

the blank solution and then filled with same. The instrument should be set to scan at a rate appropriate for the required wavelength resolution and the spectrum of the blank recorded. The sample cell should then be rinsed and filled with the test solution and the scanning repeated, preferably on the same spectrum chart, to display the baseline. The test should be carried out at 25 °C.

(c) *Data and reporting*—(1) *Treatment of results.* (i) The molar absorption coefficient  $\epsilon$  should be calculated for all absorbance maxima of the test substance. The formula for this calculation is:

$$\epsilon = \frac{A}{c_i \times d}$$

where the quantities are as defined above (see Definitions and units).

(ii) For each peak which is capable of being resolved, either as recorded or by extrapolated symmetrical peaks, the bandwidth should be recorded.

(2) *Test report.* (i) The report should contain a copy of each of the three spectra (3 pH conditions). If neither water nor methanol solutions are feasible, there will be only one spectrum. Spectra should include a readable wavelength scale. Each spectrum should be clearly marked with the test conditions.

(ii) For each maximum in each spectrum, the  $\epsilon$  value and bandwidth (when applicable) should be calculated and reported, along with the wavelength of the maximum. This should be presented in tabular form.

(iii) The various test conditions should be included, such as scan speed, the name and model of the spectrophotometer, the slit width (where available), cell type and path length, the concentrations of the test substance, and the nature and acidity of the solvent medium. A recent test spectrum on appropriate reference materials for photometric and wavelength accuracy should also be submitted (see Reproducibility and sensitivity).

(d) *Literature references.* For additional background information on this test guideline, the following references should be consulted:

(1) Milazzo, G., Caroli, S., Palumbo-Doretto, M., Violante, N., *Analytical Chemistry*, 49: 711 (1977).

(2) Katelaar, J.A.A., *Photoelectric Spectrometry Group Bulletin*, 8, (Cambridge, 1955).

(3) Chemical Rubber Company, *Atlas of Spectral Data*, (Cliffland, Ohio).

[50 FR 39472, Sept. 27, 1985]

#### § 796.1950 Vapor pressure.

(a) *Introduction*—(1) *Background and purpose.* (i) Volatilization, the evaporative loss of a chemical, depends upon the vapor pressure of chemical and on environmental conditions which influence diffusion from a surface. Volatilization is an important source of material for airborne transport and may lead to the distribution of a chemical over wide areas and into bodies of water far from the site of release. Vapor pressure values provide indications of the tendency of pure substances to vaporize in an unperturbed situation, and thus provide a method for ranking the relative volatilities of chemicals. Vapor pressure data combined with water solubility data permit the calculation of Henry's law constant, a parameter essential to the calculation of volatility from water.

(ii) Chemicals with relatively low vapor pressures, high adsorptivity onto solids, or high solubility in water are less likely to vaporize and become airborne than chemicals with high vapor pressures or with low water solubility or low adsorptivity to solids and sediments. In addition, chemicals that are likely to be gases at ambient temperatures and which have low water solubility and low adsorptive tendencies are less likely to transport and persist in soils and water. Such chemicals are less likely to biodegrade or hydrolyze and are prime candidates for atmospheric oxidation and photolysis (e.g., smog formation or stratospheric alterations). On the other hand, nonvolatile chemicals are less frequently involved in atmosphere transport, so that concerns regarding them should focus on soils and water.

(iii) Vapor pressure data are an important consideration in the design of other chemical fate and effects tests;

for example, in preventing or accounting for the loss of volatile chemicals during the course of the test.

(2) *Definitions and units.* (i) "Desorption efficiency" of a particular compound applied to a sorbent and subsequently extracted with a solvent is the weight of the compound which can be recovered from the sorbent divided by the weight of the compound originally sorbed.

(ii) "Pascal" (Pa) is the standard international unit of vapor pressure and is defined as newtons per square meter (N/m<sup>2</sup>). A newton is the force necessary to give acceleration of one meter per second squared to one kilogram of mass.

(iii) The "torr" is a unit of pressure which equals 133.3 pascals or 1 mm Hg at 0 °C.

(iv) "Vapor pressure" is the pressure at which a liquid or solid is in equilibrium with its vapor at a given temperature.

