Standard Test Method for
Oxygen Transmission Rate Through Dry Packages Using a Coulometric Sensor[1]

1. Scope

1.1 This test method covers a procedure for the determination of the steady-state rate of transmission of oxygen gas into packages. More specifically, the method is applicable to packages that in normal use will enclose a dry environment.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1434 Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting

D1898 Practice for Sampling of Plastics (Withdrawn 1998)[3]

D3985 Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *oxygen gas transmission rate (O₂GTR)—as applied to a package*, is the quantity of oxygen gas passing through the surface of the package (PKG) per unit of time.

3.1.1.1 *Discussion*—The SI unit of transmission rate is the mol/s. The test conditions, including temperature, oxygen partial pressure and humidity on both sides of the package, must be stated. A commonly used unit of O_2GTR is the cm³(STP)/(PKG·d), where 1 cm³ at Standard Temperature and Pressure (STP = 273.15K; 1.013×10^5 Pa) is 44.62×10^{-6} mol and one day is 86 400 s.

3.1.2 *oxygen permeability coefficient ($P^{'}O_2$)*—the product of the permeance and thickness of the barrier.

3.1.2.1 *Discussion*—The permeability is meaningful only for homogenous 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 in tests using several thicknesses of the material. The SI unit of permeability is the mol/(m·s·Pa). The test conditions must be stated.

3.1.3 *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 package wall.

3.1.3.1 *Discussion*—The SI unit of permeance is the mol/(s·Pa). The test conditions (see 4.2) must be stated.

4. Summary of Test Method

4.1 This test method employs a coulometric oxygen sensor and associated equipment in an arrangement similar to that described in Test Method D3985. Oxygen gas transmission rate (O_2GTR) is determined after the package has been mounted on a test fixture and has equilibrated in the test environment.

4.2 The package is mounted in such a way as to provide that the inside of the package is slowly purged by a stream of nitrogen while the outside of the package is exposed to a known concentration of oxygen. The package may be exposed in ambient room air which contains 20.8 % oxygen, or immersed in an atmosphere of 100 % oxygen. As oxygen permeates through the package walls 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 of time.

5. Significance and Use

5.1 Oxygen gas transmission rate is an important determinant of the protection afforded by barrier materials. It is not, however, the sole determinant, and additional tests, based on
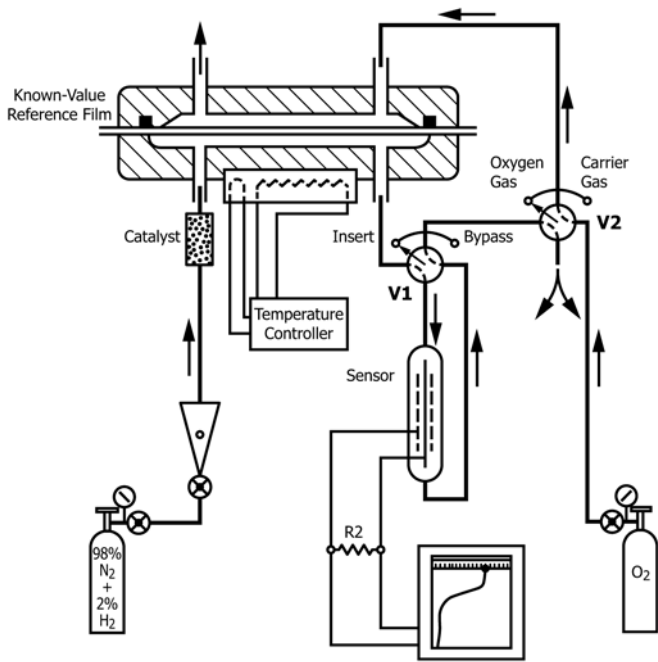

FIG. 1 Arrangement of Components when Reference Film is Used to Calibrate System for Package Testing

experience, must be used to correlate package performance with O$_2$GTR. This test method is suitable as a referee method of testing, provided that the user and source 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 diagrammed in Fig. 1 with the following:

7.1.1 *Package Test Stations,* providing a means for the introduction and exhaust of the nitrogen carrier gas stream without significant loss or leakage.

7.1.1.1 Experience has shown that arrangements using multiple package test stations are a practical way to increase the number of measurements that can be obtained from a coulometric sensor. A valving manifold connects the carrier gas side of each individual test station to the sensor in a predetermined pattern. Carrier gas is continually purging the carrier gas sides of those packages that are not connected to the sensor. Either test gas (100 % oxygen) or normal room air (20.8 % oxygen), whichever is appropriate, contacts the outside of the package.

