METHODS FOR TESTING HIGH BARRIER MATERIALS

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ABSTRACT

The permeation of packaging materials has been of importance to packaging engineers, food scientists and material engineers for decades. A brief history of permeation testing methods will be covered followed by a more detailed description of new emerging technologies and test methods. Recent advances in patented flow technology, mass transfer analysis and understanding, high speed predictive computer analysis and low cell volume construction now give engineers and scientists the ability to determine material and flavor interactions, shelf life estimations, and rapid permeability, solubility and diffusion coefficient analysis. This mass transfer analysis allows material producers, converters and end-users the ability to predict the performance of packaging materials by not only using permeability, but also understanding the importance of solubility and diffusion on this performance.

INTRODUCTION

Historically, the measurement value of interest in the polymer, material or packaging industries has been the permeation coefficient or transmission rate of a compound (typically, water vapor, oxygen, carbon dioxide or other organic vapors) in the steady state. In the most general terms, testing the permeation or barrier properties of high barrier materials involves several basic steps, irregardless of the test gas or permeant. This involves inserting the test material into some sort of test cell, closing and sealing the test cell, and then purging both sides of the test cell to establish a baseline. Then the test gas, vapor or permeant is introduced onto one side of the test material; as the gas, vapor or permeant begins to pass through the test material, it is "captured" on the opposite side of the test cell and carried into some type of detector specific to the gas, vapor or permeant in question. Typically this will generate a steady state equilibrium curve similar to that shown in Figure 1.

WATER VAPOR TRANSMISSION RATE TESTING

The original standard for testing water vapor transmission of high barrier materials is referred to in the industry as "the cup method". This method involves placing a small sample of the test materials over the top of a pre-made metal cup. The cup may contain water, in which case, the water vapor would pass through the test material and the cup would lose weight over time. In this scenario, the cups are placed into a test chamber containing a desiccant to drive the water vapor through the test material and weighed at periodic intervals until equilibrium is obtained (constant weight loss). Alternatively, the cup may contain a desiccant, be placed in a test chamber with water vapor (high humidity); in this case, the moisture pick-up by the desiccant is weighed until equilibrium. These methods were developed over many years and are now a standard ASTM Method (1). The cup method has always had several major shortcomings. It is a very tedious method and the results are very operator dependent. Secondly, it will take a very long time to measure very high barrier materials as they will take a long time to come to equilibrium; furthermore, the results obtained on very high barrier materials may not be very accurate.

In the early 1970's, several companies tried to automate water vapor transmission rate testing. Early in my career, I operated A Honeywell WVTR Tester. This machine contained a test chamber, where the test material was clamped into a test cell with moisture on one side and a gold grid moisture detector on the other. The operator simply inserted the sample, press the start button, which began the purge cycle, and then the machine automatically timed (in seconds) the amount of time it took for the moisture grid sensor to pick-up a pre-determined amount of moisture. This time was then converted into a permeation rate. This was a very easy, convenient test method that gave highly variable results. It was never approved as an ASTM Method.

This was followed in the early 1970's by a method to measure WVTR of Flexible Barrier Materials Using an Infrared Detection Technique (2). This method also involved clamping the test material into a test chamber with moist sponges on the outer chambers and an infrared photocell beam to detect the moisture in the central chamber. This method did provide measurements in far less time and with better precision than the traditional cup method (3).

In the mid-1980's, an improved infrared WVTR method was developed using a modulated infrared sensor (4). One of the big advantages of this method was its use of five samples in a "conditioning" position to help reduce time to steady state equilibrium.

In the early 90's, MAS Technologies pioneered new patented mass transfer analysis methods and a new device for the measurement of high barrier properties of films against gases. This new device employed an extremely high sampling rate of permeant gas with little or no background noise, allowing detection sensitivity, which was greatly enhanced relative to the previously referenced test methods. This led to the development of a new enhanced ASTM Method for diffusivity, solubility, and permeability of water vapor (5). This new test procedure employs mass transfer analysis that allows for high speed computer prediction of the steady state equilibrium value by analyzing the transient portion of the equilibrium curve; this has been used as a very valuable time saving technique especially when testing very high barrier materials with typically long equilibrium curves. Furthermore, by using all of the data generated in the transient portion of the curve, the diffusion coefficient and the solubility coefficient are also determined. With the analysis of this additional information, mass transfer applications such as shelf life predictions, compound absorption by food products, and loss of a compound from a food product into a packaging material (scalping) can be determined.

