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Apple Juice Aroma Compound
Sorption by Sealant Films

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APPLE JUICE AROMA COMPOUND SORPTION BY SEALANT FILMS

BY

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ABSTRACT

APPLE JUICE AROMA COMPOUND SORPTION BY SEALANT FILMS

BY

JAMES BRUCE KONCZAL

Sorption of apple juice flavor compounds by three plastic films was investigated. A dynamic headspace analysis was used to determine the levels of four aroma/flavor components found in the juice. Low density polyethylene, ethylene/vinyl alcohol copolymer of high ethylene content, and co-polyester film strips were immersed in juice at 22°C. Quantitation of flavor compounds in the juice was performed after storage intervals of 1, 3, 6, 14 and 24 days. Results were compared to data obtained from a control sample stored without film contact. Sorption of the four flavor components from the juice was significant with low density polyethylene film. Minimal change in probe concentration levels occurred in the juice in contact with the other two film types.

Contacting the test films with apple juice resulted in changes in various mechanical properties of the films. Yield point, tensile strength, percent elongation, modulus of elasticity, heat seal strength and impact resistance were affected after only one day of immersion in juice.

DEDICATION

This thesis is dedicated to my wife Sherry, without whose patience, love and support, it would not have been possible.

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INTRODUCTION

Aseptic packaging is used for the production of shelf stable foods and drinks. Both aseptic and retort processes produce shelf-stable products using similar, yet different technologies. In conventional thermal processing, the package and product are brought together in a filling operation, followed by sealing of the package. The container is then thermally processed in a retort or autoclave operation. In aseptic packaging the product and package are independently sterilized prior to filling and sealing. Sterilization techniques which cannot be used on foods but may be used on packaging materials are now feasible (ie. hydrogen peroxide) (Hotchkiss, 1988).

As a result of this technology, polymeric and paperboard materials can be used where only glass and metal could previously be. The increased usage of polymers in aseptic packaging has resulted in a higher level of concern for product/package compatibility. Contact between the product and package can result in changes in mechanical properties of packaging materials including tensile, compression, and impact strength (Halek, 1988). Sorption and desorption characteristics of flavor components in packaging materials are being studied as food companies

strive to produce a convenient, shelf-stable, yet inexpensive product/package system.

One area where the aseptic packaging concept has been employed extensively is the fruit juice and fruit drink industry. Aseptic fruit juice processing has come of age and is becoming the standard in the American juice market (Tillotsen, 1984). Aseptic processing and packaging of fruit juices has been reported to give a product of better, if not superior, flavor and shelf stability, in comparison to the same product, processed using conventional methods (Hirose et al., 1988). It has also provided a means to inexpensively package products in small sizes. Aseptic packaging of juice products virtually created a single service market for fruit juices and drinks. Aseptics are now being used in the area of frozen concentrates. Producing a shelf stable fruit juice concentrate eliminates the initial cost of freezing (and maintenance) of the concentrate in distribution and has resulted in new research in this area.

Shelf stability of the juice product is an important issue which must be addressed with the increased use of aseptics in fruit juice packaging. To insure product quality, "flavor scalping" by the package must be inhibited. "Flavor scalping" is the selective sorption of flavor components by a packaging material, resulting in a decrease of that component in the product (Harte, 1987; Hotchkiss, 1988). The overall quality of the product is thus

diminished. Fruit juices contain volatile, highly aromatic compounds. The scalping of flavor compounds is a concern for many aseptic products currently being packaged (Harte, 1987). Loss of flavor from the product to the package may result in a loss of product quality. Marshall et al. (1985) and Mannheim et al. (1986) have shown that limonene is readily absorbed by a variety of polymers. Limonene is a major flavor component in orange juice and other citrus products. The absorption of flavor components by certain packaging materials may also affect the mechanical properties of the material. Hirose et al. (1988) and Imai (1988) have shown that mechanical properties such as tensile strength, seal strength, modulus of elasticity, and impact strength changed due to limonene sorption by the polymer.

The most suitable packaging material(s) for use with a product is an important choice in today's market. Knowledge of mechanical and barrier/compatibility behavior of sealant polymers due to sorbed flavor compounds is crucial to making an informed decision. With this in mind, the major objectives of this study were:

1. To develop an efficient method of analyzing flavor volatiles in apple juice.

2. To investigate the sorption of several volatile compounds found in apple juice (ethyl-2-methylbutyrate, hexanal, trans-2-hexenal, and 1-hexanol) by selected plastic films.

3. To evaluate the influence of sorption of

volatile compounds on the mechanical properties of the respective films.

LITERATURE REVIEW

Aseptic packaging of fruit juices

The fruit juice industry has widely accepted aseptic packaging systems for the containment of shelf-stable juices. Aseptic packaging was rapidly accepted by the American fruit juice industry following approval by the FDA in 1981 of hydrogen peroxide to sterilize packaging material (Hotchkiss, 1988). Since then, flexible multilayer cartons have rapidly replaced the traditional can and glass containers for hot filled juices. The traditional method of producing a shelf-stable juice product in a can or glass container included the use of hot-fill processes. There are problems, however, in achieving high quality products using hot fill processes (Tillotsen, 1984). Hot filled juices are often subjected to high temperatures for long periods of time, thus a reduction in overall product quality results. The use of cans as a package for juice also increases the possibility of the juice picking up off flavors from the can and further reducing the quality of the juice (Tillotsen, 1984). The use of glass adds weight to the package, thus increasing distribution costs (Harte, 1984).

By late 1983, experts believed there to be more than

110 complete aseptic filling lines for carton packs in operation in the United States (Tillotsen, 1984). There probably are even more in operation today, with the advancement of aseptic technology. The majority of these lines are used for the packaging of citrus juices and drinks in a variety of sizes. A reasonable share of the lines could be used for the production of apple juice based on the fact that in 1986 17.5% of fruit juice consumption was apple juice (Stacy, 1987).

Shelf-Life of Aseptic Juice Products

Product shelf-life is controlled by three factors (Harte, 1987):

1. product characteristics
2. the product/package environment
3. the properties of the package

Shelf-life, therefore, is dependent directly upon the nature of the product and related factors, including product compatibility with the packaging system (Giacin, 1987). Gas permeation, migration of low molecular weight compounds and sorption by the food contact surface, may influence the shelf-life of systems using plastic laminates (Gilbert, 1985; Fernandes et al., 1986). Models to predict product shelf-life based on the barrier properties of the package, and rate and mode of deterioration of the food product are currently being evaluated (Hotchkiss, 1988). Optimization

of the package for the shelf-life required by the product is then possible. A substantial amount of research has been carried out to determine the shelf-life of aseptically filled juices, which are packed into laminated carton packs (Brik Pak or Combibloc), in which the food contact layer is polyethylene. A majority of this work has been performed with citrus products, particularly orange and grapefruit juice. Gherardi (1982) and Granzer (1981) evaluated the quality of juice packed in carton packs as opposed to glass. Both found that juices deteriorated faster in carton packs than in glass containers. Mannheim et al. (1987) found that the shelf-life of juices in Brik-style cartons with polyethylene as the food contact layer was significantly shorter than the shelf-life of the same juice packed in glass. The shelf-life of juice in Brik Packs was no more than 3-4 months. Marshall et al. (1985) reported that sorption of d-limonene by the contact layer reduced the organoleptic quality of citrus juices. Durr et al. (1981) reported significant losses of orange juice volatiles from juice stored in carton packs.

All the data collected to date does not repute the use of polymers as food contact layers. Potter (1985) studied the stability of citrus flavors packaged aseptically and found that aseptically packaged orange juices were acceptable for up to eight months of storage at room temperature. McLellan et al. (1987) tested an oriented polyethylene terephthalate (OPET) container for use with hot

filled apple juice. They found that no significant preferences were noted between the glass packed and quenched cooled, OPET packed juices until after 1 year of storage. Durr et al. (1981) and Mannheim and Havkin (1981) determined that a critical governing factor in establishing shelf-life of packaged orange juice is the storage temperature.

The previously cited studies, demonstrated that it would be incorrect to describe the shelf-life of aseptically packaged products, solely on the basis of the package used. The type of product and it's make-up must also be taken into consideration. Knowledge of product, package, processing, and storage temperature are necessary to accurately predict the shelf-life of an aseptic juice product. Characterization of the compatibility of polymer sealants films with aroma compounds would allow the selection of the most suitable packaging material for the product.

Product/Package Interaction

Aroma compounds often exist in food products at low concentrations, yet they may contribute extensively to the product flavor profile (Parliment, 1987). Thus, the effect of the loss of flavor and aroma compounds, due to sorption by the contacting packaging materials, can be great. In order for plastic packages to be accepted by the consumer, foods packaged in plastics must uphold the food quality with

respect to flavor and aroma. The polymer contact layer may alter the characteristic aroma and flavor of a food by selectively absorbing one or more compounds which contribute to the overall make-up of that food. The specific compound may be a key flavor component or one which combines with another to produce flavor. Polymeric materials can contribute aromas due to residual monomers, solvents or processing additives (Hricega and Stadelman, 1988). These migrants can easily upset the often delicate balance of flavor make-up. Alternatively, sorbed aroma/flavor compounds from the product could have an affect on the performance and stability of the packaging material.

Marshall et al. (1985) reported that orange juice develops a "flat taste", which is perceived as unfresh, due to loss of volatiles to the polymeric package material. Polyethylene as a food contact surface has been found to readily absorb d-limonene from orange juice, as well as to accelerate ascorbic acid degradation and browning in the juice (Mannheim et al., 1987). Durr et al. reported a 40% loss of d-limonene from orange juice within six days after filling due to sorption by the polyethylene contact layer. This compares to only a 10% loss over ninety days for orange juice packed in glass. Imai et al. (1988) found a 24% loss of limonene from orange juice in contact with polyethylene after only one day. However, only a 12% loss was observed from juice in contact with an ethylene/vinyl alcohol copolymer of high ethylene content. Marshall et al. (1985)

reported that over 60% of the d-limonene was absorbed from an orange juice sample during contact with low density polyethylene, while only a 45% decrease was observed with samples in contact with a Surlyn^R material. Hirose et al. (1988) placed orange juice in contact with several sealant films low density polyethylene, Surlyn^R (sodium type), and Surlyn^R (zinc type). Within three days of storage, all the polymer films studied had rapidly absorbed d-limonene. The zinc-type Surlyn^R reached saturation after three days. However, twelve days of storage were necessary for the polyethylene and the sodium-type Surlyn^R to reach saturation. Thus, differences in polymer chemistry can effect sorption of flavor compounds. The thickness of the food contact layer may also affect the sorption of flavor compounds (DeLassus, 1985). Shimoda et al. (1988) demonstrated that sorption of flavor volatiles by polyethylene liners increased with the carbon chain length of the flavor compounds. The distribution ratio (amount of volatile sorbed/amount of volatile remaining in product) for a given polyethylene film was proportional to film thickness. The distribution ratio also decreased with increasing percent crystallinity of a polyethylene film. Thus, the higher the percent crystallinity of the polyethylene, the less flavor sorption occurred

* Surlyn^R is a trade name of E.I. DuPont for Ethylene methacrylic acid copolymer - partial metal salt.

(Shimoda et al., 1988). Ikegami et al. (1987) reported that a greater amount of flavor compound was sorbed from a fruit flavored juice by polypropylene as compared with polyethylene when both were used as the contact layer. A distribution ratio (volatile content in film versus volatile content in solution) was used to show the influence of the molecular structure of the flavor compounds on sorption. Ratios varied depending on whether the volatile was a hydrocarbon, an alcohol, an ester or an aldehyde. In addition, the ratio was found to be inversely proportional to the polymer density. Marshall et al. (1985) found that oxygenated compounds absorb less readily than non-oxygenated compounds. The chain length of the non-oxygenated compound (or portion of the compound) will affect its sorption level. The polymer chain flexibility will limit the compound's accessibility to the holes between polymer chains, and thus limit its absorption (Marshall et al., 1985). DeLassus et al. (1988) found low density polyethylene to be a poor barrier to apple aroma. Dry ethylene/vinyl alcohol copolymer and a vinylidene/chloride copolymer film were good barriers to trans-2-hexenal, an important aroma flavor component of apple juice. An increasing area of concern with today's use of plastics is that flavor sorption by polymeric food contact films may lead to changes in permeability or mechanical property characteristics of the film. It has been suggested that, with some products, the sorption of one flavor compound changes the product and

package enough to allow other compounds to be sorbed more readily (Hotchkiss, 1988).

The effect of sorption on mechanical stability of the sealant film must be considered. Hirose et al. (1987) found that absorption of limonene by polyethylene and two types of Surlyn^{R} affected polymer mechanical properties such as modulus of elasticity, tensile strength, percent elongation, impact resistance, and seal strength. Seal strength of the sealant is an important functional property. Seal integrity is essential to maintenance of a package's integrity (Harte, 1987). The formation of a hermetic seal which functions as a bond between two polymer materials is critical to the performance of the package.

Goto (1988) studied the effect of various essence of oils (orange, lemon, eucalyptus and peppermint) in contact with low density polyethylene, ethylene/vinyl acetate copolymer and a polyacrylonitrile based films. Significant changes in tensile strength and in percent elongation were found with the polyethylene and the ethylene/vinyl acetate films as a result of contact with the essence. No significant change was found in the mechanical properties of the polyacrylonitrile. Imai (1988) investigated the influence of the sorption of orange juice volatiles on the mechanical properties of low density polyethylene, ethylene/ vinyl alcohol copolymer of high ethylene content and a co-polyester film. The co-polyester was found to sorb significantly lower amounts of d-limonene then the other

films. Mechanical properties which were affected by sorption of d-limonene included; modulus of elasticity, yield stress, heat seal strength, and impact resistance.

Flavor Analysis of Apple Juice

The volatiles responsible for the aroma and flavor of foods are often composed of low levels of flavor compounds with different volatilities (Parliment, 1987). A single volatile, can make a variety of contributions to the quality of fruit juice aroma which is subject to change during storage. The aroma of a fruit can undergo substantial changes once the fruit is crushed and processed into a fruit juice and put into storage (Durr and Schobinger, 1981). A character impact compound is one which contributes strongly to the odor/flavor of a juice. A distinctive aroma is desirable, while an off flavor aroma is undesirable. A volatile can be a precursor to an off flavor or be an intensifier of a desirable one. Some volatiles do not contribute at all, initially, to an aroma/flavor due to low thresholds, but due to chemical make-up changes in the juice (aging, oxidation, sorption, etc.) they become more significant, even if present in small quantities (Parliment, 1987). The contribution of volatiles to apple juice flavor and aroma has been described by Durr and Schobinger (1981), (see Table 1). Flath et al. (1967) and DeLassus et al. (1988) listed hexanal, trans-2-hexenal

Table 1. The contribution of volatiles to apple juice aroma.

Contribution to hedonic value

Important	Desirable	Undesirable
trans-2-hexenal	hexanal	ethanol
cis-3-hexenal	benzaldehyde	isobutanol
trans-2-hexenol	propylbutyrate	2-methylbutanol
cis-3-hexenol	pentylacetate	3-methylbutanol
ethylbutyrate	2-pentanone	beta-phenylethanol
ethyl-2-methyl-butyrate	isobutylacetate	

Contribution to aroma intensity

trans-2-hexenal

cis-3-hexenal

isobutanol

isobutylacetate

Durr and Schobinger, 1981.

and ethyl-2-methylbutyrate as important contributors to apple juice.

Distillation-extraction techniques are widely used to isolate volatiles from apples and other fruits (Flath et al., 1967; Flath et al., 1969; Seifabad, 1987). A distillation technique (Likens and Nickerson, 1964) is often used for extraction. However, a long isolation time and low percent recovery are two drawbacks of this method. McGregor et al. (1964) concentrated apple juice volatiles tenfold by stripping juice using an evaporator with a steam-jacketed heating tube and a shell type heat exchanger. Condensate was collected and frozen until needed. Analysis was conducted using a gas chromatograph with a variety of different columns. Nawar and Fagerson (1962) developed a direct sampling technique where cryogenically enhanced headspace is injected into a gas chromatograph equipped with a flame ionization detector and a capillary column. The use of capillary columns results in clearly definable peaks with discernable retention times, as compared to packed columns. Flame ionization detectors are well suited for headspace analysis because of their sensitivity to organic compounds, their range and insensitivity to inorganic gases and water (Nawar, 1966; Giacin, 1987).

A number of apple flavor analyse have been conducted by headspace sampling and/or headspace concentrating. A justification for the use of this technique is the loss of low boiling volatiles which may occur during high

temperature distillation (Seifabad, 1987). An example of this is the loss of ethyl-2-methylbutyrate from apple juice at extraction temperatures higher then 70°C. A drawback to this method, however, is that higher boiling point compounds which may contribute to overall flavor will not be extracted using this technique. Poll (1983) quantified aroma components of apple juice using a gas washing bottle. The gas washing bottle was filled with 100 ml of apple juice and placed in a 40°C water bath. The juice was purged by bubbling nitrogen through it at 60 ml/min for 60 min. Porapak Q (column packing material) in a glass tube was used to "trap" the released volatiles. A 0.5 ul sample of the elute from the trap was injected into a gas chromatograph for analysis. Poll and Flink (1984) modified this procedure by adding salt (NaCl) to the juice, prior to purging, in various concentrations. All salt-modified samples resulted in a greater release of volatile components over samples without salt.

Tenax-GC, a polymer based on 2,6 diphenyl-paraphenylene oxide has been used widely for volatile collection studies (Olafsdottir, 1985). Tenax-GC does not produce major artifacts the way other porous polymers (Porapak Q and Chromosorb) do, under certain conditions (Lewis and Williams, 1980).

A relatively new development in technology which enhances the collection of volatiles is the use of the Tekmar Model 4000 Dynamic headspace concentrator system

(Tekmar Co., Cincinnati, OH). When interfaced with a gas chromatograph equipped with a flame ionization detector and capillary column, detection of volatiles into the low parts per billion level is possible with good reproducibility and distinctive peaks (Westendorf, 1984).

MATERIALS AND METHODS

MATERIALS

Apple Juice

The apple juice used in this study was made up from Imperial brand 100% apple juice concentrate. Imperial is a brand name distributed by the Sysco Corporation (Houston, TX). The concentrate was purchased through the Michigan State University Food Stores (E. Lansing, MI). Obtained frozen, the concentrate was stored at -17.7°C ±5°C until needed. Twelve hours of thawing time was allowed at 4.5°C before dilution with water. The apple juice concentrate was diluted, following instructions on the package, by adding one part frozen concentrate to five parts distilled water.

Plastic Films

Three plastic films were utilized in this study. They were as follows:

Alathon 1645 - Low Density Polyethylene, 0.042mm (1.65 mils) thick, hereafter, referred to as Alathon.

Selar E-44762-16-1 - Ethylene/Vinyl Alcohol Copolymer of high ethylene content, 0.021mm (0.83 mils) thick, hereafter, referred to as EVOH.

Selar #24328 - Co-Polyester, 0.064mm (2.5 mils) thick, hereafter, referred to as Co-Pet.

The test films were provided by the DuPont Company (Wilmington, DE).

Probe Compounds

Four compounds were selected as flavor probes representative of apple juice. These compounds were:

Ethyl-2-Methylbutyrate (Alfa Products, Danvers, MS)
Hexanal (Aldrich Chemical Co. Inc., Milwaukee, WI)
trans-2-Hexenal (Aldrich Chemical Co.Inc.,Milwaukee,WI)
1-Hexanol (Aldrich Chemical Co. Inc., Milwaukee, WI)

They were selected based on their ease of analysis, importance to the flavor and aroma of apple juice (MacGregor et al., 1964, Flath et al., 1967, Durr and Schobinger, 1981, Poll, 1983) and in part, because of their chemical structural differences; Ethyl-2-Methylbutyrate (E-2MB) is an ester, Hexanal and trans-2-Hexenal are aldehydes, and 1-Hexanol (Hexyl Alcohol) is an alcohol. These compounds are readily separated using a gas chromatograph equipped with a

capillary column. See Appendix A for the various properties of the flavor compounds.

EXPERIMENTAL METHODS

Purge and Trap Procedure

A Dynamic Headspace analysis method was used to determine the levels of probe components in the apple juice. In this technique a purge and trap system is used to concentrate and trap the volatiles. In the purge and trap procedure, a modified gas bubbling tower was used together with a glass tube containing Tenax as a sorbent trap (See Figure 1). Three, 50 ml graduated cylinders were modified to enable the purging of a small quantity (40 ml) of juice. The small sample size reduced the possibility of overloading the GC column with flavor compounds from the juice extract (See Gas Chromatograph Analysis section). A 29/42 standard taper gas washing bottle fixture was affixed to the top of each 50 ml cylinder. This allowed a gas bubbling tower to be used to nitrogen purge the juice. The inner tube, to which the fritted glass end is attached, was extended so that the fritted end was at the 5 ml mark of the graduate cylinder. This insured that efficient purging of the test sample in the cylinder occurred. The gas outlet tube of the tower was also modified by attaching a standard taper 12/5 "ball joint" on it's end. This allowed for easy coupling of the Tenax trap to the washing bottle, by standard taper ball

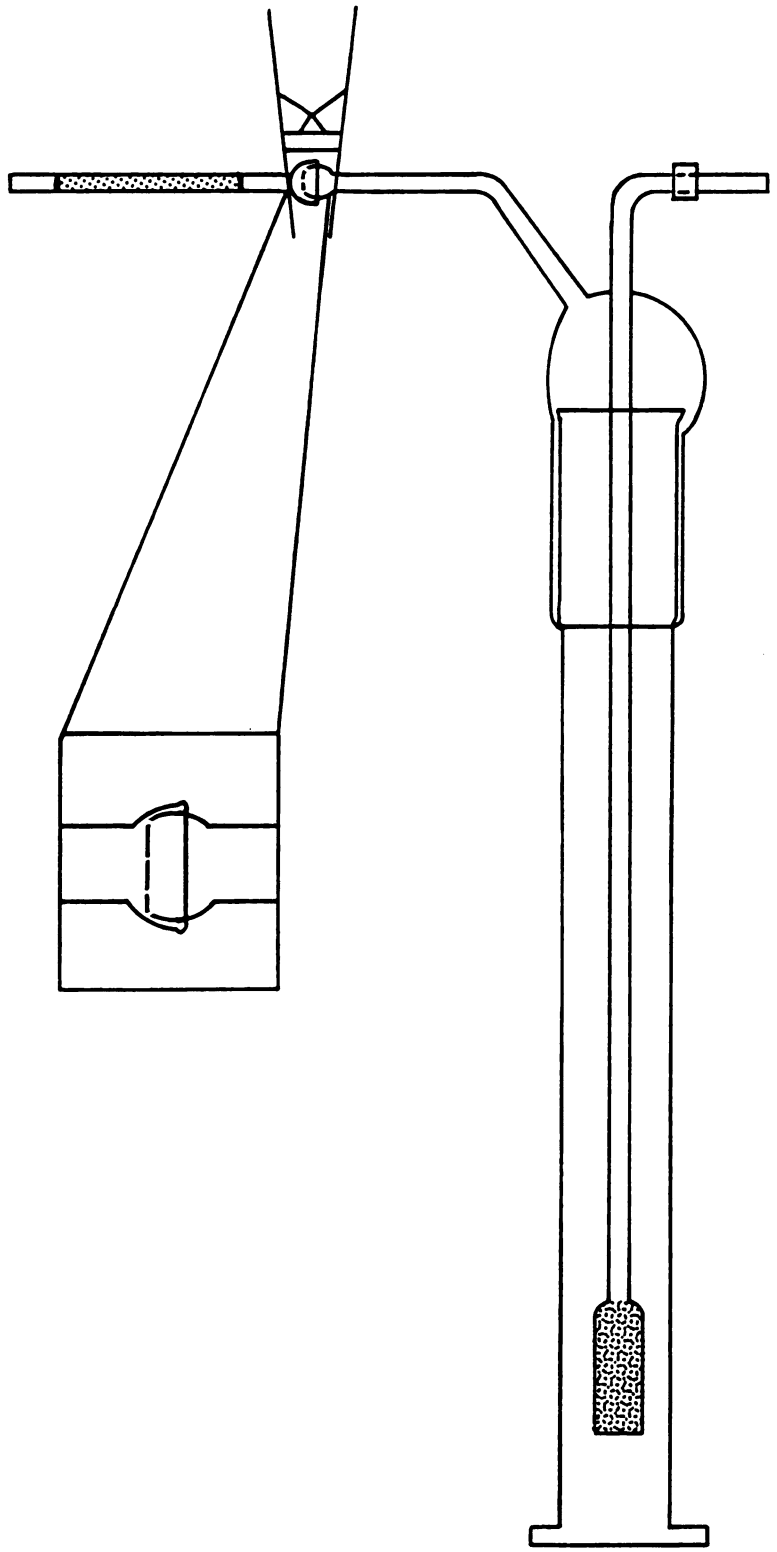

Figure 1. Purge and trap gas washing bottle

socket joints (All glass blowing was done through the Department of Chemistry, Michigan State University, E. Lansing, MI). The trap consisted of 0.35 g of Tenax-GC, 60/80 mesh (Tekmar Co., Cincinnati, OH), deposited into a glass tube (5 mm I.D., 10 cm in length) and held in place with silicanized glass wool. All traps were rinsed with acetone (distilled in glass) and conditioned at 110°C for 24 hrs prior to use. The trap was clamped to the gas outlet port of the tower and a nitrogen line attached to the gas inlet port of the tower. Nitrogen flow through the trap was controlled using a flow meter (Cole Parmer, Chicago, IL). A series of preliminary experiments were used to optimize the time-temperature conditions and to quantify the initial levels of probe flavor volatiles in the apple juice. All juice samples were made from concentrate to insure freshness of the juice. A known quantity of apple juice (40 ml) was purged at any one time. Ten grams of sodium chloride were dissolved into the 40 ml juice sample prior to purging. The salt increases the volatility of the probe compounds allowing them to be extracted efficiently at reduced time intervals (Watada et al., 1981; Poll and Flink, 1983). This is presumably related to the reduction of available solvent in the liquid phase resulting from the presence of the non-volatile solute (the salt). The gas washing cylinder, containing the juice and salt mixture, was then connected to the bubbling tower and placed in a constant temperature water bath. Each sample was purged

with nitrogen for 5 hours at a flow rate of 25 ml/min. A 65°C water bath temperature was found to be optimum with respect to recovery of probe compounds. Temperatures higher then 65°C were found to result in the loss of the more volatile probe compounds such as ethyl-2-methylbutyrate. Purge flows higher than 25 ml/min resulted in excessive foaming, which increased the risk of juice coming into contact with the Tenax trap. At higher salt contents it was difficult to dissolve the salt thoroughly in the juice. A purge time of approximately 5 hours was found to result in the quantitative removal of probe compounds from the juice. After 5 hrs the trap was disconnected from the tower and rinsed with isopentane. Isopentane was pipetted onto the top of the Tenax trap, manually, with a disposable pipet. The isopentane was allowed to drip through the trap and into a V-shaped 15 ml. glass centrifuge tube. The trap was suspended in the tube with the use of a cork stopper. To decrease the amount needed to obtain 1.5 ml of extract from the trap, the tube containing the trap was centrifuged (International Equipment Co., Boston, MA) at a speed of 425 rpm for approximately two minutes after introduction of the isopentane.

Gas Chromatographic Analysis

A Hewlett Packard (Avondale, PA) Gas Chromatograph (GC), Model #5890A was used to analyze the apple juice extracts. The GC was equipped with a flame ionization

detector and a splitless injection port. All samples were injected into the GC using a glass 10 ul syringe (Hamilton Co., Reno NV). The syringe was precooled in a refrigerator freezer at a temperature of 6°C before each injection, to decrease any sample loss due to evaporation. A sample size of 1 ul was used for all injections. The syringe was rinsed thoroughly with solvent between each injection.

GC conditions were as follows:

Column: 60 meter
0.25 mm I.D.
Fused silica capillary
Polar bonded stationary phase
Supelcowax 10 (Supelco Inc.,Bellefonte,PA)

Carrier Gas: Helium at 30.5 ml/min.

Temperatures:

Injector Port 200°C
Detector Port 275°C
Initial Oven Temperature 40°C
Initial Time 10 min.
Temperature Program Rate 2.0°C/min.
Final Temperature 120°C
Final Time 0 min.

Standard curves of response vs. concentration were constructed from standard solutions of known concentrations for each probe compound. Standard solutions were made by the addition of a known volume of probe compound to a

measured volume of dichloromethane. A 1 ul sample for each of four varying concentrations (Appendix B) was analyzed using the gas chromatographic procedure outlined above. The calibration curves for each of the probes are presented in Appendix B.

Recovery of Probe Compounds

Following development of the purge and trap procedure studies were carried out to determine the percent recovery of the respective probe compounds using this method. The juice was purged for 6 hours and 1 ul samples of the extract were injected into the GC to insure removal of probe compounds from the juice sample. A known quantity of probe compound, equal to that found in the juice, was then added to the purged juice and the sample again purged. The probe compounds were added to the juice by dissolution of pure probe compounds into isopentane, to make a standard solution of known concentration. This was followed by the transfer of a known volume of standard solution into the juice. The concentration of probe compounds in the respective standard solutions were determined (using the gas chromatographic procedure previously detailed) prior to transfer to the pre-purged juice solution. The results obtained from the spiked juice solution were compared with results from the standard solutions to determine the percent recovery.

Recovery studies were performed on three different probe solutions. Seven recovery studies were carried out

with ethyl-2-methylbutyrate, which has the lowest concentration in apple juice of all the probe compounds used. Four recovery runs were carried out using 1-hexanol, the probe of highest concentration. A third solution containing all four probe compounds was then analyzed. This solution was assayed to insure that none of the probe compounds interfered with the percent recoveries of the companion compounds during the purge and trap extraction process. A series of five recovery runs were performed with this probe solution.

