This is to certify that the

thesis entitled

Organic Vapor Permeability of High Barrier
Polymer Membranes By A Dynamic Purge And
Trap/Thermal Desorption Procedure

presented by

Yueh-Yi Chang

has been accepted towards fulfillment
of the requirements for

Master's degree in Science

Jack R. Giacin
Dr. Jack R. Giacin
Major professor

Date Dec. 10. 1996

ORGANIC VAPOR PERMEABILITY OF HIGH BARRIER POLYMER MEMBRANES BY A DYNAMIC PURGE AND TRAP/THERMAL DESORPTION PROCEDURE

By

Yueh-Yi Chang

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1996

ABSTRACT

ORGANIC VAPOR PERMEABILITY OF HIGH BARRIER POLYMER MEMBRANES BY A DYNAMIC PURGE AND TRAP/THERMAL DESORPTION PROCEDURE

By

Yueh-Yi Chang

A permeation test method based on the MAS 2000™ Permeation Test System, modified with a dynamic purge and trap system, was developed for the determination of organic vapor permeability through high barrier polymer membranes. For validation of this method, the permeation of α-pinene through a Saran coated oriented polypropylene film was determined and the results were compared with those obtained from the MAS 2000™ Permeation Test System operated in the continuous flow isostatic method. The permeance values obtained by the two procedures were found to be in good agreement.

The applicability and the sensitivity of the test method was demonstrated by measuring the permeation of α-pinene through seven high barrier polymer films. The Dynamic Purge and Trap/Thermal Desorption Procedure was found to provide an increase in sensitivity of three to four orders of magnitude over the continuous flow isostatic procedure.

Dedicated to my grandmother and my parents

ACKNOWLEDGMENTS

Dr. Jack Giacin, for his great guidance, enthusiasm, understanding, and professional advice throughout my research while serving as my major advisor.

Dr. Randy Beaudry and Dr. Susan Selke, for serving on my committee members.

CFPPR, Center for Food & Pharmaceutical Packaging Research, for providing financial support of this project.

All my friends, Shaun Chen, and Angela Tzeng, especially for Ju-Fen Lin, for their help, encouragement, and moral support throughout this research study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The permeability coefficient, P, or simply the permeability is a useful quantity for describing the rate of mass transfer through a polymer membrane at steady state.

$$\frac{\Delta M_x}{\Delta t} = \frac{P\,A\,\Delta p_x}{L} \tag{1}$$

where $\frac{\Delta M_x}{\Delta t}$ is the rate that penetrant x permeates through a polymer film with a cross-sectional area A and a thickness L, with a partial pressure gradient of Δp_x. This expression accurately describes the transport process of a penetrant from the external environment into the contents of a package, or from the contents of a package into the external environment, and is applicable for small non-interactive molecules such as oxygen and carbon dioxide, as well as for larger organic penetrants such as flavor, aroma and solvent molecules.

Numerous literature references describe the diffusion of small molecules through polymer membranes, with data for oxygen, nitrogen, carbon dioxide, water and other small molecules being reported for commercial and experimental polymers. For these cases, the diffusion coefficients (D) and the permeability coefficients (P) are large enough that transmission rates can be determined within reasonable times. For example, oxygen permeability data is available for polymer films which spans the range from high oxygen barrier to poor oxygen barrier. However, studies which considered the permeation of interactive penetrants such as organic vapors are limited, with a paucity of data describing the diffusion of organic penetrants in high barrier glassy polymers. DeLassus (1993) proposed that the principal reason for the lack of such permeability data is the low diffusion coefficients associated with high barrier glassy polymer/organic penetrant systems. For these systems, the experimental times are very long. This is illustrated in Equation (2);

$$t_{ss} = \frac{L^2}{4D} \tag{2}$$

where t_{ss} is the approximate time needed to attain the steady state transmission rate for a film of thickness L, with a diffusion coefficient D. As indicated by DeLassus (1993), when t_{ss} is less than the time of contact between film and environment, steady state conditions exist and Equation (1) is applicable. For high barrier membranes, with organic penetrants, t_{ss} can be much greater than any reasonable contact time.

Furthermore, given a low diffusion coefficient, the permeability coefficient is likely to be small as well. This can, therefore, result in transmission rates that are difficult to detect and quantify.

Berens and Hopfenberg (1982) have studied the diffusion and sorption of organic vapors at low concentration in several glassy polymers. The use of fine powdered samples by these investigators offered significant advantages in their studies of transport in glass polymers, since for powder samples, diffusion paths may be reduced by orders of magnitude below the practical limit of film thickness. In contrast, inconveniently long test times were experienced if films were used.

DeLassus (1993) described the results of permeability studies carried out with thin polystyrene, polyethylene terephthalate (PET) and Nylon 6 films, at low activities of organic penetrants. Analytical techniques based on photoionization and atmospheric pressure ionization mass spectroscopy were employed to monitor the rates of transmission (DeLassus et al., 1988; Tou et al., 1990). DeLassus (1993) reported no measurable permeation in any case, although elevated temperatures were used and experimental times ran to 16 hours.

The barrier properties of polymers are often of major importance in packaging design and selection. However, permeability data for organic vapors such as flavor, aroma and solvent molecules is not readily available and, as shown by DeLassus, for high barrier glassy polymers can not be determined by methodology currently available.

Product shelf life is affected by product characteristics, the environment to which the product/package system is exposed and the barrier properties of the packaging material. Knowledge of the barrier properties of polymer membranes can therefore be of major importance in the design and selection of a package system. Permeability data for organic vapors such as flavor, aroma and solvent molecules is however, not readily available and for high barrier polymers can not be readily determined by present techniques.

The specific objective of this present study is to use a dynamic purge and trap/thermal desorption technique as a means of attaining the analytical sensitivity necessary to monitor mass transfer rates for organic penetrants through high barrier polymer membranes.

LITERATURE REVIEW

The Importance of Studying The Permeation Behavior of Organic Vapors

The protection of food products from gas and vapor exchange with the environment primarily depends on the integrity of the package (including seals and closures), and on the permeability of the packaging materials themselves. The permeability of packaging materials to organic vapors is one of considerable interest, particularly when the package contents have to be protected against contamination from foreign odors, or where there is a requirement to insure that no loss of volatile flavoring compounds from the package occurs. The significant off-flavors found in some food products may result from the packaging material itself, or may be the result of permeation through the packaging materials from the outside environment. On the other hand, foods may contain highly desirable, but volatile organic compounds (i.e. flavor or aroma), whose loss from the packaged food would seriously destroy its quality (Robertson, 1993).

The mass transfer of flavor and aroma components from food products is an area of great concern in food packaging. Flavor and aroma molecules are present in extremely small quantities. They are, however, commonly responsible for the unique flavor or aroma of a particular food, and small losses can often cause a dramatic change in taste. Flavor degeneration of foods can result from migration or permeation of flavor, aroma or solvent molecules (Franz, 1993). Therefore, the permeation of these volatile organic compounds through packaging materials can alter the composition of aroma and flavor volatiles of foods, and thus decrease the quality of food by altering its aroma profile (Koszinowski and Piringer, 1986).

Because of the widespread use of polymeric films and rigid plastics for food packaging, the permeation and mass transport behavior of organic vapors in polymeric packaging materials has become increasingly important in recent years. Polymeric materials provide many advantages which include light weight, low cost, and microwavability, etc. However, they also present some disadvantages such as "flavor scalping" - the transport of flavor or aroma components from the food into the package, and "off-taste" - the transport of flavor and aroma components from the polymer or the outside environment to the food product (Apostolopoulos and Winters, 1991). Therefore, the organic vapor permeability characteristics of polymeric packaging materials are extremely important.

The industry has generally used the oxygen permeability values of a polymer film as a indicator of its organic vapor transmission properties. It was believed that if a polymeric membrane possessed a good oxygen barrier it would also possess a good organic vapor barrier (Hilton and Nee, 1978). As a matter of fact, this is not necessary true (Hagenbaugh, 1987). The transmission of organic vapors would be affected by several variables such as the composition of the polymer, the solubility of the organic molecules in the polymer, and the potential interaction between the polymers and the organic vapor components (Hilton and Nee, 1978). Therefore, further studies of the permeation of organic vapors through polymeric films are necessary.

A knowledge of the permeability parameters for organic vapors through polymeric packaging materials is extremely important for understanding packaging performance. It is necessary for the successful design of packaging to prevent product deterioration during distribution and storage time.

Permeation Mechanism of Organic Vapors through Polymeric Films

Permeability is often referred to as the ease of transmission of the penetrants (i.e. gases, vapors or liquids) though a resisting material which is in the absence of pinholes, cracks, or other flaws (Hilton and Nee, 1978). The transmission mechanism of gases or vapors through polymeric membranes commonly used for packaging is typically of the activated diffusion (or solution-diffusion) type (Rogers, 1964). This transport process can be described as a three-step event (DeLassus, 1985):

(1) Absorption - a gas or vapor dissolves into the polymer matrix at the high penetrant concentration surface.

(2) Diffusion - the permeant diffuses through the polymer bulk phase under a concentration gradient (or partial pressure).

(3) Desorption - the desorption or evaporation of the permeant from the lower concentration surface of the polymeric membrane.

In general, when one side of a polymeric membrane is exposed to a gas or vapor under a certain partial pressure, the first and the last steps of the transmission process (solution and evaporation) will proceed at a much faster rate than the diffusion step. Therefore, the rate of diffusion controls the penetrant flux or permeation through a polymeric membrane (Talwar, 1974).

The permeation of a gas or vapor through a polymeric material is usually described by the permeability coefficient (or permeability constant), P. It can be quantified from a knowledge of the diffusion and solubility coefficients. Equation (3) is used to express the permeation process:

$$P = D \times S \tag{3}$$

where P is a measurement of the steady state transmission rate, D is the diffusion coefficient, and S is the solubility coefficient. It is important to note that the permeability coefficient is always a function of both the diffusion coefficient and the solubility coefficient (Crank, 1968).

The diffusion coefficient (D) is a kinetic parameter, and is a measurement of how fast the transport process will occur. It indicates the ease with which a penetrant molecule moves within the polymer matrix. More specifically, it provides the time required to reach the steady state condition and allows for estimation of the effective depth of penetration of a permeant into the polymer, as a function of time.

The solubility coefficient (S) is a thermodynamic parameter, it is a measurement of the concentration of penetrant molecules sorbed in the polymer matrix. The solubility coefficient is an equilibrium partition coefficient for distribution of the penetrant between polymer matrix and vapor phase.

A polymer is a randomly arranged mass of macromolecular chains which consist of a network containing voids or "holes". The diffusion process is the result of polymer molecules having a kinetic agitation or thermal motion. Above the glass transition temperature (T_g), the holes will be constantly disappearing and re-forming in the polymer matrix as a result of thermal motion. The diffusion process takes place by the movement of diffusing molecules through these connecting holes. A penetrant molecule dissolved in a polymer film may move or "jump" from one microvoid to an adjacent one, if the motion of the macromolecular segments create a vacant space which is large enough to accommodate the diffusing molecule. These jumps by penetrant molecules are random, and thus it is possible to occur in any direction. However, under a concentration gradient or partial pressure gradient, there are many more penetrant molecules jumping from the higher to the lower concentration or partial pressure side. Therefore, a net penetrant flux in the direction of decreasing concentration or partial pressure is observed (Hilton and Nee, 1978; Baner, 1987).

In terms of the above mechanism, the rate of diffusion depends on the number and size of pre-existing holes and the ease of hole formation. The number and size of pre-existing holes is related the polymer free volume and density. The ease of hole formation refers to chain segmental mobility and depends on the chain stiffness and the cohesive energy of the polymer (Talwar, 1974). The factors involved in the rate of diffusion include size of the vapor molecules, relative structure of the vapor molecule and monomer of the polymer, thickness or density of the membrane, concentration gradient of the vapor molecule, and also the temperature and relative humidity of the environment. Any structural modifications of the polymer such as density changes, degree of crystallinity, orientation, and cross-linking, as well as additives such as plasticizers and fillers, etc., will also greatly affect the rate of diffusion (Paine, 1992).

In many food packaging applications, the transmission rate of organic compounds such as aroma, flavors and solvents through polymeric materials is of considerable interest. The permeation of organic vapors through polymer films is much more complicated than that of simple gases (i.e. oxygen, nitrogen, carbon dioxide) due to the pressure-dependent solubility coefficient and the concentration-dependent diffusion coefficient (Meares, 1965a).

Non-interactive molecules such as oxygen, nitrogen, and carbon dioxide have almost no effect on the polymer morphology, while sorbed into the polymer matrix. Several investigations have shown that the diffusion of simple gases obeys Henry's Law, with a diffusion coefficient independent of concentration (Barrer, 1939; Reitinger, 1944).

In contrast, organic vapor molecules, which are comparable in size and chemical structure with the monomer units of polymer chains, diffuse by a more complicated mechanism, which is dependent on the motions of both the polymer and the penetrant molecules (Meares, 1965a). The diffusion of organic vapors requires a co-operative motion of several continuing monomer units of the polymer to take place. This indicates that the rate of diffusion of organic vapors in a polymer is governed by the mobility of the polymer segmental unit. On the other hand, the sorbed vapor molecules may swell the polymer matrix, thus acting like a plasticizer to increase the free volume available to chain segments and to lower the glass transition temperature. Then, as a result, the jumping frequency of penetrant molecules would be increased. Since the diffusion rate depends on the frequency of molecular jumping, it will increase as the concentration of vapor in the polymer increases. Furthermore, the swelling of the polymer matrix could set up internal stresses within the polymer chains resulting in conformational changes. These conformational changes may not be instantaneous, but are controlled by the retardation time of the polymer chains. If the retardation times are long, stresses may be set up which relax slowly. Thereby, the diffusion of organic vapors can become not only a concentration-dependent process, but also a time-dependent process (Crank, 1968; Meares, 1965b).

