calibrated electronic vacuum measuring device to the vacuum source in line with the test chamber (Note 12). Apply vacuum to the test chamber. When the vacuum measuring device registers a pressure less than 0.1 kPa (0.8 mm Hg), adjust the indicator 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 the annex section on Vacuum Sensors (A6.3) of Test Method D2892 for further details concerning the calibration of electronic vacuum measuring devices and proper maintenance of McLeod gages.

10.1.3 Open the test chamber of the apparatus to atmosphere and observe the corresponding pressure value of the transducer. Ensure that the apparatus is set to display the total pressure and not a calculated or corrected value. Compare this pressure value against the value obtained from the pressure measuring device, as the pressure reference standard. If the pressure units (for example, kPa, mm Hg, mbar, etc.) differ between the pressure measuring device employed and the vapor pressure apparatus display, use the appropriate conversion factor to convert pressure values to the same units, so that the pressure values can be compared directly. 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. (Warning—Many aneroid barometers, such as those used at weather stations and airports, are

pre-corrected to give sea level readings; these must not be used for calibration of the apparatus.)

10.1.3.1 For mercury barometers used as the pressure measuring device, the barometric pressure reading shall be corrected for the change in the density of the mercury column between 0 and the operating temperature and converted to the same units of pressure as the vapor pressure apparatus display.

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

10.2 *Thermometer*—Check the calibration of the platinum resistance thermometer used to monitor the temperature of the test chamber at least every six months against a nationally traceable thermometer, such as one that is traceable from the National Institute of Standards and Technology (NIST).

#### 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 the test specimen is air saturated according to the procedure given in 8.4, and the spent test specimens are not re-used, in whole or in part. Table 1 and Table 2 provide the accepted reference value (ARV) and uncertainty limits (at least

95 % confidence interval) of reference fluids tested in the 2003 ILS<sup>6</sup> and 2014 ILS,<sup>7</sup> respectively, which are based on the total vapor pressure (P<sub>tot</sub>) measured. This information from the 2003 and 2014 interlaboratory studies was used to establish the acceptable testing or tolerance range for the reference fuels to verify instrument performance.

Note 13—In the 2003 ILS, a study was conducted to determine the effect that the % capacity of material in the 250 mL reference fluid containers supplied to the participants 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  $\geq$ 50 %.

11.2 Values obtained within the acceptable testing or tolerance range intervals in Table 1 and/or Table 2 indicate that the instrument is performing at the level deemed acceptable by this standard. If values outside the acceptable testing or tolerance range intervals are obtained, verify the quality of the pure compound(s) and re-check the calibration of the instrument (see Section 10).

# 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 DVPE 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 X2 for guidelines and suggestions for preparing, storing, and isolating QC samples for use in the test.

# 13. Procedure

- 13.1 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, uncap, and insert a transfer tube or chilled syringe (see 9.3). Draw a bubble-free aliquot of sample into a gas tight syringe or transfer tube, and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container and inserting/securing the syringe into the sealed test chamber shall not exceed 1 min.
- 13.2 Follow the manufacturer's instructions for introduction of the test specimen into the test chamber, and for operation of the instrument to obtain a total vapor pressure result for the test specimen.
- 13.3 Set the instrument to read the result in terms of total vapor pressure. If the instrument is capable of calculating a dry vapor pressure equivalent value, make sure that only the parameters in 14.2 are used.

# 14. Calculation

14.1 Record the total vapor pressure reading from the instrument to the nearest 0.1 kPa (0.01 psi). For instruments

that do not automatically record a stable pressure value, manually record the pressure indicator reading every minute to the nearest 0.1 kPa. When three successive readings agree to within 0.1 kPa, record the result to the nearest 0.1 kPa (0.01 psi).

14.2 Calculate the DVPE using Eq 1. Ensure that the instrument reading used in this equation corresponds to the total pressure and has not been corrected by an automatically programmed correction factor:

$$DVPE$$
, kPa (psi) =  $(0.965 X) - A$  (1)

where:

X = measured total vapor pressure in kPa (psi), and A = 3.78 kPa (or 0.548 psi).

