

Designation: D6377 - 14

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

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1. Scope*

1.1 This test method covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in vacuum of crude oils. This test method is suitable for testing samples that exert a vapor pressure between 25 kPa and 180 kPa at 37.8 $^{\circ}$ C at vapor-liquid ratios from 4:1 to 0.02:1 (X = 4 to 0.02).

Note 1—This test method is suitable for the determination of the vapor pressure of crude oils at temperatures from 0 $^{\circ}$ C to 100 $^{\circ}$ C and pressures up to 500 kPa, but the precision and bias statements (see Section 14) may not be applicable.

- 1.2 This test method allows the determination of vapor pressure for crude oil samples having pour points above 0 °C.
- 1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 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 warning statements, see 7.2.1 7.3.2.

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)
- D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

D5853 Test Method for Pour Point of Crude Oils

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:
- 3.1.1 platinum resistance thermometer, n—temperature measuring device constructed with a length of platinum wire, whose electrical resistance changes in relation to temperature.
- 3.1.2 *vapor-liquid ratio* (*V/L*), *n*—the ratio of the vapor volume to the liquid volume of specimen, in equilibrium, under specified conditions.
 - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *dead crude oil, n*—crude oil with sufficiently low vapor pressure that, when exposed to normal atmospheric pressure at room temperature, does not result in boiling of the sample.
- 3.2.1.1 *Discussion*—Sampling and handling of dead crude oils can usually be done without loss of sample integrity or other problems by using normal, non-pressurized sample containers such as cans.
- 3.2.2 *live crude oil, n*—crude oil with sufficiently high vapor pressure that it would boil if exposed to normal atmospheric pressure at room temperature.
- 3.2.2.1 *Discussion*—Sampling and handling live crude oils requires a pressurized sample system and pressurized sample containers to ensure sample integrity and prevent loss of volatile components.
- 3.2.3 *Reid vapor pressure equivalent (RVPE), n*—a value calculated by a defined correlation equation (see Eq X1.1) from VPCR₄ at 37.8 °C that is expected to be equivalent to the vapor pressure value obtained by Test Method D323.
- 3.2.3.1 *Discussion*—As noted in 14.3 and Appendix X1, subsection X1.2, since Eq X1.1 for estimating RVPE is not universally applicable to all crude oils, it is recommended to report the VPCR₄ (38.7 °C) result for a crude oil sample.

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.



- 3.2.4 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.
 - 3.3 Abbreviations:
 - 3.3.1 ARV, n—accepted reference value
 - 3.3.2 RVPE, n—Reid vapor pressure equivalent
 - 3.3.3 V/L, n—vapor liquid ratio
- 3.3.4 $VPCR_x$, n—vapor pressure of crude oil at x vapor liquid ratio

4. Summary of Test Method

- 4.1 Employing a measuring chamber with a built-in piston, a sample of known volume is drawn from the sample container into the temperature controlled chamber at 20 °C or higher. After sealing the chamber, the volume is expanded by moving the piston until 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 of 5 min to 30 min.
- 4.3 For results related to Test Method D323, 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. 52 1436
- Note 2—A vapor-liquid ratio of 0.02:1~(X=0.02) mimics closely the situation of an oil tanker.
- 5.2 Vapor pressure of crude oil is important to crude oil producers and refiners for general handling and initial refinery treatment.
- 5.3 The vapor pressure determined by this test method at a vapor-liquid ratio of 4:1 (VPCR₄) 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 D323 (see Appendix X1).
- 5.4 Chilling and air saturation of the sample prior to the vapor pressure measurement is not required.
- 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 $^{\circ}$ C to 100 $^{\circ}$ C. The measuring chamber shall contain a movable piston with a minimum dead volume of less than 1 $^{\circ}$ 0 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.
- 6.1.1 The measuring chamber shall be designed to have a total volume of 5 mL 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 3—The measuring chambers employed by the instruments used in generating the precision and bias statements were constructed of nickel plated aluminium, stainless steel and brass with a total volume of 5 mL. Measuring chambers exceeding a 5 mL capacity and different design can be used, but the precision and bias statement (see Section 14) may not be applicable.
- 6.1.2 The pressure transducer shall have a minimum operational range from 0 kPa to 500 kPa with a minimum resolution of 0.1 kPa and a minimum accuracy of ± 0.5 kPa. 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 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 °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 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 absolute.
- 6.3 McLeod Vacuum Gage or Calibrated Electronic Vacuum Measuring Device for Calibration, to cover at least the range of 0.01 kPa to 0.67 kPa. The calibration of the electronic measuring device shall be regularly verified in accordance with Annex A of 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 or better, at the same elevation relative to sea level as the apparatus in the laboratory.

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

7. Reagents and Materials

7.1 Purity of Reagents—Use chemicals of at least 99 % purity for verification of instrument performance (see Section 11). Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical

TABLE 1 Accepted Reference Value (ARV) and Acceptable Testing Range for Air Saturated Reference Fluids^A

Reference Fluid	ARV [P _{tot}] ± Uncertainty, (kPa)	Recommended Instrument Manufacturer Tolerance, (kPa)	Acceptable Testing Range for Reference Fuel [P _{tot}], (kPa)
Pentane	112.8 ± 0.2	± 1.0	112.8 ± 1.2 (111.6 to 114.0)
2,2 Dimethylbutane	74.1 ± 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)

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

Reagents of the American Chemical Society where such specifications are available.³ Other grades may 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 7.2.1, 7.2.2, and 7.2.3 are suggested for verification of instrument performance (see Section 11), based on the air saturated reference fuels analyzed in the Test Method D5191 2003 interlaboratory study (ILS)⁴ (see Table 1). P_{tot} used in Test Method D5191 is equivalent to VPCR₄ used in this test method). 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.
- 7.1.2 The chemicals in 7.3.1 and 7.3.2 are suggested for use as rinsing solvents capable of cleaning the measuring chamber, the valves and the inlet and outlet tubes.
 - 7.2 Verification Fluids:
- 7.2.1 2,2-Dimethylbutane, (Warning—2,2-dimethylbutane is flammable and a health hazard.)
- 7.2.2 2,3-Dimethylbutane, (Warning—2,3-dimethylbutane is flammable and a health hazard.)
- 7.2.3 *Pentane*, (Warning—Pentane is flammable and a health hazard.)
 - 7.3 Solvents:
- 7.3.1 *Toluene*, (**Warning**—Toluene is flammable and a health hazard.)
- 7.3.2 *Acetone*, (**Warning**—Acetone 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 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 D3700. Sampling in accordance with Practice D4057 shall only be used for dead crude oil and if Practice D3700 is impractical.

Note 5—Sampling in accordance with Practice D4177 may also be

used instead of Practice D4057.

- 8.1.2 For sampling in accordance with Practice D3700, 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 backpressure shall be higher than the sample vapor pressure at the introduction temperature of the measuring chamber plus 100 kPa for the shifting of the piston. The maximum backpressure shall not exceed the maximum measurement pressure of the apparatus pressure transducer. Compressed air, or any other, non-flammable 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.
- 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.

Note 6—The current precision statements were derived from the 2005 ILS using samples in 250 mL floating piston cylinders (see 14.3).

8.2.2 If the sample is taken from a non-pressurized source like a storage tank, oil tanker, drum or other container, obtain a sample and test specimen in accordance with Practice D4057. Use either a 250 mL or 1 L 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 7—The current precision statements were derived from the 2005 ILS using samples in 1 L amber glass containers (see 14.3). However, samples in containers of other sizes, as prescribed in Practice D4057, may

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 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.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1619.