7.1.2 *Diffusion Cell,* consisting of two metal halves which, when closed upon the film used for system calibration, will accurately define a circular area of that film. Typical diffusion cell areas are 100 cm^2 and 30 cm^2. The volumes inside the cell

above and below the enclosed film are not critical; they 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. Means shall be provided for the measurement of cell temperature.

7.1.2.1 *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 the 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.

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

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

7.1.2.4 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.

7.1.3 *Catalyst Bed,* a small metal tube with fittings for attachment to the inlet of the nitrogen gas pneumatic fitting containing 3 to 5 g of 0.5 % platinum or palladium catalyst on alumina to provide an essentially oxygen-free carrier gas to the diffusion cell and to each package test station.

7.1.4 *Flowmeter,* a flowmeter having an operating range of 5 to 100 mL/min is required to monitor the flow rate of nitrogen carrier gas through each test station.

7.1.5 *Flow Switching Valves*—Two or more valves for the switching of the nitrogen and test gas flow streams.

7.1.6 *Oxygen-Sensitive Coulometric Sensor,* operating at an essentially constant efficiency is employed to monitor the quantity of oxygen transmitted.

7.1.7 *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 load resistors are such that the values yield a convenient relationship between the output voltage and the oxygen transmission rate as expressed in terms of cm^3(STP)/PKG·d.

7.1.8 *Voltage Recorder*—The voltage across the load resistor is measured and recorded using a strip-chart potentiometer, data-logger or other suitable device. The instrument or system should be able to measure a full-scale voltage of 50 mV. It should be able to measure voltages as low as 0.10 mV with a resolution of at least 10 µV. An input impedance of 5000 ohm or higher is acceptable.

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

8.3 *Oxygen Test Gas*—The test gas shall be dry and contain not less than 99.5 % oxygen (except as provided for in 14.8).

9. Technical 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.

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, monitor and record the temperature, periodically, to the nearest 0.5°C. Report the average temperature and the range of temperatures found during a test.

9.3 The sensor will require a relatively long time to stabilize at 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. Take care, therefore, 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 The gas-permeability characteristics of some barrier materials are altered by exposure to water vapor. If a package is to be exposed and tested in normal laboratory air (20.8 % O_2), the ambient relative humidity should be monitored to the nearest 3 %. This may be accomplished using a sling psychrometer or other method of comparable accuracy. Report the average and range of relative humidities measured during the test.

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 D1898.

11. Test Specimens

11.1 Test packages shall be representative of the population and shall be free of non-typical defects.

12. Calibration

12.1 *General Approach*—The oxygen sensor used in this method is a coulometric device that yields a linear output as predicted by Faraday's Law. Since this sensor has an efficiency of 95 to 98 % it is almost an absolute "yardstick" that does not require calibration. 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, the method incorporates means for periodic system calibration. This calibration is derived from measurements of a known-value "Reference Package."

12.2 The reference package is essentially the lower-half of a diffusion cell (Fig. 1) in which a sheet of reference film of known O_2GTR 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 sensor is bypassed to avoid swamping it with air, that is, no flow to the sensor. Unclamp the diffusion cell and open it. Apply a thin layer of sealing grease (see 8.2) around the raised rim of the lower half of the diffusion cell. Insert the reference film in the diffusion cell 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.

12.4 *Purging the System*—Start the nitrogen carrier gas flow and purge air from the upper and lower diffusion cell chambers using a flow rate of 50 to 60 cm^3/min (as indicated by the flowmeter). After 3 or 4 min, reduce the flow rate to the desired value between 5 and 15 cm^3/min. Maintain this configuration for 30 min.

12.5 *Establishing Zero Level of Reference Film*—After the system has been flushed with nitrogen for 30 min, with the sensor bypassed, divert the nitrogen carrier gas flow to 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 low value with no significant trend in either direction. Note the observed deflection of the strip chart recorder at this time and label it E_0.

12.6 Once the zero level (E_0) has been established, switch to a flow of oxygen on the test gas side of the diffusion cell. Nitrogen will continue to flow on the downstream side of the cell.

12.7 *Establishing a Steady-State O_2GTR*—The sensor output, as displayed by the strip-chart recorder, should increase and gradually level off, approaching a constant value (E_e). Record the observed final steady-state value of E_e.

