



Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR_x (Expansion Method)¹

This standard is issued under the fixed designation D 6377; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the use of automated vapor pressure instruments to determine the vapor pressure of crude oils at temperatures between 5 and 80°C for vapor-liquid ratios from 4:1 to 0.02:1 ($X = 4$ to 0.02) and pressures from 7 to 500 kPa (1.0 to 70 psi).

1.2 The values stated in SI units are regarded as standard. The inch-pound units given in parentheses are provided for information only.

1.3 *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.*

2. Referenced Documents

2.1 ASTM Standards:²

D 323 Test Method for Vapor Pressure of Petroleum Products (REID Method)

D 2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

D 3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

D 5853 Test Method for Pour Point of Crude Oils

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

¹ 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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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 *dead crude oil*—a term usually employed for crude oils that, when exposed to normal atmospheric pressure at room temperature, will not result in actual boiling of the sample.

3.1.1.1 *Discussion*—Sampling and handling of dead crude oils can usually be done without problems in normal sample containers, such as cans and so forth. The use of pressure cylinders for (sub)sampling and sample storage is a necessary and mandatory requirement in this test method for live crude oils and, to prevent the loss of volatile material and preserve precision, is strongly recommended for dead crude oils as well.

3.1.2 *live crude oil*—a term usually employed for crude oils contained in pressurized systems that, when brought to normal atmospheric pressure at room temperature, will result in actual boiling of the sample.

3.1.2.1 *Discussion*—Sampling and handling of samples of live crude oils will necessitate the use of pressure cylinders and preclude the use of normal sample containers, such as cans and so forth.

3.1.3 *Reid vapor pressure equivalent (RVPE)*—a value calculated by a correlation equation (see 14.3 and Appendix X1) from VPCR₄, which is related to the value obtained on the sample by Test Method D 323.

3.1.4 *vapor-liquid ratio (V/L), n*—the ratio of the vapor volume to the liquid specimen volume.

3.1.4.1 *Discussion*—The total measuring chamber volume is the sum of the vapor volume and the liquid specimen volume.

3.1.5 *vapor pressure of crude oil (VPCR_x)_n*—the pressure exerted in an evacuated chamber at a vapor-liquid ratio of X:1 by conditioned or unconditioned crude oil, which may contain gas, air or water, or a combination thereof, where X may vary from 4 to 0.02.

4. Summary of Test Method

4.1 Employing a measuring chamber with a built-in piston, a sample of known volume is drawn from a pressurized sampling system (floating piston cylinder) into the temperature controlled chamber at 20°C or higher. After sealing the chamber, the volume is expanded by moving the piston until

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

the final volume produces the desired V/L value. The temperature of the measuring chamber is then regulated to the measuring temperature.

4.2 After temperature and pressure equilibrium, the measured pressure is recorded as the $VPCR_x$ of the sample. The test specimen shall be mixed during the measuring procedure by shaking the measuring chamber to achieve pressure equilibrium in a reasonable time between 5 and 30 min.

4.3 For results related to Test Method D 323, the final volume of the measuring chamber shall be five times the test specimen volume and the measuring temperature shall be 37.8°C.

5. Significance and Use

5.1 Vapor pressure of crude oil at various V/Ls is an important physical property for shipping and storage.

5.2 Vapor pressure of crude oil is important to crude oil producers and refiners for general handling and initial refinery treatment.

NOTE 1—A V/L of 0.02:1 ($X = 0.02$) mimics closely the situation of an oil tanker.

5.3 To prevent losses of high volatile compounds, the sample is always maintained at a pressure at least 100 kPa (14.5 psi) higher than the vapor pressure.

5.4 The vapor pressure determined by this test method at a V/L of 4:1 ($VPCR_4$) of crude oil at 37.8°C can be related to the vapor pressure value determined on the same material when tested by Test Method D 323 (see Appendix X1).

5.5 Chilling and air saturation of the sample prior to the vapor pressure measurement is not required.

5.6 This test method allows the determination of $VPCR_x$ samples having pour points above 0°C.

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 5 to 80°C. The measuring chamber shall contain a movable piston with a minimum 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 V/L. 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.³

6.1.1 The measuring chamber shall be designed to have a total volume of 5 to 15 mL and shall be capable of maintaining a V/L of 4:1 to 0.02:1. The accuracy of the adjusted V/L shall be within 0.01.

NOTE 2—The measuring chambers 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.

³ Vapor pressure apparatus meeting these requirements are available from Grabner Instruments, A-1220 Vienna, Dr. Neurathgasse 1, Austria.

