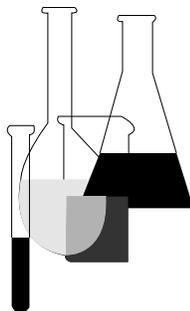




Product Properties Test Guidelines

OPPTS 830.7950 Vapor Pressure



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

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OPPTS 830.7950 Vapor pressure.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source materials used in developing this harmonized OPPTS test guideline are the OPPT guideline under 40 CFR 796.1950 Vapor pressure, OPP guideline 63–9 Vapor pressure (Pesticide Assessment Guidelines, Subdivision D: Product Chemistry, EPA Report 540/9–82–018, October 1982) and OECD guideline 104 Vapor Pressure Curve.

(b) **Guidance information**—(1) **Data required.** Melting point/melting range; boiling point/boiling range; molecular mass (for vapor pressure balance method and gas saturation method).

(2) The vapor pressure balance method and the gas saturation method are not routine procedures. Improvement of these methods in the future will depend upon further exchange of experiences and results.

(c) **Method**—(1) **Introduction, purpose, scope, relevance, application, and limits of test.** (i) The following account for the environmental relevance of vapor pressure:

(A) Vapor pressure gives an indication of the probability of the phase transitions liquid/gas and solid/gas.

(B) Vapor pressure, together with the solubility in water, is the major auxiliary variable for calculating the volatility of a substance from an aqueous solution.

(C) Vapor pressure is a significant factor for predicting atmospheric concentrations.

(D) The vapor pressure of a substance can furthermore be useful as a basis for deciding whether or not a photochemically induced degradation (in the homogeneous gas phase or in an absorbed phase) is necessary.

(E) There is no single vapor pressure measurement procedure applicable to the entire range of vapor pressures. Therefore, several methods are recommended for the measurement of vapor pressure from $<10^{-3}$ Pa to 10^5 Pa. The OECD Laboratory Intercomparison Testing Programme showed that the gas saturation method may allow measurements of considerably lower vapor pressure (as low as approximately 10^{-5} Pa). Vapor pressure testing is not required for chemicals with a standard boiling point of <30 °C.

(F) The dynamic method, static method, and isoteniscope method can be applied to pure and commercial grade substances although impurities

will affect the results. The vapor pressure balance method and the gas saturation method can only be applied to pure substances.

(2) **Definitions and units.** (i) The vapor pressure of a substance is defined as the saturation pressure above a solid or liquid substance. At thermodynamic equilibrium, the vapor pressure is a function of temperature only.

(ii) The SI unit of pressure which should be used is the Pascal (Newton/m²). Units which have been employed historically, together with their conversion factors, are:

(A) 1 Torr (mm Hg) = 1.333×10^2 Pa

(B) 1 atmosphere (physical) = 1.013×10^5 Pa

(C) 1 atmosphere (technical) = 9.81×10^4 Pa

(D) 1 bar = 10^5 Pa

(3) **Reference substances.** The following reference compounds need not be employed in all cases when investigating a new substance. They are provided primarily so that calibration of the method may be performed from time to time and to offer the chance to compare the results when another method is applied. The values presented in the following tables 1. through 6. are average and range values of vapor pressure from OECD and EEC-Laboratory Intercomparison Testing Programmes (from calculated regression curves) and not necessarily representative of the results which can be obtained with this test guideline as they have been derived from an earlier version of the test guideline.

Table 1.—Vapor Pressure of Toluene: Dynamic Method (OECD), three laboratories

Temperature, °C	Average values all labs in Pa	Range values in Pa
10	1.7×10^3	$(1.7 \text{ to } 1.8) \times 10^3$
20	3.0×10^3	$(2.9 \text{ to } 3.1) \times 10^3$
30	4.9×10^3	$(4.8 \text{ to } 5.0) \times 10^3$
40	7.8×10^3	$(7.7 \text{ to } 8.9) \times 10^3$

Table 2.—Vapor Pressure of Hexachlorobenzene: Gas saturation method¹, (OECD), two laboratories

Temperature, °C	Average values all labs in Pa	Range values in Pa
10	8.0×10^{-4}	$3.7 \times 10^{-4} \text{ to } 2.5 \times 10^{-3}$
20	2.6×10^{-3}	$1.6 \times 10^{-3} \text{ to } 5.7 \times 10^{-3}$
30	8.1×10^{-3}	$5.9 \times 10^{-3} \text{ to } 1.2 \times 10^{-2}$
40	2.3×10^{-2}	$2.1 \times 10^{-2} \text{ to } 2.5 \times 10^{-2}$
50	6.1×10^{-2}	$4.9 \times 10^{-2} \text{ to } 6.7 \times 10^{-2}$

¹ test temperature 10–50 °C

Table 3.—Vapor Pressure of Hexachlorobenzene: Vapor pressure balance¹, (EEC), two laboratories

