Designation: F 1769 – 97

Standard Test Method for Measurement of Diffusivity, Solubility, and Permeability of Organic Vapor Barriers Using a Flame Ionization Detector[1]

This standard is issued under the fixed designation F 1769; 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 covers the measurement of volatile organic-vapor-barrier properties of films, plastic sheeting, coated papers, and laminates. The specific material properties measured include diffusivity, solubility, and permeability coefficients; parameter values which are required for the solution of mass transfer problems associated with nonsteady state and steady state conditions.

1.2 Applicable test vapors include volatile organic compounds which are detectable by a flame ionization detector. Examples of applicable permeation compounds include solvents, organic film additives, flavor compounds, and aroma compounds.

1.3 This test method assumes the material being measured exhibits Fickian behavior and uses the solutions to Fick's Laws for a planar surface as the data regression model. (See Annex A1.)

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Terminology

2.1 *Definitions:*

2.1.1 *activation energy*—the thermodynamic property that describes the relationship of *P*, *D* and *S* to temperature. The relationship is Arrhenius and the parameters may be obtained by a linear fit of the natural log of the measurement value versus inverse temperature, K.

2.1.1.1 Arrhenius parameters of a material are dependent on the glass transition point of the material, and measurements spanning a glass transition point will therefore require multiple solutions (Fig. 1). The parameters of the fit are defined by the following equations:

$$P = P_0 \exp(-E_P/RT) \quad (1)$$

$$D = D_0 \exp(-E_D/RT) \quad (2)$$

$$S = S_0 \exp(-E_S/RT) \quad (3)$$

where:
P, D, and S = permeability, diffusion, and solubility coefficients,
P_0, D_0, and S_0 = Arrhenius fit intercepts,
R = gas constant,
T = temperature, and
E_P, E_D and E_S = activation energy values.

2.1.1.2 The intercept and activation energy values are essential to an understanding of a material's temperature dependence, and may be used to estimate a material's diffusion, solubility, and permeability values at any given temperature within the region of measurement. They may also be employed to estimate values outside of the region of measurement if the fit is sufficiently precise and a glass transition point has not been crossed. Methods of estimating the extrapolation error are available in current software packages and may also be obtained from standard references on statistics.

2.1.2 *diffusion coefficient*—a kinetic coefficient specific to a given material and compound that describes the relationship between molecular flux and molecular concentration change. *D* is defined by Fick's First Law:

$$F = -D\, dC/dx \quad (4)$$

where:
F = molecular flux,
D = diffusion coefficient, and
dC/dx = change in concentration in the direction of x. The SI units for D are m^2/s.

2.1.3 *permeability coefficient*—an empirical coefficient specific to a given material and compound that describes the relationship of steady state molecular flux to the partial pressure difference across a planar medium. *P* is defined by the relation:

$$F_e = P(p_1 - p_2)/L \quad (5)$$

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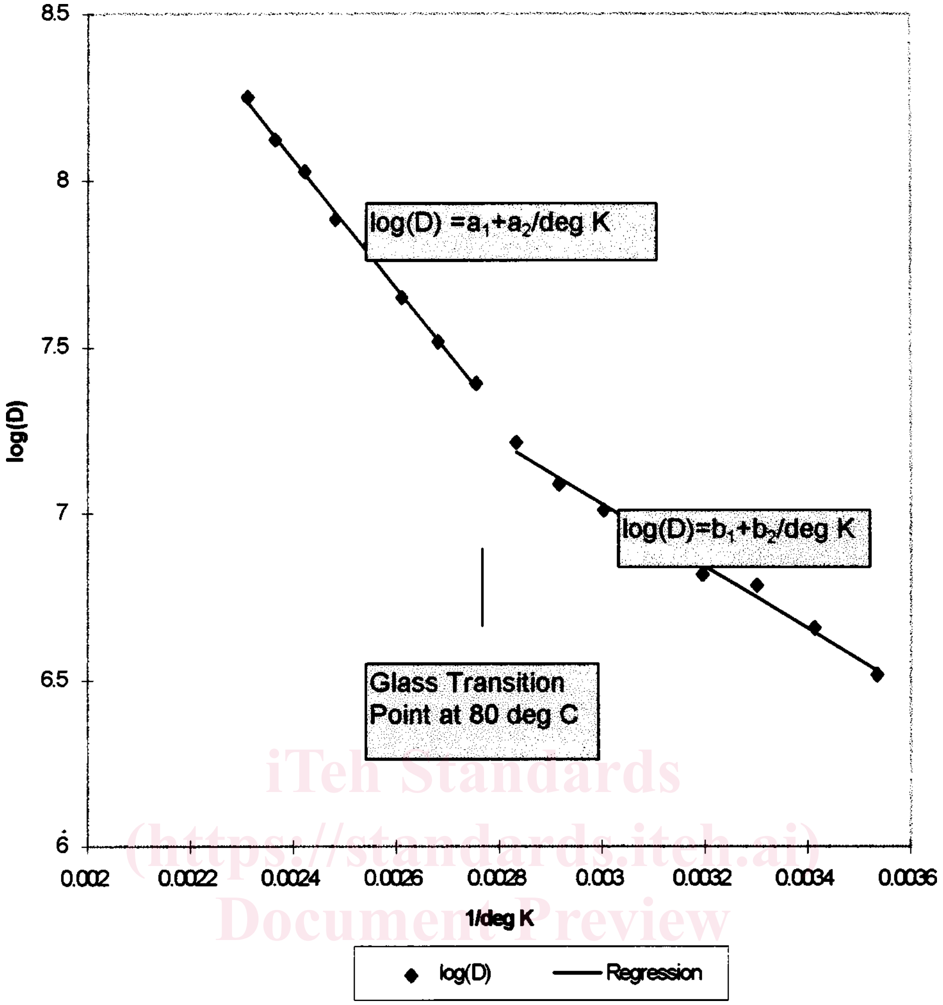

