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Designation: D 6378 – 99^{e1}


Designation: D 6378 – 03

An American National Standard

Standard Test Method for Determination of Vapor Pressure (VP_x) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)¹

This standard is issued under the fixed designation D 6378; 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.

~~ε¹ Note—Note 17 was corrected editorially in September 1999.~~

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

Current edition approved ~~Jan. 10, 1999~~; Dec. 1, 2003. Published ~~April~~ January 2004. Originally approved in 1999. Last previous edition approved in 1999 as D 6378 – 99^{ε1}.

1. Scope*

1.1 This test method covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in vacuum by volatile, liquid petroleum products, hydrocarbons, and hydrocarbon-oxygenate mixtures. This test method is suitable for testing samples with boiling points above 0°C (32°F) that exert a vapor pressure between 7 and 150 kPa (1.0 and 21psi) 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.

NOTE 1—The test method is suitable for the determination of the vapor pressure of volatile, liquid petroleum products at temperatures from 0 to 100 °C at vapor to liquid ratios of 4:1 to 1:1 (X = 4 to 1) and pressures up to 500 kPa (70 psi), but the precision statement (see Section 15.2) may not be applicable.

1.2 The VP_x determined by this test method at a vapor-liquid ratio of 4:1 (X = 4) of gasoline and gasoline-oxygenate blends at 37.8°C can be correlated to the dry vapor pressure equivalent (DVPE) value determined by Test Method D 5191 (see Section 15.2).

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 hazard statements, see Note 6.*

2. Referenced Documents

2.1 *ASTM Standards:*²

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

D 1160 Test 2892 Test Method for Distillation of Crude Petroleum Products at Reduced Pressure² (15-Theoretical Plate Column)

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)

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

D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurements

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *dry vapor pressure equivalent (DVPE)*—a value calculated by a correlation equation from the total pressure (Test Method D 5191), which is equivalent to the value obtained on the sample by Test Method D 4953, Procedure A.

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*, Vol 05.01, volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.2 *partial pressure from dissolved air (PPA), n*—the pressure exerted in vacuum from dissolved air that escapes from the liquid phase into the vapor phase.

3.1.3 *Reid vapor pressure equivalent (RVPE)*— a value calculated by a correlation equation from the TP_X , which is equivalent to the value obtained on the same by Test Method D 323.

3.1.4 *total pressure (TP_X), n*— the pressure exerted in vacuum by air- and gas-containing petroleum products, components and feedstocks, and other liquids, in the absence of undissolved water at a vapor-liquid ratio of X:1.

3.1.5 *vapor pressure (VP_X), n*— the total pressure minus the PPA in the liquid at a vapor-liquid ratio of X:1.

$$VP_X = TP_X - PPA \quad (1)$$

4. Summary of Test Method

4.1 Employing a measuring chamber with a built-in piston, a sample of known volume is drawn into the temperature controlled chamber at 20°C or higher. After sealing the chamber, an expansion is performed in three steps to a final volume of (X+1) times that of the test specimen. After each expansion, the TP_X is determined. The PPA and the solubility of air in the specimen are calculated from the three resulting pressures. The temperature of the chamber is then increased to a specified value, and the TP_X is determined. The (VP_X) is calculated by subtracting the PPA in the liquid, which has been gas corrected for the temperature, from TP_X . For DVPE results, in accordance with Test Method D 5191, the volume of the measuring chamber shall be five times that of the total test specimen and the measuring temperature shall be 37.8°C.

~~NOTE 2—~~**Caution:** For ~~2—~~For liquids containing very low levels of high vapor pressure contaminants, which behave like a gas, this test method of determination of the PPA and gases may lead to wrong results since the partial pressure of the contaminants will be included in the PPA. This effect is shown when the value of the PPA and gases exceeds the average maximum limit of 7 kPa (1 psi).

5. Significance and Use

5.1 Vapor pressure is a very important physical property of volatile liquids for shipping and storage.

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 In this test method, an air saturation procedure prior to the measurement is not required, thus eliminating losses of high volatile compounds during this step. This test method is faster and minimizes potential errors from improper air saturation. This test method permits VP_X determinations in the field.

