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**EFFECT OF 2-NONANONE VAPOR ON THE OXYGEN AND
CARBON DIOXIDE PERMEABILITY OF TWO POLYMER FILMS**

presented by

DeLynne Vail

has been accepted towards fulfillment
of the requirements for

M.S. degree in Packaging

Major professor

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**EFFECT OF 2-NONANONE VAPOR ON THE OXYGEN AND
CARBON DIOXIDE PERMEABILITY OF
TWO POLYMER FILMS**

By

DeLynne Vail

A THESIS

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

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1999

ABSTRACT

EFFECT OF 2-NONANONE VAPOR ON THE OXYGEN AND CARBON DIOXIDE PERMEABILITY OF TWO POLYMER FILMS

By

DeLynne Vail

In this study the oxygen and carbon dioxide permeability and diffusion coefficients of two polymer films were determined before and after exposure to 2-nonanone vapor. The two polymer films used were low density polyethylene, (LDPE), and a styrene – butadiene copolymer, called KR10.

The diffusion coefficient of oxygen through LDPE film increased by an average of 3.2% when exposed to low concentrations, (197 – 256 ppm), of 2-nonanone and increased by an average of 19.4% when exposed to high concentrations, (346 – 443 ppm), of 2-nonanone. The steady state oxygen permeability of the LDPE film increased by an average of 2.4% and 2.9% after exposure to low and high concentrations of 2-nonanone respectively. For KR10 film, only the high concentration of 2-nonanone had a significant effect on its diffusion coefficient for oxygen. Exposure to 2-nonanone increased KR10's diffusion coefficient by an average of 11.8%. Low and high 2-nonanone concentrations increased the steady state oxygen permeability of KR10 4.1% and 28.2% respectively. The LDPE films had an average of a 91.1% increase in carbon dioxide permeability. The KR10 films had an average increase in permeability of 52.2%.

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INTRODUCTION

In today's time-crunched society consumers are looking for convenience in their food preparation. At the same time, they are also looking for the health benefits of what they eat. To this end, supermarkets have started selling minimally processed fruits and vegetables. Minimally processed is defined as fruits and vegetables that have been washed, peeled, cored and/or sliced. Some fruits and vegetables that have been researched for this type of application include apples, potatoes, carrots, onions, kiwi, and lettuce, (Gil et al., 1996).

In order to sell minimally processed fruits or vegetables they have to be in some type of package. Packaging protects the produce from mechanical damage. It also prevents contamination by insects, dirt and consumer handling and maintains quality of the produce by reducing the evaporation of moisture. The difference between fresh fruits and vegetables and other processed produce is that they remain living and respiring until they are cooked and/or consumed. Respiring fruits and vegetables consume oxygen and release carbon dioxide and heat energy. During this process they can also be subject to attack by microorganisms or fungi.

Another hurdle in the packaging of fresh produce is condensation. Within a closed package of this type the relative humidity increases steadily as the fruit respire. This condensation makes a favorable environment for microorganism growth and decay if the temperature is warm enough. It has been shown that fungal spores that cause decay in fruit will germinate most rapidly when humidities reach 90% or higher and when the temperature is about 75° F (24° C) (Hardenburg, 1971). Some research has been done on spraying fruit with anti-fungal agents. Moyls et al. (1996) studied the effect of using

acetic acid to prevent the growth of *Botrytis cinerea* on strawberries and grapes in MAP and found it to be successful. Leepipattanawit observed that the substance 2-nonanone prevented growth of *Penicillium expansum* and *Botrytis cinerea* on apple slices, (Leepipattanawit et al., 1997). Vaughn et al. (1993) also reported that 2-nonanone inhibited the growth of the fungal species *A. alternata*, *B. cinerea*, and *C. gloeosporioides* on raspberries and strawberries.

Since polymeric packaging materials are permeable they can interact with small molecules like gases, water and organic vapors. It has been shown that polymeric materials experience physio-chemical reactions when exposed to certain permeant molecules, (Wahid, 1996). The degree to which a polymer interacts with a permeant is dependent on the sorption or diffusion capability of the permeant within the polymer and the resulting chemical reactions that may take place between the two. Sorption of certain vapors and gases causes a swelling effect or morphological change in the polymer's structure. This change can then have an effect on the polymer's permeation properties.

In modified atmosphere packaging it is important to know the permeation properties of the film being used. It is also important to know if the permeation properties will change over the shelf life of the product. It is reasonable to ask that if an organic vapor such as 2-nonanone were being used on a product in MAP if it would interact with the polymer film being used. Studies have shown that the sorption of organic vapor can have a swelling effect on the polymer matrix. This can result in additional sorption of organic vapor molecules, (Hernandez and Giacin, 1998). If 2-nonanone has a swelling effect on a polymer film this may alter the film's permeability to oxygen and/or carbon dioxide. The packaging of fresh fruits and vegetables is

determinate on specific amounts of oxygen and carbon dioxide getting through the polymer matrix. Too little oxygen can send produce into anaerobic respiration which leads to fermentation and rot. A careful equilibrium of oxygen and carbon dioxide needs to be kept in order for the fruit or vegetable to maintain freshness and withstand a decent shelf-life. There needs to be an accurate understanding of whether 2-nonanone affects certain MAP films. With this understanding it is possible to better predict the shelf life of MAP products.

In this research project the following hypothesis is examined: The presence of 2-nonanone vapor will affect the oxygen and carbon dioxide permeability and diffusion values of two polymer films. The magnitude of the change will be quantified if the hypothesis is accepted.

The goals of this research were:

1. To develop a test apparatus that can expose polymer films to 2-nonanone vapor and subsequently test their oxygen and carbon dioxide permeability after this exposure. This will include modifications to the Oxtran 100 and Permatran CIV permeability testers.
2. To apply statistical programs to analyze the resultant permeability and diffusion values (after exposure to 2-nonanone vapor).

LITERATURE REVIEW

RESPIRATION OF FRESH PRODUCE

Fruits and vegetables are different from other packaged food items in that they contain living tissue. And for this reason, they respire. The general equation of plant respiration is:



The plant takes in oxygen and together with its stores of glucose it creates water, carbon dioxide and energy in the form of heat.

Normal air is a mixture of three main gases. There is approximately .03% carbon dioxide, 21% oxygen, and 78% nitrogen. Research has shown that produce exposed to reduced oxygen and elevated carbon dioxide levels has a delayed ripening period, reduced respiration rate, reduced ethylene production rate, delayed softening, and delayed compositional changes associated with ripening. (Kader, 1980)

The speed at which a fruit ripens determines its shelf life. The faster it ripens the shorter its shelf life. If altering the gases surrounding the produce can slow the ripening process of produce it will thus extend its shelf life.

MODIFIED ATMOSPHERE PACKAGING

The most important methods to prolong shelf life of fruits and vegetables include refrigeration, maintenance of high humidity, and harvesting at optimum maturity with

minimal mechanical damage (Lee et al., 1995). Refrigeration slows down the respiration process of fruits and vegetables. High humidity keeps moisture in the cell tissue which keeps them alive. Harvesting at optimum maturity means that the fruit is taken at a point where it will not ripen to the point of decay before the consumer gets it but is ripe enough to have the taste qualities that the consumer prefers. Mechanical damage also speeds the process of fruit and vegetable ripening and decay.

More recently there have been many developments in the use of modified atmosphere packaging to prolong the shelf life of fruits and vegetables. Modified atmosphere packaging (MAP) is a passive system based on balancing produce respiration rate and package gas transmission rate, thus creating and maintaining the required CO₂ and O₂ levels under steady-state conditions in the package (Lee et al., 1996). A passive system does not introduce foreign gases to help prolong the shelf life of the commodity. Instead, this type of packaging relies on the interaction of respiration of the product and the permeability rates of the packaging film to produce the steady state levels of CO₂ and O₂.

The goal of MAP for fresh produce is to prolong shelf life by reducing the rate of respiration of the product. It has been determined that lowering oxygen concentrations below 8% will have a significant effect on slowing down fruit ripening, and the lower the oxygen concentration, the greater the effect. (Kader, et al., 1989).

Each fruit has a minimum oxygen concentration tolerance and if it is exposed to less oxygen than this level it may go into anaerobic respiration. This will increase the accumulation of ethanol and acetaldehyde causing off-flavors. Successful MAP will maintain near optimum O₂ and CO₂ levels to achieve the benefits of a modified

atmosphere but will not exceed the limits of tolerance for minimum oxygen concentration which could lead to the above mentioned anaerobic respiration.

MECHANISM OF MASS TRANSPORT

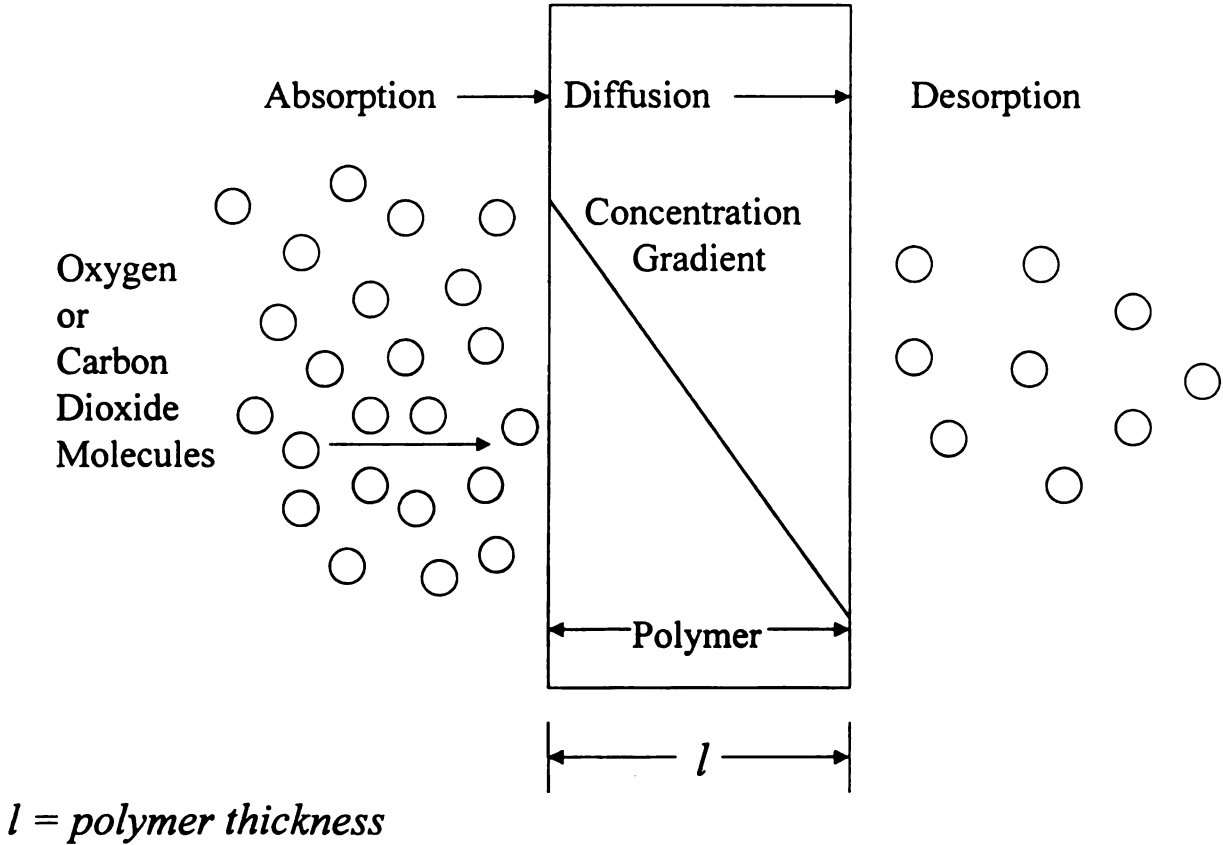
Mass transfer of molecules into or out of a package can lead to further changes in the product, package, or both.

Permeation through polymer membranes involves the transport of a gas or vapor through a homogeneous membrane. This membrane should be free of gross defects such as pores or cracks.

There are three steps to permeation which are :

- Absorption at the higher concentration surface of the polymer
- Diffusion of the permeant through the polymer bulk phase
- Desorption of the permeant on the low concentration side of the polymer

Figure 1: The Permeation Model



The process of sorption is known to follow Henry's law:

$$C = S * p \quad (1)$$

Where C is the concentration of the penetrant in the polymer,

P = the partial pressure of the penetrant in the gas/vapor phase, and

S = the solubility coefficient (Comyn, 1985)

Films along with gases and vapors all have their own solubility coefficients.

Research has shown that if a polymer and a gas or vapor have equal solubility coefficients then they will be mutually soluble (Hernandez and Giacini, 1998).

The diffusion of the permeant through the polymer membrane can be described as a series of successive jumps where the permeant particle passes over the molecular barriers of the polymer matrix from one position to the next. This means that permeation is an "activated" process.

The "jump" or particle diffusion depends on the rearrangement of the penetrant particles and the surrounding polymer. Molecular forces and movement activation energies must be overcome in order for the penetrant particles to be able to move within the polymer molecular structure. Certain types of cohesive energies such as Van der Waal's forces or hydrogen bonds must be overcome between molecules and chain segments in order to get them to break apart and let permeant particles pass. This process requires energy directed against the cohesive forces of the polymer's molecular structure. When enough energy is provided, the segments of the polymer structure begin to rearrange enough to allow for the passage of penetrant molecules. (Comyn, 1985). Diffusion thus depends on the relative mobilities of the permeant particles to their

surrounding polymer segments.