NOTE 1—The log of a mass transfer parameter such as diffusion, solubility, or permeability is expected to be linear with inverse temperature. At the glass transition point, the slope of the fit will change.

FIG. 1 Arrhenius Parameters of Hypothetical Experiment

where:

F_e = the vapor flux at equilibrium,
p_1 and p_2 = the vapor partial pressures on each side of the medium, and
L = barrier thickness. The SI units for P are kg/s·m·Pa

2.1.4 *sample diffusion coefficient, D_s*—the diffusion coefficient for a specific sample structure. The material diffusion coefficient may be calculated from the sample diffusion coefficient by the equation:

$$D = L^2 D_s \tag{6}$$

where L = thickness of the barrier layer.
The SI units for D_s are 1/s. D_2 is therefore a frequency value related to equilibrium time requirements.

2.1.5 *sample permeability flux, F_e*—a value describing the steady state permeation flux for the test structure and test gas partial pressure in kg/m^2·s. The material permeability coefficient P may be calculated from F_e by:

$$P = F_e L/(p_1 - p_2) \tag{7}$$

where:

L = barrier thickness, and
p_1 and p_2 = opposing gas vapor pressures.

2.1.6 *sample solubility coefficient, S_s*—the solubility coefficient for a specific sample structure and test vapor pressure. S_s is equal to F_e/D_s and is in units kg/m^2.

2.1.7 *solubility coefficient*—a coefficient value specific to a given material and compound defining the relationship of concentration to partial pressure. S is defined by Henry's Law:

$$C = Sp \tag{8}$$

where:

C = concentration within the medium,
S = solubility coefficient, and
p = vapor pressure of the permeating compound. The SI units for S are kg/m^3·Pa.

3. Summary of Test Method

3.1 A specific gas entity or mixture is exposed to one side of a planar sample by means of a constant gas flow within a controlled temperature cell. The test gas may be comprised of a single compound or multiple compounds (including moisture). Compounds which diffuse across the sample are swept by a carrier gas to a flame ionization detector. The resulting current signal from the detector is then amplified and tabulated in accordance with the time of exposure.

3.2 Although multiple compounds and mixtures may be employed as the test permeant, the analysis of multiple diffusion values is beyond the scope of this method. The employment of multiple compounds and mixtures will be appropriate if the compound detected by the sensor is singular and is known and the interaction effects of other compounds are desired.

3.3 The diffusion and permeability coefficients for a given sample and permeant combination are determined by a non-linear regression on the transient solution to Fick's Laws. (See Annex A1.)

3.4 The solubility coefficient is determined from the definition of the permeability coefficient and the application of Henry's Law (see Annex A1). These imply the following relationship:

$$S = P/D \tag{9}$$

3.5 The diffusion and permeability coefficients for a given sample and permeant combination are evaluated at a number of temperatures to yield the Arrhenius parameters. These values provide a measure of the temperature dependence of the permeant's transient and solubility in a given material.

4. Significance and Use

4.1 Values obtained may be used to estimate the mass transfer rate of volatile organic compounds permeating into and through a medium such as a plastic film or coating. Since the rate of transfer can sometimes be extremely slow, steady state conditions may not be achieved during the course of the experiment or in the intended end use of the material. In these situations, a reasonable estimate of the total mass transferred or absorbed requires estimates of the diffusion and solubility coefficients. In steady state situations, mass transfer may be estimated from the permeability coefficient. (These solutions are addressed in *The Mathematics of Diffusion*[2].)

