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Standard Test Method for Vapor Pressure of Liquids by Ebulliometry¹

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1. Scope

1.1 This test method describes procedures for determination of the vapor pressure of liquids by ebulliometry (boiling point measurements). It is applicable to pure liquids and azeotropes that have an atmospheric boiling point between 285 and 575 K and that can be condensed completely and returned to the ebulliometer boiler, that is, all materials must be condensable at total reflux. Liquid mixtures may be studied if they do not contain non-condensable components. Liquid mixtures that contain trace amounts of volatile but completely condensable components may also be studied, but they will produce vapor pressure data of greater uncertainty. Boiling point temperatures are measured at applied pressures of 1.0 to 100 kPa (7.5 to 760 torr).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 There is no ISO equivalent to 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1193 Specification for Reagent Water](#)

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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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.

[D2879 Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope](#)

[E1 Specification for ASTM Liquid-in-Glass Thermometers](#)

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[E1142 Terminology Relating to Thermophysical Properties](#)

[E1194 Test Method for Vapor Pressure](#)

[E1970 Practice for Statistical Treatment of Thermoanalytical Data](#)

3. Terminology

3.1 *Definitions:*

3.1.1 The following terms are applicable to this test method and can be found in Terminology E1142; *boiling temperature* and *vapor pressure*.

3.1.2 For definitions of other terms used in this test method, refer to Terminology E1142.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *ebulliometer*—a one-stage, total-reflux boiler designed to minimize superheating of the boiling liquid.

3.2.2 *manostat*—a device for maintaining constant vacuum or pressure.

3.2.3 *superheating*—the act of heating a liquid above the equilibrium boiling temperature for a particular applied pressure.

3.3 *Symbols:*

A, B, C = Antoine vapor pressure equation constants (\log_{10} , kPa, K) for the Antoine vapor pressure equation:
 $\log_{10} P = A - B / (T + C)$.
 P = vapor pressure, kPa.
 T = absolute temperature, K.

4. Summary of Test Method

4.1 A specimen is charged to the ebulliometer boiler. The ebulliometer is connected to a manostat, and coolant is circulated through the ebulliometer condenser. The manostat is set at a low pressure, and the specimen is heated to the boiling temperature. The boiling temperature and manostat pressure are recorded upon reaching a steady-state, and the manostat pressure is raised to a higher value. A suitable number (usually five or more) of boiling temperature points are recorded at

successively higher controlled pressures. The pressure-temperature data are fitted to the Antoine vapor pressure equation. Vapor pressure values required for specific reports are then computed from the derived equation.

4.2 The capability of the entire apparatus (ebulliometer, thermometer, manostat, etc.) is checked periodically by the procedure described in Annex A1. This procedure consists of measuring the boiling temperature data for a pure reference substance such as water and comparing the derived vapor pressure data to the known reference values.

5. Significance and Use

5.1 Vapor pressure is a fundamental thermodynamic property of a liquid. Vapor pressure and boiling temperature data are required for material safety data sheets (MSDS), the estimation of volatile organic compounds (VOC), and other needs related to product safety. Vapor pressures are important for prediction of the transport of a chemical in the environment; see Test Method E1194.

6. Interferences

6.1 This test method is limited to materials that are thermally stable over the measurement temperature range. Boiling temperatures that drift monotonically (not cyclically) up or down and specimen discoloration and smoking are indications of thermal instability due to decomposition or polymerization. See Test Method D2879 (9.3 and Note 8 therein). Vapor pressure data may be measured at temperatures below the initial decomposition or polymerization temperature; see 9.7 and 10.2.

6.2 The test method is limited to materials that boil smoothly under the operation conditions of the ebulliometer. Materials that “bump” continually, boil erratically, or eject material through the condenser are not suitable for study by this test method.

7. Apparatus

7.1 *Ebulliometer*³—A vapor-lift-pump, stirred-flask, or equivalent type of ebulliometer.