Storage Stability of Apple Juice

An antioxidant blend of Sustane W and Sustane 20A (UOP Process Division, McCook, IL) and an antibacterial agent, sodium azide (Aldrich Chemical Co. Inc., Milwaukee, WI) were added to the apple juice to prevent changes in the probe levels as a result of oxidation or microbial growth in the juice during storage. A weight percentage of 0.02 of each chemical was added to the juice at the beginning of the storage study. The reagents used in the microbial growth study are summarized in Table 2 (See Appendix C for components of each preservative).

The quality of the juice in storage was determined by monitoring the probe levels in the juice using the purge and trap system. Juice color and growth of microbes in the juice were also monitored. To further determine the efficacy of the sodium azide, an inoculation of

Table 2. Reagents used in the microbial growth study.

Microorganism:	LACTOBACILLUS CELLOBIOSUS
Cell Culture:	Inoculated microorganism from a single colony into MRS broth. This was placed in an incubator at 37°C for 24 hours for activation.
Agar Plate:	Two percent bacto agar was added to MRS broth. Broth was then poured into petri-dishes.
Preservatives:	SUSTANE 20A (UOP INC.) SUSTANE W (UOP INC.) SODIUM AZIDE (Aldrich Chemical Co.) (0.02% (W/V) of the preservatives were added to the juice sample.)
Sample:	100% pure apple juice from concentrate. (Imperial, Sysco Distributors Inc.)

7.5 * E 07 cells/ml cell culture was added to 3895 ml of apple juice. The cell culture used was Lactobacillus cellobious in MRS medium, while the agar plate was 2% bacto agar in MRS medium. This culture was allowed to sit at room temperature (22°C ±2°C) for 7 days. A 0.1 ml sample of juice was pipetted onto the agar plate. The plate was incubated at 37°C for 48 hours and the colonies counted and reported as the cell number per 0.1 ml of juice. Sampling was continued every 3 days for 30 days. The color tests were conducted using a Hunter color difference meter, model# D25-2 (Hunter Associates Laboratory Inc., Reston VA). The standard tile used to calibrate the meter was the yellow tile ($L\ 78.4_1$, $a\ -3.0_1$, $b\ 22.7_1$).

Extraction of Probe Compounds From Plastic Films

Preliminary studies were carried out to develop an analytical scheme to quantify the levels of sorbed probe compounds by the film. A thermal distillation and solvent extraction technique using different solvents, ethyl acetate and isopropanol (Imai, 1988) was employed to desorb probes from the films.

Two sheets of the Alathon, 12.7 cm x 10.16 cm (5" x 4") were put into a amber colored glass bottle containing 260 ml of apple juice. A lid was secured and the bottles stored at room temperature (22°C ±2°C). After 10 days, the sheets were removed from the bottles, rinsed with distilled water for 1 min., and cut into 1 cm x 1 cm pieces.

A known area of the film was placed into a 30 ml septa seal vial with either 25 ml of solvent or simply in air and sealed with silicone coated septa and tear away seals (Supelco Inc., Bellefonte DA). Two vials containing film and 25 ml of iso-propanol, and 2 vials containing 25 ml of ethyl acetate and film were stored at room temperature for 24 hrs. Two vials containing only film were placed in an oven at 80^{o}C for 24 hrs. After the allotted time period, 1 ul of solvent was taken from each vial (individually) and injected into the GC for analysis. For the vial containing only the film, 500 ul of the headspace volume was used for analysis by the GC.

No measurable quantities of probe quantities were obtained from analysis of the contents of any of the vials. Thus, it was assumed that levels of the probes sorbed by the film were below the limits of detection by gas chromatography. Therefore, quantification of the probe compounds sorbed by the plastic films was determined using the difference method (Kashtock et al., 1980; Imai, 1988). In this procedure, apple juice is put into the 260 ml amber colored glass bottle and the concentration of probe compounds are determined at the same time intervals as the juice/film system. This set serves as a control for the analysis. This data is then compared to that obtained from the film/juice samples. The probe concentrations in the juice/film system are determined using the purge and trap procedure at each time interval and the levels compared to

those of the control sample. Thus, the level of probe compound sorbed is determined by difference. It is assumed that any difference between the test sample data and the control data is due to probe compound sorption by the film.

IMMERSION STUDY - MECHANICAL PROPERTIES

Tensile Testing

Forty square inches (258.1 cm^2) of each film were placed into amber colored glass bottles containing 260 ml of apple juice. These samples were then stored at 22°C ±2°C inside a corrugated box to prevent light penetration. A volume to area ratio of juice to film was maintained at 1.01 ml/cm^2. Table 3 lists the sample sheet size of each film per volume of juice needed to maintain this ratio. Mechanical property tests were conducted initially (0 time), and after 1, 3, 6, 14, and 24 days of immersion. Probe compound concentration measurements on the juice were also conducted at these time intervals. Upon removal of the film from the juice, three 40 ml aliquots of juice were taken and the concentration of the probe compounds in the juice determined. Following removal from the juice, the film samples were rinsed with distilled water for one minute prior to measuring the different mechanical properties. Stress-strain properties were determined according to ASTM Standard D 882-83 (1984) using the Instron Testing Instrument (Instron Corporation, Canton, MA). The immersed

Table 3. Film sample size and film area/juice volume ratio.

Mechanical Property	Film	Number of Sheets	Sheet Size	Area of Film (cm^2)	Volume of Juice (ml)	Volume to Area (ml/cm^2)
Stress - Strain (a)	Alathon	10	1" x 4"(b)	258.1	260	1.01
Stress - Strain	EVOH	10	1" x 4"(b)	258.1	260	1.01
Stress - Strain	Co-Pet	6	1" x 6"(c)(d)			
		1(e)	1" x 4"(b)	258.1(f)	260	1.01
Impact Resistance	Alathon	6	7" x 6.5"(g)	1761.3	1870	1.06
Impact Resistance	EVOH	6	7" x 6.5"(g)	1761.3	1870	1.06
Impact Resistance	CoPet	6	7" x 6.5"(g)	1761.3	1870	1.06

(a) Stress-Strain properties include, modulus of elasticity, percent elongation at break, tensile strength, and heat seal strength.
(b) 2.54 cm x 10.16 cm.
(c) 2.54 cm x 15.24 cm.
(d) Extra length needed due to percent elongation at break testing requirements. If percent elongation at break is less then 100%, then a grip separation of no less then four inches is to be used (ASTM D 882-83, 1984)
(e) This 1" x 4" was not tested for stress-strain properties, but was needed to keep the film area to juice volume ratio at a constant value as compared to the other film samples.
(f) Total area of film sample immersed in juice.
(g) 17.78 cm x 16.51 cm.

samples were tested for the following mechanical properties:

a. Yield Point

b. Modulus of Elasticity

c. Tensile Strength

d. Percent Elongation at Break

e. Seal Strength

Ten specimens were tested for each sample (a-d) in the machine direction (MD) and cross direction (CD). To determine the influence of sorption on heat seal strength, samples were prepared by taking a machine direction sample, cutting it in half and then heat sealing the two pieces together. Heat seal strength was determined to see if juice contact effected the heat induced bond formed between the two pieces of film. Heat seals were made using an impulse heat sealer (Sentinel Heat Sealer Inc., Hyannis, MA). Heat sealing conditions for each film and the settings used for stress-strain testing are shown in Appendix D.

Impact Resistance

For this test, sample specimens of each film were immersed in apple juice until equilibrium (21 days) was obtained between the juice and the film. A volume to film ratio of 1.06 ml/cm^2 was utilized in order to accommodate the larger sample sizes needed for impact testing. The free-fall dart method using the staircase testing technique (ASTM D 1709-85, 1986) was used for measuring impact resistance. Initial impact resistance testing of the three

test films showed failure even with no weight on the dart at the standard drop height of 0.66m. Therefore, drop height of 0.33m was used in order to show variance in impact failure weight due to juice contact with the film. Impact failure weight (Wf) was calculated as follows:

$$Wf = Wo + [\hat{}W \{(A/N) - (1/2)\}]$$

Wf = Impact failure weight

Wo = Missile weight to which an i value of 0 is assigned (g)

$\hat{}W$ = Uniform weight increment used (g)

A = i (ni)

i : Integers 0, 1, 2, etc.

ni : number of failures in each missile weight.

Sorption of probe compounds by the sample films was determined as described for stress-strain properties prior to immersion and at equilibrium (21 days).

RESULTS AND DISCUSSION

PRODUCT CHARACTERIZATION

Probe Analysis

The purge and trap procedure, previously described, was used to analyze the apple juice. This allowed quantitation of selected aroma/flavor components in the apple juice by gas chromatography (GC) analysis. A typical chromatograph for apple juice volatiles can be found in Appendix E (Figure 42). Retention times and peak responses for the probes were identified through comparison of apple juice extracts spiked with the probe compounds, to samples of the "natural" juice extract. The GC retention times for the four probe compounds selected for study are presented below.

Ethyl-2-methylbutyrate	17.1 minutes
Hexanal	19.3 minutes
trans-2-Hexenal	30.1 minutes
1-Hexanol	40.3 minutes

It should be noted that retention times were dependent upon analytical conditions and may vary slightly from run to run.

The initial concentrations of the probe compounds in the juice are shown in Table 4. These levels were determined immediately after addition of the additive package. The flavor components in apple juice are present in the range of 0.04 - 3.20 ppm (wt/v). Thus, recoveries of the respective probes is very important. To improve percent recoveries of the probe compounds, a salting out technique was utilized to enhance removal of the probe components from the juice (Poll, 1984). It was found that the addition of salt increased the volatility of the probes. This enabled a quicker, more efficient removal of the probe components from the juice. Various amounts of salt were added to juice samples in order to determine the optimum level for probe extraction (10%, 12.5%, 25% and 37.5% (wt/v)). It was found that a 25% wt/vol addition of salt to the juice sample gave the best results. Addition of salt quantities in excess of this level resulted in difficulty in dissolving the salt in the juice prior to purging. Recovery studies were carried out by adding a known quantity of probe compound to a prepurged sample of apple juice, following the purge and trap procedure. Percent recovery for the probe compounds are shown in Tables 5, 6 and 7. As shown in Table 7, recovery levels were essentially quantitative.

Storage Stability of Apple Juice

The stability of apple juice, stored at 22^{o}C $\pm$2^{o}C, was determined by quantification of the four aroma/flavor

Table 4. Levels of probe compounds found in apple juice

Probe compound	Functionality	Concentration of Probe in Juice (ppm, wt/v)
Ethyl-2-methylbutyrate	Ester	0.038
Hexanal	Aldehyde	0.160
trans-2-Hexenal	Aldehyde	0.320
1-Hexanol	Alcohol	3.234

components and measurement of microbial growth in apple juice containing antioxidants (Sustane W and Sustane 20A) and an antimicrobial agent (sodium azide), as a function of storage time. The results are summarized in Tables 8, and 9.

The addition of preservatives to the juice prevented deterioration of product quality, as measured by change in probe compound concentration. Loss of flavor components was minimal and there was no evidence of bacterial growth after thirty days of storage at ambient temperature ($22^{o}C \pm 2^{o}C$). The preservatives used were also found to act as an anti-foaming agent in the juice during the extraction-concentration process.

Change to juice color and pH, in juice containing the preservatives were minimal (See Table 10).

Table 5. Percent recovery of ethyl-2-methylbutyrate from standard solutions via the purge and trap procedure

Concentration injected into pre-purged juice (ppm, wt/v) (a)	Concentration extracted from spiked juice (ppm, wt/v) (b)	% Recovery
1.31	1.78	136%
1.31	0.89	68%
0.86	0.83	97%
1.34	1.50	112%
1.54	1.75	114%
1.81	2.08	115%
	Average	108%

(a) Concentration level of Ethyl-2-methylbutyrate in juice after injection
(b) Concentration level of Ethyl-2-methylbutyrate detected after purging of juice

Table 6. Percent recoveries of 1-hexanol from standard solutions via the purge and trap procedure

Concentration injected into pre-purged juice (ppm, wt/v) (a)	Concentration extracted from spiked juice (ppm, wt/v) (b)	% Recovery
126	138	110%
156	169	108%
156	172	110%
145	160	110%
	Average	109.5%

(a) Concentration level of 1-hexanol in juice after injection
(b) Concentration level of 1-hexanol detected after purging of juice

Table 7. Percent recovery of aroma/flavor probes from standard solutions via the purge and trap procedure

Probe	Solution #1	Solution #2	Solution #3	Solution #4	Average of Solutions #1-#4
E-2MB (a)	140%	107%	99%	104%	113%
Hexanal	140%	107%	116%	116%	113%
trans-2-Hexenal	146%	108%	113%	111%	113%
1-Hexanol	125%	111%	112%	105%	110%

(a) Ethyl-2-methylbutyrate

Table 8. Growth of microorganisms in apple juice containing antimicrobial agents

Days of storage	Cell Count
7	0
10	0
14	0
17	0
21	0
24	0
30	0

cell counts are average of five replicates

Table 9. Probe concentration in apple juice containing antioxidant and antimicrobial agents.

Storage time (days)	E-2MB (a)	Hexanal	trans-2-Hexenal	1-Hexanol
0	0.06 ppm	0.17 ppm	0.30 ppm	3.35 ppm
14	0.05 ppm	0.16 ppm	0.37 ppm	3.33 ppm
Relative Concentration	96.1%	93.9%	122%	99.4%

storage study conducted at 22°C ±2°C

(a) Ethyl-2-methylbutyrate

Table 10. Color and pH of apple juice during storage at 22°C ±2°C containing preservatives

Storage time (in days)		L	a	b	pH
0		13.3_1	4.3_1	7.2_1	
		13.5_1	3.8_1	6.9_1	4.00
	Average	13.25_1	4.05_1	7.05_1	
7		11.4_1	6.9_1	6.2_1	
		11.5_1	6.8_1	6.1_1	3.80
	Average	11.45_1	6.85_1	6.15_1	
14		10.3_1	6.1_1	5.0_1	
		10.2_1	6.1_1	4.9_1	3.72
	Average	10.25_1	6.10_1	4.95_1	
24		9.3_1	6.4_1	4.2_1	
		9.5_1	6.3_1	4.3_1	3.64
	Average	9.40_1	6.35_1	4.25_1	
36		9.0_1	6.4_1	3.5_1	
		8.7_1	6.6_1	3.6_1	3.53
	Average	8.85_1	6.50_1	3.55_1	
0 Time Sample Frozen After 36 Days		13.2_1	2.7_1	6.5_1	
		13.2_1	2.7_1	6.5_1	3.70
	Average	13.2_1	2.7_1	6.5_1	
Standard Tile Yellow C2-12403		78.4_1	-3.0_1	22.7_1	

*All readings taken using Hunter Color Difference Meter, Model# D25-2 (Hunter Associates Lab. Inc., Reston, Va).

Sorption Measurements

Measurement of the aroma/flavor probe components (ethyl-2-methylbutyrate, hexanal, trans-2-hexenal, 1-hexanol) in the apple juice was determined as a function of storage time of the juice in contact with the individual plastic film strips (Alathon, EVOH, Co-Pet). The level of each flavor probe in the control juice sample, for each time interval, was determined and is shown in Appendix VI. For better illustration the data are presented graphically in Figures 2,3,4 and 5 where the relative concentration of the probe compounds is plotted as a function of storage time.

Using a linear regression technique (Gill, 1985) (Appendix H), it was found that the slopes of relative concentration vs. time graphs for ethyl-2-methylbutyrate, hexanal, and trans-2-hexenal, in the control juice were not statistically equal to zero. This indicates a change in concentration of the probe in the control sample, which must be taken into consideration when evaluating the results of the studies involving sorption of flavor probes by the test films. Only the slope of 1-hexanol was statistically equal to zero.

To determine the extent to which probe compounds were sorbed by a test film, a linear regression procedure of statistical analysis was employed, which allowed the incorporation of change in probe concentration due to factors other than sorption to be taken into consideration (Gill, 1985). The hypothesis that the probe control slope

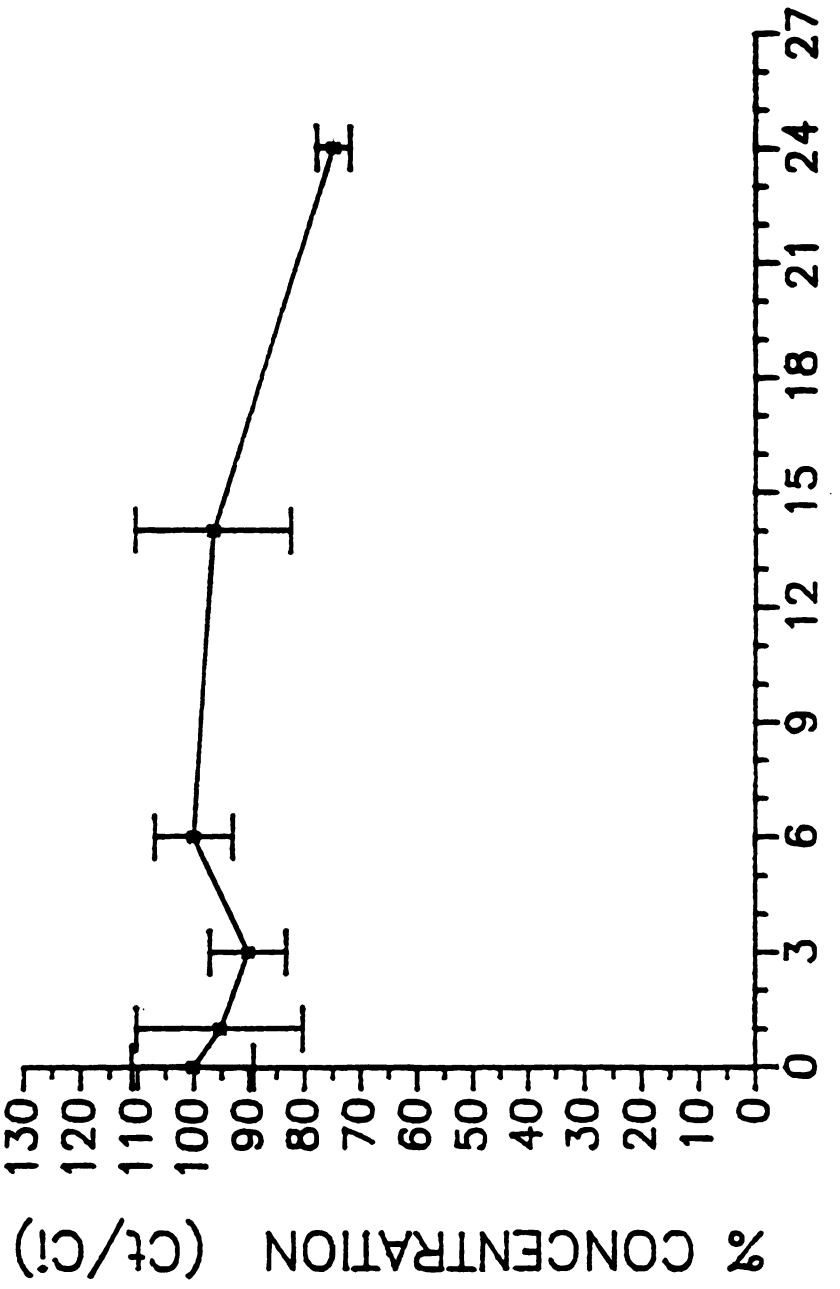

Figure 2. Relative concentration of ethyl-2-methylbutyrate control as a function of time

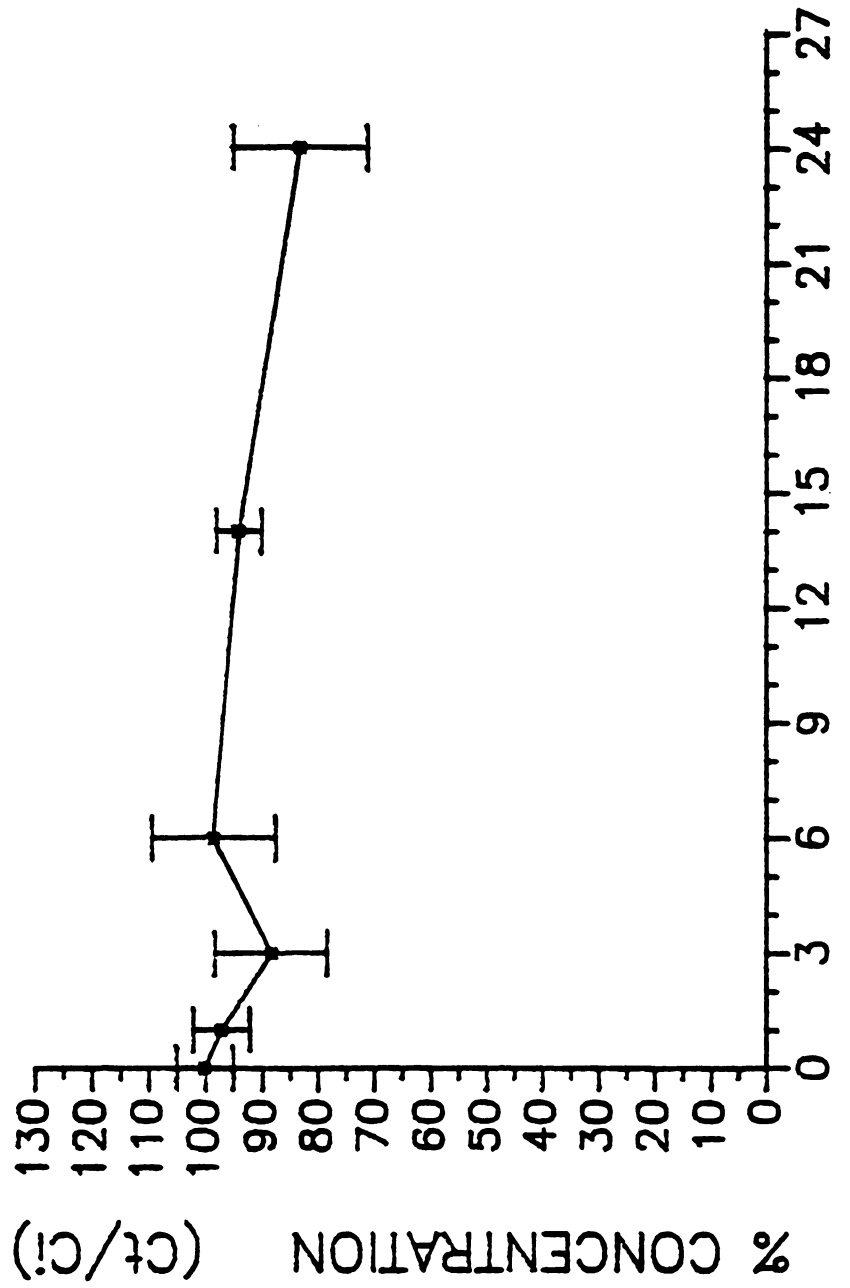

Figure 3. Relative concentration of hexanal control as a function of time

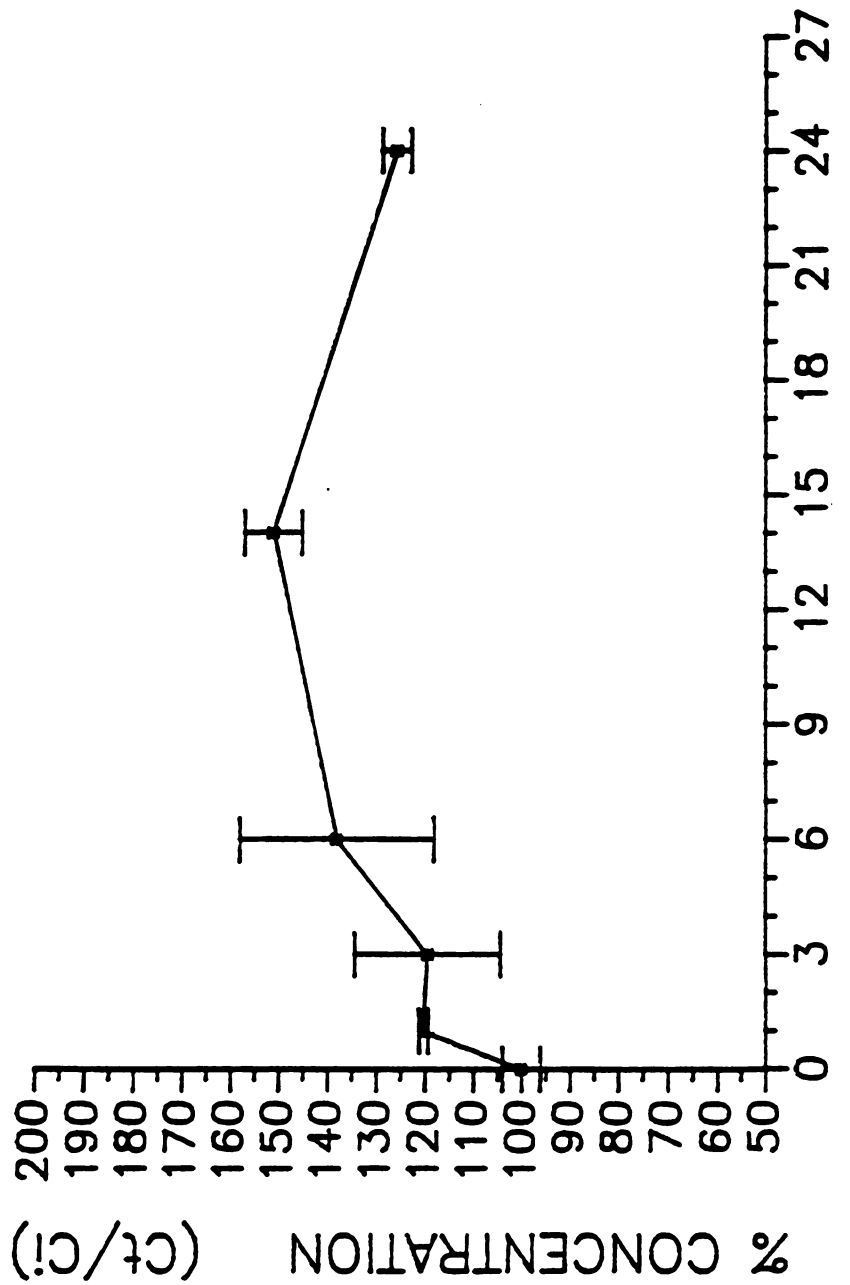

Figure 4. Relative concentration of trans-2-hexenal control as a function of time

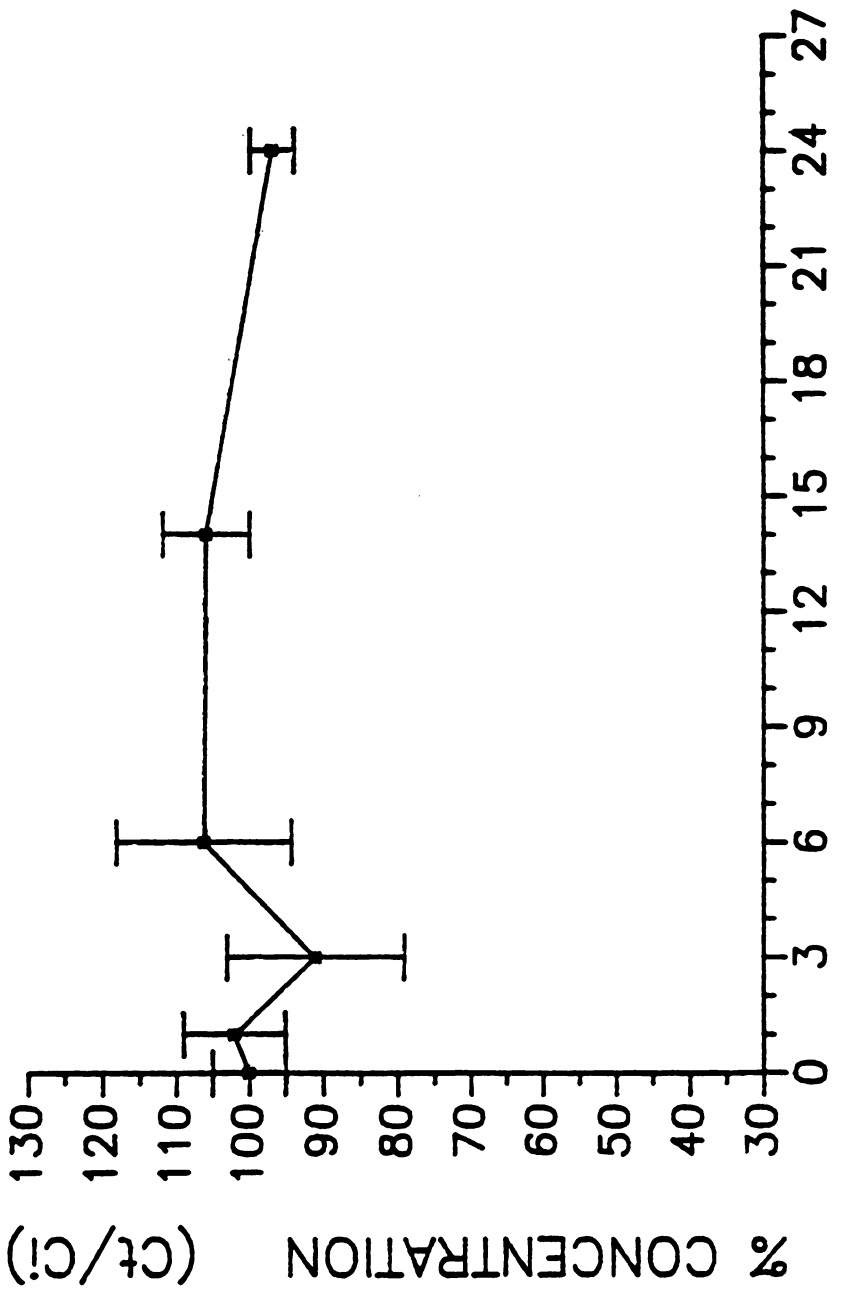

Figure 5. Relative concentration of 1-hexanol control as a function of time

was equal to the probe/film slope was tested for each film and each probe combination.

