ABSTRACT

MOELLER, LISA ANNE. Evaluation of Fresh Pack Dill Pickle Chips in Pasteurizable Plastic Containers. (Under the direction of Dr. Roger F. McFeeters.)

The pickled vegetable industry has exclusively used glass jars for fresh pack products that require a thermal process. Recent improvements in polyethylene terephthalate (PET) containers may allow them to withstand temperatures and holding times required for pasteurizing acidified foods. Previous studies on a variety of processed food products packed in plastic have identified challenges such as oxygen ingress, scalping and migration of compounds between the plastic and food matrix. We hypothesize that there will be differences in the sensory characteristics of acidified dill products pasteurized and stored in plastic versus similar product packed in glass.

Dill chips packed in several types of plastic containers and glass jars were evaluated by consumer panels, a trained descriptive sensory panel and analyzed for volatile components by comprehensive two-dimensional gas chromatography-mass spectrometry. Consumers (n=200) evaluated each product for overall liking on a nine point hedonic scale. The descriptive analysis panelists (n=18) were trained for 23 hours to scale attributes of fresh pack dill pickle chips. Volatiles extracted by solid phase microextraction were separated on a polar/less polar column combination and tentatively identified by time-of-flight mass spectrometry. Analysis of variance followed by hierarchial cluster analysis was used to discover the volatiles that were significantly different between treatments.

Significant differences in liking were found for dill chips after seven months of storage in plastic containers at 30^{o} C ($P < 0.05$) by two independent consumer

panels. Descriptive sensory analysis revealed differences in the product attributes of appearance, cure, crunchiness, firmness, fresh, oxidized and total off flavors ($P < 0.01$). Over 500 volatile compounds were detected in the dill chip brines, 81 of which were significantly different between the plastic and glass treatments ($P < 0.001$).

The results from this multidisciplinary approach showed the complex changes that occurred due to changes in packaging materials and identified challenges that need to be addressed to improve acceptability of pasteurized pickles packaged in plastic containers.

Evaluation of Fresh Pack Dill Pickle Chips in Pasteurizable Plastic Containers

by
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DEDICATION

I humbly dedicate this to:

Kelly and Kyle for keeping me grounded.

My mom who will always be an inspiration even from the Heavens.

My father who always makes me smile.

BIOGRAPHY

Lisa A. Moeller is the daughter of Robert and Elsie Moeller. She and her brother and sister were born during the 1960's in San Francisco, California. She smiles when she thinks of her childhood; great parents, great places and a great period in history.

After graduating from Serramonte High School she attended the University of California at Davis. She received a degree in Agronomy in 1983 and went on to complete a one year internship with the Dow Chemical Company's Herbicide Division in Walnut Creek, California.

The folks at Dow encouraged her to pursue a Master's Degree at the end of her wonderful year with them. But in her youthfulness she was more eager to get a "job." They gave her a beautiful send-off to Alaska and then to work with livestock in the Midwest.

In 1988, her daughter Kelly was born and during this same year she began work at Mount Olive Pickle Company in the Quality Control Department. Kyle, her son, was born in 1992 and both were raised in the country outside of Mount Olive along with their black labs, August and Scooter.

For the past 24 years she has been an employee of Mount Olive Pickle Company. Her involvement has centered on quality and environmental interests. At 47 years old she pondered going back to school and finally decided the timing was right to attempt graduate school. With the North Carolina State University campus

only 70 miles from her home and the great rapport between the pickle industry and the USDA-ARS and NCSU Food, Bioprocessing, and Nutrition Sciences Department, the plan was put into motion.

Things that once seemed black and white, she now sees in shades of grey. The journey of a Master's Program has introduced her to people, ideas, and places of great value. The word "balance" now has a fourth dimension and her outlook on the world is most optimistic.

ACKNOWLEDGEMENTS

If people were bricks in a wall, there are several that would be cornerstones. These folks have special gifts that can be seen from many angles. Through their genuine talents and inspiration they have without reservation guided others through the precious journey of learning and better understanding the world around us.

I was so fortunate to have had a “cornerstone” as a mentor for my project. Dr. Roger McFeeters could have not been more professional, inspirational, patient or helpful in supporting my interests. His career has been a monumental asset to the entire pickle industry and his willingness to give me freedom to explore many facets of the food science industry will always be greatly appreciated.

I am very grateful to have been able to work for a number of years under the direction of Doug Brock, Vice President of Operations. He is one of the rare individuals I’ve met in my lifetime with 20:20 foresight. He has been a “cornerstone” to not only my career, but to many at Mount Olive Pickle Company.

I was assigned to be a teacher’s assistant for Dr. Thomas J. Hoban IV during my second year in graduate school. The class was entitled “Food in a Global Society.” Dr. Hoban has one of the brightest spirits and minds. He has taught me “happiness” and I will always be grateful for his kind words and encouragement. He is a genuine “cornerstone” in my life.

With deepest appreciation I would also like to acknowledge the Mount Olive Pickle Company Taste Panelists who were all so devoted to the project, Dr. Van-Den Truong and Dr. K.P. Sandeep who were on my committee and added

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Introduction – Objective

Global markets, competition among food processors, and high consumer expectations are forcing companies to explore ways to improve not only their products, but their packaging and images as well. Modern technology allows many foods traditionally packaged in glass to be packaged in plastic. Unique challenges are posed to food companies because of environmental and health regulations, as well as the short shelf life of some items. Changes in packaging can affect production, transportation costs and efficiencies, waste generated and final product quality. Sensory characteristics of these products can be measured and used to describe changes in product quality that may occur.

Innovation is a process that creates and delivers additional value in the marketplace. Development of new products and processes represents an expensive and time-consuming investment. However it can create success when both consumers and the products are well understood (Hoban 1998). This requires a commitment to evaluating the entire supply chain, the values sought in the market, and changes in technology. It is increasingly important to develop internal teamwork and external partnerships as technology and markets get more complex. This is true of the entire food industry; and the pickle industry in particular.

Fermented pickles have been consumed around the world for thousands of years. Fresh pack pickles were introduced in the 1940's and now dominates the United States marketplace. The fresh pack product that undergoes a pasteurization

process has been packed solely in hermetically sealed glass containers. The traditional glass containers are made of inorganic materials that act as a complete barrier to the environment and impart no flavors to the finished product.

There has been a gradual shift from glass containers to plastic jars and flexible plastic pouches for pickled vegetable products that do not require a pasteurization process. In addition, manufacturers of plastic containers have been partnering with pickle processors over the past ten years to develop containers that are suitable for pasteurized products. This has resulted in the availability of prototype containers that can survive the thermal process, but which have not yet been used commercially.

Plastic pickle packaging is more complex than glass, in part because plastics are organic materials. They often contain multiple components that may be arranged in layers to form the final container. Unlike glass, plastic containers and lids are likely to have at least a limited level of oxygen permeability. This could be detrimental to the quality of pickled vegetables, which are known to be susceptible to oxidation (Cleary and McFeeters 2006) and reduce the shelf life of products. In addition to oxidation, quality changes could occur as a result of: migration of components from the container into the product, absorption of flavor components from the product into plastic materials, or even migration of components outside of a container.

Volatile compounds may cause off-flavors at levels below one part per billion. Such changes tend to be difficult to measure and manage. The objective of this

study was to compare changes in the sensory characteristics of fresh pack dill pickles pasteurized and stored in prototype pasteurizable plastic jars to fresh pack dill pickles pasteurized in traditional glass jars.

The experimental approach was to systematically evaluate the differences and similarities among packaging alternatives using:

1. Consumer panels (untrained) to evaluate the acceptability of products in plastic containers compared to glass containers,
2. A descriptive analysis sensory panel (trained) to quantify appearance, texture and flavor attributes, and
3. Two-dimensional gas chromatography time-of-flight mass spectrometry to identify differences in the volatile component profiles of fresh pack dill pickles in pasteurizable plastic containers compared to glass.

Food Preservation History

In 2012, each of us will be sharing the planet with almost seven billion other people. Humans have inhabited the earth as a species for over 200,000 years. For most of this period our existence was inconspicuous. High mortality due to frequent food shortages kept our numbers in check. Until humans learned to domesticate animals and cultivate crops their diets were quite limited. Agriculture allowed for the production of surplus food, which then needed to be preserved. Development of preservation methods allowed for a longer storage life of this surplus. Dehydration, salting, curing, smoking and fermentation have been used for thousands of years.

Cucumbers were first pickled 4500 years ago in Mesopotamia (Cothran 2009). Since this time the art of producing fermented pickles has been evolving. The process was not well understood, but recipes were developed for a shelf-stable and edible end product. Cucumbers were held in salt brine, while naturally occurring bacteria initiated fermentation. The pH of the fermenting cucumbers was lowered by the bacteria as they produced acids. This reduced pH helped prevent spoilage or the growth of pathogenic bacteria (Breidt et al., 2007; Hutkins 2006). Fermented cucumber products could be packed with different spices but the end product was very different from that of a fresh cucumber. Fermented cucumbers were stored in wooden barrels or earthen vessels.

Nicolas Appert, a confectioner and chef in Paris during the late 18th century experimented with ways to preserve vegetables, meats and dairy products. He placed food in glass jars, sealed them with wax and cork, and then boiled the package. He cooked the containers far in excess of what is used for pasteurization, changing the flavor of the finished product, but preserving the food with a thermal process.

