



## Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR<sub>x</sub> (Expansion Method)<sup>1</sup>

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 ( $\epsilon$ ) 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.* For specific warning statements, see Note 5.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 323 Test Method for Vapor Pressure of Petroleum Products (REID Method)<sup>2</sup>
- D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressure<sup>2</sup>
- D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder<sup>3</sup>
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>
- D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)<sup>3</sup>
- D 5853 Test Method for Pour Point of Crude Oils<sup>4</sup>

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 05.03.

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) from VPCR<sub>4</sub>, 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<sub>x</sub>), 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

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.<sup>5</sup>

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.

<sup>5</sup> 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  $\pm 0.5$  kPa ( $\pm 0.07$  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 to 5 mm Hg). The calibration of the electronic measuring device shall be regularly verified in accordance with Annex A1 of Test Method D 1160.

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 Society<sup>6</sup> 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 calibration.

<sup>6</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 *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.

2,2-Dimethylbutane (**Warning**—See Note 5)

2,3-Dimethylbutane (**Warning**—See Note 5)

Toluene (**Warning**—See Note 5)

Pentane (**Warning**—See Note 5)

Methanol (**Warning**—See Note 5)

Acetone (**Warning**—See Note 5)

NOTE 5—**Warning:** 2,2-dimethylbutane, 2,3-dimethylbutane, toluene, pentane, methanol, and acetone are flammable and a health hazard.

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 6—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 7—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. Apply vacuum to the measuring chamber. When the external gage 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 external gage as dictated by the instrument design or manufacturer's instructions.

NOTE 8—Refer to Annex A1 of Test Method D 1160 for further details concerning the calibration of pressure sensors and McLeod gages.

10.1.3 Open the measuring chamber of the apparatus to atmospheric pressure, and observe the corresponding pressure