Statistical analysis of the data showed that the slopes of all four probe/Alathon film systems (Ethyl-2-methyl-butyrate 99% CL, Hexanal 99% CL, trans-2-hexenal 99% CL, and 1-Hexanol 80% CL) were not equal to zero (See Tables 12, 14, 16 and 18). This indicates a change in the concentration levels of the probes. Slopes and slope variances utilized in the statistical analysis are tabularized in Table 11. Further analysis revealed at high confidence levels, ethyl-2-methylbutyrate/Alathon (99% CL), hexanal/Alathon (99% CL) and trans-2-hexenal/Alathon (90% CL), that the slopes of

Table 11. Slopes obtained from concentration vs. time graphs of probe compounds

Probe	Film	Slope	Slope Variance
E-2MB (a)	Control	-4.529E-04	4.378E-05
E-2MB (a)	Alathon	-1.408E-03	6.562E-05
E-2MB (a)	EVOH	3.537E-05	4.258E-05
E-2MB (a)	Co-Pet	-3.265E-04	1.651E-05
Hexanal	Control	-8.718E-04	1.655E-04
Hexanal	Alathon	-3.210E-03	7.971E-05
Hexanal	EVOH	-1.138E-03	1.630E-04
Hexanal	Co-Pet	-1.054E-03	1.019E-04
trans-2-Hexenal	Control	2.804E-03	3.037E-03
trans-2-Hexenal	Alathon	-4.104E-03	1.027E-03
trans-2-Hexenal	EVOH	1.968E-03	2.514E-03
trans-2-Hexenal	Co-Pet	1.662E-03	1.754E-03
1-Hexanol	Control	-3.456E-04	8.385E-02
1-Hexanol	Alathon	-5.611E-02	3.775E-02
1-Hexanol	EVOH	5.058E-03	8.159E-02
1-Hexanol	Co-Pet	-3.217E-03	6.819E-02

(a) Ethyl-2-methylbutyrate

Table 12. Slope of concentration vs. time statistics for ethyl-2-methylbutyrate concentrations in apple juice

Hypothesis: Slope = 0 for a given treatment

Treatment	t
Control	-10.35 (a)
Alathon	-21.46 (a)
EVOH	0.83 (b)
Co-Pet	-19.78 (a)

(a) 99% confidence level that slope is not equal to zero
(b) 60% confidence level that slope is not equal to zero

Table 13. Statisics table comparing ethyl-2-methylbutyrate concentrations among treatments

Hypothesis: Control Slope = Treatment Slope
(Conc. vs. Time) (Conc. vs. Time)

Treatment	t
Control slope is equal to Alathon slope	12.11 (a)
Control slope is equal to EVOH slope	-7.99 (a)
Control slope is equal to Co-Pet slope	-2.70 (a)

(a) 99% confidence level that control slope is not equal to film slope

Table 14. Slope of concentration vs. time statistics for hexanal in apple juice

Hypothesis: Slope = 0 for a given treatment

Treatment	t
Control	-5.27 (a)
Alathon	-40.27 (a)
EVOH	-6.98 (a)
Co-Pet	-10.34 (a)

(a) 99% confidence level that the slope is not equal to zero

Table 15. Statisics table comparing hexanal concentrations among treatments

Hypothesis: Control Slope = Treatment Slope
(Conc. vs. Time) (Conc. vs. Time)

Treatment	t
Control slope is equal to Alathon slope	12.11 (a)
Control slope is equal to EVOH slope	1.15 (b)
Control slope is equal to Co-Pet slope	-2.70 (b)

(a) 99% confidence level that film slope is not equal to zero
(b) Control slope is statistically equal to film slope

Table 16. Slope of concentration vs. time statistics for trans-2-hexenal in apple juice

Hypothesis: Slope = 0 for a given treatment

Treatment	t
Control	0.92 (b)
Alathon	-4.00 (a)
EVOH	0.78 (b)
Co-Pet	0.95 (b)

(a) 99% confidence level that the slope is not equal to zero
(b) 60% confidence level that the slope is not equal to zero

Table 17. Statisics table comparing trans-2-hexenal concentrations among treatments

Hypothesis: Control Slope = Treatment Slope
(Conc. vs. Time) (Conc. vs. Time)

Treatment	t
Control slope is equal to Alathon slope	2.16 (a)
Control slope is equal to EVOH slope	0.21 (b)
Control slope is equal to Co-Pet slope	0.33 (b)

(a) 90% confidence level that film slope is not equal to control slope
(b) Control slope is statistically equal to film slope

Table 18. Slope of concentration vs. time statistics for 1-hexanol in apple juice

Hypothesis: Slope = 0 for a given treatment

Treatment	t
Control	-0.004 (a)
Alathon	-1.490 (b)
EVOH	0.620 (a)
Co-Pet	-0.047 (a)

(a) Slope is statistically equal to zero
(b) 80% confidence level that slope is not equal to zero

Table 19. Statisics table comparing 1-hexanol concentrations among treatments

Hypothesis: Control Slope = Treatment Slope
(Conc. vs. Time) (Conc. vs. Time)

Treatment	t
Control slope is equal to Alathon slope	0.606 (a)
Control slope is equal to EVOH slope	-0.059 (a)
Control slope is equal to Co-Pet slope	0.027 (a)

(a) Control slope is statistically equal to film slope

relative concentration vs. time plots are not equal to the control slopes (See Tables 13, 15, 17 and 19). For better illustration the relative concentration vs. storage time plots for the probe/film systems are superimposed on the control plots (Figures 6, 7, 8 and 9). The results indicate that sorption of ethyl-2-methylbutyrate, hexanal, and trans-2-hexenal by the Alathon film did occur.

Statistical procedures show that the 1-hexanol/Alathon concentration vs. time slope is not equal to zero. This indicates that some change did occur. Statistical comparisons of the 1-hexanol control and the 1-hexanol/Alathon system reveal, however, that there is a high confidence level for the two slopes to be equal (See Table 19). The initial conclusion, therefore, is that no sorption is taking place. By looking at the tabular data and graphic presentation of the results (Appendix F and Figure 9), there appears to be a fairly large difference between the control and the 1-hexanol/Alathon film system. The statistical non-significance of the results is probably due to the high degree of variance among the control data. More data would need to be collected in order for a statistical difference to appear. DeLassus et al. (1988) found low density polyethylene to be a good solvent to apple flavor components. Hirose et al. (1988) and Imai (1988) both determined that low density polyethylene was a poor barrier to d-limonene in orange juice. Low density polyethylene has been found to be a poor flavor barrier, due

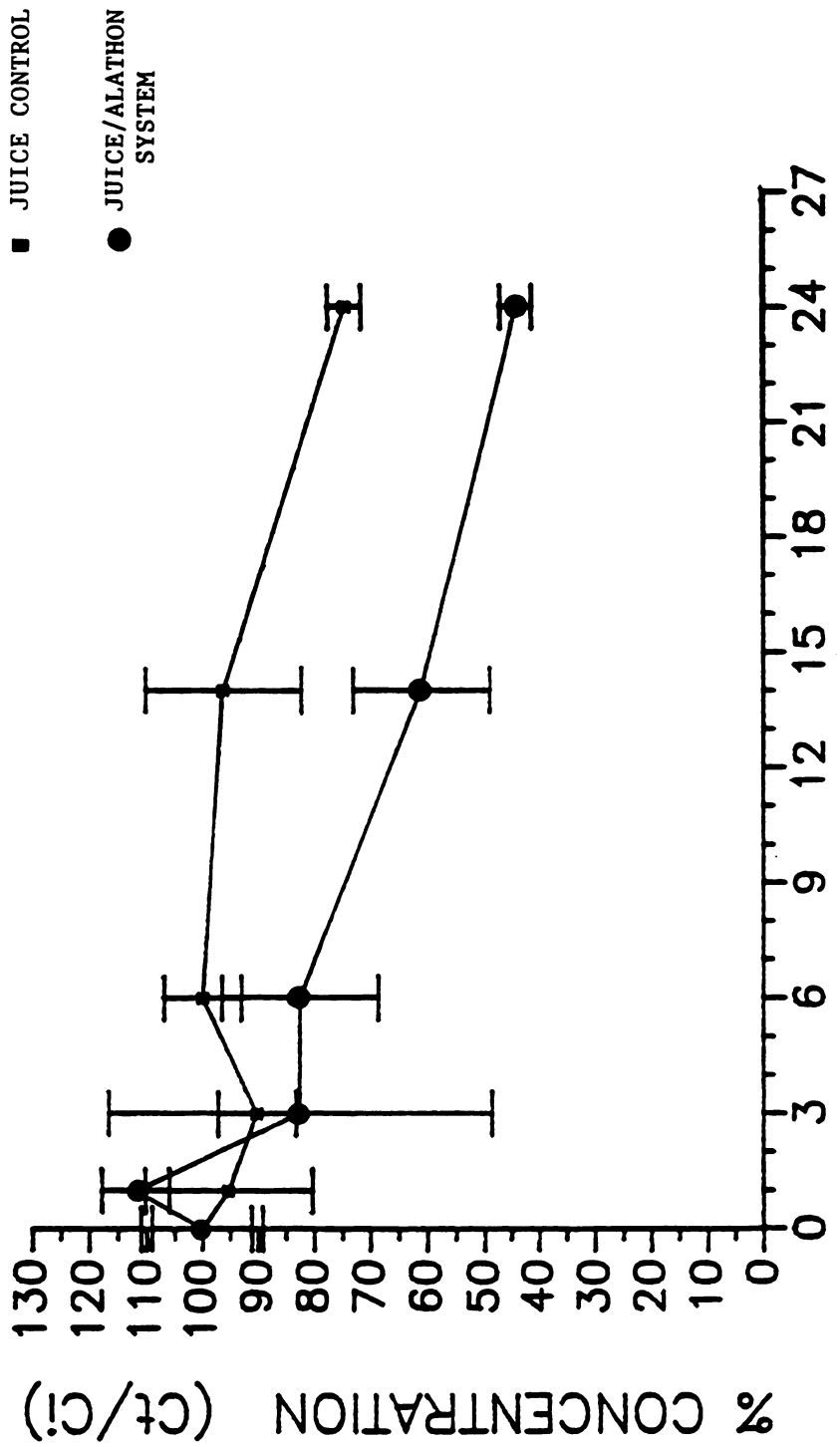

Figure 6. Relative concentrations of ethyl-2-methylbutyrate control and juice/Alathon film system as a function of time

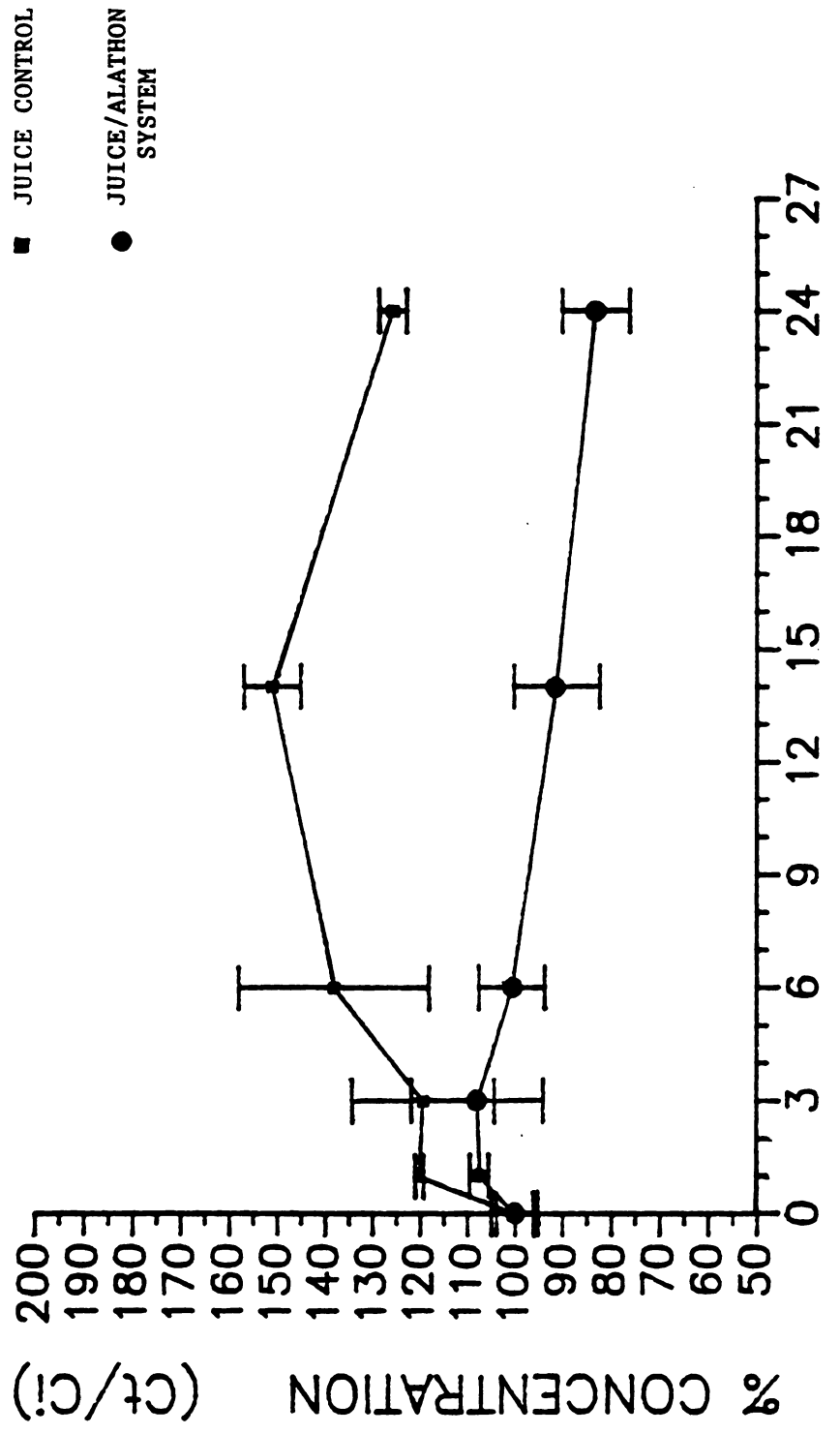

Figure 8. Relative concentrations of trans-2-hexenal control and juice/Alathon film system as a function of time

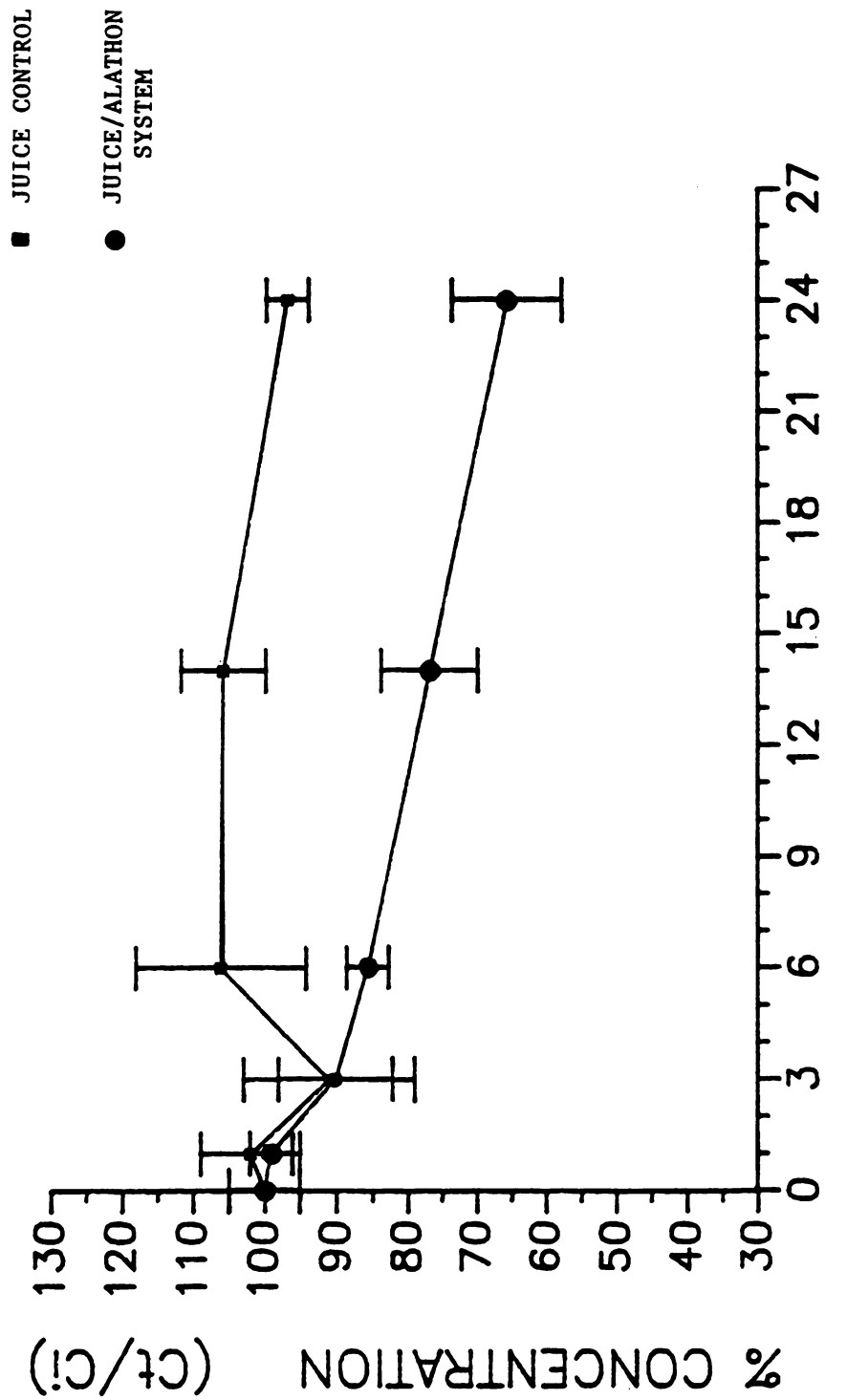

Figure 9. Relative concentrations of 1-hexanol control and juice/Alathon film system as a function of time

to it's affinity to hydrocarbons (Ikegami, 1987).

The EVOH film did not sorb hexanal, trans-2-hexenal or 1-hexanol. Statistical results demonstrated that the concentration vs. time slopes of the probe/EVOH systems were equal to the control probe slopes at a 99.9% confidence level (Tables 15, 17 and 19). See Figures 11, 12 and 13 for graphical presentation of the data (See Appendix F for the actual data collected for these probes). Statistical analysis of the ethyl-2-methylbutyrate/EVOH system suggests that there is sorption of the flavor by the EVOH film. However, graphically viewing the data (Appendix F and Figure 10) shows that the difference between the control and the EVOH film data is very small.

The Co-Pet film results were similar to those obtained for the EVOH film. The hexanal/Co-Pet, trans-2-hexenal/Co-Pet and 1-hexanal/Co-Pet system slopes were statistically equal to the control slope, confirming that sorption of these probes by the Co-Pet film had not occurred (Table 15, 17 and 19 and Figure 15, 16 and 17). The ethyl-2-methylbutyrate probe statistically, appeared to be sorbed by the Co-Pet. However, examining Figure 14 reveals little difference between the control slope and the film system slope. Any sorption which had occurred, is thus minimal.

The chemical structure of a polymer film has been shown to play a significant role in determining whether a film sorbs flavors or not. Hirose et al. (1988) and Imai (1988) both found differences between levels of d-limonene sorbed

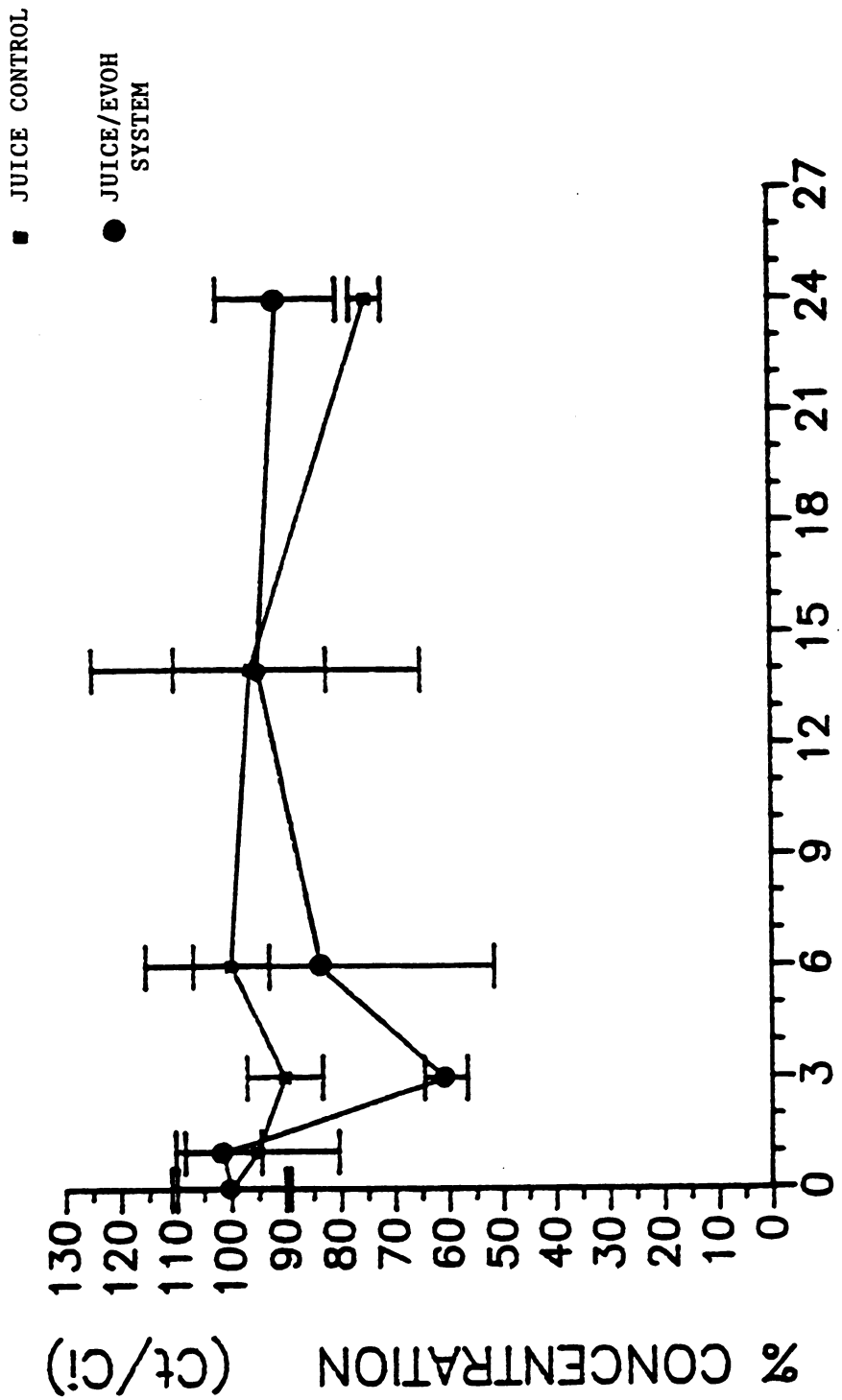

Figure 10. Relative concentrations of ethyl-2-methylbutyrate control and juice/EVOH film system as a function of time

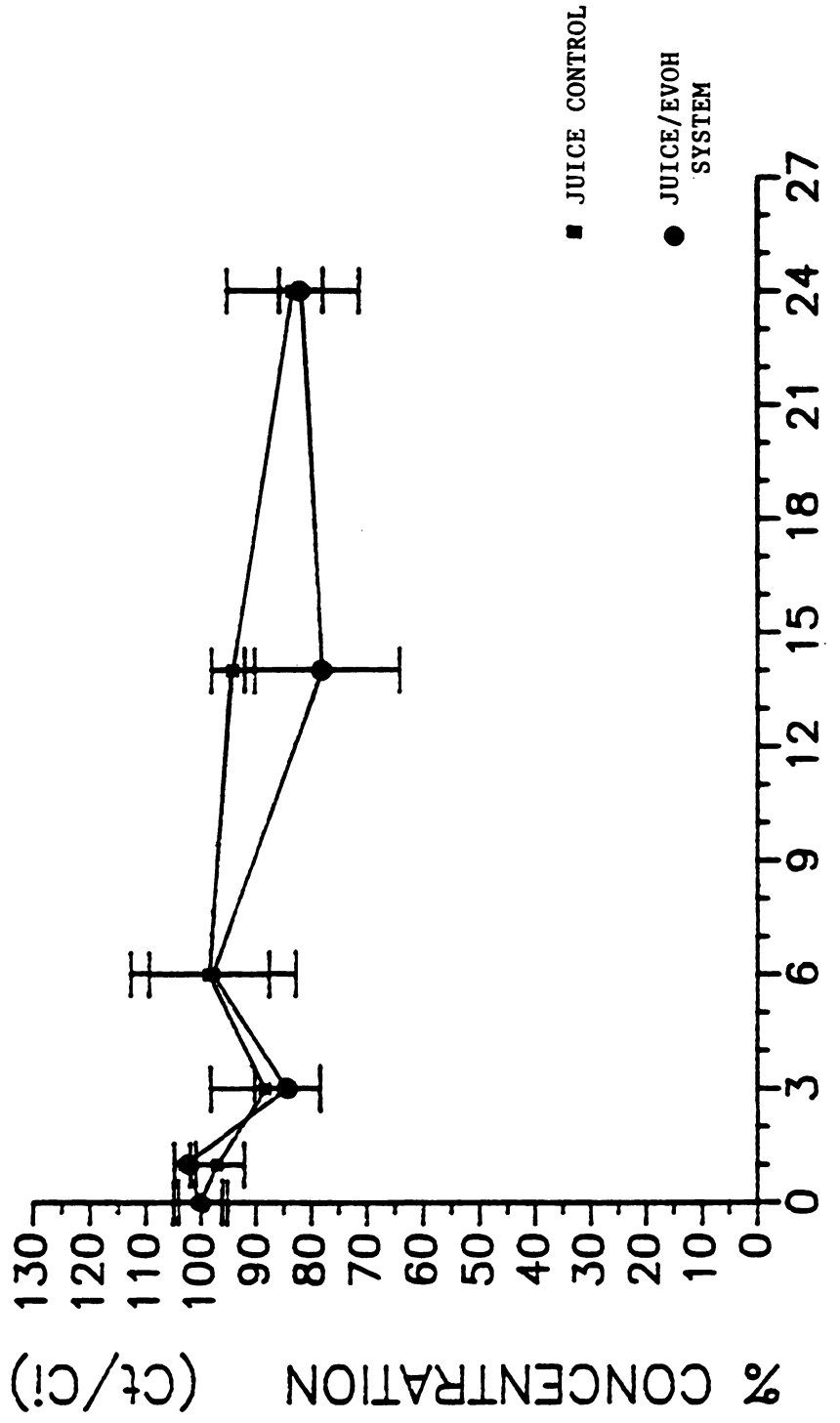

Figure 11. Relative concentrations of hexanal control and juice/EVOH film system as a function of time

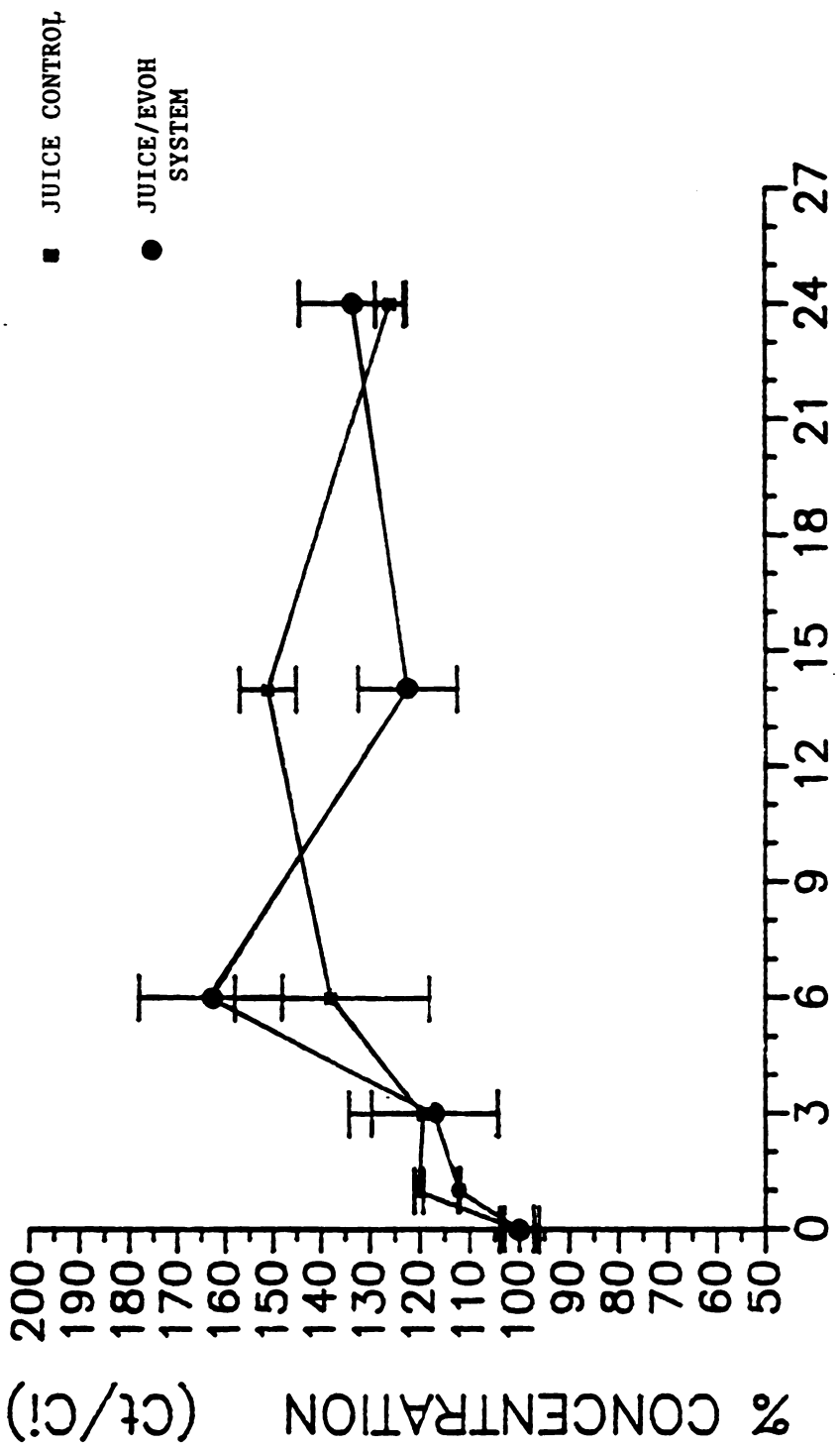

Figure 12. Relative concentrations of trans-2-hexenal control and juice/EVOH film system as a function of time