It is well known, that the diffusion process of organic vapors in polymers exhibits different features in the regions above and below the glass transition temperature, T_g, of a given polymer (Crank and Park, 1968; Meares,1965b). The process is rather simple at temperatures above T_g and extremely complex at temperatures below T_g. At temperatures well above T_g, the segmental motion of polymer molecules is active enough to reach equilibrium very rapidly, compared with the rate of diffusion. In this case, the time-dependence of the diffusion process associated with conformational changes of the polymer chain segments should disappear. As a result, at temperatures well above T_g, the diffusion coefficient of a polymer/organic vapor system becomes dependent only on the penetrant concentration. The permeation behavior of organic vapors through polymers at temperatures below the T_g, and sometimes above but within about 10°C of T_g, is anomalous and more complex and has been refered to as Non-Fickian diffusion (Fujita, 1961).

Permeability Theory

The general theory of permeation has been illustrated by many investigators (Rogers, 1964; Crank and Park, 1968; Comyn, 1985). Under the steady state condition, a gas or vapor diffuses through a polymer at a constant rate, if a constant concentration or partial pressure difference is maintained across the polymer. The diffusion flux or flow (transmission rate), F, of a permeant through a polymer is defined as the amount of permeant passing through a plane of unit area normal to the direction of diffusing flow during unit time, i.e.:

$$F = Q \ / \ A \cdot t \tag{4}$$

where Q is the total amount of permeant which has passed through area A during time t.

The mathematical theory of diffusion was first proposed by Fick (Barrar, 1951). It is based on the hypothesis that the rate of transfer of a diffusing substance through a unit area of section is directly proportional to the concentration gradient measured normal to the section. This can be expressed by Fick's first law of diffusion:

$$F = -D\frac{dc}{dx} \tag{5}$$

where c is the concentration of the permeant, D is defined as the diffusion coefficient with the unit of (length)^2(time)$^{-1}$, x is the depth variable measured normal to the direction of permeation, and dc/dx is the concentration gradient of the permeant across a thickness dx. This law can only be applied to the diffusion in the steady state, that is, where concentration is not varying with time (Crank and Park, 1968).

Steady State Permeation

Consider a polymeric material of area A, having a thickness of L, exposed to a permeant. The surfaces of the polymer, x=0, x=L, are maintained at constant concentrations c_1, and c_2, respectively. When the steady state rate of diffusion has been reached, there exists a situation in which the penetrant concentration is independent of time at all points within the polymer, where F is constant and Eq.(5) can be integrated across the total thickness of the polymer L, and between the two concentrations, assuming D to be constant and independent of c:

$$F = \frac{D(c_1 - c_2)}{L} \tag{6}$$

If the thickness L, and the surface concentrations c_1 and c_2 are known, D can be clearly obtained from a single observation of the diffusive flux, F. The above expression can also be rewritten by substituting for F using Eq.(4). This enables calculation of the quantity of permeant diffusing through a polymer of area A in time t:

$$Q = \frac{D\,(c_1 - c_2)\,A\,t}{L} \qquad (7)$$

In some systems, in which the permeant is a gas or vapor, the surface concentrations may not be known, but only the gas or vapor pressures p_1 on one side of the polymer and a lower vapor pressure p_2 on the other side are given. In these cases, the concentration of the permeant in the polymer, c, can be expressed by Henry's law:

$$c = S \cdot p \qquad (8)$$

where S is the solubility coefficient of the permeant in the polymer and p is the partial pressure of gas or vapor. By combining Eqs.(7) and (8) gives:

$$Q = \frac{D\,S\,(p_1 - p_2)\,A\,t}{L} \qquad (9)$$

The product $D \cdot S$ is defined as the permeability coefficient or permeability constant, P (Barrer, 1939). Thus:

$$P = \frac{Q\,L}{A\,t\,(p_1 - p_2)} \qquad (10)$$

or

$$\frac{P}{L} = \frac{Q}{t\,A\,\Delta p} \qquad (11)$$

The term P/L is called the permeability or permeance.

There are four assumptions required for the above simple treatment of permeation:

(1) diffusion is in a steady state condition

(2) the concentration-distance relationship through the polymer is linear

(3) diffusion takes place in only one direction

(4) both D and S are independent of the permeant concentration.

When both D and S are independent of the permeant concentration, P is a constant at any given temperature. However, when interaction between the polymer chains and the penetrant molecules is considered, P is no longer constant but will vary with c and Δp (Zobel, 1982). In this case, the transmission process is anomalous and is referred to as non-Fickian (Fujita, 1961).

Non-Steady State Permeation

When a penetrant permeates through a polymeric membrane, there is an interval from the time the penetrant first enters the membrane until the steady state of flow is established. The situation which exists during this period is illustrated by Fick's second law:

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{12}$$

There are a number of solutions to this equation which have been derived for various boundary conditions (Crank, 1975).

If a polymer film separates two test chambers which contain a gas or vapor at different partial pressures, then the gas will permeate from the high pressure chamber to the low pressure chamber in which the pressure change is then measured as a function of time. Generally, the low pressure chamber is initially free of permeant. This type of experiment, called the pressure differential method, can describe the difference between steady state and non-steady state diffusion, and it is also the basis of the time-lag method for the determination of the diffusion coefficient (Comyn, 1985).

Based on this type of experiment, a particular solution of Eq. (12) was derived by Daynes and Barrer (Paine, 1992). The test system is initially free from permeant at zero time, and then a gas at pressure p_1 is introduced into chamber 1, giving a concentration c_1 on the face of the film adjacent to chamber 1. The amount of permeant passing through the film, Q, in time t is then given by:

$$\frac{Q}{Lc_1} = \frac{Dt}{L^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-Dn^2\pi^2 t / L^2\right) \qquad (13)$$

There is an assumption in this case that equilibrium is instantaneously established at the interface. A plot of Q versus t is shown in Figure 1. It can be seen that there is an initial build-up or non-steady state period, then the amount of gas or vapor permeating through the polymer will eventually increase linearly with time. As $t \to \infty$, the steady state permeation rate is achieved, and Eq.(13) can be simplified to express the linear relationship between Q and t as the following:

$$Q = \frac{Dc_1}{L}\left[t - \frac{L^2}{6D}\right] \qquad (14)$$

If the linear portion of the steady state line is extrapolated backwards to the time axis, an intercept $t = \theta$ will be obtained, where $Q = 0$, and then Eq.(12) reduces to:

$$\theta = \frac{L^2}{6D} \tag{15}$$

The value θ is called the lag time and it is the intercept on the time axis of the extrapolated steady state portion of the permeation curve (see Figure 1).

This time-lag method provides an experimental basis for determining the diffusion coefficient D. Thus, all three parameters of interest can be calculated from a single experiment. The permeability coefficient, P, is provided by calculating the steady state permeation rate, Q/t, and substituting in Eq.(10). The diffusion coefficient is obtained from the lag time θ (Eq.(15)). Once these parameters are determined, the solubility coefficient, S, can be calculated as P/D. This general method for the estimation of D and S is very convenient and is capable of giving accurate results with various penetrant/barrier systems (Crank and Park, 1968; Meares, 1958).

There is another type of experiment that can be used for describing the non-steady state diffusion. Pasternak, et al, (1970) described a dynamic approach to investigate the permeation mechanism. A flow system in which both sides of the membrane are at atmospheric pressure is employed, the permeant is introduced into one side of the membrane, and permeation rates through the membrane are measured continuously. A typical transmission rate profile curve obtained by this procedure is presented in Figure 2.

A solution of Eq.(5) was presented by Pasternak, et al. (1970) and is given as a first approximation in Eq. (16).

$$\frac{\left(\frac{\Delta M}{\Delta t}\right)_t}{\left(\frac{\Delta M}{\Delta t}\right)_\infty} = \left(\frac{4}{\sqrt{\pi}}\right)\left(\frac{L^2}{4Dt}\right)^{1/2} \exp\left(\frac{-L^2}{4Dt}\right) \tag{16}$$

where $(\Delta M/\Delta t)_t$ and $(\Delta M/\Delta t)_\infty$ are the transmission rates of the penetrant at time t and at steady state, respectively.

For each value of $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_\infty$, a value of $(L^2/4Dt)$ can be calculated. And by plotting $(4Dt/L^2)$ as a function of time, a straight line is obtained. From the slope of the straight line, D is calculated by substitution in Eq.(17).

$$D = \frac{(slope) \cdot L^2}{4} \tag{17}$$

From a different expression for $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_\infty$, Ziegel, et al. (1969) derived Eq. (18) to solve for D:

$$D = \frac{L^2}{7.199\ t_{0.5}} \tag{18}$$

where $t_{0.5}$ is the time required to reach a rate of transmission $(\Delta M/\Delta t)_t$ equal to half the steady state $(\Delta M/\Delta t)_\infty$ value.

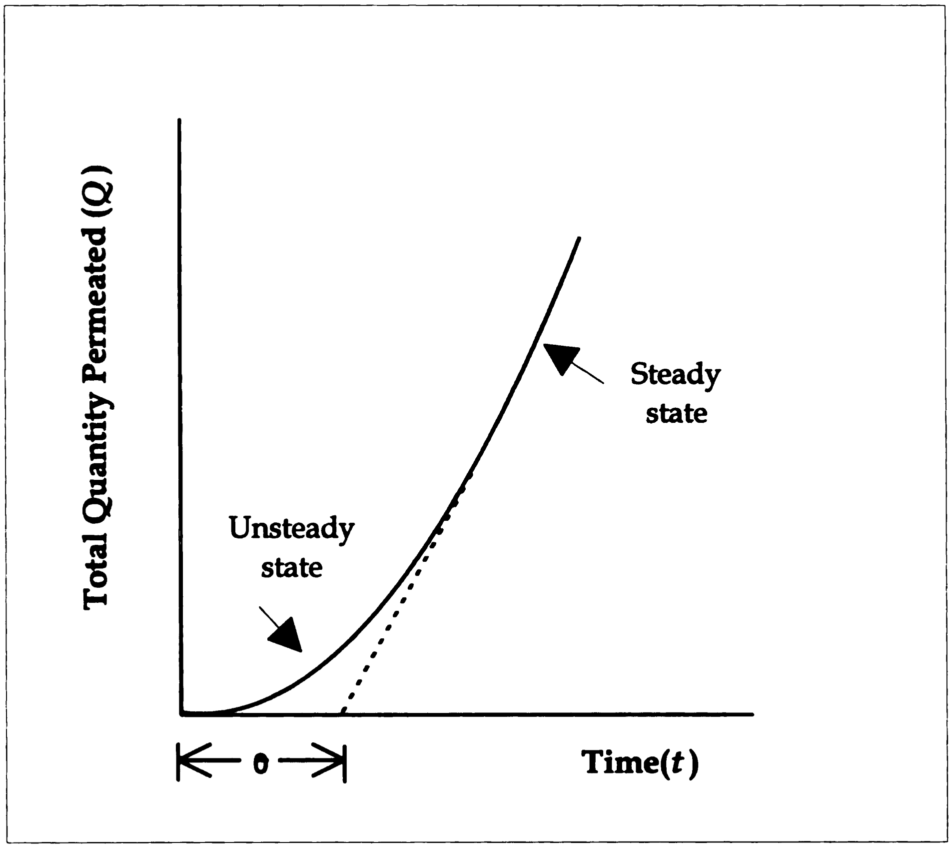


Figure 1. Typical permeation and time lag curve

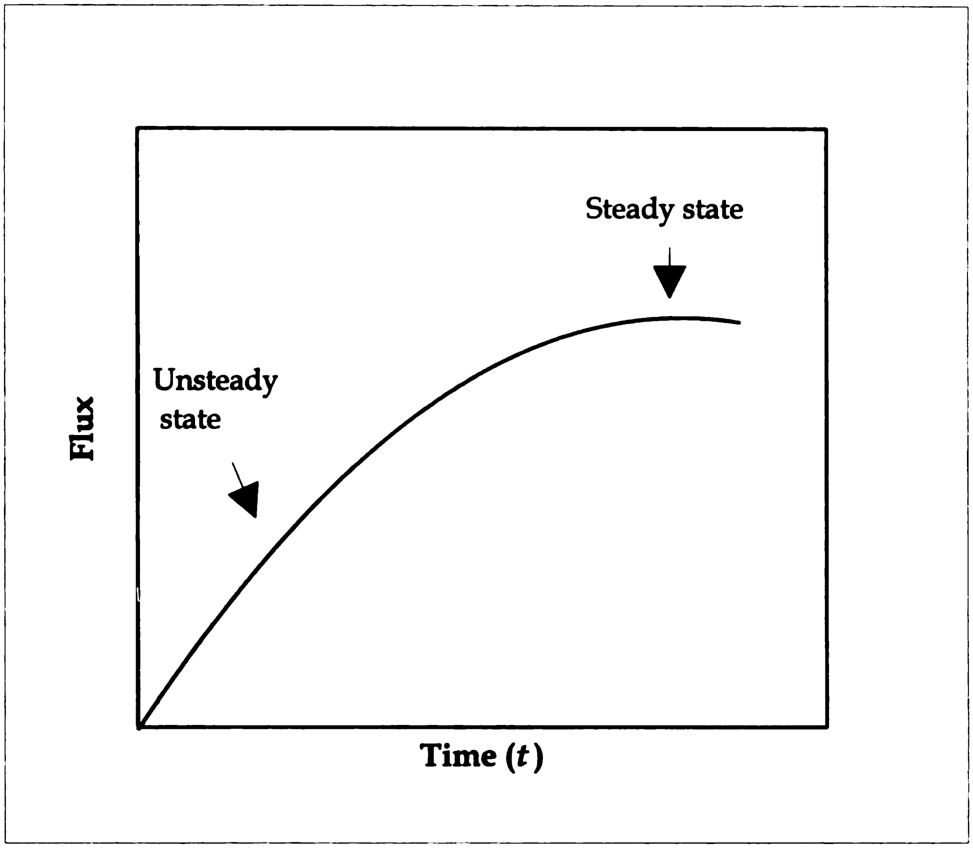


Figure 2. Typical transmission rate profile

Organic Vapor Permeation Measurement Techniques

There are no standard test methods for the measurement of organic vapor permeability, and a number of methods and test equipment have been described in the literature, for evaluating the gas or vapor permeability of organic penetrants (Paine, 1992; Robertson, 1993). However, there is a very limited number of commercial instruments available for measuring organic vapor permeability. Most researchers used a permeation test system of their own design. The various procedures developed for quantifying the rate of diffusion of organic penetrants through polymeric membranes have been described by Hernandez, et al. (1986). In general, there are four common techniques which have been used for evaluating the permeation rate of organic vapors through polymer films: (1) absolute pressure method; (2) gravimetric technique; (3) pouch method; and (4) isostatic or quasi-isostatic methods. Although a variety of test methods are available, the basic principle employed is similar. Basically, the test film is mounted in a hermetic environment between two test cell chambers; the permeant to be tested is isolated on one side of the test film and then detected on the other side as a function of time. Using these data, the transmission rate and the permeability coefficient can be calculated. The detection of the permeant is accomplished by monitoring pressure, volume, or mass increases, using appropriate techniques such as mass spectrometry or gas chromatography.