Temperature, °C	Vapor pressure, average values all labs in Pa	Range values in Pa
10	2.8×10^{-4}	9.0×10^{-5} to 3.6×10^{-4}
20	1.1×10^{-3}	4.1×10^{-4} to 1.5×10^{-3}
30	3.9×10^{-3}	$(1.7 \text{ to } 5.4) \times 10^{-3}$
40	1.3×10^{-2}	6.4×10^{-3} to 1.8×10^{-2}
50	3.9×10^{-2}	$(2.2 \text{ to } 5.8) \times 10^{-2}$

¹ test temperature 30–150 °C

Table 4.—Vapor Pressure of Dibutylphthalate: Vapor pressure balance, (EEC), two laboratories

Temperature, °C	Average values all labs in Pa	Range values in Pa
10	6.5×10^{-4}	$(4.4 \text{ to } 9.1) \times 10^{-4}$
20	2.3×10^{-3}	$(1.7 \text{ to } 3.1) \times 10^{-3}$
30	7.8×10^{-3}	$(6.1 \text{ to } 9.7) \times 10^{-3}$
40	2.4×10^{-2}	$(2.0 \text{ to } 2.8) \times 10^{-2}$
50	7.0×10^{-2}	$(6.2 \text{ to } 7.8) \times 10^{-2}$

Table 5.—Vapor Pressure of Benzoic acid: Gas saturation method (OECD), two laboratories; vapor pressure balance (OECD), two laboratories

Temperature, °C	Average values all labs in Pa		Range values in Pa
	gas saturation	vp balance	
10	0.02	0.012	0.012 to 0.03
20	0.07	0.05	0.04 to 0.07
30	0.24	0.17	0.15 to 0.26
40	0.76	0.56	0.48 to 0.89
50	2.2	1.7	1.24 to 2.9

Table 6.—Vapor Pressure of Di(2-ethylhexyl)phthalate: Gas saturation¹, (OECD), one laboratory; vapor pressure balance², (OECD), one laboratory

Temperature, °C	Regression curve values in Pa	
	balance	gas saturation
10	1.1×10^{-6}	3.2×10^{-6}
20	6.0×10^{-6}	1.3×10^{-5}
30	2.8×10^{-5}	4.7×10^{-5}
40	1.2×10^{-4}	1.6×10^{-4}
50	4.9×10^{-4}	5.0×10^{-4}

¹ test temperature 10–50 °C

² test temperature 80–120 °C

(4) **Principle of the test methods.** Five methods are proposed for determining the vapor pressure in different vapor pressure ranges. The measured results are plotted in a log p versus 1/T graph and yield rectilinear curves for limited temperature ranges.

(i) **Dynamic method.** (A) In the dynamic method, the boiling temperature which pertains to a specified pressure is measured.

(B) Recommended range is 10^3 Pa up to 10^5 Pa, between 20 °C and 100 °C.

(C) This method has also been recommended for the determination of boiling points, and is useful for that purpose up to 350 °C.

(ii) **Static method.** (A) In the static process, at thermodynamic equilibrium, the vapor pressure established in a closed system is determined at a specified temperature. This method is suitable for one-component and multicomponent solids and liquids.

(B) Recommended range is 10 Pa up to 10^5 Pa, between 0 °C and 100 °C.

(iii) **Isoteniscope.** (A) This standardized method is also a static method, but is usually not suitable for multicomponent systems. Additional information is available in ASTM method D-2879-75 under paragraph (f)(4) of this guideline.

(B) Recommended range is from 100 Pa to 10^5 Pa, between 0 °C and 100 °C.

(iv) **Vapor pressure balance.** (A) The quantity of substance leaving a cell per unit time through an aperture of known size is determined under vacuum in such a way that return of the substance into the cell is negligible (e.g., by measuring the pulse generated on a sensitive balance by a vapor jet or by measuring the weight loss).

(B) Recommended range is 10^{-3} Pa to 1 Pa, between 0 °C and 100 °C.

(v) **Gas saturation method.** (A) A stream of inert carrier gas is passed over the substance in such a way that it becomes saturated with its vapor and the vapor is collected in a suitable trap. Measurement of the amount of material transported by a known amount of carrier gas is used to calculate the vapor pressure at a given temperature.

(B) Recommended range is up to 1 Pa.

(vi) **Effusion method: loss of weight.** (A) The method is based on the estimation of the mass of test substance flowing out per unit of time of a Knudsen cell (see paragraph (f)(9) of this guideline) in the form of a vapor, through a micro-orifice under ultra-vacuum conditions. The mass of effused vapor can be obtained either by determining the loss of mass of the cell or by condensing the vapor at low temperature and determining the amount of volatilized substance using chromatography. The vapor pres-

sure is calculated by applying the Hertz-Knudsen relation with correction factors that depend on parameters of the apparatus.