Figure 2 is a diagram of the moisture diffusion apparatus referenced in this new test method. The cell used in this apparatus (see figure 3) is a low volume, four zone test cell. The advantages of this test cell include multiple material analysis during a single test sequence, replicate material analysis during a single test, and increased sample area and sensitivity. This new apparatus allows for automated temperature and relative humidity profiling of a sample material. This new method also allows for the traditional reference film calibration of the equipment or for a more accurate direct water injection procedure as used in calibrating gas chromatographs.

OXYGEN (CARBON DIOXIDE, NITROGEN) TRANSMISSION RATE TESTING

In the case of oxygen (and other similar test gases such as carbon dioxide, nitrogen, helium, etc.), the early standard was the "Dow cell" method (7). This method contains two procedures; one is a manometric method and the other is a volumetric method. These methods were very operator dependent; in fact, the precision statement in the method says "the precision of the results obtained depends strongly, but in an unpredictable manner, on the combination of material and gas being tested". This equipment also required a very high level of maintenance to keep it operational.

This method was largely replaced in the late 1970's by a method using a coulometric sensor (8). However, this method is only specific to oxygen and other test gases still had to use the older, more traditional methods. The diagram of the components used in this method is shown in Figure 4. The apparatus first developed for this method used a single head test cell as shown Figure 4; later versions of this equipment included multiple test cells (up to 10). This method was a dramatic improvement over the traditional Dow cell method in that it was much more operator friendly, required a great deal less maintenance, and allowed the equilibrium curve to be graphically displayed as the test progressed instead of calculating a single value at the end of the test.

This method will be supplemented by a new method for oxygen vapor barrier measurement of flexible materials, which is currently being balloted within ASTM Subcommittee F-2.3 on Test Methods. Extensive round robin testing by multiple laboratories is simultaneously being conducted to validate this new method. It is very similar to the new WVTR method and apparatus previously discussed except it employs a micro fuel cell oxygen sensor. This sensor allows a very wide range of oxygen permeability testing, from breathable produce materials to very sopisicated high barrier composite structures.

ORGANIC VAPOR TRANSMISSION RATE TESTING

Early testing for permeation of organic vapors was done using a modified Dow cell test technique. For many years this was the only way possible to measure the permeation of organic compounds, volatiles, flavors, etc. In the early 1990's, MAS Technologies introduced the first automated instrument to measure diffusivity, solubility, and permeability of organic vapor barriers (9). This new apparatus and technology used precise patented flow technology and a flame ionization detector. This was clearly a breakthrough in testing volatile organic compounds and flavors and was readily accepted by the industry.

Recent industry interest is being focused on several new developments in the area of helium leak detection for measuring package and seal integrity of both permeable and impermeable completed packages. These new methods claim to be able to detect package leaks in the 10 to the minus eighth range. This is very pioneering work being done under the juristicion of ASTM Committee F-2 on Flexible Barrier Materials.

CONCLUSIONS

The development of test methods to measure the water vapor transmission rate of high barrier materials has seen the most developments in the past twenty years. New techniques for oxygen (and other test gases) have also been developed and standardized. Finally, a new automated procedure for testing organic vapor and compounds has recently been approved. ASTM Committee F-2.3 on Test Methods continues to develop and standardize tests for measurement of high barrier materials.