Therefore it can be reasoned that anything which affects the arrangement of the polymer segments in their contact with permeant and the cohesive forces that hold the segments together will affect the diffusion of permeant particles. Factors that can influence the polymer/permeant relationship include:

1) Morphology of the polymer

Studies have shown that the transport of gas or vapors through a polymer occurs only in the amorphous (non-crystalline) regions (Murray and Dorschner, 1983).

The more regular the polymer chains the more easily they can pack close together. Close packing is a measure of crystallinity. The more crystalline a polymer is, the more difficult it is for a permeant to pass through it.

2) Polymer chain flexibility

This is the ability of the polymer chains to move relative to one another. This is related to the glass transition temperature, (T_g), of the polymer above which chain mobility is high and below which chain mobility is extremely low. Below the T_g the size and frequency of voids between the polymer chains is fixed. Above the T_g the size and frequency of these voids is a function of temperature. Usually the higher the temperature, the more mobility in the polymer chains. The more flexibility/mobility that the polymer has, the more free volume it has. Thus it is easier for permeant molecules to pass through it.

3) Intermolecular forces

Cohesive energy density, which produces strong intermolecular bonds and Van der Waal's forces, is the measure of the strength of the bonds between molecules. The

strength of the bonds between molecules in the polymer will affect the forces of attraction between the polymer chains. This has a strong influence on the T_g . The stronger the bonds the higher the T_g will be.

4) Concentration of permeant and permeant type

Many sorbed penetrant molecules can act as plasticizing agents in the polymer structure, (Hernandez and Giacin, 1998). Plasticizing allows for the ease of movement between polymer chains and easier diffusion of penetrant molecules.

Organic molecules are known to readily diffuse through polymer structures in which they solubilize easily, (Mohny et al., 1988).

5) Temperature

Higher temperatures usually lead to higher molecular energies. Higher molecular energy increases the speed of movement of molecules. Higher temperature makes it much easier for penetrant molecules to diffuse through polymer molecules.

Fick developed the first law of diffusion, (Equation 2). It states that the rate of transfer of a diffusing substance through a unit area is proportional to the concentration gradient measured normal the section, (Comyn, 1985).

This law can only be applied to diffusion in the steady state.

$$F = -D(C_2 - C_1)/l \quad (2)$$

Where:

F = rate of transfer of penetrant per unit area at steady state

D = diffusion coefficient (length²/time)

l = thickness of the film

Desorption takes place on the opposite side of the polymer film as absorption.

This is where the permeant moves off of the polymer surface into the environment. The amount of desorption that takes place is dependent on the concentration of permeant at or near this surface.

When Henry's Law is obeyed, the steady state rate of diffusion can be expressed as a combination of both Henry and Fick's Laws:

$$F = S * D * \frac{\Delta p}{l} = P * \frac{\Delta p}{l} \quad (3)$$

$$P = S * D \quad (4)$$

Δp = pressure difference between top and bottom faces of the polymer film

PERMEABILITY OF ORGANIC VAPORS THROUGH POLYMER FILMS

There have been many studies done on the permeation of organic vapors through polymer films. Franz studied the permeation of d-limonene across a biaxially oriented polypropylene film (Franz, 1993). Theodorou and Paik (1992) studied the permeation of linalool, citral, ethyl butyrate, and d-limonene in low density polyethylene film. These studies were conducted to determine the barrier properties of these films to certain organic vapors commonly produced by food products. The concern was over the possibility that permeation of organic vapors may lead to loss of aroma or flavor compounds. In these studies it was the organic vapor that was the permeant measured.

Studies involving organic vapors as permeants have shown that most organic vapors interact and swell the polymer (Theodorou and Paik, 1992) as a plasticizer would. At high vapor concentrations this swelling was significant enough to have an effect on the permeability coefficient of the vapor studied. Hernandez and Giacin (1998) found ethyl acetate caused PET film to swell. This penetrant-polymer interaction was attributed

to the fact that ethyl acetate and PET have a similar polarity in structure and similar solubility coefficients.

PERMEABILITY MEASUREMENTS

The permeability of a plastic film (P) is a measure of the rate at which a permeant can pass through the film in a unit of time, dependent on permeant partial pressure, film thickness and film surface area.

$$P = \frac{(q)(l)}{(a)(t)(\Delta p)}$$

q = quantity of permeant

l = film thickness

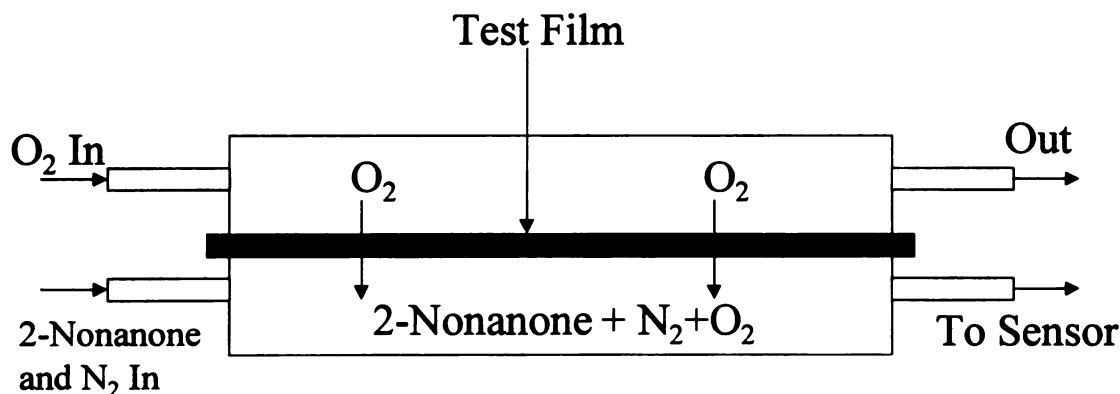
a = film area

t = time

One way to measure the permeability of a film to oxygen is the isostatic method. The isostatic method developed by MOCON, (Oxtran 100, Modern Controls Inc. Elk River, MN), involves a film sample that is mounted between two chambers (see Figure 2). The permeant gas, (oxygen), enters one chamber, creating a higher concentration of the permeant in this chamber. Because of the pressure differential the permeant diffuses through the film and thus enters the second chamber of lower concentration. From this second chamber a carrier gas transports the permeant molecules (oxygen) to a sensor which quantifies the amount permeated per unit of time and film area. It is called an isostatic method because the total pressure on both sides of the film is constant and generally is kept at atmospheric pressure.

Figure 2:

Diagram of an Isostatic Permeability Test Cell in the Modified Oxtran 100



To calculate the diffusion coefficient of a permeant through a film using the isostatic method the equation is: (Gavara and Hernandez, 1993).

$$\frac{F_t}{F_\infty} = \left(\frac{4}{\sqrt{\pi}} \right) \left(\frac{l^2}{4Dt} \right)^{1.2} \sum_{n=1,3,5} \exp\left(\frac{-n^2 l^2}{4Dt} \right) \quad (6)$$

This expression applies to the unsteady state portion of the curve only.

F_t is the flow rate of the penetrant at time (t) and F_∞ is the flow rate of the permeant at steady state.

ORGANIC VAPORS USED ON FRUITS TO PREVENT FUNGAL GROWTH

Recent studies have shown that some organic vapors have a fungistatic effect on selected fruits. Song showed that hexanal vapor was effective at the prevention of

growth of *Penicillium expansum* and *Botrytis cinerea* on apple slices, (Song, et al., 1996).

In other research, a modified atmosphere package was used in combination with fumigation with low concentrations of acetic acid on grapes and strawberries. This was shown to prevent storage rot and increase the shelf life of these two commodities. This method helped to prevent the growth of *Botrytis cinerea*, (Moyls, et al., 1996).

Anderson studied the antifungal activity among volatile C₆ and C₉ aliphatic aldehydes, ketones, and alcohols. In his research he found that they were effective in the prevention of growth of *Alternaria alternata*. He concluded that the C₉ aldehydes and ketones, including 2-nonanone, were the most potent in their antifungal activity, (Anderson et al., 1994).

Vaughn studied fifteen natural volatiles released by raspberries and strawberries during ripening. Of these fifteen volatiles he found that benzaldehyde, 1-hexanol, E-2-hexenal, and 2-nonanone inhibited the growth of three fungal species, *Alternaria alternata*, *Botrytis cinerea*, and *Coletotrichum gloeosporioides* (Vaughn et al., 1993).

Most recently, Leepipattanawit et al. (1997) used a vapor generating system to expose apple slices to 2-nonanone vapor. Through this research it was determined that 2-nonanone was effective at the prevention of *Penicillium expansum* and *B. Cinerea* growth on apple slices and potato dextrose agar.

STUDIES OF ORGANIC VAPOR INTERACTION WITH POLYMER FILMS

Numerous studies have been conducted to research the effects of organic vapors on the permeability of polymer films. Most of these studies however, have concentrated on permeation rates of these organic vapors through selected polymer films and how to

measure them, (Franz, 1993). Some studies have paired two or more organic vapors to see how the presence of the other vapor(s) may affect the permeation of the first organic vapor (Nielsen and Giacini, 1994).

There seems to be a lack of research in the area of how organic vapors influence the permeation rates of CO₂ and O₂ through polymer films. CO₂ and O₂ are of primary importance in modified atmosphere packaging of fruits and vegetables. Ampolsak (1992), studied the effect of ethanol vapor on the oxygen permeability of selected films. This was done because organic compounds such as ethanol are generated during the anaerobic phase of fruit and vegetable respiration.

MATERIALS AND METHODS

A. Materials

1. Polymer Test Films

a. Low Density Polyethylene (LDPE) $\text{H}-(\text{CH}_2)_n-\text{H}$

Dow Chemical Company, (Midland, Michigan), supplied the LDPE film used. Its thickness was 1.25 mil (0.003175 cm).

The LDPE film used had a crystallinity in the range of 40 – 50% and its density is 0.912 g / cm³.

LDPE is produced by the polymerization of ethylene gas. It is made up of both short and long chain branches. It contains no hydrogen bonding elements and has a non-polar structure. Its T_g is -120°C.

This film has good oil resistance but it is a poor barrier to most gases. It is highly permeable to oxygen and carbon dioxide. It also sorbs organic vapors easily.

b. KR10

The other film used was KR10 (Phillips Chemical Company, Bartlesville, Oklahoma). It is a styrene-butadiene amorphous block copolymer.

The thickness was 1.0 mil (0.00254 cm).

The density of KR10 is 1.01 g/cm³. Its T_g is 62 °C.

KR10 meets FDA specifications (CFR 177.1640) for use with food.

It is characterized as a film that is highly permeable to both oxygen and carbon dioxide gases.

2. Penetrant

a. 2-Nonanone

The penetrant was 2-nonanone, (Aldrich Chemical Company, Saint Louis, MO). Also called methyl-heptyl-ketone. $\text{H}_3\text{C}(\text{CH}_2)_6\text{COCH}_3$.

It was stored at 4°C until used. The density of 2-nonanone is 0.832 g/mL, molecular weight = 142.24 g/mol, and boiling point = 195°C.

2-nonanone is a colorless liquid found in the attar of rose, clove oil, passion flowers, sorghum, asparagus, tomato, corn, cheese, and beer. It has some bactericidal activity. It is an alarm pheromone in ants, hornets, and honeybees. It is moderately toxic by ingestion.

b. Acetonitrile CH_3CN

Acetonitrile, (EM Science, Gibbstown, NJ), was the solvent used to dilute 2-nonanone for the gas chromatograph tests.

3. Gases

a. Carrier Gas

Nitrogen dry grade gas containing 2% hydrogen was used for the oxygen permeability tester (Oxtran 100). Pure nitrogen gas (100%) was used for the carbon dioxide permeability tester (Permatran CIV). Both gases were supplied by AGA Gas, Inc. (Cleveland, OH).

b. Permeant Gas

Oxygen supplied in the form of compressed air (O_2 partial pressure of 0.21 atm) (AGA Gas, Inc., Cleveland, OH), was used as the oxygen source for the Oxtran 100 tests. Carbon dioxide gas, (AGA Gas, Inc., Cleveland, OH), was used as the carbon dioxide source for the Permatran CIV tests.

4. Equipment

a. Oxtran 100

The Oxtran 100, (Modern Controls Incorporated, Minneapolis, Minnesota), was the instrument used to measure the oxygen permeability of the test films. It uses the isostatic method to test oxygen permeance of films or packages. It has a single film testing station.

b. Oxygen Transmission Rate Datalogger Model DL200

Oxygen transmission was monitored using this datalogger, supplied by Modern Controls Incorporated, Minneapolis, Minnesota. Data for oxygen permeability was collected every two minutes.

c. Permatran CIV

Supplied by Modern Controls Incorporated, Minneapolis, Minnesota. It uses the Dynamic Accumulation method to test carbon dioxide permeance of films or packages. It has three film testing stations.

d. Chart Recorder Model L6512

The chart recorder, (Linseis), recorded the steady state permeation values of each film to carbon dioxide in ten-minute increments.

B. Methods

1. Setup Schematic for 2-nonanone Vapor Generation and Subsequent Oxygen Permeability Testing

The apparatus used consisted of an Oxtran 100 and a piping system to generate and control the vapor stream of 2-nonanone, and a datalogger, (Figure 3). Normally the Oxtran is connected to a test gas, (oxygen or air), and a carrier gas, (98% nitrogen and 2% oxygen). The system for this research project was modified in that the carrier gas line is split into three lines. One of these lines goes into the 2-nonanone washing bottle which contains pure (99%+) 2-nonanone liquid. The bubbler in this bottle creates 2-nonanone vapor of a concentration of approximately 2000 ppm. The required concentrations of 2-nonanone were reached by blending it with a stream of carrier gas coming from the “mixing line” shown in Figure 3. The flow of gas and vapor streams was controlled by a series of needle valves. The flow of gas and vapor streams was monitored using flow meters. Exiting off of the “mixing line” is another line of pure carrier gas. This line is used when running a regular oxygen permeability test, thus not exposing the film to any 2-nonanone.

