



Designation: D5191 – 07

## 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

### 1. Scope\*

1.1 This test method covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid petroleum products. This test method is suitable for testing samples with boiling points above 0°C (32°F) that exert a vapor pressure between 7 and 130 kPa (1.0 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 to 10 mL. No account is made for dissolved water in the sample.

NOTE 1—Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the precision and bias statements need not apply.

NOTE 2—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 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 14).

1.2 This test method is suitable for calculation of the dry vapor pressure equivalent (DVPE) of gasoline and gasoline-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 *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>2</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)

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical 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<sub>x</sub>) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)

2.2 *IP Standard:*<sup>3</sup> 56a52607/04/astm-d5191-07

IP 481 Test Method for Determination of the Air Saturated Vapour Pressure (ASVP) of Crude Oil<sup>3</sup>

2.3 *EPA Standard:*

40 CFR Part 80 Appendix E, Method 3 Test for Determining Reid Vapor Pressure (RVP) of Gasoline and Gasoline Oxygenate Blends—Evacuated Chamber Method<sup>4</sup>

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

<sup>2</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.

<sup>3</sup> Available from the Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K.

<sup>4</sup> Available from the EPA Web site at <http://www.epa.gov/docs/epacrfr40/chapt-1-info/>

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

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

3.1.1 *absolute vapor pressure*—the pressure of the air-free sample. It is calculated from the total vapor pressure of the sample by subtracting out the partial pressure of the dissolved air.

3.1.2 *dry vapor pressure equivalent (DVPE)*—a value calculated by a correlation equation (see 14.2) from the total vapor pressure.

3.1.2.1 *Discussion*—The DVPE is expected to be equivalent to the value obtained on the sample by Test Method D4953, Procedure A.

3.1.3 *total vapor pressure ( $P_{tot}$ )*—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.

### 3.2 Abbreviations:

3.2.1 DVPE—dry vapor pressure equivalent

3.2.2  $P_{tot}$ —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 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 3—The test chamber employed by the instruments used in generating the precision and bias statements were constructed of stainless steel, aluminum, or brass.

NOTE 4—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 to 177 kPa (0 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  $37.8 \pm 0.1^\circ\text{C}$  ( $100 \pm 0.2^\circ\text{F}$ ) 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  $0.1^\circ\text{C}$  ( $0.2^\circ\text{F}$ ) and an accuracy of  $0.1^\circ\text{C}$  ( $0.2^\circ\text{F}$ ).

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 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.

6.4 *Iced Water Bath, Refrigerator, or Air Bath*, for chilling the samples and syringe to temperatures between  $0$  to  $1^\circ\text{C}$  ( $32$  to  $34^\circ\text{F}$ ).

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 to 0.67 kPa (0.1 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

**TABLE 1 Accepted Reference Value (ARV) and Acceptable Testing Range for Reference Fluids<sup>6</sup>**

Reference Fluid	ARV [ $P_{100}$ ] $\pm$ Uncertainty, (kPa)	Recommended Instrument Manufacturer Tolerance, (kPa)	Acceptable Testing Range for Reference Fuel [ $P_{100}$ ], (kPa)
44.0/56.0 (m/m) Blend of Pentane/Toluene	70.0 $\pm$ 0.2	$\pm$ 1.0	70.0 $\pm$ 1.2 (68.8 to 71.2)
Pentane	112.8 $\pm$ 0.2	$\pm$ 1.0	112.8 $\pm$ 1.2 (111.6 to 114.0)
2,2 Dimethylbutane	74.1 $\pm$ 0.2	$\pm$ 1.0	74.1 $\pm$ 1.2 (72.9 to 75.3)
2,3 Dimethylbutane	57.1 $\pm$ 0.2	$\pm$ 1.0	57.1 $\pm$ 1.2 (55.9 to 58.3)

Reference Fluid	ARV [ $P_{100}$ ] $\pm$ Uncertainty, (psi)	Recommended Instrument Manufacturer Tolerance, (psi)	Acceptable Testing Range for Reference Fuel [ $P_{100}$ ], (psi)
44.0/56.0 (m/m) Blend of Pentane/Toluene	10.15 $\pm$ 0.03	$\pm$ 0.14	10.15 $\pm$ 0.17 (9.98 to 10.32)
Pentane	16.36 $\pm$ 0.03	$\pm$ 0.14	16.36 $\pm$ 0.17 (16.19 to 16.53)
2,2 Dimethylbutane	10.75 $\pm$ 0.03	$\pm$ 0.14	10.75 $\pm$ 0.17 (10.58 to 10.92)
2,3 Dimethylbutane	8.28 $\pm$ 0.03	$\pm$ 0.14	8.28 $\pm$ 0.17 (8.11 to 8.45)

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 7.3, 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). 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 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 a sample and test specimen in accordance with Practice D4057, 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. For best testing precision (reproducibility), it is recommended that a 1-L sized container be used.

