Designation: D 3985 – 95

Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor[1]

This standard is issued under the fixed designation D 3985; 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 steady-state rate of transmission of oxygen gas through plastics in the form of film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. It provides for the determination of (*1*) oxygen gas transmission rate (O_2GTR), (*2*) the permeance of the film to oxygen gas (PO_2), and (*3*) oxygen permeability coefficient $\bar{P}O_2$) in the case of homogeneous materials.

1.2 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1434 Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting[2]

D 1898 Practice for Sampling of Plastics[3]

3. Terminology

3.1 *Definitions:* :

3.1.1 *oxygen transmission rate* (O_2GTR)—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 mol/(m^2·s). The test conditions, including temperature and oxygen partial pressure on both sides of the film must be stated.

3.1.1.1 A commonly used unit of O_2GTR is the cm^3(STP)/m^2·d) at one atmosphere pressure difference where 1 cm^3(STP) is 44.62 μmol, 1 atm is 0.1013 MPa, and one day is 86.4×10^3s. The O_2GTR in SI units is obtained by multiplying the value in inch-pound units by 5.160×10^{-10}.

3.1.2 *oxygen permeance* (PO_2)—the ratio of the O_2GTR to the difference between the partial pressure of O_2 on the two sides of the film. The SI unit of permeance is the mol/(m^2·s·Pa). The test conditions (see 5.1) must be stated.

3.1.3 *oxygen permeability coefficient* ($\bar{P}O_2$)—the product of the permeance and the thickness of 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 mol/m·s·Pa. The test conditions (see 3.1.1) must be stated.

4. Summary of Test Method

4.1 The oxygen gas transmission rate is determined after the sample has equilibrated in a dry test environment. In this context, a" dry" environment is considered to be one in which the relative humidity is less than 1 %.

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 and the other chamber contains oxygen. 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 The O_2GTR 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 the purchaser and the seller have agreed on sampling procedures, standardization procedures, test conditions, and acceptance criteria.

5.2 Limited statistical data on correlations with Test Method D 1434 methods are available.[4] However, the oxygen transmission rate of a standard reference material (see 12.1) as determined manometrically by the National Bureau of Standards, is in good agreement with the values obtained in the coulometric interlaboratory test using material from the same manufacturing lot. Thus, this test method may be used as a referee method.

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 diagrammed in Fig. 1[5] with the following:

7.1.1 *Diffusion Cell* shall consist of two metal halves, which, when closed upon the test specimen, will accurately define a circular area. Typical acceptable diffusion cell areas are 100 cm^2 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 top or bottom of the cell. Each half of the diffusion cell shall be provided with a thermometer well for measuring temperature.

7.1.1.1 *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 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.

7.1.1.2 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.

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

7.1.1.4 It is desirable to thermostatically control the diffusion cell. A simple resistive heater, attached to the carrier gas side of the cell in such a manner as to ensure good thermal contact, is adequate for this purpose. A thermistor sensor and an appropriate control circuit will serve to regulate the cell temperature unless measurements are being made close to ambient temperature. In this case, it is desirable to provide cooling coils to remove some of the heat.

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 connects the carrier gas side of each individual diffusion cell to the sensor in a predetermined 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.

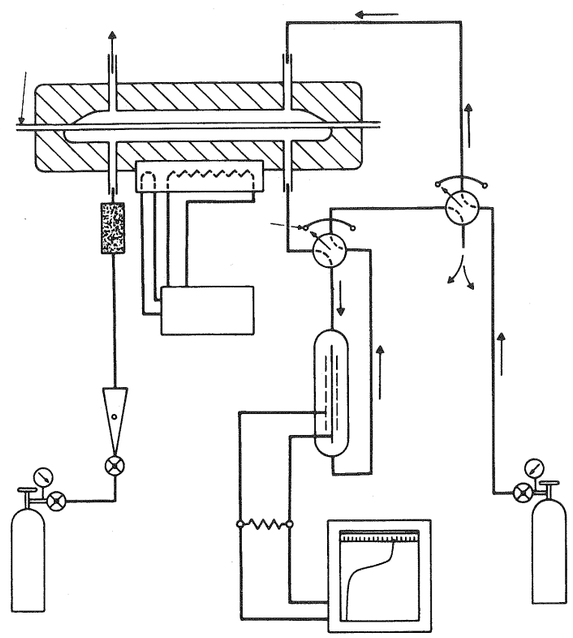

FIG. 1 A Practical Arrangement of Components for the Measurement of Oxygen Transmission Rate Using the Coulometric Method

[1] This test method is under the jurisdiction of ASTM Committee F-2 on Flexible Barrier Materials and is the direct responsibility of Subcommittee F02.30 on Test Methods.