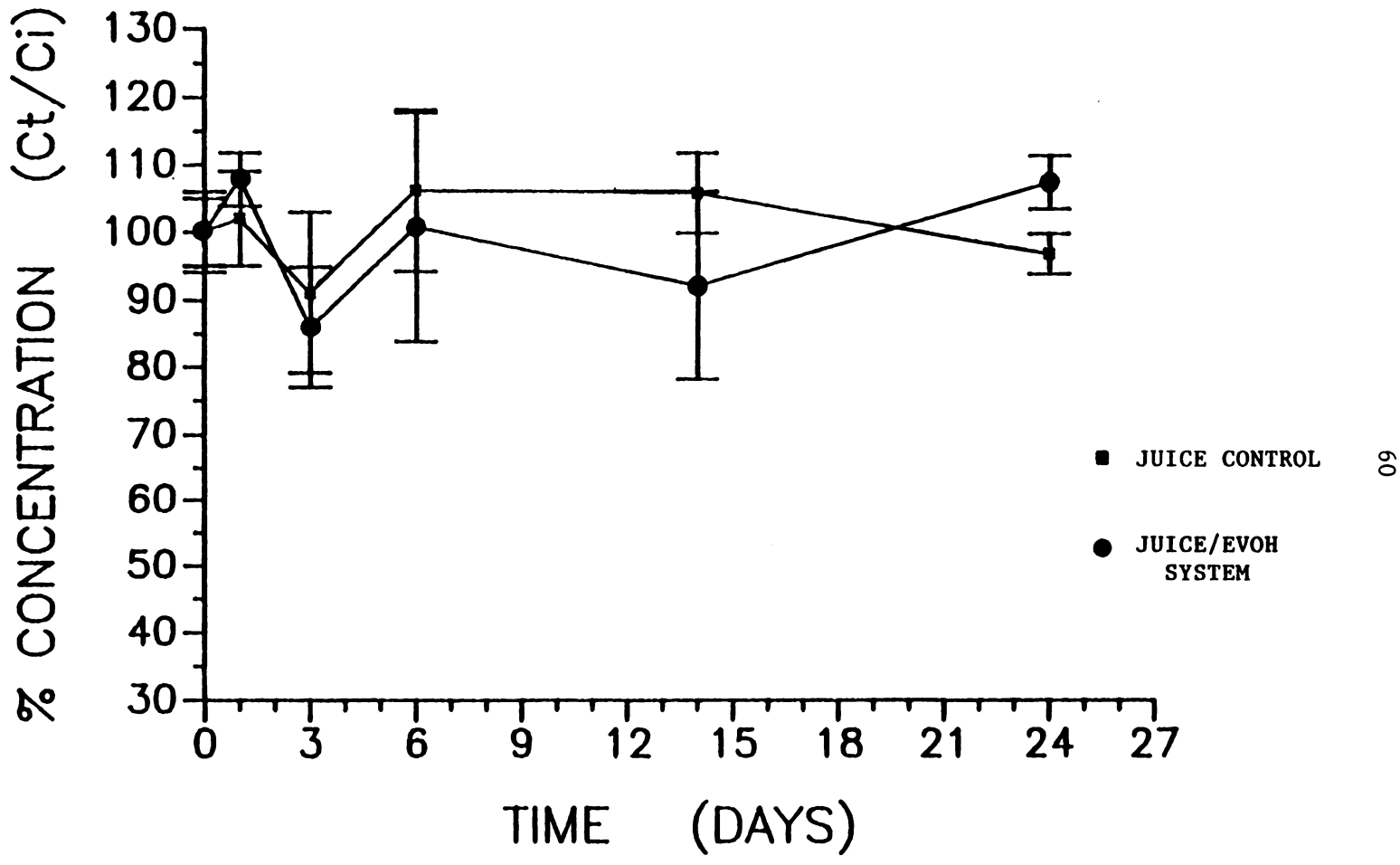

Figure 13. Relative concentrations of 1-hexanol control and juice/EVOH film system as a function of time

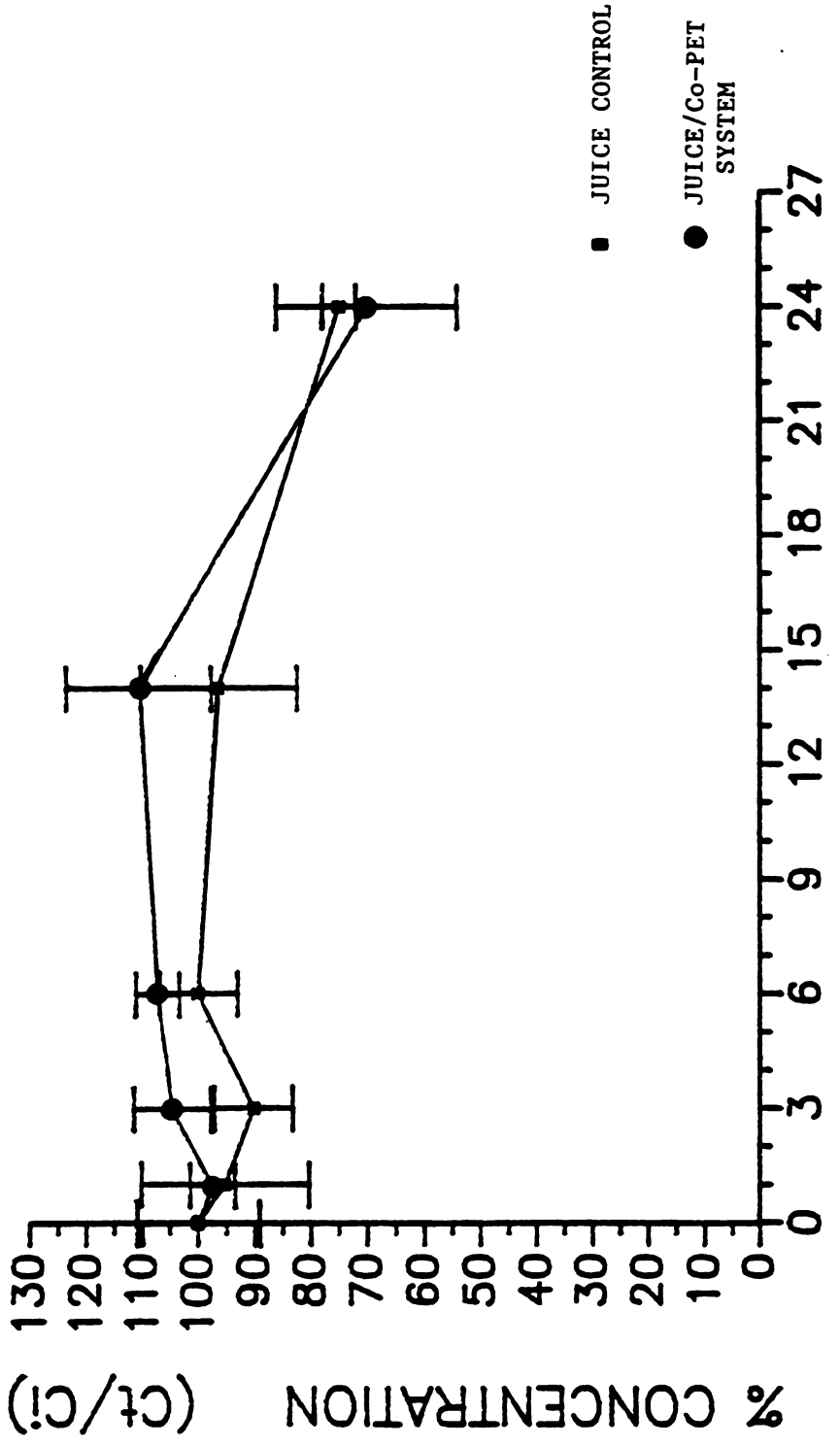

Figure 14. Relative concentrations of ethyl-2-methylbutyrate control and juice/Co-Pet film system as a function of time

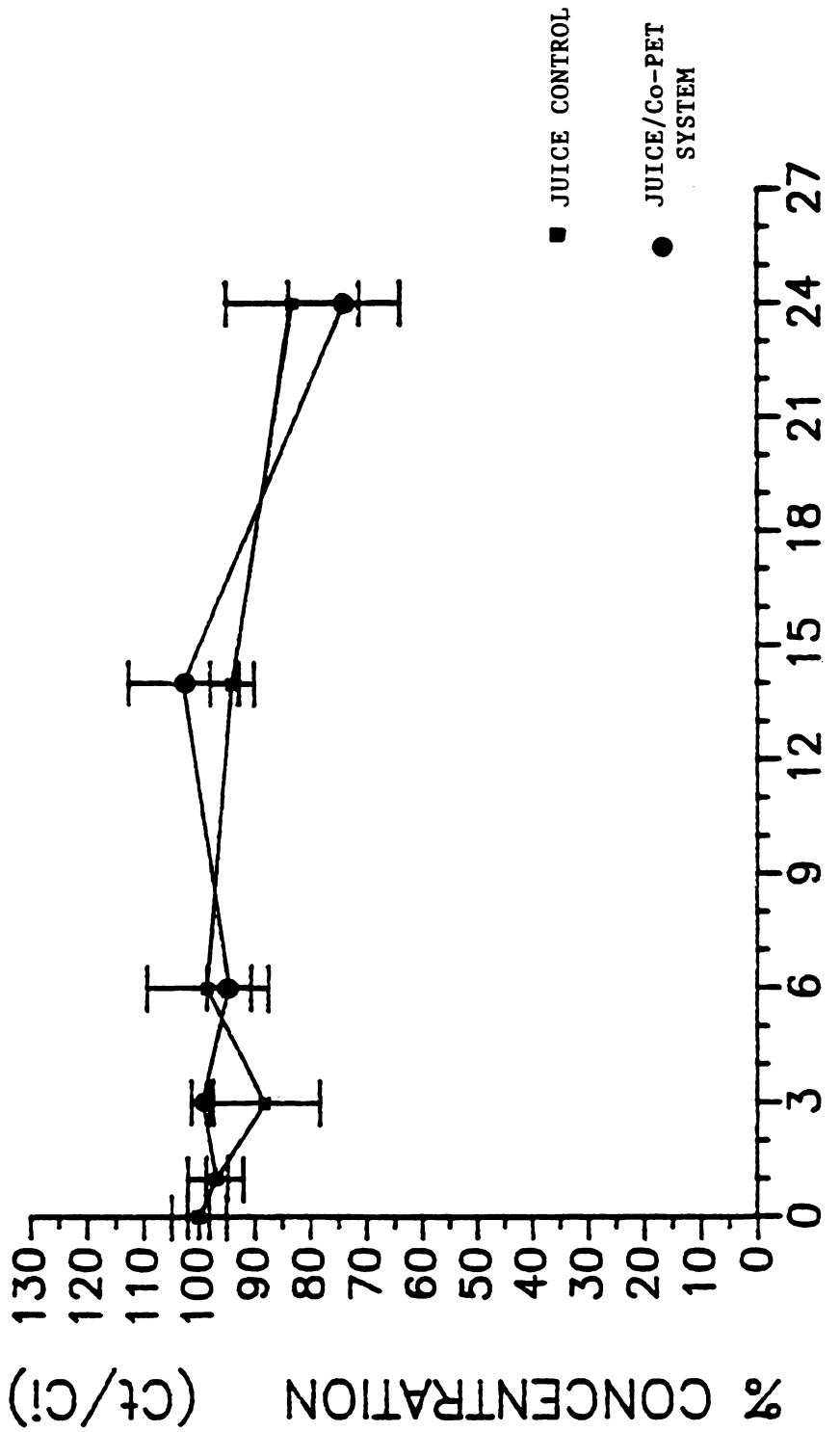

Figure 15. Relative concentrations of hexanal control and juice/Co-Pet film system as a function of time

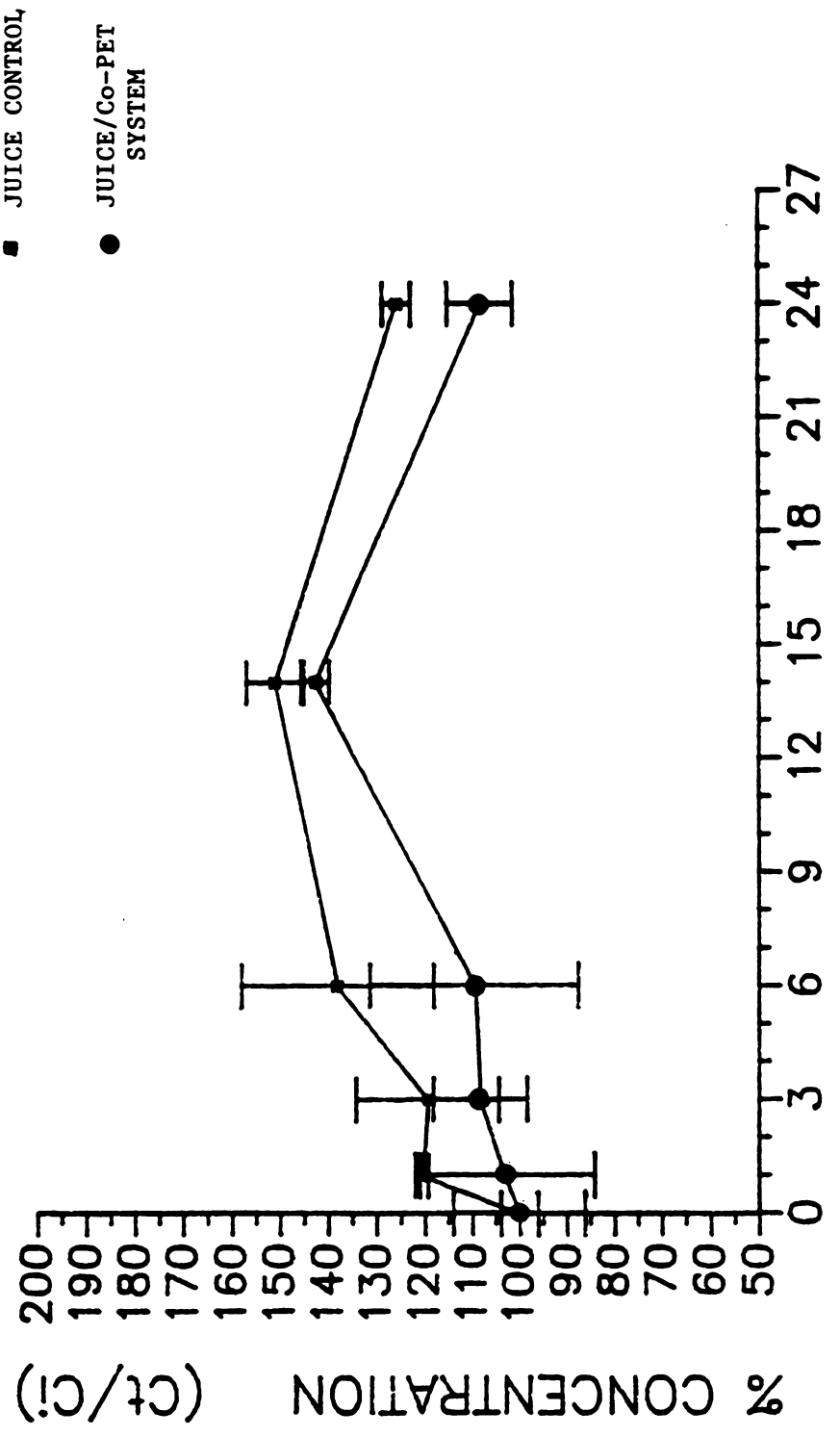

Figure 16. Relative concentrations of trans-2-hexenal control and juice/Co-Pet film system as a function of time

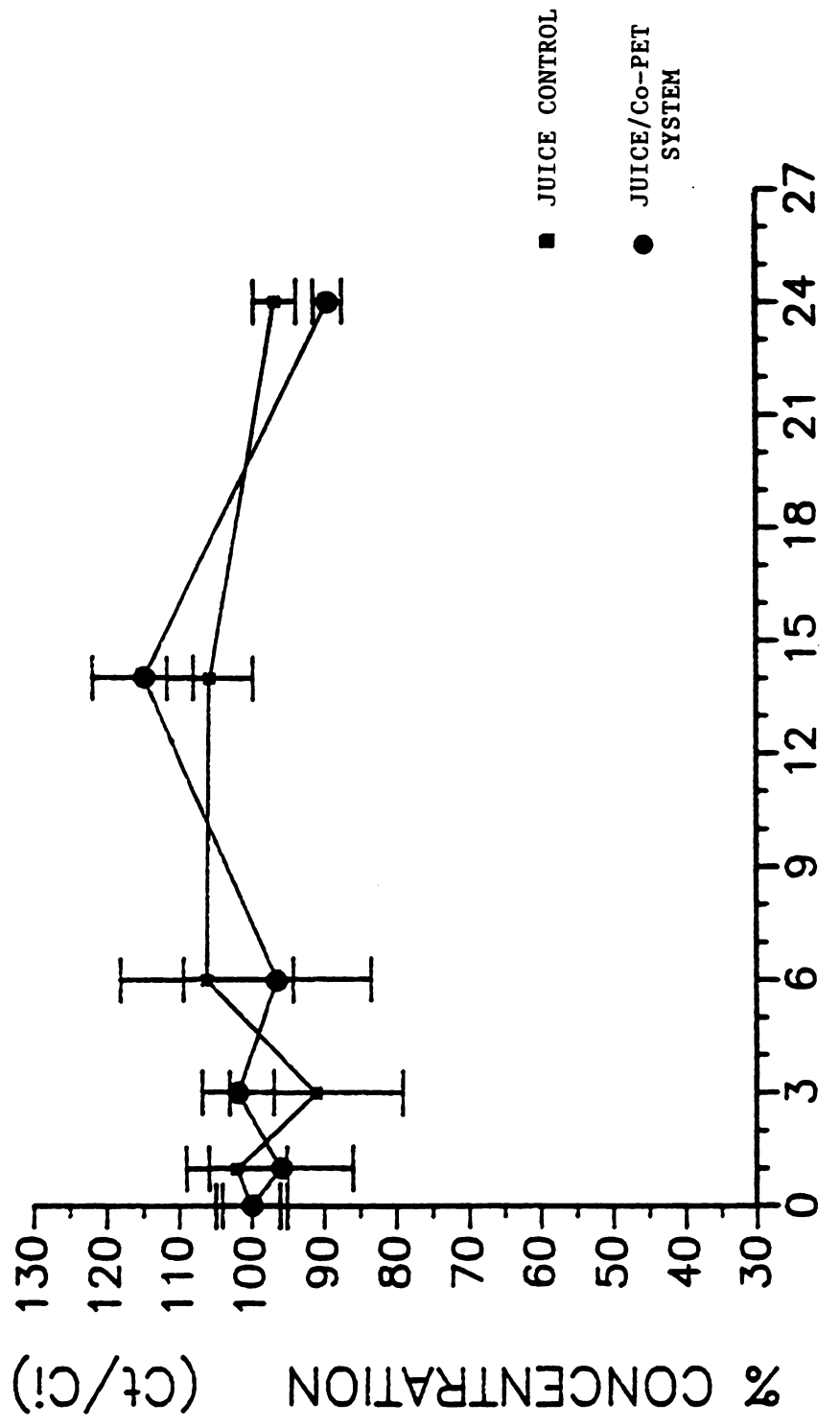

Figure 17. Relative concentrations of 1-hexanol control and juice/Co-Pet film system as a function of time

different polymer films. Hirose et al. (1988) found that low density polyethylene sorbed more d-limonene from orange juice then either a Surlyn^R sodium type film or Surlyn^R zinc type film did. Imai (1988) found no significant sorption of d-limonene from orange juice by a Co-Pet film. The same study showed d-limonene from orange juice was sorbed readily in significant levels by a low density polyethylene film and a high ethylene content EVOH film. Low density polyethylene is a hydrocarbon (as previously discussed) and is non-polar, while the high ethylene content EVOH and the Co-Pet structures, because of their functionality are more polar in nature. This difference in chemical structure contributes in part to the varying levels of sorption of the probe compounds by the respective film samples.

INFLUENCE OF FLAVOR SORPTION ON MECHANICAL PROPERTIES OF PLASTIC FILMS

The influence of flavor sorption on the yield point, tensile strength, modulus of elasticity, percent elongation at break, and heat seal strength was determined for each film. Results show that for all films, change occurred after one day of immersion with little additional change occurring after that. Statistical analysis, to determine significance of change in mechanical properties as a result of juice contact with the film, was performed using a contrast of means test (See Appendix I) (Gill, 1985). The means of the data for each mechanical test on the immersed film samples (at the pre-selected storage intervals of 1, 3,

6, 14, and 24 days) were compared as a group to the initial values obtained for the films prior to immersion in the juice product. This analysis was used rather then a day to day comparison of means because of the greater degrees of freedom associated with the test. Higher degrees of freedom result in higher confidence in the results (Gill, 1985).

It was found that changes occurred in the mechanical property of each of the three films after one day of immersion in the apple juice. Some deviation in the values occurred after one day but they were small and not significant in variation.

STRESS-STRAIN PROPERTIES

A typical stress-strain curve for low density polyethylene obtained with the use of the Instron testing equipment is shown in Appendix E.

Yield Point

The yield point is defined as the point on the stress curve after which the deformation increases more rapidly than the stress, indicating real plastic deformation (The Packaging Institute, 1979).

No significant differences were found between the films initial yield point, and the juice contact yield point in either the machine or the cross direction for the Alathon film sample. The yield point data is tabularized in

Appendix G and shown graphically for each film in Figures 18, 19 and 20 (each point on the graph represents the mean of approximately ten samples). The yield point of the EVOH film did change significantly (99.9% CL) in the machine and cross direction after one day of juice contact, with little change after that. The Co-Pet film did not exhibit a yield point initially, or at any other time during the analysis. As a result, no data was recorded for the yield point of Co-Pet.

Tensile Strength

Tensile strength of the material is defined as the maximum stress measured on a sample during the analysis (The Packaging Institute, 1979).

The influence of juice contact on the tensile strength of the sample films was determined and the results are summarized in Appendix G and in Figures 21, 22 and 23. Statistical evaluation of these data showed no change in tensile strength of the Alathon in the machine direction but a decrease in tensile strength in the cross direction, as a result of juice contact with the film (99.9% CL).

The tensile strength of the EVOH film changed in both the machine and cross directions (99.9% CL). All change occurred within one day of immersion of the film into the juice with little, if any, change after that. Plasticization of the film due to moisture contact with the film may have had an impact on these results (Nippon Gohsei, 1982).

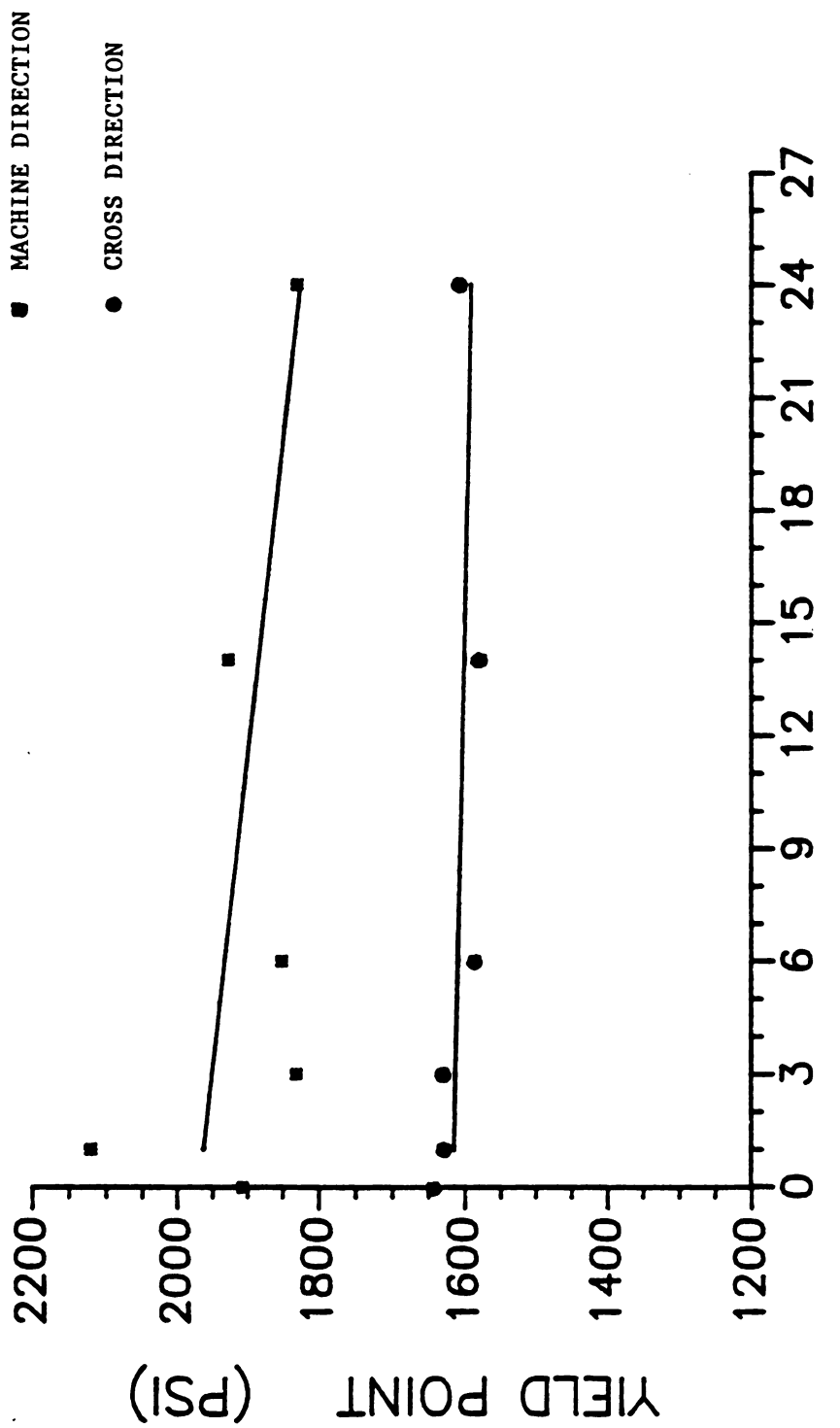

Figure 18. The yield point of Alathon as a function of immersion time in apple juice

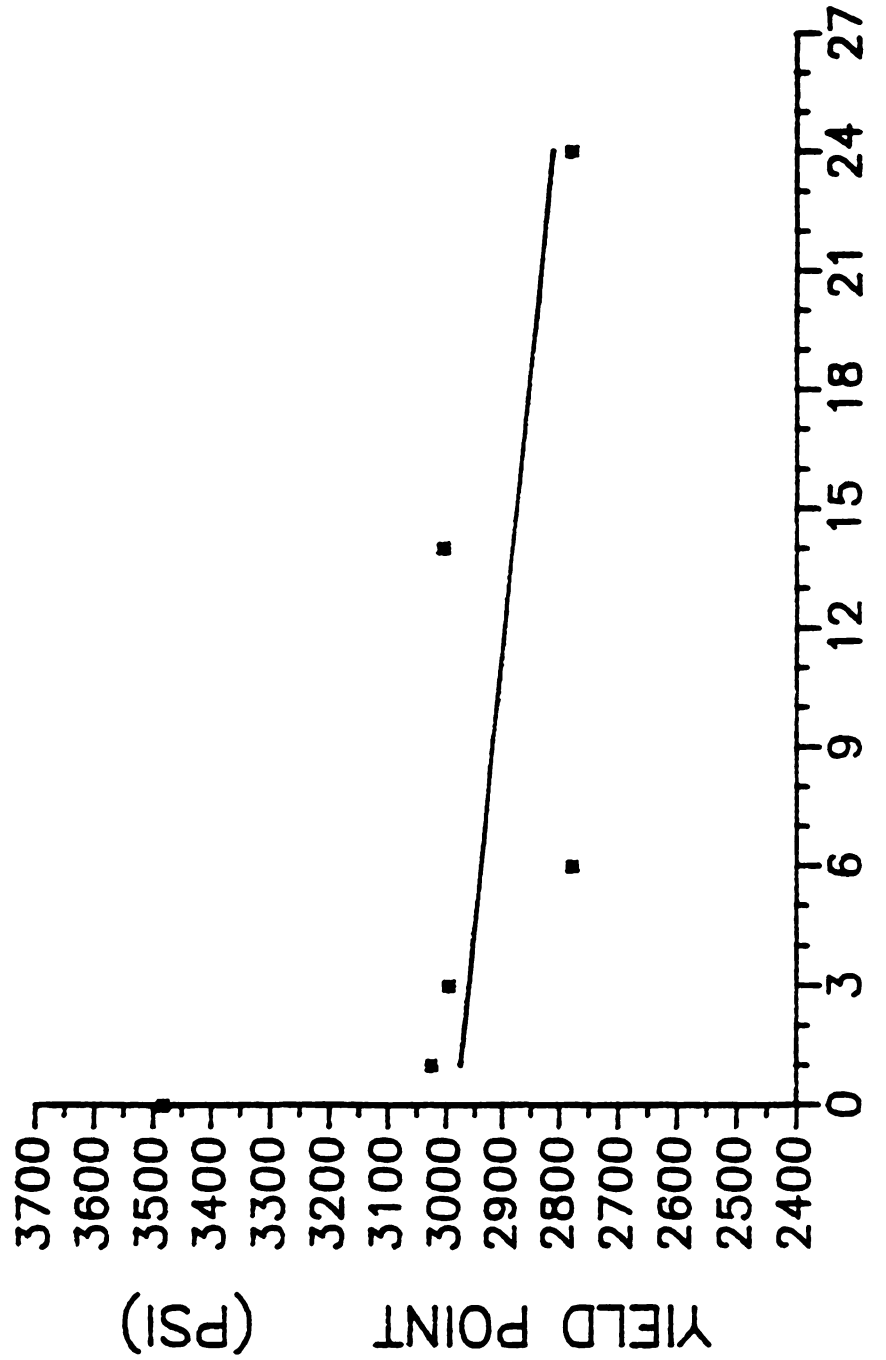

Figure 19. The yield point of machine direction EVOH as a function of immersion time in apple juice