In 1810, Peter Durand patented his method of preservation of food in a sealed container. He used soldered tin cans and created the beginning of the canning industry. In the mid 1800's the glass Mason jar, which could be hermetically sealed, was patented. This allowed for a wide variety of foods to be preserved for extended periods of time by heating the sealed containers to kill spoilage microorganisms (Etchells et al., 1942). Cucumbers were commercially packed fresh

in a vinegar brine and heat treated to prevent spoilage starting in the 1940's (Fuller et al., 1983).

Pickle Categories

The term "pickle" can refer to a variety of food items preserved in a brine or vinegar solution. There are three main types of cucumber pickles sold in the United States. They are characterized by the process used to convert green cucumbers to pickles. In the United States, cucumber pickles are prepared by fermentation, acidification and refrigeration:

1. Fermented foods are low-acid foods subjected to the action of acid-producing microorganism to reduce the pH of the food to 4.6 or below.
2. Acidified foods are low acid foods to which acid(s) or acid food(s) are added. They have a water activity greater than 0.85 and have a finished equilibrium pH of 4.6 or below (United States Code of Regulations, 2006).
3. Refrigeration is a preservation process in which food is cooled and maintained at a cold temperature. Generally, refrigerated pickle products are maintained at a pH of 4.0 to 4.6 and stored at a temperature below 4^{o}C.

Pickled cucumbers are sold, consumed, and eaten in a variety of ways. Commercial processors can pack for either an institutional or the retail market. Retail markets are dominated by acidified and refrigerated products, not fermented

pickles. Fermented cucumber stock accounts for less than 37% of the market share and is mostly converted to hamburger dill chips, salad cubes and relishes. Fermentation enables use of excess cucumbers during peak seasons, as well as reducing loss of fresh stock by fermenting pieces from cut cucumbers that are not useable as spears or chips.

Refrigerated cucumber pickles receive no thermal process (Hutkins 2006). They have gained popularity over the past few decades and now account for close to 25% of the market share (Reina et al., 2005). They are typically acidified with 0.4% to 0.6% acetic acid from the addition of vinegar and contain 0.1% sodium benzoate to inhibit growth of spoilage microorganisms (Reina et al., 2005). The lack of heat processing and cold storage helps to maintain a crisp texture and fresh appearance similar to fresh cucumbers but they tend to have a short shelf life of about three months.

Pasteurized fresh pack pickled cucumber products constitute about 40% of the pickled cucumber market. There has been a continued trend in the past forty years toward higher sales of fresh pack pickled cucumbers (Mount Olive Pickle Company Sales Reports, 2010). The product can be packed quickly, handled once compared with several times for the fermented product, and is shelf stable for 18 months or longer.

Pasteurization

A pasteurization process to assure preservation of acidified fresh pack

cucumbers was first described by Etchells and Jones (1942). Esselen and others (1951) determined heating times and temperatures required to prevent spoilage of pasteurized pickles in both laboratory and commercial packs. Later, a detailed evaluation of processing variables including temperatures, acid levels, and product pack-out ratios under commercial processing conditions was under taken (Monroe et al., 1969). This study was the basis for the standard recommended pasteurization process for fresh pack pickles of heating the product to 74^{o} C at the coldest point in the glass jar and holding it at this temperature for 15 minutes.

The pasteurization step results in shelf stable products by killing the major spoilage microorganisms, lactic acid bacteria and yeasts, as well as by inactivating enzymes that may contribute to fruit softening (Breidt et al., 2010). The thermal treatment also kills vegetative pathogens such as *Listeria*, *Salmonella,* or hemorrhagic *E. coli* that may be present on fresh product (Breidt et al., 2005). If pasteurization temperatures are too high or continued too long, it can potentially lead to development of an undesirable translucent appearance of the cucumber tissue that is referred to as curing (Mok 1992).

The container used for the pasteurization process should be able to keep its shape as the internal pressure increases during heating and then becomes lower than the outside pressure after cooling. The temperatures that the containers are subjected to are high enough to melt some plastics to the point that they deform. In some cases, the plastic expands as the pressure in the container increases and then does not return to the same volume; creating a pressure or vacuum in the container

that can greatly affect the appearance.

Additionally, there is a considerable difference in the thermal conductivity of glass versus plastic. Thermal conductivity measures the ability of a material to conduct heat and defines thermal insulation characteristics. Plastic is a better insulator than glass. Therefore, it takes more energy to heat pickled products to a pasteurization temperature in plastic containers than in glass containers.

Packaging

One of society's main goals is to satisfy their populations demand for basic necessities, such as food and water. In today's world most food is consumed at a distance in time and space from its point of production (Drury-Brun et al., 2007). This requires suitable packaging. Arvanitoyannis (2001) estimated that 50 percent of all packaging is used by the food industry. Food packaging regulation in the United States began with the passage of the Food Amendment of 1958 (Food Additives Amendment, 1958). This amendment to the Federal Food, Drug and Cosmetic Act of 1938 provided the first specific regulations for food additives (Heckman 2005). With the passage of the 1958 amendment the manufacturer became responsible for assuring safety.

The main function of food packaging is to maintain the quality and safety of products during storage (Sensodini et al., 2004; Willige et al., 2002). Food packages can also serve the important functions of maintaining the sensory attributes, adding convenience and communicating product information to consumers (Haugaard et al.,

2001). Packaging foods is a challenging task because foods are complex and diverse. The appearance, texture, aroma and flavor of foods are all important to making their consumption a pleasing experience. These four categories tend to be impacted by the processing and packaging alternatives employed.

Since the development of the commercial pasteurization process, almost all pasteurized pickles have been packaged in glass containers which do not react chemically with food components. Glass is an amorphous solid material that provides a complete barrier to gases. The glass used in the manufacturing of the pickle jars contains 10% cullet, 68% sand, 12% soda ash, and 10% limestone (Verallia Corp., 2010).

In a short period of time, plastics have become a major part of modern life in America and globally. It is estimated that 80% of the average diet in the United States comes in contact with polymeric packaging (Ackerman et al., 2009). The word “plastic” has become a common term for a range of organic materials suitable for industrial products. Many familiar plastics (e.g., nylon, Styrofoam, Teflon, and PVC) were developed in the 1930’s. Plastic bottles were first used commercially in 1947, but didn’t become main stream until the 1960’s. Their popularity was driven by their light weight, improved safety, and lower production costs compared to glass.

Plastics are polymers of high molecular weight. They can be classified by the chemical structure of the polymer and by their glass transition temperature (T_g). Figure 1 shows the chemical structure of the main food polymer packaging materials with their T_g in increasing order, under dry conditions. The T_g of the polymer

determines the flexibility of the polymer molecules. Below the glass transition temperature the plastic is glassy and stiff, while above the glass transition temperature it is in the “rubbery” state (Sajilata et al., 2007).

Unlike glass, which is an absolute barrier to oxygen and non-reactive with foods, polymeric packaging materials generally have some permeability to gases, including oxygen, and they can interact with food components. Interactions may include migration of food components into the plastic container, migration of components from the container into the food product, or chemical reactions within the containers. Understanding the unique chemical make-up of the different plastics can help predict which interactions might define success or failure with various food products (Nielsen et al., 1994).

Polyethylene terephthalate (PET) is a thermoplastic polymer resin of the polyester family. It consists of polymerized units of the monomer ethylene terephthalate with repeating $C_{10}H_8O_4$ units. It is commonly recycled and has the number “1” as its recycling symbol. Because of its ability to contain carbon dioxide it is ideal for use with carbonated soft drinks. PET has been approved as safe by the U. S. Food and Drug Administration (FDA).

In addition to the organic polymers that constitute the bulk of the package material, containers may contain other substances to improve performance in some way or reduce costs. Additives can be incorporated into the plastic for shatter-resistance, clarity, longevity, color, grease-resistance, heat stability, ink-fastness, or microwave enhancement. Plasticizers, antioxidants, and UV stabilizers (as well as

oxygen and photo-quenching compounds) are often integrated into the polymeric systems. The additives and related products are subject to frequent changes (Ackerman et al., 2009).

Oxygen scavenger technologies use iron oxidation, ascorbic acid oxidation, photosensitive dye oxidation and unsaturated fatty acids to help minimize quality changes of foods in plastic packages. Table 1 shows oxygen permeability of three widely tested packaging materials for food products.

Dury-Brun et al. (2007) defined three food product/package interactions that need to be controlled in order to have a successful package. Figure 2 depicts these different physiochemical behaviors:

1. *Migration*: Movement of volatile and non-volatile compounds from the packaging material to the food. Compounds include plastic polymerization monomers or stabilizers.
2. *Scalping:* Movement of compounds from the food or environment into the packaging. Movement depends on the interface: solid to solid, liquid to solid, or gas to solid. These interactions can involve diffusion or binding.
3. *Permeation:* Movement of volatile compounds (flavor compounds, air components, water vapor, etc.) from the food and its headspace to the environment; or movement of compounds after packaging from the environment into the food product.

Migration

The term “migration” is used to describe the process of mass transfer of a compound from a package into the food. Migration of plastic packaging compounds into foods is related to diffusion (Figge and Freytag 1984). When comparing food contamination, migration from packaging materials exceeds all other sources by a factor of 100 to 1,000 times (Grob et al., 2006).