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[2] *Annual Book of ASTM Standards*, Vol 15.09.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] Supporting data for this test method can be obtained from ASTM Headquarters. Request RR:D20-1085.

[5] Suitable apparatus, identified as Oxtran Model 100 and Oxtran Model 10–50, can be obtained from Modern Controls, Inc. 6820 Shingle Creek Parkway, Minneapolis, MN 55430.

7.1.2 *Catalyst Bed*—A small metal tube with fittings for attachment to the inlet on the nitrogen side of the diffusion cell shall contain 3 to 5 g of 0.5 % platinum or palladium catalysts on alumina[6] to provide an essentially oxygen-free carrier gas.

7.1.3 *Flowmeter*—A metal/glass, ball-in-tube flowmeter having an operating range from 5 to 100 mL/min is required to monitor the flow rate of the nitrogen carrier gas.

7.1.4 *Flow Switching Valves*—Two four-port ball valves for the switching of the nitrogen and test gas flow streams.

7.1.5 *Coulometric Sensor*—An oxygen-sensitive coulometric sensor[7] operating at an essentially constant efficiency shall be used to monitor the quantity of oxygen transmitted.

7.1.6 *Load Resistor*—The current generated by the coulometric cell shall pass through a resistive load across which the output voltage is measured. Typical values for the load resistor are 5.3 or 53 Ω. These values yield a convenient relationship between the output voltage and the oxygen transmission rate in inch-pound units (cm^3(STP)/m^2·d).

7.1.7 *Voltage Recorder*—A multirange, potentiometer strip chart recorder shall be used for measuring the voltage developed across the load resistor. The recorder should be capable of measuring a full-scale voltage of 50 mV. It should be capable of measuring voltages as low as 0.100 mV and have a resolution of at least 10 µV. An input impedance of 5000 Ω or higher is acceptable.

8. Reagents and Materials

8.1 *Nitrogen Carrier Gas* shall consist 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 14.11).

8.3 *Sealing Grease*—A high-viscosity silicone stopcock grease or a high-vacuum grease is required for sealing the specimen film in the diffusion cell.

9. Precautions

9.1 Extended use of the test unit, with no moisture in the gas stream, may result in a noticeable decrease in output and response time from the sensor (equivalent to an increase in the calibration factor, Q). This condition is due to drying out of the sensor and can often be corrected by injecting approximately 2 mL of water into the sensor at its inlet connection.

9.2 Temperature is a critical parameter affecting the measurement of O_2GTR. Careful temperature control can help to minimize variations due to temperature fluctuations. During testing, the temperature shall be monitored periodically to the nearest 0.5 K. The average temperature and the range of temperatures found during a test shall both be reported.

9.3 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 barrier such as low-density polyethylene. For this reason, materials of comparable gas transmission qualities should be tested together.

9.4 Back diffusion of air into the unit is undesirable. Care should therefore 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.

9.5 Elevated temperatures can be used to hasten specimen outgassing, provided that the treatment does not alter the basic structure of the specimen (crystallinity, density, and so forth). This can be accomplished by the use of the heaters in the diffusion cells.

10. Sampling

10.1 The sampling units used for the determination of O_2GTR shall be representative of the quantity of product for which the data are required, in accordance with Practice D 1898. Care shall be taken to ensure that samples are representative of conditions across the width and along the length of a roll of film.

11. Test Specimens

11.1 Test specimens shall be representative of the material being tested and shall be 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 cell").

12. Calibration

12.1 *General Approach*—The oxygen sensor 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 sensor for each molecule of oxygen that passes into it. Considering that the sensor is known to have a basic efficiency of 95 to 98%, it may be considered an "intrinsic" standard[8] that does not require calibration, and can thus be used as a reference method.

12.2 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 that reason, this test method incorporates means for a periodic sensor evaluation. This evaluation is derived from measurements of a known-value "reference package". Experience indicates however, that a specimen-to-specimen variability of the reference material[9] is such that a change should never be made in the calibration factor, as the result of a measurement using a single sheet of the reference material.

