Designation: E1194 – 17

Standard Test Method for Vapor Pressure[1]

This standard is issued under the fixed designation E1194; 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.

1. Scope

1.1 This test method describes procedures for measuring the vapor pressure of pure liquid or solid compounds. No single technique is able to measure vapor pressures from 1×10^{-11} to 100 kPa (approximately 10^{-10} to 760 torr). The subject of this standard is gas saturation which is capable of measuring vapor pressures from 1×10^{-11} to 1 kPa (approximately 10^{-10} to 10 torr). Other methods, such as isoteniscope and differential scanning calorimetry (DSC) are suitable for measuring vapor pressures above 0.1 kPa An isoteniscope (standard) procedure for measuring vapor pressures of liquids from 1×10^{-1} to 100 kPa (approximately 1 to 760 torr) is available in Test Method D2879. A DSC (standard) procedure for measuring vapor pressures from 2×10^{-1} to 100 kPa (approximately 1 to 760 torr) is available in Test Method E1782. A gas-saturation procedure for measuring vapor pressures from 1×10^{-11} to 1 kPa (approximately 10^{-10} to 10 torr) is presented in this test method. All procedures are subjects of U.S. Environmental Protection Agency Test Guidelines.

1.2 The gas saturation method is very useful for providing vapor pressure data at normal environmental temperatures (–40 to +60°C). At least three temperature values should be studied to allow definition of a vapor pressure-temperature correlation. Values determined should be based on temperature selections such that a measurement is made at 25°C (as recommended by IUPAC) (**1**),[2] a value can be interpolated for 25°C, or a value can be reliably extrapolated for 25°C. Extrapolation to 25°C should be avoided if the temperature range tested includes a value at which a phase change occurs. Extrapolation to 25°C over a range larger than 10°C should also be avoided. If possible, the temperatures investigated should be above and below 25°C to avoid extrapolation altogether. The gas saturation method was selected because of its extended range, simplicity, and general applicability (**2**)**.** Examples of results produced by the gas-saturation procedure during an interlaboratory evaluation are given in Table 1. These data have been taken from Reference (**3**)**.**

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

1.4 *This standard does not purport to address all of the safety problems, 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D2879 Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1782 Test Method for Determining Vapor Pressure by Thermal Analysis

2.2 *U.S. Environmental Protection Agency Test Guidelines:*

Toxic Substances Control Act Test Guidelines; Final Rules, Vapor Pressure[4]

3. Terminology Definition

3.1 *vapor pressure*—a measure of the volatility in units of or equivalent to kg/m^2 (pascal) of a substance in equilibrium with the pure liquid or solid of that same substance at a given temperature (**4**).

4. Summary of Gas-Saturation Method

4.1 Pressures less than 1.33 kPa may be measured using the gas-saturation procedure (**4**)**.**

4.2 In this test method, an inert carrier gas (for example N_2) is passed through a sufficient amount of compound to maintain saturation for the duration of the test. The compound may be coated onto an inert support (for example glass beads) or it may

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[1] This test method is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Actionand is the direct responsibility of Subcommittee E50.47 on Biological Effects and Environmental Fate.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this test method.

[3] 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.

[4] *Federal Register*, Vol 50, No. 188, 1985, pp. 39270–39273.

TABLE 1 Gas-Saturation Procedure Results Obtained During an Interlaboratory Evaluation