Absolute Pressure Method

A number of theoretical studies of permeation and diffusion of organic vapors through polymers before 1970 were carried out by the absolute pressure method (Rogers, 1964). In this method, the sample film is clamped between two cell chambers, a high pressure one and a low pressure one. A manometric or volumetric technique was then used to measure the permeated gas or vapor. Steady state permeation rate is attained when there is a constant increase in pressure or volume with time in the low pressure chamber. Several modifications of this method have been described by Rogers et al. (1956), Meares (1958), and Stannett et al. (1972). The standard procedure and equipment for determining the gas transmission rate and permeability of plastic films is described under ASTM (American Society for Testing and Materials) D-1434. This is a pressure differential method in which the pressure on one side of the film remains much larger than that on the other side (about one atmosphere difference in total pressure across the film), so the pressure difference remains essentially constant. The gas transmission rate is determined at steady state from the measurement of pressure change using the manometric technique.

The absolute pressure method has the following limitations in application: (1) permeability study can not be done at different relative humidities; (2) due to the high pressure differential, certain rigid support of the film is required; (3) it is not suitable for measuring organic vapor permeation; (4) co-permeants can not be used (Rogers, 1964; Talwar, 1974; Baner, 1987).

Gravimetric Technique

The gravimetric technique measures the permeating gas by the weight gain or loss. Lebovits (1966) used a shallow dish containing liquid penetrant with the film sealed over the top and measured the weight loss of the permeant. Laine and Osburn (1971) suspended an adsorbent-filled polymer pouch in a chamber containing the permeant vapor and measured the weight gain versus time. In these two experiments, the steady state permeation rate is attained when a constant weight gain or loss was observed. This method avoids the use of film supports, but involves difficulties with total pressure differentials due to the sealed cups (David, 1946). More recently, an electrobalance method has been used to measure the sorption and diffusion of organic vapors by polymer (Berens, 1977; Berens and Hopfenberg, 1982; Choy et al., 1984). The experiments are usually carried out at equilibrium vapor pressure, using an electrobalance which records continually the gain or loss of weight by a test specimen as a function of time. The disadvantages of these methods are: (1) only a limited vapor pressure range can be used; (2) lack of sensitivity; and (3) the inability to evaluate the permeation of co-permeants.

Pouch Method

A pouch method was developed by Becker et al. (1983) and Koszinowski and Piringer (1986). The principle of this procedure, which applies to solvent contact with the test film, is as follows: a solution of the permeant is poured into a polymer pouch, which, after heat-sealing, is dipped into a bath of the pure solvent. Then samples of this solvent bath are taken over time and analyzed by gas chromatography. This method can be applied to low concentration permeants and can measure several permeants simultaneously. The drawbacks of this method are that the test film must be sealable and the solvent must not be compatible with the test film in order to avoid swelling of the polymer. The performance of this method will depend upon film seal integrity.

Recently, the isostatic and quasi-isostatic methods were developed to study the permeation and diffusion of organic vapors through polymer membranes and have become very popular. Most of the problems associated with the above techniques can be prevented by the application of these two methods.

Isostatic Method

For the isostatic method, the total gas pressures on two sides of the test film are essentially equal, while maintaining the partial pressure differential of the test vapor across the film, at whatever level may be required. Because the total pressure on each side of the film is equal, there is no need for a rigid support of the test film and thus avoids excessive stress or compression of the test sheets. Furthermore, the condition of different partial pressures and equal total pressure on the two sides of the test film represents the usual conditions which are encountered with flexible film packages, except where vacuum packaging is used. The partial pressure difference is maintained by continuously sweeping the desired permeant concentration in an inert carrier gas stream over one side of the film, and maintaining the carrier gas flow on the other side concurrently. Thereby, the permeated vapor can be conveyed by the carrier gas stream to an appropriate detection system for quantification. The steady state permeation rate is equal to the steady state concentration of permeant in the carrier gas stream times the flow rate of carrier gas. The isostatic procedure allows for the continuous monitoring of the transmission rate of organic vapors through test films from the initial time zero until steady state conditions. Furthermore, since the method of measuring the concentration of the permeated vapor can be specific to that vapor, even in the presence of other gases or vapors, equipment can be developed to control the relative humidity of the permeant vapor and carrier gas. Therefore, the study of permeability at different relative humidity levels can be achieved.

A number of isostatic permeation test systems, with various detection devices, have been reported to date. Davis (1946) described an isostatic system which employed chemical sorption methods for determining the amount of permeated gas at various temperatures and relative humidities. However, this system has a lack of sensitivity. Ziegel et al. (1969) and Pasternak et al. (1970) used a thermal conductivity detector to measure the permeation and diffusion of permeant gases. Yasuda et al. (1970) developed a method in which small thermistors were incorporated in the detection system. Both systems worked well for a wide temperature range and single permeants, but they can not be applied for studying co-permeants. Also, calibration of detector response for the specific permeant was complicated. Zobel (1982) introduced a more sophisticated instrument in which the permeated vapor was directly conveyed to a flame-ionization detector. However, the ultimate sensitivity is limited by the long-term drift of the signal baseline, since at low permeation levels it becomes more difficult to distinguish between a real increase in signal and baseline drift. However, this method is still incapable of measuring the permeation rates of mixed gases or vapors. In 1984, the same investigator reported a modification of this system, which incorporated an absorption/desorption cycle to increase the detection sensitivity. In the later study, in order to attain the flexibility of operation, a permeability cell in conjunction with a more sensitive detection system was developed. With such a system, the choice of permeant is unlimited; mixtures of permeants, and the effect of relative humidity, pressure and temperature can also be studied. Pye et al. (1976) utilized gas chromatographic analysis with a thermal conductivity detector to determine the permeability of mixed gases and vapors. Baner et al. (1984), Landois-Garza and Hotchkiss (1988), and Booma et al. (1993) used gas chromatography (GC) equipped with a flame ionization detector (FID) to determine the permeability of barrier membranes. Other techniques based on either a photoionization detector or atmospheric pressure ionization mass spectrometer were employed by Caldecourt and Tou (1985) and DeLassus (1985). Both of these two detection systems were found to be very sensitive and useful in the characterization of the permeability of barrier membranes. The photoionization detector is simple and inexpensive. However, it suffered from lack of specificity. Only single component permeants can be used, and it must be used dry. The atmospheric pressure ionization mass spectrometric technique is specific and sensitive, but is instrumentally complex and expensive. DeLassus et al. (1988a,b) and Tou et al. (1990) utilized an electron impact mass spectrometric technique to monitor the permeated vapors through respective test films. Temperatures up to 150°C and relative humidities from 0 to 100% are able to be used by this instrument; this makes it possible to obtain data on the permeation of polymeric materials used in retortable pouches. The system exhibited parts per billion sensitivity to organic vapors. Leufven and Stollman (1992) and Johansson and Leufven (1994) used an adsorbent material to collect permeated vapors and then thermal desorption to a GC/FID for quantification. This technique has been successful at very low levels of permeated vapor.

More recently, there are two commercial instruments available for performing organic vapor permeability measurements. One is the MAS 2000™ Organic Permeation Detection System (Testing Machines Inc., Amityville, NY) and the other is the MOCON's AROMATRAN Permeation Test System (Modern Controls Inc., Minneapolis, MN). Both systems are based on the isostatic procedure. The MAS 2000™ Organic Permeation Detection System incorporates a FID, which provides sensitivity levels in the low parts per billion region. This system allows rapid evaluation of the diffusion, solubility, and permeability coefficient of organic vapors through a packaging material. Huang (1996) has used this system to successfully determining the barrier properties of a series of commodity polymeric films. The MOCON's AROMATRAN system also incorporates a FID to allow the measurement of the permeation rate of aromas, flavors, and solvents through barrier films and packages. It can test both single and multiple permeants at different humidities.

Quasi-Isostatic Method

In a modification of the isostatic method, known as the "quasi-isostatic method", the low concentration chamber of permeation cells is initially filled with the carrier gas and completely closed. The permeated gas or vapor is then accumulated in the lower concentration cell chamber and monitored at predetermined time intervals, typically by gas chromatography.

Hilton and Nee (1978) developed an accumulation or quasi-isostatic test system for determining the permeability of organic vapors through packaging films. Murray (1983, 1985), Hatzidimitriu et al. (1987), and Theodorou and Paik (1991) expanded and modified test apparatus employing this quasi-isostatic procedure to study the transport behavior of organic vapors through polymer membranes. These studies, however, were limited to only saturated solvent vapors of liquid penetrants at a given temperature. Although this data is useful in estimating how well a packaging material will withstand accidental high-level contamination, it is not suitable to estimate permeability at much lower vapor concentrations encountered in typical retailing situations. Recently, in order to study the concentration dependence of permeation, many investigators (Gilbert et al., 1983; Hatzidimitriu et al., 1987; Mohney et al., 1988; Apostolopoulos and Winters, 1991; Sajiki, 1993) employed a more sophisticated apparatus, which involved flushing a carrier gas through volatile permeant, to allow measurement of permeation for organic vapors at any desired low concentration level. These methods can establish a constant and highly variable feed concentration of permeants and numerous compounds can be monitored simultaneously. An apparatus that could permit permeability measurements to be made at low vapor levels was described by Franz (1993). It is a variation of the quasi-isostatic procedure for evaluating high barrier film properties at low permeant vapor pressures. An adsorption trap and solvent desorption techniques were incorporated with gas chromatographic analysis. The applicability and high sensitivity of this technique was demonstrated. However, the procedure is very complicated and time-consuming. Since many new polymeric structures with improved high barrier properties have been increasely used, better techniques with very sensitive detectability are required to understand their permeation properties.

In addition to the permeation methods described above, the transfer of organic vapor molecules through polymers can also be evaluated by sorption-desorption methods (Fujita, 1961; Bischoff et al., 1984; Choy et al., 1984; Berens, 1978; Thalmann, 1990; Nielsen et al., 1992).

Technique for Trapping Volatile Compounds

Numerous analytical techniques for the quantitation, collection and identification of volatile organic compounds have been employed to date. Generally, there are three major techniques that are commonly used: distillation/extraction methods, direct (or static) headspace technique, and the dynamic headspace (or purge and trap) technique (Sugisawa, 1981; Risch, 1989). Dynamic headspace/gas chromatography has been recognized as one of the most powerful and sensitive analytical techniques for analyzing a wide range of volatile organic compounds. It is the most suitable technique for the analysis of trace flavor or aroma compounds (Krzymien and Elias, 1990; Vallejo-Cordoba, 1993).

Direct Headspace Technique

Direct headspace sampling has been widely used. Several investigators confirmed the validity of this technique as a reliable means of quantifying volatile components which contribute to food flavor, and their application to product quality and shelf life (Dupuy et al., 1973; Alberola and Izquierdo, 1976). This is the simplest, fastest and one of the most precise techniques for analyzing volatile compounds. This technique is based on an equilibrium distribution of volatiles between the sample and gas phase in a closed and thermosetted vessel

(Kolb, 1984). The "headspace" was defined by Wyllie (1978) as the gaseous mixture surrounding a sample within a closed system at equilibrium. In the closed system, the headspace gas is withdrawn using a gas-tight syringe, and then is directly injected into the gas chromatograph (GC) or gas chromatograph/mass spectrometer (GC/MS) for analysis.

Despite the advantage of no loss of volatiles due to handling and wide spread acceptance, this method has many shortcomings as a result of the relatively low analytical sensitivity. In many instances, the concentration of volatile constituents which occurs in the headspace is too low for direct headspace analysis (Murray, 1977; Buckholz et al., 1980), and a large volume of headspace gas is required for detection. However, direct injection of a large volume of gas can result in band broading and poor resolution. Application of this method is limited to the situation in which the volatile partial pressure levels in the headspace are equal to concentrations above 10^{-7} g/L (Schaefer, 1981). Therefore, it can not provide adequate sensitivity for trace compound analysis. For these reasons, collection and concentration of sample substances is necessary to achieve the needed analytical sensitivity.