Measuring chambers exceeding a 5 mL capacity and having a different design can be used, but the precision and bias statements (see Section 14) are not known to apply.

6.1.2 The pressure transducer shall have a minimum operational range from 0 to 500 kPa (0 to 72.5 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ± 0.5 kPa (± 0.07 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 $\pm 0.1^\circ\text{C}$ for the duration of the test.

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 to 100°C with a resolution of 0.1°C and an accuracy of $\pm 0.1^\circ\text{C}$.

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

6.1.6 The vapor pressure apparatus shall have provisions for shaking the sample during the measuring procedure with a minimum frequency of 1.5 cycles per second.

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 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 Annex A6.3 of Test Method D 2892.

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

7. Reagents and Materials

7.1 *Purity of Reagents*—Use chemicals of at least 99 % purity for quality control checks (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 Society⁴ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

NOTE 4—The chemicals in this section are suggested for cleaning and quality control procedures (see Section 11) and are not used for instrument

⁴ *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 *Analar 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.

calibration. (**Warning**—2,2-dimethylbutane, 2,3-dimethylbutane, toluene, pentane, methanol, and acetone are flammable and health hazards.)

7.2 *Cleaning Solvents*—Use suitable solvents capable of cleaning the measuring chamber, the valves, and the inlet and outlet tubes. Two commonly used solvents are toluene and acetone.

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 requires the utmost precaution and the most meticulous care in the drawing and handling of samples. Sampling of live crude oil shall be performed in accordance with Practice D 3700. Sampling in accordance with Practice D 4057 shall only be used for dead crude oil and if Practice D 3700 is impractical.

NOTE 5—Sampling in accordance with Practice D 4177 may also be used instead of Practice D 4057.

8.1.2 A floating piston cylinder with a minimum sample volume of 200 mL shall be used if the overall volume of the test specimen required for the vapor pressure determination, including the rinsing procedure, is not larger than 20 mL. Larger floating piston cylinders can be used. The minimum piston back-pressure shall be higher than the sample vapor pressure at the introduction temperature of the measuring chamber plus 100 kPa (15 psi) for the shifting of the piston. The maximum back-pressure shall not exceed the maximum measurement pressure of the apparatus pressure transducer. Compressed air, or any other compressed gas, can be used as the back-pressuring agent. The floating piston cylinder shall have provisions for mechanical stirring of the sample and a second valve at the inlet for rinsing.

NOTE 6—The present precision statement was derived using samples in 250-mL floating piston cylinders.

8.1.3 Do not unnecessarily expose the samples to temperatures exceeding 30°C during sampling and storage. For prolonged storage, store the samples in an appropriate room or refrigerator.

8.1.4 Perform the vapor pressure determination on the first test specimen withdrawn from the cylinder after the rinsing step in 9.3. Do not use the remaining sample in the floating piston cylinder for more than three repeat vapor pressure determinations.

8.1.5 In the case of quality control checks with pure compounds (see 11.1), smaller sample containers without applied pressure can be used.

8.2 Sampling Procedures:

8.2.1 If the sample is contained in a pressurized source like a pipeline, use a floating piston cylinder and obtain the sample directly from the source under pressure. Rinse the cylinder by opening the rinsing valve until the crude oil emerges at the second inlet. Close the rinsing valve, and let the piston move slowly until at least 200 mL of sample has entered the cylinder. Close the inlet valve, and apply the back pressure immediately. Check the filling of the cylinder to be at least 200 mL.

8.2.2 If the sample is taken from a nonpressurized source like a storage tank, oil tanker, drum, or other small container,

obtain the sample in accordance with Practice D 4057 and fill the sample into an open floating piston cylinder at ambient pressure. Close the floating piston cylinder, and apply the back-pressure immediately after the cylinder is filled with the sample. Turn the cylinder in a vertical position so that the inlet is on top, and open the inlet valve of the cylinder until the crude oil emerges at the inlet to discharge the captured air. Close the valve, and check the filling of the cylinder to be at least 200 mL.

8.3 *Sample Transfer*—Transfer the sample from the cylinder into the measuring cell at room temperature but at least 5°C above the pour point (as determined by Test Method D 5853) of the sample. Apply a back-pressure that is higher than the vapor pressure of the sample at the introduction temperature plus a minimum of 100 kPa (15 psi) for the piston movement. The applied back-pressure shall not exceed the maximum limit of the pressure transducer used in the vapor pressure apparatus.

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. Toluene has a 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 12.4).