PET is a condensation polymer derived from terephthalic acid and ethylene glycol. PET is itself biologically inert if ingested (PETRA 2011). However to make plastics more useful for specific functions, low molecular weight additives are used to color, increase flexibility, thermal stability, clarity, or reduce static charges. Migration of these plastic additives into food products during processing or storage can be undesirable due to health or environmental issues.

Additives react differently depending on the type of polymeric system and conditions of use. As different plastic formulations have been developed to provide improved package performance the range of chemicals used has increased (Arvantoyannis et al., 2004). Priority-based Assessment of Food Additives (PAFA) contains information on over 3000 substances mentioned in Title 21 of the *U.S. Code of Federal Regulations* (21CFR) Parts 175, 176, 177, and 178. These parts of 21CFR deal with what are known as "indirect" food additives. These are substances that may come into contact with food as part of the packaging system, but are not intended to be added directly to food. Section 409 of the Food, Drug and Cosmetic Act defines Food Contact Substances (FCS) “as any substance that is intended for

use as a component of material used in manufacturing, packing, packaging, transporting or storage, but are not intended to have any technical effect in such food." There are a number of chemicals of concern in the manufacturing of PET. Antimony, acetaldehyde and phthalates are just a few that have been researched in the past several years.

Antimony is widely used as a catalyst in the forming of PET containers (Pang et al., 2006). The resin typically contains concentrations of 100,000-300,000 ppb antimony. Shotyk and Krachler (2007) measured antimony levels in 132 brands of water in 28 countries and found levels as high as 2 ppb. They surmised the levels were dependent on the time and temperature water was stored in the bottles. The United States Environmental Protection Agency (US EPA) has established a maximum contaminant level (MCL) of 6 ppb for antimony. Choe et al. (2003) found that antimony chloride had estrogenic activity in two different *in vitro* assays (Sax 2010).

When PET degrades, one of the end products is acetaldehyde. When acetaldehyde is formed as a by-product in the production of a plastic container some of it remains in the wall of the container. The presence of 10-20 ppb acetaldehyde can modify the organoleptic properties and if present in high enough concentrations cause health problems (Guart et al., 2011). Acetaldehyde is a known carcinogen. Mutsuaga et al. (2006) investigated the migration of acetaldehyde into mineral water in PET bottles and found it was present in commercial products in Japan, Europe and the United States.

Phthalates are by-products of the polymerization reaction. They are added to improve flexibility (Guart et al., 2011). They have endocrine disruptor activity and may leach into the food. Sax (2010) reports evidence that phthalates have been found to leach from water bottles made of PET. Levels are affected by temperature, storage time and the food matrix in the container. When vinegar is added to the containers and the pH is lowered the phthalate levels in the food usually rise (Sax 2010). Ingesting several servings of a salad dressing held in a warm warehouse may result in a dose of di (2-ethylhexyl) phthalate (DEHP) that exceeds the U.S. EPA reference dose of 20 micrograms per kilogram per day (Sax 2010).

Recently phthalates have become more of a concern environmentally (Cao 2008). Addressing the problem of limiting certain compounds from the degradation of the polymers into the environment becomes complicated when you consider that since 2008, 27 percent of PET bottles already in circulation were recycled. These containers come from a wide variety of sources. If bottles intended for food use were recycled from shampoo bottles they might contribute high concentrations of phthalates (Sathyanarayana 2008). New regulations in the United States require the recycling of plastic bottles, so there has been much research in understanding the risks (Dole et al., 2006).

Scalping

Whereas, migration involves the movement of compounds from the packaging into the food, scalping is a term used to describe the absorption of food

constituents into the packaging material. Two mechanisms contribute to a loss of sensory attributes during long term storage: the food degradation process and the absorption process (Ducruet et al., 2007). Absorption is related to the partitioning and diffusion of chemicals (Sajilata et al., 2007) which is determined by environmental factors, such as temperature and concentration and physiochemical properties of the food components, such as molecular weight, structure, polarity and hydrophobicity. Highly branched molecules tend to absorb more than linear molecules. The solubility of esters, aldehydes and benzoate increases three times for every added methylene group (Dury-Brun et al., 2007).

Results from sorption studies show scalping can be explained by enthalpy and entropic effects (Willige et al., 2002). It is observed that flavor absorption by polycarbonate (PC), PET, and polyethylene naphthalate (PEN) is much less than the polyfilms, linear low-density polyethylene (LLDPE), and oriented polypropylene (OPP). However experiments by Willige et al. (2002) show that storage temperature does not influence the amount of absorption onto the rubbery polymers, but does affect the rate and quantity of absorption onto glassy polymers like PET.

Scalping of flavors can cause decreased consumer acceptance of a product based on either loss of flavor intensity or the development of an unbalanced profile. For example, the loss of limonene from orange juice in low density polyethylene (LDPE) containers has been shown to both reduce flavor intensity and impart an unbalanced flavor to the final product (Nielsen et al., 1994). In contrast, Berlinet et al. (2005) found loss of aroma compounds in orange juice when stored at 20^{o}C for

five months was comparable between glass and PET. Their results suggest losses were attributable to high acidity of the matrix and not specifically dependent on container type.

Widen et al. (2004) studied how compounds added to food such as benzaldehyde, limonene, anethole, and benzophenone react when present in multilayer containers. They stressed the importance of layer thicknesses, storage conditions, temperature affects, and concentration of the food on these reactions.

Scalping can have a detrimental effect on the integrity of the package as well as on product quality (Arvantoyannis et al., 2004). The absorption of fats or organic acids by the food contact layer can cause delaminating of layered packages. T. M. Hensley at Michigan State in 1991 studied chemicals found in food systems that had the potential to act as plasticizers, causing plastic polymers to swell (Nielsen and Jägerstad 1994). Widen et al. (2004) also examined the bottle shrinkage that occurs when PET is exposed to high temperatures. Increased polymer chain mobility occurs at the glass transition temperature. It was determined that 1.5 liter bottles shrunk by approximately 50 ml when held at 40^{o} C.

Permeation

The third physiochemical interaction Dury-Brun referred to as permeation. Permeation is the movement of volatile flavor compounds, water vapor, oxygen, nitrogen, carbon dioxide, etc. from the food to the environment or from the environment to the food (Lopez-Cervantes, et al., 2003). In many cases there are

reasons to consider packaging that may not provide a complete barrier to certain compounds. Besides cost, availability, aesthetics and safety, the choices may involve convenience and familiarity (Ayhan et al., 2001).

The unique properties of the product and package influence food interactions, as do storage conditions such as temperature, humidity and light intensity (Nielson et al., 1994). Oxygen ingress is a concern for pickled vegetable products. Oxygen can be a major detriment to shelf life. It can contribute to oxidation of lipids and is necessary for the growth of some spoilage microorganisms (Maloba et al., 1996). Figure 3 depicts oxygen permeability versus water permeability for a variety of polymeric systems. Packaging material selection as well as processing influence the quality of foods during storage due to permeation of compounds especially oxygen that affect color, nutrients, and the degradation of flavor components.

Active Packaging

Some plastic packaging materials for food can be layered, coated or formed as a composite of compounds in an attempt to prolong shelf life and preserve quality. The resulting material is known as “active packaging.” The aim of active packaging is to modify the atmosphere inside the package or slow down natural reactions such as oxidation and microbial growth (Lopez-Cervantes et al., 2003).

Active packaging techniques are concerned with absorbing oxygen, ethylene, moisture, carbon dioxide or releasing carbon dioxide, antimicrobial agents, antioxidants and flavors. In many cases, food deterioration is directly related to

oxidation (Vermeiren et al., 1999). The active packaging agents used to absorb oxygen are readily oxidizable chemicals. The synthetic compounds such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) have been replaced to a large extent with iron, ascorbic acid and their salts as well as enzymes such as glucose oxidase (Lopez-Cervantes et al., 2003). The behavior of the tocopherols (vitamin E), carotenoids, and polyphenols (such as carvacrol) are being studied in different polymeric systems with different food products and storage conditions to assess their advantages and disadvantages as packaging additives (Peltzer et al., 2009).

Peltzer et al. (2009) investigated the use of carvacrol (found in oregano) as an agent for active packaging in plastic containers. Carvacrol is a natural extract with both antioxidant and antimicrobial properties. It migrates from packaging into both oil and aqueous solutions. The main drawback is its organoleptic alteration of the foodstuff. Interestingly, this oil's migration into the product is desirable. In fact, controlled migration would have value in terms of quality and safety.

Thirteen month evaluations of extra virgin olive oil stored in PET showed improved quality characteristics when an oxygen scavenger was incorporated into the plastic matrix (Ceechi et al., 2009). Antioxidants such as iron salts can be incorporated into some polymeric systems and have been shown to slow down the degradation of ascorbic acid better than glass containers under the same conditions (Baiano et al., 2004).

Plastic containers have also been compared to glass jars for use with

mayonnaise. For polymeric packaging systems, oxygen scavenger technologies utilizing iron powder oxidation have proven to be effective in improving shelf-life (Sensodini, et al., 2004). With some oxygen scavenging systems the rate of oxygen absorption is slow. Some of the iron based scavenging systems take as much as four days to reduce the oxygen to less than 100 ppm (Maloba et al., 1996). Eosin and naturally occurring curcumin have been evaluated using sunflower oil in an attempt to reduce the time required for oxygen scavenging.