Several investigators have sought a means of enriching the headspace sample prior to its introduction into the GC. Such techniques as cryogenic trapping and steam distillation-solvent extraction (Clark and Cronin, 1975; Hartman et al., 1993) have been described. The cryogenic trapping involves purging the sample compounds with an inert gas and condensing the sparged volatiles in a series of cold traps (usually fused silica capillaries) maintained at liquid nitrogen (or liquid carbon dioxide) temperatures before the chromatographic analysis. This methodology offered a great opportunity for the collection of all volatiles and contributed to a decrease of artifacts. However, there are some inherent problems related to this method, namely: (1) loss of volatiles during purging out the liquified sample; (2) the presence of condensed water in traps limits the usefulness of this method. If sampling was continued for longer periods, crygenic trapping accumulated water in the trap, and the freezing water could act to block the trap. Therefore, sample purging might be limited to only 10-20 min, which results in the sensitivity to be limited as well (Talka, 1986; Linforth and Taylor, 1993; Ehret-Henry et al., 1994).

Dynamic Purge and Trap Technique

There are other alternate methods for enriching headspace volatiles which have grown in popularity. They are commonly termed the dynamic purge and trap technique. This technique involves the use of adsorbents to concentrate headspace volatiles. In this method, the sample is continuously purged with an purified inert carrier gas such as nitrogen or helium, which strips volatile constituents from the sample, and is then sorbed onto adsorbent traps. The vapors concentrated in the adsorbent trap are subsequently recovered by a desorption system and transferred into a GC or GC/MS for analysis. This technique provides greatly increased analytical sensitivity. Normally, it can provide a sensitivity ten times greater than the sensitivity achieved by the static headspace technique (Lin, 1995).

The sample recovery from the trap can be achieved by either solvent desorption or thermal desorption. The latter one is termed the purge and trap/thermal desorption (P&T-TD) technique. It has been accepted widely in the research area of food, beverage, packaging and environment (Wyllie et al., 1978, Buckholz et al., 1980; Soderhjelm and Eskelinen, 1985; Krzymien and Elias, 1990). Most of the pioneering researchers using this method utilized custom-made trapping and desorbing apparatus, which were not readily available to interested researchers. Since then, commercial P&T-TD instruments have been provided, and many of them were reviewed by Ioffe and Vitenberg (1984) and Bicchi and Joulain (1990). The thermal desorption procedure offers several advantages over the solvent desorption procedure, which include: (1) higher sampling flexibility; (2) higher overall sensitivity; (3) more homogeneous behavior to different substances; (4) absence of the solvent peak; and (5) reduced solvent usage and waste generation (Bruner et al., 1978; McCaffrey, 1994).

The most common adsorbents that have been used include: activated carbon, charcoal, silica gel, porous polymers (i.e. Tenax, Porapaks, Chromsorbs), and Carbotrap, etc. Among these, Tenax is probably the most popular one.

Research into improved adsorbents is the subject of ongoing studies, and the carbon-based materials have received much attention and are referred to as possible alternates to Tenax (Bruner et al., 1978; Mangani et al., 1982).

The choice of adsorbents is one of the most critical aspects of dynamic headspace sampling, which governs the range of volatile compounds that can be effectively trapped. Ideally, the adsorbent should retain sample compounds during the entire sampling period, and release them completely during the desorption period. In addition, an ideal adsorbent should be so hydrophobic that it will not adsorb water during the purging step and thus interfere with the gas chromatographic analysis. Furthermore, adsorbents with the highest surface area will tend to have the highest sampling capacities. Adsorbents should be chosen on the basis of their selective adsorption characteristics. However, no single adsorbent polymer will be capable of trapping and efficiently releasing all compounds. Thus, the adsorbent must be chosen to fit a particular problem (Buckholz et al., 1980). Usually, an ideal adsorbent trap may be a mixed bed design with any number of combinations of different adsorbents. The multi-bed adsorbent trap allows for analysis of a wider range of compounds in a single sampling (Supelco, 1995). The evaluation of different adsorbents with regard to trapping efficiencies has been carried out by Jenning et al. (1972) and McCaffrey and MacLachlan (1994).

Withycombe et al., (1978) indicated that the sampling capacity depended on the nature of adsorbants, as well as on the sorbates. The adsorption capacity of an adsorbent towards a given compound is described by the breakthrough volume (BTV). It represents the gas (i.e. air) volume passing through the trap, above which a given compound is no longer totally trapped. The larger the value, the better the adsorbate was retained. The BTV depends on numerous factors, such as temperature, concentration of sample compounds, chemical composition of the gaseous mixture, relative humidity, the flow rate of carrier gas, dimensions of the trap, and pore diameter and specific surface area of the adsorbent (Simon et al., 1995; Krzymien and Elias, 1990). Among these factors, the adsorption temperature and the concentration of the sample compound are the major critical parameters affecting the BTV value. A safe sampling volume has been suggested to be two thirds of the BTV.

Generally, most adsorbents begin to efficiently trap most classes of volatile organic compounds when their carbon skeletons are above C-3. Activated carbon traps have a strong affinity and high capacity for most aroma constituents. The pore diameter and particle size distribution of activated carbon significantly affects the breakthrough volumes of analities. The ones with smaller particles and pores are more efficient for trapping highly volatile low molecular weight hydrocarbons such as C2 - C4 species. Silica gel has been used to trap low molecular weight polar compounds. However, it has the disadvantage of trapping water (Hartman et al., 1993; Supelco, 1990). Charcoal offers some advantages in that it has absolute thermal and chemical stability, and is not deactivated by water. However, incomplete recoveries and artifact formation in adsorbed samples are the reasons for its limited use (Clark and Cronin, 1975).

Tenax is a porous polymer based on *p*-2,6-diphenylene oxide. It has been a very popular adsorbent for aroma/flavor trapping (Bruner et al., 1978; Galt, 1984; Olafsdottir et al., 1985). In many comparative studies, Tenax was reported to give the best overall trapping efficiency (Withcombe et al., 1978; Vallejo-Cordoba and Nakai, 1993; Linforth and Taylor, 1993). Tenax provides several advantages. It has a very high affinity for organic compounds and is relatively hydrophobic, which is important in view of the large volume of water vapor produced upon heating food products for aroma/flavor analysis. In addition, Tenax has good thermal stability. It can efficiently trap volatiles at room temperature but also permits efficient desorption of volatiles at temperatures that reach up to 375°C (Glat and MacLeod, 1984). It is also good for the collection of volatiles with higher molecular weight (Sugisawa, 1981; Hartman et al., 1993).

There are many investigators who have reported the use of Carbotrap as the adsorbent (Mangani and Mastrogiacomo, 1982; Connick et al., 1989; Krzymien and Elias, 1990). Carbotrap adsorbents are graphitized carbon blacks. Investigators at Supelco, Inc (Bellefonte, PA) found that Carbotrap can adsorb and release a much wider range of airborne organic compounds than other adsorbents such as Tenax. Carbotrap has no surface ions or active functional groups; therefore, the entire surface is available for interaction that depends solely on dispersion (London) forces. In contrast, the other widely used adsorbents such as Tenax have localized surface charges for specific adsorbent/adsorbate interactions. Carbotrap adsorbents are manufactured at temperatures above 2000°C; therefore, they can offer excellent thermal stability and are not susceptible to solvent degradation. Furthermore, Carbotrap adsorbents are more hydrophobic in nature, thus minimizing sample displacement by water, and allowing their performance to be unaffected by humidity. Bertoni et al. (1981) indicated that Carbotrap is particularly useful at room temperature for the evaluation of air pollution in the working place. The studies of the adsorptive capacity and effectiveness of release by Carbotrap has been carried out by Bruner et al. (1978), Mangani and Mastrogiacomo (1982), and Supelco Inc. (1988).

Porous polymer and carbon-type adsorbents have a low affinity for water vapor. However, problems could still occur if water condensation takes place while trapping (Vallejo-Cordoba and Nakai, 1993). The condensation of water vapor could block the pores of the adsorbent and inhibit the diffusion of volatile compounds into the resins, thereby decreasing the trapping efficiency. This problem can be solved by introducing a "bone dry" make-up gas line into the purge gas outlet directly before the adsorbent trap. The dry make-up gas serves to lower the relative humidity of the purge gas to a level that will not promote condensation (Hartman et al., 1993). Ehret-Henry et al. (1994) also used a water condenser before the purged gas is brought to the trap in order to remove water. However, volatiles might also be trapped on the condenser and excessive purging might result in loss of low-boiling compounds. The temperatural control could be critical in this case (Boyko et al., 1975).

There has been a recent innovation in dynamic headspace techniques, named Microwave Desorption Technique (Risch and Reineccius, 1989). This method involves trapping the purged volatiles onto a charcoal based trap and then desorbing the trapped volatiles by using microwave heating. Rapid desorption is the major advantage of this technique, where volatiles are normally desorbed in 4-5 seconds. It can also save time and decrease cost. The major disadvantages of this method are the concern of artifact formation on the charcoal based material and trap to trap reproducibility.

MATERIALS AND METHODS

Materials

Film Samples

Seven commercial high barrier film structures were evaluated in the present study. The barrier layers of these polymeric structures are based on Ethylene vinyl alcohol copolymer (EVOH), Nylon, and Silica deposited polyethylene terephthalate (SiO_xPET). The seven polymer structures evaluated included:

A. HDPE/tie/EVOH/EVOH/tie/HDPE - 2.0 mil

0.9 mil HDPE
0.7 mil tie
0.4 mil EVOH (DuPont BX228)

B. HDPE/tie/EVOH/ionomer - 2.3 mil

1.1 mil HDPE
0.2 mil tie
0.6 mil EVOH
0.4 mil ionomer

C. HDPE/tie/Nylon/Nylon/tie/HDPE - 2.9 mil

1.1 mil HDPE
0.9 mil tie
0.9 mil Nylon (Nylon 6,6/9 copolymer)

D. HDPE/Nylon/ionomer - 2.9 mil

2.2 mil HDPE
0.3 mil Nylon
0.4 mil ionomer

E. Acrylic Coated OPP - 1.7 mil

F. PP/SiO_xPET - 2.9 mil

G. PET/SiO_xPET/CPP - 3.4 mil

0.5 mil PET
0.5 mil SiO_xPET
2.4 mil CPP

where: HDPE = High density polyethylene
tie = Adhesive layer
PET = Polyethylene terephthalate
PP = polypropylene
CPP = Cast polypropylene

Film A, B, C, and D were obtained from Tredegar Film Products (Richmond, VA). The supplier of film E and F is Mobil Chemical Co. Film Division (Macedon, N.Y.) and Energy Conversion Devices, Inc. respectively. Film G was obtained from Toppan Printing Co., Ltd. (Tokyo, Japan).

Permeant

α-Pinene ([1s,5s]-2,6,6-trimethyl-bicyclo[3,1,1]hept-2-ene) was used as the permeant. Research grade α-pinene was obtained from SIGMA Chemical Co. (St. Louis, MO). α-Pinene is used in household pine oil cleaners that act as mild disinfectants. It was therefore selected to simulate supermarket storage conditions, where packaged foods might be affected by their proximity to non-food products such as household cleaners (Kontominas, 1985). The chemical structure of α-pinene is shown in Figure 3.

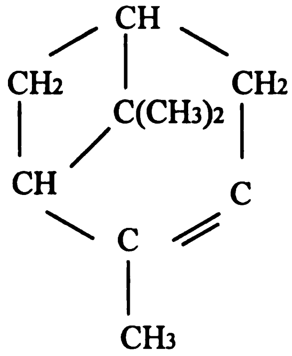


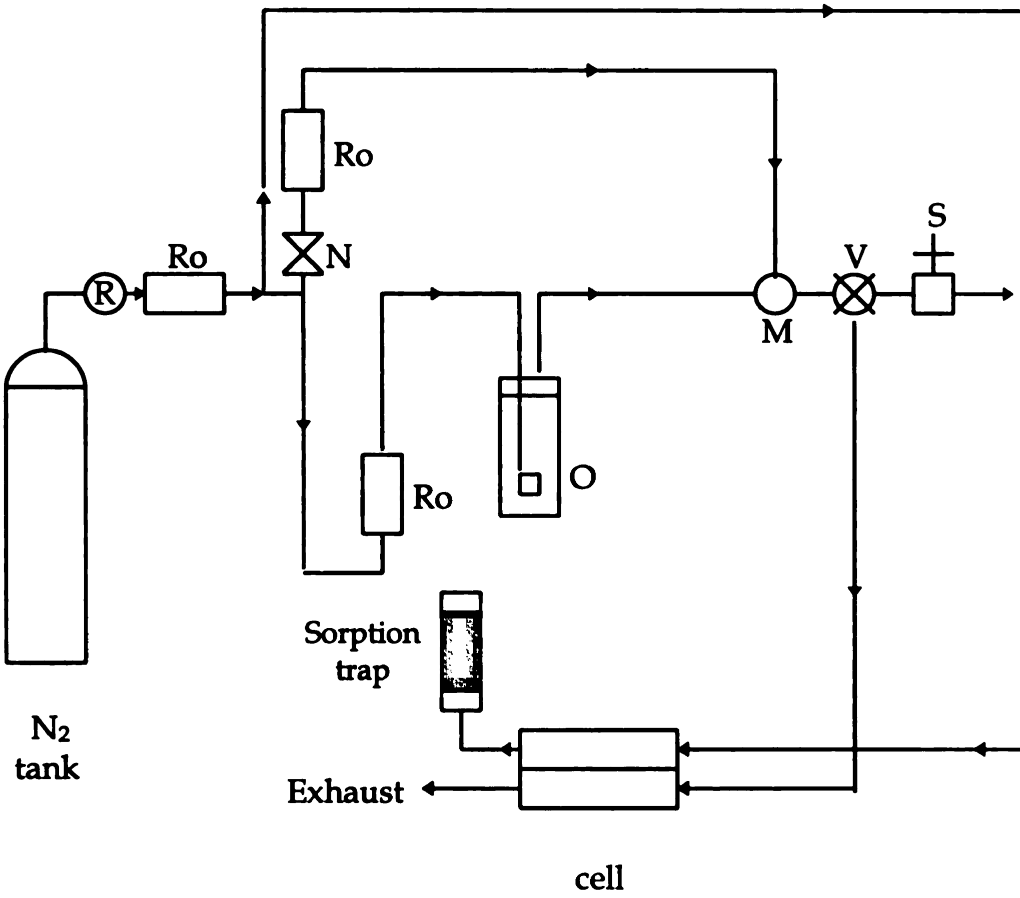
Figure 3. The chemical structure of α-Pinene

Methods

Permeation Test System

Permeability studies were carried out with a MAS 2000™ Organic Permeation Detection System (Testing Machines Inc., Amityville, NY), which was modified with a device for trapping permeated organic vapors employing a dynamic purge and trap technique. The trapping device was designed and fabricated by MAS Technologies, Inc. (Zumbrota, MN) in collaboration with the School of Packaging (Michigan State University, East Lansing, MI). The MAS 2000™ Organic Permeation Detection System is based on an isostatic permeation test procedure. This system allows for the continuous collection and measurement of the permeation rate of the organic vapor through a polymer membrane, from the initial time zero to steady state conditions. The MAS 2000™ system incorporates a flame ionization detector (FID), and precisely controls the cell temperature (range from ambient to 100°C) and all gas flow rates (nitrogen as carrier, air and hydrogen as fuel). An IBM 486SX computer system with a very user friendly software package was interfaced to the system to control many of the test parameters. The computer can also activate and deactivate the gas flow direction, cell opening/closing, as well as display data, while recording all pertinent instrument parameters. All permeation data can be stored in the computer hard drive, and LOTUS 1-2-3 is used to recall the permeation data to calculate the respective mass transfer parameters and give the transmission rate profile curve.