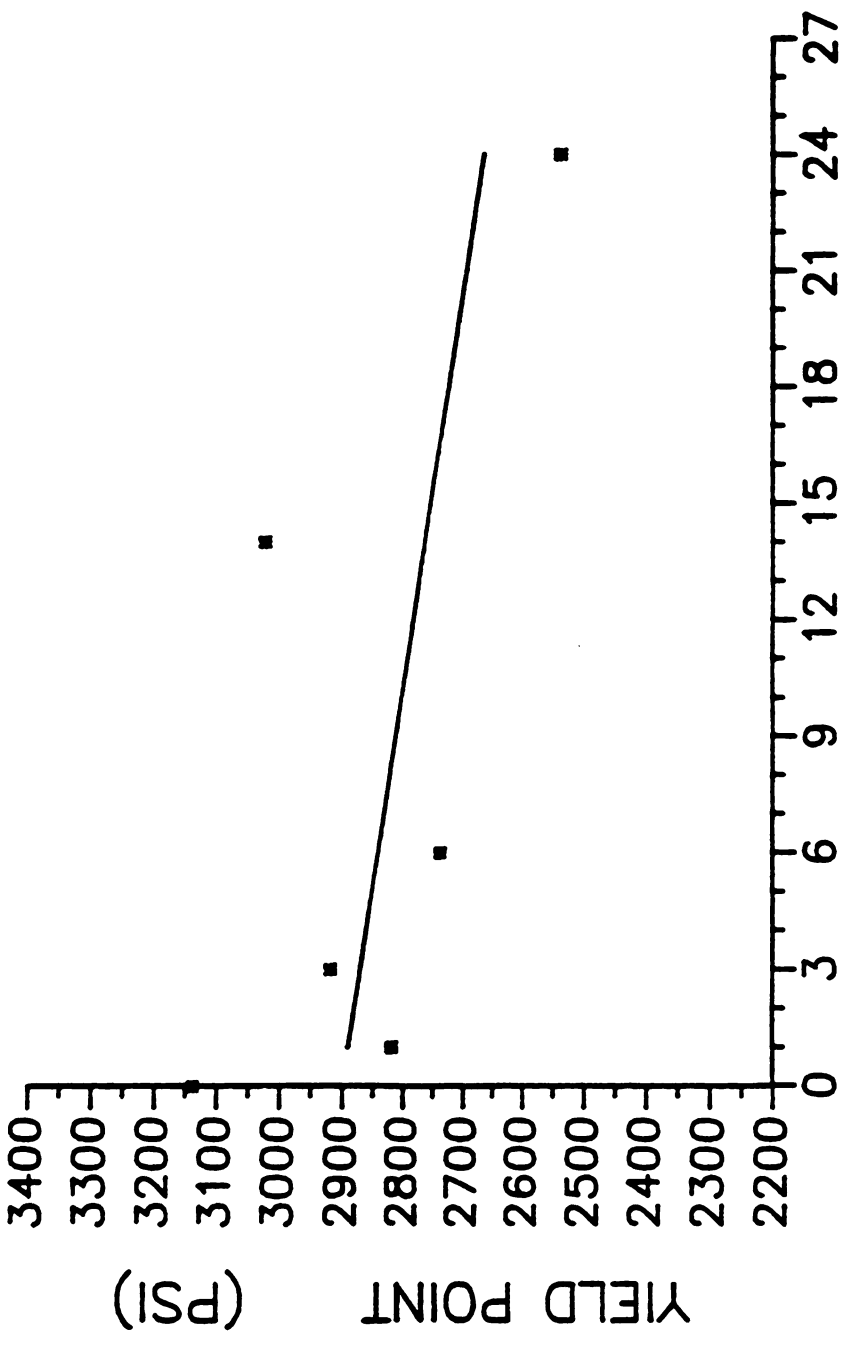

Figure 20. The yield point of cross direction EVOH as a function of immersion time in apple juice

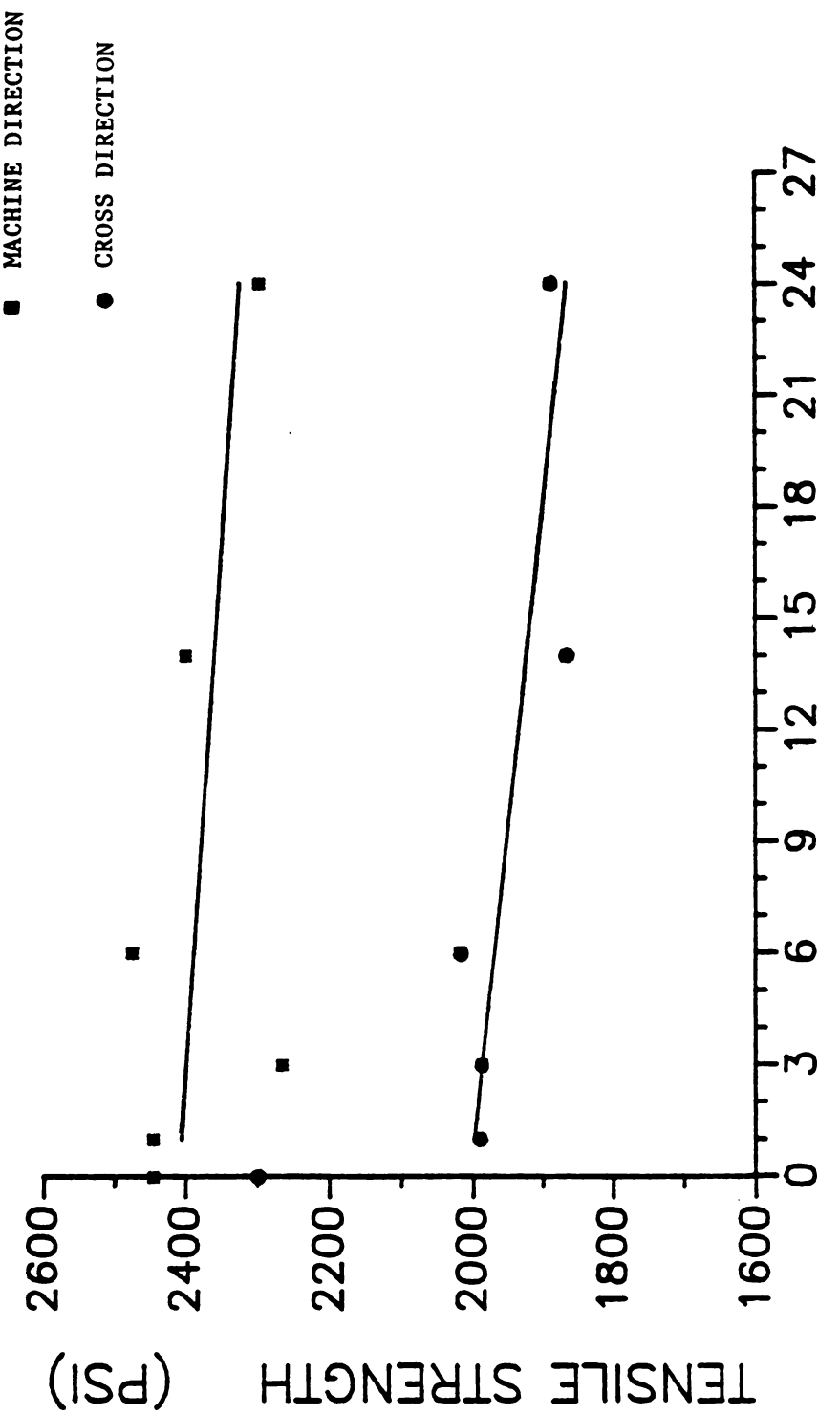

Figure 21. The tensile strength of Alathon as a function of immersion time in apple juice

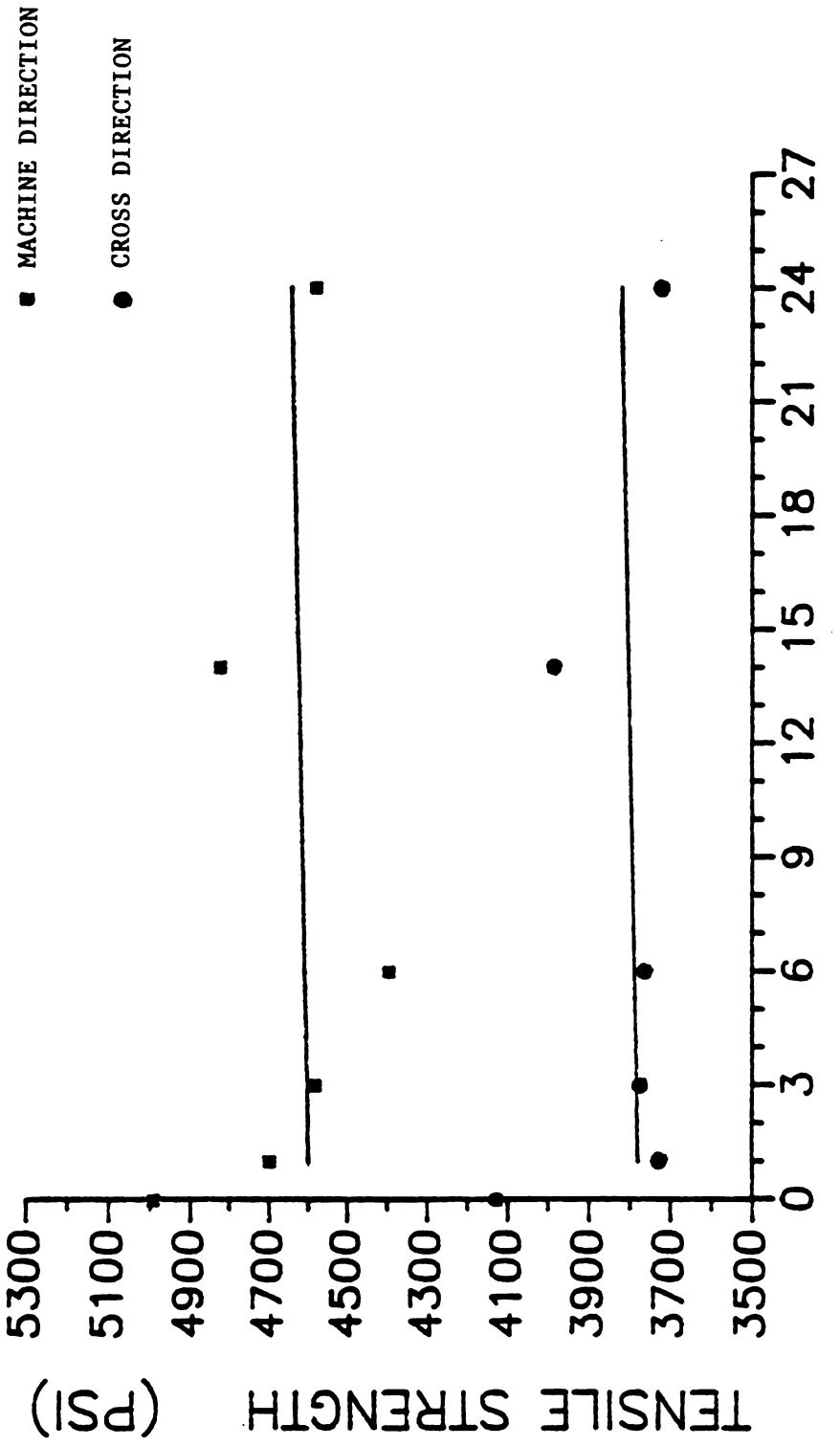

Figure 22. The tensile strength of EVOH as a function of immersion time in apple juice

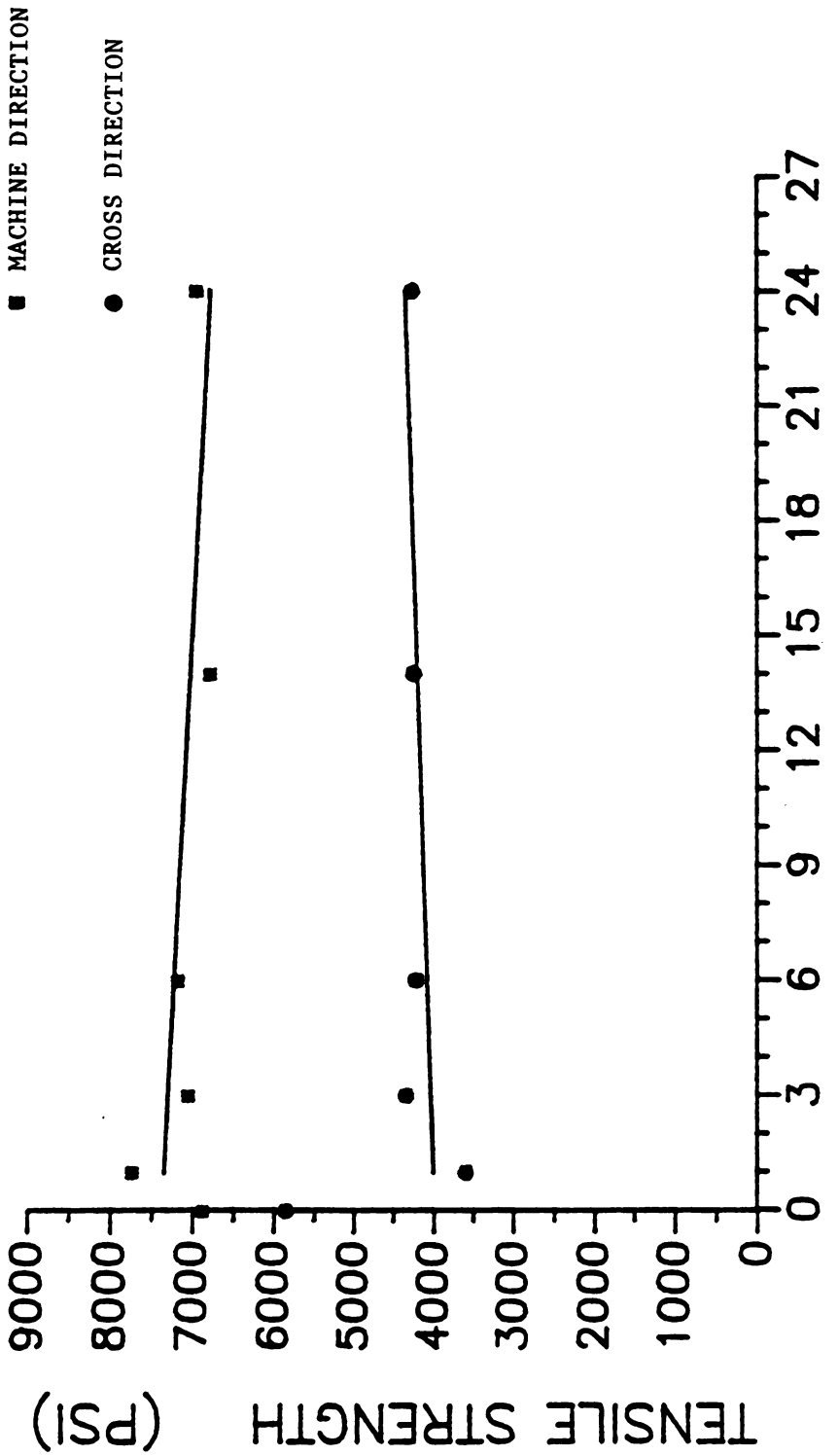

Figure 23. The tensile strength of Co-Pet as a function of immersion time in apple juice

Statistical analysis of the machine direction tensile strength data for the Co-Pet film did give support for a slight increase (See Appendix G). Tensile strength measured in the cross direction showed a decrease in tensile strength of the Co-Pet film, after one day of juice contact. No significant change was found after the first day of immersion.

Percent Elongation at Break

Percent elongation is found by dividing the elongation at the moment of rupture of the sample by the initial gage length of the sample and multiplying by 100 (ASTM, 1984).

The data for elongation at break of the three films is shown in Appendix G and plotted in Figures 24-28. For the Alathon film samples significant changes in both the machine and cross directions were noted. An average decrease of 130% was found after juice contact in the cross direction. A 51% decrease was found in the machine direction.

EVOH machine direction samples showed a significant decrease in the percent elongation at break (90% CL). Cross direction EVOH samples also showed a significant decrease in elongation as a result of juice contact (99.9% CL).

Percent elongation at break for the Co-Pet samples were very low compared to those of the other films. Statistically significant decreases were found in both the machine (99.9% CL) and cross direction (99.9% CL) samples, due to immersion in apple juice. Initial values of 3.75%

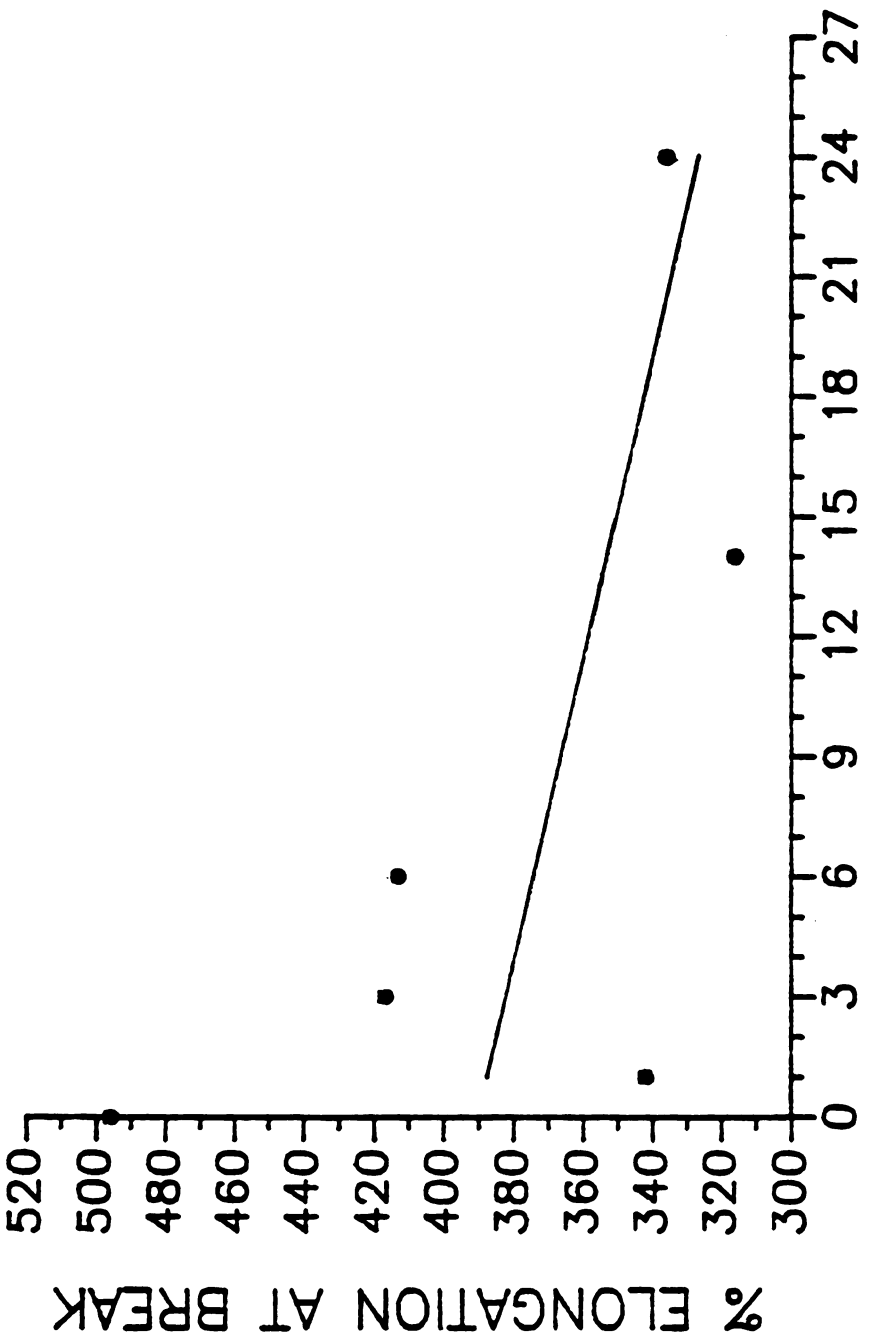

Figure 25. The percent elongation at break of cross direction Alathon as a function of immersion time in apple juice

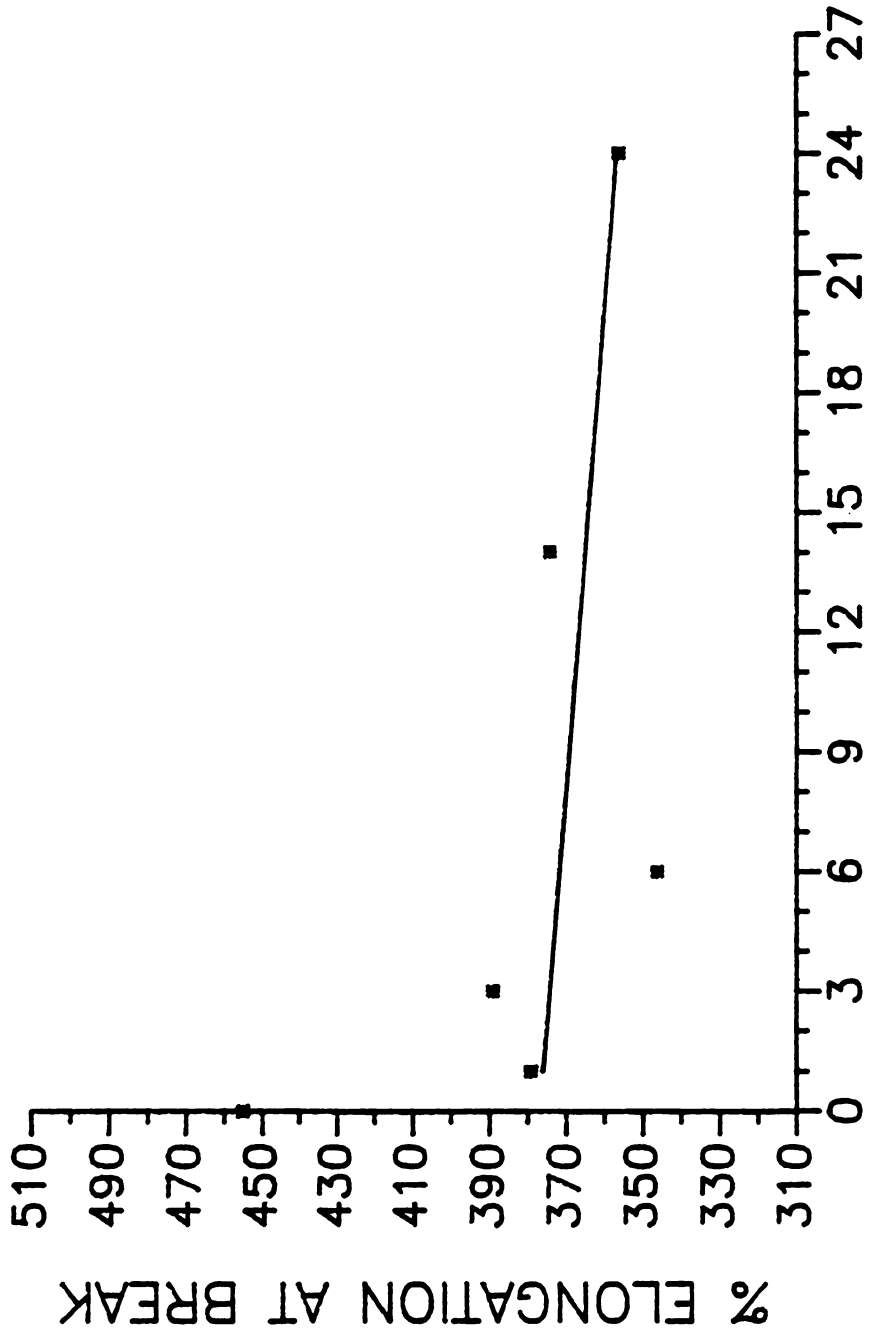

Figure 26. The percent elongation at break of machine direction EVOH as a function of immersion time in apple juice

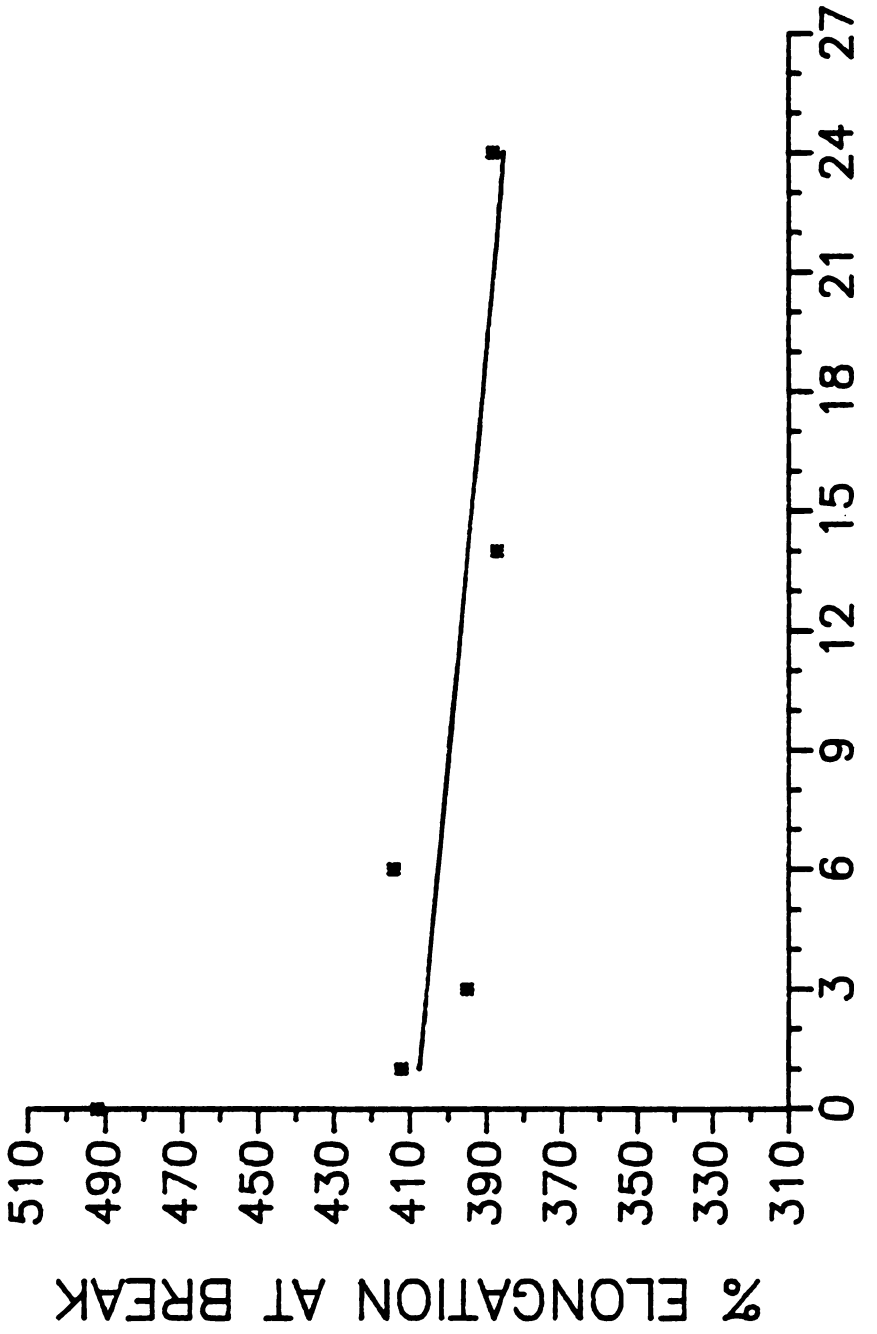

Figure 27. The percent elongation at break of cross direction EVOH as a function of immersion time in apple juice

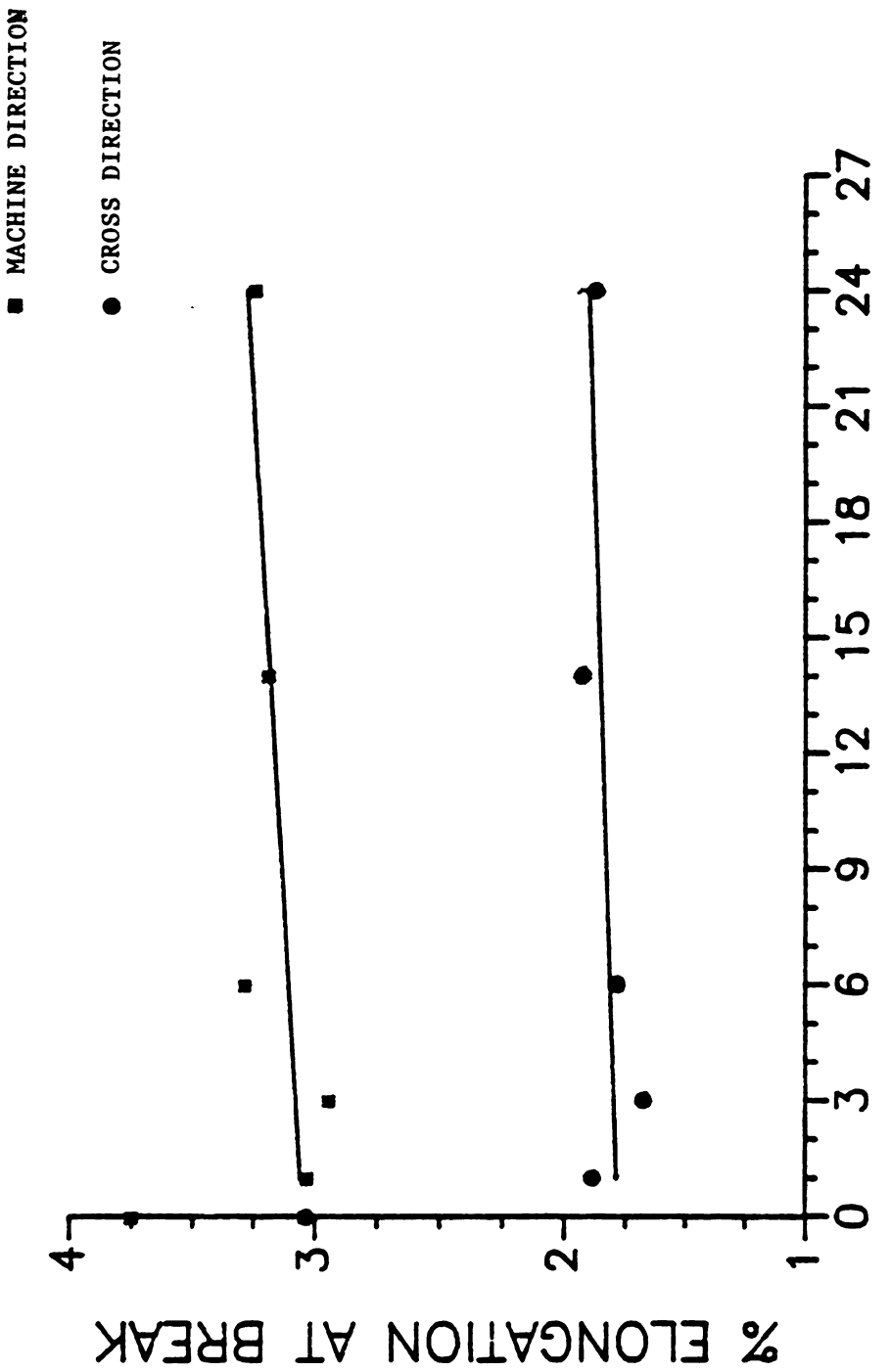

Figure 28. The percent elongation at break of Co-Pet as a function of immersion time in apple juice

and 3.04% were found in the machine and cross direction samples respectively for the Co-Pet film. After one day of juice immersion, this changed to 3.13% in the machine direction and 1.82% for the cross direction.