7.1.1 *For Example, a Vapor-Lift-Pump Ebulliometer*⁴—Fig. 1 shows the dimensions for an example twin-arm ebulliometer, which is a one-stage, total-reflux boiler equipped with a vapor-lift pump to spray slugs of equilibrated liquid and vapor on a thermometer well. The boiler (e), which is constructed from concentric pieces of 200-mm glass tubing (5 and 10-mm outside diameter), has powdered glass fused to the heated surface to promote smooth boiling. The boiler is wrapped with an electrical heater. Twin vapor-lift pumps (d-constructed of 270-mm lengths of 5-mm outside diameter glass tubing) spray liquid and vapor slugs on a 100-mm thermometer well (c) that is wrapped with a glass spiral to promote thermal equilibration. The vapor-lift pumps dissipate the effects of superheating. The ebulliometer is connected to the manostat through a 200-mm reflux condenser (b); see 7.3. The side view in Fig. 1 shows a

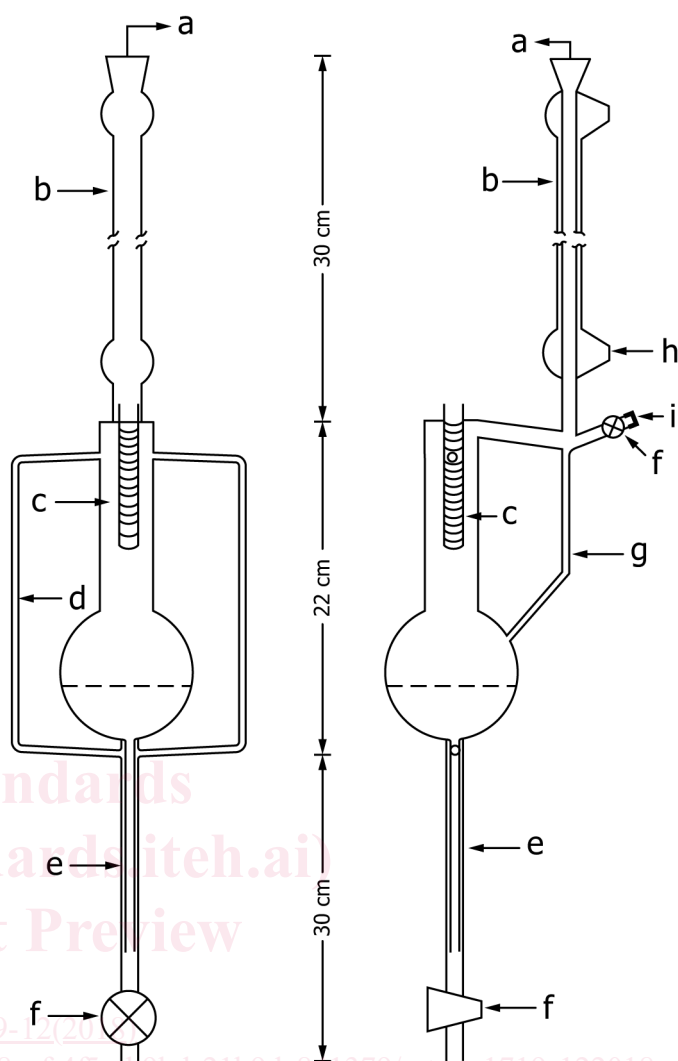


FIG. 1 Vapor-Lift-Pump Ebulliometer

septum port and stopcock (f and i) where materials may be charged to the apparatus. Except for the condenser, septum port, and stopcock, the entire ebulliometer is insulated with a suitable case or wrapping. A window should be left to observe the smoothness of boiling and the return rate (drop rate) of condensed vapor into the 125-mL boiler return reservoir.

7.1.1.1 For example, a Swietoslawski-type ebulliometer⁵ may be used instead.

7.1.2 For example, a *Stirred-Flask Ebulliometer*, Fig. 2 shows an example of a stirred-flask ebulliometer, which is a one-stage, total-reflux boiler equipped with a magnetic stirrer to circulate the boiling liquid past a thermometer well which is immersed in the liquid. The boiler is a 250-mL, round-bottomed, single-neck boiling flask modified with a 7-mm inside diameter thermometer well positioned diagonally toward the bottom of the flask. The bottom half of the boiler has powdered glass fused to the inner surface to promote smooth

³ An ebulliometer can be assembled from readily available lab glassware.