(B) Recommended range is 10^{-3} to 1 Pa.

(vii) **Spinning rotor method.** (A) This method uses a spinning rotor viscosity gauge, in which the measuring element is a small steel ball which, suspended in a magnetic field, is made to spin by rotating fields (see paragraph (f)(9) of this guideline. Pick-up coils allow its spinning rate to be measured. When the ball has reached a given rotational speed, usually about 400 revolutions per second, energizing is stopped and deceleration, due to gas friction, takes place. The drop of rotational speed is measured as a function of time. The vapor pressure is deduced from the pressure-dependent slow-down of the steel ball.

(B) The recommended range is 10^{-4} to 0.5 Pa.

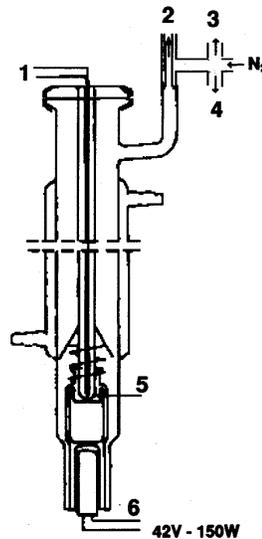
(5) **Quality criteria.** The various methods of determining the vapor pressure are compared as to application, repeatability, reproducibility, measuring range, and ability to standardize in the following table 7:

Table 7.—Quality criteria

Measuring method	Substance		Estimated repeatability	Estimated reproducibility	Recommended range	Ability to standardize
	solid	liquid				
Dynamic method		X	up to 25% 1–5%	up to 25% 1–5%	10^3 Pa to 2×10^3 Pa 2×10^3 Pa to 10^5 Pa	—
Static method	X	X	5–10%	5–10%	10 Pa to 10^5 Pa	—
Isoteniscope	X	X	5–10%	5–10%	10^2 Pa to 10^5 Pa	ASTM-D-2879-75
Effusion method: Vapor pressure balance	X	X	5–20%	up to 50%	10^{-3} Pa to 1 Pa	—
Gas saturation method	X	X	10–30%	up to 50%	$<10^{-3}$ Pa to 1 Pa	—
Effusion method: Loss of weight	X	X	10–30%	X	10^{-3} Pa to 1 Pa	—
Spinning rotor method	X	X	10–20%		10^{-4} Pa to 0.5 Pa	—

(d) **Description of the test procedures—(1) Dynamic measurement procedure—(i) Apparatus.** (A) The measuring apparatus typically consists of glass, metal, and glass-metal connections and is composed of a boiling vessel with attached cooler (see figure 1 under this paragraph), equipment for regulating and measuring the temperature and equipment for regulating and measuring the pressure.

Figure 1.—Apparatus for Determining the Vapour Pressure Curve According to the Dynamic Method



- 1 = thermocouple
- 2 = vacuum buffer volume
- 3 = pressure gauge
- 4 = Cottrell pump
- 5 = measuring point
- 6 = heating element 42 voltage DC, 150 W.

(B) A typical measuring apparatus shown in the drawing is made from heat resistant glass and is composed of five parts: The large, partially double-walled tube consists of a ground jacket joint, a cooler, a cooling vessel, and an inlet.

(C) The glass cylinder with a Cottrell pump is mounted in the boiling section of the tube and has a rough surface of crushed glass for avoiding “bumping” in the boiling process.

(D) The temperature is measured by using a thermocouple or resistance thermometer which is immersed in a small quantity of oil. It is inserted into the charging tube which has a male ground joint and is sealed on the bottom.

(E) The cross-piece makes the necessary connections to the pressure regulation and measurement equipment.

(F) The bulb, which acts as a buffer volume, is connected with the measuring apparatus by means of a capillary tube.

(G) A cartridge heater, which is inserted into the glass apparatus externally from below, is used for heating the boiling vessel. The desired heating current is set by means of a voltage-regulating transformer and is monitored by means of an amperometer.

(H) An oil pump is used for setting the desired vacuum between 10^2 and roughly 10^5 Pa.

(I) A nitrogen cylinder is used for setting a desired pressure and is connected via a valve which is also used for ventilating the apparatus.