5.5 This test method can be applied in on-line 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 to 100 °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 vapor-liquid ratio. 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 contain between 5 and 15 mL of liquid and vapor and be capable of maintaining a vapor-liquid ratio of 4:1 to 1:1. The accuracy of the adjusted vapor-liquid ratio shall be within 0.05.

~~NOTE 3—~~The measuring chamber 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. Measuring chambers exceeding a 5-mL capacity can be used, but the precision and bias statements (see Section 15) are not known to apply.

6.1.2 The pressure transducer shall have a minimum operational range from 0 to 200 kPa (0 to ~~74~~ 29 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ± 0.2 kPa (~~± 0.002~~ (± 0.03 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 20 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 ~~from~~ for rinsing the measuring chamber with a solvent of low vapor pressure or with the next sample to be tested.

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

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 ~~A1~~ A6.3 of Test Method ~~D 1160~~ 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 4—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 10). Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society⁴ where such specifications are available. 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.

NOTE 5—The chemicals in this section are suggested for quality control procedures (see Section 11) and are not used for instrument calibration.

~~2,2-Dimethylbutane (Warning—See Note 6)~~

~~2,3-Dimethylbutane (Warning—See Note 6)~~

~~Toluene (Warning—See Note 6)~~

~~Pentane (Warning—See Note 6)~~

~~Methanol (Warning—See Note 6)~~

~~Acetone (Warning—See Note 6)~~

NOTE 6—~~Warning: 2,2-dimethylbutane, 2,3-dimethylbutane, toluene, pentane, methanol, and acetone are flammable and health hazards.~~

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 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 D 4057, D 4177, D 5842, or D 5854 when appropriate, except do not use the Sampling by Water Displacement section for fuels containing oxygenates. Use a container not less than 300 mL and not more than 1 L in size filled at least 70 % with sample.

NOTE 7~~6~~—The present precision statement was derived using samples in 1 L (1 qt) containers. However, samples in containers of other sizes as prescribed in Practice D 4057 can be used, with the same filling requirement, but the precision can be affected.

8.1.3 Perform the VP_X determination, including the rinsing (see 9.4), on the first test specimen withdrawn from a sample container. Do not use the remaining sample in the container for a second VP_X determination. If a second determination is necessary, obtain a new sample.

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*—Cool the sample container and contents in a ice bath or refrigerator to the 0 to 1°C (32 to 34°F) range prior to opening the sample container. Allow sufficient time to reach this temperature. Verify the sample temperature 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.

NOTE 8~~7~~—Cooling of the sample may be omitted if provisions are provided that avoid loss of high volatile components during the sample introduction. Sample introduction with a pressurized sample container is a useful procedure. If a statement for hazy sample is required, cooling to the required temperature is necessary.

8.3 *Verification of Sample Container Filling*—With the sample at a temperature below 10°C, take the container from the cooling bath and wipe dry with absorbent material. If the sample is contained in a transparent container, verify that the container is at least 70 % full by suitable means, such as by using a marked ruler or by comparing it to a like container that has the 70 % levels clearly marked. If the container is not transparent, unseal it and, using a suitable gage, confirm that the sample volume equals at least 70 % of the container capacity.

8.3.1 Discard the sample if the container is filled to less than 70 %, by volume, of the container capacity.

⁴ *Annual Book of Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of ASTM reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, Vol 05-03, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.3.2 Reseal the container, if opened, and place it back in the cooling bath or refrigerator.

8.4 *Verification of Single Phase Sample*—After drawing the test specimens and transferring them 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, shake the sample thoroughly and immediately pour a portion of the remaining sample into a glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into distinct phases. If the sample separates into two distinct phases with a discernible common boundary, then discard the test and the sample. If the sample has a hazy appearance, but does not have two distinct phases, then phase separation has not occurred. The test is valid, but the precision and bias in Section 15 may not apply (see Section 14).

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. Methanol 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 12.24).

9.4 If a syringe is used for introduction of the test specimen, chill the syringe to the temperature of the sample (below 10°C) in an air or water bath before drawing in the specimen. Avoid water contamination of the syringe reservoir by suitably sealing the syringe during the cooling process.