12.8 *Temperature of the Reference Film*—It is desirable that system calibration should be conducted at the temperature for which the reference film's O_2GTR is cited. Apply an appropriate correction to the rate that the temperature differs from that value. Temperature shall be obtained by monitoring thermometers or thermocouples placed in the thermometer wells on both sides of the reference film. The film temperature may be assumed to be midway between the two values.

12.9 *Standby Procedure*—At the conclusion of system calibration, but when it is expected that package tests will be performed soon, the instrument should be placed in a standby condition by taking the following steps: (*1*) stop the flow of O_2 test gas to the sensor, and switch to nitrogen carrier gas on the

test gas side of the diffusion cell, (2) turn off the oxygen supply, and (3) reduce the nitrogen flow rate to less than 5 mL/min. 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.

12.10 *Establish System Calibration Constant*—Determine the exposed area, *A*, of the calibrating reference film (see 7.1.2.1). Using the permeance value furnished with the reference film, determine the O_2GTR through a film of that area (*A*). Use this value to determine the calibration constant, *Q* :

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

where:

O_2GTR	=	oxygen transmission rate through a film of area *A*, as calculated from data supplied with the reference film,
R_L	=	value of load resistance (see 7.1.7),
E_0	=	observed steady-state zero-level before oxygen gradient is applied (see 12.5), and
E_e	=	observed steady-state voltage with oxygen gradient across test film (see 12.7).

Repeat the calibration using additional sheets of the reference film until the confidence interval for *Q* defined by the measurements is within acceptable limits. When operating an instrument with multiple diffusion cells, it is desirable to keep a sheet of the reference film in one of the diffusion cells to ensure the reliability of the rates being measured.

12.11 In principle, each molecule of oxygen that enters the sensor causes the transfer of four electrons. Experience indicates that production models of the sensors achieve efficiencies of 95 to 98 %. Any significant drift in the calibration factor *Q* should, therefore, be investigated as to its cause and corrective action should be undertaken.

12.12 The value of *Q* will be a function of the units in which the results are to be expressed. If it is desired to change units, *Q* can be transformed to its proper value in the new set of units using the appropriate relationships between base units (quantity of matter, length, and time) in the new and the old sets of units.

13. Preparation of a Package for Test

13.1 The method by which a package is prepared for attachment to the instrument for testing depends upon the package shape, type, and test objectives. For a majority of tests, the package may be exposed to ambient air (20.8 % O_2). If the package is an extremely good barrier, however, it may be helpful to increase the test gradient by immersing the package in 100 % oxygen. This is accomplished by securing a plastic bag, pouch overwrap, or other container around the test package and flooding the bag with oxygen as shown in Fig. 2. This will increase the transmission rate by a factor equal to the ratio:

$$\frac{100\%}{21\%} = 4.8 \qquad (2)$$

Whenever 100 % oxygen is used to establish the test gradient, the operator should use care not to pressurize the
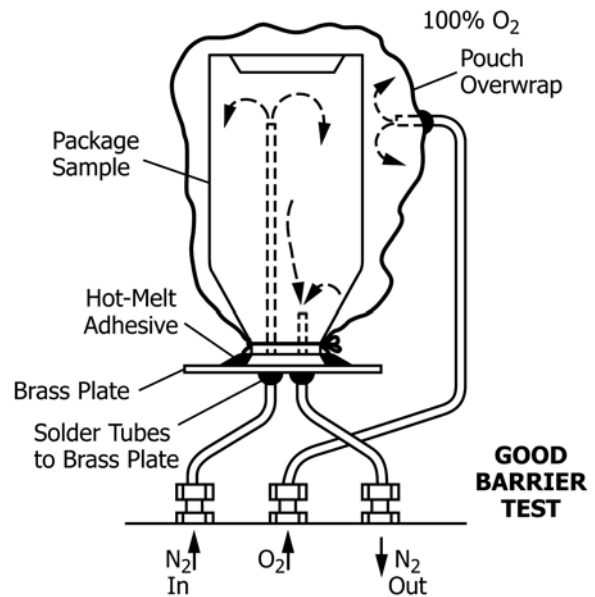

FIG. 2 Typical Method of Attaching a Plastic Bottle or Tub

oxygen-containing structure. (Oxygen partial pressure should be equal to the prevailing atmospheric pressure.) Pressurization may be avoided by providing a small vent and by injecting the oxygen at a low rate on the order of 10 to 20 mL/min. Bottles, thermoformed plastic cups, and tubs are usually mounted as shown in Fig. 2. Flat pouches and bags may be mounted using some variation of Fig. 3. In attaching a pouch, it is important that the copper tubes first be connected securely to the fittings and then bent to the desired angles. Corners of the pouch may then be snipped off to provide openings just large enough for the tubes. After the package has been slipped over the tube ends, a fast-curing epoxy or hot-melt adhesive is carefully applied to seal cut openings.