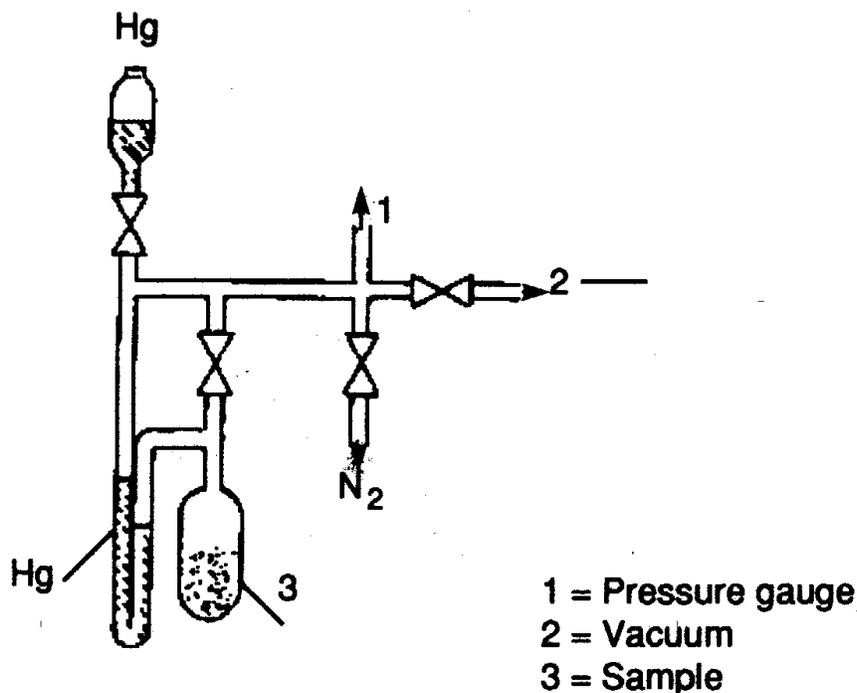
(J) A precision pressure gauge which is connected to the cross-piece is used for pressure measurement.

(ii) **Measurement procedure.** (A) The vapor pressure is measured by determining the boiling point of the sample at various specified pressures between roughly 10^3 and 10^5 Pa. The temperature constancy (at a constant pressure) indicates that the boiling point (boiling equilibrium in the case of a mixture) has been reached.

(B) All glass parts are first thoroughly cleaned and dried and evacuated under a gas ballast. The substance is introduced into the apparatus. If solids are not in a powdered form, problems may occur during the filling process, but they can be circumvented by heating the cooling water jacket. Frothing substances cannot be measured using this method. After filling, the apparatus is flanged together and the substance degassed. The lowest desired pressure is set, and the heating system is switched on. Simultaneously, the thermocouple or the resistance thermometer is connected to a recorder. Equilibrium is reached when a constant boiling temperature can be read at a constant pressure. After recording this equilibrium point, a higher pressure is set. The process is continued in this manner until 10^5 Pa has been reached (approximately 5 to 10 points in all). As a control, equilibrium points must be repeated at decreased pressures.

(2) **Static measurement procedure**—(i) **Apparatus.** (A) A typical measuring apparatus (see figure 2 under this paragraph) consists of glass, metal and glass-metal connections. The measuring apparatus also includes a heating and a cooling system for bringing the sample to a regulated temperature and for measuring the temperature, as well as equipment for setting and measuring the pressure.

Figure 2.—Apparatus for Determining the Vapour Pressure Curve According to the Static Method



(B) The sample chamber is terminated on one side in a high-vacuum valve made of stainless steel and on the other side by a U-tube containing a suitable manometric fluid. The other end of the U-tube terminates in a cross-piece, one branch of which leads to the vacuum pump, another to the nitrogen cylinder, and the third to the pressure gauge.

(C) For bringing the substance to a regulated temperature, the entire sample chamber, including the valve vertical support and a sufficiently large section of the U-tube (for practical purposes, up to the height of the valve vertical support), is placed in an appropriate constant temperature bath. The temperature is measured using a thermocouple or resistance thermometer very close to the outside of the sample chamber and can be recorded.

(D) Liquid nitrogen or a Dry Ice-ethyl alcohol mixture is suitable for supercooling the sample. An ultra-cryomat is used for measuring at low temperatures.

(E) A suitable pump is used to evacuate the apparatus to the required pressure.

(F) The vapor pressure of a substance is usually measured indirectly via a zero indicator. The zero indicator is usually a liquid, but membrane

capacity manometers, for example, also exist. In a temperature-controlled bath, the vapor pressure moves the liquid in the U-tube out of equilibrium. Nitrogen is allowed into the apparatus from a connected nitrogen cylinder via a valve to compensate the effect of the vapor pressure and to bring the pressure gauge fluid back to zero. The nitrogen pressure required for this is read off at a pressure gauge which is at ambient temperature and corresponds to the vapor pressure of the substance at a corresponding temperature constancy. There are various precision pressure gauges for the pressure range from 10 Pa up to 10^5 Pa.

(G) There are various liquids available, according to pressure range and the chemical behaviour of a substance, which can be used as U-tube liquids for zero balancing at the temperature of the substance: Mercury, silicone oils, and phthalates. Mercury may be used from 10^2 Pa up to 10^5 Pa, silicone oils and phthalates from below 10^2 Pa down to 10 Pa; the membrane capacity manometer can be applied even below 10^{-1} Pa.