4.2 Test measurement values are applicable to a number of issues associated with the interaction of a packaging material with volatile organic compounds. Examples include shelf life estimation when used in conjunction with other information; the evaluation of solvent release rates in a converting process; the evaluation of ingredient scalping into a packaging material.

4.3 Activation energy values may be employed to estimate the dependence of the measured mass transfer parameters on temperature. Since product end use conditions often vary, the effect of temperature on a material's performance can be critical to assessing a material's ability to meet its required function. These values also allow construction of a database by which materials may be compared for a wide range of end use temperature conditions.

5. Apparatus

5.1 *Impinger or Bubbler*, for production of the permeant test gas at the desired concentration.

NOTE 1—Other methods of permeant generation include the use of a packed column (for granular compounds) and gas cylinders containing a mixture of compounds. These are acceptable test gases if the permeant concentration values remain constant during the course of the test.

5.2 *Thermal Dewars or a Cold Temperature Bath*, capable of maintaining the permeant bubbler at a room temperature condition or lower.

5.3 *Two Stage Regulators*, for each of the required gas supplies which include a carrier gas such as helium or nitrogen, and detector fuels which include hydrogen and air (or oxygen).

5.4 *Means to Precisely Control the Flow of Each Required Gas*—As gas flow is critical to the precision of the measurement, a flow rate precision of at least ±0.1 mL/min is required.

5.5 *Temperature-Controlled Test Cell*, as diagrammed in Fig. 2 consisting of two chambers diametrically opposed and with a means of supporting the measurement sample so as to separate the two chambers without leakage. Test cell parameters critical to the measurement process include the following:

5.5.1 *O-Ring*, constructed of Viton (or another known inert material) for sealing the film is mounted within the cell to prevent leakage. The O-ring is to be mounted on the test permeant side of the cell so as to eliminate its effect on the detection of compounds diffusing across the test sample.

5.5.2 *Cell Chamber Volumes*, in the range of 10 to 15 cc. Larger volumes are known to interfere with the measurement process as they incorporate a significant delay time in test gas concentration changes.

5.5.3 *Film Sample Area*, as defined by the O-ring diameter in the range of 80 to 100 cm^2.

5.5.4 *Means to Control the Temperature*, on both sides of the cell (exposure and detector sides) to a precision of ±0.05°C.

5.6 *Valving and Stainless Steel Plumbing*, allowing operator selection of the permeant chamber gas (either the test permeant or the carrier gas) and transport of the selected gas into the permeant chamber and away from the permeant chamber to an exhaust.

5.7 *Flame Ionization Detector and Amplifier*, capable of detecting gas concentration differences to at least 1 ppm and the means to record the resulting signal with respect to time.

5.8 *Flow Controls and Stainless Steel Plumbing*, allowing the maintenance of a constant flow of carrier gas into the detector chamber and then out to the detector. As the measurement signal is dependent on flow rate changes, a flow rate precision of at least± 0.1 mL/min is required.

5.9 *Injection Port*, located prior to the test cell detector chamber for injections of known calibration compounds.

5.10 *Syringes*, of varying size (10 to 1000 µL) for injection of gas calibration samples. Syringe needles will need to be of a side port type in order to prevent plugging of the syringe and to assure consistent calibration values.

5.11 *Septum Vials*, with a volume capacity of 50 to 100 mL for preparation of calibration standards. The septum material will be TFE-fluorocarbon or another material known to not interact with the calibration compound.

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[2] *The Mathematics of Diffusion*, J. Crank, Clarendon Press, Oxford, 1975.