Modulus of Elasticity

The modulus of elasticity was calculated by drawing a tangent to the initial linear portion of the stress-strain curve, selecting a point on this tangent, and dividing the tensile stress by the corresponding strain (ASTM, 1979). This value is often used as a measurement of stiffness (The Packaging Institute, 1979). The higher the modulus of elasticity, the higher the stiffness of the film.

Modulus of elasticity data for all three films is found in Appendix G and plotted in Figures 29-33. The modulus of elasticity for Alathon decreased in both the machine and cross direction. The change in machine direction was approximately 34% while the change in the cross direction samples was slightly lower, at 33%. The EVOH machine direction sample and the Co-Pet cross direction sample showed no statistical evidence (95% CL) of change between the initial evaluation and subsequent time intervals. No change was found (based on statistical analysis) between the initial evaluation and the time interval evaluations for the EVOH cross direction and the Co-Pet machine direction samples.

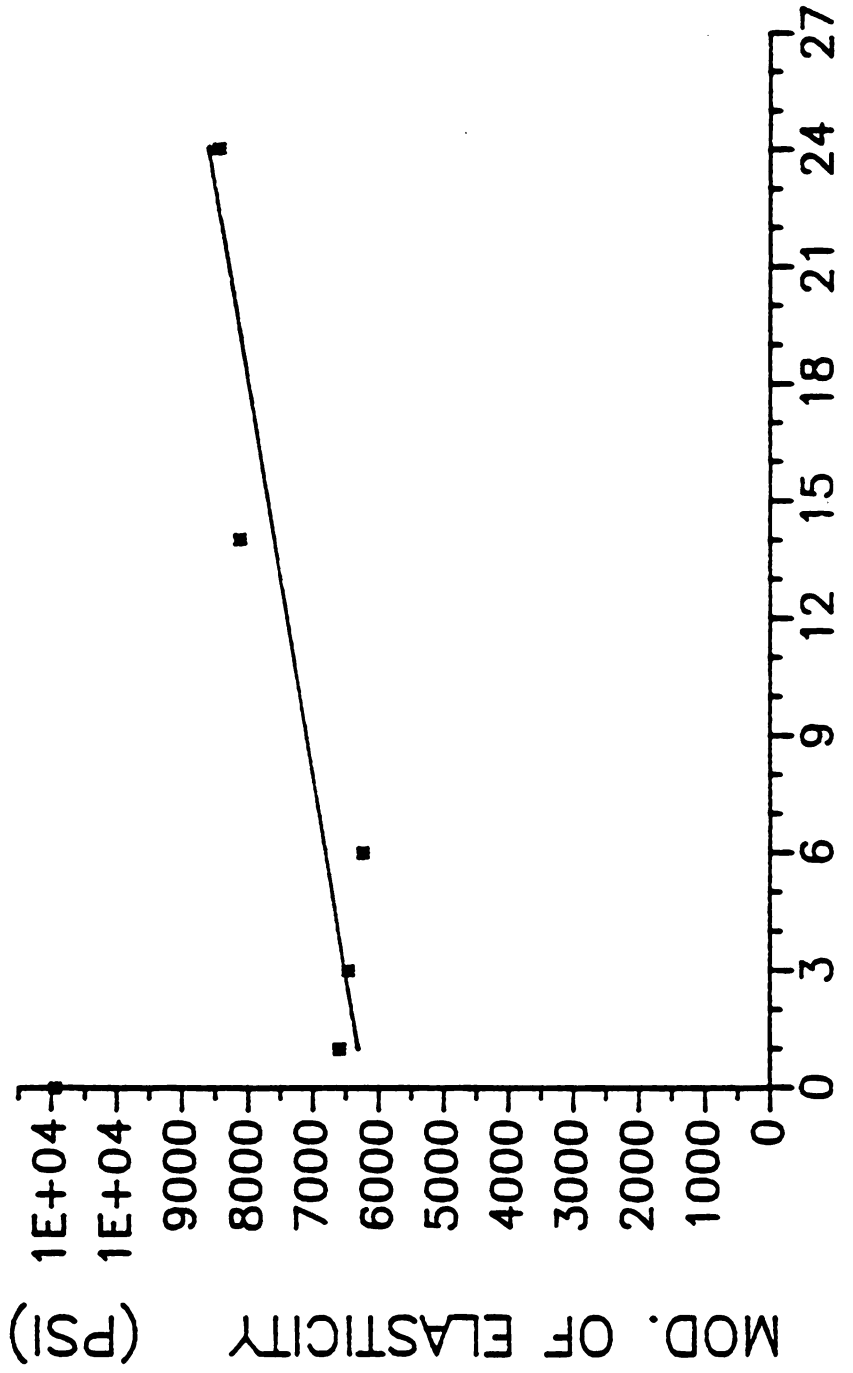

Figure 29. The modulus of elasticity of machine direction Alathon as a function of immersion time in apple juice

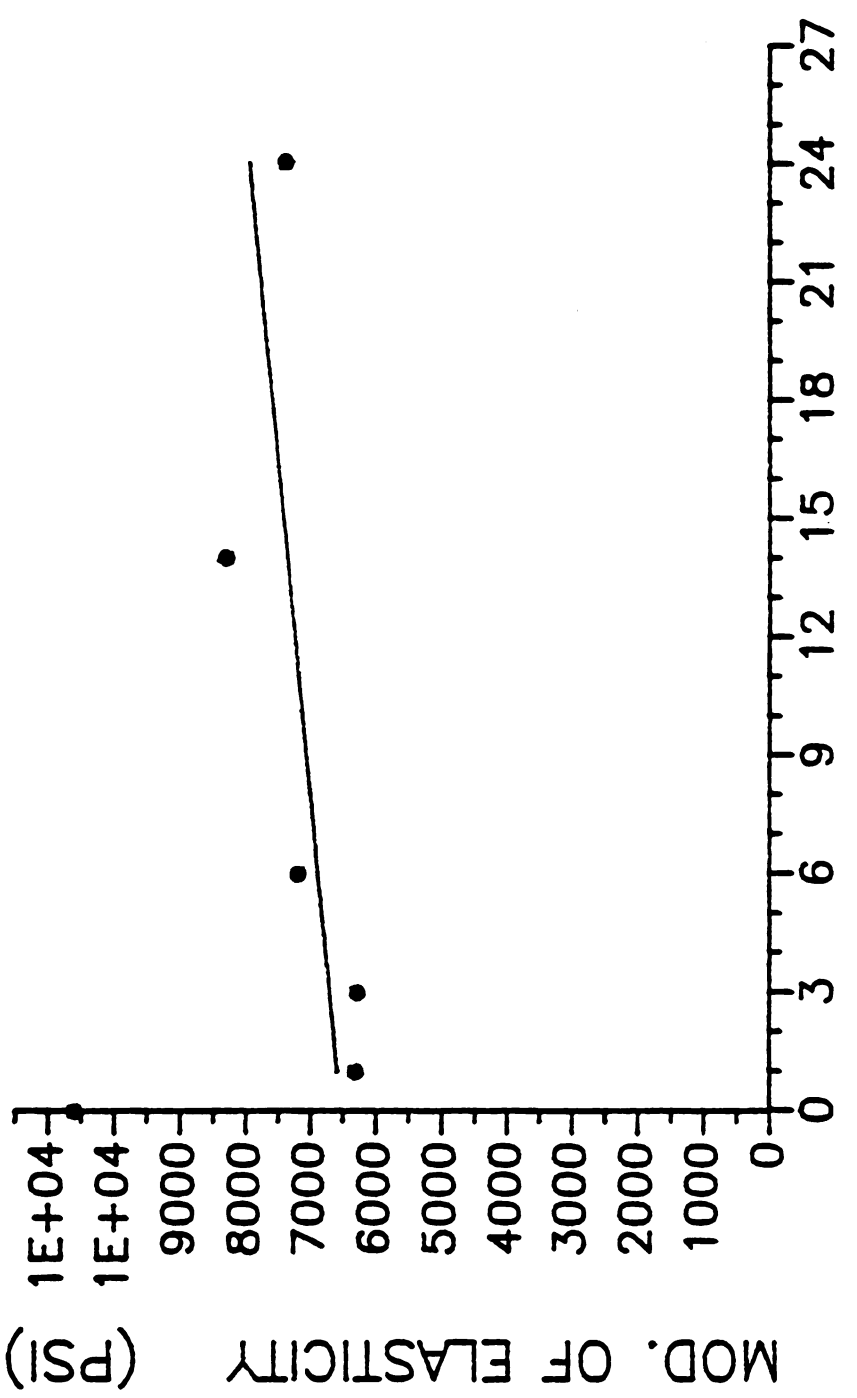

Figure 30. The modulus of elasticity of cross direction Alathon as a function of immersion time in apple juice

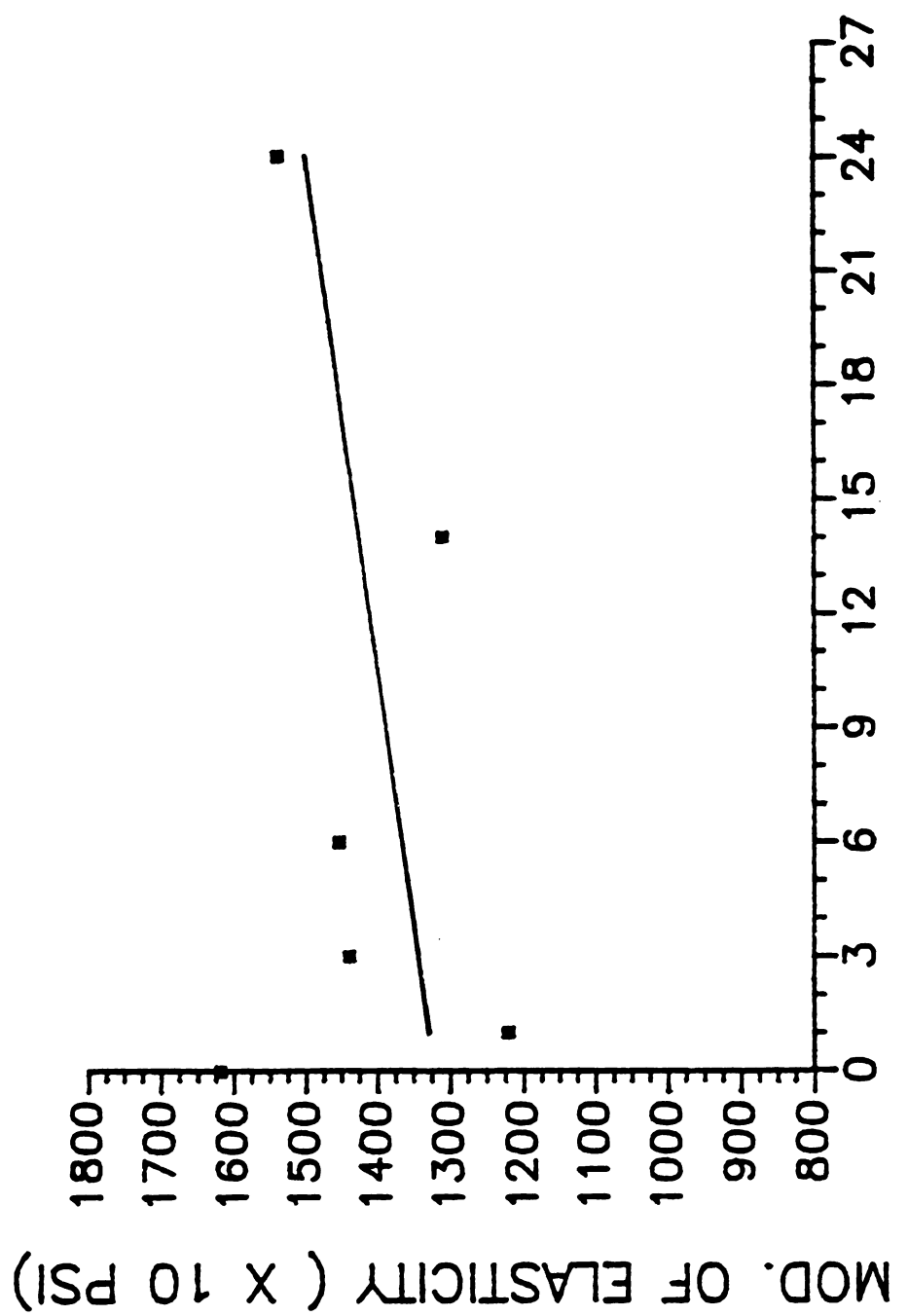

Figure 31. The modulus of elastictiy of machine direction EVOH as a function of immersion time in apple juice

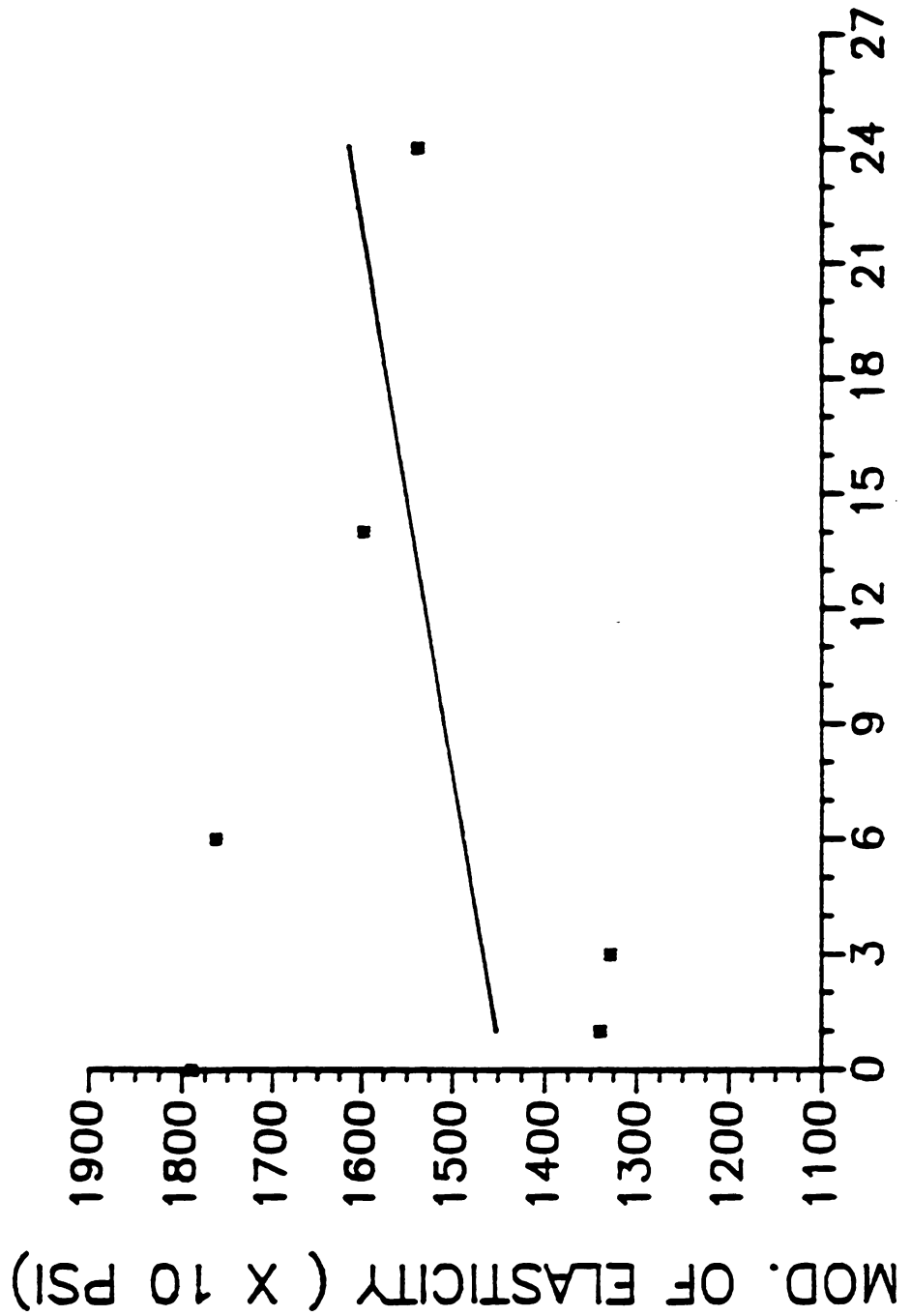

Figure 32. The modulus of elasticity of cross direction EVOH as a function of immersion time in apple juice

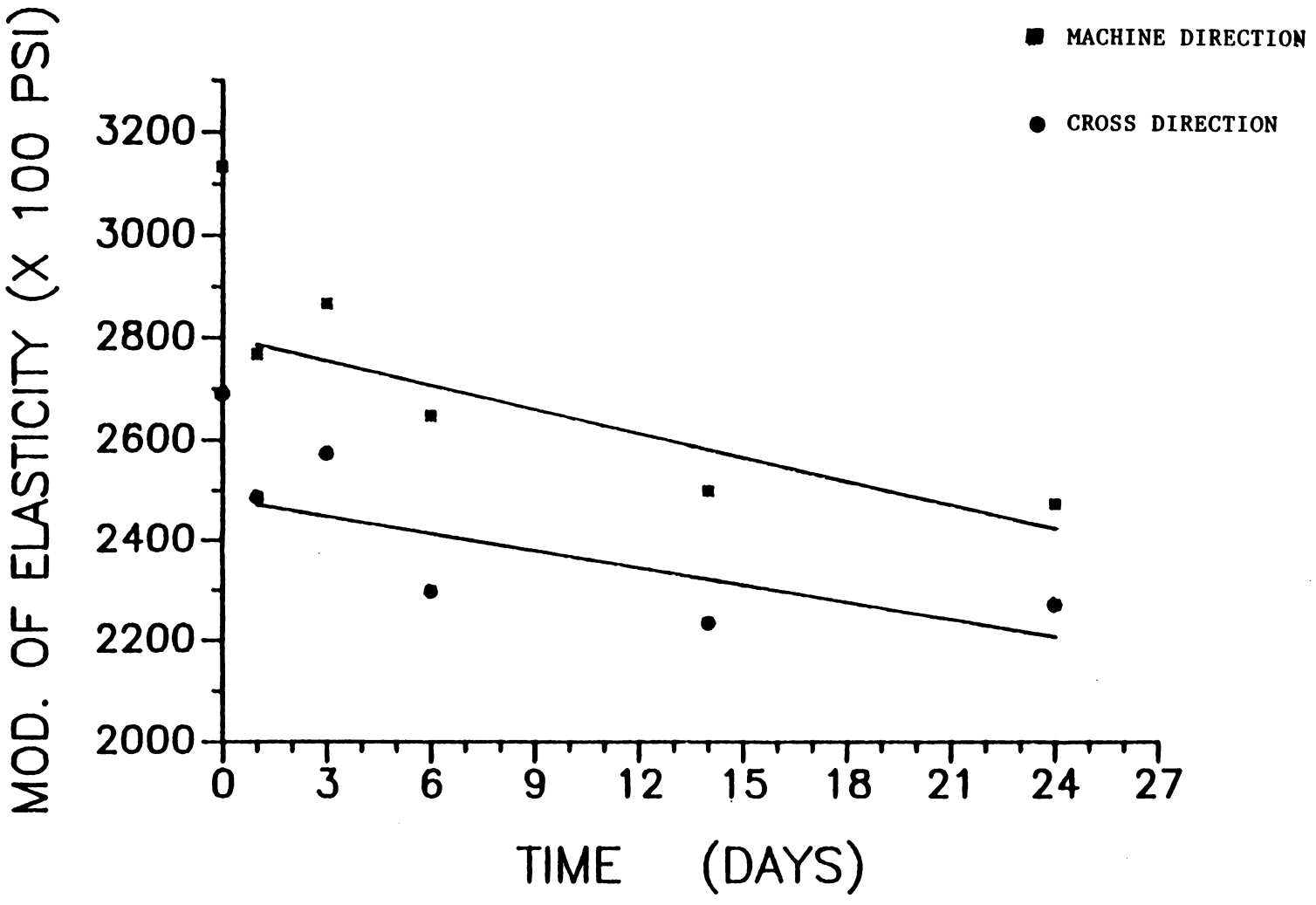

Figure 33. The modulus of elastictiy of Co-Pet as a function of immersion time in apple juice

Heat Seal Strength

Heat seal strength is defined as the maximum stress a heat bonded sample will withstand under an applied load (The Packaging Institute, 1979).

Little evidence was found to support the hypothesis that heat seal bond strength would change due to contact with apple juice. The change determined in the heat seal bond strength for Alathon, EVOH, and Co-Pet had confidence levels of 80%, 75% and 90% respectively. The high values for the Co-Pet film are a result of the large variance found in the data (Appendix G and Figures 34, 35 and 36).

Impact Resistance

The results of the impact resistance tests are summarized in Table 20. As shown, the impact resistance of the Alathon and Co-Pet films was effected minimally as a result of contact with apple juice. An increase of 1.7% occurred in the Alathon film (109.5g to 111.3g). A decrease from 47.67g to 44.21g (7.8%) resulted with the Co-Pet film. However, the EVOH's film impact resistance showed a marked effect as a result of contact with apple juice. Initially the impact resistance was 68.84g. After 21 days in contact with apple juice impact resistance had increased to 111.43g, which represents an increase of 61.9% (See Figure 37). The change in impact resistance of the EVOH film sample is most likely due to the plasticizing of the film's structure due to moisture contact.

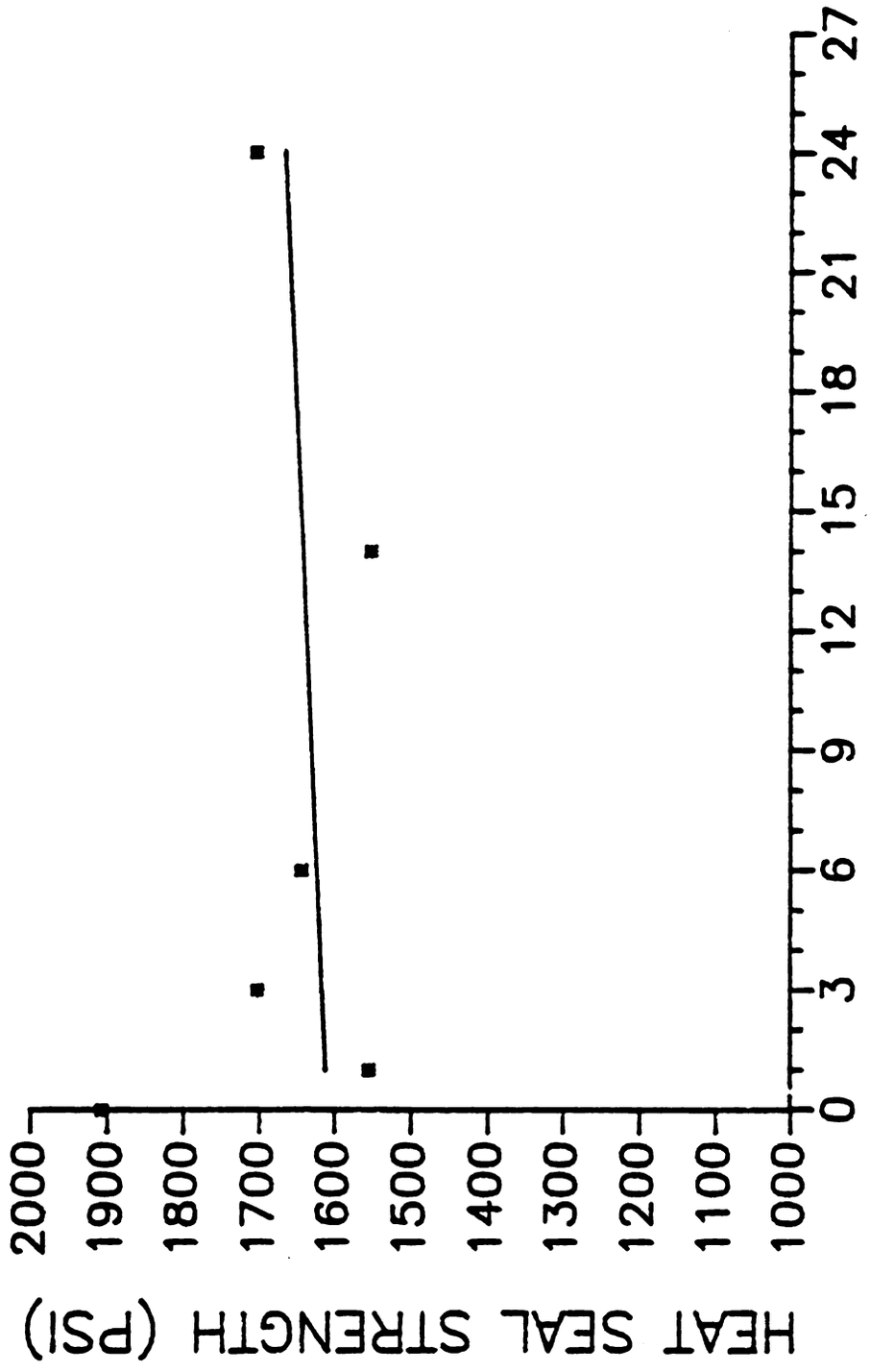

Figure 34. The heat seal strength of Alathon as a function of immersion time in apple juice