OXYGEN MEASUREMENTS

The oxygen permeability of the film samples was determined in accordance with the ASTM Standard D3985-81, “Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor”. The Oxtran 100 Permeability Tester (Modern Controls, Inc., Elk River, MN), employs an isostatic method. The gas that permeates the film is conveyed to the sensor by a carrier gas. Each film sample was

tested three times. The first and second measurements were for oxygen permeability control, where the film sample was not exposed to 2-nonanone vapor. These tests were done in duplicate to ensure stability of the baseline before the film was exposed to the 2-nonanone. After each measurement was finished, the film was allowed to equilibrate in the test cell for approximately four hours before the next test. When the two non-exposed oxygen tests were completed the valves were adjusted on the system of piping to allow for the carrier gas to generate a 2-nonanone vapor stream and for the vapor to enter into the Oxtran carrier gas stream.

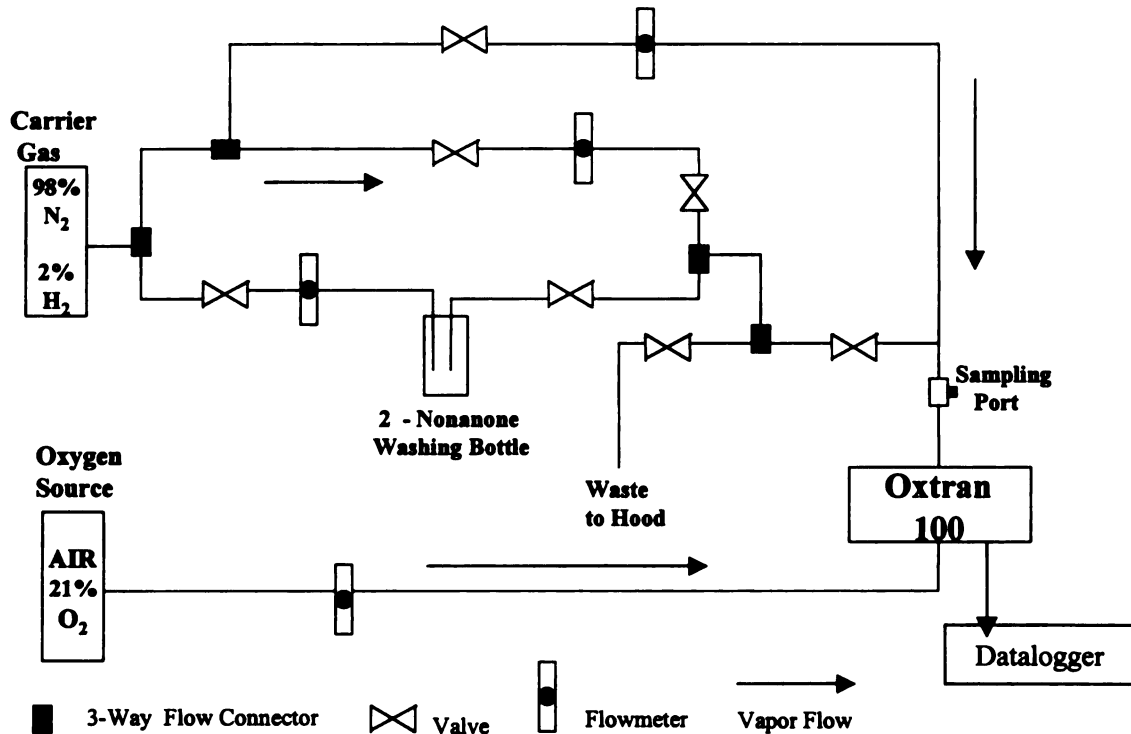
The Oxtran was left in the “carrier purge” mode in order to expose both sides of the film to the 2-nonanone/carrier gas stream. The LDPE films were exposed in this fashion for approximately 5 to 6 hours and the KR10 film were exposed for approximately 3 1/2 days. After the designated exposure time was reached, an oxygen permeability test was run on the film, while continuing exposure to 2-nonanone vapor on one side only.

The output for these tests was collected by the DL 200 Datalogger. The datalogger converted the voltage response on the coulometric detector to an oxygen permeance response. Readings were recorded every 2 minutes and were reported in units of $\text{cc/m}^2 \cdot \text{day}$.

The results of this third test, after 2-nonanone exposure, were then compared statistically to the average of the results of the first two regular oxygen tests to determine if there was a significant difference in the “before 2-nonanone exposure” oxygen permeation values to the “after 2-nonanone exposure” oxygen permeation values. We

were interested in the effect of the first exposure therefore only one measurement was carried out on each film.

Figure 3: Schematic of the 2-Nonanone Exposure System for Oxygen Permeability Testing



Both of the test films, LDPE and KR10, are known to be highly permeable to oxygen and thus an aluminum mask was used to reduce the exposed surface area of the film by a factor of ten. Compressed air was used as the oxygen test gas source to reduce the amount of permeated oxygen conveyed to the sensor, as it contains only 21% oxygen.

CARBON DIOXIDE MEASUREMENTS

The setup for the carbon dioxide testing was very similar to that for the oxygen testing. (Figure 4). There were, however, two differences compared to the Oxtran 2-nonanone setup (Figure 3). The first was that the 2-nonanone vapor was generated using the test gas stream, (carbon dioxide), and not the carrier gas stream. The reason for this was that the carbon dioxide stream is in constant contact with the film samples whereas the carrier gas stream is only in contact with the films periodically during the actual testing period. The other difference was that the 2-nonanone vapor generating line was physically taken off -line when not exposing the films to the vapor. The pure carbon dioxide line was hooked up straight from the source tank when running the regular carbon dioxide tests.

The Permatran CIV system is similar to the Oxtran 100 in that as the molecules of carbon dioxide permeate through the test film they are transported to a sensor by the carrier gas. The sensor on the Permatran is different from the Oxtran in that it is an infrared sensor.

The continuous flow method was employed to analyze the test films. This method is used for the evaluation of moderate to high transmitting films such as LDPE and KR10. When the continuous flow method is used, the Permatran is acting as a comparator in which the test films are being compared to a given reference film value. In order to do this the value of the reference film has to be determined. Running a dynamic accumulation test on the reference film provides a method for determining the permeability of the test film under control conditions. Once the reference film value has been determined, then the reference film is run along side the test films in the

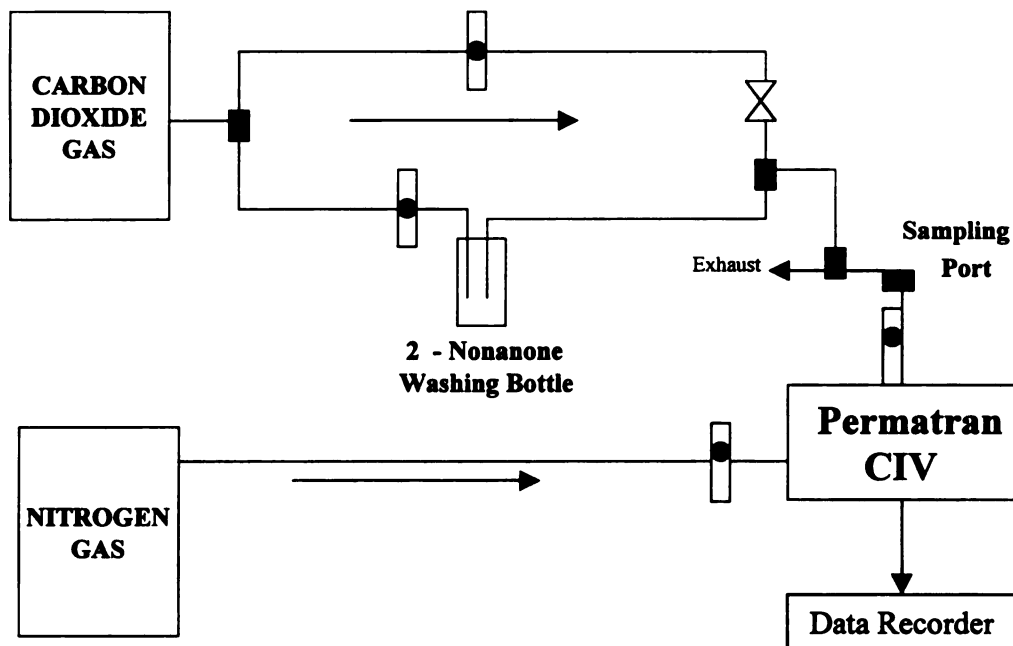
continuous flow method and through a series of calculations the values of the test films can be determined using the value of the reference film. The continuous flow test method was run on the films six times before 2-nonanone exposure and then six times after 2-nonanone exposure.

Unlike the single station Oxtran 100, the Permatran had three stations for testing films. Once the 2-nonanone vapor generating system was interfaced to the Permatran CIV system the three test stations were being exposed simultaneously to the 2-nonanone vapor. After the designated exposure time the vapor was allowed to continue flowing while the last set of six tests were run.

The output from the Permatran CIV system was monitored on a strip chart recorder, with lines denoting a certain amount of voltage created by the test samples. The voltage response was compared to that of the reference film. Through a series of calculations involving the value of the reference film, (see Appendices 4 and 5), the CO₂ permeation values of the test films were determined.

The results were analyzed statistically to determine if the CO₂ permeation values before 2-nonanone exposure were significantly different from the CO₂ permeation values after 2-nonanone exposure.

Figure 4:
Schematic of the 2-Nonanone Exposure System for
Carbon Dioxide Permeability Testing



2-NONANONE CONCENTRATION DETERMINATION

Two different concentrations of 2-nonanone were used during the oxygen permeability testing and one concentration was used for the carbon dioxide testing.

Quantification of 2-nonanone concentration in the test chamber(s) was determined by a gas chromatographic analysis using a flame ionization detector. The settings for the gas chromatograph are shown in Appendix 1.

CALIBRATION CURVE

Standard concentrations were prepared by diluting a certain amount of known concentration stock solution of 2-nonanone and acetonitrile. In this way, several concentrations of 2-nonanone in acetonitrile were prepared. A calibration curve was generated using a gas chromatograph. The quantity injected versus area unit response was plotted, (Appendix 1). The equation of the line describing the relationship between the quantity injected and detector response is $y=20,644,615x$, where y equals area unit response (AU), and x equals quantity of 2-nonanone injected ($\times 10^{-6}$ grams). $R^2 = 1.00$.

At various times during the exposure period of the film to the 2-nonanone a sample of the vapor stream was taken at the sampling port using a 500 μ l syringe. As shown in figures 3 and 4, the sampling port was located just before the entrance of the carrier gas line on the Oxtran and just before the carbon dioxide entrance on the Permatran. The contents of the syringe were then injected into the gas chromatograph and analyzed for area unit response. This response was then converted into a concentration amount using the calibration curve.

DETERMINATION OF FILM EXPOSURE TIME TO 2-NONANONE VAPOR

Each film needed to be exposed to the 2-nonanone vapor long enough for the 2-nonanone vapor to reach steady state permeation through the film before exposing it to oxygen. The equation used to estimate the time to reach steady state of a permeant through a film is: (Hernandez, 1996)

$$T = \frac{l^2}{D} \quad (7)$$

T = lagtime

l = thickness of the film

D = diffusion coefficient of the permeant through the film

The diffusion coefficient of 2-nonanone through LDPE is known to be $D = 3.1 \times 10^{-14} \text{ m}^2/\text{sec}$ (Wahid, 1996). The thickness of LDPE film used in this study was $31.75 \times 10^{-6} \text{ meter}$, (1.25 mil). Solving for T here we get 4.5 hours of exposure time to reach steady state permeation of 2-nonanone vapor through LDPE film.

The diffusion coefficient of 2-nonanone through KR10 film is not known and therefore had to be estimated. The diffusion coefficients of d-limonene and ethyl acetate through KR10 film (McDowell, 1997). 2-nonanone has a molar volume of 171, d-limonene of 162, and ethyl acetate of 98. Therefore 2-nonanone is likely to behave more like d-limonene than ethyl acetate when diffusing through the KR10 film and therefore have a similar diffusion coefficient. When substituting the diffusion coefficient of ethyl acetate ($3.3 \times 10^{-14} \text{ m}^2/\text{sec}$) (McDowell, 1997) into the above equation, the exposure time to reach steady state is about 3 hours. If one substitutes the diffusion coefficient of d-limonene through KR10 film ($3.0 \times 10^{-15} \text{ m}^2/\text{sec}$) (McDowell, 1997) into the above equation the exposure time to reach steady state is 30 hours. (The thickness of KR10 film used was $2.54 \times 10^{-6} \text{ meter}$ or 1 mil). Because the molar volume of 2-nonanone is larger than that of d-limonene it is estimated that the time to reach steady state permeation will be longer. Therefore a safe estimate was determined to be 80 hours.

CONSISTENCY TEST

The data from the Oxtran permeability tests was subjected to a consistency test developed by Gavara and Hernandez, (1993), specifically for continuous flow experimental data.

When running an oxygen permeability test, the need arises to detect variations in the system's parameters such as temperature and concentration variations and to determine if they have affected the consistency of the data. The correctness of the permeability data will affect all future calculations regarding diffusion coefficients and/or steady state values.