Test Compound	Temperature, °C	Mean Vapor Pressures, kPa	Standard Deviation Estimate, S_r [A]	Square Root, S_R [B]	Precision Estimate, S_R [C]
Naphthalene	25	1.3×10^{-2}	0.31	0.39	0.50
	35	3.5×10^{-2}	0.55	1.23	1.35
Benzaldehyde	25	1.8×10^{-1}	0.31	1.24	1.28
	35	2.8×10^{-1}	0.33	1.12	1.17
Aniline	25	7.9×10^{-2}	1.9	3.8	4.3
	35	1.5×10^{-1}	0.25	0.28	0.38
2-Nitrophenol	25	1.2×10^{-2}	0.33	0.41	0.53
	35	3.2×10^{-2}	0.53	1.57	1.66
Benzoic Acid	25	1.5×10^{-4}	0.32	1.69	1.72
	35	5.7×10^{-4}	2.3	5.2	5.7
Phenanthrene	25	1.6×10^{-5}	0.36	0.46	0.58
	35	4.7×10^{-5}	2.41	2.39	2.42
2,4-Dinitrotoluene	25	7.1×10^{-5}	1.9	6.3	6.6
	35	2.3×10^{-4}	1.0	3.2	3.4
Anthracene	25	6.0×10^{-6}	3.7	13.8	14.3
	35	1.1×10^{-5}	0.23	2.29	2.30
Dibutylphthalate	25	6.8×10^{-6}	4.4	8.8	9.8
	35	2.0×10^{-5}	0.49	2.28	2.33
p,p'-DDT	25	1.7×10^{-7}	0.55	1.66	1.75
	35	5.7×10^{-7}	11.1	4.7	12.1

[A] S_r is the estimated standard deviation within laboratories, that is, an average of the repeatability found in the separate laboratories.

[B] S_R is the square root of the component of variance between laboratories.

[C] S_R is the between-laboratory estimate of precision.

be in a liquid or solid granular form. The compound is removed from the gas stream using a suitable agent (sorbent or cold trap). The amount of the test sample collected is then measured using gas chromatography or any other sensitive and specific technique capable of suitable mass detection limit for the intended purpose.

5. Significance and Use

5.1 Vapor pressure values can be used to predict volatilization rates (**5**). Vapor pressures, along with vapor-liquid partition coefficients (Henry's Law constant) are used to predict volatilization rates from liquids such as water. These values are thus particularly important for the prediction of the transport of a chemical in the environment (**6**).

6. Reagents and Materials

6.1 The purity of the substance being tested shall be determined and documented as part of the effort to define the vapor pressure. If available, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[5]

6.2 Every reasonable effort should be made to purify the chemical to be tested. High sample purity is required for accurate evaluation of vapor pressure using direct mass loss measurement.

6.3 For the gas-saturation method, the results can be reported in terms of the partial pressure for each component of the mixture that is identified and quantified through the trapping procedure. However, unless the pure component vapor pressures and the vapor/liquid activity coefficients of the contaminants are known, the results cannot be interpreted any more clearly. If the activity coefficient of the major constituent is defined as one (= 1), the indicated partial pressure and analytical purity data can be converted to a pure component vapor pressure.

7. Gas-Saturation Procedure

7.1 The test sample can be (*1*) coated onto clean silica sand, glass beads, or other suitable inert support from solution; prior to data measurement, the solvent must be completely removed by application of heat and flow (*2*) in solid state, possibly using a method similar to the previous one or by melting the solid to maximize surface area prior to data measurement; or (*3*) a neat liquid. If using a coated-support procedure, the thickness of the coating must be sufficient to ensure that surface energy effects will not impact vapor pressure or vaporization rate. Following volatilization the surface must remain completely coated with the test compound.

7.2 Coat the support prior to column loading, to ensure the support is properly coated. Use sufficient quantity of material on the support to maintain gas saturation for the duration of the test.

7.3 Put the support into a suitable saturator container. The dimensions of the column and gas velocity through the column should allow complete saturation of the carrier gas and negligible back diffusion.

7.4 Connect the principal and back-up traps to the column discharge line downstream from the saturator column. Use the back-up trap to check for breakthrough of the compound from the principal trap. For an example of such a system, see Fig. 1.

7.5 Surround the saturator column and traps by a thermostated chamber controlled at the test temperature within ±0.05°C.

7.6 If test material is detected in the second trap, breakthrough has occurred and the measured vapor pressure will be too low. To eliminate breakthrough, take one or both of the following steps:

7.6.1 Increase trapping efficiency by using more efficient traps, such as a larger higher capacity or a different type of trap.