(v) "Volatilization" is the loss of a substance to the air from a surface or from solution by evaporation.

(3) *Principle of the test methods.* (i) The isoteniscope procedure uses a standardized technique [ASTM 1978] that was developed to measure the vapor pressure of certain liquid hydrocarbons. The sample is purified within the equipment by removing dissolved and entrained gases until the measured vapor pressure is constant, a process called "degassing." Impurities more volatile than the sample will tend to increase the observed vapor pressure and thus must be minimized or removed. Results are subject to only slight error for samples containing nonvolatile impurities.

(ii) Gas saturation (or transpiration) procedures use a current of inert gas passed through or over the test material slowly enough to ensure saturation and subsequent analysis of either the loss of material or the amount (and sometimes kind) of vapor generated. Gas saturation procedures have been described by Spencer and Cliath (1969) under paragraph (d)(2) of this section. Results are easy to obtain and can be quite precise. The same procedures also can be used to study volatilization from laboratory scale environmental simulations. Vapor pressure is com-

puted on the assumption that the total pressure of a mixture of gases is equal to the sum of the pressures of the separate or component gases and that the ideal gas law is obeyed. The partial pressure of the vapor under study can be calculated from the total gas volume and the weight of the material vaporized. If  $v$  is the volume which contains  $w$  grams of the vaporized material having a molecular weight  $M$ , and if  $p$  is the pressure of the vapor in equilibrium at temperature  $T$  (K), then the vapor pressure,  $p$ , of the sample is calculated by

$$p = (w/M)(RT/v),$$

where  $R$  is the gas constant (8.31 Pa m<sup>2</sup> mol<sup>-1</sup> K<sup>-1</sup>) when the pressure is in pascals (Pa) and the volume is in cubic meters. As noted by Spencer and Cliath (1970) under paragraph (d)(3) of this section, direct vapor pressure measurements by gas saturation techniques are more directly related to the volatilization of chemicals than are other techniques.

(iii) In an effort to improve upon the procedure described by Spencer and Cliath (1969) under paragraph (d)(2) of this section, and to determine the applicability of the gas saturation method to a wide variety of chemical types and structures, EPA has sponsored research and development work at SRI International (EPA 1982) under paragraph (d)(1) of this section. The procedures described in this Test Guideline are those developed under that contract and have been evaluated with a wide variety of chemicals of differing structure and vapor pressures.

(4) *Applicability and specificity.* (i) A procedure for measuring the vapor pressure of materials released to the environment ideally would cover a wide range of vapor pressure values, at ambient temperatures. No single procedure can cover this range, so two different procedures are described in this section, each suited for a different part of the range. The isoteniscope procedure is for pure liquids with vapor pressures from 0.1 to 100 kPa. For vapor pressures of 10<sup>-5</sup> to 10<sup>3</sup> Pa, a gas saturation procedure is to be used.

(ii) With respect to the isoteniscope method, if compounds that boil close to

or form azeotropes with the test material are present, it is necessary to remove the interfering compounds and use pure test material. Impurities more volatile than the sample will tend to increase the observed vapor pressure above its true value but the purification steps will tend to remove these impurities. Soluble, nonvolatile impurities will decrease the apparent vapor pressure. However, because the isoteniscope procedure is a static, fixed-volume method in which an insignificant fraction of the liquid sample is vaporized, it is subject to only slight error for samples containing nonvolatile impurities. That is, the nonvolatile impurities will not be concentrated due to vaporization of the sample.

(iii) The gas saturation method is applicable to solid or liquid chemicals. Since the vapor pressure measurements are made at ambient temperatures, the need to extrapolate data from high temperatures is not necessary and high temperature extrapolation, which can often cause serious errors, is avoided. The method is most reliable for vapor pressures below  $10^3$  Pa. Above this limit, the vapor pressures are generally overestimated, probably due to aerosol formation. Finally, the gas saturation method is applicable to the determination of the vapor pressure of impure materials.

(b) *Test procedures*—(1) *Test conditions.*

(i) The apparatus in the isoteniscope method is described in paragraph (b)(2)(i) of this section.