The consistency test involves determining the $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ values. These values correspond to the $1/4$ time it takes to reach steady state, $1/2$ the time it takes to reach steady state, and $3/4$ the time to reach steady state, respectively. These values are used to determine values for K_1 and K_2 . $K_1 = (t_{1/4}) / (t_{3/4})$. $K_2 = (t_{1/4}) / (t_{1/2})$. The range for the accepted consistent experimental values of K are $0.42 \leq K_1 \leq 0.46$ and $.65 \leq K_2 \leq 0.69$. Tables 11 and 12 show the results of the consistency tests for the Oxtran tests of LDPE and KR10.

STATISTICAL ANALYSIS

The statistical methods employed in this study were used to determine whether to accept or reject our hypothesis. Specifically, we wanted to know if there were significant differences between:

- 1) The oxygen diffusion coefficients (D) corresponding to zero 2-nonanone exposure, low concentration 2-nonanone exposure, and high concentration 2-nonanone exposure.
- 2) The steady state rate of oxygen permeation values at zero 2-nonanone concentration versus low 2-nonanone concentration and high 2-nonanone concentration exposed films.
- 3) The carbon dioxide permeation coefficient values at zero 2-nonanone concentration versus the ones exposed to 2-nonanone vapor.

All of the statistical analyses were carried out using the SAS computer software program using an input of all the data for the LDPE and KR10 films. (SAS/STAT User's Guide. Version 6, 4th Edition, 1990, SAS Institute, Cary, NC). This program was not used to compare any data between LDPE and KR10.

1) Singular Film Comparison of Diffusion Coefficients

Each film had a series of three oxygen tests run on it. The first two tests were control tests, where the film was not exposed to 2-nonanone vapor. The third test was run on the film after it was exposed to the 2-nonanone vapor. The results of the two control tests were compared to the result of the test after 2-nonanone exposure. There were five replicates of LDPE films tested at low 2-nonanone concentration exposure, five replicates of LDPE films tested at high 2-nonanone concentration exposure, five replicates of KR10 films tested at low 2-nonanone exposure and five replicates of KR10 films tested at high 2-nonanone concentration exposure. We refer to a "run" as an individual permeation experiment. Using the SAS program PROC NLIN (SAS, 1990)

the data, for one film at a time, was then fitted to a non-linear regression curve using the equation: (Gavara and Hernandez, 1993)

$$\frac{F_t}{F_\infty} = \left(\frac{4}{\sqrt{\pi}} \right) \left(\frac{l^2}{4(D + \delta)t} \right)^{1.2} \sum_{n=1,3,5} \exp\left(\frac{-n^2 l^2}{4(D + \delta)t} \right) \quad (8)$$

where: $\delta = 0$, if treatment = control

$\delta \neq 0$, if treatment = 2-nonanone

The parameter $(D + \delta)$ was estimated for each film. The diffusion coefficient value, D , was the control, (at zero 2-nonanone concentration). The (δ) was the difference between the control and the treated diffusion coefficient value. $(D + \delta)$ is the value of the diffusion of oxygen in the presence of 2-nonanone. A 95% confidence interval was provided for both parameters. If the confidence interval for (δ) did not contain zero then the estimated difference between the control D -value and the treated D -value was statistically significant, at a Type I error rate of 5%.

2) Comparison of All Diffusion Coefficients

Each polymer film, LDPE and KR10, had ten sections of data. Five sections were used to compare low concentration of 2-nonanone vapor to control and five were used to compare high concentration of 2-nonanone vapor to control. This design further allowed an indirect comparison of low to high 2-nonanone concentration.

HYPOTHESIS

The data was labeled according to three treatments. Treatment 1, (trt1), corresponded to no 2-nonanone exposure (regular oxygen test). Treatment 2, (trt 2),

corresponded to low concentration 2-nonanone exposure. Treatment 3, (trt 3), corresponded to high concentration 2-nonanone exposure.

Using SAS PROC NLIN on all sets of data a non-linear regression analysis was used to estimate 3 D-values: those for 1) zero 2-nonanone exposure, 2) low 2-nonanone concentration exposure, and 3) high 2-nonanone concentration exposure. The effect of films was also accounted for in the analysis. The effect of films was also accounted for in the analysis. The 95% confidence intervals for each D-value are also computed. If any two confidence intervals do not overlap then the corresponding D-values are surely known to be significantly different ($P < 0.05$). Nevertheless, two D-values may be statistically different even if their confidence intervals overlap.

3) Comparison of Steady State Values of Oxygen Permeation

Data was entered and labeled according to one of the three treatments, film number and the corresponding steady state oxygen permeation value observed. To determine if the steady state values of permeation differed between treatments an ANOVA test was run on SAS. Pair-wise t-tests were run to compare each of the three treatments' steady state values to the others. The analyses used blocked on film. If the p-value between a comparison of two treatments is less than 0.05 this means that the films were significantly different at steady state.

4) Comparison of Steady State Values of Carbon Dioxide Permeation

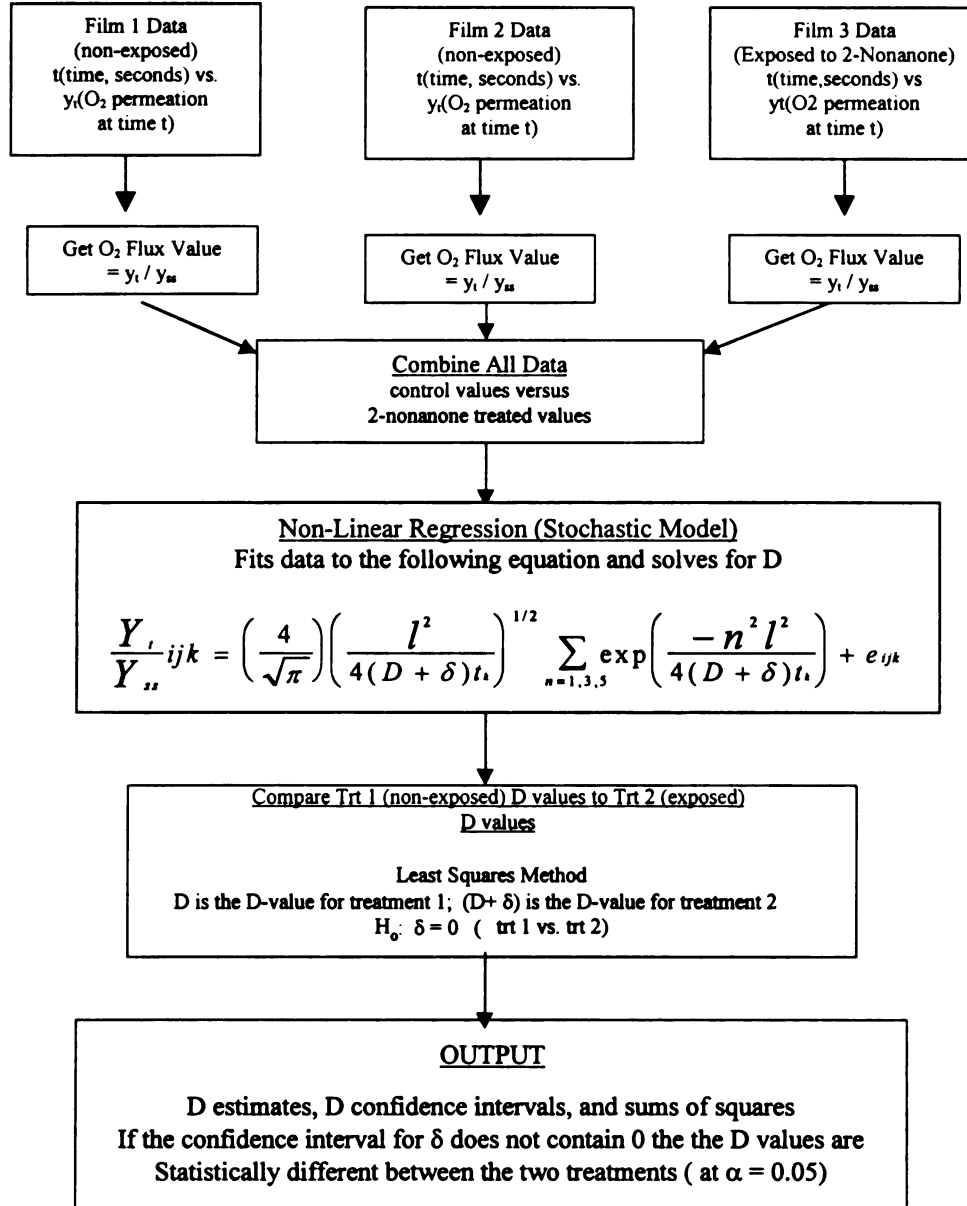
With the Permatran tests there were only two treatments. Treatment 1 was no 2-nonanone exposure and treatment 2 was high concentration 2-nonanone exposure.

First, all the data for one type of film (LDPE or KR10) is entered and labeled according to treatment 1 or treatment 2 and film section.

An analysis of variance (ANOVA) based on the use of SAS PROC GLM was used, (SAS, 1990). Treatment differences were assessed by an analysis of variance by blocking on film section.

Figures 5 – 8 are flowcharts of how the above-mentioned statistical programs ran.

Figure 5: SAS Single Film Comparison Test



Note: D is the diffusion coefficient of the non-exposed (control), f_j is the effect of the jth film, e_{ijk} is the error pertaining to the kth time period on the jth film, and $e_{ijk} \sim N(0, \sigma^2)$.

Figure 6: SAS Overall Comparison of Diffusion Coefficients

D_i is the diffusion coefficient for the i th treatment, f_j is the effect of the j th film and e_{ijk} is the error term pertaining to the i th treatment, j th film and k th time period. $e_{ijk} \sim N(0, \sigma^2)$.