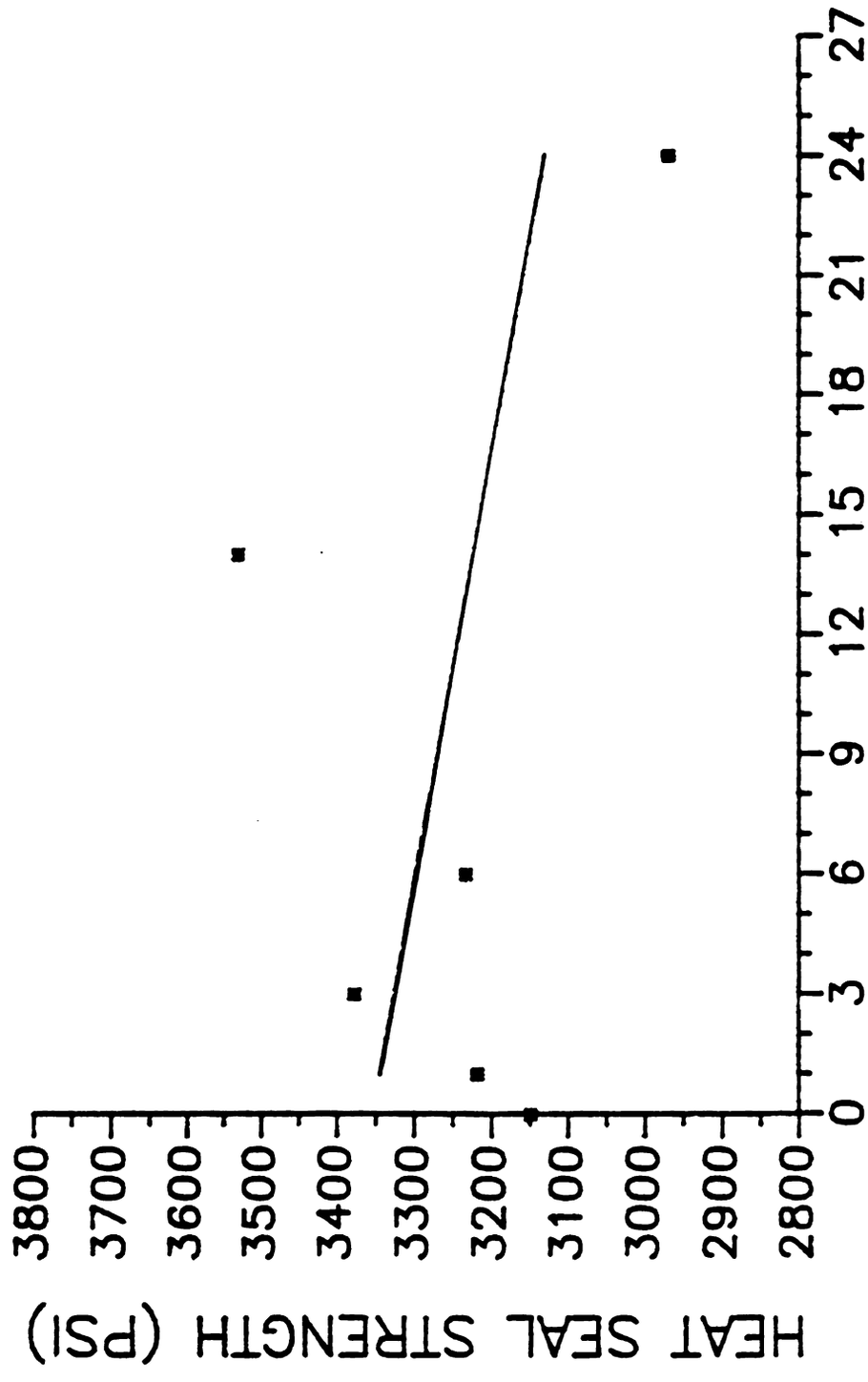

Figure 35. The heat seal strength of EVOH as a function of immersion time in apple juice

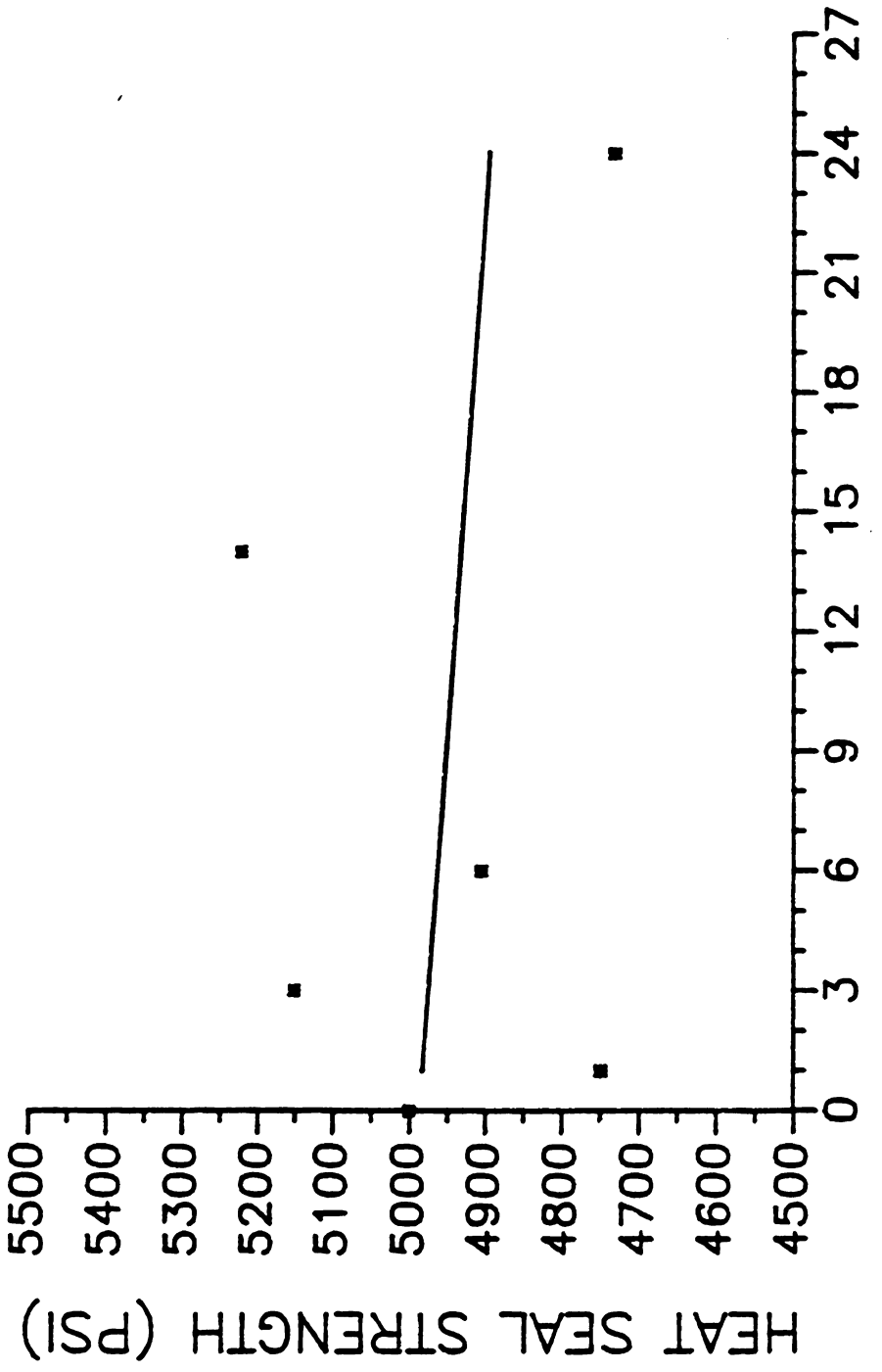

Figure 36. The heat seal strength of Co-Pet as a function of immersion time in apple juice

Table 20. Impact resistance change of the plastic films as a result of juice immersion for 21 days at 22°C ±2°C

Film	Initial Failure Weight	Final Failure Weight
Alathon	109.50 g	111.43 g
EVOH	64.84 g	111.43 g
Co-Pet	47.67 g	44.21 g

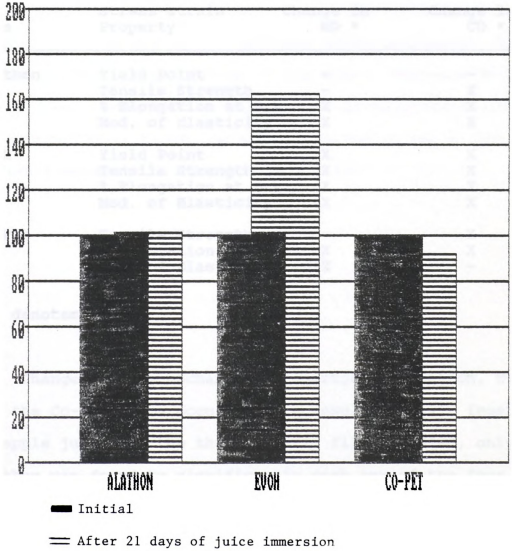

Figure 37. Relative percent change in impact resistance of the sample films

To recapitulate, the mechanical properties which did change significantly, as a result of juice contact with the films, are summarized in Table 21.

Table 21. Mechanical properties changes which occurred as a result of apple juice contact

Film	Stress-strain Property	Change in MD *	Change in CD *
Alathon	Yield Point	-	-
	Tensile Strength	-	X
	% Elongation at Brk.	X	X
	Mod. of Elasticity	X	X
EVOH	Yield Point	X	X
	Tensile Strength	X	X
	% Elongation at Brk.	X	X
	Mod. of Elasticity	X	X
Co-Pet	Tensile Strength	-	X
	% Elongation at Brk.	X	X
	Mod. of Elasticity	X	-

* X denotes change

Changes in the mechanical properties of Alathon, EVOH and the Co-Pet films occurred as a result of their immersion in apple juice. Of the three plastic films studied, only Alathon was found to significantly sorb any of the four aroma/flavor components analyzed. Mechanical property changes with EVOH and Co-Pet samples may be a result of sorption of flavor components not considered in this study, or morphological changes in the film due to juice contact. EVOH films have been shown to sorb water when placed in contact with an aqueous solution (Nippon Gohsei, 1982). The

water sorbed by the film can cause plasticization. Plasticization of this structure is related to the breaking and reforming of hydrogen bonds in a polymer (Tan, 1986). The "loosening" of the chemical structure of the film due to juice or water contact is a result of water vapor swelling the structure, thus reducing the cohesive energy density and increasing the chain flexibility of the polymer (Giacin, 1988). This change in the film may cause subsequent changes in the mechanical properties of the film. DeLassus et al. (1988) found that EVOH is plasticized by moisture which in turn resulted in higher permeation values of apple flavor (trans-2-hexenal) through the EVOH film.

CONCLUSIONS

This study was designed to determine the extent of sorption of aroma/flavor components in apple juice by three polymeric films, and to investigate the influence of sorption of these compounds on the mechanical properties of the plastic films. The major findings of the study are summarized below:

(1) The purge and trap procedure developed was found to work efficiently in the concentration extraction of the flavor components from the apple juice.

(2) Sorption of the four probe flavor components by the Alathon film was indicated.

(3) Little or no sorption of the four probe flavor components by either the EVOH or Co-Pet films was found.

(4) Change in the stress-strain mechanical properties occurred after one day of juice contact with the Alathon, EVOH, and Co-Pet films, with minimal change thereafter.

(5) Significant changes in the stress-strain mechanical properties of the EVOH and Co-Pet films do not appear to be the direct result of sorption

of the aroma/flavor components considered in this study, since these films were shown not to have sorbed measurable levels of test aroma/flavor components. Mechanical property changes in the EVOH film may be due to plasticization of the film by sorbed water.

(6) Some change in heat seal strength for each of the films was found. However, low confidence levels for change with the Alathon and EVOH samples and large variances within the Co-Pet sample data are responsible for these results.

(7) Minimal change was found in the impact resistance of the Alathon and the Co-Pet films as a result of film immersion into apple juice, while an increase of approximately 62% was found with the EVOH film.

The results of this study indicate that the EVOH and Co-Pet films performed better as a contact phase with apple juice than did the Alathon films, since the films sorbed little or no aroma/flavor components. Film mechanical property requirements must be considered in the selection of a contact layer, because of the change which occurred as a result of juice contact. Further tests are needed to make a more qualified choice. At this point it is not known whether the mechanical property changes observed were a result of sorption of components other than those studied or some other phenomenon. Within one day of immersion,

changes in mechanical properties were noted. However, the actual amount of immersion time before significant changes in film mechanical properties are observed may be even less.

Further research in the area of product/package compatibility is needed. A study such as this could be conducted when actual changes in package performance characteristics due to apple juice containment are monitored. The induction period of the package (the heating of the polymer contact layer due to the hot filling of the juice) or the heat sealing process exercised may have an effect on the sorption characteristics of the food contact layer or package performance.

This work, together with previous studies reported in the literature, shows that the shelf-life of aseptically packaged juice cannot be determined solely on the type of packaging used. The make-up of the product must also be considered. Knowledge of product, package, processing, and storage temperatures are necessary to accurately predict the shelf-life of an aseptic juice product. Characterization of the compatibility of the polymer sealant films with aroma/flavor components in the product would allow the selection of the most suitable packaging material for the product.

APPENDICES

LIST OF APPENDICES

APPENDIX A

Table 22. Ethyl-2-methylbutyrate properties

Property	
Density	0.869
Molecular Weight	130.19
Solubility	insoluble in water
Boiling Range	131-133°C
Refractive Index	1.3964
Flash Point	
Chemical Formula	$CH_3CH_2CH(CH_3)CO_2C_2H_5$
Typical Assay (GLC)	90%

CRC Handbook of Chemistry and Physics 67th ed.

Table 23. Hexanal properties

Property	
Density	0.834
Molecular Weight	100.16
Solubility	insoluble in water
Boiling Range	128°C
Refractive Index	1.4039
Flash Point	32°C
Chemical Formula	$CH_3(CH_2)_4CHO$
Typical Assay (GLC)	99%

Aldrich Chemical Company, Milwaukee, WI

Table 24. Trans-2-hexenal properties

Property	
Density	0.846
Molecular Weight	98.14
Solubility	insoluble in water
Boiling Range	146-147°C
Refractive Index	1.4480
Flash Point	38°C
Chemical Formula	$CH_3CH_2CH_2CH=CHCHO$
Typical Assay (GLC)	99%

Aldrich Chemical Company, Milwaukee, WI

Table 25. 1-Hexanol properties

Property	
Density	0.814
Molecular Weight	102.18
Solubility	insoluble in water
Boiling Range	156-157°C
Refractive Index	1.417
Flash Point	60°C
Chemical Formula	$CH_3(CH_2)_5OH$
Typical Assay (GLC)	98%

Aldrich Chemical Company, Milwaukee, WI

APPENDIX B

Table 26. Ethyl-2-methylbutyrate standard calibration curve data: GC model #5890 equipped with a capillary column

AREA RESPONSE (Y-axis)	ABSOLUTE QUANTITY INJECTED (E-8 GRAMS) (X-axis)
16224	0.4350
33141	0.8700
79217	2.1750
160170	4.3500

Resulting line slope equation (See Figure 38):

$$y = 472 + (3.664 * E\ 12)\ X$$

Table 27. Hexanal standard calibration curve data: GC model #5890 equipped with a capillary column

AREA RESPONSE (Y-axis)	ABSOLUTE QUANTITY INJECTED (E-8 GRAMS) (X-axis)
16743	0.4170
35169	0.8340
74932	1.6680
161715	3.7530
371280	8.3400

Resulting line slope equation (See Figure 39):

$$y = -1979 + (4.461 * E12)\ X$$

Table 28. Trans-2-hexenal standard calibration curve data: GC model #5890 equipped with a capillary column

AREA RESPONSE (Y-axis)	ABSOLUTE QUANTITY INJECTED (E-8 GRAMS) (X-axis)
0	0
17178	0.4230
33122	0.8460
64339	1.6920
141290	3.3840

Resulting line slope equation (See Figure 40):

$$y = -1563 + (4.157 * E12)\ X$$

Table 29. 1-Hexanol standard calibration curve data: GC model #5890 equipped with a capillary column

AREA RESPONSE (Y-axis)	ABSOLUTE QUANTITY INJECTED (E-8 GRAMS) (X-axis)
21275	0.4070
42553	0.8140
84427	1.6820
169083	3.2560
411450	8.1400

Resulting line slope equation (See Figure 41):

$$y = 2134 + (5.041 * E12)\ X$$

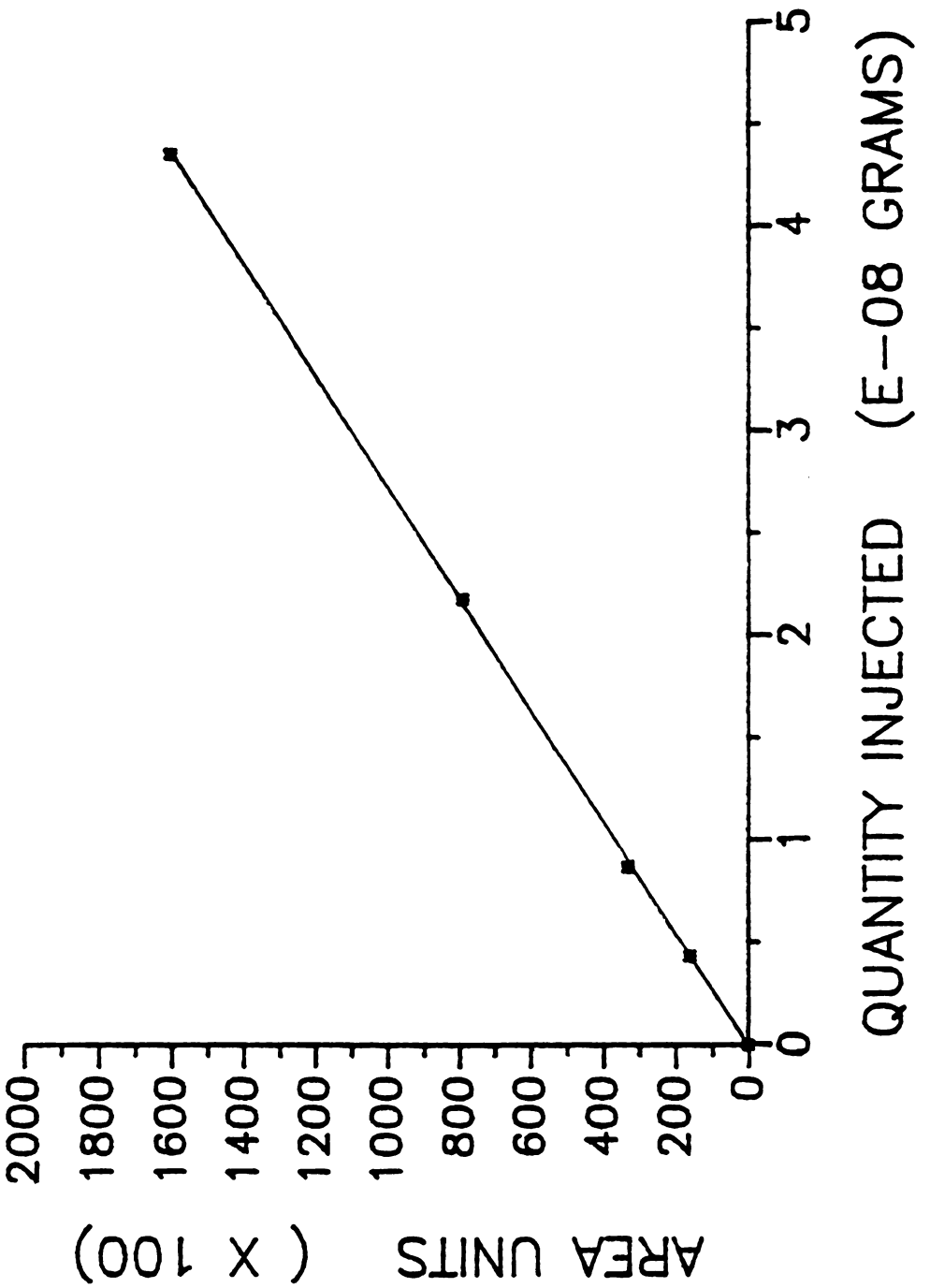

Figure 38. Standard curve for ethyl-2-methylbutyrate area response as a function of quantity

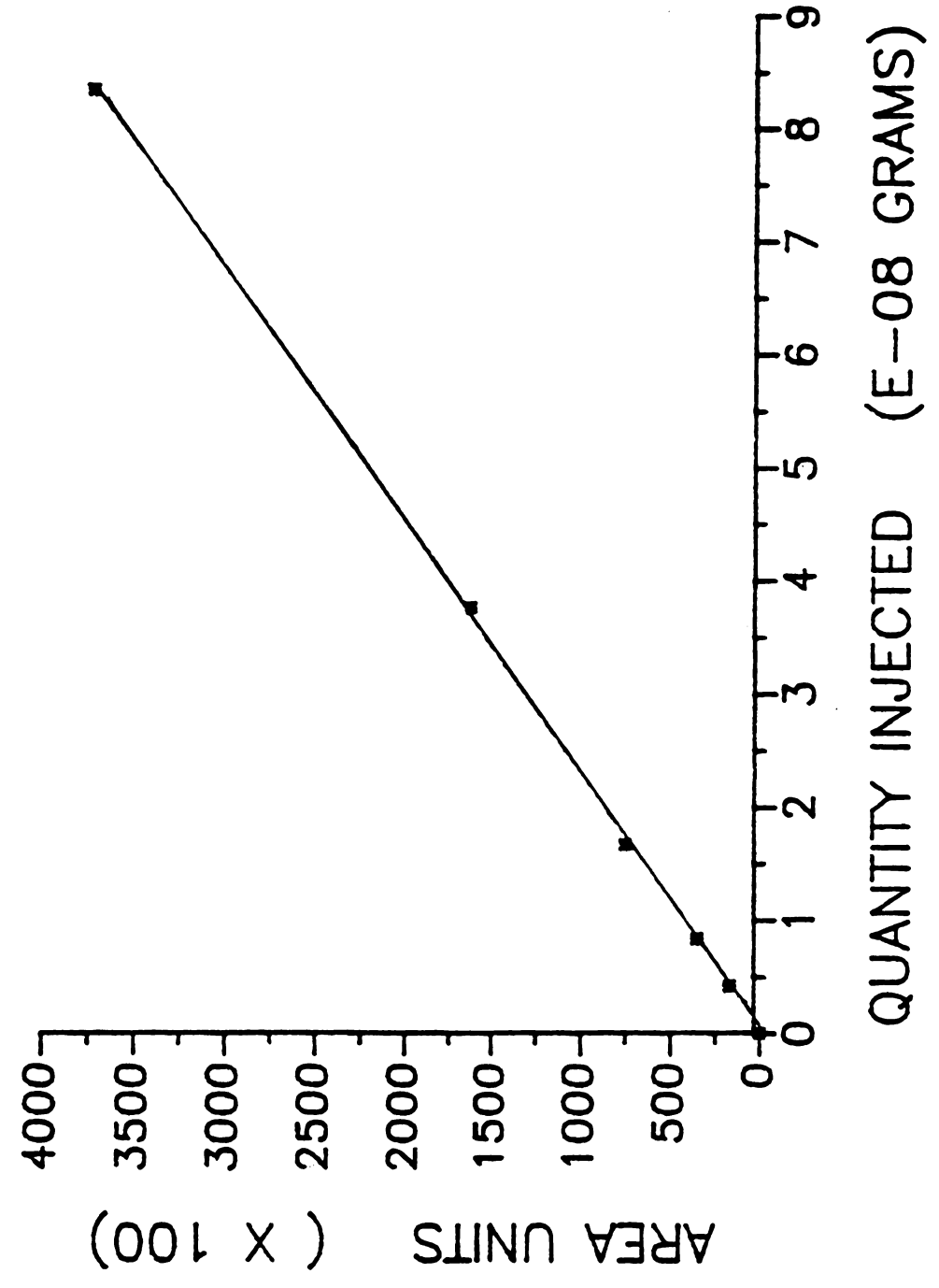

Figure 39. Standard curve for hexanal area response as a function of quantity

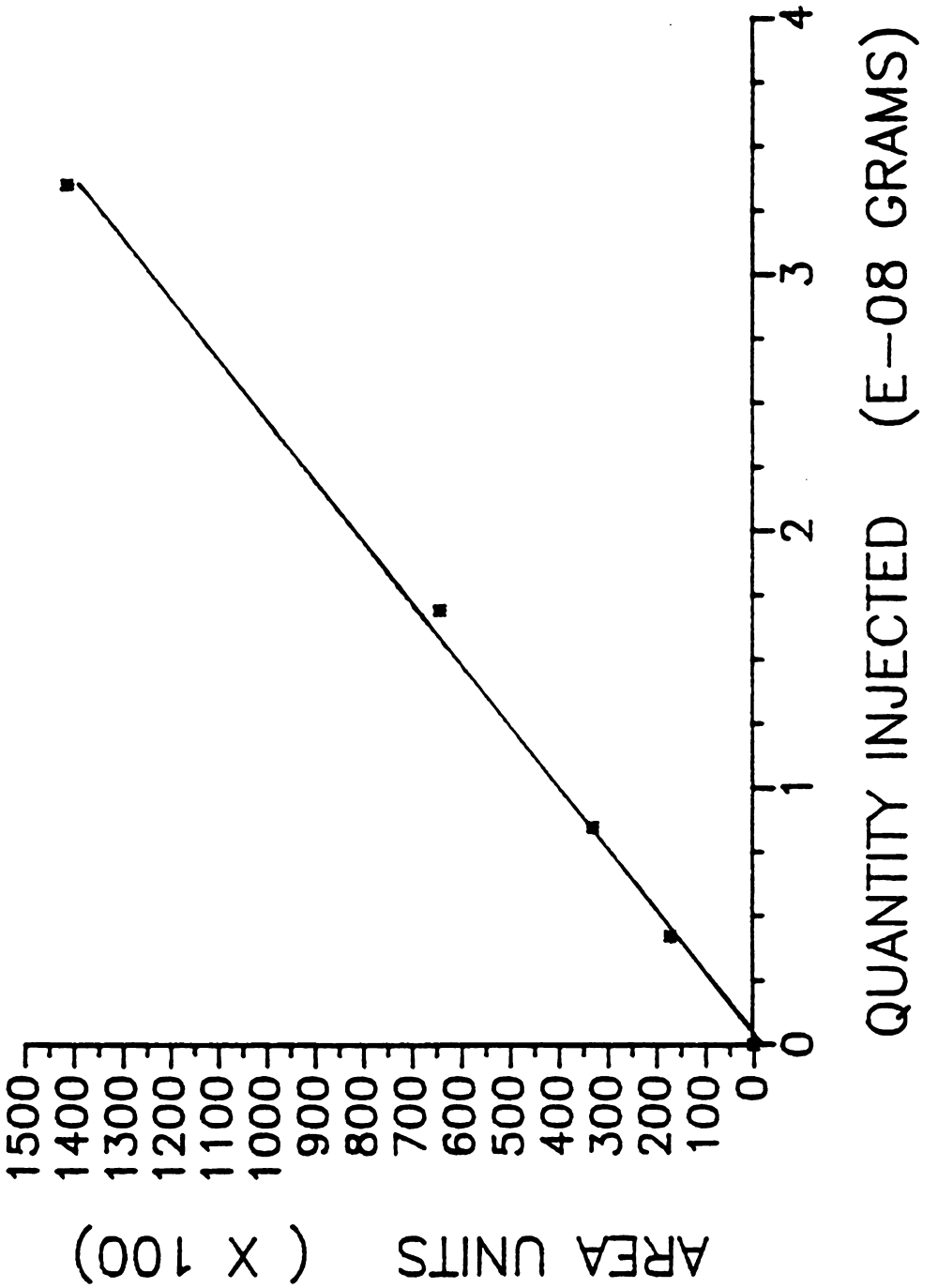

Figure 40. Standard curve for trans-2-hexenal area response as a function of quantity

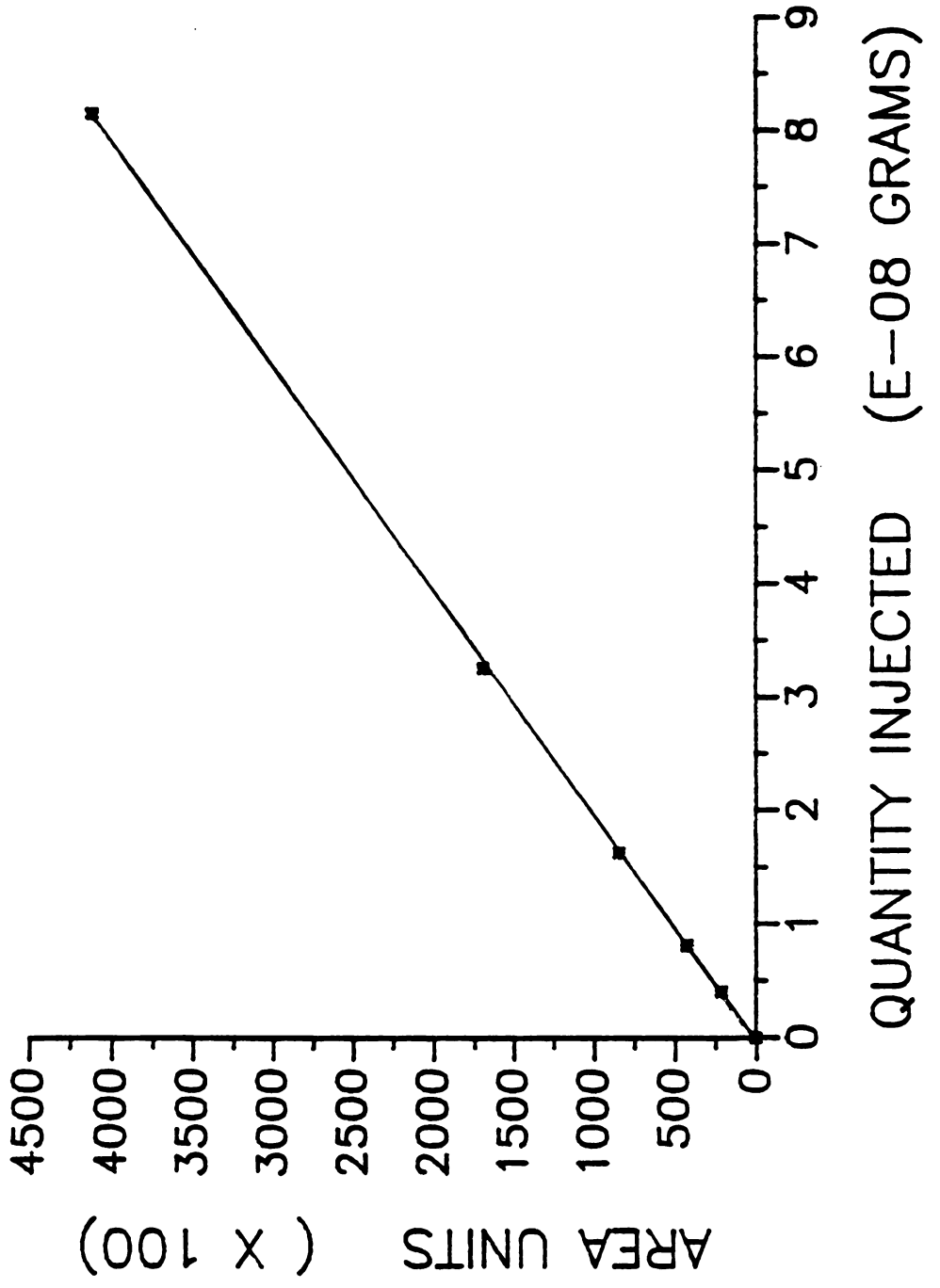

Figure 41. Standard curve for 1-hexanol area response as a function of quantity

APPENDIX C

Table 30. The components of the preservatives

SUSTANE W (UOP INC.) Antioxidant

Ingredients (weight percent)

(a) Mono-tertiary-butyl-r-hydroxy anisole (BHA) (10)

(b) 2,6-Di-tert-butyl-para-cresol (BHT) (10)

(c) N-propyl-3,4,5-trihydroxy benzoate (PG) (6)

(d) Citric acid (6)

(e) Propylene glycol (8)

(f) Edible oil (28)

(g) Mono and diglycerides of fatty acids (32)

SUSTANE 20A (UOP INC.) Antioxidant

Ingredients (weight percent)

(a) Tertiary-butyl hydroquinone (TBHQ) (20)

(b) Citric acid (3)

(c) Propylene glycol (15)

(d) Edible oil (30)

(e) Mono and diglycerides of fatty acids (20)

SODIUM AZIDE (Sigma Chemical Co.) Antibacterial agent

APPENDIX D

Table 31. Film heat sealing conditions.