Graham Packaging (York, PA) has developed a plastic container called CPTX-312. CPTX-312 is a passive and active barrier package made of multilayer PET that was developed to block carbon dioxide and scavenge oxygen. This package is intended to extend the shelf life of oxygen sensitive food and beverage products, such as catsup (Hartman 2003). CPTX-312 has a layer of Nylon MXD6 (poly-m-xylylenediamene) which contains 50-2000 ppm cobalt as an oxidation catalyst to increase the rate of oxygen scavenging and minimize oxygen permeation into the container (Patel 1992).

Turmeric

Oxygen absorbing package systems can provide options that are often economically viable in reducing packaging costs (Ozedemir et al., 2004). Another option can be the addition of antioxidant ingredients to products to prevent detrimental changes in food products caused by the reactions of oxygen with food components. Turmeric has a long history as an ingredient in pickled cucumber

products. Turmeric oleoresin (8.5% cucurmin in polysorbate 80) was the main colorant used in pickle products for a number of years. However, the stability of the pigment is adversely affected by exposure to light. As a result tartrazine (FD&C Yellow #5) has replaced turmeric as the more common colorant in pickled vegetable products (Buescher et al., 1990). Recent research (Cleary and McFeeters 2006) has shown that the addition of turmeric inhibited formation of aldehydes in dill pickles exposed to oxygen that are typically associated with the formation of oxidative off-flavors in foods.

Sensory Evaluation

Pasteurized pickles are a complex product. Cucumbers that are converted to pasteurized fresh pack products undergo many physical and chemical changes throughout the production and storage process. At the same time, consumers expect a consistent product on store shelves. Though some quality aspects can be measured with accuracy, arrays of aromatic compounds found in many foods can best be assessed by sensory panels (Alverado et al., 2010).

It has become common to assess products by both descriptive sensory profiling and consumer acceptability (Mukisa et al., 2009). Untrained, consumer panels are often used to sample a group of product users in a target market. From data collected, consumer preferences and other opinions are assessed.

On the other hand, trained descriptive panels involve discrimination and description of both qualitative and quantitative sensory attributes. Trained panels

have the advantage of generating information about specific characteristics of interest, as well as product changes over time. Data from such trained panels helps evaluate relationships among perception, chemical analysis and physical properties. Such information also helps identify changes in intensity for specific attributes of appearance, texture and flavor.

Sensory science has foundations in biology, biochemistry, biophysics and statistics. Sensory programs focus on relationships between different types of sensory and non-sensory information (Lundahl 1998). The attributes of a food item are typically perceived in terms of appearance, aroma, texture and flavor. Sensory science measures these perceptions through the senses of sight, smell, touch and taste. Sensory evaluations also have an underlying social and cultural dimension (e.g., some groups are better able to critically evaluate various attributes of traditional ethnic foods).

A trained sensory panel is a group of people selected based on their ability to describe products on the basis of taste, smell or feel (Stuckey 2012). Sensory panelists are initially trained to describe their sensory experiences using words they generate in training sessions. These words are more detailed than those used by consumers, and hence, very useful for R&D departments. Linking sensory panel data with consumer tests is a powerful product development tool.

Sensory evaluation begins with understanding what the research wants to accomplish. The most common objectives usually pertain to new product development or quality assurance. Sensory panels identify flavor, aroma and

texture characteristics and then rate these characteristics on an intensity scale. Trained sensory panels do not determine acceptability. Rather, they help determine whether a flavor characteristic is detected and to what degree (Stuckey 2012).

The acceptability of foods has traditionally been measured primarily by untrained consumer taste panels. By the early 1950s, the US Army Food and Container Institute developed a nine-point hedonic scale which has high discriminative power and reliability (Lawless et al., 2010). It uses the following nine anchor terms*: like extremely, like very much, like moderately, like slightly, neither like nor dislike, dislike slightly, dislike moderately, dislike very much and dislike extremely.*

The Labeled Affective Magnitude (LAM) scale has been proposed as an alternative to the nine-point hedonic scale. Lawless et al. (2010). compared the nine-point hedonic scale with the LAM scale for food acceptability ratings of a well-liked food (potato chips). Though both scales performed well in discriminating this product, the nine-point scale showed somewhat higher reliability. Using scales with high discriminative power, good reliability and predictive value is critical to the potential of a sensory evaluation.

Moyssiadia et al. (2004) found that milk bottles made of pigmented high density polyethylene (HDPE) and pigmented PET protected milk against vitamin A and riboflavin degradation more effectively than those of clear PET. Based on sensory evaluations and chemical analysis they determined the shelf life of low-fat, pasteurized milk to be approximately five days. The best overall protection in terms

of vitamin retention was provided by pigmented HDPE bottles. They concluded that packaging is important for protecting products from microbial recontamination and can directly prevent development of light-induced, off flavors. Problems with all-plastic containers did include light transmission and oxygen permeability.

Chapman et al. (2002) also examined milk products by both a trained sensory panel and untrained consumer panel to detect off flavors due to light. Milk in HDPE containers was exposed to a fluorescent light. Samples were evaluated by 10 trained panelists and by 94 consumers to assess the presence and intensity of sensory differences from unexposed control samples. They concluded the majority of commercial milk products in light-transmissible plastic containers are at-risk for detectable off flavors (i.e. old vegetable oil, cardboard, “goaty” or “metallic”) after as little as fifteen minutes exposure to medium intensity fluorescent light.

Liquids are known to react differently than solids in many food packages. Sensidoni et al. (2004) assessed the effects of various plastic-based packages on quality changes in mayonnaise during storage as compared to glass. The three plastic packaging materials examined were: PET, PET with an oxygen scavenger incorporated during extrusion (PET with Amosorb, ColorMatrix Corporation, Cleveland, Ohio), and PET coated with an oxygen diffusion barrier (PET with epoxy-amine, PPG Industries, Pittsburgh, PA.). Packaged mayonnaise was stored at 20°C and removed monthly for chemical, microbiological, sensory and rheological analysis over a six month period. A sensory panel was unable to distinguish samples stored in glass from samples stored in PET with either the added oxygen scavenger or

outer oxygen barrier coating. The panel was able to perceive differences between mayonnaise packaged in glass and monolayer PET. Containers made from PET (incorporating Amosorb as an oxygen scavenger) were found to provide an attractive and suitable form of packaging for mayonnaise because they protect the product against lipid oxidation.

In addition to milk, orange juice has also been evaluated for the effects of packaging on sensory attributes. Ayhan et al. (2001) investigated the effects of packaging materials, storage temperature, and time on the stability of orange juice processed with pulsed electric field (PEF). The retention of eight orange juice aroma compounds, color, and vitamin C in glass, polyethylene terephthalate (PET), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) were evaluated at 4°C and 22°C for 112 days. Packaging material had a significant effect on the retention of orange juice aroma compounds, color, and vitamin C. They concluded that packaging material influences the quality of foods during storage due to the absorption of flavor compounds and by permeation through the packaging. Packaging also impacted degradation of flavor, color and nutrients by oxygen transmission. The retention of all flavor compounds, vitamin C and color was significantly higher in glass and PET than in HDPE and LDPE (Figure 3).

Glass is typically used as the reference when comparing packaging types. Del Noble et al. (2004) found that glass containers are generally preferred to plastic for bottling virgin olive oil. This is due to marketing aspects and the fact that glass containers prevent permeation of oxygen into the bottle. Exclusion of oxygen

prevents auto-oxidation of unsaturated fatty acids. Their results showed that by increasing the barrier properties of the polymer used to manufacture the plastic bottles it was possible to obtain rates of quality deterioration in plastic as slow as that obtained for olive oil bottled in glass containers.

Obushera is one of the many popular traditional fermented products in Asia and Africa whose production has not yet been commercialized. Mukisa et al. (2010) used both a trained and untrained sensory panel to describe the sensory characteristics of obushera and to assess product acceptability. They used results of these panels to evaluate each characteristic that had an influence on consumer acceptability using focus group discussions. Important sensory characteristics of obushera included thickness, cereal aroma, sweetness, honey aroma, sourness and fruity aroma. Significant variation in the sensory attributes was due to different raw materials used, stage of fermentation and manufacturer practices and processes.

Watermelon-rind pickles are a popular condiment in areas of the southern United States, but until recently little scientific information was available for this product. Simonne et al. (1999) at Auburn University evaluated seven existing watermelon-rind pickle formulations (representing various soaking pretreatments including lime, brine and water) for their chemical, physical, sensory and safety properties. Sensory data were collected using a mixed-gender consumer panel to identify consumer preferences. Their goal was to examine consumer acceptance and safety of existing watermelon rind pickles in order to promote product marketability and future production.

Volatiles Analysis Using Gas Chromatography-Mass Spectrometry

The role of sensory evaluation is to provide critical quality data about a food product. The overall flavor profile of a food is determined by volatile and non-volatile components. The human nose has enormous discriminatory power and allows individuals to detect thousands of aroma compounds; having 10- or 100-fold more sensitivity than the best laboratory equipment (Meilgaard et al., 2007). Detection of compounds by sniffing can be used to compare or rank samples, but in complex mixtures deciphering what is happening chemically is impossible using human senses alone. Using taste panels as measuring instruments can provide valid and reliable information that becomes a powerful tool when combined with instrumental analysis.