Trt 1 = no 2-nonanone exposure

D = diffusion coefficient for trt 1

Trt 2 = low concentration 2-nonanone exposure

D_1 = diffusion coefficient for trt 2

Trt 3 = high concentration 2-nonanone exposure

D_2 = diffusion coefficient for trt 3

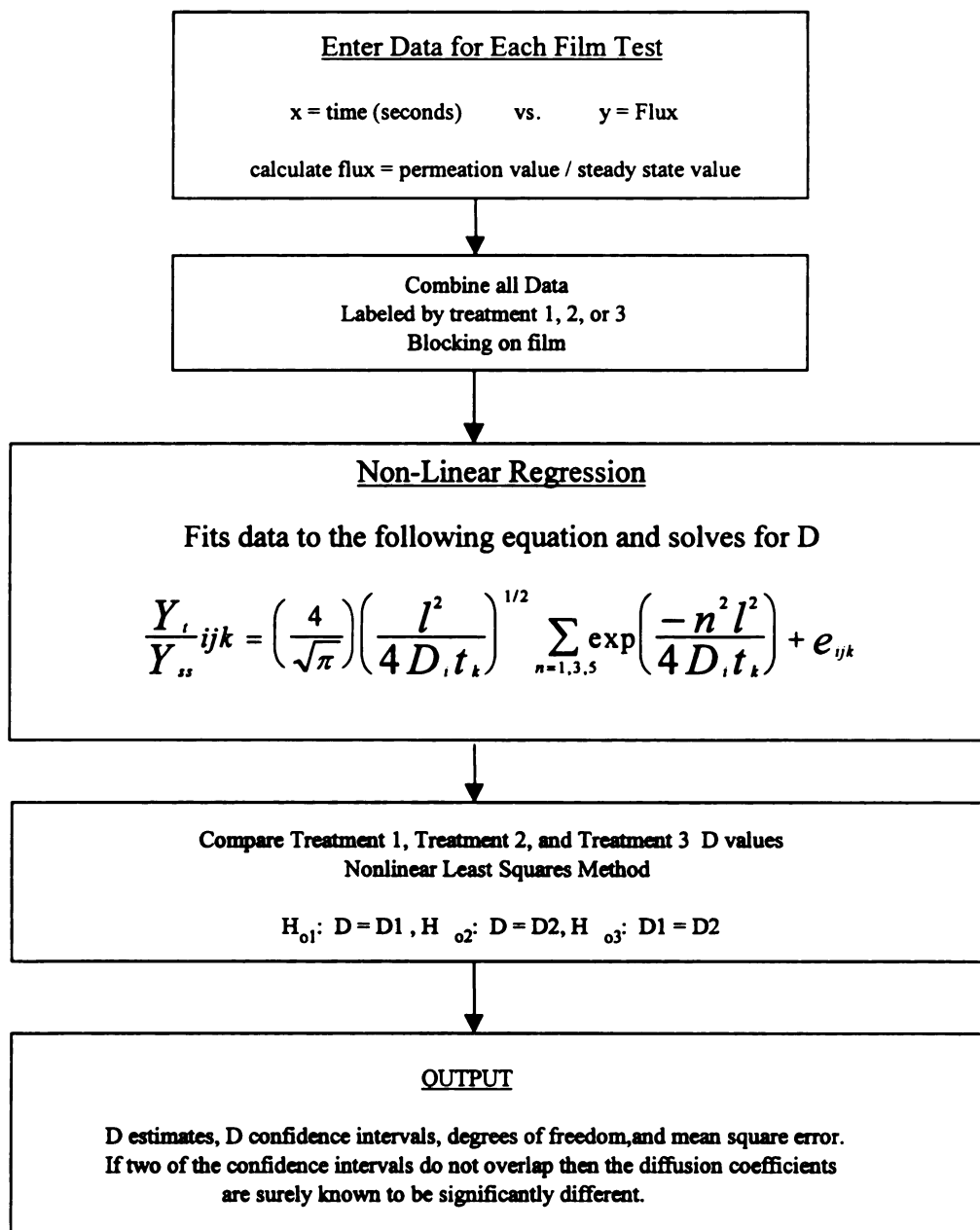


Figure 7: SAS Comparison of Steady State Oxygen Permeation Values

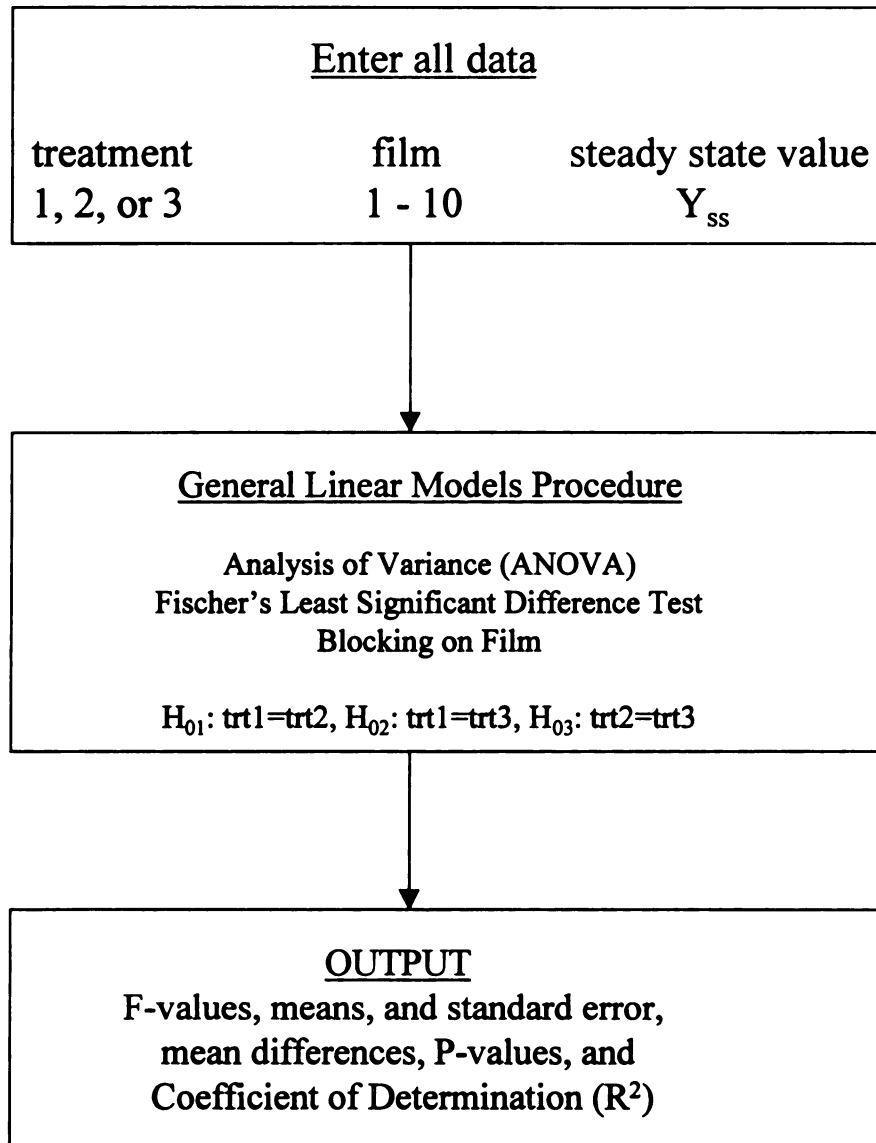
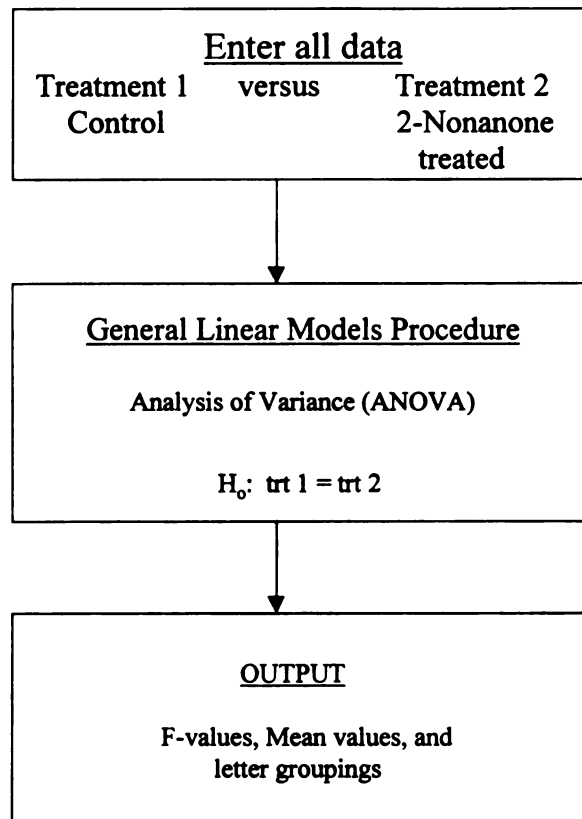


Figure 8: SAS Comparison of Steady State CO₂ Permeation Values



RESULTS AND DISCUSSION

The Standard Calibration Curve.

The relationship between the GC response and 2-nonanone concentration was found to be linear (See Appendix 1). The GC-response was linear with 2-nonanone concentration according to the following equation

$$Y = 20644615 X$$

where X is the quantity of 2-nonanone injected (μg) and Y is the GC response in area units. The coefficient of determination (r^2) was 0.995. The original hypothesis of this research project was whether the presence of 2-nonanone vapor affected the oxygen and carbon dioxide permeability and diffusion values of the two films studied.

The statistical analysis of the data was done using four different SAS programs. The first SAS program, called the Single Film Comparison Test, was used to compare the diffusion coefficients (D) of oxygen an a film by film basis. This test takes the data through non-linear regression and a least squares method to determine the D values and whether they are statistically different between the non-exposed and exposed film. Each film sample had three tests run on it that included two oxygen control tests and one test after the exposure to 2-nonanone vapor. The two control tests were denoted as treatment 1 while the third test was denoted treatment 2. Tables 5A, 5B, 6A, and 6B show the results of this analysis.

Tables 1 and 2 summarize the concentration of 2-nonanone at which each film sample was exposed to before testing for oxygen permeability and the effect on oxygen permeability that was measured after 2-nonanone exposure.

Table 1: Oxygen Permeability of LDPE Films

Run Number	Concentration of 2-nonanone Exposure (ppm)	Change in Permeability (%)
1	240	0.8
2	256	4.2
3	197	2.4
4	209	4.1
5	220	0.7
6	443	4.1
7	381	0.6
8	386	-0.3
9	346	6.5
10	358	3.5

Table 2: Oxygen Permeability of KR10 Films

Run Number	Concentration of 2-nonanone Exposure (ppm)	Change in Permeability (%)
1	283	5.0
2	317	5.6
3	279	3.9
4	335	1.1
5	282	5.1
6	322	28.3
7	337	29.2
8	300	27.5
9	433	22.7
10	518	33.1

Tables 3 and 4 summarize the concentration of 2-nonanone at which each film sample was exposed to before testing for carbon dioxide permeability and the effect permeability that was measured after 2-nonanone exposure.

Table 3: Carbon Dioxide Permeability of LDPE Films

Run #	Concentration of 2-nonanone Exposure (ppm)	Change in Permeability (%)
1	351	78.7
2	351	110.8
3	351	93.5
4	333	59.0
5	333	82.2
6	333	100.0
7	454	77.2
8	454	73.8
9	454	144.4

Table 4: Carbon Dioxide Permeability of KR10 Films

Run #	Concentration of 2-nonanone Exposure (ppm)	Change in Permeability (%)
1	370	51.0
2	370	44.3
3	370	34.7
4	349	28.8
5	349	29.4
6	349	31.1
7	446	78.8
8	446	63.3
9	446	108.0

Tables 5A and 6A show the results for the low concentration 2-nonanone exposure to the LDPE and KR10 films respectively. Listed as D in these tables are the diffusion coefficient values for the control oxygen tests that were conducted. The $D + \delta$ values represent the diffusion coefficients of the same films after exposure to 2-nonanone. The last column denotes whether or not H_0 was rejected. If the answer is YES this means that we reject the null hypothesis ($P < 0.05$) and therefore the diffusion coefficient values were significantly different. δ is the incremental difference in diffusion. The null hypothesis is $H_0: \delta = 0$ meaning that the incremental difference in diffusion is zero after exposure to 2-nonanone. The confidence intervals given in this program are for δ . Therefore if the confidence interval does not include zero then δ does not equal zero and therefore H_0 must be rejected.

The tables 5A and 5B show the original and after exposure D-values and the difference between the two for low and high concentration 2-nonanone exposure respectively. The values are shown for each run.

Table 5C gives an overall comparison, combining all the data to show the difference between the D-values of low and high concentration exposure. All values are for LDPE film samples.

Table 5A: Nonlinear Regression Estimates of D-Coefficients for Low 2NN Concentration (A) Exposure of LDPE Films

All values are in units of m^2/sec

RUN	D	D + δ	δ	H ₀ Rejected?
1a	4.91 E-13	5.21 E-13	2.96 E-14	YES
2a	5.10 E-13	5.28 E-13	1.79 E-14	YES
3a	5.10 E-13	5.22 E-13	1.19 E-14	YES
4a	4.97 E-13	5.02 E-13	5.16 E-15	NO
5a	5.11 E-13	5.28 E-13	1.73 E-14	YES

Table 5B: Nonlinear Regression Estimates of D-Coefficients for High 2NN Concentration (B) Exposure of LDPE Films

All values are in units of m^2/sec

RUN	D	D + δ	δ	H ₀ Rejected?
1b	5.52 E-13	5.70 E-13	1.77 E-14	YES
2b	4.95 E-13	5.91 E-13	9.63 E-14	YES
3b	4.94 E-13	5.05 E-13	1.12 E-14	YES
4b	4.53 E-13	4.64 E-13	1.10 E-14	YES
5b	4.61 E-13	4.74 E-13	1.30 E-14	YES

The second analysis, “Overall Comparison of Diffusion Coefficients”, was used to average all the diffusion coefficients at a given concentration of 2-nonanone exposure. The D value for the control tests was called D1. The D value for the low 2-nonanone concentration tests was D2, and the D value for the high concentration tests was D3. Nonlinear regression analyses were used to estimate D1, D2, and D3. Table 5C for LDPE shows that none of the confidence intervals for D1, D2, or D3 overlaps meaning that all diffusion coefficients differed from each other. In other words, both the low concentration 2-Nonaone and the high concentration 2-nonanone exposure of the films had an effect on the D value of LDPE, the latter having the stronger effect. Table 6C for KR10 shows that the D1 and D2 confidence intervals overlap with each other but neither D1 nor D2’s confidence intervals overlap with that of D3. This means that the low

concentration 2-nonanone exposed KR10 film did not appear to have a significantly different D value than the control and the low concentration 2-nonanone treated film.

Table 5C: Overall Comparison of D Values for LDPE
All values are in units of m^2/sec

Parameter	Estimate	95% Confidence Interval	
		Lower	Upper
D	4.96 E-13	4.94 E-13	4.98 E-13
D1	5.12 E-13	5.07 E-13	5.16 E-13
D2	5.92 E-13	5.86 E-13	5.98 E-13

D = No 2-NN exposure

D1 = Low Conc. 2-NN exposure

D2 = High Conc. 2-NN exposure

The tables 6A and 6B show the original and after exposure D-values and the difference between the two for low and high concentration 2-nonanone exposure respectively. The values are shown for each run.

Table 6C gives an overall comparison, combining all the data to show the difference between the D-values of low and high concentration exposure. All values are for KR10 film samples.

**Table 6A: Nonlinear Regression Estimates of D-Coefficients for Low 2NN
Concentration (A) Exposure of KR10 Films**

All values are in units of m^2/sec

RUN	D	D + δ	δ	H ₀ Rejected?
1a	2.84 E-13	3.19 E-13	3.45 E-14	YES
2a	3.08 E-13	2.90 E-13	-1.77 E-14	YES
3a	2.37 E-13	3.08 E-13	7.14 E-14	NO
4a	2.34 E-13	2.38 E-13	4.09 E-15	NO
5a	2.40 E-13	1.70 E-13	-7.00 E-14	NO

**Table 6B: Nonlinear Regression Estimates of D-Coefficients for High 2NN
Concentration (B) Exposure of KR10 Films**

All values are in units of m^2/sec

RUN	D	D + δ	δ	H ₀ Rejected?
1b	2.36 E-13	2.55 E-13	1.91 E-14	YES
2b	2.65 E-13	2.91 E-13	2.62 E-14	YES
3b	2.50 E-13	3.31 E-13	8.05 E-14	YES
4b	3.12 E-13	3.11 E-13	-8.76 E-16	NO
5b	2.76 E-13	3.08 E-13	3.17 E-14	YES

As seen in tables 5A, for LDPE, four out of five film runs, (runs 1a,2a,3a, and 5a), at low 2-nonanone concentrations had different D values after exposure. Table 6A, KR10, shows that three out of five film runs, (3b, 4b, and 5b), showed no significant difference in their before and after exposure D values. Tables 5B and 6B are set up in a similar manner to that of 5A and 6A. The difference is that the 2-nonanone concentration that the films were exposed to was higher. Again, D1 was the D value of the control films and D1+ δ was the D value of the films after exposure to 2-nonanone.

Tables 5B and 6B show that both the LDPE and KR10 films had all of their D values increase significantly as a consequence of the exposure to the higher concentration of 2-nonanone vapor.

