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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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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.

[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.

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.

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

[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.

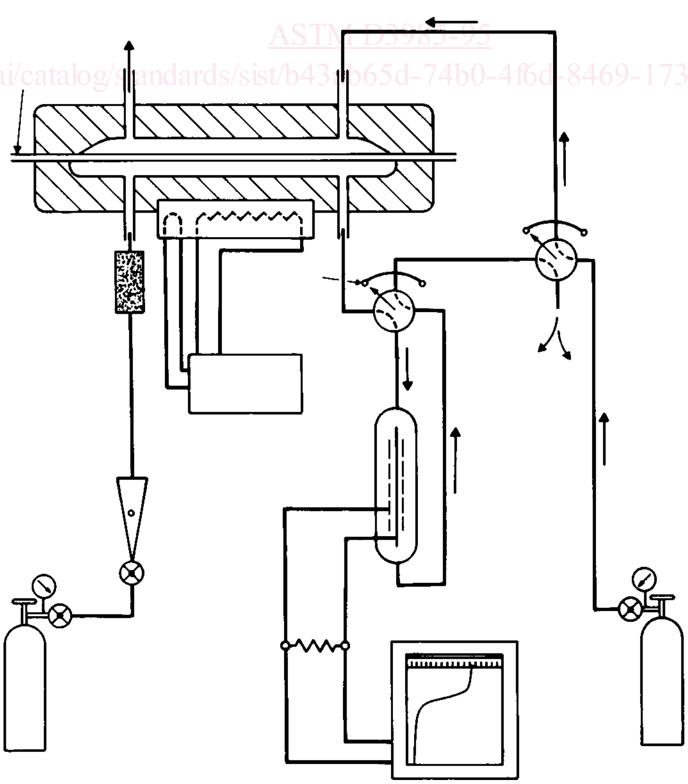

FIG. 1 A Practical Arrangement of Components for the Measurement of Oxygen Transmission Rate Using the Coulometric Method

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)/$m^2 \cdot d$).

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

[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.