10. Calibration

10.1 Pressure Transducer:

10.1.1 Check the calibration of the transducer on a monthly basis or when required as indicated from the quality control checks (see Section 11). The calibration of the transducer 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 8). Apply vacuum to the measuring chamber. When the ~~external gage 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 ~~external gage vacuum measuring device~~ as dictated by the instrument design or manufacturer's instructions.

NOTE 98—Refer to Annex A1 A6.3 of Test Method ~~D H60 D 2892~~ for further details concerning the calibration of ~~pressure sensors~~ 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 TP_X and not a calculated or corrected value. Compare this pressure value with the pressure obtained from a mercury barometer, or equivalent, 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.

NOTE 10—~~Caution: Many~~ Many aneroid barometers, such as those used at weather stations and airports, are precorrected 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. If the observed VP_X 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 vapor pressures at 37.8°C and a vapor-liquid ratio of 4:1 (VP_4) include:

2,2-Dimethylbutane	$VP_4=$	68.0 kPa	(9.86 psi)
2,3-Dimethylbutane	$VP_4=$	51.1 kPa	(7.41 psi)
Pentane	$VP_4=$	107.4 kPa	(15.57 psi)
Methanol	$VP_4=$	32.0 kPa	(4.63 psi)
Toluene	$VP_4=$	7.1 kPa	(1.03 psi)

NOTE 140—The value for 2,2-dimethylbutane in this list was derived from the 1991 interlaboratory cooperative test program⁵ and represents the VP_4 values of the air saturated liquid. The other values were determined in limited cross check programs.

NOTE 121—It is recommended that at least one type of verification fluid used in 11.1 have a vapor pressure representative of the fuel(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 132—**Caution:** The use of single component verification materials, such as 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 as 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.

12.2 Set the vapor-liquid ratio to the desired value X:1 (for test results related to Test Method D 5191, set the vapor-liquid ratio to 4:1).

12.3 Connect an aliquot of sample either in a syringe, pressurized sample container, or a tubing immersed in the sample to the inlet of the apparatus. Make provisions to avoid loss of high volatiles in the sample. The overall volume of the sample shall exceed the volume of three rinsing cycles plus the final test volume. Follow the manufacturer's instructions for introducing the test specimen into the measuring chamber.

12.4 Perform the three rinsing cycles (see 9.3) immediately after connecting the sample.

12.5 Introduce the test specimen into the measuring chamber by a stroke of the piston. The volume of the specimen shall be such that after the expansion to the final volume the programmed vapor-liquid ratio is achieved.

12.6 Close the inlet valve, and make the first expansion by a stroke of the piston.

12.7 Monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,1}$.

12.8 Make the second expansion, and monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,2}$.

12.9 Repeat 12.8 for the third expansion, and record the resulting total pressures as $TP_{X,3}$.

12.10 Allow the temperature of the measuring chamber to increase to within 0.1°C of the desired test temperature. Monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,t}$.

12.11 *Check for Sample Separation* —After introducing the test specimen into the instrument for analysis, check the remaining sample for sample separation (see 8.4)

13. Calculation

13.1 Calculate the partial pressure of the air, PPA_i , after the sample has been introduced into the measuring chamber and expanded to the final volume, using the following equation:

$$PPA_i = \frac{(TP_{X,1} - TP_{X,3})(TP_{X,2} - TP_{X,3})}{\frac{V_3 - V_1}{V_2 - V_1}(TP_{X,1} - TP_{X,2}) - (TP_{X,1} - TP_{X,3})} \quad (2)$$

where:

$TP_{X,1}$ = total pressure after first expansion,

$TP_{X,2}$ = total pressure after second expansion,

$TP_{X,3}$ = total pressure after third and final expansion,

V_1 = volume after the first expansion,

V_2 = volume after the second expansion, and

V_3 = final volume after the third expansion.

13.2 Calculate the partial pressure of the air at test temperature t , PPA_t , using the following equation:

$$PPA_t = PPA_i (273.2 + t) / (273.2 + t_i) \quad (3)$$

where:

t_i = temperature of the measuring chamber when the test specimen is introduced and expanded, in degrees Celsius, and

t = temperature, in degrees Celsius.

