

California Environmental Protection Agency

 **Air Resources Board**

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PROCEDURE FOR THE DETERMINATION OF THE REID VAPOR PRESSURE
EQUIVALENT OF GASOLINE

SOP NO. MLD 125

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1 Introduction

- 1.1 This test method covers the determination of the total pressure, exerted in vacuum, by air-containing, volatile, petroleum products. The test method is suitable for testing samples with boiling points above 0EC (32EF) that exert a vapor pressure between 7 and 130 kPa (1.0 and 19 psi) at 37.8EC (100EF) at a vapor-to-liquid ratio of 4:1. The test method is suitable for testing gasoline samples which contain oxygenates. No account is made of dissolved water in the sample. (Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the Precision and Bias as described in section 11 do not necessarily apply.)
- 1.2 This method covers the use of automated vapor pressure instruments that perform measurements on liquid specimen sizes in the range from 1 to 10 mL.
- 1.3 Standard values are specified in SI units (International System of Units). The values given in parentheses are provided for information purposes only.
- 1.4 This test method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see section 7.5.

2 Test Method

- 2.1 A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled test chamber, the internal volume of which is five times that of the total test specimen introduced into the chamber. A vacuum is applied to the chamber in accordance with the manufacturer's instructions. After introduction into the test chamber the test specimen is allowed to reach thermal equilibrium at the test temperature, 37.8EC (100EF). The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator.
- 2.2 Only the sum of the partial pressure of the sample and the partial pressure of the dissolved air (commonly known as the total pressure) are used in this test method. Note that some instruments may call this pressure measurement by another term. Also note that some instruments are capable of measuring the absolute pressure of the specimen as well.
- 2.3 The measured total vapor pressure is converted to a Reid Vapor Pressure Equivalent (RVPE) by use of a calibration equation (section 9.1). This calculation converts the

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measured total pressure to the Reid Vapor Pressure (RVP) expected from the American Society of Testing and Materials (ASTM) Test Method D323-58.

3 Apparatus or Instrument

- 3.1 Vapor Pressure Apparatus - An appropriate instrument, designed for the intended use should be selected. The minimum performance level for the automated vapor pressure test instrument is that the instrument shall perform as well as, or better than, the precision criteria set forth in the ASTM D323-58. The ASTM D323-58 states a repeatability value of 0.2 psi and a reproducibility value of 0.3 psi. The instrument shall provide accurate results which are comparable to the RVP measured by the ASTM 323-58. Typically, 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.
- 3.2 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.
- 3.3 The pressure transducer shall have a minimum operational range from 0 to 177 kPa (0 to 25.6 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ± 0.3 kPa (± 0.05 psi). The pressure measurement system shall include associated electronics and readout devices to display the resulting pressure reading.
- 3.4 The thermostatically controlled heater shall be used to maintain the test chamber at 37.8 ± 0.1 EC (100 ± 0.2 EF) for the duration of the test.
- 3.5 A platinum resistance thermometer shall be used for measuring the temperature of the test chamber. The minimum temperature range of the measuring device shall be from ambient to 60EC (140EF) with a resolution of 0.1EC (0.2EF) and accuracy of 0.1EC (0.2EF).
- 3.6 The vapor pressure apparatus shall have provisions for introduction of the test specimen into the test chamber and for the cleaning or purging of the chamber following the test.
- 3.7 A vacuum pump (if required by the manufacturer's instructions) shall be capable of reducing the pressure in the test chamber to less than 0.01 kPa (0.001 psi) absolute.
- 3.8 A syringe (optional, depending on sample introduction mechanism employed with each instrument) shall be gas-tight. The syringe shall be 1 to 20mL capacity with a $\pm 1\%$ or better precision. The capacity of the syringe should not exceed two times the volume of the test specimen being dispensed.

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- 3.9 Ice Water Bath or Refrigerator (Air Bath): for chilling the samples and syringe to temperatures between 0° and 1°C (32 to 34°F).
- 3.10 Mercury Barometer (if required by the manufacturer's instructions): in the 0 to 120 kPa (0 to 17.4 psi) range.
- 3.11 McLeod Vacuum Gage (if required by the manufacturer's instructions): to cover at least the range from 0 to 0.67 kPa (0 to 5mm Hg).

4 Sampling

- 4.1 Obtain a sample in accordance with Section 2261 of Title 13 of the California Code of Regulations.
- 4.2 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 most meticulous care in the handling of samples.
- 4.3 Protect samples from excessive high temperatures prior to testing. This can be accomplished by storage in an appropriate ice water bath or refrigerator.
- 4.4 Do not test samples stored in leaky containers. Discard and obtain another sample if leaks are detected.

