Designation: F3136 – 15

Standard Test Method for
Oxygen Gas Transmission Rate through Plastic Film and Sheeting using a Dynamic Accumulation Method[1]

1. Scope

1.1 This test method covers a procedure for determination of the transmission rate of oxygen gas through plastics in the form of film, sheeting, laminates, coextrusions, coated or uncoated papers or fabrics.

1.2 This test method is not the only method for measurement of the oxygen transmission rate (OTR). There are other methods of OTR determination that use other oxygen sensors and procedures.

1.3 The values stated in SI units are to be regarded as standard. Commonly used metric units used to report Oxygen Transmission Rate are included in Terminology, Procedure, Precision and Bias sections and in the Calculation section of the Appendix.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

F2622 Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using Various Sensors

F2714 Test Method for Oxygen Headspace Analysis of Packages Using Fluorescent Decay

3. Terminology

3.1 *Definitions:*

3.1.1 *Oxygen Transmission Rate (OTR)*—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 $mol/(m^2 \cdot s)$. The test conditions including temperature, relative humidity and oxygen partial pressure on both sides of the film must be stated in the report.

3.1.1.1 *Discussion*—A commonly used unit of OTR is the cm^3 (STP)/($m^2 \cdot day$) at one atmosphere pressure difference where 1 cm^3 (STP) is 44.62 μmol, 1 atmosphere is 0.1013 MPa, and one day is 86.4×10^3 s. The OTR in SI units is obtained by multiplying the value in commonly used units by 5.160×10^{-10}.

4. Summary of Test Method

4.1 The specimen is mounted as a sealed semi-barrier between two chambers, which together make up the permeation apparatus. The sensing well which contains the oxygen sensor is slowly purged by a stream of pure nitrogen or other oxygen deficient gas mixture until the oxygen concentration represents that of the purge gas. A commercial grade of compressed nitrogen containing less than 0.05% oxygen is recommended. A gas of known oxygen concentration, typically air or pure oxygen, is directed into the opposite chamber, the driving well. Oxygen concentration in the sensing well containing the oxygen sensor is measured periodically and the accumulating oxygen concentration recorded. The Oxygen Transmission Rate (OTR) parameter is determined from the slope of the logarithm of accumulated oxygen concentration in the sensing well versus time as described in 14.2.

5. Significance and Use

5.1 The Oxygen Transmission Rate is an important determinant of packaging functionality afforded by packaging materials for a wide variety of packaged products including food, pharmaceuticals and medical devices. In some applications, sufficient oxygen must be allowed to permeate into the package. In others, the oxygen ingress must be minimized to maintain product quality.

5.2 Other ASTM Standard Methods to measure the oxygen transmission rate are described in Standard Test Method D3985 and Standard Test Method F2622.

6. Interferences

6.1 Any leakage within the permeation apparatus or mounted packaging film will affect results. A means to assess leakage is described in paragraph 9.2.

6.2 The condition of the sample film must be noted such as wrinkles or other defects can affect results.

7. Apparatus

7.1 *Oxygen Gas Transmission Apparatus,* as diagrammed in Fig. 1 with the following:

7.1.1 *Permeation Apparatus (diffusion cell)* shall consist of two metal halves, which, when closed upon the test specimen, will define a known gas transmission area. The volume of the sensing well containing the oxygen sensor must be accurately known.

7.1.1.1 *O-ring*—A circular transmission area permits application of a static O-ring in a properly constructed O-ring groove in the side of the permeation apparatus that does not contain the oxygen sensor. The test area of the sensing well is considered to be that area established by the inside contact diameter of the compressed O-ring when the permeation apparatus is clamped shut. 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 permeation apparatus.

7.1.1.2 The sensing well of the permeation apparatus 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 The sensing well of the permeation apparatus shall have a low-permeability window transparent to wavelengths used to activate and read the oxygen sensor which is mounted within the sensing well.

7.1.1.4 The oxygen sensor incorporates a fluorophore that fluoresces in response to a certain wavelength of light, but is quenched in the presence of oxygen. The oxygen quenching effect is calibrated to oxygen concentration. This sensing technology is identical to the sensing technology described in ASTM F2714.

7.1.1.5 The permeability apparatus shall incorporated suitable fittings for the introduction and exhaust of gases without significant loss or leakage.