In order to increase the analysis sensitivity, the MAS 2000™ permeation test unit employed in the present study incorporated a dynamic purge and trap system to allow accumulation of the permeated vapor. In the original MAS 2000™ system, the permeated vapor is directly conveyed to a flame ionization detector (FID) for quantification. However, in the modified system, a bypass line was inserted to convey the permeated vapor to the adsorption trap. The trapping system was designed to ensure that the sample cell chamber is continuously flushed with the carrier gas and the permeated vapor is conveyed to the trapping tube attached. The sorption trap was connected to the exit port of the bypass line, which is incorporated on the instrument chassis, via a 1/4" thumb wheel swagelok fitting (Supelco Inc., Bellefonte, PA) for easy removal. Figure 4 shows a schematic of the permeation test and trap system. The glass thermal desorption tubes - Carbotrap™ 300 (6mm O.D. × 4mm I.D. × 11.5cm length) were employed as adsorption traps, which were prepacked by Supelco Inc. (Bellefonte, PA). The trapping tubes contain 300 mg of Carbotrap C adsorbent, 200 mg of Carbotrap B adsorbent, and 125 mg of Carbosieve S-III adsorbent.



R: Regulator
Ro: Rotameter
N: Needle valve
O: Organic vapor generator
M: Mixing device
V: Three way valve
S: Sampling port

Figure 4. Schematic diagram of permeation test and trap apparatus

Permeability Measurements

The permeability studies were carried out at 60°C, and 0.4 organic vapor activity. Due to the high barrier properties of the test films, elevated temperature and high permeant vapor concentration conditions were required to obtain measurable rates of permeation. Prior to initiating a test run, the test film was conditioned at 50°C ± 1°C for 48 hours, to desorb any residual monomer, or other low molecular weight volatiles from the film which could interfere with detection of permeated vapor. For each test run, a sample film approximately 6" × 6 1/2" was cut, mounted on a paperboard film holder with tape, and then placed in the permeability cell. The area of the test film was 0.0081 m^2 (12.6 in^2). A schematic drawing of the permeation test cell is shown in Figure 5.

A constant concentration of permeant vapor for the high concentration cell chamber was produced by bubbling nitrogen through the liquid permeant, with the flow rate equal to 30 ml/min. The liquid permeant is contained in a vapor generator consisting of a Kontes Fritted Midget Bubbler (Fisher Scientific, Pittsburgh, PA). The organic vapor stream was then mixed with a diluent nitrogen stream. Rotameters were used to provide an indication of settings required for the desired permeant vapor activity (partial pressure gradient). The gas flows to the rotameters were regulated by Nupro "M" series needle valves. The vapor generator system was maintained at a temperature of 23 ± 1°C.

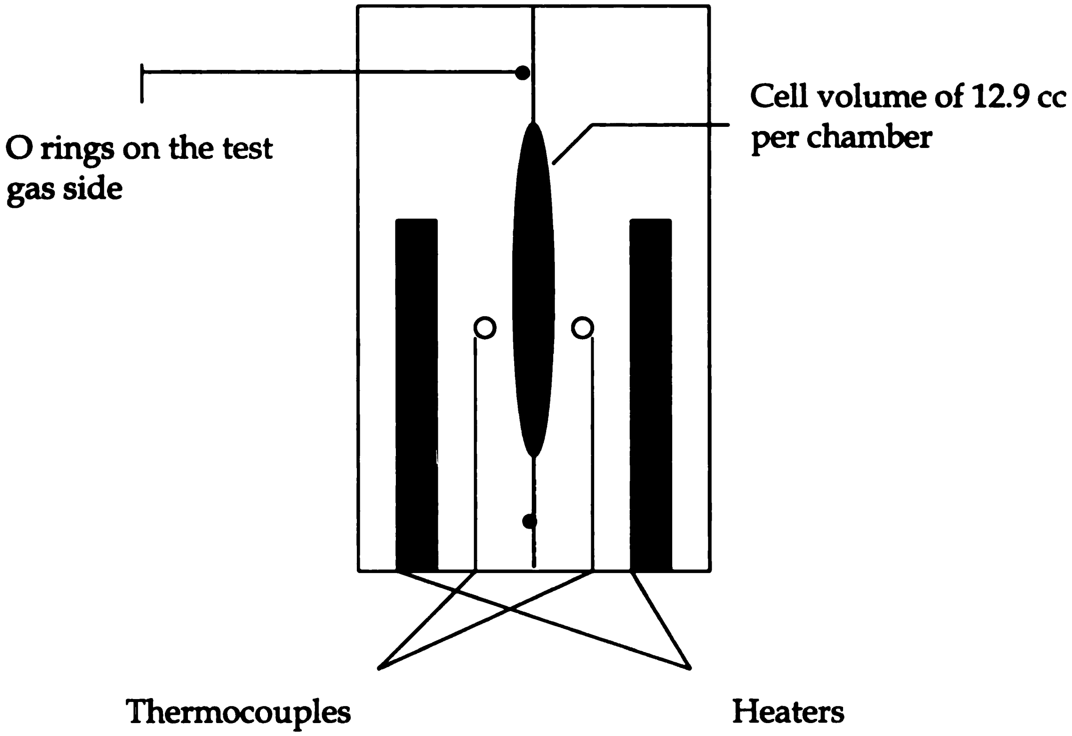


Figure 5. The schematic drawing of permeation test cell

Determination of the Vapor Activity

In the present studies, the partial vapor pressure gradient for the permeability experiments was expressed as the vapor activity. Before a test was conducted, flow meter settings were determined to provide a vapor activity (*a*) value of approximately 0.4. The vapor activity value was calculated by dividing the experimentally determined vapor pressure by the saturated vapor pressure of the permeant (Eq.19).

$$\textit{Vapor activity}\ (a) = \frac{p}{p_0} \tag{19}$$

where: p = partial vapor pressure

p_0 = saturated vapor pressure

All vapor pressure values were determined at 23 ± 1°C. To determine the saturated vapor pressure of α-pinene, 5 ml of liquid α-pinene was added to septa seal vials equipped with Teflon-faced silicone septums and aluminum crimp caps. The sealed vials were stored at 23 ± 1°C for 48 hours to allow equilibration of saturated vapor pressure in the vial headspace. A 100 μl sample were then withdrawn from the headspace by a 500 μl gas-tight syringe (Hamilton Co., Reno, Nevada) and directly injected into the gas chromatograph for quantification. The gas chromatographic analysis was carried out with a Hewlett-Packard Model 5890 gas chromatograph, equipped with a flame ionization detector and interfaced to a Hewlett-Packard integrator (Model 3395, Avondale, PA). The gas chromatography (GC) conditions were as follows:

Column: SPB-5 (30 m × 0.32 mm, 0.25 μm)
(Supelco Inc., Bellefonte, PA)

Carrier gas: Helium at 7.5 ml/min

Range: 2

Attenuation: 0

Temperature cycle:

Injection temperature	220°C
Detector temperature	250°C
Initial temperature	50°C
Initial time	1 min
Temperature rate	5°C/min
Final temperature	200°C
Final time	10 min

α-Pinene was eluted at a retention time of 7.1 minutes.

In order to provide an accurate measurement of the permeant vapor concentration or activity, a gas sampling port was installed between the dispensing manifold and the test cell. To determine the specific vapor concentration, a 100 μl sample was withdrawn from the sampling port with a 500 μl gas-tight syringe (Hamilton Co., Reno, Nevada), and injected directly into the gas chromatograph for quantification. The GC analysis conditions were the same as that for determining the saturated vapor pressure.

In both cases, a standard calibration curve of response versus permeant quantity was constructed from standard solutions of known concentration.

Standard solutions were prepared by dissolving known quantities of α-pinene in acetonitrile. A 1.0 μl sample was withdrawn from the respective standard solutions and directly injected into the gas chromatograph for quantification. The GC conditions are the same as that described previously. The standard calibration curve for α-pinene is shown in Appendix A.

Dynamic Purge and Trap/Thermodesorption Procedure

Once the operational parameters of gas flow rates, temperature, vapor pressure, and signal base line have become stable, the permeation test was started. In conducting a permeability run, the test film is initially exposed under isostatic conditions for a period of 72 hours at the required test temperature and vapor activity, during which time it is assumed that a concentration gradient is established within the film and a steady state transmission rate is attained. Following exposure of the film to the standard isostatic test procedure for a 72 hour period, the switching valve was activated and the system was operated in the accumulation or dynamic purge and trap mode for a predetermined time interval. The sorbant tube was then removed and replaced by a new trapping tube and the permeated vapor again accumulated for quantification. This procedure was repeated in triplicate, with a 3 hour time interval between sampling. The sorbant tube removed from the permeability test system was then transferred to a thermal desorption unit (Model 890, Dynatherm Analytical

Instruments, Inc., Kelton, PA), which thermally desorbs any organic volatiles from the sorbant tube and transfers them to the gas chromatograph for quantification. The sorbed volatiles were desorbed by heating for 6 minutes at 340°C, with the valve and transfer line held at 230°C to maintain the desorbed compounds in the vapor phase, while being transferred to the gas chromatograph. Helium was used as a carrier gas through the thermal desorption unit at a flow rate of 7.5 ml/minute at 40 psi. After sample desorption, the sorbant tubes were conditioned at 340°C for 40 minutes prior to re-use. The trapping and subsequent thermal desorption of volatiles allows their effective release, undiluted, and allows monitoring of otherwise undetectable levels of penetrant concentration.

Assuming an initial quantity of permeant was detected, the test system was conditioned for an additional 15-20 hours and the accumulation step was repeated. The results of the detection levels were then compared, to insure the system was at steady state.

After each test run, the switching valve of the permeation test system was heated to approximately 100°C by wrapping the valve with heating tape (OMEGA Engineering, Inc., Stamford, CT), and the valve heated for a period of at least 72 hours. The temperature of the permeation cell was also maintained at 100°C simultaneously, to remove any residual sorbed permeant from the previous experiment.

Analysis of Test Permeant by Thermal Desorption/Gas Chromatography Procedure

Gas chromatographic (GC) analyses were carried out with a Hewlett-Packard Model 5890 gas chromatograph, equipped with a flame ionization detector and interfaced to a Hewlett-Packard Model 3395 integrator (Avondale, PA), for quantification of permeated vapor. The GC conditions are presented as following:

Column: SPB-5 (30 m × 0.32 mm, 1.0 µm)
(Supelco Inc., Bellefonte, PA)

Carrier gas: Helium at 7.5 ml/min

Range: 2

Attenuation: 0

Temperature cycle:

Injection temperature	220°C
Detector temperature	250°C
Initial temperature	50°C
Initial time	6 min
Temperature rate	5°C/min
Final temperature	200°C
Final time	10 min

α-Pinene was eluted at a retention time of 12.5 minutes.

The transmission rate of α-pinene through the barrier film was determined by substitution into the following equation:

$$Transmission\ rate\,(wt./time) = \frac{AU \times C.F.}{trapping\ time} \qquad (20)$$

where: AU = average area unit response from integrator

$C.F.$ = calibration factor (gm/AU)

To prepare a standard calibration curve to establish the linearity and sensitivity of the thermal desorption procedure, standard solutions of α-pinene of known concentration were prepared by dissolution of α-pinene in acetonitrile. A 1.5 µl sample was withdrawn from the respective standard solutions and directly injected onto the Carbotrap tube. The Carbotrap tube was then transferred to the thermal desorption unit, which is interfaced to the gas chromatograph for quantification. The conditions of thermal desorption and GC analysis were the same as that described previously. The calibration data are shown in Appendix B.

RESULTS AND DISCUSSION

The primary objective of the studies described hereafter was to determine the applicability and validation of the dynamic purge and trap/thermal desorption test method proposed for determining the permeability of high barrier polymer film structures. A Saran coated oriented polypropylene film was used in the preliminary studies to demonstrate validation of the dynamic purge and trap/thermal desorption procedure for determining the permeability of high barrier polymer films. Following validation of the method, seven multi-layered or coated packaging films, with outstanding barrier properties, were selected to demonstrate method applicability. Thus, allowing permeation measurements of high barrier polymer structures within a reasonably short time period, with high sensitivity. α-Pinene was selected as the permeant.