10. Calibration

10.1 Pressure Transducer:

10.1.1 Check the transducer calibration on a monthly basis or when required as indicated from the quality control checks (see Section 11). The transducer calibration is checked using two reference points: zero pressure (<0.1 kPa) and the ambient barometric pressure.

10.1.2 Connect a McLeod gage or a calibrated electronic vacuum measuring device to the vacuum source in line with the measuring chamber (see Note 7). 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 7—Refer to Annex A6.3 of Test Method D 2892 for further details concerning the calibration of electronic vacuum measuring devices and proper maintenance of McLeod gages.

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 total pressure and not a calculated or corrected value. Compare this pressure value with the pressure obtained from a pressure measuring device (see 6.4), 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. When the instrument is used over the full pressure range, a calibration with a dead weight balance shall be carried out.

NOTE 8—Caution: Many aneroid barometers, such as those used at weather stations and airports, are pre-corrected 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 thermometer 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. Quality Control Checks

11.1 Use a verification fluid of known volatility as an independent check against the instrument calibration each day the instrument is in use. For pure compounds, multiple test specimens may be taken from the same container over time. Pressurization of the verification fluid may be omitted, provided the pure compound is air saturated between 0 and 1°C, as described in Test Method D 5191 (see 8.4). Follow the manufacturer’s instruction for sample introduction of verification fluids. The temperature of the verification fluid shall be between 0 and 3°C during the sample introduction, and the measuring procedure shall be in accordance with Section 12 with a V/L of 4:1 and a measuring temperature of 37.8°C. If the observed vapor pressure $VPCR_4$ (37.8°C) differs from the reference value by more than 1.0 kPa (0.15 psi), then check the instrument calibration (see Section 10).

11.2 Some possible materials and their corresponding air saturated vapor pressures at 37.8°C and a V/L of 4:1 ($VPCR_4$) include:

| | | | |
|--------------------|--------------------------------|-----------|-------------|
| 2,2-dimethylbutane | $VPCR_4(37.8^\circ\text{C}) =$ | 73.4 kPa | (10.65 psi) |
| 2,3-dimethylbutane | $VPCR_4(37.8^\circ\text{C}) =$ | 57.4 kPa | (8.32 psi) |
| Pentane | $VPCR_4(37.8^\circ\text{C}) =$ | 112.1 kPa | (16.26 psi) |
| Methanol | $VPCR_4(37.8^\circ\text{C}) =$ | 38.9 kPa | (5.64 psi) |
| Toluene | $VPCR_4(37.8^\circ\text{C}) =$ | 12.9 kPa | (1.87 psi) |

NOTE 9—The value for 2,2-dimethylbutane in this list was derived from the 1991 interlaboratory cooperative test program⁵ and represents the total pressure of the air saturated liquid at 37.8°C at a V/L of 4:1. The other values were determined in limited cross check programs.

NOTE 10—It is recommended that at least one type of verification fluid used in 11.1 have a vapor pressure representative of the crude(s) regularly tested by the equipment. The vapor pressure measurement process (including operator technique) can be checked periodically by performing this test method on previously prepared samples from one batch of product, as per procedure described in 8.1.2. Samples should be stored in an environment suitable for long term storage without sample degradation. Analysis of result(s) from these quality control samples can be carried out using control chart techniques.⁶

NOTE 11—Caution: The use of single component verification materi-

als, such as those listed in 11.2, will only prove the calibration of the equipment. It will not check the accuracy of the entire test method, including sample handling, because losses due to evaporation will not decrease the sample vapor pressure that happens with losses of light ends in multi-component mixtures.

12. Procedure

12.1 Set the sample introduction temperature of the measuring chamber between 20 and 37.8°C. For crude oil samples with a pour point higher than 15°C, set the injection temperature at least 5°C above the pour point temperature of the sample.

12.2 Set the V/L to the desired value X:1 (For test results related to Test Method D 323, set the V/L to 4:1).

12.3 Mix the sample in the pressurized floating piston cylinder vigorously with the mechanical stirrer to ensure a homogenous sample, and connect the outlet of the cylinder to the inlet of the apparatus.

12.4 Follow the manufacturer’s instructions for introducing the test specimen into the measuring chamber. The volume of the specimen shall be such that after the expansion to the final volume the programmed V/L is achieved.

12.5 After closing the inlet valve, expand the volume of the measuring chamber to the final volume.

12.6 Switch-on the shaker, and leave it on during the entire measuring procedure

12.7 Adjust the temperature control to the measuring temperature (for results related to Test Method D 323, adjust to a temperature of 37.8°C). The measuring temperature shall not be lower than at least 10°C above the pour point temperature of the sample.