Note 14—The correlation equation was derived from the results of the 1988 cooperative program<sup>8</sup> and confirmed in the 1991 interlaboratory study.<sup>9</sup>

14.3 The calculation described by Eq 1 can be accomplished automatically by the instrument, if so equipped, and in such cases the user shall not apply any further corrections.

# 15. Report

- 15.1 Report the DVPE value to the nearest 0.1 kPa (0.01 psi) without reference to temperature, along with the volume container size (250 mL or 1 L) in which the result was obtained.
- 15.2 If the sample was observed to be hazy in 8.5, report the test result as in 15.1, followed by the letter H.

Note 15—The precision and bias statements have not been determined for hazy samples since these types of samples have not been evaluated as part of an interlaboratory study.

Note 16—The inclusion of the letter H in 15.2 is intended to alert the data recipient that the sample analyzed was hazy. In the event that a laboratory has a computer system that is incapable of reporting alphanumeric results in accordance with the requirements in 15.2, it is permissible for the laboratory to report the result obtained as in 15.1, along with a statement or annotation that clearly conveys to the data recipient that the analyzed sample was hazy.

# 16. Precision and Bias<sup>6</sup>

- 16.1 *Precision*—The precision of this test method was developed in a 2003 interlaboratory cooperative test program. See X1.1 and X1.3 for additional information concerning the number and nature of the sample types and instruments evaluated.
- 16.1.1 Repeatability—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 follows only in one case in

<sup>&</sup>lt;sup>8</sup> Supporting data (the results of this program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1260

<sup>&</sup>lt;sup>9</sup> Supporting data (the results of this test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1286.

TABLE 3 Repeatability and Reproducibility Values for Nominal DVPE Values Determined by D5191

	250 mL C	Containers	1 L Co	ntainers		250 mL C	Containers	1 L Coi	ntainers
DVPE	r	R	r	R	DVPE	r	R	r	R
(kPa)	(kPa)	(kPa)	(kPa)	(kPa)	(psi)	(psi)	(psi)	(psi)	(psi)
20.0	1.47	2.75	1.08	1.83	2.50	0.21	0.40	0.15	0.26
25.0	1.47	2.75	1.11	1.88	3.00	0.21	0.40	0.16	0.27
30.0	1.47	2.75	1.14	1.93	3.50	0.21	0.40	0.16	0.27
35.0	1.47	2.75	1.17	1.98	4.00	0.21	0.40	0.16	0.28
40.0	1.47	2.75	1.20	2.03	4.50	0.21	0.40	0.17	0.28
45.0	1.47	2.75	1.23	2.08	5.00	0.21	0.40	0.17	0.29
50.0	1.47	2.75	1.26	2.13	5.50	0.21	0.40	0.17	0.29
55.0	1.47	2.75	1.29	2.18	6.00	0.21	0.40	0.18	0.30
60.0	1.47	2.75	1.32	2.23	6.50	0.21	0.40	0.18	0.30
65.0	1.47	2.75	1.35	2.28	7.00	0.21	0.40	0.18	0.31
70.0	1.47	2.75	1.38	2.33	7.50	0.21	0.40	0.18	0.31
75.0	1.47	2.75	1.41	2.38	8.00	0.21	0.40	0.19	0.32
80.0	1.47	2.75	1.44	2.43	8.50	0.21	0.40	0.19	0.32
85.0	1.47	2.75	1.47	2.48	9.00	0.21	0.40	0.19	0.33
90.0	1.47	2.75	1.50	2.54	9.50	0.21	0.40	0.20	0.33
95.0	1.47	2.75	1.53	2.59	10.00	0.21	0.40	0.20	0.34
100.0	1.47	2.75	1.56	2.64	10.50	0.21	0.40	0.20	0.34
					11.00	0.21	0.40	0.21	0.35
					11.50	0.21	0.40	0.21	0.35
					12.00	0.21	0.40	0.21	0.36
					12.50	0.21	0.40	0.21	0.36
					13.00	0.21	0.40	0.22	0.37
					13.50	0.21	0.40	0.22	0.37
					14.00	0.21	0.40	0.22	0.38
					14.50	0.21	0.40	0.23	0.38

twenty across the nominal DVPE range of 17.5 kPa to 102.5 kPa (2.5 psi to 14.9 psi).