Estimation of the Detection Sensitivity for the Dynamic Purge and Trap/Thermal Desorption Procedure

Outlined below is the method used to estimate the lower limit of detectability for the vapor transmission rate, based on the Dynamic Purge and Trap/Thermal Desorption Procedure.

The lowest area response for detecting α-pinene with good precision and accuracy by gas chromatography analysis was assumed to be 5,000 area units (AU). According to the calibration curve, an area response of 5,000 AU is equivalent to 0.2 ng of α-pinene transferred to the gas chromatograph. Based on a dynamic purge time of one hour and a detectability level of 0.2 ng, the minimum measurable α-pinene transmission rate is equal to 0.2 ng/hr. Huang (1996) reported that the lower limit of detectability for the vapor transmission rate ranged from 0.2 μg/hr to 0.4 μg/hr, based on the MAS 2000™ Organic Vapor Permeation Test System operated in the isostatic test mode. The 0.2 ng/hr detectability of the Dynamic Purge and Trap/Thermal Desorption Procedure represents an increase in sensitivity of three to four orders of magnitude over the continuous flow isostatic procedure. Furthermore, if the dynamic purge time is extended, the minimum measurable transmission rate will be lower.

Comparison of Permeance Values for Saran Coated Oriented Polypropylene by MAS 2000™ Isostatic Procedure and Dynamic Purge and Trap/Thermal Desorption Procedure

The general utility and validation of the MAS 2000™ Organic Vapor Permeation test system has been demonstrated by Huang (1996). The suitability of the proposed dynamic purge and trap/thermal desorption method for measuring permeation rates of organic vapors through barrier films was demonstrated by comparing the permeance values obtained by the isostatic procedure and the dynamic purge and trap/thermal desorption procedure. For α-pinene as the permeant and Saran coated OPP as the barrier film, permeance values were determined from permeability studies utilizing the MAS 2000™ Permeation Test System, operated in the typical isostatic mode, as well as by the Dynamic Purge and Trap/Thermal Desorption Procedure based on modification of the MAS 2000™ test system. Both tests were conducted at a vapor activity of α-pinene of 0.4 and 60°C. The test results obtained by the two procedures are presented in Table 1. As shown, there was good agreement between permeance values obtained by the two procedures, with the deviation between the two permeance values being within 10%. Therefore, the validity of the developed test procedure is evidenced by the agreement between the permeance values obtained by the two test methods. According to the agreement between the results obtained by the MAS 2000™ isostatic procedure and the higher sensitivity Dynamic Purge and Trap/Thermal Desorption procedure, the latter method should have the ability to provide a precise and useful technique for determining the permeation rates of high barrier polymeric membranes.

Table 1. Comparison of the permeance values of α-pinene through Saran coated OPP film obtained from the two test procedures.

Test procedure	Permeance (Kg/m^2·sec·Pa)	
		Average
Isostatic MAS 2000 System	1.30×10^{-13} 1.34×10^{-13}	1.32×10^{-13}
Dynamic Purge/Trap MAS 2000 System modified to allow accumulation	1.39×10^{-13} 1.45×10^{-13}	1.42×10^{-13}

Permeability Studies of High Barrier Packaging Films by the Dynamic Purge and Trap/Thermal Desorption Procedure

In this aspect of the study, seven commodity packaging films, with outstanding barrier properties, were evaluated to determine the general utility and applicability of the Dynamic Purge and Trap/Thermal Desorption Procedure for determining the organic vapor barrier characteristics of high barrier polymer films. All studies were carried out with α-pinene (a = 0.4) at 60°C. The transmission rates and permeance values obtained for the selected polymeric films are summarized in Tables 2 through 8, respectively. As shown, measurable but low transmission rates were obtained after 3 to 4 days of continual testing. Additional measurements were then made, for up to more than 6 days, to establish with sufficient confidence that a steady state permeation rate had been attained. Since all the films investigated in the present study are multi-layered or coated structures, which have different layer thicknesses and combinations of layers, permeance values ($Kg/m^2{\cdot}sec{\cdot}Pa$) were calculated to describe the barrier properties of the total structure. From the consistency of each triplicate measurement, it was assumed that there was no significant breakthrough losses of the permeant from the adsorption tubes. The results of the permeability studies are summarized in Table 9. According to the results, Acrylic coated OPP film, exhibited the highest permeance value, which is one order of magnitude greater than the permeance of other films. However, from the permeance values obtained, both SiO_xPET based films appeared to provide the highest organic vapor barrier properties among the seven polymeric films evaluated.

Table 2. The permeation data of α-pinene through
HDPE/tie/EVOH/EVOH/tie/HDPE film at a = 0.4, 60°C.

Total Run Time(a) (day)	Transmission Rate (µg/hr)		Permeance(b) ($Kg/m^2 \cdot sec \cdot Pa$)
		Average	
4	2.2×10^{-4} 1.6×10^{-4} 1.7×10^{-4}	1.8×10^{-4}	3.3×10^{-17}
5	1.7×10^{-4} 1.7×10^{-4} 1.7×10^{-4}	1.7×10^{-4}	3.1×10^{-17}
6	1.9×10^{-4} 1.4×10^{-4} 1.5×10^{-4}	1.6×10^{-4}	2.9×10^{-17}
Steady State Value(c)		1.7×10^{-4}	3.1×10^{-17}

(a) Samples conditioned for a period of 96 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 3. The permeation data of α-pinene through HDPE/tie/EVOH/ionomer film at a = 0.4, 60°C.

Total Run Time[a] (day)	Transmission Rate (μg/hr)		Permeance[b] (Kg/m²·sec·Pa)
		Average	
3	6.4×10^{-5} 7.4×10^{-5} 7.0×10^{-5}	6.9×10^{-5}	1.3×10^{-17}
4	2.4×10^{-4} 1.8×10^{-4} 1.9×10^{-4}	2.0×10^{-4}	3.7×10^{-17}
5	1.9×10^{-4} 1.6×10^{-4}	1.8×10^{-4}	3.3×10^{-17}
6	1.6×10^{-4} 1.7×10^{-4} 1.9×10^{-4}	1.7×10^{-4}	3.1×10^{-17}
Steady State Value[c]		1.8×10^{-4}	3.4×10^{-17}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 4. The permeation data of α-pinene through HDPE/tie/Nylon/Nylon/tie/HDPE film at a = 0.4, 60°C.

Total Run Time[(a)] (day)	Transmission Rate (μg/hr)		Permeance[(b)] (Kg/m²·sec·Pa)
		Average	
3	1.1×10^{-4} 1.1×10^{-4} 1.5×10^{-4}	1.2×10^{-4}	2.2×10^{-17}
4	1.2×10^{-4} 1.3×10^{-4}	1.3×10^{-4}	2.4×10^{-17}
5	1.9×10^{-4} 2.2×10^{-4} 1.4×10^{-4}	1.8×10^{-4}	3.3×10^{-17}
6	2.2×10^{-4} 1.8×10^{-4} 1.9×10^{-4}	2.0×10^{-4}	3.7×10^{-17}
7	2.0×10^{-4} 2.0×10^{-4} 2.2×10^{-4}	2.1×10^{-4}	3.9×10^{-17}
Steady State Value[(c)]		2.0×10^{-4}	3.6×10^{-17}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 5. The permeation data of α-pinene through HDPE/Nylon/ionomer film at a=0.4, 60°C.

Total Run Time(a) (day)	Transmission Rate (μg/hr)		Permeance(b) (Kg/m²·sec·Pa)
		Average	
3	1.3×10^{-4} 1.2×10^{-4} 1.3×10^{-4}	1.3×10^{-4}	2.4×10^{-17}
4	1.6×10^{-4} 1.3×10^{-4} 1.7×10^{-4}	1.5×10^{-4}	2.8×10^{-17}
5	1.6×10^{-4} 1.8×10^{-4} 1.2×10^{-4}	1.5×10^{-4}	2.8×10^{-17}
6	1.9×10^{-4} 2.2×10^{-4} 1.6×10^{-4}	1.9×10^{-4}	3.5×10^{-17}
Steady State Value(c)		1.6×10^{-4}	3.0×10^{-17}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 6. The permeation data of α-pinene through Acrylic coated OPP film at a=0.4, 60°C.

Total Run Time(a) (day)	Transmission Rate (µg/hr)		Permeance(b) (Kg/m^2·sec·Pa)
		Average	
3	0.001 0.001 0.001	0.001	1.8×10^{-16}
4	0.002 0.001 0.001	0.001	1.8×10^{-16}
5	0.002 0.002 0.002	0.002	3.7×10^{-16}
6	0.002 0.002 0.002	0.002	3.7×10^{-16}
7	0.002 0.002 0.002	0.002	3.7×10^{-16}
Steady State Value(c)		0.002	3.7×10^{-16}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 7. The permeation data of α-pinene through PET/SiO_xPET/CPP film at a=0.4, 60°C.

Total Run Time[a] (day)	Transmission Rate (μg/hr)		Permeance[b] ($Kg/m^2 \cdot sec \cdot Pa$)
		Average	
3	1.0×10^{-4} 0.8×10^{-4} 0.8×10^{-4}	0.9×10^{-4}	1.7×10^{-17}
4	1.2×10^{-4} 1.0×10^{-4} 1.0×10^{-4}	1.1×10^{-4}	2.0×10^{-17}
5	1.1×10^{-4} 1.0×10^{-4} 1.0×10^{-4}	1.0×10^{-4}	1.8×10^{-17}
6	1.2×10^{-4} 1.0×10^{-4} 1.0×10^{-4}	1.1×10^{-4}	2.0×10^{-17}
Steady State Value[c]		1.1×10^{-4}	2.0×10^{-17}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 8. The permeation data of α-pinene through PP/SiO$_x$PET film at a = 0.4, 60°C.

Total Run Time(a) (day)	Transmission Rate (μg/hr)		Permeance(b) (Kg/m^2·sec·Pa)
		Average	
3	0.9×10^{-4} 0.8×10^{-4} 0.8×10^{-4}	0.8×10^{-4}	1.5×10^{-17}
4	0.9×10^{-4} 0.9×10^{-4} 0.8×10^{-4}	0.9×10^{-4}	1.7×10^{-17}
5	1.1×10^{-4} 0.9×10^{-4} 0.9×10^{-4}	1.0×10^{-4}	1.8×10^{-17}
6	0.9×10^{-4} 1.0×10^{-4} 0.9×10^{-4}	1.0×10^{-4}	1.8×10^{-17}
7	1.1×10^{-4} 1.0×10^{-4} 1.0×10^{-4}	1.0×10^{-4}	1.8×10^{-17}
Steady State Value(c)		1.0×10^{-4}	1.8×10^{-17}

(a) Samples conditioned for a period of 72 hours prior to test.

(b) Calculated from the average transmission rate.

(c) Values reported are the average of data obtained from the last three days.

Table 9. The permeance values of α-pinene at a = 0.4, 60°C.

Test Film	Permeance[a] (Kg/m^2·sec·Pa)
HDPE/tie/EVOH/EVOH/tie/HDPE	3.1×10^{-17}
HDPE/tie/EVOH/ionomer	3.4×10^{-17}
HDPE/tie/Nylon/Nylon/tie/HDPE	3.6×10^{-17}
HDPE/Nylon/ionomer	3.0×10^{-17}
Acrylic coated OPP	3.7×10^{-16}
PET/SiO$_x$PET/CPP	2.0×10^{-17}
PP/SiO$_x$PET	1.8×10^{-17}

(a) Values reported are the average of data obtained from the last three days.

The permeability of gases such as oxygen and carbon dioxide across high barrier membranes has been studied in detail by a number of researchers (Allison, 1985; Anon, 1986; Yoshi, 1990; Furrer, 1994; Fishman, 1995). However, investigations which consider the permeation of interactive penetrants such as organic vapors through high barrier packaging films are extremely limited because of the lack of high detection sensitivity by conventional test procedures.

Hatzidimitriu et al. (1987) used a permeation cell method, based on the Quasi-Isostatic procedure, to study the odor barrier properties of several Nylon and EVOH based multi-layer packaging films. The authors found no measurable level of permeated vapor. In these cases, the permeation rates were expressed as a value below the detection limit.

DeLassus (1993) described the results of permeability studies carried out with thin polystyrene, polyethylene, PET and Nylon 6 films, for several organic penetrants at low vapor activities. Analytical procedures were based on the photoionization and atmospheric pressure ionization mass spectroscopy techniques (DeLassus et al., 1988a; Tou et al., 1990). DeLassus (1993) indicated that no measurable permeation rates were observed in any case, although elevated temperatures were used and experimental times ran to 16 hours.

Huang (1996) used the MAS 2000™ Organic Vapor Permeation Test System, operated in the isostatic test mode, to determine the organic vapor barrier properties of a series of commodity polymer membranes. For α-pinene and limonene as the permeant, and Acrylic coated OPP as the tested film, there was no measurable level of permeation detected, even following continuous testing for 44 hours at 60°C and vapor activity of permeant equal to 0.4. The Dynamic Purge and Trap/Thermal Desorption Procedure provided a method which accurately determined the permeance of α-pinene through the same Acrylic coated OPP film, thus establishing the enhanced sensitivity provided by this method.

Several investigators reported conducting permeability studies at saturation vapor pressure to determine the permeation rates of barrier films such as a HDPE/EVOH/HDPE laminate (Hatzidimitriu et al., 1987; Theodorou and Paik, 1991). The rationale for the penetrant being at saturation vapor pressure was that a high vapor pressure can cause polymer swelling, thus leading to an increase in permeation rates (Crank and Park, 1968). On the other hand, for low vapor pressures, the permeated levels of test compounds can be in such low concentration ranges that they would remain below the detection limit of the test method. However, it is best that the permeation test be conducted under conditions as close as possible to practice (Franz, 1993).

It can be assumed that the vapor concentration employed in the present study may cause swelling of the films to some extent, thus increasing the solubility and diffusivity of the penetrant in the polymer film structure. In addition, the test temperature is much higher than ambient temperature.