7.6.2 Decrease the quantity of material trapped by decreasing the flow rate of carrier gas or reduce the sampling period.

7.7 After temperature equilibration, the carrier gas contacts the specimen and the sorbent (or cold) traps and exits from the thermostated chamber. The thermostatically-controlled chamber should utilize liquid baths to facilitate heat transfer. Liquid (for example, ethylene-glycol-water or oil) baths are suggested because of the difficulty in controlling temperatures in accordance with the tight specifications required (**7**) using air baths. Variations in the ambient temperature in facilities designed for hazardous chemical work make this a critical requirement.

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[5] "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 States Pharmacopeia."

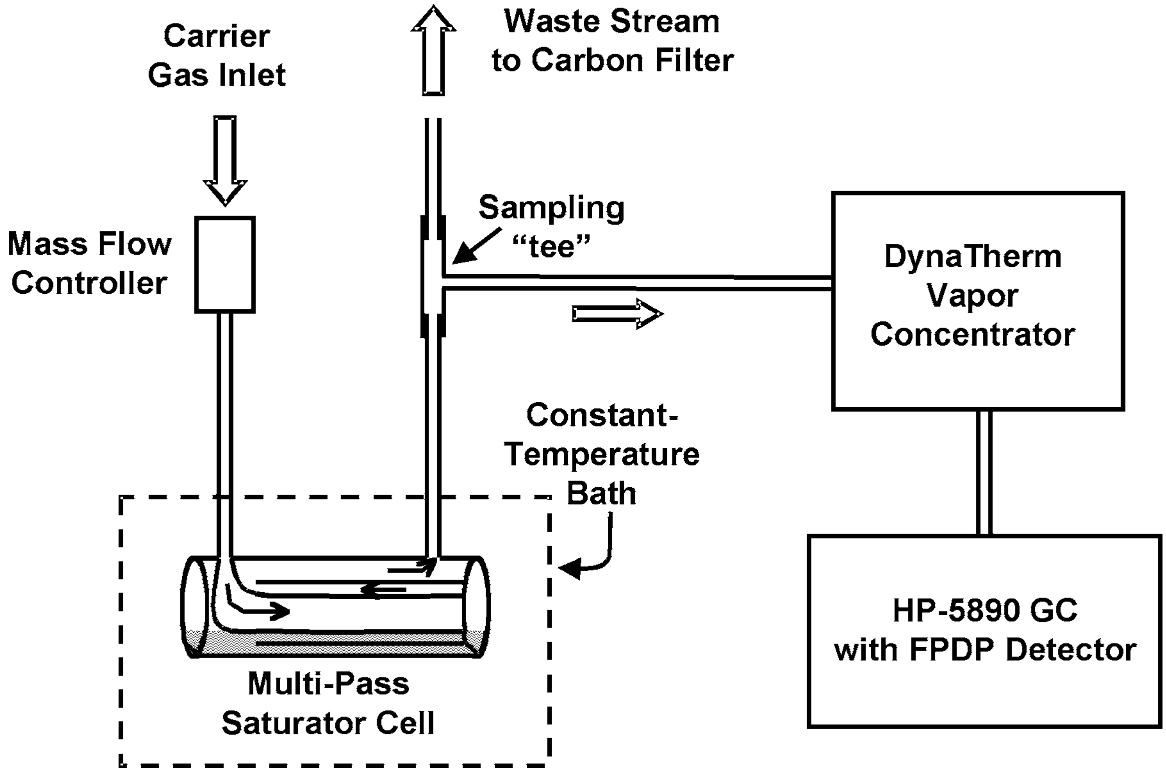

FIG. 1 Configuration of Analytical Apparatus

7.8 Measure the flow rate of the effluent carrier gas at the adiabatic saturation temperature using a calibrated mass flow meter bubble meter or other, nonhumidifying devices considered suitable. Check the flow rate frequently during the procedure to ensure that the total volume of carrier gas is accurately measured. Use the flow rate to calculate the amount of gas that has passed through the specimen and sorbent or trap. ((volume/time) (time) = volume or (mass/time) (time) = mass)).