5 Preparation of Apparatus

- 5.1 Prepare the instrument for operation in accordance with the manufacturer's instructions.
- 5.2 Clean and prepare the test chamber as required to avoid contamination of the test specimen.
- 5.3 For instruments that require that the test chamber be evacuated prior to the introduction of the test specimen: Prior to specimen introduction, visually determine from the instrument display that the test chamber pressure is stable and does not exceed 0.1 kPa (0.01 psi). When the pressure is not stable or exceeds this value check that the chamber is clean of volatile materials remaining in the chamber from a previous specimen or check the calibration of the transducer.

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- 5.4 If a syringe is used for introduction of the specimen, chill it to between 0EC and 4.5EC (32 and 40EF) in an ice water bath or a refrigerator before drawing in the specimen. Avoid water contamination of the syringe reservoir by suitably sealing the outlet of the syringe during the cooling process.
- 5.5 For instruments using a pre-heated test chamber: Prior to introduction of the test specimen, check that the temperature of the test chamber is within the required range from $37.8 \pm 0.1^{\circ}\text{C}$ ($100 \pm 0.2^{\circ}\text{F}$).

6 Calibration

- 6.1 Pressure Transducer:
- 6.2 Check the calibration of the pressure transducer on a monthly basis or when needed as indicated from the quality control checks (section 7). The calibration of the pressure transducer is checked using two reference points: zero pressure (0.1 kPa) and the ambient barometric pressure.
- 6.3 Connect a McLeod gage to the vacuum source in line with the test chamber. Apply a vacuum to the test chamber. When the McLeod gage registers a pressure less than 0.1 kPa (0.8 mm Hg or 0.01 psi), adjust the pressure transducer control to zero or to the actual reading on the McLeod gage as dictated by the instrument design and manufacturer's instructions.
- 6.4 Open the test chamber to the atmosphere and observe the pressure transducer reading. If the pressure reading is not equal to the ambient barometric pressure, then adjust the pressure transducer span control until the appropriate reading is observed. Ensure that the instrument is set to display the total pressure and not a calculated or corrected value.
- 6.5 Repeat steps 6.3 and 6.4 until the zero and barometric pressures read correctly without further adjustments.
- 6.6 Thermometer - Check the calibration of the platinum resistance thermometer used to monitor the temperature of the test chamber at least every six months against a National Institute on Standards and Technology (NIST) traceable thermometer.

7 Quality Control Checks

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7.1 Check the performance of the instrument each day it is in use by running a quality control sample consisting of a pure solvent of known vapor pressure similar to the vapor pressure of the samples to be tested. Treat the pure solvent quality control check sample in the same manner as a sample (section 8). Record the total vapor pressure (do not calculate a Reid vapor pressure equivalent) in a log for the purpose of tracking the instrument's performance. If the total vapor pressure differs from the previous entry (for the same pure solvent) in the log by more than ± 1.0 kPa (0.15 psi), then check the instrument calibration (section 6). If the trend of the log shows variations of more than ± 1.0 kPa (0.15 psi) (for the same pure solvent), also check the instrument calibration.

7.2 Some of the possible reference pure materials and their corresponding absolute vapor pressures¹ include:

cyclohexane	22.5 kPa	(3.27 psi)
cyclopentane	68.3 kPa	(9.92 psi)
2,2-dimethylbutane	67.9 kPa	(9.86 psi)
2,3-dimethylbutane	51.1 kPa	(7.41 psi)
2-methylpentane	46.7 kPa	(6.77 psi)
toluene	7.1 kPa	(1.03 psi)

7.3 Purity of Reagents - Use chemicals of at least 99% purity for quality control checks. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society where such specifications are available.² 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.

7.4 The chemicals in this section are suggested for use in quality control procedures; not for instrument calibration.

7.5 WARNING--Cyclohexane, cyclopentane, 2,2-dimethylbutane, 3,2-dimethylbutane, 2-methylpentane, and toluene are extremely flammable. They are an aspiration hazard and are harmful if inhaled. They are also a skin irritant on repeated contact.

¹ The total pressure values cited were obtained from Phillips Petroleum Co., Bartlesville, OK, or the Table of Physical Constants, National Gas Producer Association.

² "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United State Pharmacopeia."