Volatile compounds can be detected and quantified chemically by a number of different instruments. The laboratory equipment used to detect volatile compounds has improved greatly in the past twenty years. For a long time, one-dimensional gas chromatography was the leading way to detect volatile compounds in food matrices. In complex mixtures, there were problems with co-eluting compounds that had overlapping peak areas because of the single column. In the 1990's, John Phillips helped develop the concept of two-dimensional gas chromatography (Harynuk 2009). Two-dimensional gas chromatography (GCxGC) utilizes two independent gas chromatographic separations by using two independent columns with different selectivity.

A sample is injected onto the first chromatographic column (primary column).

As molecules elute, they are trapped and sampled periodically by a cryogenic modulator (interface). The modulator releases the trapped components onto a second column at regular predetermined intervals (two to six seconds). The dimension and phase properties of the columns are chosen based on the molecules to be evaluated. The molecules take different amounts of time (retention time) to elute from the columns. Since Phillip's conceptualization of two columns, much work has been done to better understand how to optimize column combinations. For example, Zhu (2009) developed a method to optimize column combination orthogonality, specifically for two-dimensional gas chromatography.

The GCxGC unit separates the volatiles with great resolution, but doesn't identify the compounds. Detectors such as flame ionization detectors (FID), electron capture detectors (ECD), and time-of-flight mass spectrometers (ToFMS) are used to acquire the data. Time-of-flight mass spectrometers capture, ionize, accelerate, deflect and detect the ionized particles separately. Because of its high-speed, ToFMS has become the technique of choice for many volatile studies. ToFMS allows for the separation of very narrow peaks from the two-dimensional gas chromatography instrument (Wojtowicz et al., 2010).

In complex food systems that are susceptible to subtle changes, a discovery-based approach can be enlightening. Two-dimensional gas chromatography with time-of-flight mass spectrometry has been used for pickle fermentation brines to provide robust metabolite information (Johanningsmeier and McFeeters 2011). Non-targeted profiling can lead to the discovery of previously misunderstood or unknown

relationships between compounds that may affect the perception of the end product. An enormous amount of data is produced with this testing that new computer programs can handle.

JMP Genomics is a statistical discovery software that allows compounds from the GCxGC with ToFMS to be arranged in meaningful patterns. This software offers the user the ability to explore data mining techniques such as hierarchial cluster analysis (HCA). Cluster analysis involves assigning a set of objects to groups such that objects in the same cluster are more similar to each other than those in other clusters.

Marketing reports have shown that Chinese consumers prefer potherb mustard pickles with a savory taste. Detection of the actual compounds associated with the preferred taste is now possible with improved technological advances and data analysis systems. Zhoa et al. (2007) evaluated 28 samples of pickles collected from 14 cities around the Yangtzee River Delta. They compared descriptive sensory information with physio-chemical parameters. This confirmed which compounds were important for the potherb mustard pickle umami taste.

Ducruet et al. (2007) monitored the sorption of 14 aroma compounds from strawberry syrup into PET and PVC for one year. They found that the absorption of aroma compounds by plastic materials produced both weaker flavor and changes to the organic profile of packaged food products. They found 2-ethylhexanol, benzaldehyde and acetophene migrated from the PET polymers into the strawberry syrup. Sucrose in the syrup was thought to reduce diffusion of flavor compounds by

creating a hydrophobic environment which interacts with the aroma compounds. The sucrose reduced the potential effects of the packaging on strawberry syrup as compared to what might be expected in other food products with less sugar (Ducruet et al., 2007).

Orange juice is the most widely consumed juice, with 90 percent made from concentrate (Berlinet et al., 2005). Orange juice aromas are absorbed in plastic packaging to different degrees. Factors that affect absorption include the molecular size of the aroma compounds, the polarity of the compounds, and their solubility properties. Numerous studies have reported correlations between sensory perceptions and vitamin content; as well as specific aroma and color compounds (Sajilata et al., 2007, Ayhan et al., 2001, Berlinet et al., 2005). Ascorbic acid is an important nutritional component of many juices and the nutritional claims made on the package must be valid. Studies comparing ascorbic acid concentrations through time (in various package types) have been researched (Conrad et al., 2005, Ayhan et al., 2001, Fronz et al., 2008).

Widen et al. (2004) studied the migration of model contaminants from PET as influenced by temperature, food type and functional barrier. They discovered how an increase in storage temperature from 20^{o}C to 40^{o}C resulted in an up to nine-fold increase in migration.

Cherry wine is a common drink in China. Because the volatile compounds play an important role in the perceived quality, Niu et al. (2011) studied the correlations between sensory analysis, gas chromatography-olfactory and gas

chromatography-mass spectrometry data. Their research showed not only strong correlations, but led to the prediction of what fermentation parameters could be altered to give more pleasing aromas to the cherry wine produced.

Rodrigues et al. (2011) investigated ways to shorten the time it took to gather chromatographic data by using multivariate analysis. Their work in Portugal centered on the organoleptic stability of beer. They determined that flavor deterioration was affected by packaging, temperature, light, oxygen content, pH, antioxidant content and precursor concentrations of key aroma compounds. They accelerated changes by exposing the beer to temperatures of 45^{o}C for 18 days. They were able to analyze enough samples to comfortably decrease resolution of the chromatograms without losing critical spectral information.

Much work has been done at North Carolina State University to relate sensory scores for the intensity of oxidized odors in fermented pickles to actual compounds (Zhou et al., 2000, Cleary and McFeeters 2006). Recently, a non-targeted GC X GC-ToFMS was developed for analysis of volatile compounds in fermented cucumbers (Johanningsmeier and McFeeters 2011). It was hopeful that procedures developed the past few years for pickled products could be used to analyze the volatile components in the various treatments and help explain the differences among dill chips packed in glass and plastic packaging.

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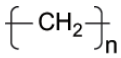
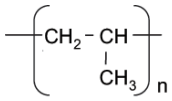
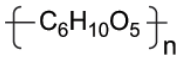
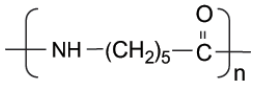
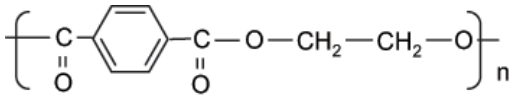
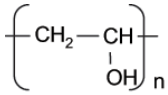
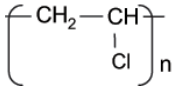
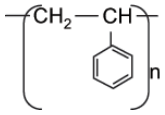
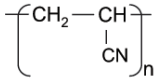
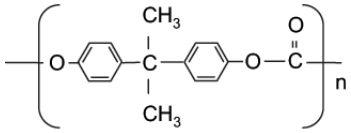
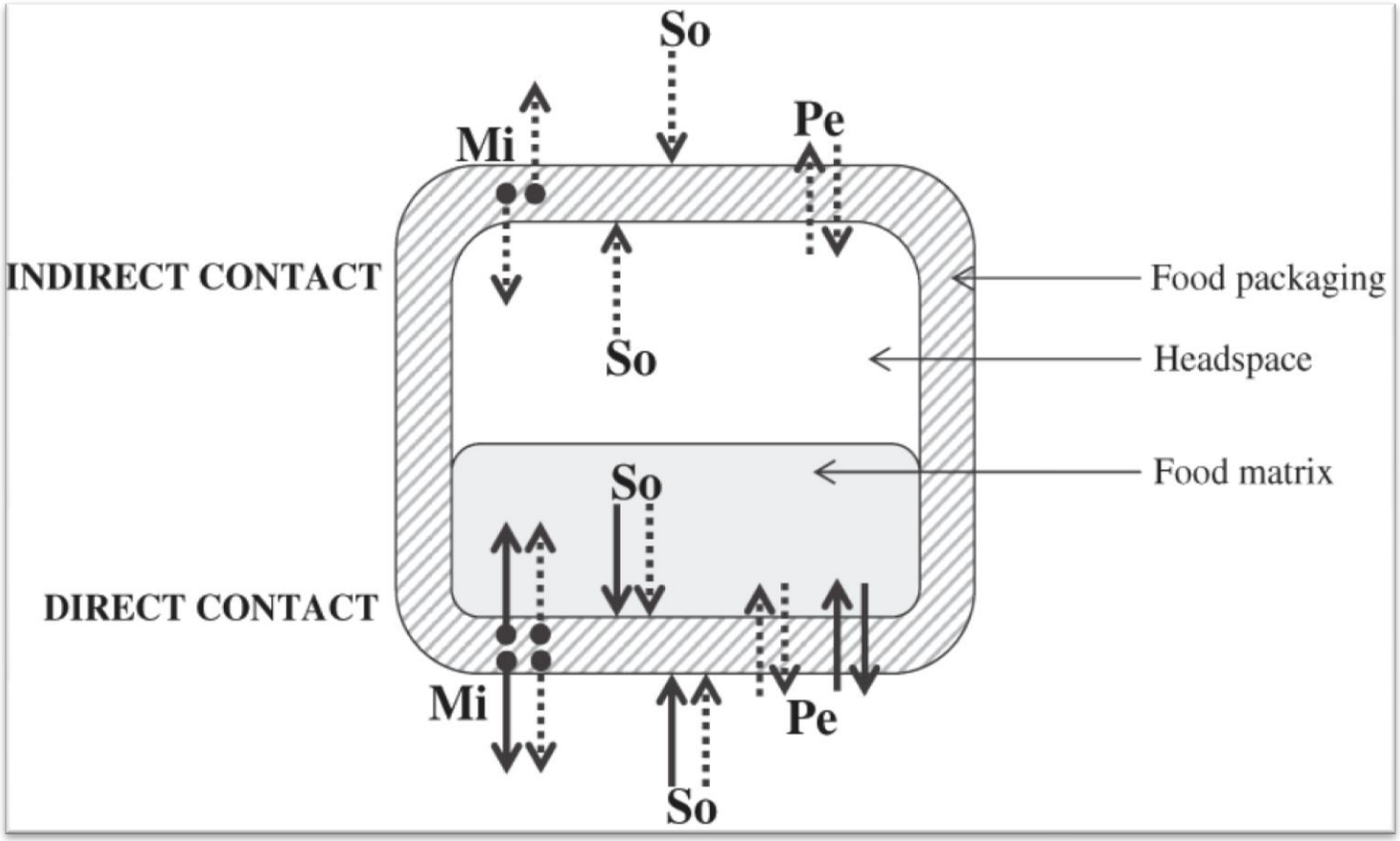
Common name	Abbreviation	Chemical structure	Tg (°C)
Polyethylene	PE		-110
Polypropylene	PP		-15 to 5
Cellulose	-		40
Nylon-6	PA-6		50
Poly(ethylene terephthalate)	PET		70
Poly(vinyl alcohol)	PVOH		85
Poly(vinyl chloride)	PVC		90
Polystyrene	PS		94
Polyacrylonitrile	PAN		104
Polycarbonate	PC		150

