



Standard Test Method for Determination of Oxygen Gas Transmission Rate, Permeability and Permeance at Controlled Relative Humidity Through Barrier Materials Using a Coulometric Detector¹

This standard is issued under the fixed designation F 1927; 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 a procedure for determination of the rate of transmission of oxygen gas, at steady-state, at a given temperature and %RH level, through film, sheeting, laminates, co-extrusions, or plastic-coated papers or fabrics. This test method extends the common practice dealing with zero humidity or, at best, an assumed humidity. Humidity plays an important role in the oxygen gas transmission rate (O_2 GTR) of many materials. This test method provides for the determination of oxygen gas transmission rate (O_2 GTR), the permeance of the film to oxygen gas ($P'O_2$), the permeation coefficient of the film to its thickness (PO_2), and oxygen permeability coefficient ($P'O_2$) in the case of homogeneous materials at given temperature and %RH level(s).

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

- D 1434 Test Method for Gas Transmission Rate of Plastic Film and Sheet
- D 1898 Practice for Sampling of Plastics
- D 3985 Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheet Using a Coulometric Sensor

¹ This test method is under the jurisdiction of ASTM Committee F02 on Flexible Barrier Materials and is the direct responsibility of Subcommittee F02.30 on Test Methods.

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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.

E 104 Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 Definitions:

3.1.1 *oxygen permeability coefficient* ($P'O_2$)—the product of the permeance and the thickness of the film. The permeability is meaningful only for homogeneous materials, in which case it is a property characteristic of the bulk material. This quantity should not be used unless the relationship between thickness and permeance has been verified on tests using several different thicknesses of the material. The SI unit of oxygen permeability is the $\text{mol}/\text{m} \cdot \text{s} \cdot \text{Pa}$. The test conditions (see 3.1.4) must be stated.

3.1.2 *oxygen permeance* ($P'O_2$)—the ratio of O_2 GTR to the difference between the partial pressure of O_2 on the two sides of the film. The SI unit of permeance is the $\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$. The test conditions (see 3.1.4) must be stated.

3.1.3 *oxygen permeation coefficient* (PO_2)—the ratio of O_2 GTR to the thickness of the film. The SI unit of permeance is the $\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{cm}$. The permeation coefficient is meaningful only for homogeneous materials, in which case it is a property characteristic of the bulk material. This quantity should not be used unless the relationship between thickness and transmission rate is known.

3.1.4 *oxygen transmission rate*—at a given temperature and %RH (O_2 GTR), the quantity of oxygen gas passing through a unit area of the parallel surfaces of a plastic film per unit time under the conditions of test. The SI unit of transmission rate is the $\text{mol}/\text{m}^2 \cdot \text{s}$. The test conditions, including temperature, %RH and oxygen partial pressure on both sides of the film must be stated.

3.1.5 *transmission rate* (O_2 GTR)—a commonly used metric unit of O_2 GTR is the $\text{cm}^3(\text{STP})/\text{m}^2 \cdot \text{d}$ at one atmosphere pressure differential where: 1 $\text{cm}^3(\text{STP})$ is 44.62 μmol , 1 atm is 0.1013 MPa, and one day is 86.4×10^3 s. O_2 GTR in SI units is obtained by multiplying the value in metric units by

5.165×10^{-10} or the value in inch-pound units $[(\text{cm}^3/\text{STP}/100 \text{ in.}^2 \cdot \text{d})]$ by 8.005×10^{-9} .

4. Summary of Test Method

4.1 The oxygen gas transmission rate is determined after the sample has equilibrated in a given temperature and humidity environment.

4.2 The specimen is mounted as a sealed semi-barrier between two chambers at ambient atmospheric pressure. One chamber is slowly purged by a stream of nitrogen at a given temperature and %RH and the other chamber is purged by a stream of oxygen at the same temperature as the N_2 stream but may have a different %RH than the N_2 stream. In this case the environment would more closely simulate actual shelf conditions. As oxygen gas permeates through the film into the nitrogen carrier gas, it is transported to the coulometric detector where it produces an electrical current, the magnitude of which is proportional to the amount of oxygen flowing into the detector per unit time.

