# METHOD 28

REF: Reg 8-5-101 8-5-602

# DETERMINATION OF VAPOR PRESSURE OF ORGANIC LIQUIDS FROM STORAGE TANKS

#### 1) PRINCIPLE

This method provides for the determination of the absolute vapor pressure of an organic liquid at its storage temperature. The procedure is basically the same as that prescribed in ASTM D-323-82 (**Reid Method**), the exception being that the test is performed at the tank storage temperature of the sample.

The liquid chamber portion of a Reid vapor pressure apparatus is filled with a chilled sample and connected to the air chamber at test temperature. The apparatus is immersed in a constant temperature bath **(equivalent to the storage tank temperature)** and shaken periodically until equilibrium is reached. The gage reading, suitably corrected, is reported as the absolute pressure of the material at its stored temperature.

#### 2) APPARATUS

- 2.1 Refrigerator and/or Cooling Bath.
- 2.2 Reid Vapor Pressure (RVP) Bomb. A unit as described in Fig. 11.
  - **2.2.1 Test Gauge.** A gauge with a range of 0 to 5 psia capable of being read to 0.025 psia. A manometer or other equivalent pressure reading devise maybe used.
- **2.3 Constant Temperature Bath.** A bath capable of maintaining a constant temperature setting between ambient temperature and 120°F (± 0.5°F).

## 3) ANALYTICAL PROCEDURE

- 3.1 Handling of Sample.
  - **3.1.1** 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 handling of samples. The provisions of this section shall apply to all samples taken for vapor pressure determination. Sampling shall be done in accordance with **Practice D 4057.**

3.1.2 Sample Container Size. The size of the sample container from which the vapor pressure sample is taken shall be 1 QT. (1 L). It shall be 70 to 80% filled with the sample. In the case of referee testing, the 1 qt. (1 L) sample container shall be mandatory.

#### 3.2 Precautions

- **3.2.1** The Reid vapor pressure determination shall be the first test run on a collected sample, and no more than one sample shall be withdrawn from the sample container for testing.
- **3.2.2** Samples shall be protected from excessive heat prior to testing.
- **3.2.3** Samples in leaky containers shall not be tested. They should be discarded and new samples obtained.
- **3.3** Sample Handling Temperature. In all cases, the sample container and contents shall be cooled to 32 to 34°F (0 to 1°C) before the container is opened. Sufficient time to reach this temperature shall be assured by direct measurement of the temperature of a similar liquid in a like container placed in the cooling bath or equivalent at the same time as the sample.

#### 3.4 Preparation For Test.

- **3.4.1** Verification of Sample Container Filling. With the sample at a temperature of 32 to 34°F (0 to 1°C), take the container from the cooling bath, unseal it, and examine its ullage. The sample content, as determined by use of a suitable gage, shall equal 70 to 80% of the container capacity.
- **3.4.2** Discard the sample if its volume is less than 70% of the container capacity.
- **3.4.3** If the container is more than 80% full, pour out enough sample to bring the container contents within the 70 to 80% range. Under no circumstance may any sample poured out be returned to the container.

#### 3.5 Air Saturation of Sample in Sample Container.

**3.5.1** With the sample again at a temperature of 32 to 34 °F (0 to 1°C), take the container from the cooling bath, unseal it momentarily, reseal it, and shake it vigorously. Return it to the bath for a minimum of 2 minutes.

- **3.5.2** Repeat **3.5.1** twice more. Return the sample to the bath until the beginning of the procedure.
- **3.6 Preparation of Liquid Chamber.** Completely immerse the open liquid chamber (in an upright position) and the sample transfer connection in the bath at 32 to 34°F (0 to 1°C) for at least 10 minutes.
- 3.7 Preparation of Air Chamber. After purging and rinsing the air chamber and pressure gage, connect the gage to the air chamber. Immerse the air chamber to at least 1 in. above its top in the water bath maintained at the temperature at which the RVP test is to be run, for not less than 10 minutes just before coupling it to the liquid chamber. Do not remove the air chamber from the bath until the liquid chamber has been filled with sample as described in 4.1.

## 4) PROCEDURE

- 4.1 Sample Transfer. With everything in readiness, remove the chilled sample container from the bath, uncap it, and insert the chilled transfer apparatus (See Fig. 1). Quickly empty the water from the chilled liquid chamber and place it, in an inverted position, over the sample delivery tube of the transfer apparatus. Invert the entire system rapidly so that the liquid chamber is upright with the end of the delivery tube touching the bottom of the liquid chamber. Fill the liquid chamber to overflowing. Withdraw the delivery tube from the liquid chamber while allowing the sample to continue flowing up to the moment of complete withdrawal. CAUTION: Provision should be made for suitable restraint and disposal of the overflowing liquid to avoid fire hazard.
- **4.2** Assembly of Apparatus. Immediately remove the air chamber from the water bath and, as quickly as possible, attach the air chamber to the liquid chamber (NOTE: 1). Not more than 10 seconds shall be consumed in coupling the two chambers.
  - NOTE 1: When the air chamber is removed from the constant temperature bath, allow it to drain only briefly and, without shaking, connect it to the liquid chamber without undue movements through the air which could promote exchange of room temperature air with the air (sample storage temperature) in the chamber.
- **4.3 Introduction of Apparatus to Bath.** Turn the assembled vapor pressure apparatus upside down to allow the sample in the liquid chamber to run into the air chamber and shake vigorously in a direction parallel to the length of the apparatus. Immerse the assembled

apparatus into the bath, maintained at the desired temperature  $(\pm 0.5^{\circ}F)$ , in an inclined position so that the connection of the liquid and air chamber is below the water level and may be observed closely for leaks. If no leaks are observed, immerse the apparatus to at least 1 in. above the top of the air chamber. Observe the apparatus for leaks throughout the test. If a leak is detected, discard the test.

4.4 Measurement of Vapor Pressure. After the assembled vapor pressure apparatus has been immersed in the bath for at least 5 minutes, tap the pressure gage lightly and observe the reading. Withdraw the apparatus from the bath and repeat 4.3. At intervals of not less than 2 min, perform 4.3 until a total of not less than five shaking and gage readings have been made and continuing thereafter if necessary until the last two consecutive gage readings are constant, indicating equilibrium attainment. These operations normally require 20 to 30 min. Read the final gage pressure to the nearest 0.025 psi and record this value as the "uncorrected vapor pressure" of the sample. Without undue delay remove the pressure gage (NOTE 2), and without attempting to remove any liquid which may be trapped in the gage, check its reading against that of a manometer while both are subjected to a common steady pressure which is no more than 0.2 psi different from the recorded "uncorrected vapor pressure". If a difference is observed between the gage and mercury manometer readings, the difference should be added to or subtracted from the "uncorrected vapor pressure" recorded for the sample being tested and the resulting value recorded as the absolute pressure of the sample.

# NOTE 2: Cooling the assembly prior to disconnecting the gage will facilitate disassembly and reduce the amount of hydrocarbon vapors released into the room.

## 5) PRECISION

**5.1** Interlaboratory testing by the BAAQMD and five refineries was performed on three samples in the 0-1 psi range. At the 95% confidence level the estimate for the precision was found to be approximately 0.05 psi. Based on this testing an enforcement guideline tolerance of  $\pm$  0.15 psi has been deemed appropriate for Method 28.

## 6) **REFERENCES**

6.1 Vapor Pressure of Petroleum Products (Reid Method), ASTM Designation D-323-82 Volume 05.01, Section 5 (1984).