NOTE 6—The current precision statements were derived from the 2003 ILS<sup>6</sup> 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 significant, whereas there was no statistically observable bias 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 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 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 7—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.

8.1.4 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 Temperature*—Place the sample container and contents in an ice bath or refrigerator to the 0 to

<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>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1619.

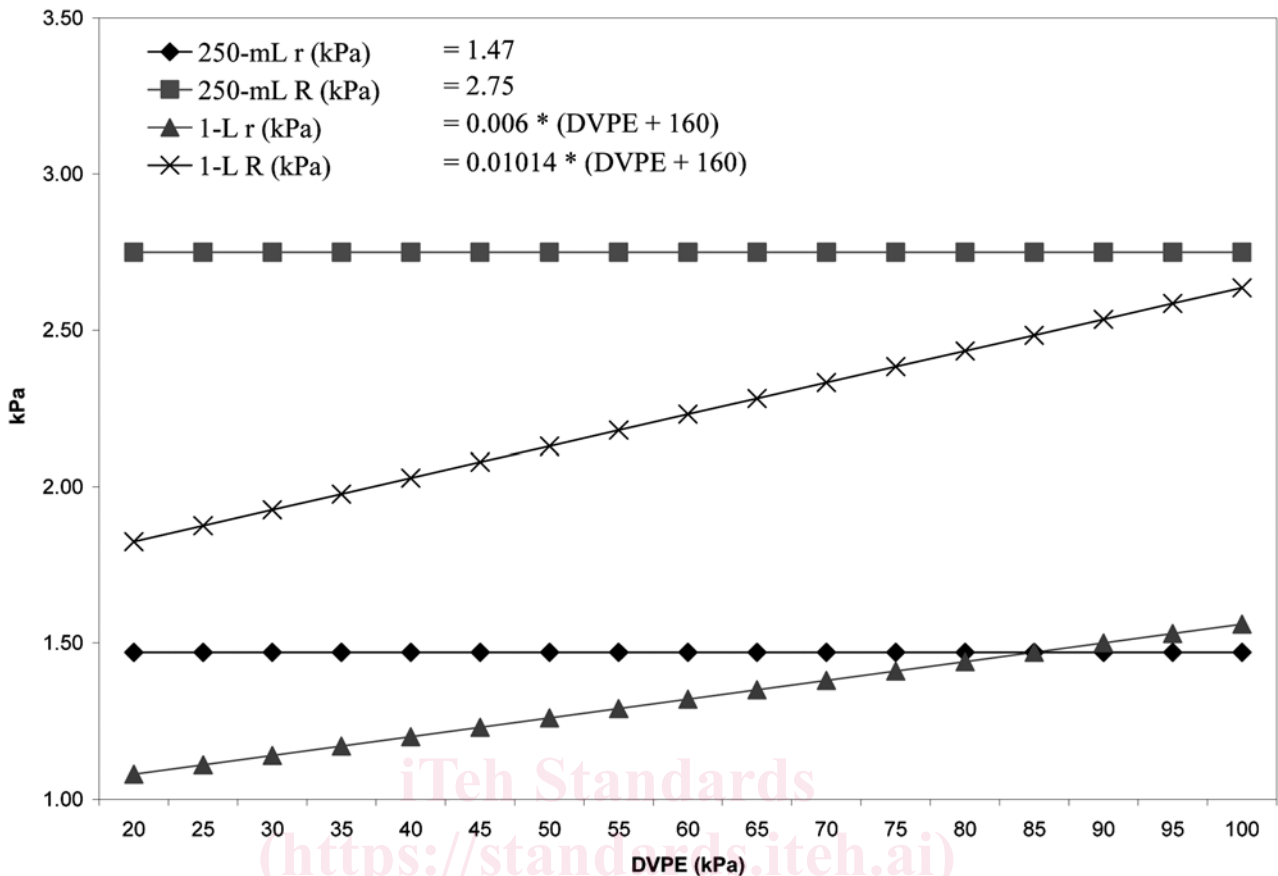


FIG. 1 Plot of DVPE Precision (kPa) by Container Size at Nominal DVPE (kPa) Values Determined

1°C (32 to 34°F) range prior to opening the sample container. Allow sufficient time to reach this temperature.

NOTE 8—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 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 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 9). If the sample is contained in a transparent glass container, verify that the container is 70 to 80 % full by suitable means (see Note 9).

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 9—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.

8.4.2 With the sample again at a temperature of 0 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.