⁴ Olson, J. D., *Journal of Chemical Engineering Data*, Vol 26, 1981, pp. 58–64.

⁵ Malanowski, S., *Fluid Phase Equilibria*, Vol 8, 1982, pp. 197–219.

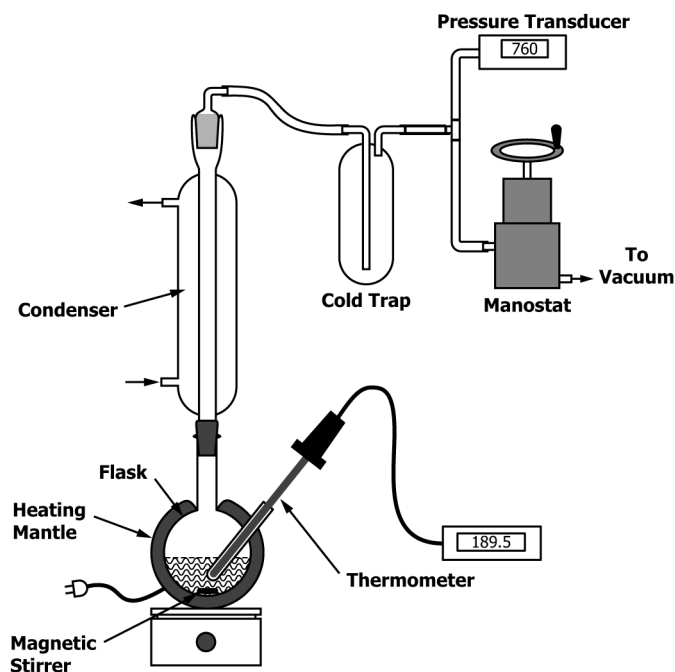


FIG. 2 Stirred-Flask Ebulliometer

boiling.⁶ The thermometer well is positioned to have a length of at least 20 mm below the surface of the liquid when 125 mL of liquid is charged to the flask. The thermometer well must be positioned to allow a magnetic stirring bar to rotate freely in the bottom of the flask. The magnetic stirrer dissipates the effects of superheating. The flask is connected to the manostat through a reflux condenser; see 7.3. An electrical heating mantle covers the lower half of the flask; see 7.2. The upper half of the flask is insulated with a suitable wrapping.

NOTE 1—Ebullimeters that use thermometer wells that are immersed directly in the boiling liquid are more susceptible to data errors due to superheating. Vapor-lift-pump ebulliometers are preferred except if “bumping” occurs, as discussed in 6.2 and 9.5.

7.1.3 *Other Ebulliometers*—Other ebulliometers, for example, those that require smaller specimen charges, may be used if the operation and capability of the ebulliometer is demonstrated by the procedure described in Annex A1.

7.2 *Heater or Heating Mantle*—An electrical heater or heating mantle equipped with a suitable controller of power input. Indirect heating by circulating a thermostatted hot fluid through a jacketed boiler may be used.

7.3 *Condenser*, which shall be of the fluid-cooled, reflux, glass-tube type, having a condenser jacket of at least 200 mm in length. A smaller condenser may be used, particularly for smaller volume systems, provided that no condensed specimen is found in the cold trap.

NOTE 2—Suitable condenser designs include Allihn, Graham, Liebig, and equivalent condensers.

⁶ The stirred-flask ebulliometer shown in Fig. 2 (with the inner boiling surface coated with powdered glass) is available from Lab Glass, Inc., P.O. Box 5067, Fort Henry Drive, Kingsport, TN 37663.

7.4 *Coolant Circulating System*—Cooling water below 300 K, circulated through the condenser for tests on materials that freeze below 273 K and boil above 325 K at the lowest applied pressure. For other test materials, a circulating thermostat shall be used that is capable of supplying coolant to the condenser at a temperature at least 2 K above the freezing point and at least 30 K below the boiling point at the lowest applied pressure.