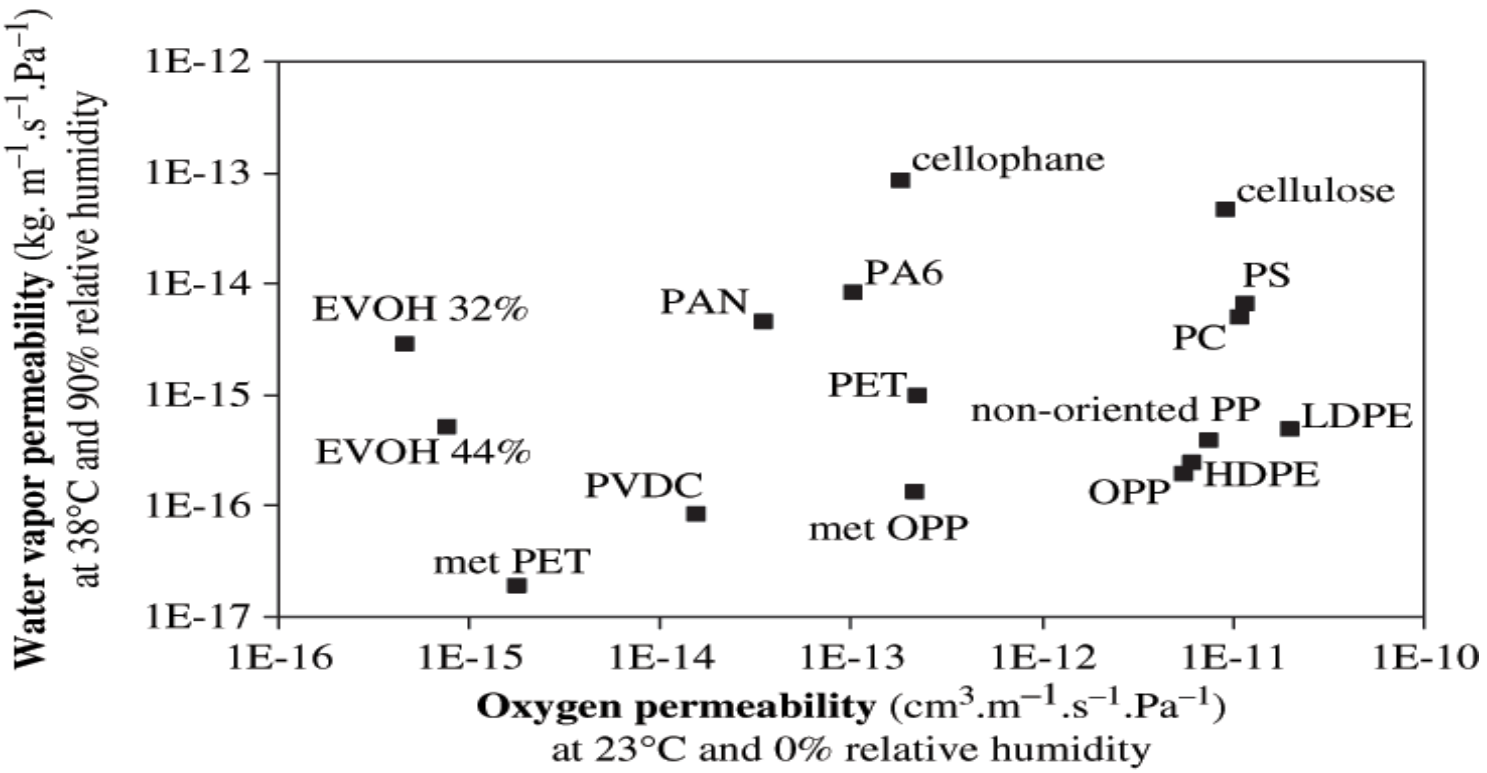
(Adapted from Dury-Brun et al., 2007)

Figure 1. Chemical structure of food packaging polymers and glass transition temperature (T_g) in dry conditions.



(Adapted from Dury-Brun et al., 2007)

Figure 2. Different types of physiochemical behaviors, namely migration (Mi), absorption (So), and permeation (Pe) between a food matrix, its environment, and packaging both under conditions of direct and indirect contact.



(Adapted from Dury-Brun et al., 2007)

Figure 3. Oxygen permeability versus water permeability for polymeric systems. EVOH 32% (32 mol ethylene vinyl alcohol), EVOH 44% (44 mol ethylene vinyl alcohol), met PET (metallized polyethylene terephthalate), PVDC (polyvinylidene chloride), PAN (polyamides), PA6 (nylon 6), PET (polyethylene terephthalate), met OPP (metalized oriented polypropylene), PS (polystyrene), PC (polycarbonate), OPP (oriented polypropylene), LDPE (low density polypropylene), HDPE (high density polypropylene).

Table 1. Oxygen permeability of three common plastic packaging materials.

Packaging Material	Thickness (mm)	Oxygen Permeability (cm^3/day/atm)
PET	0.48 +/-0.01	0.143
PET + Epoxy-amine	0.48 +/-0.01	0.076
PET + Amosorb	0.47 +/-0.01	0.012

(Adapted from Sensidoni 2004)

CHAPTER 2: IMPACTS OF PACKAGING ON FRESH PACK DILL PICKLE CHIP QUALITY AS MEASURED BY CONSUMER AND TRAINED DESCRIPTIVE ANALYSIS PANELS

2.1 Abstract

Consumer acceptance of plastic packaging has increased for many products, but pickles in plastic remain a novelty. Packing pasteurized pickle products in plastic instead of glass has the advantages of reduced weight, possible ease of opening, reduced breakage and the ability to be taken into ball parks, schools and other areas where glass is restricted. In this study, fresh pack dill pickle chips were prepared and stored in several variations of polyethylene terephthalate (PET) and glass containers and evaluated by both consumer acceptance (n=200) and trained descriptive analysis (n= 18) sensory panels. Pickles packaged in glass and monolayer PET with higher oxygen barrier lids (Fresh Seal II™) were found to be better liked than other treatments by consumer panels ($P < 0.05$). Descriptive sensory analysis was used to identify attributes that might cause differences in consumer preference. Significant differences between plastic and glass packaging existed in several key product attributes. Descriptive sensory analysis revealed degradation in overall appearance, crunchiness, firmness, and fresh flavor and increases in cured appearance, oxidized and total off-flavor within 4 months of storage ($P < 0.01$). The data suggests that modifications to the process, formulation and/or packaging materials are necessary to improve the products in plastic containers such that they are rated and scaled closer to that which was packed in glass. Determining the differences between treatments will be used to help understand the changes in the dill chips and potential modifications for future trials that might be most promising.

2.2 Introduction

Packaging is an indispensable element in the manufacturing of pickled vegetables. Although the main function of a package is to preserve inherent product quality (Nielsen et al., 1994), it also conveys messages about the product and manufacturer (Mahalik et al., 2010). Most companies are trying to create a stronger image, become more sustainable and improve safety and quality. They focus on streamlining processing as well as evaluating and implementing changes in product packaging.

In a relatively short period of time plastics have become a major part of modern life. It is estimated that 80% of the average diet in the United States comes in contact with plastic packaging (Ackerman et al., 2009). Sometimes the changes in packaging are the result of requirements by the retail grocery store buyers. Shipping, handling and safety demands are often forcing food manufacturers to consider replacing glass with plastic containers. There are many types of plastics, possible additives to the materials, and interactions that can take place, so shelf life testing of products is necessary.

Pasteurized pickles are a complex product. Cucumbers that are converted to pasteurized fresh pack products undergo many physical and chemical changes throughout the production and storage process. At the same time, consumers expect a consistent tasting food product on store shelves. Though some quality aspects can be measured by instrumental analysis, arrays of aromatic compounds

found in many foods can best be assessed by sensory panels (Alverado et al., 2010). It has become common to assess products by both descriptive sensory profiling and consumer acceptability (Mukisa et al., 2009).

