Designation: F2476 – 13

Standard Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO_2TR) Through Barrier Materials Using An Infrared Detector[1]

This standard is issued under the fixed designation F2476; 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 method covers a procedure for determination of the steady-state rate of transmission of carbon dioxide gas through plastics in the form of film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. It provides for the determination of (1) carbon dioxide gas transmission rate (CO_2TR), (2) the permeance of the film to carbon dioxide gas (P'CO_2) , and (3) carbon dioxide permeability coefficient (P"CO_2) in the case of homogeneous materials.

1.2 *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]

D1898 Practice for Sampling of Plastics (Withdrawn 1998)[3]

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

3. Terminology

3.1 *Definitions:*

3.1.1 *carbon dioxide permeability coefficient* (P"CO_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 carbon dioxide permeability is the mol/m·s·Pa. The test conditions (see 3.1.3) must be stated.

3.1.2 *carbon dioxide permeance* (P'CO_2) —the ratio of the CO_2 TR to the difference between the partial pressure of CO_2 on the two sides of the film. The SI unit of permeance is the mol/(m^2·s·Pa). The test conditions (see 3.1.3) must be stated.

3.1.3 *carbon dioxide transmission rate* (CO_2TR) —The quantity of carbon dioxide gas passing through a unit area of the parallel surfaces of a plastic film per unit time under the conditions of the test. The SI unit of transmission rate is the mol/(m^2·s). The test conditions, including temperature and carbon dioxide partial pressure on both sides of the film, must be stated.

3.1.3.1 *Discussion*—A commonly used metric unit of CO_2TR is the cc(STP)/(m^2·day) at one atmosphere driving force pressure differential where: 1 cc(STP) is 44.62 µmol. 1 atm is 0.1013 MPa. and one day is 86.4 x 10^3 s. CO_2 TR in SI units is obtained by multiplying the value in metric units by 5.164 x 10^{-10} or the value in inch-pound units cm^3(STP) / (100 $in.^2$ · day) by 8.004 x 10^{-9}.

4. Summary of Test Method

4.1 The carbon dioxide 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 with carbon dioxide. As carbon dioxide gas permeates through the film into the nitrogen carrier gas, it is transported to an infrared detector where an electrical output is produced whose magnitude is proportional to the amount of CO_2 flowing into the detector per unit of time.

5. Significance and Use

5.1 Carbon dioxide gas transmission rate (CO_2 TR) is an important determinant of the packaging protection afforded by

[1] This test method is under jurisdiction of ASTM Committee F02 on Flexible Barrier Packaging and is the direct responsibility of Subcommittee F02.10 on Permeation.

Current edition approved Dec. 15, 2013. Published February 2014. Originally approved in 2005. Last previous edition approved in 2005 as F2476-05. DOI: 10.1520/F2476-13.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

barrier materials. It is not, however, the sole determinant, and additional tests, based on experience, must be used to correlate packaging performance with CO_2TR. It is suitable as a referee method of testing, provided that purchaser and seller have agreed on sampling procedures, standardization procedures, test conditions and acceptance criteria.

6. Apparatus

6.1 *Carbon Dioxide Gas Transmission Apparatus,* as diagrammed in Fig. 1 or Fig. 2, with the following:

6.1.1 *Diffusion Cell*—shall consist of two metal halves, which, when closed upon the test specimen, will accurately define a circular area. A typical acceptable diffusion cell area is 50 cm^2. The volume enclosed by each cell half, when clamped, in not critical: it should be small enough to allow for rapid gas exchange, but not so small that an unsupported film that happens to sag or bulge will contact the top or bottom of the cell.

6.1.1.1 *O-Ring Groove*—an appropriately sized groove, machined into the CO_2 (or test gas) side of the diffusion cell, retains an elastomer 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.

6.1.1.2 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.

6.1.1.3 *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.

6.1.1.4 It is desirable to thermostatically control the diffusion cell. Because the transmission rate is a function of temperature, it shall be controlled to within ± 0.1°C.

6.1.1.5 Experience has shown that arrangements using multiple diffusion cells are a practical way to increase the number of measurements that can be obtained from an infrared 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 side 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.

6.1.2 *Flowmeter*—a means shall be provided to establish and maintain test gas and carrier gas flows. An operating range in the order of 5 to 100 ml/min for CO_2 and up to 300 ml/min for N_2.

6.1.3 *Flow Switching Valves*—needed to perform the tasks of (1) purging, (2) accumulating, if needed, for static or dynamic testing methods, and (3) maintaining flow for continuous flow methods.

6.1.4 *Infrared Sensor*—a 4.3 µm infrared filter to measure the quantity of CO_2 in the carrier gas going to the sensor.

NOTE 1—The infrared sensor is not an absolute measuring device. Therefore, some standard has to be used to establish a point of reference. A means of providing a known quantity of CO_2 has been used and has been found satisfactory for this application. The use of a calibrated valve enables the system to establish the point of reference against which the

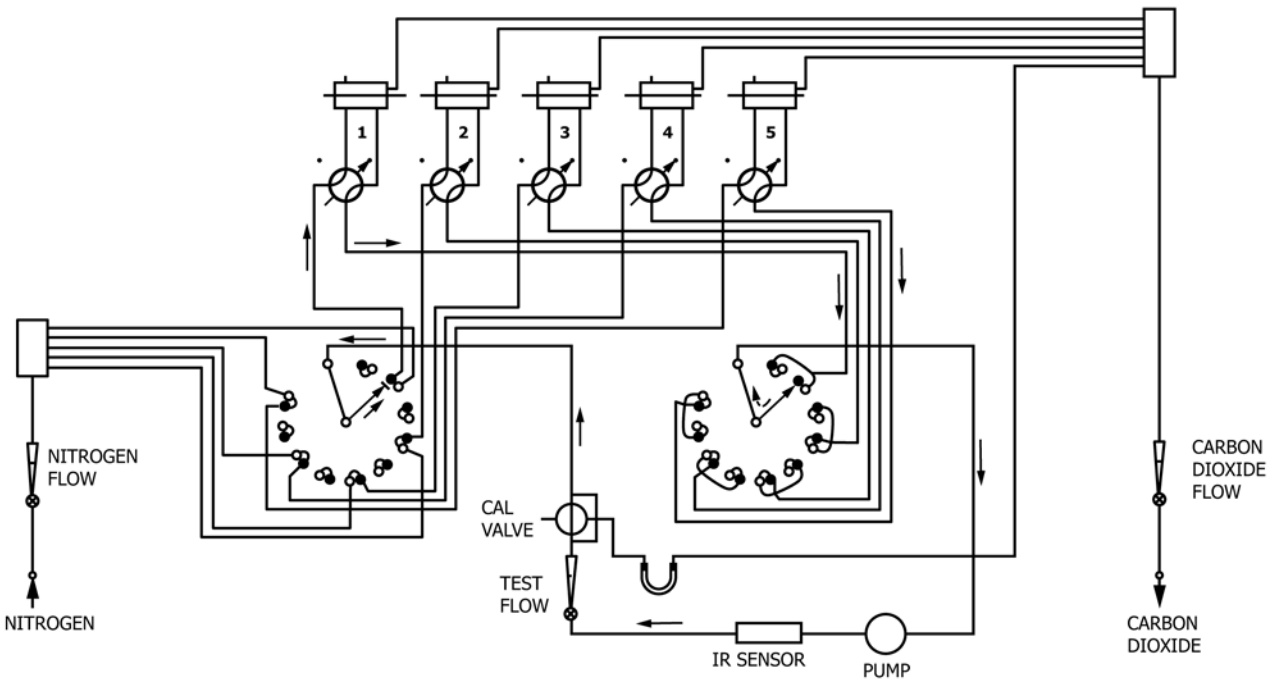

FIG. 1 A practical arrangement of components for the measurement of carbon dioxide transmission rate using a non-computerized system

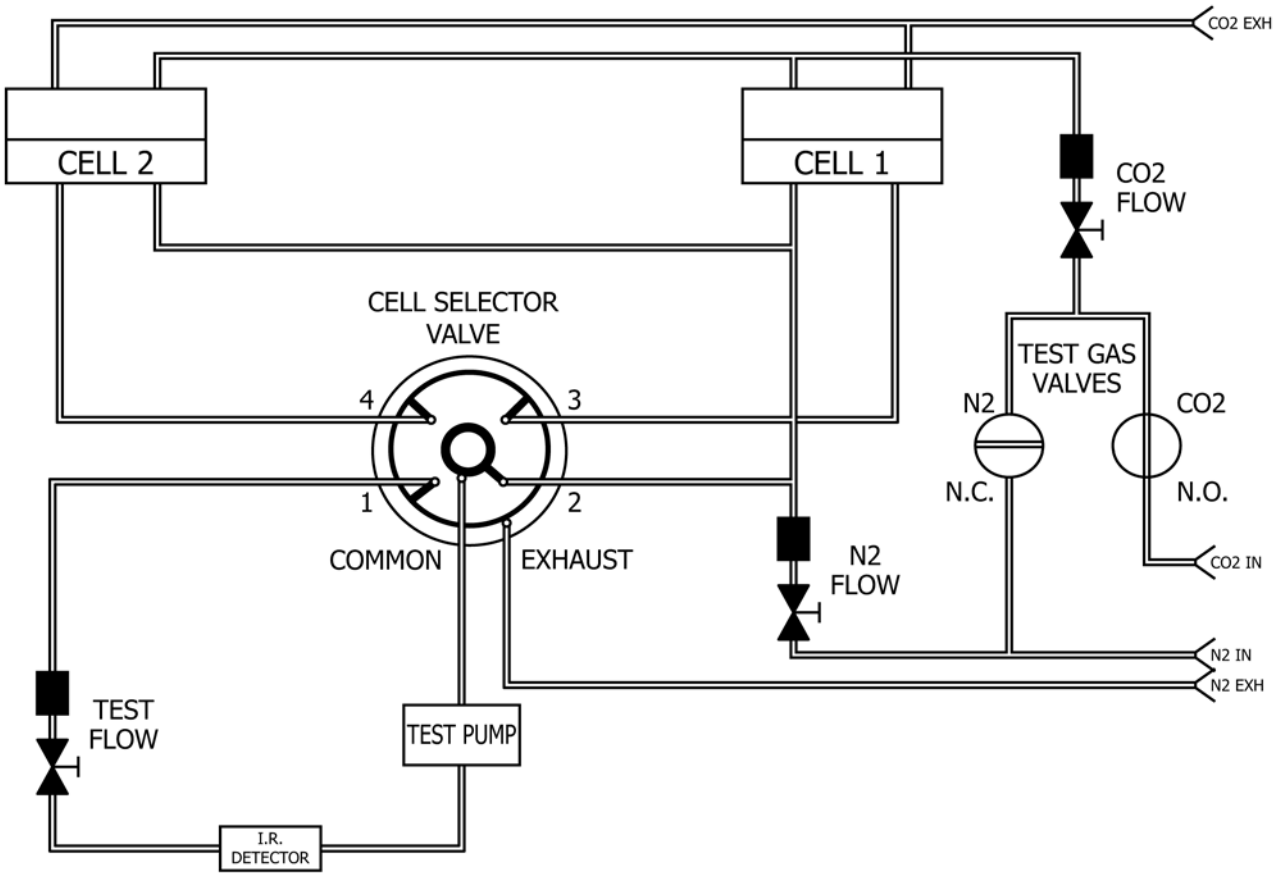

FIG. 2 A practical arrangement of components for the measurement of carbon dioxide transmission rate using a computerized system

unknown film is compared or the system may also be calibrated with a reference film.

6.1.5 *Recording Device*—a strip chart recorder or, if the system is computer- controlled, a monitor and a printer have been found to be adequate.

7. Reagents and Materials

7.1 *Nitrogen Gas*—grade need not be higher than "High Purity" or "Extra Dry," which is readily available in most of the principal cities at low cost. A regulator with auxiliary metering valve and outlet fittings for ⅛ in. tubing should be used.

7.2 *Carbon Dioxide Gas*—a carbon dioxide concentration of 99.9 % or greater is suitable for this application.

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

7.4 *Aluminum Foil Reference Blank*—The term "reference blank" or "blocking plate" refers to a non-transmitting, zero reference aluminum foil sheet. Used in some instruments to establish system zero prior to testing film specimens.

8. Precautions

8.1 Temperature is a critical parameter affecting the measurement of CO_2TR. Careful temperature control will help to minimize variations due to temperature fluctuations. During testing, the temperature shall be maintained within ± 0.1°C. The average temperature and the range of temperatures found during a test shall both be reported. Accurate temperature control is easier to maintain if the instrument is placed in a temperature-controlled environment.

8.2 The sensor will require time to stabilize to a low reading characteristic of a good CO_2 barrier after it has been used to test a high transmission barrier. For this reason, materials of comparable gas transmission qualities should be tested together.

8.3 Calibration should be performed with the appropriate amount of CO_2 that is comparable to the CO_2 TR of the specimens being tested.

9. Sampling

9.1 The sampling units used for the determination of CO_2TR shall be representative of the quantity of product for which the data are required, in accordance with Recommended Practice D1898. Care shall be taken to ensure that samples are representative of conditions across the width and along the length of a roll of film.

10. Test Specimens

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

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

10.3 If the test specimen is of an asymmetrical (multilayer) 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 2 was mounted facing the CO_2 side of the diffusion cell").

11. Conditioning

11.1 If a specific conditioning procedure is used, it should be included in the report.

12. Calibration

12.1 *Computerized Instruments*—Systems that utilize computer linearization technology allow a one-point calibration for a wide range of CO_2TR values. This one-point reference is accomplished by utilizing a known value reference film.

12.1.1 Systems that utilize computer linearization technologies normally require calibration to be accomplished before the samples are tested, or during the test of a sample. Follow the manufacturer's standard calibration procedure as called out in the manufacturer's operating manual.

12.2 *Non-Computerized Instruments* —Because the IR sensor voltage output on non-computerized systems is dependent on variables such as detector response and carrier gas flow, a calibrated point of reference must be determined against which the unknown can be compared. This is achieved through the use of a measured quantity of CO_2 being injected into the system, utilizing a calibration valve (the volume of which has been determined) or with a known value reference film.

12.2.1 On the manually operated systems, calibration is performed after the samples have been tested and before the test cells have been opened and the samples removed. Follow the manufacturer's standard calibration procedure as called out in the manufacturer's operating manual.

12.2.2 It should be noted that the system response may not be perfectly linear. Therefore, the amount of CO_2 injected into the system during the calibration cycle should be as close to the estimated value as possible.

13. Test Procedure

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

13.2 Unclamp the diffusion cell and open it. Apply a thin layer of sealing grease around the raised rim of the diffusion cell. Place the test specimen upon the greased surface, taking care to avoid creases or wrinkles. Clamp both halves of the diffusion cell tightly together.

13.3 In some instruments, it may be necessary to establish a system zero prior to testing. This is accomplished by using an aluminum foil reference blank that is free from wrinkles, creases, scratches and pinholes. This foil is mounted in one diffusion cell using sealing grease. The output of this cell, where there is no contribution from permeation since foil is essentially impervious, is the system zero.

If a system zero is not required prior to testing, proceed to 13.4.

13.4 Introduce carbon dioxide gas into the test gas side of the diffusion cell, following the manufacturer's instructions. This marks the start of the conditioning period during which a gradient is established within the film and a steady-state transmission rate is achieved. The length of time it takes to achieve a steady-state condition is dependent on many factors, such as temperature and thickness of the film. Steady state is defined as the point at which the transmission rate no longer changes with time. Users will initially have to experiment with conditioning times to establish a suitable time for their materials.

13.5 Depending on the equipment used, the following is offered as a guide when testing flat materials with a manual system (non-computerized):

Static Accumulation—A method generally used for testing low transmitting barriers (transmission rates of <50 cc/(m^2 · day).

Dynamic Accumulation—A method applied to barriers of moderate transmission rate generally >50 cc/(m^2 · day) but <300 cc/(m^2 · day).

Continuous Flow—A method suited to measurement of moderate-to-high transmitting barriers [(300 cc/(m^2 · day)] to [(10 000 cc/(m^2 · day)].

Please refer to the manufacturer's manual for a more complete description of each method and follow the manufacturer's instructions regarding the specifics of each technique.

13.6 *Computerized Instruments*—Allows a wide range to be tested using a continuous flow technique. The typical usable range is from 1 cc/(m^2 · day) to 10 000 cc/(m^2 · day). Follow the manufacturer's instructions regarding the operation of such instrumen

13.7 Once it has been determined that the films have reached steady state, the test may be terminated (this is done automatically by the computer for computer-controlled systems).

14. Calculations

14.1 For computer controlled equipment, all calculations are performed by the computer and CO_2TR is presented in units of cc/(m^2 · day).

14.2 For equipment that is not computer-controlled, closely follow the equipment manufacturer's suggested data reduction procedures.

14.3 Calculate the carbon dioxide permeance (P'CO_2)

$$P'CO_2 = (CO_2TR)/p \quad (1)$$

where p is the partial pressure of carbon dioxide, which is the mole fraction of CO_2 multiplied by the total pressure (normally one atmosphere) in the test gas side of the diffusion cell. The partial pressure of CO_2 on the carrier gas side is considered to be zero.

14.4 Calculate carbon dioxide permeability coefficient ($P''CO_2$)

$$P''CO_2 = P'CO_2 \times l \quad (2)$$

where l is the average thickness of the specimen (see 10.2). This is only meaningful for homogeneous materials. This value should not be used unless the relationship between the thickness and permeance has been verified in tests using several different thicknesses of the material.

15. Report

15.1 The report shall include the following:

15.1.1 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.

15.1.2 The average thickness of the test specimen as determined in 10.2, and the standard deviation of the thickness values.

15.1.3 The partial pressure of the carbon dioxide gas on the test gas side of the diffusion cell and a statement as to how it was determined.

15.1.4 The rate of flow of the nitrogen carrier gas during the test.

15.1.5 The conditioning procedure used on the test specimens prior to testing.

15.1.6 The temperature of the test specimen (to the nearest 0.1°C) and the method used to determine the temperature.

15.1.7 The values of CO_2TR, permeance (if desired), and permeability (if desired).

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

15.1.9 A statement of the procedure used to calibrate the instrument.

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

15.1.11 The time to reach steady state after introduction of the carbon dioxide gas into the test gas side of the diffusion cell..

16. Precision and Bias

16.1 The precision of this test method is based on an interlaboratory study conducted in 2013. Eight laboratories tested two different materials. Every "test result" represents an individual determination. Each laboratory was asked to submit two replicate test results, from a single operator, for each material. Practice E691 was followed for the design and analysis of the data; the details are given in RR:F02-1035.[4]

TABLE 1 Summary of ILS Results, cc/(m² · day)

Material	Average,[A] $\bar{\chi}$	Repeatability Standard Deviation, S_r	Reproducibility Standard Deviation, S_R	Repeatability Limit, r	Reproducibility Limit, R
A	331	14.6	15.2	16.2	42.4
B	56.7	2.98	3.16	4.21	8.85

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

16.1.1 *Repeatability Limit, r*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the *r* value for that material; *r* is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

16.1.1.1 Repeatability limits are listed in Table 1.

16.1.2 *Reproducibility Limit, R*—Two test results shall be judged not equivalent if they differ by more than the *R* value for that material; *R* is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

16.1.2.1 Reproducibility limits are listed in Table 1.

16.1.3 The 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 have an approximate 95% probability of being correct.

16.2 *Bias*—The bias for this method has not been determined because there is no known reference available.

16.3 The precision statement was determined through statistical examination of twenty-eight results, from eight laboratories, on two materials. Both results from Laboratory 5, Material A were excluded due to h-outliers. Both results from Laboratory 7, Material B were excluded due to h-outliers. These two materials were described as follows:

Material A: nominally 1 mil polyethylene terephthalate
Material B: nominally 5 mil polyethylene terephthalate

16.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:F02-1035. Contact ASTM Customer Service at service@astm.org.