Sample	Alathon	EVOH	Co-Pet
Impulse Time (seconds)	0.4	0.5	0.6
Cooling Time (seconds)	2.5	2.5	2.5
Jaw Pressure (psi)	25	30	30

Table 32. Instron machine settings for stress-strain testing.

Sample	Alathon			EVOH			Co-Pet		
Test Parameter	MD	CD	HS	MD	CD	HS	MD	CD	HS
Crosshead Speed (in/min)	20	20	20	20	20	20	0.5	0.5	0.5
Chart Speed (in/min)	20	20	20	20	20	20	10	20	20
Full Scale Load (lbs)	5	5	5	5	5	5	50	20	20
Grip Seperation (in)	2	2	2	2	2	2	4	4	4

MD = Machine Direction
CD = Cross Diorection
HS = Heat Seal

APPENDIX E

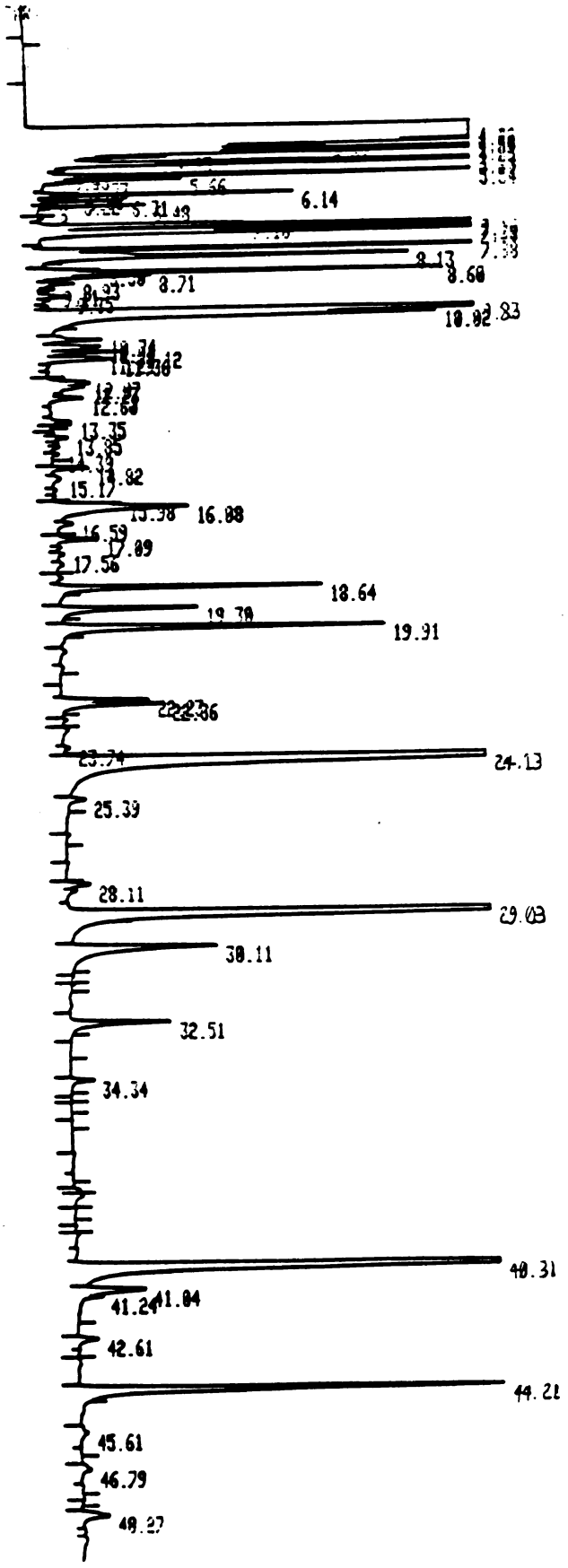

Figure 42. GC analysis of apple juice extract

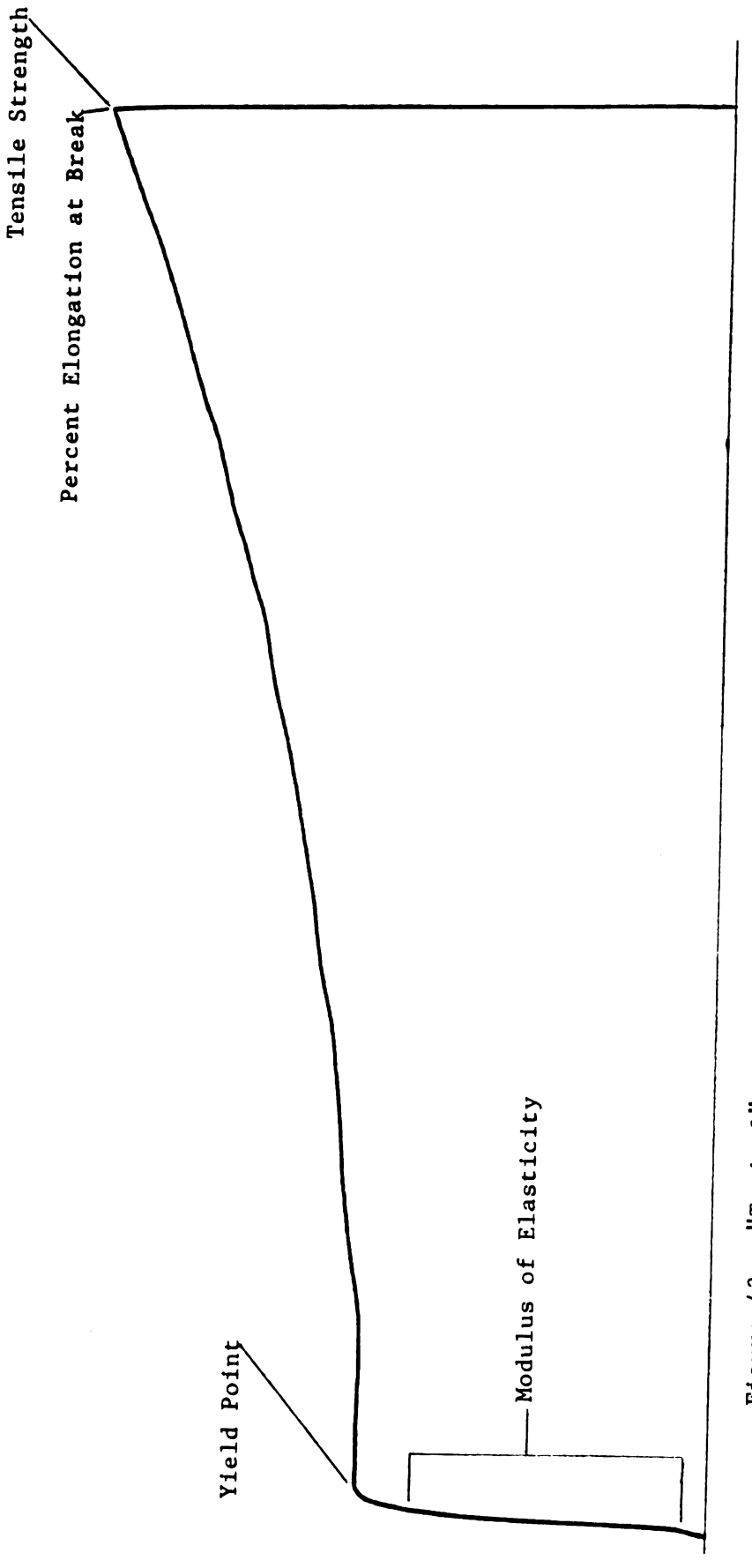

Figure 43. "Typical" stress-strain curve for a low density polyethylene material

APPENDIX F

Table 33. Change in concentration of ethyl-2-methylbutyrate in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.
0	0.057	0.006	0.056	0.005	0.034	0.003	0.031	0.004
1	0.054	0.008	0.063	0.004	0.034	0.002	0.030	0.001
3	0.051	0.004	0.047	0.002	0.020	0.001	0.033	0.002
6	0.057	0.012	0.046	0.007	0.028	0.009	0.033	0.001
14	0.055	0.007	0.034	0.004	0.032	0.009	0.034	0.003
24	0.043	0.006	0.025	0.001	0.031	0.003	0.021	0.003

(a) values in ppm (wt/v)
(b) data based on three different runs and three injections per run

Table 34. Relative percent of ethyl-2-methylbutyrate remaining in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Ct ppm	Ct/Co	Ct ppm	Ct/Co	Ct ppm	Ct/Co	Ct ppm	Ct/Co
0	0.057	100%	0.056	100%	0.034	100%	0.031	100%
1	0.054	95%	0.063	112%	0.034	102%	0.030	97%
3	0.051	90%	0.047	83%	0.020	61%	0.033	105%
6	0.057	100%	0.046	82%	0.028	84%	0.033	107%
14	0.055	96%	0.034	61%	0.032	95%	0.034	110%
24	0.043	75%	0.025	44%	0.031	91%	0.021	70%

(a) Co = initial concentration
Ct = concentration in the juice at time = t (ppm, wt/v)
(b) Ct/Co = (Ct/Co)x 100 = relative percent remaining in the apple juice at time t

Table 35. Change in concentration of hexanal in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.
0	0.168	0.009	0.196	0.006	0.136	0.005	0.126	0.003
1	0.163	0.008	0.184	0.009	0.140	0.003	0.122	0.007
3	0.148	0.015	0.170	0.011	0.115	0.007	0.125	0.002
6	0.166	0.019	0.166	0.006	0.133	0.020	0.119	0.005
14	0.158	0.006	0.146	0.009	0.106	0.015	0.129	0.013
24	0.140	0.017	0.108	0.015	0.111	0.005	0.093	0.009

(a) values in ppm (wt/v)
(b) data based on three different runs and three injections per run

Table 36. Relative percent of hexanal remaining in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Ct ppm	Ct/Co	Ct ppm	Ct/Co	Ct ppm	Ct/Co	Ct ppm	Ct/Co
0	0.057	100%	0.056	100%	0.034	100%	0.031	100%
1	0.054	97%	0.063	94%	0.034	103%	0.030	97%
3	0.051	88%	0.047	87%	0.020	84%	0.033	99%
6	0.057	98%	0.046	85%	0.028	98%	0.033	95%
14	0.055	94%	0.034	75%	0.032	78%	0.034	103%
24	0.043	83%	0.025	55%	0.031	82%	0.021	75%

(a) Co = initial concentration
Ct = concentration in the juice at time = t (ppm, wt/v)
(b) Ct/Co = (Ct/Co)x 100 = relative percent remaining in the apple juice at time t

Table 37. Change in concentration of trans-2-hexenal in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.
0	0.305	0.012	0.424	0.023	0.229	0.006	0.237	0.032
1	0.366	0.003	0.456	0.011	0.257	0.006	0.244	0.047
3	0.363	0.055	0.458	0.062	0.268	0.034	0.256	0.025
6	0.422	0.084	0.423	0.031	0.373	0.058	0.258	0.058
14	0.459	0.029	0.387	0.036	0.280	0.028	0.337	0.007
24	0.382	0.010	0.351	0.026	0.306	0.035	0.256	0.019

(a) values in ppm (wt/v)
(b) data based on three different runs and three injections per run

Table 38. Relative percent of trans-2-hexenal remaining in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
	Ct		Ct		Ct		Ct	
(Days)	ppm	Ct/Co	ppm	Ct/Co	ppm	Ct/Co	ppm	Ct/Co
0	0.305	100%	0.424	100%	0.229	100%	0.237	100%
1	0.366	120%	0.456	108%	0.257	112%	0.244	103%
3	0.363	120%	0.458	108%	0.268	117%	0.256	108%
6	0.422	138%	0.423	101%	0.373	163%	0.258	109%
14	0.459	151%	0.387	91%	0.280	122%	0.337	142%
24	0.382	126%	0.351	83%	0.306	133%	0.256	108%

(a) Co = initial concentration
Ct = concentration in the juice at time = t (ppm, wt/v)
(b) Ct/Co = (Ct/Co)x 100 = relative percent remaining in the apple juice at time t

Table 39. Change in concentration of 1-hexanol in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
(Days)	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.	Avg.	s.d.
0	3.346	0.160	4.019	0.220	2.577	0.160	2.634	0.100
1	3.427	0.240	3.984	0.110	2.778	0.110	2.526	0.250
3	3.046	0.380	3.620	0.280	2.215	0.200	2.682	0.120
6	3.549	0.440	3.439	0.100	2.594	0.450	2.541	0.330
14	3.536	0.210	3.085	0.210	2.372	0.330	3.028	0.200
24	3.232	0.100	2.635	0.210	2.764	0.100	2.355	0.040

(a) values in ppm (wt/v)
(b) data based on three different runs and three injections per run

Table 40. Relative percent of 1-hexanol remaining in apple juice during storage at 22°C ±2°C following contact with test films (a) (b)

Storage Time	Apple Juice Control		Juice Contact with Alathon		Juice Contact with EVOH		Juice Contact with Co-Pet	
	Ct		Ct		Ct		Ct	
(Days)	ppm	Ct/Co	ppm	Ct/Co	ppm	Ct/Co	ppm	Ct/Co
0	3.346	100%	4.019	100%	2.577	100%	2.634	100%
1	3.427	102%	3.984	99%	2.778	108%	2.526	96%
3	3.046	91%	3.620	90%	2.215	86%	2.682	102%
6	3.549	106%	3.439	86%	2.594	101%	2.541	96%
14	3.536	106%	3.085	77%	2.372	92%	3.028	115%
24	3.232	97%	2.635	66%	2.764	107%	2.355	90%

(a) Co = initial concentration
Ct = concentration in the juice at time = t (ppm, wt/v)
(b) Ct/Co = (Ct/Co)x 100 = relative percent remaining in the apple juice at time t

APPENDIX G

Table 41. Change of yield point of Alathon film immersed in apple juice at 22°C ±2°C

ALATHON	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	1907	146	100%	1644	58	100%
1	2120	278	111%	1629	122	99%
3	1830	208	96%	1630	84	99%
6	1851	172	97%	1586	89	96%
14	1927	171	101%	1579	101	96%
24	1829	147	96%	1607	79	98%
Average of Day 1 through Day 24	1911	195	100%	1606	95	98%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Alathon Machine Direction — f = 0.0036
No statistical difference between initial and day 1 through day 24 data.

Alathon Cross Direction — f = 1.3846
No statistical difference between initial and day 1 through day 24 data.

Table 42. Change of tensile strength of Alathon film immersed in apple juice at 22°C ±2°C

ALATHON	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	2445	247	100%	2299	130	100%
1	2445	267	100%	1989	235	87%
3	2265	271	93%	1987	242	86%
6	2474	409	102%	2071	210	90%
14	2398	221	98%	1865	288	81%
24	2295	239	94%	1888	179	82%
Average of Day 1 through Day 24	2375	281	97%	1960	231	85%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Alathon Machine Direction	f = 0.0194 No statistical difference between initial and day 1 through day 24 data.
Alathon Cross Direction	f = 18.2600 99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Table 43. Change of percent elongation of Alathon film immersed in apple juice at 22°C ±2°C

ALATHON	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	398%	67%	100%	496%	26%	100%
1	350%	37%	88%	342%	117%	69%
3	342%	47%	86%	417%	79%	84%
6	351%	70%	88%	413%	91%	83%
14	331%	61%	83%	316%	132%	79%
24	360%	51%	90%	336%	99%	84%
Average of Day 1 through Day 24	347%	53%	87%	365%	104%	74%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Alathon Machine Direction — f = 3.1000
90% CL of a statistical difference between initial and day 1 through day 24 data.

Alathon Cross Direction — f = 8.7035
99.5% CL of a statistical difference between initial and day 1 through day 24 data.

Table 44. Change of modulus of elasticity of Alathon film immersed in apple juice at 22°C ±2°C

ALATHON	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	10939	1062	100%	10605	1515	100%
1	6588	1074	60%	6303	1203	59%
3	6455	607	59%	6273	543	59%
6	6229	846	57%	7172	495	68%
14	8121	811	74%	8273	665	78%
24	8424	1003	77%	7364	1076	69%
Average of Day 1 through Day 24	7163	868	66%	7077	797	67%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Alathon Machine Direction — f = 105.8367
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Alathon Cross Direction — f = 95.5533
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Table 45. Change of heat seal strength of Alathon film immersed in apple juice at 22°C ±2°C

ALATHON Machine direction

Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial
Initial	1907	146	100%
1	1554	367	82%
3	1702	204	89%
6	1643	224	86%
14	1551	320	81%
24	1704	230	89%
Average of Day 1 through Day 24	1631	269	86%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Alathon Machine Direction f = 2.4234
80% CL of a statistical difference between initial and day 1 through day 24 data.

Table 46. Change of yield point of EVOH film immersed in apple juice at 22°C ±2°C

EVOH	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	3482	297	100%	3137	80	100%
1	3023	230	87%	2817	173	90%
3	2993	170	86%	2917	176	93%
6	2776	202	80%	2735	128	87%
14	3001	195	86%	3019	283	96%
24	2775	175	80%	2533	158	81%
Average of Day 1 through Day 24	2914	195	84%	2804	184	89%

*Relative Percent Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

EVOH Machine Direction f = 52.0987
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

EVOH Cross Direction f = 26.4383
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Table 47. Change of tensile strength of EVOH film immersed in apple juice at 22°C ±2°C

EVOH	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	4992	394	100%	4128	351	100%
1	4698	446	94%	3727	478	90%
3	4580	546	92%	3773	539	91%
6	4393	455	88%	3761	334	91%
14	4819	509	97%	3984	497	97%
24	4575	850	92%	3719	374	90%
Average of Day 1 through Day 24	4613	561	92%	3793	444	92%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

EVOH Machine Direction f = 3.5066
90% CL of a statistical difference between initial and day 1 through day 24 data.

EVOH Cross Direction f = 4.4176
95% CL of a statistical difference between initial and day 1 through day 24 data.

Table 48. Change of percent elongation of EVOH film immersed in apple juice at 22°C ±2°C

EVOH	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	455%	35%	100%	492%	41%	100%
1	379%	38%	83%	412%	82%	84%
3	389%	19%	85%	395%	61%	80%
6	346%	45%	76%	414%	31%	84%
14	374%	54%	82%	387%	47%	79%
24	356%	80%	78%	388%	56%	79%
Average of Day 1 through Day 24	369%	47%	81%	399%	55%	81%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

EVOH Machine Direction f = 15.6093
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

EVOH Cross Direction f = 3.4316
90% CL of a statistical difference between initial and day 1 through day 24 data.

Table 49. Change of modulus of elasticity of EVOH film immersed in apple juice at 22°C ±2°C

EVOH	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent Of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	16185	1914	100%	17891	764	100%
1	12199	722	75%	13387	2691	75%
3	14383	2437	89%	13277	1805	74%
6	14525	1642	90%	17620	1372	98%
14	13081	770	82%	15964	2159	89%
24	15362	1043	98%	15361	2991	86%
Average of Day 1 through Day 24	14053	2161	87%	15522	2204	87%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

EVOH Machine Direction f = 3.6410
90% CL of a statistical difference between initial and day 1 through day 24 data.

EVOH Cross Direction f = 5.2449
95% CL of a statistical difference between initial and day 1 through day 24 data.

Table 50. Change of heat seal strength of EVOH film immersed in apple juice at 22°C ±2°C

EVOH Machine direction

Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial
Initial	3148	377	100%
1	3217	272	102%
3	3376	180	107%
6	3232	171	103%
14	3529	144	112%
24	2967	278	94%
Average of Day 1 through Day 24	3264	209	104%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

EVOH Machine Direction f = 1.5569
75% CL of a statistical difference between initial and day 1 through day 24 data.

Table 51. Change of tensile strength of Co-Pet film immersed in apple juice at 22°C ±2°C

Co-Pet	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	6872	470	100%	5852	990	100%
1	7735	731	113%	3590	359	61%
3	7046	676	103%	4344	908	74%
6	7168	1078	104%	4218	215	72%
14	6766	644	98%	4251	269	73%
24	6932	350	101%	4268	166	73%
Average of Day 1 through Day 24	7129	625	104%	4134	383	71%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Co-Pet Machine Direction f = 4.4872
95% CL of a statistical difference between initial and day 1 through day 24 data.

Co-Pet Cross Direction f = 63.8692
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Table 52. Change of percent elongation of Co-Pet film immersed in apple juice at 22°C ±2°C

Co-Pet	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	3.75%	0.32%	100%	3.04%	0.42%	100%
1	3.03%	0.18%	81%	1.88%	0.51%	62%
3	2.94%	0.25%	78%	1.67%	0.32%	55%
6	3.28%	0.38%	87%	1.78%	0.15%	59%
14	3.18%	0.25%	85%	1.92%	0.20%	63%
24	3.23%	0.36%	86%	1.86%	0.14%	61%
Average of Day 1 through Day 24	3.13%	0.28%	83%	1.82%	0.26%	60%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Co-Pet Machine Direction f = 19.3553
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Co-Pet Cross Direction f = 88.7805
99.9% CL of a statistical difference between initial and day 1 through day 24 data.

Table 53. Change of modulus of elasticity of Co-Pet film immersed in apple juice at 22°C ±2°C

Co-Pet	Machine direction			Cross direction		
Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial	Avg.	s.d.	Relative Percent of Initial
Initial	313333	35777	100%	269067	38872	100%
1	276802	30777	88%	248587	80440	92%
3	286584	48589	91%	257342	80785	96%
6	264667	82855	84%	229733	30476	85%
14	249867	23059	80%	223333	30412	83%
24	247282	22942	79%	226977	30282	84%
Average of Day 1 through Day 24	265040	41644	85%	237194	50479	88%

*Percent Change is equal to $Avg._T/Avg._I$ x (100)

STATISTICAL EVALUATION

Co-Pet Machine Direction f = 4.7690
95% CL of a statistical difference between initial and day 1 through day 24 data.

Co-Pet Cross Direction f = 2.6456
75% CL of a statistical difference between initial and day 1 through day 24 data.

Table 54. Change of heat seal strength of Co-Pet film immersed in apple juice at 22°C ±2°C

Co-Pet Machine direction

Storage Period (Days)	Avg.	s.d.	Relative Percent of Initial
Initial	5000	129	100%
1	4748	557	95%
3	5150	574	103%
6	4904	784	99%
14	5220	724	104%
24	4729	547	95%
Average of Day 1 through Day 24	4971	837	99%

*Relative Percent of Initial is equal to $(Avg._T/Avg._I)100$

STATISTICAL EVALUATION

Co-Pet Machine Direction f = 4.5264
90% CL of a statistical difference between initial and day 1 through day 24 data

APPENDIX H

LINEAR REGRESSION

The purpose of this analysis was to determine the significance of sorption of the aroma/flavor probes by the plastic film samples.

Each slope, resulting from a concentration versus time graph, was tested to see if it was significantly different from zero. This was done in the following manner:

H:Slope = 0 for a given treatment.

$$t = \frac{b_1}{SE\ b_1} \qquad v = \text{degrees of freedom} = r - 2$$

r = the total of all values per data point

b_1 = the slope of the concentration vs. time graph for the given treatment

SE b_1 = the variance of the concentration vs. time slope for the given treatment

Reject H if: $t > t_{\alpha/2,\ v}$ (Student's t distribution, two tailed procedure.)

Upon learning whether the slope was equal to zero, each treatment slope was then tested to see if it was equal to it's control slope:

H:Control slope = Treatment slope

$$t = \frac{bA_1 - b^B_1}{\sqrt{(SE\ b^A_1)^2 + (SE\ b^B_1)^2}} \qquad v = (r_1 - 1) + (r_2 - 1)$$

b^A_1 = Control slope for probe

b^B_1 = Treatment slope for probe

SE b^A_1 = Slope variance for control slope for probe

SE b^B_1 = Slope variance for treatment slope for probe

Reject H if : $t > t_{D,\tilde{},m,v}$ (Dunnett's t distribution for two-sided comparisons with control.)

m = number of total comparisons

CONTRAST OF MEANS

The purpose of this analysis was to determine the significance of any change in mechanical properties as a result of juice contact with the juice. In all cases change occurred between day 0 and day 1. Therefore, the initial data was compared to the remainder of the storage data obtained as a whole. This was done using a contrast of means.

$$f = \left(\frac{[\{n - r_1\} * \bar{y}_1 - r_1 * \{\sum_{i=2}^{6} \bar{y}_i\}]^2}{MS_E \left[\sum_{i=1}^{6} \{c^2{}_i / r_i\}\right]} \right)$$

$$MS_E = \frac{\sum_{i=1}^{6} (SS_i)}{(n - 6)}$$

(six is the total number of treatments in the study)

$$SS_i = \left(\{\sum_{j=1}^{r} Y2_{ij}\} - [\{\sum_{j=1}^{r} Y_{ij}\}^2 / r\} \right)$$

r = number of values per treatment

$$c^1 = n - r_1$$

$$c_2, c_3, \ldots . c_i = -r_1$$

Reject f if:

$$f > f_{\alpha,1,n-6}$$ (Fisher variance ratio)

APPENDIX I

Table 55. Impact failure weight of Alathon film.

INITIAL

Missile Weight (grams)

Initial	ni	i	i*ni
124.9g X X X X X	5	1	5
109.5g O X X X X O O O X O	5	0	0
94.1g O O O O O			
	N = 10		A = 5
	Wo = 109.5g		^W = 15.4g
	Wf = 109.5g		

IMMERSED

Missile Weight (grams)

Initial	ni	i	i*ni
136.07g X X	2	2	4
120.67g X X O X O X X	5	1	5
105.27g O X O X X O O O	3	0	0
89.87g O O O O			
	N = 10		A = 9
	Wo = 105.27g		^W = 15.4g
	Wf = 111.43g		

X denotes failure
O denotes non-failure

Test conditions: drop height 0.33m
dart head diameter 38.1mm

Table 56. Impact failure weight of EVOH film.

INITIAL

Missile Weight (grams)

Initial	ni	i	i*ni
94.1g X X	0	2	0
78.7g O O X X X X X X	6	1	6
63.3g X X O O O O O X X O	4	0	0
47.9g O O O O			

N = 10 A = 6

Wo = 63.3g ^W = 15.4g

Wf = 64.84g

IMMERSED

Missile Weight (grams)

Initial	ni	i	i*ni
136.07g X X	2	2	4
120.67g X X X O O X X	5	1	5
105.27g X O O O O X O X	3	0	0
89.87g O O O			

N = 10 A = 9

Wo = 105.27 ^W = 15.4

Wf = 111.43

X denotes failure
O denotes non-failure

Test conditions: drop height 0.33m
dart head diameter 38.1mm

Table 57. Impact failure weight of Co-PET film.

INITIAL

Missile Weight (grams)

Initial	ni	i	i*ni
63.30g X X X X X X	5	1	5
47.67g O O XXXO O XO O XOOOO	5	0	0

N = 10 A = 5

Wo = 47.67g ^W = 15.4g

Wf = 47.67g

IMMERSED

Missile Weight (grams)

Initial	ni	i	i*ni
57.93g X X X X X X X	6	1	6
42.67g XO XXXXO O XXO O O O OOO	4	0	0

N = 10 A = 6

Wo = 42.67g ^W = 15.4g

Wf = 44.21g

X denotes failure
O denotes non-failure

Test conditions: drop height 0.33m
dart head diameter 38.1mm

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