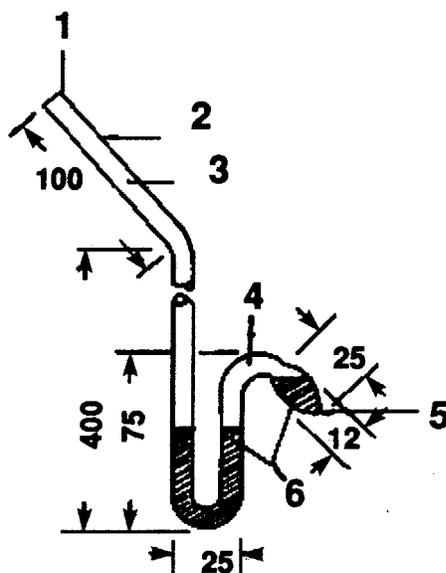
(ii) **Measurement procedure.** (A) Before measurement, all parts of the apparatus shown in figure 2 are thoroughly cleaned with solvents and dried in a vacuum. The U-tube is filled with the desired pressure gauge fluid, which should be degassed at elevated temperature prior to filling.

(B) After having been filled with the substance the apparatus is flanged together and the sample chamber sufficiently supercooled. The enclosed air is pumped out of the apparatus for several minutes with the valve open above the sample chamber. The valve above the substance is closed, the sample is brought to the selected temperature, and the resulting displacement of the columns is observed and compensated to the zero position with nitrogen, if necessary, until a constant temperature is reached. The sample chamber is again supercooled. If residual pressure is observed in the supercooled condition, it is due either to air contained in the sample which is released during the heating process and which can be drawn off, or to the cooling temperature's not being low enough. Liquid nitrogen must be used as a coolant.

(C) After the sample has been sufficiently degassed, the temperature dependency of the vapor pressure is determined at sufficiently small temperature intervals. The vapor pressure values are given in Pa in a table. In addition, a semilogarithmic graph is prepared in which $\log p$ is plotted as a function of $1/T$.

(3) **Isoteniscope.** (i) For a complete description of this method see ASTM-D 2879-75 under paragraph (f)(4) of this guideline. For the principle of the measuring device see the following figure 3:

Figure 3.—Isoteniscope (according to ASTM D 2879–75)



1 = pressure control measurement system

2 = tube, o.d. 8 mm

3 = dry nitrogen in pressure system

4 = sample vapor

5 = small tip

6 = liquid sample

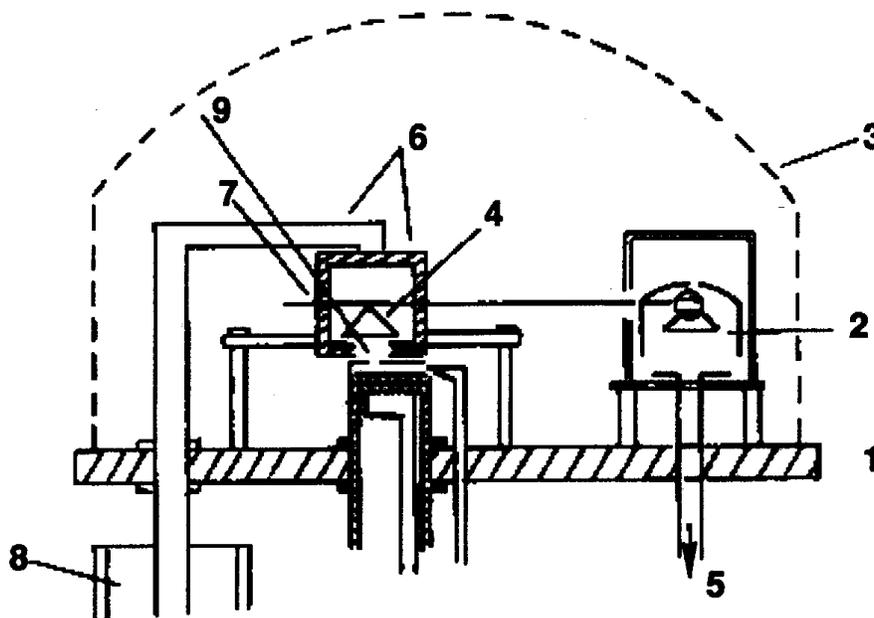
(A) Similarly to the static method described under paragraph (d)(2), the isoteniscope is appropriate for the investigation of solids and liquids. In the case of liquids, the substance itself serves as the packing fluid in the auxiliary manometer. In the case of solids, depending on the pressure and temperature range, the manometer liquids listed in the description of the static method under paragraph (d)(2)(ii)(G) of this guideline are used. The sphere of the isoteniscope for liquids is filled with the substance to be investigated, which is degassed at elevated temperature during boiling.