5. Significance and Use

5.1 O_2GTR at a given temperature and %RH is an important determinant of the packaging protection afforded by barrier materials. It is not, however the sole determinant, and additional tests, based on experience, must be used to correlate packaging performance with O_2GTR . It is suitable as a referee method of testing, provided that purchaser and seller have agreed on sampling procedures, standardization procedures, test conditions and acceptance criteria.

6. Interferences

6.1 The presence of certain interfering substances in the carrier gas stream may give rise to unwanted electrical outputs and error factors. Interfering substances include free chlorine and some strong oxidizing agents. Exposure to carbon dioxide should also be minimized to avoid damage to the sensor through reaction with the potassium hydroxide electrolyte.

7. Apparatus

7.1 *Oxygen Gas Transmission Apparatus*, as diagramed in Fig. 1 and described following. Alternative systems need to be evaluated to ensure equivalent performance.

7.1.1 *Diffusion Cell*, consisting of two metal halves, that, when closed upon the test specimen, will accurately define a circular area. Typical acceptable diffusion cell areas are 100 and 50 cm^2 . The volume enclosed by each cell half, when clamped, is not critical: it should be small enough to allow for rapid gas exchange, but not so small that an unsupported film which happens to sag or bulge will contact the sides of the cell. The diffusion cell shall be provided with a temperature measuring and controlling capability and a means to measure and control relative humidity.

7.1.1.1 Temperature control is critical because RH can vary as much as 5 % RH/ $^{\circ}\text{C}$ in certain temperature regions. A compact design of the diffusion cell structure with associated controls would lend itself to better temperature control. The temperature should be controlled to $\pm 0.5^{\circ}\text{C}$ or better.

7.1.1.2 *O-Ring*—An appropriately sized groove, machined into the oxygen (or test gas) side of the diffusion cell, retains a neoprene O-ring. The test area is considered to be that area

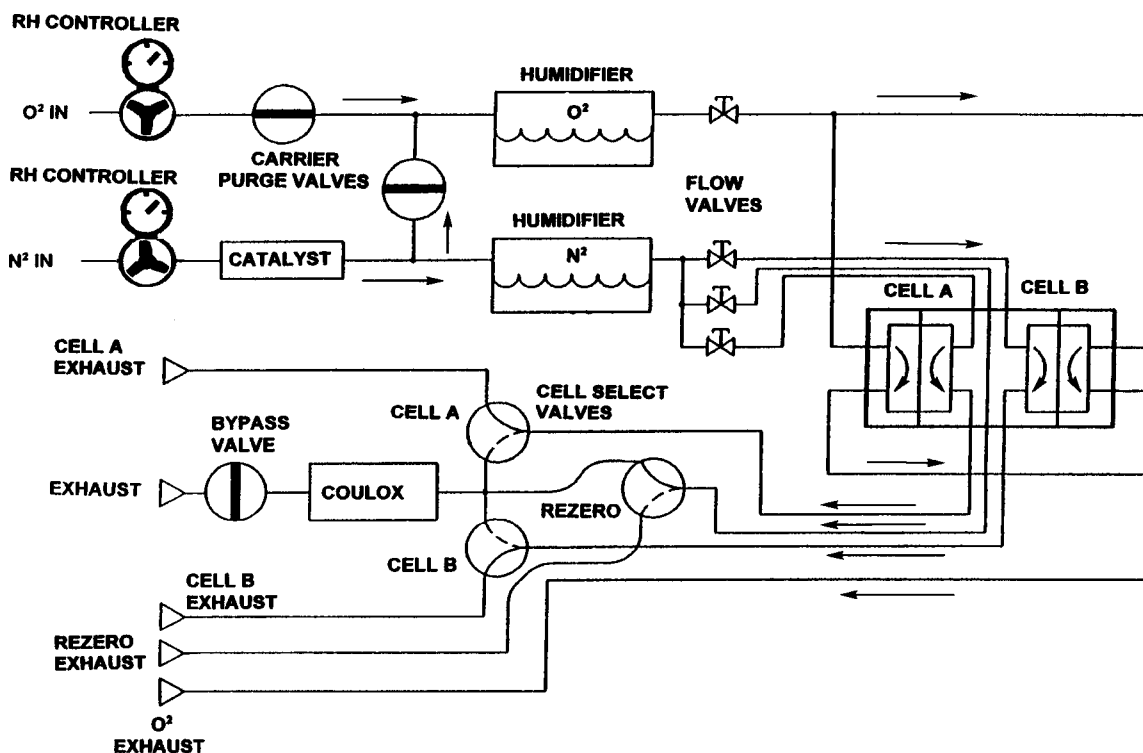


FIG. 1 A Practical Arrangement of Components for the Measurement of Oxygen Transmission Rate Under Precise Relative Humidity Conditions Using the Coulometric Method