13.3 Calculate the vapor pressure $VP_{X,t}$ at test temperature t , using the following equation:

$$VP_{X,t} = TP_{X,t} - PPA_t \quad (4)$$

⁶ Vapor pressure apparatus meeting these requirements are available from Grabner Instruments, A-1220 Vienna, Dr. Neurathgasse 1, Austria.

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

Reagent Chemicals, American Chemical Society Specifications;

⁶ Reference ASTM MNL 7, American Chemical Society, Washington, DC. For suggestions *Manual on the testing Presentation of reagents not listed by the American Chemical Society, see Analar Standards Data Control Chart Analysis, 6th Edition, Section 3: Control Charts 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. Individuals.*

where:

$TP_{X,t}$ = total pressure at temperature t , and

PPA_t = partial pressure of the air at temperature t .

13.4 See Appendix X1 for the derivation of the equations.

14. Report

14.1 Report the results to the nearest 0.1 kPa (0.02 psi), and specify the test temperature and vapor-liquid ratio.

$$VP_X(Tm^{\circ}C) = \#\#\.# \text{ kPa or } \#\#\.#\#\ \text{ psi} \quad (5)$$

$$Pair(Tm^{\circ}C) = \#\#\.# \text{ kPa or } \#\#\.#\#\ \text{ psi} \quad (6)$$

Tm

where:

X = vapor-liquid ratio,

$Pair$ = partial pressure of the dissolved air, and

Tm = measuring temperature.

14.2 If a haze was observed in 8.4, state on the report document that the test sample was hazy. Examples of acceptable reporting statements are a result of xx.xH or the statement “Sample Hazy - Yes.”

15. Precision and Bias

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

15.1.1 *Repeatability*— The difference between successive test results obtained by 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 following value only in one case in twenty:

$$\text{repeatability} = 0.50 \text{ kPa (0.07 psi)}$$

NOTE 143—The listed repeatability value was derived with 208 measurements on four different gasoline samples. The vapor pressure ranges were from 58 to 75 kPa at a vapor to liquid ratio of 4:1. Further data are to be developed in an interlaboratory cooperative test program before the five year reapproval required by the society.

15.1.2 *Reproducibility*— The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty:

$$\text{reproducibility} = 1.63 \text{ kPa (0.22 psi)}$$

NOTE 154—These precision data were developed in a 1995 interlaboratory cooperative test program from SHELL, CARB, and EPA over a time period of two years. Samples were sent and analyzed weekly. Participants analyzed sample sets comprised by hydrocarbons and hydrocarbon-oxygenate blends. The vapor pressure ranged from 46 to 100 kPa (6.5 to 13.9 psi) nominal. A total of 50 laboratories including EPA and CARB participated. Comparison was performed against Test Method D 5191.

15.2 *Relative Bias to Test Method D 5191*—A statistically significant relative bias was observed using this test method for VP_4 at 37.8°C (vapor-liquid ratio of 4 to 1) and the DVPE obtained by using Test Method D 5191. This bias can be corrected by applying the correlation Eq 7:

$$DVPE = VP_4(37.8^{\circ}C) - \text{Relative bias} \quad (7)$$

where:

Relative bias = 1.027 kPa (0.15 psi).

NOTE 165—The precision and bias statements may not be applicable to gasolines observed to be hazy in 8.4.

NOTE 176—Different correlation formulas have been developed for Test Method D 5191 by various agencies to correlate either to Test Method D 4953, Procedure B, or to Test Method D 323. The relative bias for the VP_X calculated by these different formulas are as follows:

Correlation formula for Test Method D 4953, Procedure B, used by the EPA.