(B) Simultaneously, a part of the liquid is distilled out of the sphere and is condensed in the upper cooled sphere and returned to the U-tube. When the latter is sufficiently filled with degassed liquid, the lower sphere with the U-tube in a thermostat-controlled bath is brought up to the chosen temperature, and the resulting vapor pressure is indirectly measured as described under paragraph (d)(2)(ii) of this guideline.

(C) In the case of solids, the degassed packing fluid is filled into the bulge on the long arm of the isoteniscope. The solid to be investigated is filled into the lower sphere and is degassed at elevated temperature. The isoteniscope is tilted so that the manometer liquid can flow into the U-tube. The measurement of vapor pressure as a function of temperature is done as in the static method under paragraph (d)(2) of this guideline.

(4) **Effusion method: vapor pressure balance**—(i) **Apparatus.** (A) There are several different designs presented under paragraphs (f)(2) and (f)(3) of this guideline. The one described here is illustrative of the principles involved. A number of parts can be seen in the following figure 4:

Figure 4.—Apparatus for Determining the Vapour Pressure Curve According to the Vapour Jet Method



- 1 = base plate
- 2 = moving coil instrument
- 3 = bell jar
- 4 = balance with scalepan
- 5 = vacuum measuring device
- 6 = refrigeration box and cooling bar
- 7 = evaporator furnace

8 = Dewar flask with liquid nitrogen

9 = shield

(B) These are base plate and bell jar, a pump with a vacuum measuring device and equipment for measuring the vapor pressure with a visual display of the pointer deflection. The following built-in equipment is mounted on the base plate:

(1) An evaporator furnace with flange and rotary feed-through. The evaporator furnace is a flat, cylindrical copper vessel. (The furnace can also be made of glass surrounded by a copper wall.) It is placed in a copper retainer which is screwed onto a piece of stainless steel by its lower protruding edge. The piece of stainless steel, in turn, is mounted on the base plate by means of a flange so that it can be rotated about the axis of the furnace. Heating is provided by a heater coil inside the piece of stainless steel, closed off from the vacuum chamber.

(2) The furnace lid is made of copper and has three evaporation openings of various diameters which are located at 90° to one another. By rotating the furnace, the desired opening or an intermediate position can be placed under the slot in the cooler which is positioned eccentrically to the furnace, aiming the molecular beam at the balance pan or diverting it. A thermocouple or resistance thermometer is mounted in the furnace wall for temperature measurement.

(3) The balance is a moving-coil instrument. The pointer is replaced by a small tube on which are mounted the balance beam and counterweight. The balance beam has a replaceable pan made of a thin piece of gold-plated aluminium. A 0.1 mm thick constantan wire onto which calibration weights can be set is attached to the approximate center of the balance beam. The vapor pressure can be recorded using a photoelectric null-point recording method.

(4) A cylindrical brass pot surrounds the balance pan on all sides with the exception of the two slots for the movement of the balance beam and a narrow opening for the entrance of the molecular beam. Heat dissipation to the outside is provided by a copper bar on top of the brass pot. It is routed via a stainless steel tube through the base plate and thermally insulated from it. The bar is immersed in a Dewar flask containing liquid nitrogen under the base plate.

(ii) **Measurement procedure.** (A) The copper furnace is filled with the substance, the lid closed, and the plate orifice, shield, and cooler slid over the furnace. The bell is mounted, and the vacuum pumps are switched on. The final pressure before beginning measurement is roughly 10^{-4} Pa. The cooling of the refrigeration box is begun from 10^{-2} Pa downwards. After a period of time, the balance will have attained a sufficiently low temperature to allow the escaping vapor jet to condense on the scale pan.

This condensation produces a signal on the connected recorder. This signal can be used in two ways. For the particular apparatus described here, the vapor pressure is determined directly from the pressure on the scale pan (the molecular mass is not required). At the same time the mass condensed is determined, and the evaporation rate can therefore be calculated from the time of deposition. This latter property applies to more general apparatus.

(B) The vapor pressure may also be calculated from the evaporation rate and molecular mass using the Herz relationship,