7.9 Measure the pressure at the outlet of the saturator. Determination of the saturator operating pressure is critical because it will always be above ambient pressure due to a pressure drop through the system. Measure either by including a pressure gage between the saturator and traps or by determining the pressure drop across the particular trapping system used in a separate experiment for each flow rate.

7.10 Calculate the test specimen vapor pressure (which is its partial pressure in the gas stream) from the total gas volume (corrected to the volume at the temperature at the saturator) and the mass of specimen vaporized.

7.11 Record the ambient pressure frequently during the test to ensure an accurate saturator pressure value. Laboratories are seldom at normal atmospheric pressure, and this fact is often overlooked.

7.12 Determine the time required for collecting the quantity of test specimen necessary for analysis in preliminary runs or by estimates based on experience. Before calculating the vapor pressure at a given temperature, carry out preliminary runs to determine the flow rate that will completely saturate the carrier gas with sample vapor. To check, determine whether another flow rate at the same system temperature gives a different calculated vapor pressure.

7.13 Measure the desorption efficiency for every combination of sample, sorbent, and solvent used. To determine the desorption efficiency, inject a known mass of sample onto a sorbent. Then desorb and analyze it for the recovered mass.

7.14 For each combination of sample, sorbent and solvent used, make triplicate determinations at each of three concentrations. Desorption efficiency may vary with the concentration of the actual sample and it is important to measure the efficiency at or near the concentration of the sample under gas saturation test procedure conditions. It is usually necessary to interpolate between two measured efficiencies.

7.15 If the test specimen vapor pressure is very low, check and make sure significant amounts of the test specimen are not lost on the surface of the apparatus. This is checked by a material compatibility test prior to loading the sorbent into the traps or saturation column. If the tested chemical has a significant affinity for the traps or saturation column material of construction, select and test an alternative material of construction.

7.16 When testing elevated temperature conditions, it is necessary that the system is operating at a uniform temperature. Contaminant condensation on cold spots will give low vapor pressure values.

7.17 The choice of the analytical method, trap, and desorption solvent depends upon the nature of the test specimen and the temperature conditions of interest.

7.18 Advantages of this test method when used with an analysis specific for the compound of interest are:

7.18.1 Minor impurities are not likely to interfere with either the test protocol or the accuracy of the vapor pressure results, and the effects of impurities on the indicated vapor pressure can be corrected for in the final calculation.

7.18.2 Pressures of two or more compounds may be obtained simultaneously, providing the compounds do not have significant vapor/liquid activity interaction.

7.18.3 If the analytical method chosen is preceded by a separation step such as GC, the sample purity correction may be possible.

8. Alternative Procedures

8.1 Although the procedures stated in Section 7 are preferred for vapor pressure measurement at ambient temperatures, many laboratories have employed other successful methods. If an alternative is chosen, determine the vapor pressure in triplicate at each of three temperatures and report the average value at each temperature. As stated in 1.2, determine a value at 25°C by direct measurement, interpolation, or reliable extrapolation.

9. Calculation

9.1 For the gas-saturation procedure, compute the vapor pressure based on the volume of gas passing through the saturator and traps and the quantity of chemical removed from the saturated gas stream. The calculations involve a series of equations that convert wet gas flow and mass of organic to the vapor pressure of the chemical in the dry gas at the saturator column outlet. The equations (**7**) used for the calculations are as follows:

$$Q_w = q(\Delta T) \quad (1)$$

$$Q_D = Q_w\left(P_T - P_{H_2O}\right)/P_T \quad (2)$$

$$m_{gas} = Q_D/22.414\left((273.15+t_{exh})/(273.15)(760)/\left(P_T - P_{H_2O}\right)\right) \quad (3)$$

$$m_{org} = W_{org}/M \quad (4)$$

$$y = m_{org}/m_{gas} \quad (5)$$

$$P = y\left(P_T - P_{H_2O} + \Delta P\right) \quad (6)$$

where:

T = elapsed time, min,
q = wet gas flow rate, L/min,
Q_w = wet gas flow, L,
Q_D = dry gas flow, L,
W_{org} = weight of trapped test chemical, g,
m_{org} = test chemical, mol,
m_{gas} = carrier gas, mol
P_T = total ambient pressure, Pa,
P_{H2O} = saturation water vapor pressure at adiabatic saturation temperature, Pa
ΔP = pressure drop through the system, Pa,
P = vapor pressure, Pa,
M = molecular weight of test chemical, g/mol,
t_{exh} = exhaust gas temperature, °C, and
y = fraction of test chemical in carrier gas, mol.

9.1.1 When using mass flow control to measure the carrier, the calculation simplifies to

$$P = P_{sat}\left(n_{analyte}/\left(n_{carrier}+n_{analyte}\right)\right) \quad (7)$$

where:

P = Calculated vapor pressure, Pa
P_{sat} = Total saturator pressure = $P_{amb}+\Delta P$, Pa
$n_{analyte}$ = Moles analyte, determined experimentally
$n_{carrier}$ = Moles carrier gas, determined by multiplying sampling time (t) by sampling rate (Q)
t = sampling time, min
Q = Mass flow rate of carrier gas sampled by analytical system, standard cc/min
P_{amb} = Measured ambient pressure, Pa
ΔP = Pressure drop through the system, PA

9.1.2 Report pressure in kilopascals (kPa).

10. Report

10.1 Report the following information:

10.1.1 The test method used, along with any modification.

10.1.2 A complete description of all analytical methods used to analyze the test material and all analytical results.

10.1.3 The procedure, calculations of vapor pressure at three or more gas flow rates at each test temperature showing no dependence on flow rate.

10.1.3.1 Describe the sorbents and solvents employed and the desorption efficiency calculation.

10.1.4 Vapor pressure reported in kilopascals (kPa) at the experimental temperatures. It is suggested that at least three replicate samples be used at each temperature and the mean values obtained.

10.1.5 Average calculated vapor pressure at each temperature including the calculated standard deviation and the number of data points.

10.1.6 A description of any difficulties experienced or any other pertinent information such as possible interferences.

10.1.7 Plot of log P vs 1/t or similar.

10.1.8 Correlation equation as appropriate.

10.1.9 Enthalpy of volatilization based on measured data.

10.1.10 Entropy of volatilization based on measured data.

11. Precision and Bias

11.1 An interlaboratory evaluation was conducted at eight laboratories using the gas-saturation procedure and ten chemicals (**8**). The evaluation results are summarized in Table 1. Table 1 follows the format given in Practice E691.

12. Keywords

12.1 gas saturation procedure; vapor pressure; vapor pressure temperature correlation

APPENDIX

(Nonmandatory Information)

X1. HEAT OF VOLATILIZATION

X1.1 Heat of volatilization may be obtained from a plot of log of vapor pressure versus the reciprocal of the temperature in K. The heat of volatilization is the heat of sublimation for a solid and heat of vaporization for a liquid. The change in vapor pressure with temperature is related to the molar heat of volatilization, H_{vol}, by the Clapeyron expression (**4**):

$$dP/dT = H_{vol}/T(\Delta V) \quad (X1.1)$$

where:

ΔV is the increase in volume when one mole of compound is vaporized.

At a sufficiently low temperature, when the vapor pressure is less than 10 to 20 kPa, the vapor may be assumed to obey the perfect gas law. Under these conditions, the above equation reduces to:

$$-d\ln P/d(1/T) = \Delta H_{vol}/R \quad (X1.2)$$

where:

ΔH_{vap} or ΔH_{sub} may now be determined directly from the slope of the above plot.

X1.2 Heat of volatilization may also be obtained by multiplying the derivative with respect to T of the vapor pressure equation by RT2. In the case of the Antoine equation, the expression is:

$$\Delta H_{vol} = bR*(T/(c + T))^2 \quad (X1.3)$$

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