EPA:

$$DVPE = (0.956 P_{tot}) - 2.39 \quad \text{in kPa}$$

$$DVPE = (0.956 P_{tot}) - 0.347 \quad \text{in psi}$$

$$\text{Relative bias} = 0.137 \text{ kPa (0.02 psi)}$$

Correlation formula for Test Method D 323, used by CARB

CARB:

$$RVPE = (0.972 P_{tot}) - 4.93 \quad \text{in kPa}$$

$$RVPE = (0.972 P_{tot}) - 0.715 \quad \text{in psi}$$

$$\text{Relative bias} = 1.575 \text{ kPa (0.23 psi)}$$

16. Keywords

16.1 dry vapor pressure; gasoline; hydrocarbon-oxygenate blends; mini method; petroleum products; vapor pressure; variable volume method

APPENDIX

(Nonmandatory Information)

X1. DERIVATION OF EQUATIONS USED TO CALCULATE VP_X

X1.1 Theory

X1.1.1 The measured TP_X of the air containing liquid is the sum of the VP_X of the liquid and the PPA in the liquid.

X1.1.2 *Derivation of Equation*—The derivation is based on the assumption that the VP_X of the liquid is constant within the accuracy of the measurement for all three vapor-liquid ratios.

X1.1.2.1 The TP_X after the three expansions may be expressed by the following equations.

$$TP_{X,1} = VP_X + PPA_{V,1} \quad \text{or} \quad PPA_{V,1} = TP_{X,1} - VP_X \quad (X1.1)$$

$$TP_{X,2} = VP_X + PPA_{V,2} \quad \text{or} \quad PPA_{V,2} = TP_{X,2} - VP_X \quad (X1.2)$$

$$TP_{X,3} = VP_X + PPA_{V,3} \quad \text{or} \quad PPA_{V,3} = TP_{X,3} - VP_X \quad (X1.3)$$

X1.1.2.2 The free volume V_A for the air in the sample can be defined as follows:

$$V_A = (k/100) V_L \quad (X1.4)$$

where:

k = solubility of air in the sample in %, and

V_L = sample volume.

X1.1.2.3 Applying the gas law equation for the three different volumes and using the term V_A for the free air volume the following relationship can be defined:

$$(V_1 + V_A)PPA_{X,1} = (V_2 + V_A)PPA_{X,2} = (V_3 + V_A)PPA_{X,3} \quad (X1.5)$$

X1.1.2.4 Using Eq X1.1-X1.3, the two following equations are derived:

$$(V_1 + V_A)(TP_{X,1} - VP_X) = (V_2 + V_A)(TP_{X,2} - VP_X) \quad (X1.6)$$

$$(V_1 + V_A)(TP_{X,1} - VP_X) = (V_2 + V_A)(TP_{X,2} - VP_X) \quad (X1.6)$$

$$(V_1 + V_A)(TP_{X,1} - VP_X) = (V_3 + V_A)(TP_{X,3} - VP_X) \quad (X1.7)$$

X1.1.2.5 Solving the Eq X1.6 and X1.7 the formula for the PPA in the final volume can be derived.

$$PPA_{X,3} = \frac{(TP_{X,1} - TP_{X,3})(TP_{X,2} - TP_{X,3})}{\frac{V_3 - V_1}{V_2 - V_1}(TP_{X,1} - TP_{X,2}) - (TP_{X,1} - TP_{X,3})} \quad (X1.8)$$

where:

$TP_{X,1}$ = total pressure after first expansion,

$TP_{X,2}$ = total pressure after second expansion,

$TP_{X,3}$ = total pressure after third and final expansion,

V_1 = vapor volume after the first expansion,

V_2 = vapor volume after the second expansion, and

V_3 = final vapor volume after the third expansion.

X1.1.2.6 The air corrected vapor pressure is calculated by

$$VP_X = TP_{X,3} - PPA_{X,3} \quad (X1.9)$$

X1.2 Air Correction at Test Temperature

X1.2.1 The partial pressure of the air at the test temperature, PPA_t , can be determined using the following equation derived from the gas laws as follows:

$$PPA_t = PPA_C (273.2 + t) / (273.2 + t_C) \quad (X1.10)$$

where:

t_C = temperature of the measuring chamber during the gas determination procedure, in °C, and

t = test temperature, in° C.

SUMMARY OF CHANGES

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D 6378 – 99⁶) that may impact the used of this standar.

(1) Updated 2.1 to replace the D 1160 reference with one to D 2892.

(2) Updated 6.3 to reference D 2892 requirements and 10.1.2 to explicitly reference Note 8.

(3) Updated Note 8.

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