12.8 Wait for temperature equilibrium between measuring chamber and specimen, and monitor the total vapor pressure every 30 ± 5 s. When three successive readings agree within 0.3 kPa, record this resulting vapor pressure as $VPCR_x$ ($T_m^\circ\text{C}$).

13. Report

13.1 Report the results to the nearest 0.1 kPa (0.02 psi), and specify the test temperature and V/L.

$$VPCR_x (T_m^\circ\text{C}) = \text{##.## kPa or ##.## psi} \quad (1)$$

where:

X = vapor-liquid ratio, and
 T_m = measuring temperature.

14. Precision and Bias

14.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

NOTE 12—The following precision data are provisional and further data are to be developed in an interlaboratory cooperative test program before the five year reapproval required by the society.

14.1.1 *Repeatability*— The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values calculated as per the following equations only in one case in twenty:

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1286.

⁶ Reference ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th Edition, Section 3: Control Charts for Individuals.

V/L = 4 and 37.8°C: repeatability = 0.015 VPCR₄ (37.8°C) (2)

V/L = 0.1 and 37.8°C: repeatability = 0.055 VPCR_{0.1} (37.8°C) (3)

V/L = 0.2 and 37.8°C: repeatability = 0.065 VPCR_{0.02} (37.8°C) (4)

NOTE 13—The listed repeatability data were derived on more than 30 different crude oil samples in three different laboratories. The vapor pressure ranges were from 2.8 to 16.6 kPa at V/L of 4:1, and vapor pressures up to 240 kPa at a V/L of 0.02:1. Further data are to be developed in an interlaboratory cooperative test program before the five year reapproval required by the society.

14.1.2 *Reproducibility*—The reproducibility of this test method is being determined and will be available within five years.

14.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedures in this test method, a bias cannot be determined.

14.3 *Relative Bias to Test Method D 323 for Crude Oil*—A statistically significant relative bias was observed for crude oil in a limited interlaboratory test program between VPCR₄(37.8°C) obtained using this test method and the vapor pressure obtained using Test Method D 323 (see Appendix X1).

15. Keywords

15.1 crude oil; mini method; Reid vapor pressure; vapor pressure

APPENDIXES

(Nonmandatory Information)

X1. RELATIVE BIAS TO TEST METHOD D 323 FOR VAPOR PRESSURE OF CRUDE OIL

X1.1 The VPCR_x at a V/L of 4:1 and a measuring temperature of 37.8°C determined by this test method can be related to the value determined by Test Method D 323.

X1.2 The sample is collected in accordance with Section 8.

X1.3 The bias is corrected by the use of Eq X1.1 to calculate the equivalent RVP value from the observed VPCR₄ at a measuring temperature of 37.8°C.

$$RVPE = A \times VPCR_4(37.8^\circ C) + B \quad (X1.1)$$

where:

$A = 0.752$, and

$B = 6.07$ kPa (0.88 psi).

NOTE X1.1—This relative bias was developed in a limited interlaboratory cross check program on live and dead crude oil samples. The sample set consisted of 141 samples with vapor pressures ranging from 18.9 to 113.7 kPa (2.75 to 16.5 psi). The standard deviation was calculated as 1.86 kPa (0.27 psi). Further data are to be developed in an interlaboratory cooperative test program before the five year reapproval required by the society.

X2. VAPOR PRESSURE OF CRUDE OIL VERSUS TEMPERATURE

X2.1 For several purposes, for example, transport and storage, it may be useful to measure the vapor pressure behavior of crude oil versus temperature. To obtain such information proceed as follows.

X2.1.1 Follow the instructions outlined in 12.1-12.8. The initial measuring temperature is programmed to the lowest temperature of interest but not lower than the temperature stated in 12.7.

X2.1.2 Increase the measuring temperature in steps to the highest temperature of interest but not higher than 80°C. Each step is measured in accordance with 12.7 and 12.8.

X2.1.3 The result is either recorded as a series of values, or plotted as log (VPCR_x) versus 1/T, where T is the absolute measuring temperature in° K (°C + 273.2).

NOTE X2.1—No precision data have been developed for temperatures different from 37.8°C.

SUMMARY OF CHANGES

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D 6377 – 99) that may impact the use of this standard.

- (1) Updated 2.1 to replace references to D 1160 with references for D 2892. explicitly reference Note 7.
- (2) Updated 6.3 to reference D 2892 requirements and 10.1.2 to (3) Updated Note 7.

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