(ii) The apparatus used in the gas saturation method is described in paragraph (b)(2)(ii) of this section.

(2) *Performance of the tests*—(i) *Isoteniscope Procedure.* The isoteniscope procedure described as ANSI/ASTM Method D 2879-86 is applicable for the measurement of vapor pressures of liquids with vapor pressures of 0.1 to 100

kilopascals (kPa) (0.75 to 750 torr). ASTM D 2879-86 is available for inspection at the Office of the Federal Register, 800 North Capitol Street, NW., suite 700, Washington, DC. This incorporation by reference was approved by the Director of the Office of the Federal Register. This material is incorporated as it exists on the date of approval and a notice of any change in this material will be published in the FEDERAL REGISTER. Copies of the incorporated material may be obtained from the Non-Confidential Information Center (NCIC) (7407), Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Room B-607 NEM, 401 M St., SW., Washington, DC 20460, between the hours of 12 p.m. and 4 p.m. weekdays excluding legal holidays, or from the American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia, PA 19103. The isoteniscope method involves placing liquid sample in a thermostated bulb (the isoteniscope) connected to a manometer and a vacuum pump. Dissolved and entrained gases are removed from the sample in the isoteniscope by degassing the sample at reduced pressure. The vapor pressure of the sample at selected temperatures is determined by balancing the pressure due to the vapor of the sample against a known pressure of an inert gas. The vapor pressure of the test compound is determined in triplicate at  $25 \pm 0.5$  °C and at any other suitable temperatures ( $\pm 0.5^\circ$ ). It is important that additional vapor pressure measurements be made at other temperatures, as necessary, to assure that there is no need for further degassing, as described in the ASTM method.

(ii) *Gas saturation procedure.* (A) The test procedures require the use of a constant-temperature box as depicted in the following Figure 1.

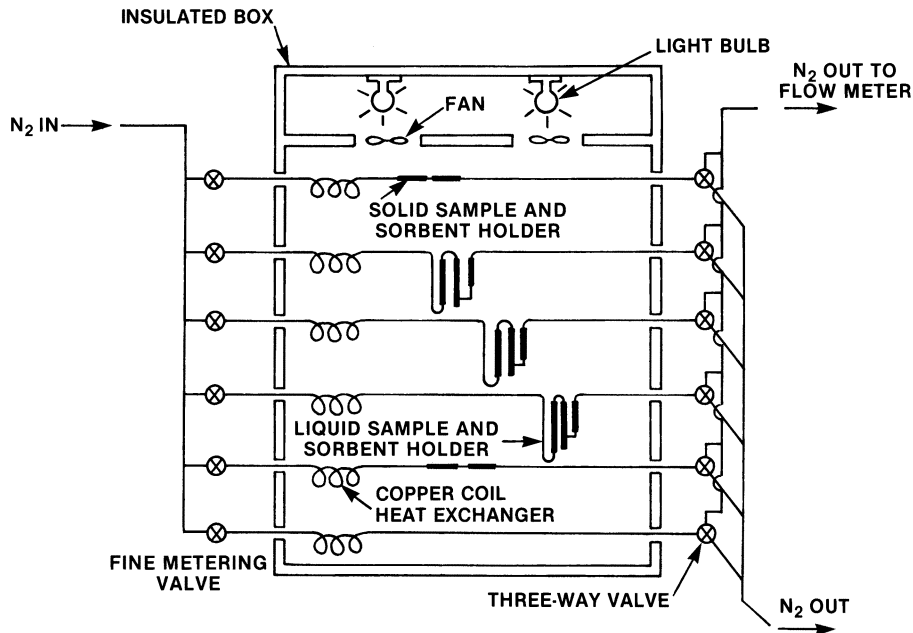


FIGURE 1—SCHEMATIC DIAGRAM OF VAPOR SATURATION APPARATUS

The insulated box, containing sample holders, may be of any suitable size and shape. The sketch in Figure 1 shows a box containing three solid sample holders and three liquid sample holders, which allows for the triplicate analysis of either a solid or liquid sample. The temperature within the box is controlled to  $\pm 0.5^\circ$  or better. Nitrogen gas, split into six streams and controlled by fine needle valves (approximately 0.79 mm orifice), flows into the box via 3.8 mm (0.125 in.) i.d. copper tubing. After temperature equilibration, the gas flows through the sample and the sorbent trap and exits from the box. The flow rate of the effluent carrier gas is measured at room temperature with a bubble flow meter or other suitable device. The flow rate is checked frequently during the experiment to assure that there is an accurate value for the total volume of carrier gas. The flow rate is used to calculate the total volume (at room tem-