7.2 It is necessary to control the temperature of the permeability apparatus during the test period. A simple heating/cooling chamber regulated to ±0.5°C, is adequate for this purpose in which the apparatus is housed during the test period.

7.3 Flow meters having an operating range from 1 to 100 cm^3/min are required to monitor the flow rate of the nitrogen purge stream and, if used, the oxygen or compressed air circulation stream. Sufficiently low flow rates and/or balanced pressures on each side of the film are required to avoid stretching the specimen which would modify the effective sensing well volume.

7.4 An external light source provides sufficient light in the appropriate wavelength to activate the oxygen sensor.

7.5 A light detector, and associated electronics, determines the fluorescence decay constant, which is proportional to oxygen concentration.

7.6 A computer is used to calculate the oxygen concentration at specified time intervals based on decay rates. The oxygen transmission rate of the film is calculated from that data.

8. Reagents and Materials

8.1 Nitrogen enriched purge gas shall contain a known concentration of nitrogen. Commercial grade compressed nitrogen (<0.05% oxygen), certified pure nitrogen gas, cryogenically stored nitrogen or nitrogen enriched gas produced using on-site generators may be used.

8.2 Transmission gas shall be of a known oxygen concentration with an oxygen concentration at least 10% greater than the purge gas. Typically, commercial grade compressed oxygen, certified gas or air is used. Also, regulated compressed air can be used or the driving well can simply be left open to ambient air.
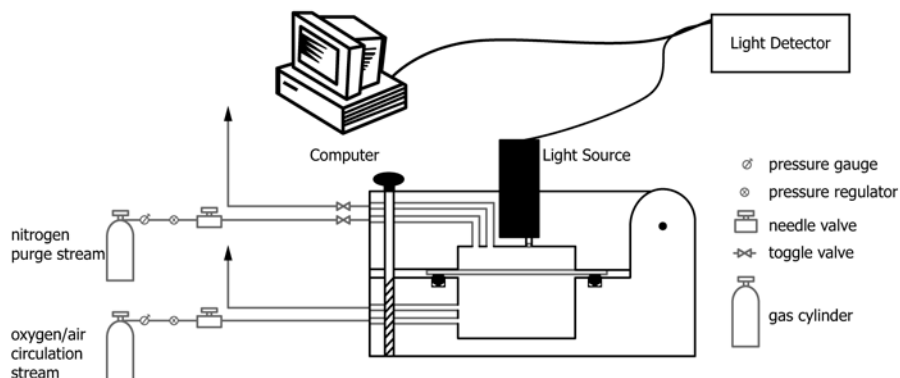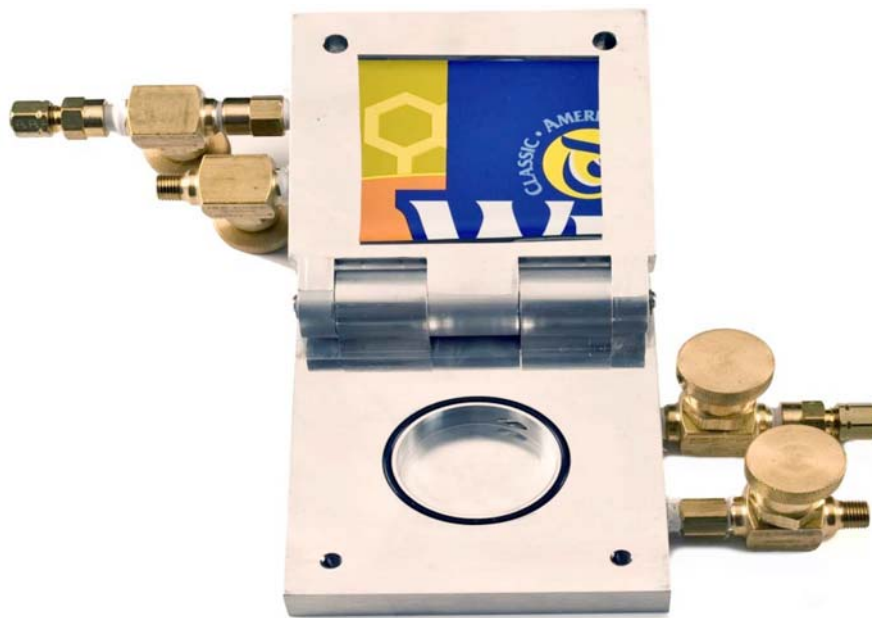

FIG. 1 A Practical Arrangement of Components for the Measurement of Oxygen Transmission Rate Using an Optical Florescent Oxygen Sensor and a Permeation Apparatus

An acceptable Permeation Apparatus (aka Diffusion Cell) is available from OxySense, Inc., 6000 S. Eastern Ave., Suite 14G, Las Vegas, NV 89119, USA.

FIG. 2 Permeation Apparatus as described in this method (film specimen is shown adhered to the sensing well)

8.3 *Sealing Grease*—High-viscosity silicone stop cock grease or 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 OTR. Careful temperature control can help to minimize variations due to temperature fluctuations. During testing, the temperature shall be monitored and controlled to ± 0.5°C. Temperature variations should be minimized. The average temperature and a range of temperatures during a test shall both be recorded.

9.2 Oxygen that leaks into the sensing well through faulty valves, fittings, or through an improperly sealed window can significantly affect the accuracy of the measurement. Periodic leak checks using impervious films such as metal foils with thicknesses ≥25 μm (with their expected permeations of zero) should be taken to identify suspected system leaks. Leak check permeation tests should be run at least every 3-6 months and each test should be run for a minimum of 12 hours.

10. Sampling

10.1 Film samples used for the determination of OTR shall be representative of materials for which the data are required. 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 and shall be free of defects including wrinkles, creases, and pinholes, unless these are characteristics of the material being tested and included in the material description.

11.2 Average thickness shall be determined ± 3 μm 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. Sample thickness need not be measured for determination of sample OTR only.

11.3 If the test specimen is of an asymmetrical construction, the two surface shall be marked by appropriate distinguishing marks and the orientation of the test specimen within the permeation apparatus shall be reported.

12. Calibration

12.1 *General Approach*—The oxygen sensor fluoresces when exposed to certain wavelengths of light. Oxygen quenches the fluorescent decay response. The sensor apparatus utilizes a light source to deliver light to the oxygen sensor which, in turn, fluoresces. This light is measured by the detector. The detector determines the exponential fluorescent response decay constant, which is calibrated to oxygen concentration.

12.2 *Calibration*—The sensor system is calibrated by measuring oxygen concentration at two known values, typically air (20.9% oxygen) and pure nitrogen (0% oxygen). These values define a calibration curve from which unknown oxygen levels may be determined. Alternatively, 2 gases of known concentrations nearer to the level under test may prove to yield a better calibration value (perhaps 3% and 0% oxygen).

13. Procedure

13.1 Apply a thin layer of sealing grease (see 8.3) around the raised rim of the sensing well opposite the O-ring. Place the specimen on the greased surface, taking care to avoid wrinkles or creases. Close and secure the permeation apparatus.

13.2 The system can be calibrated with the test specimen in place.

13.2.1 Open both the inlet and outlet valves connected to the sensing well of the permeation apparatus. If using air as the upper oxygen level calibration gas, there is no need to purge the sensing well as it already contains air and readings from the sensor can be taken immediately. If using other than air as the upper oxygen level calibration gas, then the sensing well must be purged with that gas. Purge the sensing well with the higher oxygen level calibration gas at 5-10 cm^3/min. Note that whenever purging with a sample in the chamber, care must be taken to avoid stretching or bulging the film. A flow rate of 5-10 cm^3/min with valves open has been determined to not cause undue sample bulging or stretching. Oxygen concentration should be monitored until the reported value does not change. Expect to purge with at least 5 chamber volumes of gas (typically 5-10 minutes). Once the indicated concentration remains steady, calibrate the oxygen sensor to this known value.

13.2.2 Purge the sensing well with the lower oxygen level calibration gas (typically nitrogen) at a flow rate of 5-10 cm^3/min. Again, observe the indicated oxygen concentration until it does not change. Once the concentration reading is steady, calibrate the oxygen sensor to this known value. From these two readings of calibrated/known gas concentrations, the system can determine the calibration curve parameters (see Section 14 below). By purging the sensing well with the lower oxygen concentration lastly, the step also serves to prepare the chamber for the commencing of the test.

13.3 Initiate the test with the specimen mounted as a sealed semi-barrier between the two halves of the permeation apparatus.

13.3.1 The sensing well which contains the oxygen sensor is slowly purged (5-10 cm^3/min) by a stream of nitrogen until the sensing well is either essentially free of oxygen or to a known reduced oxygen level (based on indicated oxygen concentration reading shown by the instrument). Close the inlet valve of the sensing well prior to the outlet valve to eliminate pressure within the sensing well.

13.3.2 A gas of known oxygen concentration, typically 100% oxygen, is applied to the driving well at a rate of approximately 5-10 cm^3/min for 5-10 minutes. The driving well may be sealed off after flushing by closing the inlet valve first then the outlet valve. Alternatively, if air (20.9% oxygen) is to be used as the driving gas, the valves can be left open. As stated previously, care must be taken to prevent any pressure differential on either side of the film specimen which may distort it, changing the sensing well volume.

13.3.3 Oxygen concentration in the sensing well is measured periodically at time increments sufficient to indicate a small gain in oxygen with each reading (changes of 0.05% oxygen have been found satisfactory between readings).

13.3.4 The test should continue until such time as the experimenter is satisfied that the indicated increase in oxygen concentration during the test period is consistent with results obtained from previous periods.

13.4 *Start/End Points*—The permeation of the sample and the permeation precision sought will determine the oxygen levels at which to start and end recording data. As guidance, the following table can be used.

Barrier Level	Range	Start %	End %
Medium	2 to 100 cm^3(STP)/(m^2·day)	0.50	2.00
Poor	greater than 100 cm^3(STP)/(m^2·day)	1.00	3.00

13.4.1 The time between oxygen concentration measurements should be such that a minimum of 8-10 reading are taken between the starting and ending oxygen points in the data accumulation period.

14. Calculation

14.1 A computer and detection system will be required to convert the decay time into partial pressure of oxygen using the Stern Volmer equations.

14.1.1 The fluorescent signal decay depends on the oxygen partial pressure (pO$_2$). The typical fluorescent life time τ varies between 1 μs in air (pO$_2$ = 212 mbar at sea level) and 5 μs in zero oxygen.

14.1.2 As the fluorescence decays, its lifetime can be derived from the following equation.

$$\frac{I}{I_0} = \exp\left(\frac{-t}{\tau}\right) \tag{1}$$

where:

I = fluorescent intensity at a certain time,
I_0 = fluorescent intensity at the start of the decay,
t = time (μs), and
τ = fluorescence lifetime or time (TC).

14.1.3 The software calculates the time constant τ from the a least squares fit of the fluorescence signals generated by the chemical coating on the oxygen sensor and from the time constant the oxygen concentration is calculated. The relationship between the oxygen partial pressure and the measured fluorescence lifetime (time constant) is given by the Stern Volmer Equation.

$$\frac{\tau_0}{\tau} = 1 + K_{SV} \cdot pO_2 \tag{2}$$

where:

τ = time constant at current concentration,
τ_0 = time constant in the absence of oxygen,
K_{SV} = Stern-Volmer constant, and
pO_2 = oxygen partial pressure in mbar.

14.1.4 This linear Stern Volmer equation is transposed in the software to;

$$\frac{1}{TC} = A \cdot pO_2 + B \tag{3}$$

where:

TC = time constant at current oxygen concentration in μs,
A = slope of Stern Volmer line, and
B = intercept of Stern Volmer line.

14.1.5 The calibration process determines the slope and intercept (dA and dB) of the Stern Volmer line for a low and a high oxygen concentration. These values are used by the computer system to convert fluorescent decay data into oxygen concentration (pO$_2$).

TABLE 1 Oxygen Transmission Rate (cm³ (STP)/(m²·day))

Material	Average[A] $\bar{x}$	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
PE/nylon/PE	28.61	2.74	5.51	7.67	15.43
72 µm PET	68.33	6.01	10.31	16.83	28.87
3 mil PE	2289	256.1	320.7	717.1	898.1

[A] The average of the laboratories' calculated averages.

14.2 The oxygen permeation is calculated as shown below. A linear regression from the plot of the accumulation ratio calculated from data collected between the starting and ending points as suggested in 13.4 is used to determine the oxygen permeation.

14.2.1 The fundamental equation used to derive OTR is:

$$\ln\frac{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{initial}}\right)}{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{time=t}}\right)} = \frac{OTR \cdot Area}{Volume} \cdot time \qquad (4)$$

where:

$p_{O_2}^{Driving}$ = partial pressure oxygen in driving well,
$p_{O_2}^{Sensing_{initial}}$ = partial pressure oxygen in sensing well at time 0,
$p_{O_2}^{Sensing_{time=t}}$ = partial pressure oxygen sensing well at any time t,
OTR = oxygen transmission rate,
Area = film specimen area,
Volume = volume of sensing well, and
Time = unit time.

14.2.2 Therefore, the slope of the plot of the left hand side versus time is used to calculate OTR as follows:

$$OTR = \frac{|Slope| \cdot Volume}{Area} \qquad (5)$$

where:

OTR = oxygen transmission rate,
Slope = slope of the described calculated variable versus time,
Volume = volume of the sensing well, and
Area = film specimen area.

14.2.3 The oxygen transmission rate, OTR, is determined in units of $\frac{cm^3 O_2 STP}{m^2 \cdot day}$ when time is reported in days, Area in m² and chamber volume in cm³.

14.2.4 It is also possible to invert the accumulation ratio in order to plot relative accumulation over time. For example:

$$\ln\frac{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{time=t}}\right)}{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{initial}}\right)} \qquad (6)$$

where:

$p_{O_2}^{Driving}$ = partial pressure oxygen in driving well,
$p_{O_2}^{Sensing_{initial}}$ = partial pressure oxygen in sensing well at time 0,
$p_{O_2}^{Sensing_{time=t}}$ = partial pressure oxygen sensing well at any time t.

14.2.4.1 This provides the same magnitude for slope, but with an opposite sign. Using the absolute value of the resulting slope as shown above ensures estimation of OTR with the proper, positive sign.

14.3 See Appendix X1 for an example of an OTR calculation based on oxygen ingress accumulation during the pre-defined test period.

15. Report

15.1 Report the following information:

15.1.1 A description of the test specimen, including each of its component layers or coatings, and the film orientation (i.e. which side of the structure is facing the oxygen sensor).

15.1.2 The average thickness of the test specimens as determined in 11.2 and the standard deviation of the thickness values.

15.1.3 The permeation apparatus used.

15.1.4 The barometric pressure, temperature, date, and time for each measurement.

15.1.5 The oxygen permeation as calculated in 14.2 based on the dynamic oxygen accumulation data.

16. Precision and Bias

16.1 The precision of this test method is based on an interlaboratory study conducted in 2014. Four laboratories participated in this study. Each of the four laboratories reported five replicates of three different plastic films, being tested for oxygen permeability. Every test result reported represents an individual determination. Except for the use of only four laboratories, Practice E691 was followed for the design and analysis of the data; the details are given in RR:F02-1039[3]

16.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

16.1.1.1 Repeatability can be interpreted as the maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.1.2 Repeatability limits are listed in Table 1.

16.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

16.1.2.1 Reproducibility can be interpreted as the maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.2.2 Reproducibility limits are listed in Table 1.

16.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

16.1.4 Any judgment in accordance with statements 16.1.1 and 16.1.2 would normally have an approximate 95% probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of materials tested and laboratories reporting results guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95% probability limit would imply. The repeatability limit and the reproducibility limit should be considered as general guides, and the associated probability of 95% as only a rough indicator of what can be expected.

16.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

16.3 The precision statement was determined through statistical examination of 60 results, from four laboratories, on three types of film.

17. Keywords

17.1 dynamic accumulation; fluorescence; OTR; oxygen transmission rate; permeability; permeation; plastic film

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APPENDIX

(Nonmandatory Information)

X1. CALCULATION OF OXYGEN GAS TRANSMISSION RATE USING DYNAMIC ACCUMULATION DATA

X1.1 Calculation of oxygen transmission rate for a given sample is described below. The fundamental equation used to derive OTR is:

$$\ln \frac{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{initial}}\right)}{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{time=t}}\right)} = \frac{OTR \cdot Area}{Volume} \cdot time \quad (X1.1)$$

where:

$p_{O_2}^{Driving}$ = partial pressure oxygen in driving well,
$p_{O_2}^{Sensing_{initial}}$ = partial pressure oxygen in sensing well at time 0,
$p_{O_2}^{Sensing_{time=t}}$ = partial pressure oxygen sensing well at any time t,
OTR = oxygen transmission rate,
$Area$ = film specimen area,
$Volume$ = volume of sensing well, and
$Time$ = unit time.