established by the inside contact diameter of the compressed O-ring when the diffusion cell is clamped shut against the test specimen. The area, A , can be obtained by measuring the inside diameter of the imprint left by the O-ring on the specimen after it has been removed from the diffusion cell.

7.1.1.3 The nitrogen (or carrier gas) side of the diffusion cell shall have a flat raised rim. Since this rim is a critical sealing surface against which the test specimen is pressed, it shall be smooth and flat, without radial scratches.

7.1.1.4 *Diffusion Cell Pneumatic Fittings*—Each half of the diffusion cell shall incorporate suitable fittings for the introduction and exhaust of gasses without significant loss or leakage.

7.1.1.5 Experience has shown that arrangements using multiple diffusion cells are a practical way to increase the number of measurements which can be obtained from a coulometric sensor. A valving manifold shall connect the carrier gas side of each individual diffusion cell to the sensor in a preselected pattern. Carrier gas is continually purging the carrier gas sides of those cells that are not connected to the sensor. Either test gas or carrier gas, as is appropriate, purges the test gas chamber of any individual cell.

7.1.2 *Catalyst Bed*—Should be used on the carrier gas (N_2) side of the diffusion cell assembly to provide an essentially oxygen free carrier gas. Palladium catalyst on alumina³ converts O_2 molecules into H_2O , thus virtually eliminating O_2 molecules in the carrier gas.

7.1.3 Oxygen gas transmission apparatus⁴ shall have the capability of measuring, at a variety of relative levels including, zero RH to 90 % RH at a wide range of temperatures.

7.1.4 Package testing at given temperature and %RH levels to be optional if it is not included in the basic configuration.

7.1.5 *Coulometric Sensor*—An oxygen-sensitive coulometric sensor operating at an essentially constant efficiency shall be used to monitor the quantity of oxygen transmitted.⁴

7.1.6 With computer controlled systems, the results are printed out giving final results, time-history of equilibration, ambient conditions of test, material being tested and date. Should a failure occur, the time of this occurrence and its cause and correction taken should be documented for operator analysis as to the validity of continued testing.

7.1.7 *RH Detectors*—Water sensitive solid-state devices are used to monitor the relative humidity of the gases directly in the upper and lower halves of the cell.

7.1.7.1 Placement of the RH detectors in the diffusion cells is important because relative humidity will change whenever the temperature of the relative humidity source and diffusion cells differ.

7.1.7.2 The RH detectors should periodically be calibrated against saturated salt solutions (see Practice E 104) or NIST traceable devices.⁵

8. Reagents and Materials

8.1 *Nitrogen Carrier Gas*, consisting of a nitrogen and hydrogen mixture in which the percentage of hydrogen shall fall between 0.5 and 3.0 volume %. The carrier gas shall be dry and contain not more than 100 ppm of oxygen. A commercially available mixture known as “forming gas” is suitable.

8.2 *Oxygen Test Gas*, shall be dry and contain not less than 99.5 % oxygen (except as provided in 14.10).

8.3 *Water to Generate %RH*—Double or triple-distilled water is recommended (not deionized water) for precise relative humidity generation and to avoid scale build up.

8.4 *Sealing Grease*—A high-viscosity hydrocarbon grease⁶ (preferred) or a high-vacuum grease is required for sealing the specimen film in the diffusion cell.

9. Precautions

9.1 Temperature is a critical parameter affecting the measurement of O_2 GTR. Careful temperature control will help to minimize variations due to temperature fluctuations. During equilibration and testing the temperature shall be monitored periodically. Should this temperature exceed $\pm 0.5^\circ C$ after reaching the desired temperature, report the average temperature and the range of temperatures found during the test.

9.2 The sensor will require a relatively long time to stabilize to a low reading characteristic of a good barrier after it has been used to test a poorer barrier such as low density polyethylene. For this reason, materials of comparable gas transmission qualities should be tested together.