Foods are preferred for many different reasons. Understanding the food, its package, processing and storage conditions; as well as markets are all important. This is true both for continued success of established products, as well as the introduction of new ones. To realize the potential advantages of plastic containers for pasteurized pickle products it is critical that products can be produced and stored which have sensory characteristics similar to that which is obtained with traditional containers. The objective of this investigation was to evaluate consumer acceptability and changes in product attributes of fresh pack dill cucumber chips packaged in different types of polyethylene terephthalate bottles as compared to glass bottles during storage.

2.3 Materials and Methods

2.3.1 Preparation of Cucumbers

Freshly-harvested, size-2A, pickling cucumbers (25-32 mm diameter) were collected from Mount Olive Pickle Company. Packing was done on five separate days using different lots of cucumbers (two lots for untrained consumer acceptance testing and three lots for trained descriptive analysis testing). Each group of

cucumbers was transported to North Carolina State University where they were washed and cut into slices. The cucumbers were flat cut, 8 mm thick, using a food processor (Hobart, Model PF150. Troy, Ohio).

2.3.2 Preparation of Cover Brine

Cover brine was prepared the day before packing. Morton's pickling salt was purchased from a local grocery store. Food grade sodium benzoate, anhydrous calcium chloride, FD&C Yellow #5 colorant, Polish dill flavor concentrate, 200 grain vinegar (20% acetic acid), antifoam C mixture and turmeric (8.5% curcumin) were obtained from Mount Olive Pickle Company. Two formulations were used (Table 2). One was prepared with FD&C Yellow #5 as the colorant and the other with turmeric. It has been shown that turmeric at commercial coloring levels (250 mg/l) may be effective in minimizing the formation of oxidative, off-flavors in pasteurized dill pickles (Cleary and McFeeters 2006).

2.3.3 Selection of Packaging Materials

According to Berlinet et al. (2005), polyethylene terephthalate (PET) is the most widely accepted plastic packaging material used for food storage. Several manufacturers have designed plastic containers that can withstand the high temperatures needed for pasteurization. They are either made from virgin PET or PET in combination with additives or layers of different components. Initial testing showed that the most promising containers were a 16 ounce (473 ml) monolayer

virgin PET bottle and a 16 ounce (473 ml) bottle with an oxygen scavenger incorporated into the center layer of a composite plastic (CPTX-312). Both containers were obtained from Graham Packaging Co. (York, PA). Clarity, rigidity, jar opening size and the ability to stack jars on a shelf were important considerations in deciding the final packaging types to evaluate.

Closures are likely to be an important factor in limiting the amount of oxygen that can migrate into a sealed container. Glass jars are typically capped with metal lids including a built-in, plastic liner that allows minimal oxygen into the container. Plastic jars are commonly enclosed with a plastic lid that also has a plastic liner.

OptiSeal™ is a plastic lid with good sealing characteristics but with low gas barrier properties. Fresh Seal II™ on the other hand was designed to provide a barrier to gases such as oxygen. These two type lids were obtained from Rexum PLC (London, UK). Six different packaging and storage combinations were evaluated for their effect on fresh pack dill pickles after a pasteurization process to assure preservation and microbiological safety (Table 3).

2.3.4 Packing and Pasteurization

The 16-ounce jars were packed with cucumber slices to give a 60:40 pack-out ratio. This required 283 grams of cucumber slices to be added and then 207 grams of cover solution. The lids were heated and then applied by hand to form a hermetic seal. The containers were pasteurized in a steam-jacketed kettle until they reached 74^{o} C at the coldest point in the container, held at that temperature for 15 minutes

and rapidly cooled to room temperature in cold tap water.

2.3.5 Storage Conditions

Interactions between a food and its package continue to occur until the container is opened and the product is consumed. Commercially prepared fresh pack pickles in glass jars are expected to have at least an 18 month shelf life. The pickles were incubated at 30^{o} C to accelerate changes during storage for this project. The pasteurized containers were labeled and placed in an appropriate temperature-controlled environment. The treatment containers were held in an incubator at 30^{o} C. A set of product samples in glass containers was stored at 5^{o}C to minimize changes. Those jars were used as reference samples for the trained panel. A reference sample was included in each set of unknown samples evaluated by both the trained and untrained panels. Products were stored for 16-19 days prior to the first sensory evaluation by the trained panel. Jars of product were equilibrated at ambient temperature (approx. 21^{o} C) before they were served to sensory panelists.

2.4 Sensory Evaluation by a Consumer Acceptability Panel

All consumer acceptability samples were evaluated using a nine-point hedonic scale. Consumers were asked to choose a term that best described their overall opinion of each sample. The terms of the scale were *dislike extremely, dislike very much, dislike modestly, dislike slightly, neither like nor dislike, like slightly, like modestly, like very much or like extremely.* Panelists rated six samples.

2.4.1 Consumer Panel Selection and Data Collection9

Four separate consumer sessions were conducted at a university dining hall (North Carolina State University, Raleigh, NC). Two lots of cucumbers packed two weeks apart were evaluated by independent panels after seven and twelve months of storage. The morning of the evaluation, pickle chips from the six treatments were placed in a 2.0 ounce cup with lid. Each cup was assigned a three digit code. Samples were presented to panelists in a randomized order to avoid bias that could be introduced by order of presentation. All samples were served at room temperature.

Individuals were initially asked if they would like to participate in a sensory evaluation of fresh pack dill chips - packed in plastic and glass. Each panelist was given an evaluation sheet (Figure 4), an IRB consent form (Figure 5) and a brief survey (Figure 6). Participants were also provided with a bottle of water and several unsalted crackers to cleanse their palate between samples.

2.4.2 Consumer Panel Statistical Analysis of Data

Data collected included scores for each sample, as well as participant's age, fresh pack dill pickle consumption, and frequency of visits to the grocery store. Table 4 shows the major variables used in this study.

Panel means were evaluated using SAS® System Type 3 statistical software (SAS® Institute, Cary, N.C.) Analysis of Variance (ANOVA) to compare all variables and the GLM procedure to determine the Tukey's standardized range test scores.

The test controls the Type I, experiment-wise error rate and allows for an easy comparison of similarities and differences among treatments. Tukey Grouping was used to make comparisons between the treatment means for both lots combined for the seven and twelve month evaluation dates.

2.5 Trained Panel Selection and Data Collection

2.5.1 Panelist Selection (n=18)

Sixteen employees of Mount Olive Pickle Company were selected as panelists by company staff. Panelists were selected from various departments. Individuals were chosen based on their willingness to be good "team players," their communication skills and ability to distinguish basic tastes. In addition, two panelists were recruited from the USDA-ARS Research Lab on the North Carolina State University campus in Raleigh.

2.5.2 Panelist Training

The North Carolina State University Institutional Review Board approved an "exempt" status (IRB exemption # 203) for this project as all food products were prepared in accordance with FDA guidelines. Panelists were trained in descriptive sensory analysis for a variety of attributes using a modification of the Spectrum™ method (Meilgaard et al., 2007). Most panelists had no background in formal sensory science, but all were very familiar with pickled cucumber products.

Panelists were trained for an average of 23 hours to use a 15 point scale to assess 14 different attributes.

Training was done to evaluate the basic tastes (sour, salty, sweet and bitter), and vinegar, Polish dill, astringency, oxidized flavor, fresh flavor, “off” flavor, overall appearance, firmness, and crunchiness. The percent cured appearance of slices was evaluated as a percentage of the total area of the slices. Solutions of sodium chloride, sucrose, citric acid, alum, Polish dill emulsion, acetic acid and caffeine were prepared to scale the intensity of salty, sweet, sour, astringency, Polish dill, vinegar and bitter respectively (Figure 7). Panelists were given a reference chart (Figure 8) to estimate the percentage of the area of slices that had a cured appearance. Overall appearance was rated in terms of how the sample compared to the reference. Panelists were trained not to consider the degree of cure in doing this assessment. A score for each attribute was assigned to the reference fresh pack dill chip samples which were maintained at 5^{o}C during storage. For several weeks before beginning the packaging study, panelists trained by tasting the reference sample and scaling the attributes accordingly using solutions and samples of pasteurized fresh pack and fermented dill chips altered to deliver different intensities of key attributes.

2.5.3 Descriptive Sensory Analysis Panel Testing

For each sensory analysis session, panelists were given a tray with 2 ounce cups with lids that contained three pickle chips for evaluating each of the

five treatments. Each cup was identified by a three digit code. In addition to the samples the panelists were given reference solutions for sour, salty, vinegar and Polish dill at intensities of 2, 5 and 10. All samples were served at room temperature. Trays also contained several unsalted crackers and a bottle of water. Each panelist tasted the samples in a predetermined, randomized order to eliminate bias based on the order of sample presentation. One of the unknown samples identified by a three digit code was the reference. A cup labeled as containing the reference dill pickles stored at 5^{o} C was provided to panelists at each evaluation so they could recalibrate themselves for each attribute. Reference intensities were noted on the score sheets (Figure 9).

For each storage time, participants tasted each of the three cucumber lots, on three different occasions at least one day apart. Participants were given a two-hour time slot in which to visit a designated tasting room that was away from the production area where they were isolated from noise and odors associated with the processing plant. An evaluation sheet was assigned to each coded sample and collected when the panelist finished their tasting session.