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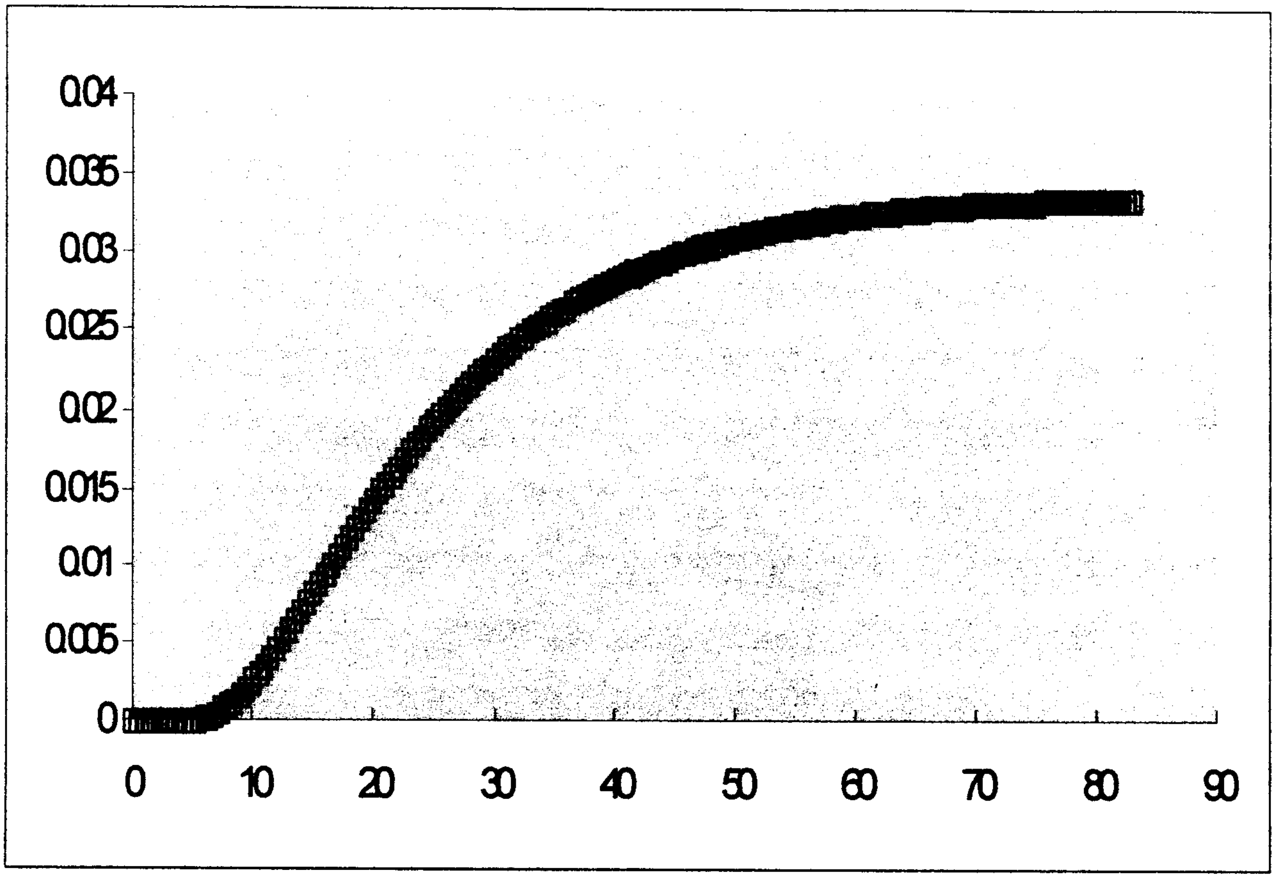