NOTE 3—The suitability of the circulating coolant temperature shall be demonstrated by the absence of freezing of the specimen in the condenser and the absence of specimen in the cold traps at the conclusion of the test.

7.5 *Cold Trap*, capable of freezing or condensing the test material, connected in series to the condenser. Ice plus water, dry ice plus solvent, or liquid nitrogen may be used as the cold trap coolant, depending on the characteristics of the test material.

7.6 *Temperature Measuring Device*—Liquid-in-glass thermometers accurate to 0.1 K (after calibration and immersion corrections), or any other thermometric device of equal or better accuracy. See Specification E1.

7.7 *Thermometer Well Fluid*—A low-volatility, thermally inert fluid such as silicone oil or glycerin, charged to the thermometer well of the ebulliometer. The amount of fluid added should be such that the fluid level in the thermometer well is not above the flask boundary when the ebulliometer is at the measurement temperature.

7.8 *Pressure Regulating System*—A manostat, capable of maintaining the pressure of the system constant within ± 0.07 kPa (± 0.5 torr). Connect the pressure regulating system to the exit of the cold trap. A T-connection from the pressure regulating system near the exit of the cold trap should be used to connect the manometer. A ballast volume may be used to dampen pressure fluctuations.

7.9 *Pressure Measuring System*—A manometer, capable of measuring absolute pressure with an accuracy of ± 0.07 kPa (± 0.5 torr).

7.9.1 A comparative ebulliometer may be used to measure pressure. The comparative ebulliometer is connected to the same pressure-controlled atmosphere as the test ebulliometer and contains a reference fluid (for example, distilled water). The observed boiling temperature in the comparative ebulliometer is used to compute the applied pressure from the known vapor pressure-temperature relationship of the reference fluid.

7.10 *Software*, to perform multiple linear regression analysis on three variables.

8. Safety Precautions

8.1 There shall be adequate provisions for the retention and disposal of spilled mercury if mercury-containing thermometers, pressure measurement, or controlling devices are used.

8.2 Vapor pressure reference materials (Annex A1) and many test materials and cold trap fluids will burn. Adequate precautions shall be taken to eliminate ignition sources and provide ventilation to remove flammable vapors that are generated during operation of the ebulliometer.

8.3 Adequate precautions shall be taken to protect the operator in case debris is scattered by an implosion of glass apparatus under vacuum.

9. Procedure

9.1 Start with clean, dry apparatus. Verify the operation and capability of the apparatus as described in **Annex A1** for a new ebulliometer setup or an ebulliometer setup that has not been used recently.

9.2 Charge a specimen of appropriate volume to the ebulliometer boiler. Charge 75 ± 1 mL for the vapor-lift ebulliometer (**Fig. 1**). Close all stopcocks on the vapor-lift ebulliometer. Charge 125 ± 1 mL for the stirred-flask ebulliometer (**Fig. 2**). Add a magnetic stirring bar to the stirred-flask ebulliometer. Connect the stirred-flask ebulliometer to the reflux condenser.

9.3 Connect the ebulliometer reflux condenser to the cold trap. Connect the cold trap exit to a glassware T-connection. Connect one side of the T-connection to the manostat and the other side to the manometer. If a comparative ebulliometer is used as the manometer, charge the reference fluid to the comparative ebulliometer and connect it through a cold trap to the T-connection.

9.4 Start the condenser coolant flow. Set the manostat for the lowest pressure to be studied. (This pressure should produce a boiling temperature at least 30 K above the condenser coolant temperature.) Turn on the magnetic stirrer if using a stirred-flask ebulliometer. Turn on the electrical heater, and heat the specimen to produce steady-state reflux. A 30-mm reflux zone should be visible in the bottom of a 200-mm long reflux condenser at steady-state. Decrease the heating power if the reflux zone extends above half the height of the condenser. The reflux return rate from the condenser at steady-state should be at least two drops/s. <https://www.astm.org/catalog/standards/sist/754ec238-12>

9.5 See **6.2** if the specimen “bumps”. If “bumping” invalidates the test, two remedies can be tried to see whether it is eliminated: the test can be repeated at a higher initial pressure, or a stirred-flask ebulliometer can be tried in place of the vapor-lift-pump ebulliometer.