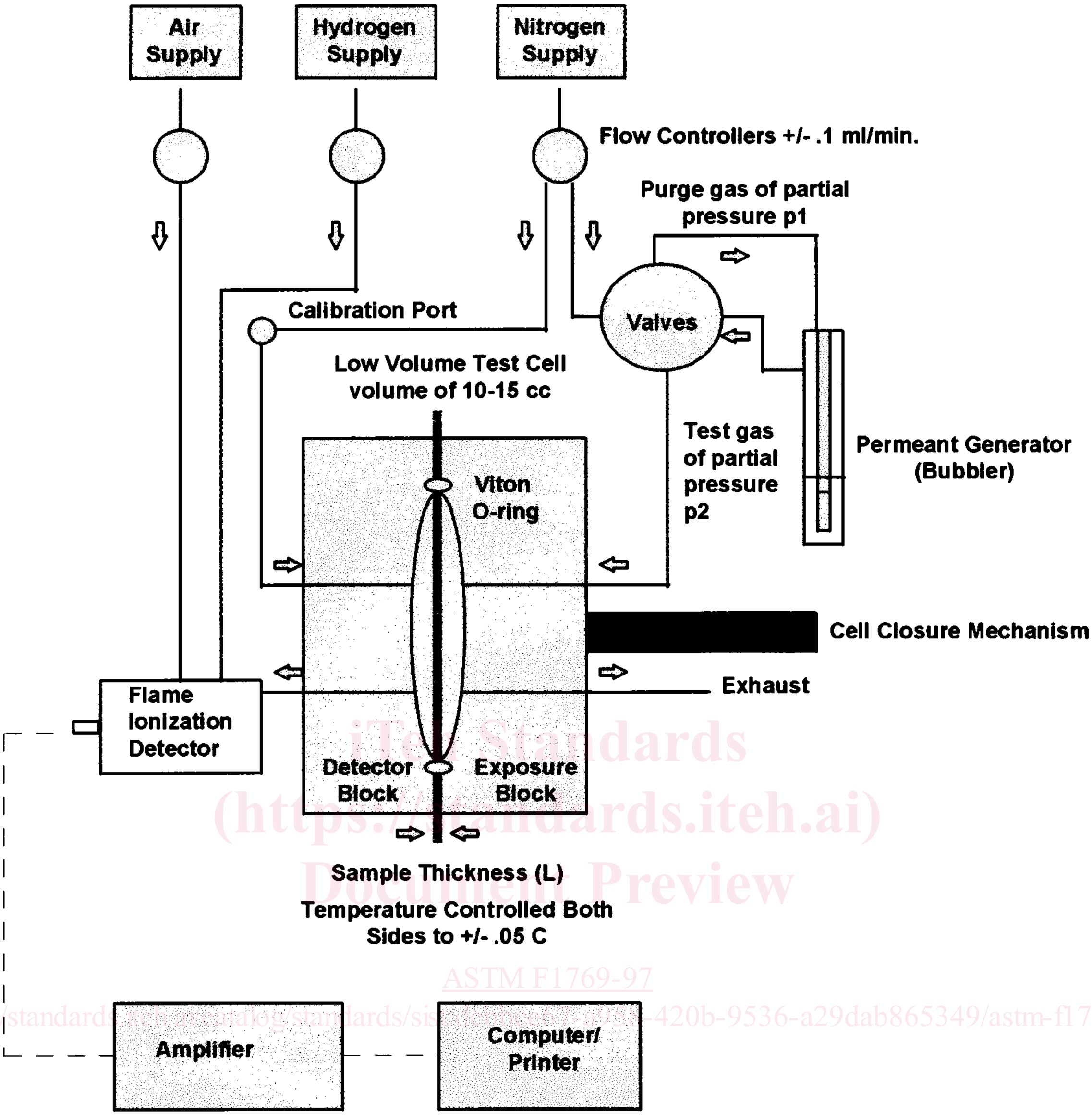

FIG. 2 Equipment Diagram

6. Reagents and Materials

6.1 *Gas Supplies*, of a GC grade or better to include nitrogen as a carrier gas (or helium), and flame ionization detector fuels of hydrogen and air.

6.2 *Vapor Generation Compounds or Mixtures*, for generating the test gas stream and to prepare calibration standards.

7. Sampling

7.1 Select samples representative of the lot or the material to be tested. Samples should be free of wrinkles or pinholes and of a size sufficient for placement within the test cell area.

8. Permeant Preparation

8.1 Fill the bubbler or impinger to a specified level with the compound to be evaluated and place in a dewar of ice water or a controlled temperature bath. Note the fill level and the bubbler specification. Maintain the bubbler at a constant temperature and level and record the temperature value to the nearest degree centigrade by means of a thermometer, thermocouple, or other temperature probe.

8.1.1 Maintaining a constant bubbler temperature is critical to minimize variation in the test vapor pressure. In most experimental situations, an ice bath will be the preferred means of temperature control in order to produce a vapor pressure more typical of end use applications and to avoid condensation in the plumbing from the bubbler to the test cell. Obtain the vapor pressure of the compound at the temperature of generation from a standard reference manual (*CRC Handbook of Chemistry and Physics*[3]) or evaluate by GC analysis.

8.2 Prepare septum vials containing 10 mL of the compound to be evaluated for use as calibration standards. These vials should be kept in a controlled temperature water bath at a temperature equal to or less than room temperature. Note the vial specification, fill level, and temperature.

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[3] *Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, FL.