perature) of gas that has passed through the sample and sorbent [(vol/time)  $\times$  time = volume]. The vapor pressure of the test substance can be calculated from the total gas volume and the mass of sample vaporized. If  $v$  is the volume of gas that transported mass  $w$  of the vaporized test material having a molecular weight  $M$ , and if  $p$  is the equilibrium vapor pressure of the sample at temperature  $T$ , then  $p$  is calculated by the equation

$$p = (w/M)(RT/v).$$

In this equation,  $R$  is the gas constant ( $8.31 \text{ Pa m}^3\text{mol}^{-1} \text{ K}^{-1}$ ). The pressure is expressed in pascals (Pa), the volume in cubic meters ( $\text{m}^3$ ), mass in grams and  $T$  in kelvins (K).  $T = 273.15 + t$ , if  $t$  is measured in degrees Celsius ( $^\circ\text{C}$ ).

(B) Solid samples are loaded into 5 mm i.d. glass tubing between glass wool plugs. The following Figure 2 depicts a drawing of a sample holder and absorber system.

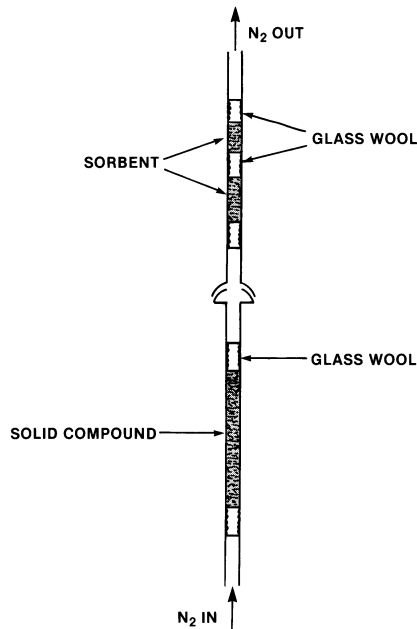


FIGURE 2—SOLID COMPOUND SAMPLING SYSTEM

(C) Liquid samples are contained in a holder as shown in the following Figure 3.

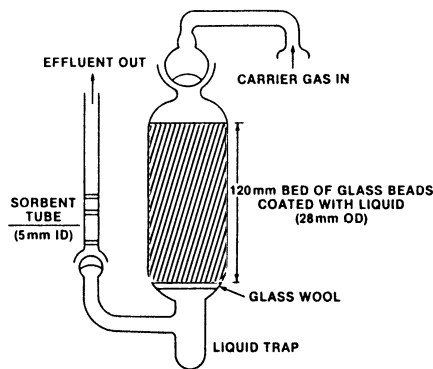


FIGURE 3—LIQUID COMPOUND SAMPLING SYSTEM

The most reproducible method for measuring the vapor pressure of liquids is to coat the liquid on glass beads and to pack the holder in the designated place with these beads.

(D) At very low vapor pressures and sorbent loadings, adsorption of the chemical on the glass wool separating the sample and the sorbent and on the glass surfaces may be a serious problem. Therefore, very low loadings should be avoided whenever possible. Incoming nitrogen gas (containing no interfering impurities) passes through a coarse frit and bubbles through a 38 cm column of liquid sample. The stream passes through a glass wool column to trap aerosols and then through a sorbent tube, as described above. The pressure drop across the glass wool column and the sorbent tube are negligible.