9.3 Back diffusion of air into the unit is undesirable. Care should be taken to ensure that there is a flow of nitrogen through the system at all times. This flow can be low when the instrument is not being used.

9.4 Elevated temperatures to hasten specimen out gassing is not recommended. RH is a function of temperature and, therefore, equilibrating at some other temperature than the test temperature would expose the sample to an incorrect RH during the equilibration process. The entire test should be run at constant temperature and constant RH.

10. Sampling

10.1 The samples used for the determination of O_2 GTR shall be representative of the quality of product for which the

³ The sole source of supply of the apparatus, a suitable catalyst, known to the committee at this time is Englehard Industries Division, Chemical Department, 429 Delancey Street, Newark, NJ 07105. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

⁴ The sole source of supply of suitable apparatus such as that embodied in several later OX-TRAN models known to the committee at this time is available from MOCON/Modern Controls, Inc. 7500 Boone Ave N, Minneapolis, MN 55428. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

⁵ Hasegawa, S. (NIST) “National Basis of Accuracy in Humidity Measurements,” *ISA Transactions*, Vol 25, No. 3, 1986, pp. 15–24.

⁶ The sole source of supply of the apparatus, a suitable hydrocarbon grease such as Apiezon T, known to the committee at this time is, Biddle Instruments, 510 Township Road, Blue Bell, PA 19422. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

data are required, in accordance with Practice D 1898.⁶ Care shall be taken to ensure that film samples are representative of conditions across the width and along the length of the film being tested.

11. Test Specimen

11.1 Test specimens shall be representative of the material being tested and free of defects, including wrinkles, creases, and pinholes, unless these are a characteristic of the material being tested.

11.2 Average thickness shall be determined to the nearest 2.5 μm (0.0001 in.), using a calibrated dial gage or equivalent at a minimum of five points distributed over the entire test area. Maximum, minimum, and average values shall be recorded.

11.3 If the test specimen is of an asymmetrical construction, the two surfaces shall be marked by appropriate distinguishing marks and the orientation of the test specimen in the diffusion cell shall be reported (for example, "Side II Was Mounted Facing the Oxygen Side of the Diffusion Cells").

12. Calibration

12.1 *General Approach*—The oxygen detector used in this test method is a coulometric device that yields a linear output as predicted by Faraday's Law. In principle, four electrons are produced by the detector for each molecule of oxygen that passes into it. Considering that the detector is known to have a basic efficiency of 95 to 98 % it may be considered an "intrinsic" standard.⁷

12.1.1 Experience has shown, however, that under some circumstances the sensor may become depleted or damaged to the extent that efficiency and response are impaired. For this reason, this test method incorporates means for periodic detector evaluation. This evaluation is derived from measurements of a known-value "Reference Package".

12.2 *Detector Evaluation*—The reference package is a diffusion cell in which a sheet of reference of known O_2TR has been sealed and clamped. This creates a "package" into which oxygen will diffuse at a known rate.

12.3 *Assembling the Reference Package*—Ensure the carrier gas stream is diverted away from the detector to avoid exposing the detector to room oxygen. Unclamp the diffusion cell and open it. Apply a thin layer of sealing grease⁸ around the raised rim of the one half of the diffusion cell. Insert the sheet of reference film⁸ in the diffusion cell and place it upon the greased surface, taking care to avoid wrinkles or creases. Clamp both halves tightly together.

12.4 *Testing The Reference Film*—Determine the specimen area in units in which results are to be reported. Determine the O_2GTR provided at equilibrium with the reference film in the diffusion cell in units which results are to be reported. Use these values in the equation found in Item Number 15.1; use the result to adjust the system gain so that its output agrees with the stated reference film O_2GTR .

NOTE 1—**Caution**—The O_2GTR of the reference film may be adversely affected by water vapor in the test gas or the carrier gas, therefore detector evaluation tests should be run at 0 % RH.

13. Conditioning

13.1 Trim the test specimen to a size appropriate for the diffusion cell in which it will be mounted. In general, this means that the seal around the edge of the diffusion cell should not be impaired if the specimen bulges or sags slightly.