Container Size	Repeatability (r)	
250 mL	1.47 kPa (0.21 psi)	
1 L	0.006 ( <i>DVPE+B</i> )	
where:	h by Eq.1 and	

B = 160 kPa (23.2 psi).16.1.2 Reproducibility—The difference between two single

and independent test results obtained by different operators working in different laboratories on identical test material withdrawn from 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 follows only in one case in twenty across the nominal DVPE range of 17.5 kPa to 102.5 kPa (2.5 psi to 14.9 psi).

Container Size	Reproducibility (R)
250 mL	2.75 kPa (0.40 psi)
1 L	0.01014 ( <i>DVPE</i> + <i>B</i> )
where:	

DVPE = kPa (psi) value determined by Eq 1, and B = 160 kPa (23.2 psi).

- 16.1.3 See Table 3 and Figs. 1 and 2 for a summary of the precision values determined for nominal DVPE values determined in kPa (psi) from 16.1.1 and 16.1.2.
- 16.2 Bias—Since there is no accepted reference material suitable for determining the bias for the procedures in this test method, bias cannot be determined.
- 16.3 Relative Bias—A statistically significant relative bias was observed in the 1991 interlaboratory cooperative test program between the total pressure obtained using this test method and the dry vapor pressure obtained using Test Method D4953, procedure A. This bias is corrected by the use of Eq 1 (see 14.2), which calculates a DVPE value from the observed total pressure. Secondly, in the 2003 ILS<sup>6</sup>, no observable bias was detected between results obtained in 250 mL and 1 L containers.

# 17. Keywords

17.1 dry vapor pressure; gasoline; hydrocarbon-oxygenate blends; mini method; petroleum products; vapor pressure



#### APPENDIXES

(Nonmandatory Information)

# X1. INFORMATION RELATING TO THE 2003 INTERLABORATORY STUDY (ILS)<sup>6</sup> INVOLVING ANALYSES BY D5191 AND D6378

# X1.1 Samples

X1.1.1 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 (see Eq 1) of the samples ranged from approximately 22 kPa to 110 kPa (3.2 psi to 16.0 psi), which corresponds to an approximate DVPE range of 17.5 kPa to 102.5 kPa (2.5 psi to 14.9 psi).

### **X1.2 Reference Fuels**

X1.2.1 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.

# X1.3 D5191 Instrument Types and Data Sets Evaluated

X1.3.1 A total of 29 data sets were received from 27 laboratories that analyzed samples by D5191, using one or more of the following four instrument types (with the number of data sets submitted by vendor or model, or both, given in parentheses): Grabner VP (9), Grabner VPS (8), Herzog HVP970 and MP970 (6), and Setavap Tester and Analyzer (6).

# X2. GUIDELINES AND SUGGESTIONS FOR PREPARING, STORING, AND ISOLATING QC SAMPLES FOR USE IN THIS TEST

X2.1 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,  $\geq 20$  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). This bulk supply should be kept in a refrigerated location, such as a "cold room" maintained at an approximate temperature of 0 °C to 1 °C. Portions of the bulk supply may be transferred into smaller pre-chilled containers with a total volume of no less than 50 mL and no greater than 1 L<sup>10</sup> filled to 70 % to 80 % capacity and stored in the "cold room" or refrigerator until needed for analysis or transferred from the bulk supply container just prior to analysis.

X2.2 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 Measurement<sub>initial</sub> – Measurement<sub>final</sub>) 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).

X2.2.1 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.

<sup>&</sup>lt;sup>10</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1708.

# **SUMMARY OF CHANGES**

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D5191 - 13) that may impact the use of this standard. (Approved Oct. 1, 2015.)

- (1) Updated subsection 13.1.
- (2) Updated Table 1.
- (3) Updated subsections 7.1.1, 11.1, and 11.2.

(4) Added new Table 2 and new footnote 7 (also footnoted in Table 2).

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