(E) With both solid and liquid samples, at the end of the sampling time, the front and backup sorbent sections are analyzed separately. The compound on each section is desorbed by adding the sorbent from that section to 1.0 ml of desorption solvent in a small vial and allowing the mixture to stand at a suitable temperature until no more test compound desorbs. It is extremely important that the desorption solvent contain no impurities which would interfere with the analytical method of choice. The resulting solutions are analyzed quantitatively by a suitable analytical method to determine the weight of sample desorbed from each section. The choice of the analytical method, sorbent, and desorption solvent is dictated by the nature of the test material. Commonly used sorbents include charcoal, Tenax GC, and XAD-2. Describe in detail the sorbent, desorption solvent, and analytical methods employed.

(F) Measure the desorption efficiency for every combination of sample, sorbent, and solvent used. The desorption efficiency is determined by injecting a known mass of sample onto a sorbent and later desorbing it and analyzing for the mass recovered. For each combination of sample, sorbent, and solvent used, carry out the determination in triplicate 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 sample under gas saturation test procedure conditions.

(G) To assure that the gas is indeed saturated with test compound vapor, sample each compound at three differing gas flow rates. Appropriate flow rates will depend on the test compound and test temperature. If the calculated vapor pressure shows no dependence on flow rate, then the gas is assumed to be saturated.

(c) *Data and reporting.* (1) Report the triplicate calculated vapor pressures for the test material at each temperature, the average calculated vapor pressure at each temperature, and the standard deviation.

(2) Provide a description of analytical methods used to analyze for the test material and all analytical results.

(3) For the isoteniscope procedure, include the plot of  $p$  vs. the reciprocal of the temperature in K, developed during the degassing step and showing linearity in the region of 298.15 K (25°C) and any other required test temperatures.

(4) For the gas saturation procedure, include the data on the calculation of vapor pressure at three or more gas flow rates at each test temperature, showing no dependence on flow rate. Include a description of sorbents and solvents employed and the desorption efficiency calculations.

(5) Provide a description of any difficulties experienced or any other pertinent information.

(d) *References.* For additional background information on this test guideline the following references should be consulted:

(1) U.S. Environmental Protection Agency. *Evaluation of Gas Saturation Methods to Measure Vapor Pressures: Final Report*, EPA Contract No. 68-01-5117 with SRI International, Menlo Park, California (1982).

(2) Spencer, W.F. and Cliath, M.M. "Vapor Density of Dieldrin," *Journal of Agricultural and Food Chemistry*, 3:664-670 (1969).

(3) Spencer, W.F. and Cliath, M.M. "Vapor Density and Apparent Vapor Pressure of Lindane," *Journal of Agricultural and Food Chemistry*, 18:529-530 (1970).

[50 FR 39252, Sept. 27, 1985, as amended at 53 FR 12525, Apr. 15, 1988; 53 FR 21641, June 9, 1988; 60 FR 34466, July 3, 1995]

## Subpart C—Transport Processes

### § 796.2750 Sediment and soil adsorption isotherm.

(a) *Introduction—(1) Background and purpose.* The adsorption of chemicals to sediments and soils is an important process that affects a chemical's distribution in the environment. If a chemical is adsorbed to soil particles, it will remain on the soil surface and will not reach ground water. If a chemical is not adsorbed, it will leach through the soil profile and may reach ground waters and then surface waters. Similarly, if a chemical adsorbed to sediment, it will accumulate in the bed and suspended load of aquatic systems. If a chemical is not adsorbed to sediment, it will accumulate in the water column of aquatic systems. Information on the adsorption potential is needed under certain circumstances to assess the transport of chemicals in the environment. This section describes procedures that will enable sponsors to determine the adsorption isotherm of a chemical on sediments and soils.

(2) *Definitions and units.* (i) The "cation exchange capacity" (CEC) is the sum total of exchangeable cations that a sediment or soil can adsorb. The CEC is expressed in milliequivalents of negative charge per 100 grams (meq/100g) or milliequivalents of negative charge per gram (meq/g) of soil or sediment.

(ii) "Clay mineral analysis" is the estimation or determination of the kinds of clay-size minerals and the amount present in a sediment or soil.

(iii) "Organic matter" is the organic fraction of the sediment or soil; it includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the microbial population.

(iv) "Particle size analysis" is the determination of the various amounts of the different particle sizes in a sample (i.e., sand, silt, clay), usually by sedimentation, sieving, micrometry, or combinations of these methods. The names and diameter range commonly used in the United States are: