WHITE PAPER

A COMPARISON OF THE ASTM F1115 AND F2476 TEST METHODS FOR CO_2TR MEASUREMENT

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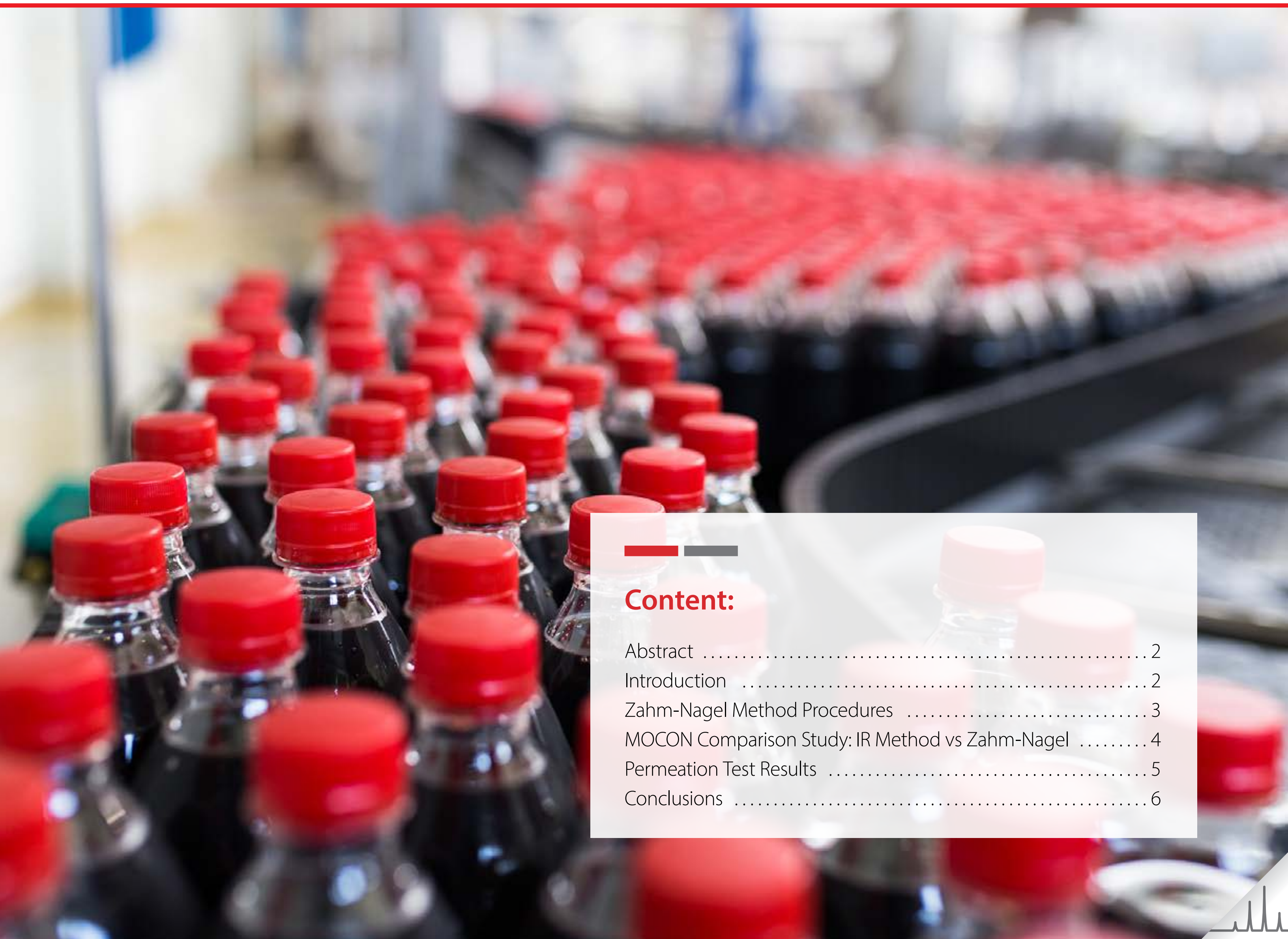


Content:

TWO MAJOR METHODS FOR CO_2TR ANALYSIS

As carbonation is critical to the flavor profile of carbonated beverages, carbon dioxide gas transmission rate (CO_2TR) is the most important determinant of shelf life for a carbonated soft drink package.

Abstract

When assessing carbon dioxide (CO_2) barrier properties in the food and beverage industry, there are two major test methods: ASTM F1115 "Standard Test Method for Determining the Carbon Dioxide Loss of Beverage Containers," and ASTM F2476 "Standard Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO_2TR) Through Barrier Materials Using an Infrared Detector." This whitepaper compares these two methods in detail. It will also offer an assessment of their uses at different stages of the CO_2 barrier packaging design process, with relation to MOCON® permeation analyzers (Figure 1).

Introduction

With a long history dating back to the early 1900s, Zahm-Nagel equipment is well known for measuring air and CO_2 content in containers or bottles for industries including beer, carbonated soft drinks, and sparkling water. The method involves the use of sensitive pressure and temperature monitoring equipment where a high degree of accuracy is essential. For example, a micro-pressure transducer and thermocouple are used for measuring pressure and temperature of the package in a closed system (Figure 2). The purpose of the test is to determine the CO_2 loss from polymer beverage containers after a specified period of storage time.

Factors contributing to this pressure loss include volume expansion and the gas transport characteristics of the package, including permeation and leakage. Depending on the barrier level and seal quality of the bottles, the monitoring of pressure loss

Figure 1. MOCON PERMATRAN-C 4/30 L

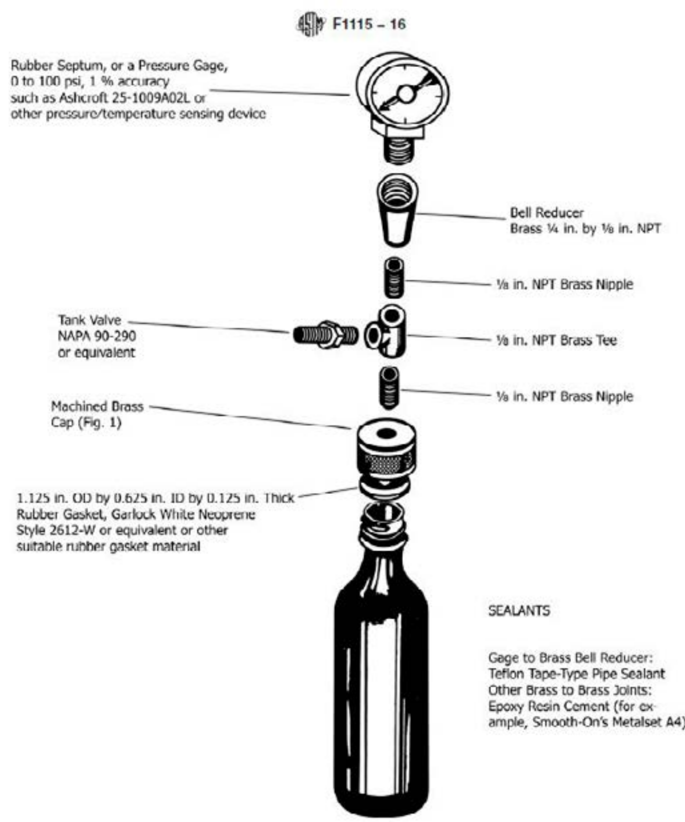


Figure 2. Zahm-Nagel Method (Procedure A) Testing Pre-filled Carbonated Bottle

ZAHM-NAGEL METHOD PROCEDURES

could be long or short in time. For any bottles or packages with poor barriers or seals, the pressure drops quickly, and the test could be short. Alternatively, for bottles with good barriers and seals, the testing could be very long, from 2 months (smaller bottles) to 4-5 months (larger bottles).

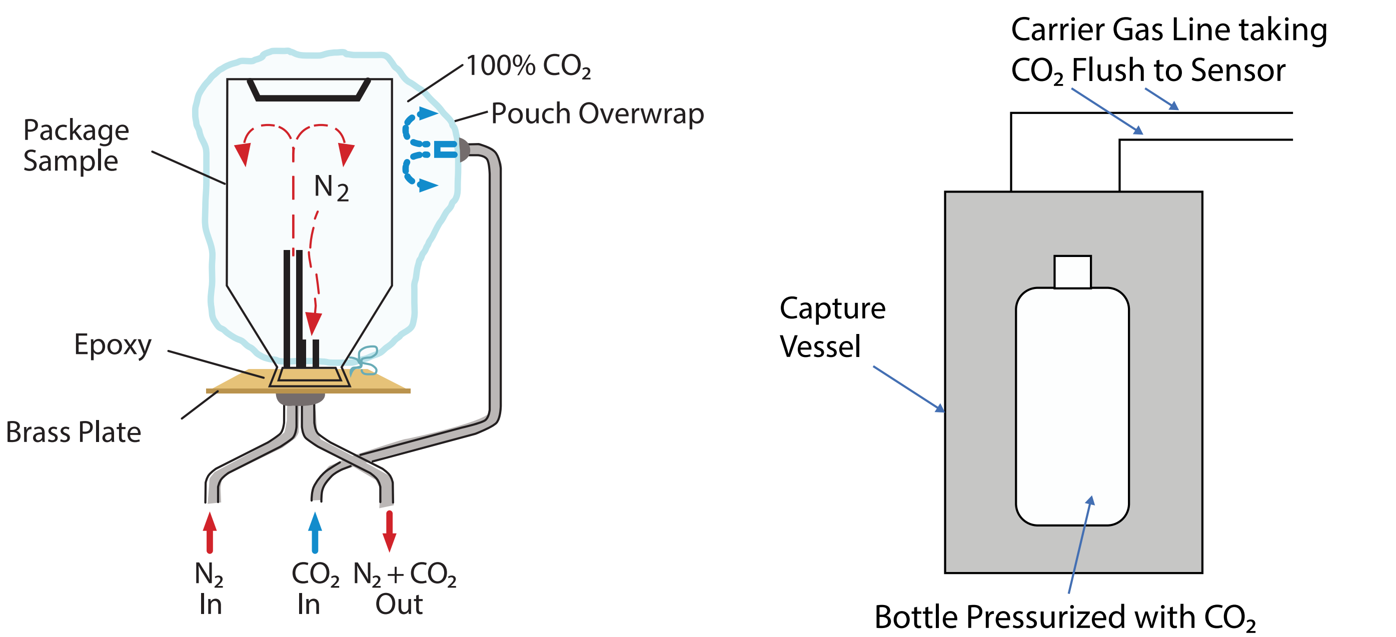
The Zahm-Nagel Method comprises two procedures, A and B:

- Procedure A is used mostly by package development engineers who focus on the package function. It allows use of a specially designed closure with attached pressure transducer and thermocouple. It needs a minimum set of 5 bottles for each type of sample.
- Procedure B is recommended for use in beverage filling operations as a quality control (QC) tool. Procedure B uses manual measurement, which means that each test destroys the bottle at the test interval. Therefore a minimum of 50 bottles are needed for this procedure.

In practice, Zahm-Nagel Method is a good tool for manufacturers and brand owners to monitor the real-time shelf life of their carbonated liquid products. However, it is not time effective for R&D engineers working on barrier evaluation during new package designs or trying newly invented materials, or for the bottle manufacturing QA/QC process.

The industry needs a method to evaluate CO_2 barriers in a reasonably short time. This whitepaper introduces ASTM F2476 — the IR CO_2TR Method, represented by the MOCON® PERMATRAN-C® 4/30. This method quantifies CO_2 loss with an Infrared (IR) sensor, unlike the Zahm-Nagel Pressure Method.

In the IR Sensor Method, the CO_2 sensor uses a pressure modulated IR sensor. The measurement system consists of a bellows pump, a sensing chamber, an infrared source, a 4.3 micrometer infrared filter, a lead selenide photo detector, and an amplifier. Only CO_2 molecules that match the same wavelength can be detected by the sensor. The signal from the detector is amplified, filtered, and converted to a DC signal which is directly proportional to the CO_2 in the exhaust of the Test Cell. The signal is therefore proportional to the CO_2TR of the barrier material. Both film samples and package samples can be tested with this method. When testing packages, there are ways to test either the empty package with an opening, or the sealed package (such as a bottle) with pre-filled carbonated liquid product pressurized to the product specification (Figure 3).



Empty Bottle Test Setup

Pre-filled Carbonated Bottle Test Setup

Figure 3. IR Sensor Method

With the obtained CO_2TR transmission rate data, along with minor spreadsheet calculations, the shelf life can be estimated for any carbonated drink, assuming the start point and end of shelf life parameters are known (Refer to separate technical note: "How To Use CO_2TR Results Of Carbonated Drink Bottles For Shelf Life Estimation").

Because the IR sensor is specific to CO_2 molecules, other gases (such as air) in the system will not be measured, which greatly increase the accuracy of CO_2 measurement compared to the Zahm-Nagel Method. The test duration could be just days with the IR Sensor Method, verses months with the Zahm-Nagel Method.

The IR Sensor Method can not only measure the CO_2TR of polymer materials and packages faster, but is also proven to produce CO_2TR results that match data derived from the Zahm-Nagel Method.

MOCON Comparison Study: IR Method vs Zahm-Nagel Method

In order to compare ASTM F1115-87 (Zahm-Nagel Method) and ASTM F2476 (MOCON IR Sensor Method) and determine any differences, MOCON R&D engineers conducted a comparison study with both methods for the following samples and test conditions:

Six PET 20 ounce bottles from the same mold were used to perform the CO_2TR test with the IR Sensor Method (Figure 4). All permeation tests were done at room temperature (22-23° C).

Prior to the main study, a few side tests were conducted to guarantee the accuracy of the final test results:

- **A helium leak check** was performed on all specially made closures and toggle valves, to ensure that they did not have any gross leaks.
- **A creep test** was done to determine the rate of deformation of the bottle under pressure. This was done by pressurizing four PET bottles with nitrogen to 60 PSIG. The pressure gauge was monitored, and a time was determined for how long it took for the pressure to stop falling. PET is a very good barrier to nitrogen; results determined that any creep happens almost immediately (over the first several hours), and can be determined negligible after this time.
- **Closure permeation tests** were done on a set of the special MOCON closures. Glass bottles were used to ensure that the permeation came only from the special closures. First the bottles were carefully flushed with CO_2. The closures were then added, and the bottle was pressurized to 60 PSIG. The bottles were then put into the capture volumes and tested. Closures took about 5 days to come to equilibrium. Results are as follows. Closure A = 0.3926 cc/pkg•day, closure B = 0.3745 cc/pkg•day. Results when normalized for PSIA of CO_2 are as follows:
  - Closure 1 = 0.00528 cc/pkg•day•PSIA
  - Closure 2 = 0.00504 cc/pkg•day•PSIA
  - This value will be added to the following empty bottle testing results

Then, the major tests for this study were performed, and the results were listed in Table 1.

Figure 4. MOCON PERMATRAN-C 4/30 used to test pre-filled carbonated drink bottle

PERMEATION TEST RESULTS

Bottle Permeation Test (Empty Bottle Without Closure, CO_2 Going In)

Permeation tests were done on a set of bottles using the standard MOCON method. This consists of gluing the bottle to a package adapter and placing the bottle in a metalized bag. A small quantity of water was added to the bottom of the bag to create 100% relative humidity. The bag was then flushed with CO_2. The package adapter was then connected to the PERMATRAN-C instrument. Nitrogen was flushed through the inside of the bottle and then measured by the detector. With this method, one atmosphere of CO_2 permeates from the outside into the bottle. Equilibrium time is about six days. Below are the results when normalized for PSIA of CO_2 and the closure results are added:

- Bottle 1 = 0.1028 cc/pkg•day•PSIA
- Bottle 2 = 0.1019 cc/pkg•day•PSIA

Bottle Permeation Test (Partial Full Bottle, CO_2 Going Out)

With this method, 100 ml of water is added to the bottle and the special closure is then attached to the bottle. The special closure was designed to attach a pressure gauge and a shutoff valve that can be connected to a tank gas line. The bottle is then pressurized with CO_2 gas to 60 PSIG (75 PSIA, or five atmospheres of CO_2 in the bottle). It is then conditioned with a constant 60 PSIG applied for 6 days. The bottle is then placed in the Capture Vessel Cartridge and tested with the PERMATRAN-C. The results are as follows: bottle 1 = 6.174 cc/(pkg•day), bottle 2 = 6.396 cc/(pkg•day). Results when normalized for 1 PSIA of CO_2 are as follows:

- Bottle 1 = 0.1029 cc/pkg•day•PSIA
- Bottle 2 = 0.1066 cc/pkg•day•PSIA

Bottle Permeation Test (Full Bottle, CO_2 Going Out)

The same above special closure was used to attach a pressure gauge and a shutoff valve that can be connected to a tank gas line. The bottles were filled with water and pressurized with CO_2 to 60 PSIG (75 PSIA, or five atmospheres of CO_2 in the bottle). The bottles were then conditioned for a minimum of 6 days and then placed into the capture volume for testing. The results are as follows: bottle 1 = 8.2027 cc/(pkg•day), bottle 2 = 8.1879 cc/(pkg•day). Results when normalized for 1 PSIA of CO_2 are as follows:

- Bottle 1 = 0.1104 cc/pkg•day•PSIA
- Bottle 2 = 0.1102 cc/pkg•day•PSIA

Shelf Life Test with Zahm-Nagel Method (Full Bottle, CO_2 Going Out)

Shelf life tests were done following the ASTM test method F 1115-16 (Zahm-Nagel method). Two bottles (with the same design and size as those used in the IR method testing) were filled with water and pressurized to 60 PSIG. The same closure/valve system was used to pressurize the bottle and measure the pressure. The filled bottle was monitored and recorded for pressure and temperature change, for an extended length of time. After gas volumes are calculated, transmission rate per PSIA can then be calculated. The whole test duration was over a few months.

Table 1 summarizes the test results from above tests.

Table 1. CO_2TR Results Comparison

Method	MOCON IR Sensor *			Zahm-Nagel *
Sample ID	Empty Bottle cc/(pkg•day•PSIA)	Partial Full Bottle cc/(pkg•day•PSIA)	Full Bottle cc/(pkg•day•PSIA)	Full Bottle cc/(pkg•day•PSIA)
BOTTLE A	0.1028	0.1029	0.1104	0.1067
BOTTLE B	0.1019	0.1066	0.1102	0.1080
Time to complete Test	Equilibrium in 6 days	Conditioning 6 days + 2 days testing	Conditioning 6 days + 2 days testing	2.5 months

**Note: Due to the IR Sensor Method and the Zahm-Nagel Method using different test gas pressures, above results are normalized to 1-PSIA for comparison purposes.*

CONCLUSIONS

Conclusions

The above data demonstrates that using the MOCON IR Sensor CO_2 permeation instrument, the CO_2TR test results were comparable with that from the Zahm-Nagel Test Method.

Several considerations, best practices, and suggested further reading are listed below.

- The Zahm-Nagel Method is historically a good tool for brand owners to monitor the real-time shelf life of the carbonated liquid products.
- Zahm-Nagel tests are often time consuming. The longer the test takes, the longer the shelf life, which is good news for the brand owner. However, the longer testing time may not be favorable to R&D and the design process.
- At least 50 bottles are needed if measured manually for the Zahm-Nagel long-term test. Since a bottle is destroyed at each test, a minimum of five bottles are needed at each interval.
- MOCON's IR Sensor Method following ASTM F2476 methodology provides test results that are highly correlated to Zahm-Nagel shelf life results in much shorter time.
- The MOCON IR Sensor Method enables R&D to accomplish new designs and QA/QC tasks in a more effective way.
- MOCON's IR Sensor Method provides CO_2TR measurements for samples in the form of film, multi-layer laminations, empty bottles/containers, as well as bottles with pre-filled carbonated liquid products.
- A separate technical note describes how to test CO_2TR with the MOCON PERMATRAN C 4/30 and how to use CO_2TR results from ASTM F2476 IR Sensor Method to estimate a carbonated drink product's shelf life.

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: F2476 – 20

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 (PCO_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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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* (PCO_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 86.4×10^3 s. CO_2TR in SI units is obtained by multiplying the value in metric units by 5.164×10^{-10} or the value in inch-pound units cm^3(STP) / (100 $in.^2$ · day) by 8.004×10^{-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

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

Current edition approved June 1, 2020. Published July 2020. Originally approved in 2005. Last previous edition approved in 2013 as F2476 – 13. DOI: 10.1520/F2476-20.

[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.

Figure 5. ASTM F2476 IR Sensor Method

Reference:

ASTM F2476: Standard Test Method for Determining the Carbon Dioxide Loss of Beverage Containers (Figure 5).

ASTM F1115: Standard Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO_2TR) Through Barrier Materials Using an Infrared Detector.

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