However, regardless of the swelling and temperature effects, the results still indicate a general applicability of the test method for determining the permeability of organic vapors through high barrier polymer membranes. By carrying out permeability experiments at several lower temperature conditions, the permeation behavior of polymeric packaging materials at temperatures more typical of food packaging applications can be obtained by application of the Arrhenius Equation. Thus, permeation rates can be determined in a more reliable manner.

SUMMARY AND CONCLUSIONS

A permeation test method based on the MAS 2000™ Permeation Test System, modified with a dynamic purge and trap system, was developed for the determination of organic vapor permeability through high barrier polymer membranes. For validation of the method, the permeation of α-pinene through a Saran coated OPP film was determined by the purge and trap procedure and the results compared with those obtained from the continuous flow Isostatic MAS 2000™ Permeation Test method. The applicability and the sensitivity of the test method was demonstrated by measuring α-pinene permeation through seven high barrier polymeric films at 60°C. The method developed in this study offers a practical and sensitive procedure for measuring the organic vapor permeability of high barrier polymer film structures.

Based on the results presented in the previous section, the conclusions which can be drawn from this study are summarized below:

1. By using the Dynamic Purge and Trap/Thermal Desorption procedure described in this study, a lower limit of detection sensitivity of 0.2 ng/hr can be reached for monitoring organic vapor permeability. This value represents an increase in sensitivity of three to four orders of magnitude, over the continuous flow isostatic procedure.

2. The developed method was found to be a suitable and precise procedure, based on the agreement between the permeance values determined by the Isostatic MAS 2000™ Permeation Test System and the Dynamic Purge and Trap/Thermal Desorption Procedure.
3. The results of this study illustrate the general applicability of the developed method. The Dynamic Purge and Trap/Thermal Desorption Procedure has been shown to have the ability to determine the permeation rate of high barrier packaging films.
4. The detection sensitivity increase by this procedure allows use of this method for determining aroma/flavor permeation rates through high barrier films. Again, this technique is especially applicable in determining the permeability of packaging films exhibiting high barrier properties, where the conventional techniques fail.

FUTURE STUDIES

The results of this study demonstrate the general applicability and high sensitivity of the Dynamic Purge and Trap/Thermal Desorption Procedure for determining the barrier properties of high barrier packaging films. Temperature, relative humidity, and concentration dependence were not evaluated in the present investigation. With respect to the effect of these factors, examination of temperature, relative humidity, and penetrant concentration levels will be necessary for better understanding of the transport process associated with the respective barrier membranes. A humidifier system can be connected to the permeation device for controlling the relative humidity.

Similar studies should be carried out with other organic vapor penetrants, representing a range of polarities and molecular size, to compare their relative behavior. In addition, the effect of co-permeants on the diffusivity may be investigated. Experiments can be conducted to determine the permeability of binary organic vapor mixture of varying composition through polymeric barrier films. These will contribute to further developments in commercial use of high barrier polymeric membranes.

APPENDICES

APPENDIX A

Standard Calibration

Table 10. Calibration data of α-pinene by GC-FID procedure

Solution Conc. (ppm, g/cm^3)	Quantity Injected (g)	Area Response (AU)
0	0	0
10	1.30×10^{-8}	136465
20	2.70×10^{-8}	274501.7
30	4.10×10^{-8}	471341
40	5.30×10^{-8}	557413

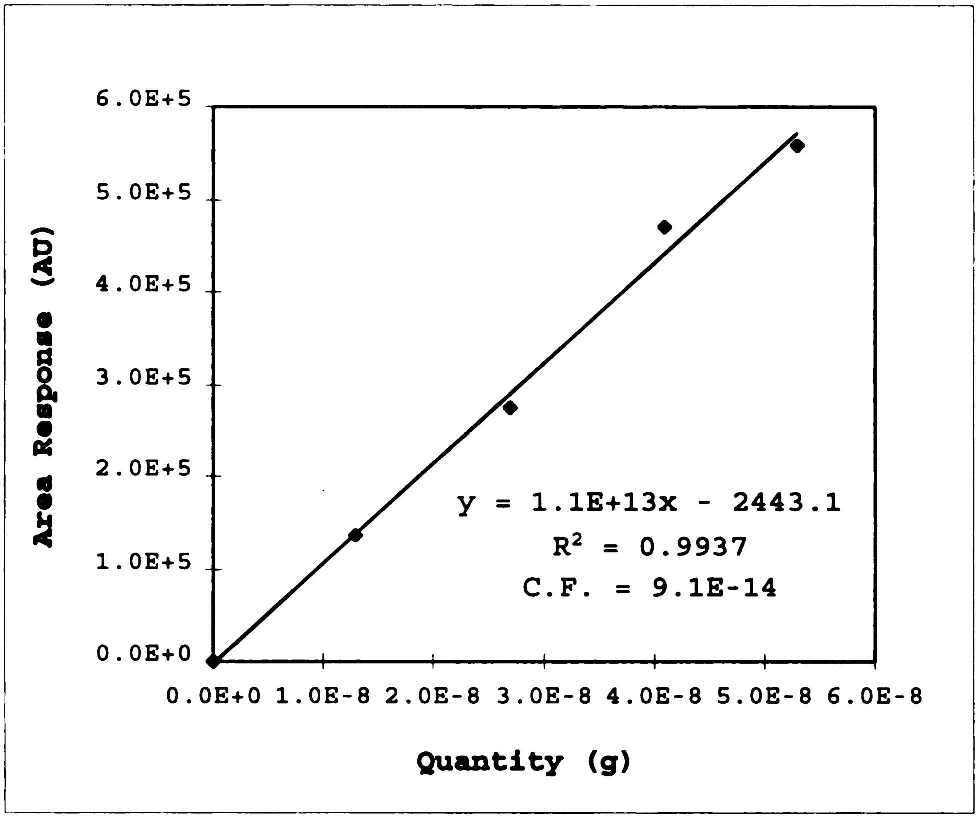


Figure 6. Calibration curve of α-pinene by GC-FID procedure

APPENDIX B

Standard Calibration

Table 11. Calibration data of α-pinene by Thermal Desorption/Gas Chromatography Procedure

Solution Conc. (ppm, g/cm^3)	Quantity Injected (g)	Area Response (AU)
0	0	0
10	1.287×10^{-8}	315598
20	2.574×10^{-8}	582505
30	3.861×10^{-8}	918056
40	5.148×10^{-8}	1204582

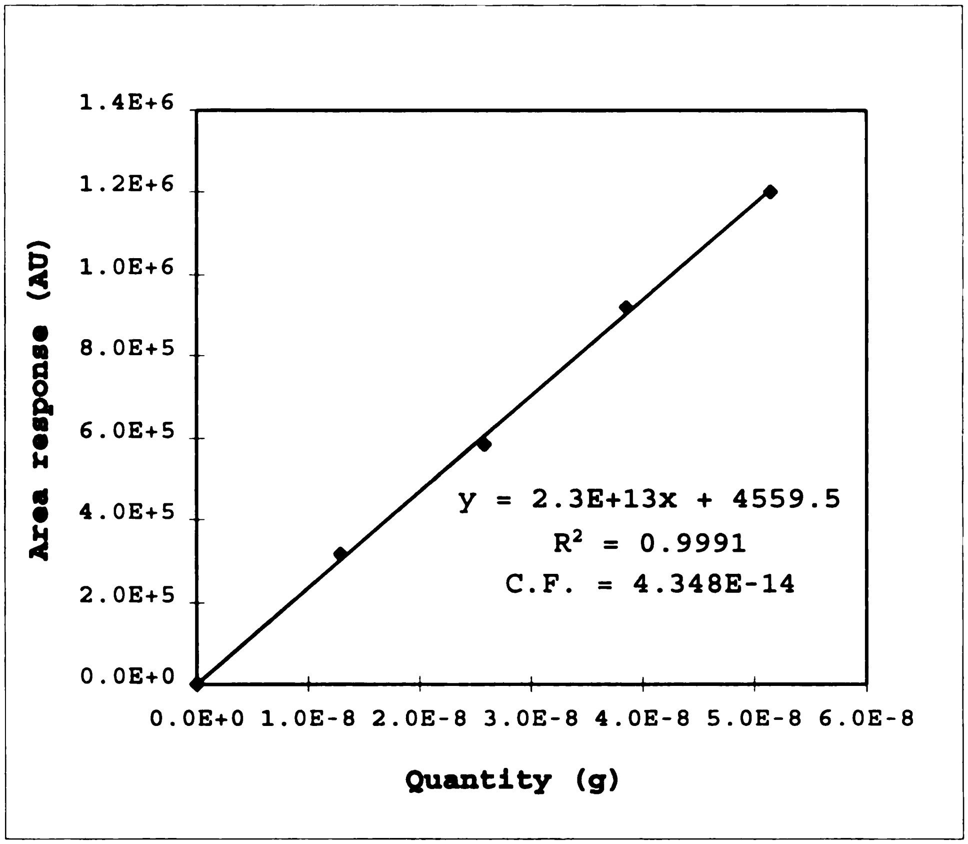


Figure 7. Calibration curve of α-pinene by Thermal Desorption/Gas Chromatography Procedure

BIBLIOGRAPHY

BIBLIOGRAPHY

Alberola, J. and Izquierdo, L.J., 1976. The Volatile Fraction of Orange Juice, Methods for Extraction and Study of Composition. In *Flavor of Foods and Beverages - Headspace Techniques.* G. Charalambous (Ed.), 263-304. Academic Press, New York.

Apostolopoulos, D. and Winters, N., 1991. Measurement of Permeability for Packaging Films to d-Limonene Vapour at Low Levels. Packag. Technol. Sci. 4(3):131-138.

Baner, A.L., Hernandez, R.J., Jayaraman, K., and Giacin, J.R., 1984. Isostatic and Quasi-Isostatic Methods for Determining the Permeability of Organic Vapors through Barrier Membranes. In *Current Technologies in Flexible Packaging,* M.L. Troedel (Ed.), 49-62. American Society for Testing and Materials, Philadel phia, PA.

Baner, A.L., 1987. The Measurement and Analysis of the Diffusion of Toluene in Polymeric Films. Master Thesis. Michigan State University, East Lansing, MI.

Barrar, R.M., 1951. *Diffusion in and through Solid.* Cambridge Press, London.

Barrer, R. M., 1939. Permeation, Diffusion and Solution of Gases in Organic Polymers. Trans. Faraday Soc., 35:628.

Becker, K., Koszinowski, J., and Piringer, O., 1983. *Deutsche Lebensm.-Rundschau.* 79:257.

Berens, A.R., 1977. Diffusion and Relaxation in Glassy Polymer Powders: 1. Fickian Diffusion of Vinyl Chloride in Poly (Vinyl choride). Polymer. 18:697-704.

Berens, A.R., 1978. Analysis of Transport Behavior in Polymer Powders. J. Membrane Sci. 3:247-264.

Berens, A.R. and Hopfenberg, 1982. Diffusion of Organic Vapors at Low Concentrations in Glassy PVC, Polystyrene, and PMMA. J. Membrane Sci. 10:283-303.

Bertoni, G., Bruner, F., Liberti, A., and Perrino. C., 1981. Some Critical Parameters in Collection, Recovery and Gas Chromatographic Analysis of Organic Pollutants in Ambient Air Using Light Adsorbents. J. Chromatography. 203:263-270.

Bicchi, C. and Joulain, D., 1990. Headsapce-Gas Chromatographic Analysis of Medicinal and Aromatic Plants and Flowers. Flav. Fragr. J. 5(3):131-145.

Bischoff, M. and Eyerer, P., 1984. Effect of Orientation on the Sorption of Toluene by High Density Polyethylene. J. Membrane Sci. 21:333-342.

Booma, M., Hoojjat, H., and Giacin, J.R., 1993. Permeability of Fragrance Volatiles through an Ethylene-Vinyl Acetate Co-Polymer Membrane Based Delivery System: The Effect of Time and Temperature. Paper presented at 1993 Polymers, Laminations and Coatings Conference. 255-261.

Boyko, A.L., Morgan, M.E., and Libbey, L.M., 1978. Porous Polymer Trapping for GC/MS Analysis of Vegetable Flavors. In *Analysis of Foods and Beverages-Headspace Techniques*, G. Charalamons (Ed.), 57-59. Academic Press, Inc., N.Y.

Bruner, F., Bertoni, G., and Crescentini, G., 1978. Critical Evaluation of Sampling and Gas Chromatographic Analysis of Halocarbons and Other Organic Air Pollutants. J. Chromatography. 167:399-407.

Buckholz, L.L., Withycombe, D.A., and Daun, H., 1980. Application and Characteristics of Polymer Adsorption Method Used to Analyze Flavor Volatiles from Peanuts. J. Agric. Food Chem. 28(4):760-765.

Caldecourt, V. and Tou, J., 1985. Atmospheric Pressure Ionization Mass Spectrometric an Photoionization Techniques for Evaluation of Barrier Film Permeation Properties. TAPPI Proceedings: Polymers, Laminations and Coatings Conference. 441-444.

Choy, C.L., Leung, W.P., and Ma, T.L. 1984. Sorption and Diffusion of Toluene in Highly Oriented Polypropylene. J. Polymer Sci.: Polymer Physics Edition. 22:707-719.

Clark, R.G. and Cronin, D.A., 1975. The Use of Activated Charcoal for the Concentration and Analysis of Headspace Vapours Containing Food Aroma Volatiles. J. Sci. Fd. Agric. 26:1615-1624.

Comyn, J., 1985. Introduction to Polymer Permeability and the Mathematics of Diffusion. In *Polymer Permeability*. J. Comyn (Ed.), Elsevier Applied Science Publishers, New York.

Connick, W.J., Bradow, J.M., and Legendre, M.G., 1989. Identification and Bioactivity of Volatile Allelochemicals from Amaranth Residues. J. Agric. Food Chem. 37(3):792-796.