Table 6C: Overall Comparison of D Values for KR10All values are in units of m^2/sec

Parameter	Estimate	95% Confidence Interval	
		Lower	Upper
D1	2.62 E-13	2.60 E-13	2.65 E-13
D2	2.66 E-13	2.60 E-13	2.71 E-13
D3	2.93 E-13	2.88 E-13	2.99 E-13

D = No 2-NN exposure

D1 = Low Conc. 2-NN exposure

D2 = High Conc. 2-NN exposure

The third analysis, “Comparison of Oxtran Steady State Values”, was an analysis of variance (ANOVA) used to determine if the steady state oxygen permeation values of the films tested changed significantly after exposure to 2-nonanone. The control, (non-exposed), steady state values were compared to the 2-nonanone exposed steady state values of each film tested. The values are all shown in tables 7A and 8A with their corresponding percent changes in permeance, along with the concentration of 2-nonanone that each film was exposed to. Table 7A shows that the LDPE film samples did not show as large of a change in permeance compared to the KR10 film results in table 8A. The percent change in permeance for the LDPE films ranged from –0.3% up to 6.5% whereas the percent change in permeance for the KR10 films ran from 1.1% up to 33.1%.

Treatment 1 corresponds to the steady state values for the non-exposed film tests, treatment 2 corresponds to the steady state values after exposure to low concentration 2-nonanone vapor, and treatment 3 corresponds to the steady state values of the films treated with high concentration 2-nonanone vapor. Tables 7B and 8B use a grid design to compare treatments with their p-values calculated using the SAS program.

As seen in Table 7B, treatments 1 and 2 are significantly different from one another as denoted by a P-value less than 0.05. A p-value of less than 0.05 means that you can say with 95% confidence that the two treatments compared are different.

Treatments 1 and 3 are also significantly different from one another because their comparison P-value is 0.015. In contrast, treatments 2 and 3 have a corresponding p-value of 0.8008 that denotes a non-significant difference between treatments. This basically means that the steady state oxygen permeation values did change significantly when comparing non-exposure to either low or high concentration exposure of 2-nonanone. But the difference between the low concentration exposure effect and the high concentration exposure effect was not statistically significant. In the table 8B, for KR10, it is shown that all the comparisons of treatments give a significant p-value meaning that they are all significantly different from one another.

The KR10 film steady state oxygen permeation was affected significantly by the exposure to 2-nonanone vapor. This is demonstrated by the fact that the p-values for treatment 1 versus 2 is below 0.05 and the p-value of the comparison between treatment 1 and 3 was also below 0.05. In addition, the p-value of the comparison between low concentration exposure (trt2) and high concentration exposure (trt 3) is significant. This means that the change in concentration of exposure had a significant effect on the change in oxygen permeation.

Table 7A: Oxtran Steady State Oxygen Permeation Results for LDPE

*Appendix 4 shows the calculations used to determine the quantity of 2-nonanone injected

Run Number	Steady State Flow Non-Exposed cc/m ² ·day	Steady State Flow Exposed cc/m ² ·day	Percent Change in Flow (%)	2-nonanone Concentration (ppm) (vol vapor/ vol air)	Quantity of 2-nonanone in 0.5 ml Injected (μ g)
1	1029	1037	0.8	240	100
2	1118	1165	4.2	256	106
3	1134	1161	2.4	197	82
4	1096	1141	4.1	209	87
5	1038	105	0.7	220	92
6	1085	112	4.1	443	184
7	1105	1112	0.6	381	158
8	1098	1094	-0.3	386	161
9	1060	1129	6.5	346	144
10	1100	1139	3.5	358	149

Table 7B is a grid which compares the p-values of ANOVA tests run on the steady state oxygen flow rates between treatments.

Table 7B: ANOVA p-Values for Steady State Results in LDPE

Treatment	1	2	3
1	---	0.0318**	0.0150**
2	0.0318**	---	0.8008
3	0.0150**	0.8008	---

**Values below 0.05 indicate a statistically significant difference between treatments

Figure 9:
Relationship Between Concentration of 2-Nonanone Exposure and
Steady State Oxygen Flow in 1.25 mil LDPE

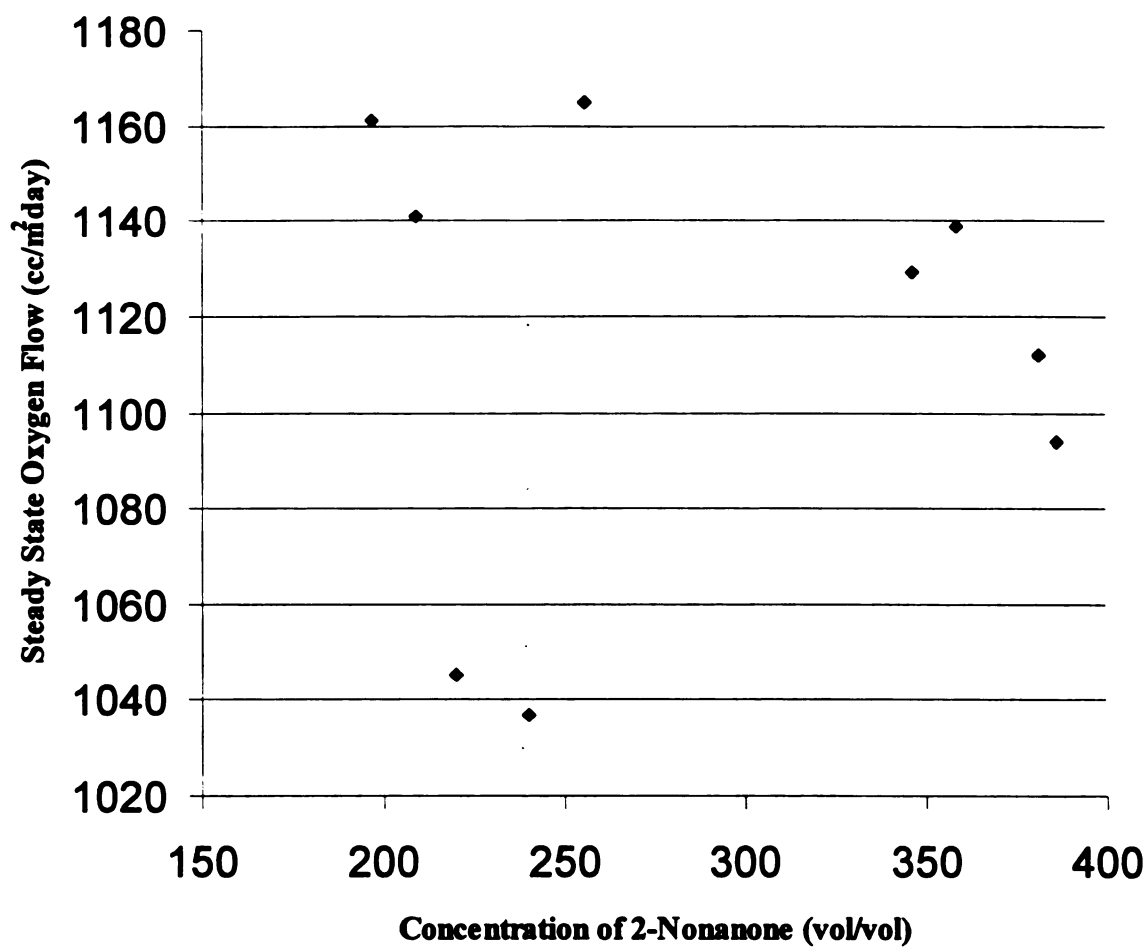


Table 8A shows steady state oxygen flow rates for KR10 before and after exposure to varied concentrations of 2-nonanone and the percent change in steady state oxygen flow after exposure.

Table 8A: Oxtran Steady State Oxygen Permeation Results for KR10

Run Number	Steady State Flow Non-Exposed cc/m ² •day	Steady State Flow Exposed cc/m ² •day	Percent Change in Flow (%)	2-nonanone Concentration (ppm) (vol vapor/ vol air)	Quantity of 2-nonanone in 0.5 ml Injected (μ g)
1	1347	1414	5.0	283	118
2	2662	2811	5.6	317	132
3	1478	1535	3.9	279	116
4	1416	1432	1.1	335	139
5	1454	1528	5.1	282	117
6	1907	2447	28.3	322	134
7	2144	2771	29.2	337	140
8	1391	1774	27.5	300	125
9	1560	1914	22.7	433	180
10	1910	2542	33.1	518	215

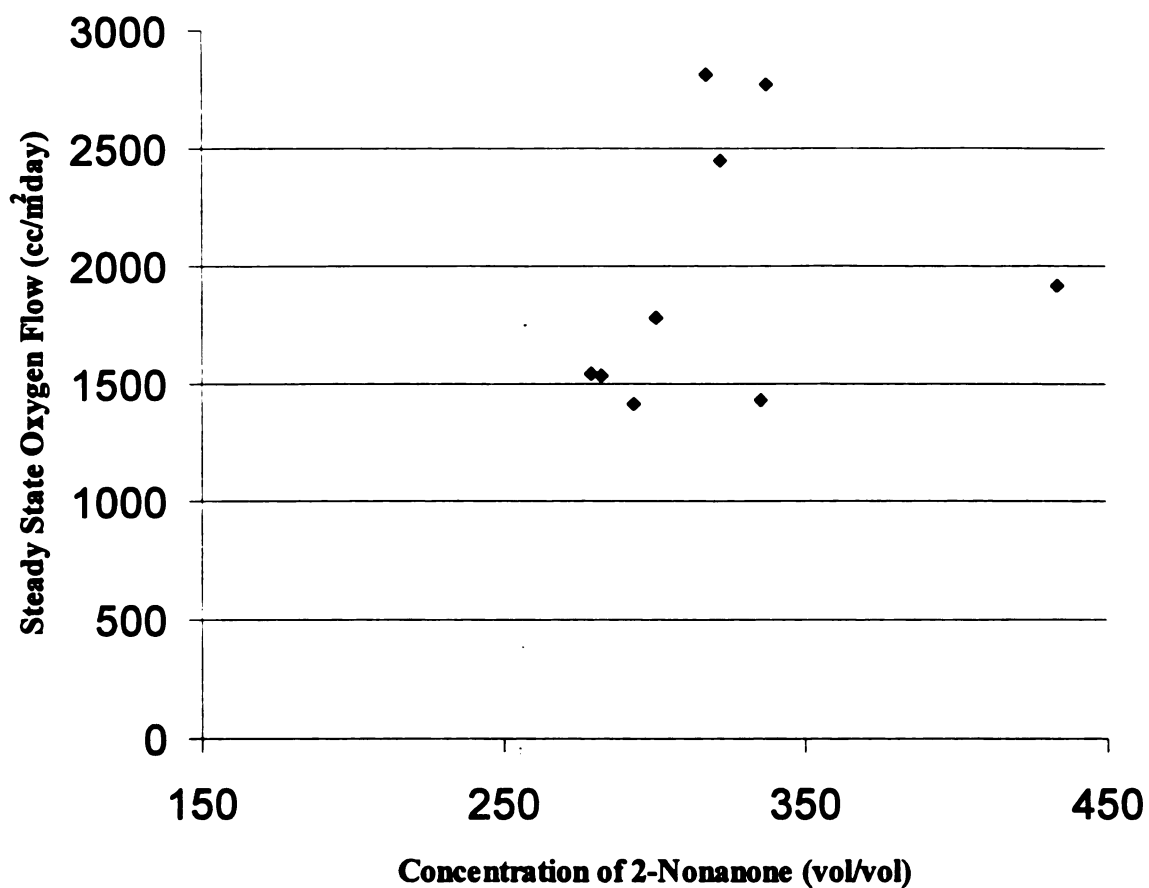
Table 8B is a grid which compares the p-values of ANOVA tests run on the steady state oxygen flow rates between treatments.

Table 8B: SAS Comparison P-Values for Steady State Results in KR10

Treatment	1	2	3
1	---	0.0410*	0.0001*
2	0.0410*	---	0.0001*
3	0.0001*	0.0001*	---

*Values below 0.05 indicate a statistically significant difference between treatments

Figure 10:
Relationship Between Concentration of 2-Nonanone Exposure and
Steady State Oxygen Flow in 1.0 mil KR10



The fourth analysis, “SAS Comparison of Steady State Permeation Values”, was used to compare the steady state permeation of carbon dioxide values of non-exposed films to the permeation values after these films were exposed to a given concentration of 2-nonanone vapor. The difference between this SAS program and the program for oxygen steady state values is that this program is only comparing two treatments, non-exposed versus exposed.

Tables 9A and 10A show the actual steady state values before and after exposure to 2-nonanone for LDPE and KR10, respectively, along with their corresponding percent changes in permeance. These tables also show the concentration at which these tests were run. Table 9A and 10A show that both the LDPE and KR10 films had a relatively large percent change in carbon dioxide permeance after exposure to 2-nonanone. Tables 9B and 10B show the results of the SAS program analysis for the Permatran results. This was again an analysis of variance. The program just denotes by a letter grouping next to each mean value whether the means are statistically considered the same or different. As shown in both tables 9B and 10B the letter grouping for both means, non-exposed and 2-nonanone exposed, are different for both films. This means that the mean carbon dioxide permeation values were significantly affected by 2-nonanone exposure for both the LDPE and KR10 films studied.