13.2 Measure O_2GTR in a temperature-controlled environment with the apparatus placed in a draft free location.

14. Procedure

14.1 *Controlled RH Test Procedure*—Disable the detector to avoid exposing it to air. Unclamp the diffusion cell and open it. Apply a thin layer of sealing grease (see 8.4) around the raised rim of the diffusion cell. Place the test specimen upon the greased surface, taking care to avoid wrinkles or creases. Clamp both halves tightly together.

14.2 *Purging the System*—Adjust the RH of the test and carrier gases to the desired levels using the appropriate controls. Place the system into the mode where both sides of the film are being purged. Start the nitrogen carrier gas flow and purge the air from both sides of the diffusion cell chambers, using a flow rate between 5 and 15 mL/min. After the RH stabilizes, make any necessary adjustments to the RH controls to achieve the desired levels. Let the RH stabilize.

14.3 *Establish Zero Level (E_0)*—After the system has been flushed with nitrogen for a minimum of 30 min, divert the carrier gas which has passed through the diffusion cell into the detector. At this time, the detector output will usually increase abruptly, indicating that oxygen is entering the detector with the carrier gas. The most likely sources of this oxygen are out-gassing of the sample, leaks in the system, or a combination of both of these. The operator shall observe the zero level until the detector output current stabilizes at a constant value with no significant trend in either direction. Thick samples may require a purge of several hours, overnight, or longer before a steady low value of zero level is obtained.

14.4 Once the carrier gas "zero" (E_0) has been established, cut off the flow of nitrogen into the test-gas side of the diffusion cell and substitute a flow of oxygen test gas into the diffusion cell. This is automated on computer controlled systems.

14.5 *Establish Equilibrium Level (E_e)*—The O_2GTR should increase gradually, ultimately stabilizing at a constant value. While some thin films with high diffusion coefficients may reach equilibrium in 30 to 60 min, thicker, or more complex structures may require several hours or days to reach a steady state of gas transmission. The equilibrium value of the O_2GTR shall be recorded.

NOTE 2—If, after attainment of an apparent steady-state condition, any doubt exists as to whether this is a true steady-state condition, perform a check as follows:

- (1) Divert the carrier gas away from the detector.
- (2) Allow unit to stabilize for an additional time period of 2 to 8 h.
- (3) Divert the carrier gas back through the detector and again monitor the O_2GTR . An increased output indicates steady-state conditions had not been reached, while the same output (no increase) indicates steady-state conditions had been obtained initially.

⁷ Garner, E. L. and Raspberry, S. D., "What's New in Traceability" *Journal of Testing and Evaluation*, Vol 21, No. 6, November 1993, pp. 505–509.

⁸ Reference material available from Modern Controls, Inc., has been found satisfactory.

14.6 Obtain temperature by monitoring the temperature of the specimen.

14.7 *Standby and Shutoff Procedures*—At the conclusion of a test, but at a time when it is expected that other tests will be performed soon, the instrument should be placed in a standby condition by taking the following steps:

14.7.1 Divert the carrier gas away from the detector.

14.7.2 Turn off the oxygen supply.

14.7.3 Reduce the nitrogen flow rates to less than 5 mL/min.

14.7.4 These steps will economize on carrier and test gases and will minimize the danger of ruining the detector because of a film failure while the instrument is not being used for testing. It is desirable to maintain a slow flow of nitrogen through the instrument when it is not being used in order to reduce the back diffusion of air into the system. When the instrument is not being used for a long period of time, the electrical power may be turned off.

14.8 *Tests Using %RH Environment*—The coulometric method has been used routinely in RH environments. Passing through the detector are N₂, H₂, H₂O, and O₂, which is similar to previous “DRY” testing procedures (see Test Method D 3985). The basic change is that there may be more H₂O molecules in the flow to the detector during high %RH testing. A higher H₂O content in the carrier gas has been proven to have no discernible effect on the detector output.

14.9 O₂GTR at environmental temperatures other than ambient may be determined by thermostatically controlling the diffusion cell provided that the temperature of the carrier gas does not adversely affect the operation of the detector.