13.2 The detector output is governed by Faraday's Law, and the calibration does not vary with temperature. It should be noted, however, that the oxygen transmission rate of most plastic materials will vary 3 to 9 %/°C. Since the package test attachment does not provide means for control of package temperature, it will prove advantageous from the standpoint of data reproducibility to locate the instrument in a draft-free, constant-temperature environment.

14. Package Test 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 to desorb residual moisture. Water must be removed from nitrogen and test-gas bubblers. The system can then be dried by slowly purging overnight using dry carrier gas (sensor bypassed).

14.2 *Attachment of the Package*—Ensure that the sensor is bypassed to avoid swamping it with air. Each package test station consists of three fittings in a triangular array, or two adaptor fittings in a lower cell half. The package shall be attached to the two carrier gas fittings with brass or nylon ferrules. Ferrules should only be used once. When the test gradient is to be established by immersing the package in normal room air (20.8 % O_2), the third (oxygen supply) fitting
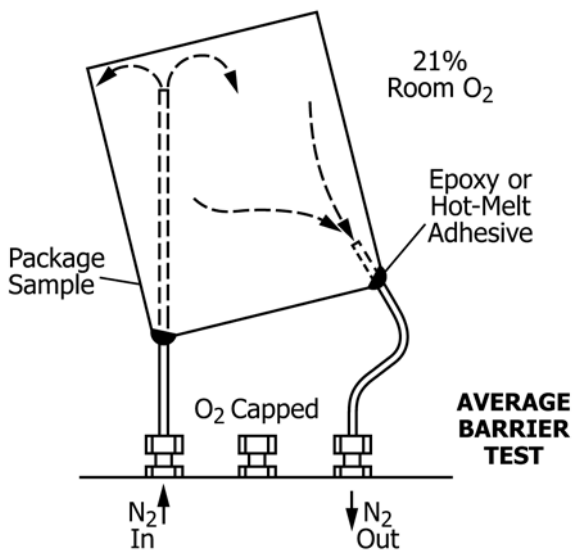
FIG. 3 Attachment Method for Flexible Pouches

should be capped. In making the copper tube connections to the fittings it is important that a good seal be achieved.

14.3 *Purging the System*—Start the nitrogen gas flow and purge air from the package using a flow rate of 50 to 60 mL/min (as indicated by a flow meter). Maintain this rate for a period determined by the volume of the package:

$$\text{Volume less than } 100 \text{ m}L = 30\text{min} \tag{3}$$

$$100 \text{ to } 200 \text{ m}L = 1 \text{ h}$$

$$200 \text{ to } 500 \text{ m}L = 2 \text{ h}$$

$$500 \text{ to } 1000 \text{ m}L = 3 + \text{h}$$

After the package has been purged for the appropriate period, reduce the rate to a value between 5 and 15 mL/min. Maintain this rate for the next 30 min (sensor bypassed).

14.4 *Establish Package* E_e—After the system has been flushed with nitrogen for 30 min at the new rate, divert the flow of nitrogen carrier gas to the sensor. At this time, the sensor output, as displayed by 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 package, (*2*) system leaks, (*3*) initial permeation of oxygen into the package, or (*4*) a combination of all three factors. The operator shall periodically observe the recorder trace until the sensor output current stabilizes at a constant value with no significant trend in either direction. The sensor output current, as indicated by the strip-chart recorder, should increase gradually, ultimately stabilizing at a constant value. Packages may require several hours, or days, to reach a steady value of diffusion equilibrium. During this time, the sensor should be bypassed except for brief intervals when the equilibrium level is being checked. When consecutive sensor readings begin to yield the same value, the operator should record this value and label it E_e (package).

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*) stop the flow of gas to the sensor (sensor bypassed),

(*2*) allow the package to stabilize for an additional period of time (minimum of 6 h), and (*3*) restart the flow of gas to the sensor. Observe the voltage as displayed by the recorder. If the value rises to the same level as before, this is indicative that steady-state (equilibrium) has been achieved. If the value is substantially different from that previously observed, the operator should repeat (*1*), (*2*), and (*3*) until satisfied that a steady-state condition has been achieved.