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. After trimming, condition the specimens in a desiccator over calcium chloride or another suitable desiccator for a minimum of 48 h. This does not imply that 48 h will be sufficient to bring all materials to a condition where their measured O_2GTRs will be reproducible. Previous experience should serve as the primary guide to the suitability of a given conditioning regimen. If a material is being tested with which the user has no previous experience, the effect of conditioning time should be investigated and a regimen selected such that there is no significant effect due to conditioning time. In any case, the conditioning procedure used should be included in the report section.

13.2 Elevated temperature may be used to accelerate outgassing of films, provided that the temperatures are not so high as to cause alterations of the physical and chemical state of the film (see 9.5).

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

14. Procedure

14.1 *Preparation of Apparatus*—If preceding tests have exposed the apparatus to high moisture levels, it will be necessary to outgas the system, particularly the catalyst bed, to desorb residual moisture. Water shall be removed from the nitrogen and test gas bubblers. The system can then be dried by slowly purging overnight using dry carrier gas and with the sensor bypassed. Heating the apparatus will speed the drying and outgassing process.

14.2 *Inserting the Specimen*—Place Valve V_1(Fig. 1) in the SENSOR BYPASS position to avoid swamping the detector with air. Unclamp the diffusion cell and open it. Apply a thin layer of sealing grease (see 8.3) around the raised rim of the lower half of the diffusion cell. Remove the test specimen from the desiccator and place it upon the greased surface, taking care to avoid wrinkles or creases. Lower the upper half of the diffusion cell into place and clamp both halves tightly together.

14.3 *Purging the System*—Place Valve V_2(Fig. 1) in the CARRIER PURGE position. Start the nitrogen carrier flow and purge air from the upper and lower diffusion cell chambers, using a flow rate of 50 to 60 mL/min (as indicated by the flowmeter). After 3 or 4 min, reduce the flow rate to the desired value between 5 and 15 mL/min. Maintain this configuration for 30 min.

14.4 *Establish E_0*—After the system has been flushed with nitrogen for 30 min, move Valve V_1 to the INSERT SENSOR position. This diverts the carrier gas which has passed through both sides of the diffusion cell into the sensor. At this time, the sensor output, as displayed on the voltage recorder, will usually increase abruptly, indicating that oxygen is entering the sensor with the carrier gas. The most likely sources of this oxygen are (*1*) outgassing of the sample, (*2*) leaks in the system, or (*3*) a combination of (*1*) and (*2*). The operator shall observe the recorder trace until the sensor output current stabilizes at a constant value with no significant trend in either direction. Thick samples may require a purge of several hours, or even overnight, before a steady low value of sensor current is obtained. During this time, Valve V_1 should be in the SENSOR BYPASS position except for brief periods when the zero level is being checked. Once a steady low value of sensor current has been obtained, Valve V_1 should be switched to the INSERT SENSOR position and left there. The observed deflection of the stripchart recorder at this time is recorded and labelled E_0. It has been found helpful to periodically test the O_2GTR of a piece of brass shim stock in order to ascertain that no leaks or contamination of the carrier gas have developed.

14.5 Once E_0 has been established, switch V_2 into the OXYGEN PURGE position. This cuts off the flow of nitrogen into the test-gas side of the diffusion cell and substitutes a flow of test gas into the diffusion cell.

14.6 The sensor output current, as indicated by the strip chart recorder, 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 a number of hours to reach a steady state of gas transmission. The constant value of the voltage on the strip-chart recorder shall be recorded and labelled E_e.

NOTE 1—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*) turn V_1 to SENSOR BYPASS, (*2*) allow unit to stabilize for an additional period of time (minimum of 6 h), and (*3*) turn V_1 to INSERT SENSOR position and again monitor voltage output on the strip-chart recorder. 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.

14.7 Temperature shall be obtained by monitoring the temperature in the thermometer wells on both sides of the specimen. The specimen temperature may be assumed to be midway between the two values.

14.8 *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: (*1*) turn V_1 to SENSOR BYPASS, (*2*) turn V_2 to CARRIER PURGE, (*3*) turn off the oxygen supply, and (*4*) reduce the nitrogen flow rate to less than 5 mL/min. These steps will economize on carrier and test gases and will minimize the danger of ruining the sensor 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 sensor. When the instrument is not being used for a long period of time, the electrical power may be turned off.