Figure 1 - Typical Steady State Equilibrium Curve

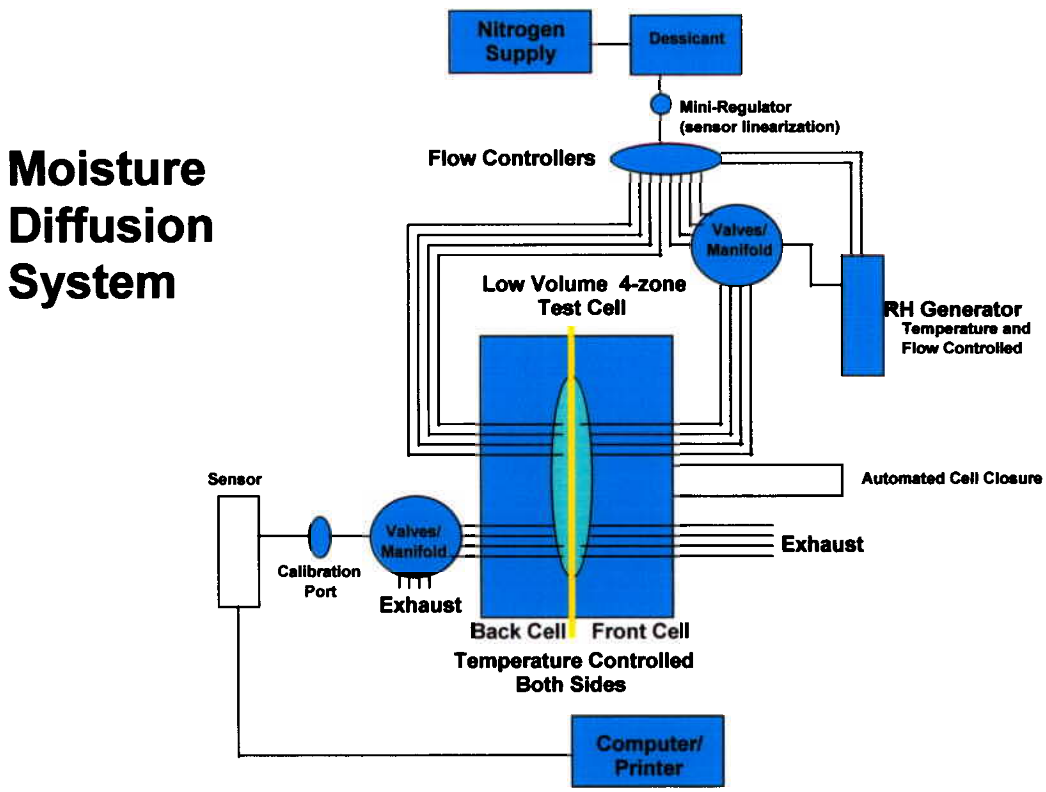
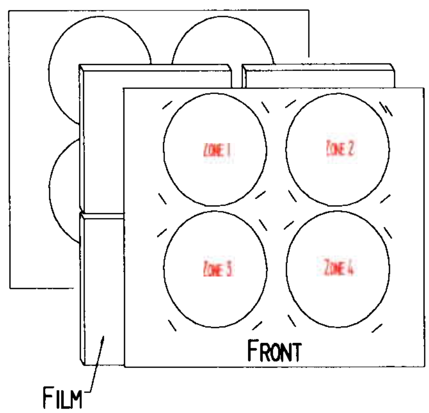


Figure 2 - Moisture Diffusion System

4 Measurement Zones For:



- **Material Variability Measuremnt**
- **Increased Sample Area & Sensitivity**
- **Multiple Material Setup**

Figure 3 - Multi-zone, low volume test cell

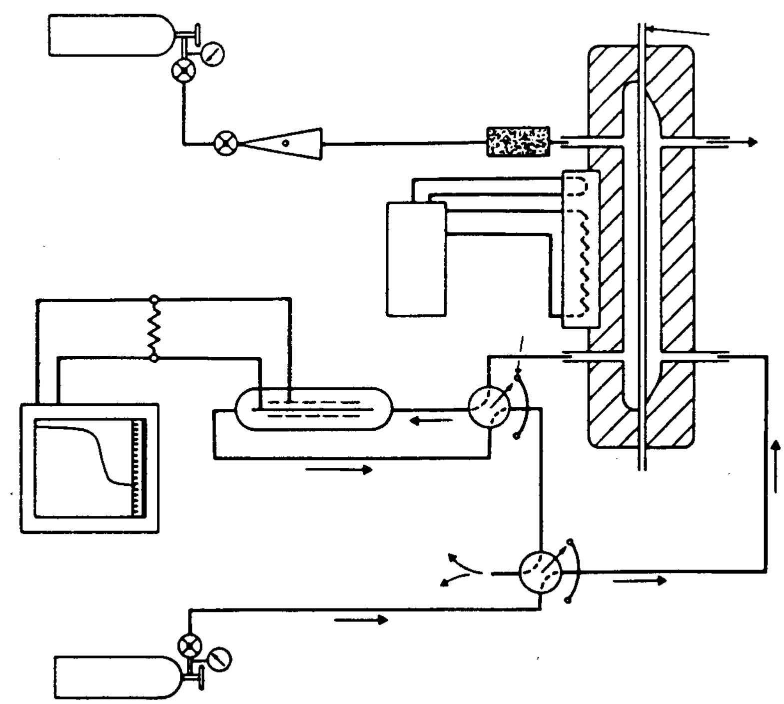


Figure 4 - Oxygen Transmission Rate Using the Coulometric Method