14.5 *Establish Package Zero Level* (E_o)—After steady-state conditions have been achieved and the value E_e has been recorded, put the sensor in bypass once again. Remove the package from the package fittings and install a stainless steel "perfect package" loop between the carrier gas fittings. After 10 to 15 min, divert the flow of carrier gas to the sensor. Maintain this configuration for 30 min, or until the sensor output current has descended to a constant low value. Note this value and record as E_0 (package).

14.6 *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, place the instrument in a standby condition by taking the following steps: (*1*) stop the flow of gas to the sensor and switch to nitrogen carrier gas, (*2*) turn off the oxygen supply, and (*3*) 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 or package 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 it is expected that the instrument will stand idle for a long period of time, the electrical power may be turned off.

14.7 Tests at temperature other than laboratory ambient may be performed by thermostatically controlling the ambient air around the package within an environmental chamber, provided that the temperature of the carrier gas does not adversely affect the operation of the sensor.

14.8 *Testing Poor Barriers*—The maximum oxygen transmission rate can be measured using the coulometric method is on the order of 2 cm^3(STP) per package per day. Depending upon wall thickness, some packages may have rates in excess of this when immersed in air. Typical examples include packages fabricated from polyethylene, polycarbonate, and polystyrene. High oxygen concentrations in the carrier gas, as encountered when testing poor barriers, will tend to produce detector saturation. One way to avoid this problem is to immerse the package in a test-gas mixture that provides a lower concentration of oxygen than is found in air. Any subsequent data conversions will require that the O_2 partial pressure of such a test gas be known.

15. Calculation

15.1 Determine package oxygen transmission rate as follows:

$$O_2GTR = \frac{(E_e - E_0)}{R_L} \times Q \tag{4}$$

where:

E_e = steady-state voltage with oxygen gradient applied to test package (see 14.4),

TABLE 1 Precision Statement

Materials	Average	Sr[A]	SR[B]	r[C]	R[D]
Bottle 23	0.116280	0.006856	0.015455	0.019196	0.043275
Bottle 25	0.124300	0.013138	0.015831	0.036786	0.044327
Cup 23	0.002983	0.001719	0.002948	0.004813	0.008256
Cup 25	0.000750	0.000094	0.000394	0.000264	0.001103
Pouch 23	0.035050	0.002500	0.008731	0.007000	0.024446
Pouch 25	0.026613	0.001096	0.003656	0.003068	0.010236

[A] Sr = Repeatability Standard Deviation.
[B] SR = Reproducibility Standard Deviation.
[C] r = Repeatability Limit (2.8 times Sr) or 95 % Probability Level.
[D] R = Reproducibility Limit (2.8 times SR) or 95 % Probability Level.

E_0 = steady-state, zero-level voltage (see 14.5),
Q = system calibration constant (see 12.10), and
R_L = value of load resistance (see 7.1.7).

15.2 Determine the permeance ($PO_2^{'}$) of the specimen as follows:

$$PO_2^{'} = \frac{O_2 GTR}{p} \qquad (5)$$

where :

p = partial pressure of oxygen in the test gas. The partial pressure of O_2 inside the package is considered to be zero.

16. Report

16.1 Report the following information:

16.1.1 A description of the test package and the location of the specimen in the lot of material of which it is representative,

16.1.2 The barometric pressure at the time of the test,

16.1.3 The partial pressure of oxygen in the test gas and a statement as to how it was determined,

16.1.4 The rate of flow of the nitrogen carrier gas,

16.1.5 A description of the pre-test conditioning procedure,

16.1.6 The temperature of the package during the test (to the nearest 0.5°C) and the method used to measure the temperature,

16.1.7 The relative-humidity environment in which the package was immersed (average and range),

16.1.8 The calculated values of oxygen transmission rate and, if required, permeance and permeability coefficients,

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, and the value of calibration factor Q, and

16.1.11 The time to reach steady-state equilibrium after introduction of the oxygen test gradient.

17. Precision and Bias

17.1 *Precision:*

17.1.1 The repeatability and reproducibility given in Table 1 are in accordance with the definitions of these terms in Practice E691 using the E691 Interlaboratory Data Analysis Software. These values have been calculated for test results obtained as specified in this test method. The values are based on an interlaboratory study involving six laboratories in which each laboratory made two determinations of the package oxygen transmission rate on each of three package types. For each package, the total number of required test specimens for all laboratories together were taken from single lots and randomized before distribution to the laboratories.

17.1.2 The precision, characterized by repeatability, Sr, r, and the reproducibility, by SR, R, has been determined for following materials 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.

18. Keywords

18.1 coulometric; oxygen transmission rate; packages; permeability; permeation