X1.1.1 Therefore, the slope of the plot of the left hand side versus time is used to calculate OTR as follows:

$$OTR = \frac{|Slope| \cdot Volume}{Area} \quad (X1.2)$$

where:

OTR = oxygen transmission rate,
$Slope$ = slope of the described calculated variable versus time,
$Volume$ = volume of the sensing well, and
$Area$ = film specimen area.

X1.1.2 OTR is determined in units of $\frac{cm^3 O_2 STP}{m^2 \cdot day}$ when time is reported in days, Area in m^2 and sensing well volume in cm^3.

X1.2 As an example, assume the data in Table X1.1 was obtained using a permeability apparatus with a sample surface area of 20 cm^2 (0.0020 m^2) and an sensing well volume of 6 cm^3.

X1.2.1 This same data is presented in graphical form in Fig. X1.1 with a linear regression line added to determine its slope.

X1.2.2 The oxygen transmission rate (OTR) is determined from the given slope of the linear regression line as follows:

OTR = 0.0129 day^{-1} × 6 cm^3 / 0.002 m^2 = 38.6 cm^3 O$_2$ STP/(m^2·day)

TABLE X1.1 Oxygen Accumulation Data with Calculation

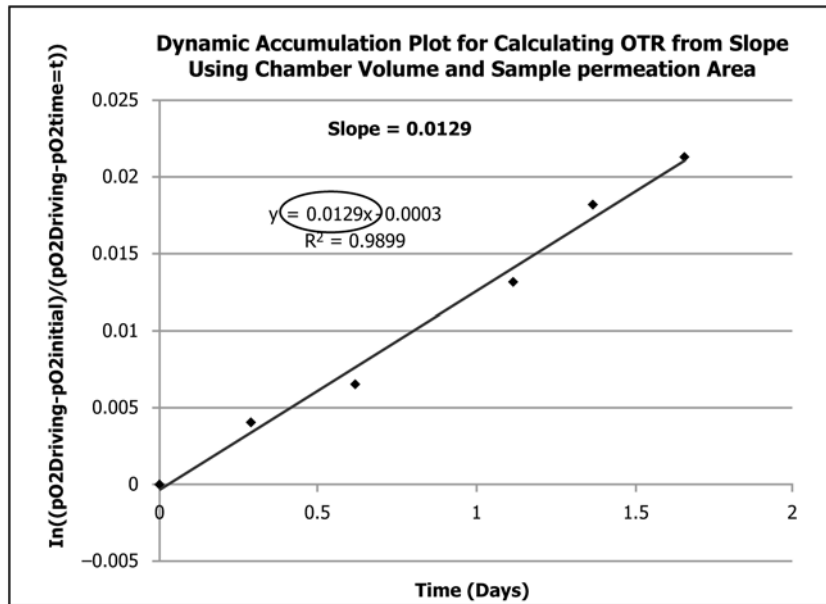| Date and Time	Days from Start (days)	Oxygen Concentration (%)	Calculated Column for Plot $\ln \frac{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{initial}}\right)}{\left(p_{O_2}^{Driving} - p_{O_2}^{Sensing_{time=t}}\right)}$
Day 1 05:12	0.00	0.10	0.0
Day 1 12:04	0.29	0.50	0.004012
Day 1 20:00	0.62	0.75	0.006528
Day 2 08:00	1.12	1.40	0.013098
Day 2 14:00	1.37	1.90	0.018182
Day 2 21:00	1.66	2.20	0.021245

FIG. X1.1 Plot of Oxygen Accumulation Data

X1.3 The determination of the oxygen concentration within the permeation apparatus by measuring the quenching effect of oxygen on the fluorophore is accomplished using automated sensors and a computer system as described in 14.1.