Table 9A: Permatran Carbon Dioxide Steady State Results for LDPE

Run Number	Steady State Flow Rate Non-Exposed cc / m²•day	Steady State Flow Rate Exposed cc / m²•day	Percent Change in Flow (%)	2-nonanone Concentration (ppm)	Quantity of 2-nonanone in 0.5 ml Injected (μ g)
1	5020	8969	78.7	351	146
2	5217	10998	110.8	351	146
3	5217	10096	93.5	351	146
4	5231	8316	59.0	333	139
5	4829	8799	82.2	333	139
6	4628	9255	100.0	333	139
7	5043	8936	77.2	454	189
8	4906	8528	73.8	454	189
9	4770	11662	144.4	454	189

Table 9B: Statistical Comparison of LDPE Permatran Values

Mean values with a different letter grouping are significantly different

Letter Grouping	Mean Steady State Flow Rate (cc / m² • day)	Treatment
A	4985	Non-Exposed
B	9506	Exposed

Figure 11:
Relationship Between Concentration of 2-Nonanone Exposure and
Steady State Carbon Dioxide Flow in 1.25 mil LDPE

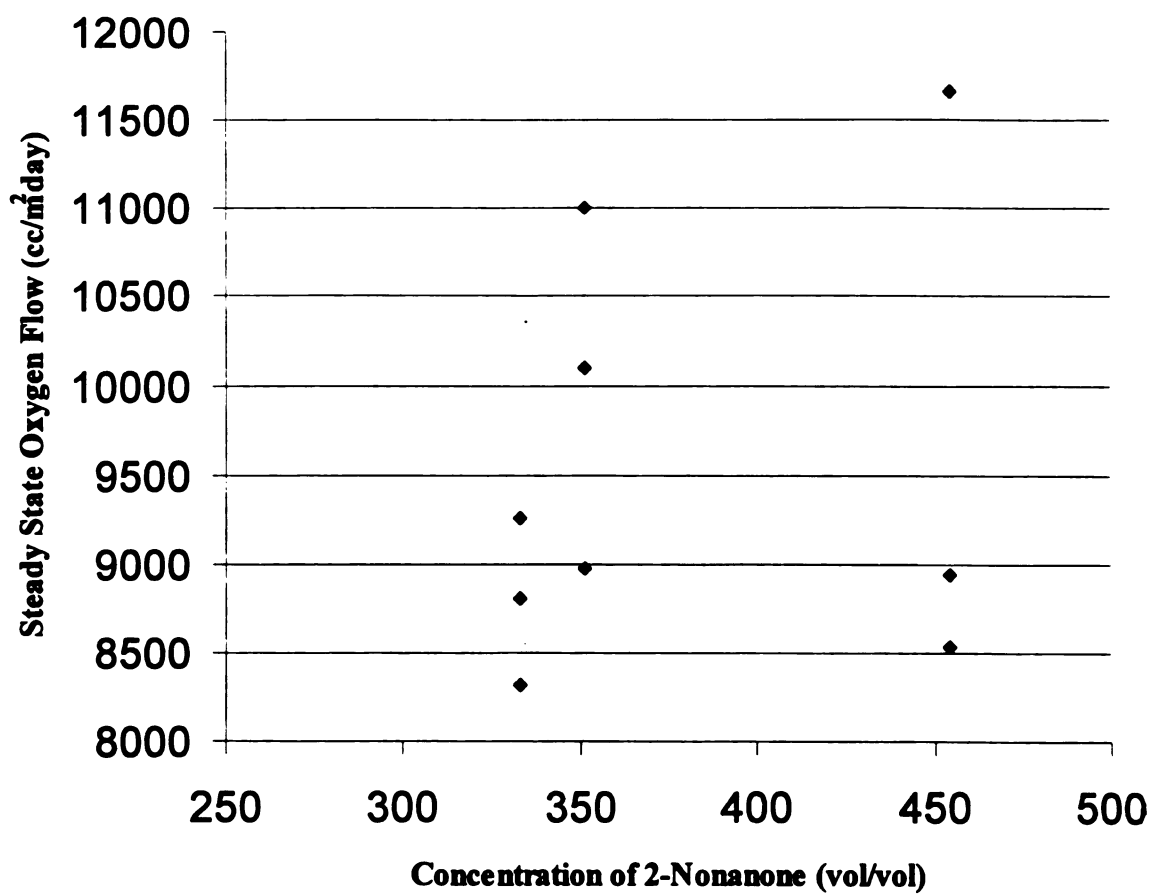


Table 10A: Permatran Carbon Dioxide Steady State Permeation Results for KR10

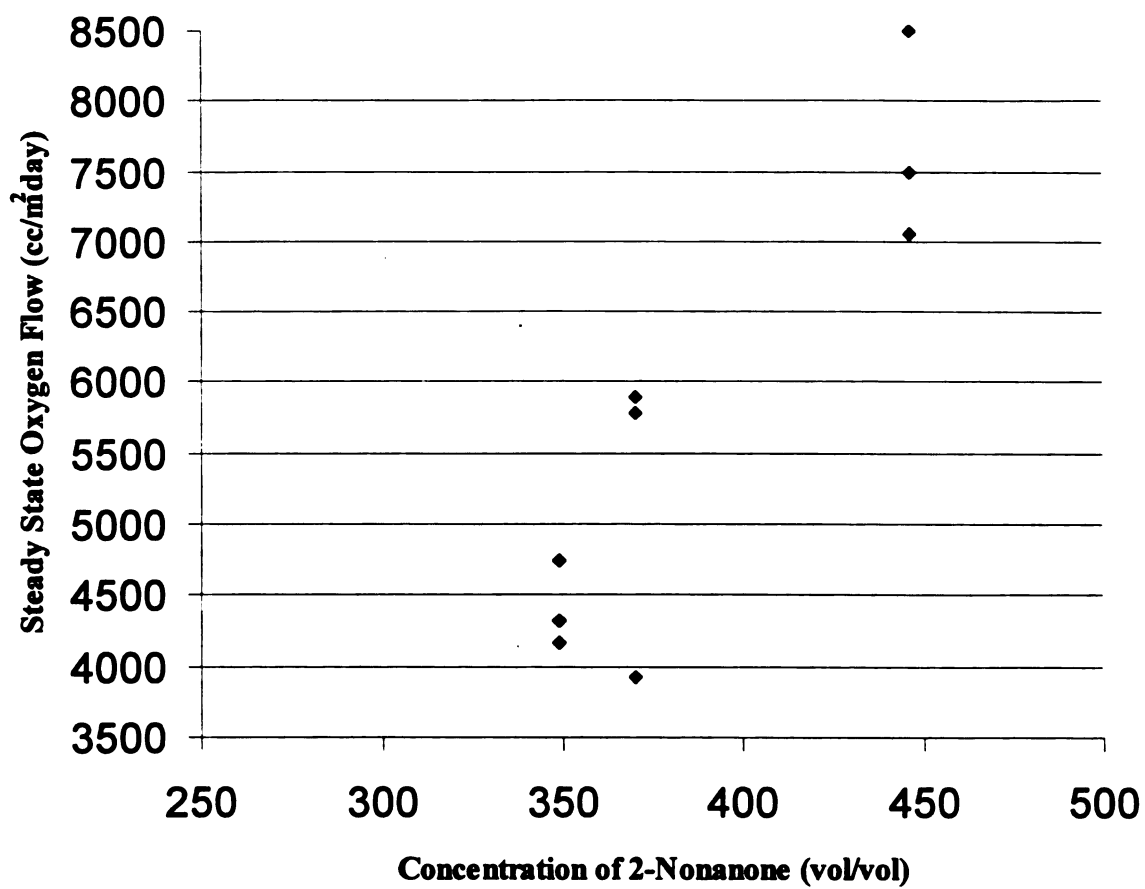
Run Number	Steady State Flow Rate Non-Exposed cc / m ² •day	Steady State Flow Rate Exposed cc / m ² •day	Percent Change in Flow (%)	2-nonanone Concentration (ppm)	Quantity of 2-nonanone in 0.5 ml Injected (μ g)
1	3823	5774	51.0	370	154
2	4084	5895	44.3	370	154
3	3883	3923	34.7	370	154
4	3360	4326	28.8	349	145
5	3219	4165	29.4	349	145
6	3622	4748	31.1	349	145
7	4752	8496	78.8	446	186
8	4320	7056	63.3	446	186
9	3600	7488	108.0	446	186

Table 10B: Statistical Comparison of KR10 Permatran Values

Means with a different letter grouping are significantly different

Letter Grouping	Mean Steady State Flow Rate (cc / m ² • day)	Treatment
A	3851	Non-Exposed
B	5909	Exposed

Figure 12:
Relationship Between Concentration of 2-Nonanone Exposure and
Steady State Carbon Dioxide Flow in 1.0 mil KR10



Tables 11 and 12 show the results of the consistency tests run on the data from the Oxtran tests. The study by Gavara and Hernandez (1993) states that the resulting K values have to be within certain limits in order to call the data consistent. The values for K1 must be within the range of 0.42 and 0.46 and the values for K2 must be within the range of 0.65 and 0.69. The K1 and K2 values reflect that the Oxtran tests were within range for consistency.

Table 11: Consistency Test Results for LDPE Tested on the Oxtran

Test Number	K1	K2
1	0.45	0.67
2	0.44	0.66
3	0.44	0.67
4	0.45	0.67
5	0.45	0.67
6	0.43	0.67
7	0.45	0.67
8	0.45	0.67
9	0.44	0.67
10	0.44	0.67
11	0.43	0.66
12	0.43	0.66
13	0.44	0.67
14	0.45	0.67
15	0.44	0.67
16	0.45	0.70
17	0.45	0.69
18	0.43	0.70
19	0.46	0.67
20	0.46	0.67
21	0.44	0.71
22	0.46	0.67
23	0.46	0.67
24	0.44	0.72
25	0.47	0.68
26	0.48	0.68
27	0.43	0.70
28	0.46	0.68
29	0.47	0.68
30	0.42	0.70

Table 12: Consistency Test Results for KR10 Tested on the Oxtran

Test Number	K1	K2
1	0.50	0.70
2	0.49	0.70
3	0.47	0.69
4	0.44	0.67
5	0.46	0.68
6	0.46	0.68
7	0.60	0.85
8	0.47	0.69
9	0.47	0.69
10	0.46	0.68
11	0.46	0.68
12	0.43	0.66
13	0.42	0.65
14	0.43	0.65
15	0.43	0.65
16	0.44	0.66
17	0.44	0.66
18	0.43	0.65
19	0.43	0.66
20	0.44	0.66
21	0.47	0.68
22	0.47	0.69
23	0.44	0.67
24	0.48	0.77
25	0.45	0.68
26	0.45	0.67
27	0.44	0.69
28	0.44	0.67
29	0.45	0.67
30	0.41	0.76

SUMMARY TABLES

Tables 13 and 14 are to be read in columns. The first column describes which type of exposure to 2-nonanone. The following columns list, by letter designation, if the diffusion, permeation, or flow coefficients were significantly different from one another.

A different letter designation means statistically significant difference.

Percent change is that between the given value and the non-exposed value.

Table 13: Oxygen Test Results Summary Table

TREATMENT	LDPE		KR10	
	Diffusion Coefficient	Permeation Coefficient	Diffusion Coefficient	Permeation Coefficient
1 (non-exposed)	A	A	A	A
2 (low concentration exposure)	B 3.2%	B 2.4%	A 1.5%	B 4.1%
3 (high concentration exposure)	C 19.4%	B 2.9%	B 11.8%	C 28.2%

Table 14: Carbon Dioxide Test Results Summary Table

TREATMENT	FILM	
	LDPE	KR10
Non-Exposed	A	A
Exposed	B (91.1%)	B (52.2%)

CONCLUSIONS

- 1) Two testing systems were successfully developed to expose polymer films to 2-nonanone vapor and subsequently test their oxygen and carbon dioxide permeability.**
- 2) Four different analyses were designed in SAS. One can statistically analyze the diffusion coefficients of oxygen through single films before and after exposure to 2-nonanone. Another analyzes the diffusion coefficients of a group of films with three different treatments. The last two compare the steady state permeation rates of control versus treated films for both oxygen and carbon dioxide.**
- 3) Table 13 shows that the low concentration exposure of 2-nonanone to LDPE film increased the LDPE's diffusion coefficient by 3.2% and also increased its steady state oxygen permeation by 2.4%. Exposure of LDPE film to high concentration 2-nonanone vapor increased its diffusion coefficient by 19.4%. It also increased its steady state oxygen permeation by 2.9%. In addition, Table 13 shows the results of KR10's exposure to 2-nonanone. Low concentration exposure caused a 1.5% increase in its diffusion coefficient and a 4.1% increase in its steady state oxygen permeation. Exposure to high concentration 2-nonanone caused an 11.8% increase in the diffusion coefficient and a 28.2% increase in its steady state oxygen permeation.**
- 4) Table 14 shows that after exposing the LDPE film to 2-nonanone its steady state carbon dioxide diffusion increased by 91.1%. Table 14 also shows that after exposing KR10 to 2-nonanone vapor the steady state rate of carbon dioxide increased by 52.2%.**

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Appendix 1

2 - Nonanone Calibration Curve for Gas Chromatography

Instrument: Hewlett Packard 5890 Gas Chromatograph (GC)
Column - SPB – 5 (non-polar column)

Conditions: Oven Temperature : 100 °C
Initial Temperature: 60 °C
Initial Time: 1 minute
Rate: 7.5 degrees / minute
Final Time: 30 minutes
Final Temperature: 200 °C
Injection Temperature: 220 °C
Range: 2
Attenuation: 0

Reagents: 1. Acetonitrile - HPLC Grade CH_3CN
EM Science, Gibbstown, NJ.