14.9 *Tests in a Moist Environment*—Although the coulometric method may prove to be suitable for testing barrier materials in a moist environment, test data on which to base suitable precision and accuracy statements are not available. Specific procedures for testing in a moist environment are planned for development.

14.10 The O_2GTR at temperatures other than ambient may be determined by thermostatically controlling the diffusion cell

[6] A suitable catalyst can be obtained from Englehard Industries Division, Chemical Dept., 429 Delancey Street, Newark, NJ 07105.

[7] It is deemed advisable upon initial setup of the voltage recorder and periodically thereafter to check the response of the recorder on all ranges to a suitable voltage input.

[8] 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.

[9] Reference material available from Modern Controls, Inc., has been found satisfactory.

or by using the heater referred to in 7.1.1.4, provided that the temperature of the carrier gas does not adversely affect the operation of the sensor. Experience has shown that the unit can be operated satisfactorily in the range from 4 to 50°C. Efficiency of the sensor may be changed somewhat below normal laboratory temperature, however.

14.11 *Testing Poor Barriers*—Films having transmission rates in excess of 200 cm^3(STP)/(m·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. Another way to reduce the oxygen concentration in the carrier gas when testing poor barriers is to mask off most of the area of the test specimen using a mask of thin metal or aluminum foil on both sides of the test specimen by use of a suitable adhesive such as contact cement or epoxy. The specimen area then becomes equal to the open area of the mask. The effect of varying the area of the open hole in the mask should be tested to ensure that the mask is performing properly.

15. Calculation

15.1 Determine the O_2GTR as follows:

$$O_2GTR = \frac{(E_e - E_o) \times Q}{A \times R_L} \quad (1)$$

where:

E_e = steady-state voltage level (see 14.6),
E_o = zero voltage level (see 14.4),
A = specimen area (see 7.1.1.1),
Q = calibration constant (see Section 12), and
R_L = value of load resistance (see 7.1.6).

15.2 Determine the permeance (PO_2) of the specimen as follows:

$$PO_2 = \frac{O_2GTR}{p} \quad (2)$$

where p = partial pressure of oxygen, which is the mol fraction of oxygen multiplied by the total pressure (normally, one atmosphere), in the test gas side of the diffusion cell. The partial pressure of O_2 on the carrier gas side is considered to be zero.

15.3 Determine the oxygen permeability coefficientPO_2) as follows:

$$\bar{P}O_2 = PO_2 \times t \quad (3)$$

where t = 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 determined.

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 specimens 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 The values of O_2GTR, permeance (if desired), and the permeability (if desired).

16.1.9 A description of the apparatus used including, if applicable, the manufacturer's model number and serial number.

16.1.10 A statement of the means used to obtain the calibration factor, Q.

16.1.11 The effective area for permeation, A, and a description of how it was obtained.

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

17. Precision and Bias

17.1 The data given were obtained at a temperature of 20 to 25°C from statistical analysis of an interlaboratory test program in which sheets of a polyester film nominally 23 μm thick were distributed to 17 participants.[3] The participants used two different models of a commercially available coulometric gas transmission measuring instrument, corrected the data for atmospheric pressure and temperature fluctuations, and reported permeance values. No significant difference was found between results obtained from the two models, and the results from the two models were pooled.

17.2 *Variability*—The statistical analysis of the data took the unequal number of replicates from each respondent into account. The between-laboratory standard deviation, σ_b, is 5.0 cm^3(STP)/(m^2·d·atm), and within-laboratory standard deviation, σ_w, is 1.2 cm^3(STP)/m^2·d·atm. The standard deviation for the uncertainty of a single measurement is, therefore, 5.1 cm^3(STP)/(m^2·d·atm).

17.3 A weighted average material value, X, and its standard error were calculated from the data, taking the within- and between-laboratory variability into account. The weighted average material value was found to be 59.36 cm^3(STP)/(m^2·d·atm) and the standard error of 1.21 cm^2(STP/m^2·d·atm).

17.4 The material used in the interlaboratory test was from the same manufacturing lot as NIST Standard Reference Material 1470, which NIST has found to possess an O_2GTR equal, at a pressure differential of one atmosphere (0.10133 MPa), to 63.8 cm^3(STP)/(m^2·d·atm) with a standard error of 0.4 cm^3(STP)/(m^2·d·atm). This discrepancy may be attributable to differences in sampling, test methodology, or analysis of the data.

O_2 Permeability