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8 Procedure

- 8.1 Sample Temperature - Cool the sample container and contents in an ice water bath or refrigerator to the 0E to 1EC (32E to 34EF) range prior to opening the sample container. Allow sufficient time to reach this temperature.
- 8.2 Verification of Sample Container Filling - After the sample reaches thermal equilibrium at 0EC to 1EC, take the container from the ice water bath or refrigerator, wipe dry with an absorbent material, unseal and examine the ullage. With a suitable gage, determine that the liquid content in the container is between 70% and 80% of the volume of the container capacity.
- 8.3 Discard the sample if the liquid content of the container is less than 70% of the volume of the container capacity.
- 8.4 If the liquid content of the container is more than 80% of the volume of the container capacity, pour out enough sample to bring the liquid contents within the 70% and 80% volume range.
- 8.5 Air Saturation of Sample in Sample Container.
- 8.6 After determining that the liquid content in the sample container is between 70% and 80% full, reseal the container and shake vigorously. Return the container to the ice water bath or refrigerator for a minimum of two minutes.
- 8.7 Remove the sample from the ice water bath or refrigerator, dry the exterior of the container with absorbent material, uncap, insert a transfer tube or syringe (section 4). Draw a bubble-free aliquot of sample into a gas tight syringe or transfer tube and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container and inserting/securing the syringe into the sealed test chamber shall not exceed one minute.
- 8.8 The vapor pressure determination shall be performed on the first test specimen withdrawn from a sample container. Successive vapor pressure determinations can be made on the remaining test material in the same container if the container had been tightly sealed immediately after the previous vapor pressure determination.
- 8.9 Follow the manufacturer's instructions for the introduction of the test specimen into the test chamber and for the operation of the instrument to obtain a total vapor pressure result for the test specimen.

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- 8.10 Set the instrument to read the result in terms of total vapor pressure. If the instrument is capable of calculating a RVPE value, ensure that only the parameters described in section 7.2 are used.
- 8.11 Verification of Single Phase - After drawing a test specimen and introducing it into the instrument for analysis, check the remaining sample for phase separation. If the sample is contained in a glass container, this observation can be made prior to sample transfer. If the sample is contained in a non-transparent container, mix the sample thoroughly and immediately pour a portion of the remaining sample into a glass container and observe for evidence of phase separation. If the sample is not clear and bright or if a second phase is observed, discretion shall be used to determine if the sample is truly representative.
- 8.12 Record the total vapor pressure reading from the instrument to the nearest 0.1 kPa (0.01 psi). For instruments that do not automatically record or display a stable pressure value, manually record the pressure indicator reading every minute to the nearest 0.1 kPa; and, when three successive readings agree to within 0.1 kPa, record the result to the nearest 0.1 kPa (0.01 psi).

9 Calculation

- 9.1 Calibration Equation - Calculate the RVPE using the following calibration equation. Ensure that the instrument reading used in this equation corresponds to the total pressure and has not been corrected by an automatically programmed correction factor.

Equation 1:
$$RVPE = aX - b$$

where:

$ARVPE$ \cong is the vapor pressure value (in psi) that would be expected from test method ASTM D323-58;

Aa \cong is the correlative relationship of test data from the specific automated vapor pressure test instrument and test data from ASTM D323-58;

AX \cong is the total vapor pressure value (in psi) as determined by the specific automated vapor pressure test instrument;

Ab \cong is the offset of the test data between the specific automated vapor pressure test instrument and the test data from ASTM D323-58.

The data used for determining the calibration equation for each instrument shall be obtained during an Air Resources Board vapor pressure test program. The data shall consist of test results obtained from the analysis of identical samples by the automated

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instrument and by ASTM D323-58. Vapor pressure test programs may be conducted on a periodic basis as needed. The Air Resources Board conducted such a program and determined that the following automated vapor pressure test instruments meet the requirements of section 3. The data from the test program were used to arrive at the calibration equations for these instruments. The calibration equations are as follows:

1. Grabner Instruments,
Model: CCA-VP (laboratory Grabner) $RVPE = (.965)X - .304$
2. Grabner Instruments,
Model: CCA-VPS (portable Grabner) $RVPE = (.972)X - .715$
3. Stanhope-Seta Limited,
Model: Setavap $RVPE = (.961)S - .577$

- 9.2 The calculation described in section 9.1, above, can be accomplished automatically by the instrument, if so equipped, and in such cases the user shall not apply any further corrections.

10 Report

- 10.1 Report the Reid vapor pressure equivalent to the nearest 0.1 kPa (0.01 psi).

11 Precision And Bias

- 11.1 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 correct operation of the test method exceed the following value only in one case in 20. The repeatability values for the specific automated vapor pressure test instruments listed in section 9.1 were equal to or less than 0.2 psi. For the purposes of determining compliance with Sections 2251 and 2251.5, the repeatability value for this method shall be 0.20 psi.
- 11.2 Reproducibility - The difference between two single and independent test results obtained by different operators working in different laboratories using the same make and model test instrument on identical test material would, in the long run, exceed the following value only in one case in 20. The reproducibility values for the specific automated vapor pressure test instruments listed in paragraph 9 (9.1) were equal to or less than 0.3 psi. For the purposes of determining compliance with Sections 2251 and 2251.5, the reproducibility value for this method shall be 0.30 psi.

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- 11.3 Bias - A relative bias was observed between the total pressure obtained using this test method and the Reid vapor pressure obtained using ASTM Test Method D323-58. This bias is corrected by the use of the calibration equation in section 9.1 which calculates a Reid vapor pressure equivalent value from the observed total pressure.