14.10 *Testing Poor Barriers*—Films having transmission rates in excess of 200 cm³(STP)/(m²-d) when tested with an oxygen partial pressure difference of one atmosphere are defined as poor barriers. Examples of such materials, depending on thickness, include polyethylene, polycarbonate, and polystyrene. High oxygen concentrations in the carrier gas, from the testing of poor barriers, will tend to produce detector saturation. One way to avoid this problem is to use a test gas that is a mixture with a known concentration of oxygen in nitrogen. The permeance of the film should be calculated using the known value of oxygen partial pressure, and then a transmission rate should be calculated for the appropriate partial pressure difference from the permeance and the desired partial pressure difference.

15. Calculation

15.1 Determine the O₂GTR as follows:

$$O_2GTR = \frac{(E_e - E_o)}{A}$$

where:

E_e = steady state test O₂GTR level (see 14.6),

E_o = “zero” O₂GTR level (see 14.4), and

A = specimen area (see 7.1.1.2).

15.2 Determine the permeance (PO₂) of the specimen as follows:

$$PO_2 = \frac{O_2GTR}{P}$$

where:

P = partial pressure of oxygen, which is the mol fraction of oxygen multiplied by the total pressure (nominally, one atmosphere), in the test gas side of the diffusion cell. The partial pressure of O₂ on the carrier gas side is considered to be zero.

15.3 Determine the oxygen permeability coefficient P'O₂ as follows:

$$P'O_2 = PO_2 \times l$$

where:

l = average thickness of the specimen (see 11.2). Results should be expressed as permeabilities only in cases where materials have been determined to be homogeneous by investigation of the relationship between specimen thickness and permeance.

16. Report

16.1 Report the following information:

16.1.1 A description of the test specimen, including an identification of the two sides of the material if they are different, a statement as to which side was facing the test gas, the location of the specimen in the lot of material of which it is representative, and the dimensions of the test specimen,

16.1.2 The average thickness of the test specimens as determined in 11.2 and the standard deviation of the thickness values,

16.1.3 The barometric pressure at the time of the test. This information is not required if the pressure of the gas on the test gas side of the diffusion cell is maintained by any accurate pressure regulating device,

16.1.4 The partial pressure of the oxygen gas on the test-gas side of the diffusion cell and a statement as to how it was generated,

16.1.5 The rate of flow of the nitrogen carrier gas during the test,

16.1.6 The conditioning procedure used on the test specimen prior to testing,

16.1.7 The temperature of the test specimen (to the nearest 0.5°K) and the method used to determine the temperature,

16.1.8 RH values used, state both test gas RH and carrier gas RH,

16.1.9 The values of O₂GTR, permeance (if desired), and the permeability (if desired),

16.1.10 A description of the apparatus used including, if applicable, the manufacturers' model number and serial number,

16.1.11 A statement of the means, if any, used to adjust the detector gain factor,

16.1.12 The effective area for permeation, A , and

16.1.13 The time to reach the steady-state after introduction of the oxygen gas into the test-gas side of the diffusion cell.

17. Precision and Bias ⁹

17.1 *Precision:*

⁹ A research report is available from ASTM headquarters. Request RR:F02-1012.

17.1.1 The repeatability and reproducibility given in Table 1 are in accordance with the definitions of these terms in Practice E 691 using the Interlaboratory Data Analysis Software given in Practice E 691. These values have been calculated for test results obtained as specified in this test method. The values are based on an interlaboratory study involving two laboratories in which each laboratory made six determinations of the oxygen transmission rate on each of four film types. For each film, the

total number of required test specimens for all the laboratories together were taken from single lots and randomized before distribution to the laboratories.

17.1.2 The precision, characterized by repeatability, S_r ; r , and reproducibility, by SR , R , has been determined for the following materials, and is given in Table 1.

17.2 Bias:

17.2.1 The bias for this test method has not been determined because there is no known reference available.

17.2.2 The number of laboratories in this study does not meet the minimum requirements for determining precision as prescribed in Practice E 691. A full round robin following this test method will be organized and the results of that round robin testing will be accumulated and analyzed and will be made part of this test method.

TABLE 1 Precision Statement for Test Method O₂ Wet

Materials	Average	S_r	SR	r	R
0.5 Mil PET	93.4880	1.8221	1.9270	5.1018	5.3956
1 Mil PET	48.7670	0.3981	1.0506	1.1148	2.9416
2 Mil Multi	04.0370	0.1839	0.1839	0.5149	0.5149
10 Mil Nylon	01.6110	0.0893	0.0893	0.2501	0.4401

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