Crank, J. and Park, G.S., 1968. *Diffusion in Polymers.* Academic Press, New York.

Crank, J. 1975. *The Mathematics of Diffusion*, 2nd ed. Clarendon Press, Oxford, England.

Davis, D.W. 1946. Gas Permeability, An Isostatic Test Method. Modern Packaging. May:145.

DeLassus, P., 1985. Transport of Unusual Molecules in Polymer Films. TAPPI Proceedings, Polymers, Laminations and Coating Conference. 445.

DeLassus, P.T., 1993. Proceedings of Permeation of Flavors and Aromas through Glassy Polymers. Tappi 263.

Delassus, P.T., Strandburg, G., and Howell, B.A., 1988a. Flavor and Aroma Permeation in Barrier Film: The Effects of High Temperature and High Humidity. Tappi Journal 71:177.

DeLassus, P.T., Tou, J.C., Babinec, M.A., Rulf, D.C., Karp, B.K., and Howell, B.A., 1988b. Transport of Apple Aromas in Polymer Films. Ch.4 in *Food and Packaging Interactions*. J.H. (Ed.) Hotchkiss, American Chemical Society, Washington, DC.

Demarest, R.I., 1987. Measuring Oxygen Transmission Rates of EVOH at Precise Relative Humidities. J. Packaging Technology. 1(6):186-187, 203, 205.

Dupuy, H.P., Fore, S.P., and Goldblatt, L.A., 1973. Direct Gas Chromatographic Examination of Volatiles in Salad Oils and Shortenings. JAOCS 50:340.

Ehret-Henry, J., Ducruet, V., Luciani, A., and Feigenbaum, A., 1994. Styrene and Ethylbenzene Migration from Polystyrene into Dairy Products by Dynamic Purge-and-Trap Gas Chromatography. J. Fd. Sci. 59(5):990-992.

Franz, R., 1993. Permeation of Volatile Organic Compounds across Polymer Films-Part I: Development of a Sensitive Test Method Suitable for High-barrier Packaging Films at Very Low Permeant Vapour Pressures. Packaging Technol. and Sci. 6:91-102.

Fujita, H., 1961. *Diffusion in Polymer-Diluent Systems*. Fortsch. Hochpolym. Forsch. 3:1-47..

Galt, A.M. and MacLeod, G., 1984. Headspace Sampling of Cooked Beef Aroma Using Tenax GC. J. Agric. Fd. Chem. 32:59-64.

Gilbert, S.G., Hatzidimitriu, E., Lai, C., and Passy, N., 1983. Study of Barrier Properties of Polymeric Films to Various Organic Aromatic Vapors. In *Instrumental Analysis of Foods*, Volume 1, G. Charalambous and G. Inglett (Ed.), 405-411. Academic Press, London.

Hagenbaugh, J., 1987. Flavor and Odor Protection of Packaging Films. The Manufacturing Confectioner 67(6):111-114.

Hartman, T.G., Lech, J., Karmas, K., Salinas, J., Rosen, R.T., and Ho, C.T., 1993. Flavor Characterization Using Adsorbent Trapping-Thermal Desorption or Direct Thermal Desorption-Gas Chromatography and Gas Chromatography-Mass Spectrometry. In *Flavor Measurement*. C.T. Ho and C.H. Manley (Ed.), 37-60. Marcel Dekker. Inc. N.Y.

Hatzidimitriu, E., Gilbert, S.G., and Loukakis, G., 1987. Odor Barrier Properties of Multi-Layer Packaging Films at Different Relative Humidities. J. Fd. Sci. 52(2): 472-474.

Hernandez, R.J., Giacin, J.R., and Baner, A.L., 1986. The Evaluation of the Aroma Barrier Properties of Polymer Films. J. Plastic Film & Sheeting. 2:187-211.

Hilton, B.W. and Nee, S.Y., 1978. Permeability of Organic Vapor through Packaging Films. 1. Ind Eng. Chem. Prod. Res. Dev. 17(1):80.

Huang, S.J., 1996. Evaluation Isostatic and Quasi-isostatic Procedures for Determining the Organic Vapor Barrier Properties through Polymer Membranes. Master Thesis. Michigan State University, East Lansing, MI.

Ioffe, B.V. and Vitenberg, A.G., 1984. Headspace Analysis and Related Methods in Gas Chromatography. John Wiley & Sons, N.Y.

Jennings, W.G., Wohleb, R., and Lewis, M.J., 1972. Gas Chromatographic Analysis of Headspace Volatiles of Alcoholic Beverages. J. Food Sci. 37:69.

Johansson, F. and Leufven, A., 1994. Food Packaging Polymer Films as Aroma Vapor Barriers at Different Relative Humidities. J. Fd. Sci. 59(6):1328-1331.

Kolb, B., 1984. Analysis of Food Contaminants by Headspace Gas Chromatography. In *Analysis of Food Contaminants.* J. Gilbert (Ed.), 117-156. Elsevier Applied Science, London.

Kontominas, M.G., 1985. Determination of Permeation Rates of Polymeric Films to Various Organic Vapors in Relation to Retention of Flavor Quality of Packaged Stuffs. Sciences Des Aliments. 5:321-329.

Koszinowski, J. and O. Piringer., 1986. Influence of the Packaging Material and the Nature of the Packed goods on the Loss of Volatile Organic Compounds: Permeation of Aroma Compounds. Ch. 16 in *Food Packaging and Preservation Theory and Practice.* M. Mathlouthi (Ed.), Elserier Applied Science Publishers Ltd., Essex, England.

Krzymien, M.E. and Elias, L. 1990. Feasibility Study on the Determination of Fish Freshness by Trimethytlamine Headspace Analysis. J. Fd. Sci. 55(5):1228-1232.

Laine, R. and Osburn, J.O., 1971. Permeability of Polyethylene Film to Organic Vapors. J. Applied Polymer Sci. 15:327-339.

Landois-Garza, J. and Hotchkiss, J.H., 1988. Permeation of High-Barrier Films by Ethyl Esters. Ch.4 in *Food and Packaging Interactions.* J.H. Hotchkiss (Ed.), American Chemical Society, Washington, DC.

Lebovits, A., 1966. Permeability of Polymers to Gases, Vapors and Liquid. Modern Plastics. 43:139.

Leufvsn A. and Stollman, U., 1992. Polymer Films as Aroma barrier at Different Temperatures. Zeitschrift fur Lebensmittel-Untersuchung und-Forschung. 194:355-359.

Lin, C.H., 1995. Permeability of Organic Vapors through a Packaged Confectionery Product with a Cold Seal Closure: Theoretical and Practical Consideration. Master Thesis. Michigan State University, East Lansing, MI.

Linforth, R.S.T. and Taylor, A.J., 1993. Measurement of Volatile Release in the Mouth. Food Chem. 48:115-120.

Mangani, F. and Mastrogiacomo, A.R., 1982. Evaluation of the Working Conditions of Light Adsorbents and Their Use as Sampling Material for the GC Analysis of Organic Air Pollutants in Work Areas. Chromatographia. 15(11):712.

McCaffrey, C.A. and MacLachlan, J., 1994. Adsorbent Tube Evaluation for the Preconcentration of Volatile Organic Compounds in Air for Analysis by Gas Chromatography-Mass Spectrometry. Analyst. 119:897-902.

Meares, P. 1958. Diffusion of Allyl Chloride in PVA. Part I. The Steady State of Permeation. J. Polymer Sci. 27:391.

Meares, P. *1965*a. *Polymers: Structure and Bulk Properties*. Van Nostrand & Co. LTD. London.

Meares, P. 1965b. Transient Permeation of Organic Vapors through Polymer Membranes. J. Applied Polymer Sci. 9:917-932.

Mohney, S.M., Hernandez, R.J., Giacin, J.R., Harte, B.R., and Miltz, J., 1988. Permeability and Solubility of d-Limonene Vapor in Cereal Package Liners. J. Fd. Sci. 53(1):253-257.

Murray, K.E., 1977. Concentration of Headspace, Airborne and Aqueous Volatiles on Chromosorb 105 for Examination by Gas Chromatography and Gas Chromatography-Mass Spectrometry. J. Chromatography. 135:49-60.

Murray, L.J., 1985. An Organic Vapor Permeation Rate Determination for Flexible Packaging Materials. J. Plastic Film and Sheeting. 1:104.

Murray, L.J. and Dorschner, R.W., 1983. Permeation Speeds Tests, Aids Choice of Exact Material. Package Engineering. March:76.

Nielsen, T.J., Jagerstad, I.M., Oste, R.E., and Wesslen, B.O., 1992. Comparative Absorption of Low Molecular Aroma Compounds into Commonly Used Food Packaging Polymer Films. J. Fd. Sci. 57:490.

Olafsdottir, G., Steinke, J.A., and Lindsay, R.C., 1985. Quantitative Performance of a Simple Tenax-GC Adsorption Method for Use in the Analysis of Aroma Volatiles. J. Fd. Sci. 50:1431-1436.

Paine, F.A. and Paine, H.Y., 1992. *A Handbook of Food Packaging*. 2nd ed. Blackie Academic & Professional. London, England.

Pasternak, R.A., Schimscheimer, J.F., and Heller, J., 1970. A Dynamic Approach to Diffusion and Permeation Measurements. J. Polymer Sci. Part A-2. 8:467-479.

Pye, D.G., Hoehn, H.H., and Panar, M., 1976. Measurement of Gas Permeability of Polymers. I. Permeabilities in Constant Volume/Variable Pressure Apparatus. J. Applied Polymer Sci. 20:1921-1931.

Risch, S.J. and Reineccius, G.A., 1989. Ch.5 in *Isolation of Thermally Generated Aromas*. American Chemical Society.

Robertson. G.L., 1993. Ch.4 in *Food Packaging: Principles and Practice*. Marcel Dekker, Inc. N.Y.

Rogers, C.E., 1964. Permeability and Chemical Resistance of Polymers. Ch.9. in *Engineering Design for Plastics*. Baer, E. (Ed.) Rheinhold, N.Y.

Rogers, C.E., Meyer, J.A., Stannett, V., and Szwarc, M., 1956. Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers. Part I. Determination of the Permeability Constant. TAPPI. 39(11):737.

Sajiki, T. and Giacin, J.R., 1993. Permeation of Ethyl Acetate Vapor through Silica Deposited Polyethylene Terephthalate Film and Composite Structures. J. Plastic Film & Sheeting 9:97-111.

Schaefer, J., 1981. Isolation and Concentration from the Vapour Phase. In *Handbook der Aroma Forschung*. H. Mearse and R. Belz (Ed.), p.44. Akademia-Verlag, Berlin.

Simon, A., Riba, M., Waldhart, A., and Torres, L., 1995. Breakthrough Volume of Monoterpenes on Tenax TA: Influence of Temperature and Concentration for α-Pinene. J. of Chromatrgraphy. 704:465-471.

Soderhjelm, L., and Eskelinen, S., 1985. Characterization of Packaging Materials with Respect to Taint and Odour. Appita. 38(3):205-209.

Stannett, V., Hopfengerg, H.B., and Petropoulols, J.H., 1972. Diffussion in Polymers. Ch.8 in *Macromolecular Science.* Baum, C.E. (Ed.), 8:329.

Sugisawa, H., 1981. Sample Preparation: Isolation and Concentration. Ch.2 in *Flavor Research.* R. Teranishi, R.A. Flath, H. Sugisawa (Ed.), Marcel Dekker, Inc., N.Y.

Talka, E., 1986. Fractionation and Identification of Some Biologically Active Compounds in Bleached Kraft Mill Dffluents. Part 1. Volatile Compounds. Pap. Puu. 68(9):670-673.

Talwar, R. 1974. Plastic in Packaging: Gas and Vapor Permeability. Package Development. Sep./Oct.:101.

Thalmann, W.R., 1990. Sorption of Solvents in Plastics and Solvent Desorption and Retention. Packag. Technol. Sci. 5(1):21-25.

Theodorou, E. and Paik, J.S., 1992. Effect of Organic Vapour Interaction on Permeation Rate through Polymer Films. Packag. Technol. Sci. 5(1):21-25.

Tou, J.C., Rulf, D.C., and DeLassus, P.T., 1990. Mass Spectrometric System for the Measurement of Aroma/Flavor Permeation Rates across Polymer Films. Analytical Chem. 61:592.

Vallejo-Cordoba, B. and Nakai, S., 1993. Using a Simultaneous Factor Optimization Approach for the Detection of Volatiles in Milk by Dynamic Headspace Gas Chromatographic Analysis. J. Agric. Fd. Chem. 41:2378-2384.

Withycombe, D.A., Mookherjee, B.C., and Hruza, A., 1978. Isolation of Trace Volatile Constituents of Hydrolyzed Vegetable Protein via Porous Polymer Headspace Entrainment. In *Analysis of Foods and Beverages, Headspace Techniques.* G. Charalambous (Ed.), 81-94. Academic Press, N.Y.

Wyllie, S.G., Alives, S., Filsoof, M., and Technings, W.G., 1978. Headspace Sampling: Use and Abuse. In *Analysis of Foods and Beverages-Headspace Techniques*, G. Charalamons (Ed.), 57-59. Academic Press, Inc., N.Y.

Yasuda, H. and Rosengren, K., 1970. Isobaric Measurement of Gas Permeability of Polymers. J. Applied Polymer Sci. 11(14):2839.

Ziegel, K.D., Frensdorff, H.K., and Blair, D.E., 1969. Measurement of Hydrogen Isotope Transport in Polyvinyl Flouride Films by Permeation Rate Method. J. Polymer Sci. A2. 7:809.

Zobel, M. G. R., 1982. Measurement of Odour Permeability of Polypropylene Packaging Films at Low Odourant Levels. Polymer Testing. 3:133.