2. 2 - Nonanone - 99+ % $\text{CH}_3(\text{CH}_2)_6\text{COCH}_3$
Aldrich Chemical Company, Milwaukee, WI.
Density 0.832 gm/ml

Units: 1 μL of 2-nonanone / Liter of Acetonitrile corresponds to 1 ppm (v/v)

Example: 1300 μL of 2-nonanone / L = 1300 ppm

Procedure:

1. A 1300 ppm stock solution of 2-nonanone in acetonitrile was made.
A 100 ml flask was used. The amount of 2-nonanone weighed out into the flask to achieve 1300 ppm was figured by:

$$0.13 \text{ ml} \times 0.832 \text{ g/ml} = 0.1082 \text{ g}$$

$$\text{Density of 2-nonanone} = 0.832 \text{ g/ml}$$

0.1082 g of 2-nonanone was placed into the 100 ml flask and was then diluted with acetonitrile to the line to achieve the 1300 ppm stock solution.

1. Three different dilutions of the stock solution were made in 25 ml flasks to achieve 200 ppm, 400 ppm, and 800 ppm concentrations. The equation used for this was:

$$V_o C_o = V_n C_n$$

Where

V_o = volume of original solution (stock solution) to add

C_o = concentration of original solution (1300 ppm)

V_n = volume of new solution (25 ml)

C_n = concentration of new solution (200, 400, or 800 ppm)

For 200 ppm:

$$V_o (1300 \text{ ppm}) = (25 \text{ ml})(200 \text{ ppm})$$

$$V_o = 3.85 \text{ ml}$$

3.85 ml of stock solution was pipetted into a 25 ml flask and diluted to the line with acetonitrile.

This procedure was repeated for the 400 and 800 ppm solutions.

2. Volume conversions of the four different concentrations (200,400,800, and 1300 ppm) in there injected form are as follows:

200 ppm :

$$200 \times 10^{-6} \text{ ml/ml} \times 0.832 \text{ g/ml} = 166.4 \times 10^{-6} \text{ g 2-nonanone /ml acetonitrile}$$

$$166.4 \times 10^{-6} \text{ g/ml} \times 0.001 \text{ ml} = 1.082 \text{ } \mu\text{g of 2-nonanone} \\ \text{(quantity injected)}$$

The above calculation was repeated for 400, 800, and 1300 ppm.

Table 15: Calibration Curve Values

Concentration of 2-nonanone (ppm)	Quantity of 2-nonanone Injected (* 10⁻⁶ g)	Average Area Unit Response (AU)
0	0	0
200	0.166	2,880,563
400	0.333	5,829,077
800	0.666	13,699,297
1300	1.082	22,773,886

Seven injections at each concentration were run on the GC to determine the average area unit response for each of the four different concentrations. The resulting calibration curves are shown in figures 13 and 14.

Figure 13: 2-Nonanone Calibration Curve for the GC (1)

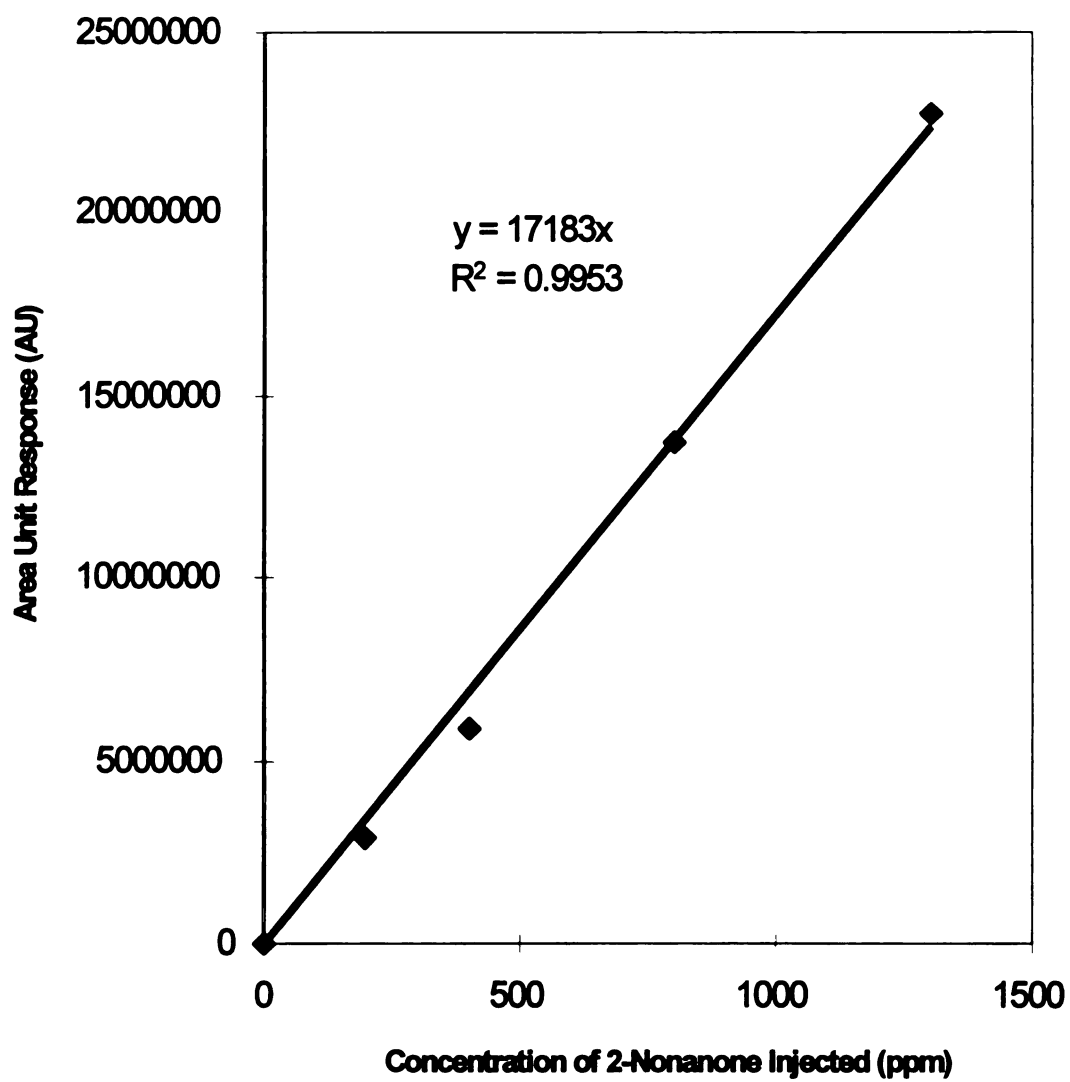
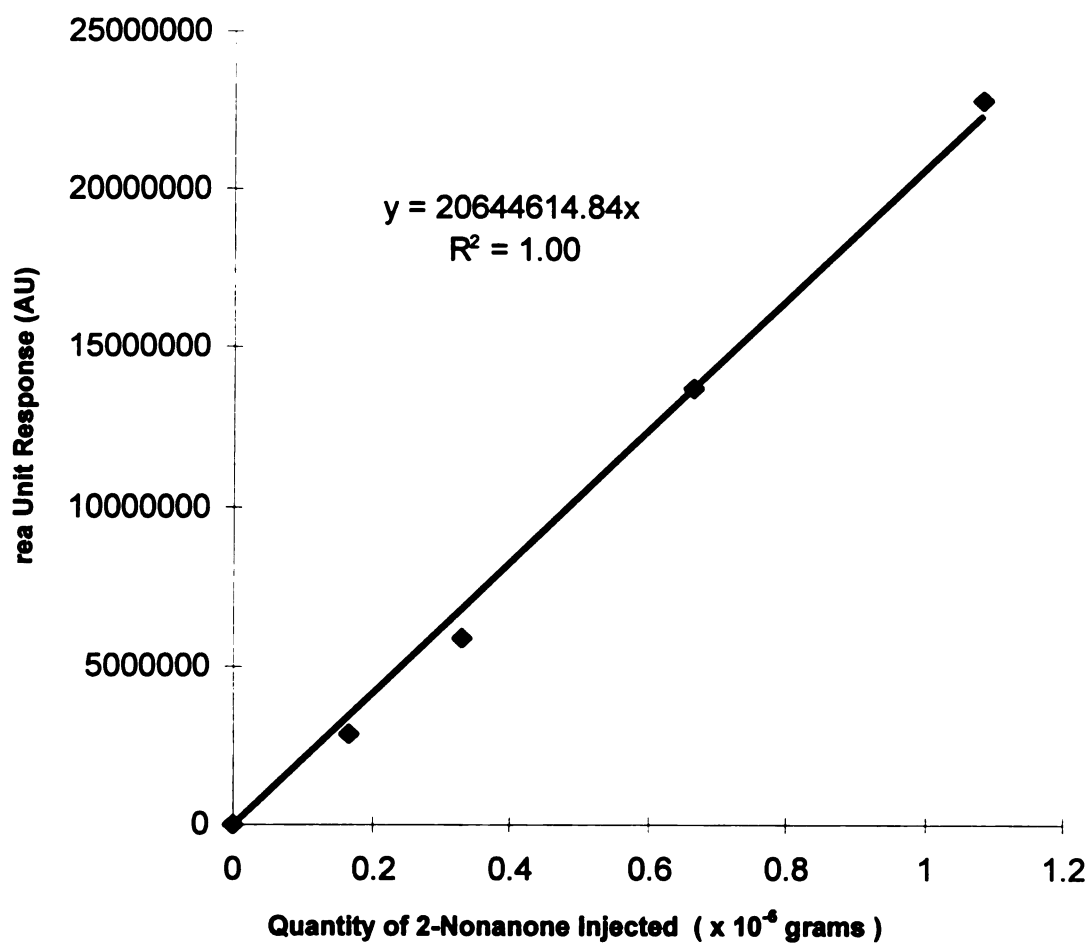


Figure 14:
2-Nonanone Calibration Curve for the GC (2)



Appendix 2

Determination of Reference Film Carbon Dioxide Permeation Value Using the Dynamic Method

Given:

Volume of CO ₂ detected, cc (V _d)	0.0248
Area of sample film, cm ² (A _s)	50
Pressure differential, atm	1
Recorder velocity, mm/sec (R _v)	0.167 (1 cm/min)
Recorder paper advance, measured, mm (R _p)	57**
Film Thickness, measured, mil (l)	2**

** example numbers

1. Calculate Time of Permeation θ :

$$\theta = R_p / R_v = \frac{57 \text{ mm}}{0.167 \text{ mm/sec}} = 341 \text{ seconds} = 5.69 \text{ minutes}$$

3. Calculate Gas Transmission Rate (GTR) :

$$\text{GTR} = V_d / (\theta * A_s) = \frac{0.0248 \text{ cc}}{5.69 \text{ min} * 50 \text{ cm}^2} = 8.72 \times 10^{-5} \frac{\text{cc}}{\text{min} * \text{cm}^2}$$

4. Calculate Permeability Constant (P):

$$P = \frac{\text{GTR} * l}{\Delta p}$$

$$P = \frac{8.72 \times 10^{-5} \text{ cc}}{\text{minutes} * \text{cm}^2} \times \frac{2 \text{ mil}}{1} \times \frac{1}{1 \text{ atm}} \times \frac{100^2 \text{ cm}^2}{1 \text{ m}^2} \times \frac{1440 \text{ minutes}}{1 \text{ day}}$$

$$P = 2511 \frac{\text{cc} * \text{mil}}{\text{m}^2 * \text{day} * \text{atm}}$$

Appendix 3

Determination of Test Film Carbon Dioxide Permeation Values

Given:

Pre-determined permeation value of reference film to be 2511 $\frac{\text{cc} \cdot \text{mil}}{\text{m}^2 \cdot \text{day} \cdot \text{atm}}$

(See Appendix 2)

The Permatran CIV Continuous Method was used running three test films against this reference film. The voltage values were found as follows:

Reference film: 0.56 volt
Test Film A : 0.64 volt
Test Film B : 0.62 volt
Test Film C : 0.54 volt

1. Determine Ratios:

$$\text{Film A / Reference Film} = 0.64 \text{ volt} / 0.56 \text{ volt} = 1.14$$

$$\text{Film B / Reference Film} = 0.62 \text{ volt} / 0.56 \text{ volt} = 1.11$$

$$\text{Film C / Reference Film} = 0.54 \text{ volt} / 0.56 \text{ volt} = 0.96$$

2. Determine Transmission Rates:

$$\text{Rate of Test Film} = \text{Rate of Reference Film} \times \text{Ratio}$$

$$\text{Film A} = 2511 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}} \times 1.14 = 2863 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}}$$

$$\text{Film B} = 2511 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}} \times 1.11 = 2787 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}}$$

$$\text{Film C} = 2511 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}} \times 0.96 = 2411 \frac{\text{cc}}{\text{m}^2 \cdot \text{day}}$$

Appendix 4

Calculation for the Conversion of ppm to μg For 2-Nonanone Concentration

- 1) A 500 μL sample was drawn during testing of the 2-nonanone vapor stream and injected into the gas chromatograph.
- 2) The gas chromatograph gave out readings in area units (AU). The AU value was then put into the equation for a line from the calibration curve seen in Figure 13 as y and the equation was solved for x which was the concentration of 2-nonanone in ppm (vol/vol).

- 1) ppm was then converted to μg by the following example:

$$240 \text{ ppm (vol/vol)} = 240 * 10^{-6} \text{ ml/ml}$$

$$(240 * 10^{-6} \text{ ml/ml}) * (0.832 \text{ g/ml}) = 199.68 * 10^{-6} \text{ g/ml}$$

density of 2-nonanone

$$(200.88 * 10^{-6} \text{ g/ml}) * 0.500 \text{ ml} = 99.84 * 10^{-6} \text{ g} = 99.84 \mu\text{g}$$

sample size measured

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