$$p = G \sqrt{2 RT/M_r}$$

where

G = evaporation rate

M_r = relative molecular mass

T = temperature in K

R = universal molar gas constant

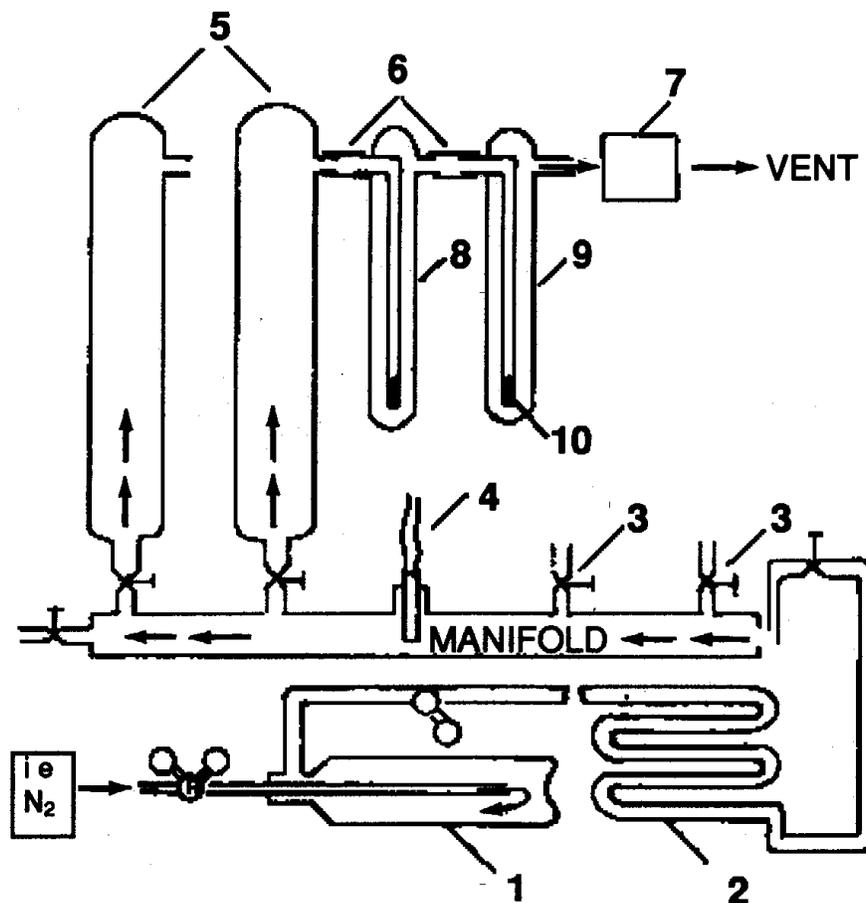
P = vapor pressure

(C) After the necessary vacuum is reached, the series of measurements commences at the lowest desired measuring temperature. The necessary orifice is opened, and the vapor jet passes the shield directly mounted above the cover and strikes the cooled scale pan. The size of the scale pan is chosen so that the entire jet is collected in its cosinal distribution. The momentum of the vapor jet results in a force onto the scale pan where the molecules condense on its cooled surface. Due to the force of the vapor jet, the scale beam will be deflected from the equilibrium state. At the end of the scale beam is a small tab which is registered optically via a prism system and two photodiodes. A connected control circuit momentarily regulates and resets the debalanced scale beam back to the balanced state. The required torque is recorded and corresponds, after a calibration with weights, to the vapor pressure of the substance.

(D) For further measurements, the temperature is increased by small steps until the maximum desired temperature value is reached. The sample is cooled again, and a second curve of the vapor pressure may be recorded. The two series will only be reproducible if the sample being measured is sufficiently pure. If the third run fails to confirm the results of the second run, it is possible that the substance may be decomposing in the temperature range being measured.

(5) **Gas saturation method**—(i) **Apparatus.** (A) A typical apparatus used is designed essentially according to paragraph (f)(5) of this guideline. It consists of a number of components shown in the following figure 5:

Figure 5.—An Example of a Flow System for the Determination of Vapour Pressure By the Gas Saturation Method Under Paragraph (e)(6) of this Guideline



- 1 = flow regulator
- 2 = heat exchanges
- 3 = needle valves
- 4 = sensor (% relative humidity)
- 5 = saturation columns
- 6 = PTFE joints
- 7 = flow meter
- 8 = trap (absorber)
- 9 = oil trap
- 10 = fritted bubbler

(B) Components. (1) Inert gas. The carrier gas must not react chemically with the test substance. Nitrogen is usually sufficient for this purpose, but occasionally other gases may be required. The gas employed must be dry.

(2) Flow control. A suitable gas control system is required to ensure a constant and selectable flow through the saturator column.

(3) Traps to collect vapor. These are dependent on the particular sample characteristics and the method of analysis chosen. The vapor should be trapped quantitatively and in a form which permits subsequent analysis. For some test substances, traps containing liquids such as hexane or ethylene glycol will be suitable. For others, solid absorbants may be applicable.

(4) Heat-exchanger. For measurements at different temperatures it may be necessary to include a heat-exchanger in the assembly.

(5) Saturator column: The test substance is a solution coated onto a suitable inert support. The coated support is packed into the saturator column, the dimensions and the flow rate of which should be such that complete saturation of the carrier gas is ensured. The saturator column must be thermostated. For measurements at temperatures above 20 °C, the region between the saturator column and the traps should be heated to prevent condensation of the test substance.