NOTE 4—“Bumping” in the ebulliometer boiler is usually caused by the inability of the apparatus to dissipate the effects of superheating of the specimen. This problem occurs more often at lower pressures, approximately 1 to 15 kPa (8 to 110 torr).

NOTE 5—Some materials may “bump” a few times and then boil smoothly. These materials can be studied provided that material is not ejected from the condenser during the “bumping” period.

9.6 Record the temperature and manostat pressure after the boiling point temperature is at a steady-state (± 0.10 K) for at least 10 min. Raise the manostat pressure to the next highest pressure to be studied, and repeat the steady-state measurement. Continue until five or more pressure-temperature data points are determined.

9.6.1 Vary the heater power, and observe the effect on the boiling temperature before recording the first data point. If increasing the heater power raises the boiling temperature, this indicates that there is insufficient reflux to the thermometer well. Raise the power level in this case until a “heater power

plateau” is reached at which the observed temperature is independent of the heater power.

9.6.2 At steady-state, the boiling temperature should be independent of the heater power (applied voltage) over a modest range (approximately 5 V for an ebulliometer with a variable transformer).

9.7 Discontinue the test if the specimen begins to decompose or polymerize. Decomposition may be indicated by a decreasing boiling point temperature, smoking or extreme discoloration of the specimen, or failure to reach a steady-state. Polymerization of the specimen usually causes the temperature to continue to increase instead of reaching a steady-state.

9.8 Check the cold trap for the presence of condensed volatiles from the specimen upon completion of the test. Discard the results from the test if condensate is found in the cold trap.

NOTE 6—If the test material is a pure chemical (99.9 % by weight) or an azeotropic mixture, a small amount (approximately 2 mL) of cold trap condensate is allowable.

NOTE 7—Take care not to permit water from humid laboratory air to condense inside the cold traps. Analyze the cold trap condensate in a questionable case to verify that it is from the specimen under study.

10. Calculation

10.1 Apply any calibration corrections to the pressure-temperature data points. Plot the logarithms of the pressure ($\log_{10} P$) versus the reciprocal of the absolute temperature ($1/T(K)$). Examine this plot for abrupt deviation from linearity as evidence of decomposition or polymerization; see **10.2**. Proceed to **10.3** if there is no evidence of decomposition or polymerization.

NOTE 8—Deviations from linearity due to the expected decrease in enthalpy of vaporization with temperature (the cause of curvature due to the Antoine equation C constant <0) should not be confused with the abrupt deviation due to decomposition or polymerization. Curvature in normal data is barely perceptible in a visual examination of a $\log_{10} P$ versus $1/T(K)$ plot (for example, see **Fig. 3**).

10.2 The initial decomposition or polymerization temperature is the temperature at which the logarithmic vapor pressure plot first deviates abruptly from linearity. Data points in the linear region at temperatures below the initial decomposition or polymerization temperature may be used to determine vapor pressure equation constants, as described in **10.3**.

10.3 Calculate the Antoine vapor pressure equation constants, A , B , and C , retaining all available decimals. Use a nonlinear least-squares regression program to fit the Antoine equation, $\log_{10} P = A - B/(T + C)$, to the measured pressure-temperature data points.

NOTE 9—If a nonlinear least-squares regression program is not available, a linear least-squares regression program (see Practice **E1970**) may be used for Antoine equation fitting by making the following variable transformations:⁷ $a = A$, $b = A * C - B$, and $c = -C$. The fitting equation, now linear in the parameters, is as follows:

$$T * \log_{10} P = a * T + b + c * \log_{10} P \quad (1)$$

NOTE 10—Antoine equation constants (for \log_{10} , kPa, and K units)

⁷ This procedure was described by Willingham, et al., *Journal of Research NBS*, Vol 35, 1945, pp. 219–244.