(ii) **Test conditions.** Determinations with the sample should be made in triplicate, preferably at each of three temperatures: 10, 20, and 30 °C. For some substances, it may be necessary to carry out the procedures at elevated temperatures (<100 °C) and extrapolate to these temperatures.

(iii) **Performance of test—(A) Preparation of the saturator column.** A solution of the test substance in a highly volatile solvent is added to a suitable amount of support. Sufficient test substance should be added to maintain saturation for the duration of the test. The solvent is totally evaporated in air or in a rotary evaporator, and the thoroughly mixed material is added to the saturator column. After thermostating the sample, dry nitrogen is passed through the apparatus.

(B) Measurement procedure. (1) The traps are connected to the column effluent line and the time recorded. The flow rate is checked at the beginning and at regular intervals during the experiment, using a bubble meter (or continuously, with a mass flow-meter). The pressure at the outlet to the saturator must be measured. This may be done either by including a pressure gauge between the saturator and traps (this because of increased dead space and adsorptive surface), by determining the pressure drops across the particular trapping system used as a function of flow rate in a separate experiment (may be not very satisfactory for liquid traps).

(2) The time required for collecting the quantity of test substance that is necessary for the different methods of analysis is determined in preliminary runs or by estimates. Before calculating the vapor pressure at a given temperature, preliminary runs are to be carried out to determine the maximum flow rate that will completely saturate the carrier gas with substance vapor. This is guaranteed if the carrier gas is passed through the saturator slowly enough that a still lower rate gives no greater calculated vapor pressure.

(3) The specific analytical method will be determined by the nature of the substance being tested (e.g., gas chromatography or gravimetry).

(4) The quantity of substance transported by a known volume of carrier gas is determined.

(C) **Calculation of vapor pressure.** Vapor pressure is calculated from the vapor density, W/V , by means of the equation:

$$p = W/V \times PT/M_r$$

where

p = vapor pressure in Pa

W = mass of adsorbed test substance in grams

V = volume of saturated gas in cubic meters

R = universal molar gas constant

T = temperature in K

M_r = relative molecular mass

Measured volume must be corrected for pressure and temperature differences between the flow meter and the thermostated saturator. If the flow meter is located downstream from the vapor trap, corrections may be necessary to account for any vaporized-trap ingredients, as discussed under paragraph (f)(6) of this guideline.

(e) **Data and reporting**—(1) **Treatment of results.** The vapor pressure from any of the preceding methods should be determined for at least three temperatures in the range 0–50 °C. If the chosen method has required measurement at temperatures above this range, the vapor pressure curve (log p versus $1/T$) should be extrapolated to these temperatures. Care must be taken when extrapolating over large temperature ranges.

(2) **Test report.** (A) For all methods, the vapor pressure at 20 or 25 °C should be reported. This value should preferably be an experimental one, but may be interpolated or extrapolated if necessary. Data need not be reported if vapor pressure is less than 10^{-5} PA (10^{-7} TORR).

(B) In addition, the test report should include the minimum three vapor pressure and temperature values used to determine the above value. It should also include all of the raw data and the log p versus 1/T curve used to determine these values.

(C) The report should also include a description of the apparatus and method employed if they deviate from those described in this test guideline. Difficulties encountered and any other pertinent information should be reported. If transitions (change of state, decomposition) were encountered, the following information should be noted:

(1) Nature of the change.

(2) Temperature at which the change occurs at atmospheric pressure.

(3) Vapor pressure at 10 and 20 °C above and below the transition or change of state temperature (unless the transition is from solid to gas).

(f) **References.** The following references should be consulted for additional background material on this test guideline.

(1) Report by D. I. Mennicken in AP of the Bayer AG, 5090 Leverkusen, Federal Republic of Germany, December 17, 1968.

(2) Report by the Leybold Company, Bonner Str. 504, 5000 Köln-Bayenthal, Federal Republic of Germany, 1951.

(3) Herlet, A. and G. Reich. *Zeitschrift für angewandte Physik* 9:14–23 (1957).

(4) ASTM D 2879–75, Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope.

(5) Spencer, W.F. and M. M. Cliath. Vapor Density of Dieldrin, *Environmental Science and Technology* 3:670–74 (1969).

(6) Thompson, G.W. and D. R. Douslin. “Vapor Pressure” in *Physical Methods of Chemistry*, Arnold Weissberger and W. B. Rossiter (eds.), Vol. 1, Part 5, pp. 47–89, Wiley-Interscience New York, (1971).

(7) Friedrich, K. and K. Stambach. *Journal of Chromatography* 16:22–28 (1964).

(8) OECD Guideline for The Testing of Chemicals, Guideline 104, Vapor Pressure (1995).

(9) *Organization for Economic Cooperation and Development*, Guidelines for The Testing of Chemicals, OECD 104, Vapor Pressure Curve, OECD. Paris, France.