2.5.4 Trained Descriptive Analysis Panel Analysis of Data

SAS® statistical software (version 9.1.3, SAS® Institute, Cary, N.C.) was used for all statistical analysis. Analysis of variance (ANOVA) was performed on the panel mean intensity scores for each attribute. To test whether the mean intensity score of the attributes differed among treatments at each time point, LSD (Least

Significant Difference) values were determined for α = 0.05 and plotted on a graph of the treatment means as a function of time. This was done to visually display results and be able to make comparisons between treatments and through time.

2.6 Results and Discussion

2.6.1 Evaluation of Fresh-Pack Pasteurized Dill Chips by Consumer Panels

Packaging materials clearly affected the quality of fresh pack dill chips during the storage period. Two lots of cucumbers were tasted on two different days by 189 different consumers after seven months of storage and by 196 consumers on two separate days after twelve months of storage. Consumer liking scores expressed as the mean +/- the standard deviation were compared using the Tukey Groupings (Table 5).

Acceptability of fresh pack dill chips after seven months of storage in plastic and glass containers.

Two lots of cucumbers harvested about a week apart were used to provide two independent sets of samples for analysis. All treatments for the consumer panel testing were subjected to an extended storage for seven or twelve months. The reference samples were stored in glass containers at 5^{o} C so as to minimize changes in the dill chips after jars were pasteurized. The treatment designated "glass" was packed in identical glass containers, but the jars were stored at 30^{o} C as were all of the treatments in which product was packed in plastic containers.

Consumer panel ratings for the two lots of product were not significantly different. This showed there were not factors unique to a particular lot of cucumbers or cover solution that substantially influenced the panel responses. Therefore, results from the two lots of cucumbers were combined for the final analysis of the data.

After seven months of storage the ranking of acceptance scores were as follows: reference > glass > monolayer PET with a high oxygen barrier lid > monolayer PET with a low oxygen barrier lid, but with added turmeric > CPTX-312 > monolayer PET with a low oxygen barrier lid.

Fresh pack dill chips in the reference, glass and monolayer PET with high oxygen barrier lid containers were found to be liked significantly better than fresh pack dill chips in the other three treatments ($P < 0.05$). This is critical for several reasons. It shows that the lid is critical, active packaging is not always better (in this case CPTX-312) and that turmeric while being an antioxidant that reduces formation of aldehydes associated with oxidized flavors in foods (Cleary and McFeeters 2006) did not show that this translated into improved consumer acceptability.

Figures A.1 through A.12 depict for all six treatments after seven and twelve months of storage the percentage of panelists that choose each acceptability score. This information is critical to understanding the results. These figures show that the results between panels and lots of cucumbers were very reproducible, but also that the spread of scores covered the full range of the scale.

From the combined data for two independent lots of product, the reference dill chips stored at 5^{o} C to maintain their quality characteristics as closely as possible to

newly prepared product, received a mean score of 5.77. The product in the glass treatment stored at 30^{o} C was able to maintain acceptability equal to that of the reference after seven months with a mean liking score of 5.75. The liking score for the fresh pack dill chips in monolayer PET with a high oxygen barrier lid was 5.26. This was not significantly different from those chips stored in glass at 5 or 30^{o} C ($P > 0.05$). However, it was also not significantly different from the turmeric treatment.

Use of the low barrier lid, which would have allowed more oxygen into the dill chips during storage, resulted in a significant reduction of product acceptability. The product in the CPTX-312 container with oxygen scavenging capability incorporated into the jar had lower consumer acceptability with a score of 4.75 even though it had a lid with high barrier properties. The chemical changes that occur to scavenge oxygen may have resulted in release of components from the plastic into the product that had a detrimental effect on product quality (Dury-Brun et al., 2007). Turmeric proved to be ineffective as a substitute for the use of a more costly high barrier lid for pasteurized fresh pack pickles in plastic containers.

Acceptability of fresh pack dill chips after twelve months of storage in plastic and glass containers.

After twelve months of storage the order of acceptability changed. At this point the ranking was; reference > glass > CPTX-312 > monolayer PET with a high oxygen barrier lid > monolayer PET with a low oxygen barrier lid > monolayer PET with a low oxygen barrier lid, but with added turmeric.

After twelve months of storage the fresh dill chips in glass held at 30^{o} C were found to be significantly different from the fresh dill chips stored in glass held at 5^{o} C ($P < 0.05$). The difference in these products was related to temperature. The relationship between the monolayer PET with a high and low oxygen barrier lid still existed, but the CPTX-312 through time appeared to improve in the ranking. On the other hand the average liking score for the monolayer PET with a low oxygen barrier lid, but with added turmeric dropped to 3.67 (dislike slightly to dislike modestly).

The impacts of consumer demographics were also evaluated. The scores for the panels were compared to see if there was a difference in liking scores between lots of cucumbers, males and females, age of panelists, consumption of pickles or number of trips to the grocery store. Tukey groupings were used again to make comparisons. There was found to be no significant differences ($P > 0.05$) among the different groups of panelists for any of the factors that were evaluated (Figures10-14).

2.6.2 Evaluation of Fresh Pack Pasteurized Dill Chips by a Trained Descriptive Analysis Panel

In order to better understand the results from the consumer panels and the suitability of plastic containers as a substitute for glass jars, a descriptive analysis panel was trained to evaluate fresh pack dill chips. The combined information from the two types of panels could then be analyzed to better describe the differences among the treatments. From previous unpublished studies it was

understood that there were a variety of appearance, texture and flavor attributes that should be evaluated. Panelists were trained to scale fourteen attributes that were identified as factors that would be indicative of the quality of the product and could affect marketability.

Figures 15-28 show results from the trained descriptive analysis panel. The fourteen attributes evaluated included cure, appearance (as related to reference), firmness, crunchiness, sweet, sour, salty, Polish dill, vinegar, astringency, bitter, oxidized, fresh and off. Cure was scaled as a percentage and all other attributes were rated on a 15 point scale. Each panelist evaluated triplicate samples of each of the three lots of cucumbers over a 2-3 day period at each sampling.

It was found that there were no significant differences among packaging treatments ($P > 0.01$) at any of the time points for seven of the attributes: astringency, bitter, Polish dill, salty, sour, sweet, and vinegar. The other seven attributes related to appearance, texture and flavor showed significant differences among the fresh pack dill pickle packaging treatments from the first sampling time onward through the storage period. Differences in least squares means of the intensity scores for all 14 attributes, the four plastic packaging treatments and all time points as compared to glass is depicted in A.13.

Appearance

The amount of cured appearance in a fresh pack pickle product is a very important quality characteristic. Fresh pack pickle slices pasteurized in glass

containers typically should have minimal cured appearance after pasteurization. The plastic packaging developed a higher vacuum as a result of the thermal process. This resulted in more rapid removal of gas from the cucumber tissue which caused the cucumber tissue to develop a cured appearance (Mok 1992). Higher storage temperature also results in more rapid development of cured appearance.

At the initial and four month storage evaluation, the fresh dill chips stored in glass and held at 30^{o} C was found to have a higher percentage of cured appearance than the product held at 5^{o} C (Figure 19). Initially there was no significant difference among the samples in glass containers held at 30^{o} C compared to plastic jars stored at the same temperature, but after four months the chips stored in glass were found to have significantly less cured appearance than any of the chips stored in plastic. All samples in plastic were rated very close to each other indicating that the type of PET plastic or the barrier properties of the lids did not greatly affect the rate at which cure developed in plastic containers.

Texture

Texture is very important to the quality of fresh pack pickle products. Many packers advertise their products “crunch.” For this study, products were evaluated for both crunchiness and firmness on a 15 point scale. Panelists were trained to understand the difference between these two quality attributes. Firmness is dependent on the amount of pressure required to compress the food in between your teeth, while crunch is also an important part of the eating experience and

represents the audible part of the experience.

Crunchiness was affected by packaging. Fresh pack chips in glass after four months of storage were found to be crunchier than the products stored in any of the plastic containers ($P < 0.01$). At the six month storage point the glass and plastic containers were rated the same for the product held at 30^{o} C, but were significantly different than the reference product (Figure 18).

Similar results were obtained for firmness (Figure 20). There was a significantly higher firmness score for product stored in glass as compared to all the plastic treatments ($P > 0.01$) and by six months these differences had disappeared.

Flavor

As is the case with most food products, flavor is a critical attribute for pasteurized fresh pack dill pickles. The intensity of salty, sweet, sour, vinegar, bitter, astringency and Polish Dill were found to remain similar between the packaging types after the various storage periods Three of the flavor attributes (fresh flavor, oxidized flavor and off flavor other than oxidized) were found to be significantly different among the packaging types evaluated for this project.

Fresh Flavor

Though fresh pack products do not taste like fresh cucumbers, these products have a mild, slightly sweet almost water melon-like taste after they are processed. If this fresh attribute is missing or altered this is expected to result in reduced

consumer acceptability. A substantial decline in fresh taste score occurred in all of the products packed in the plastic containers compared to the glass containers (Figure 21). At the initial sampling time, the fresh taste score was not significantly different among the plastic container treatments. This indicates loss or alteration of key components related to fresh flavor are taking place due to changes that cannot be eliminated by barrier lids or the types of plastic materials chosen in this study.

Oxidized Flavor

Oxidized flavor and off flavor were rated separately. Oxidation occurs when material comes in contact with oxygen and chemically changes. Oxidation of food products can affect sensory properties. Oxidation is often related to rancidity. For fresh pack chips an oxidized flavor is highly undesirable. Glass jars can be a complete barrier to oxygen, whereas through time plastic containers generally allow ingress of air depending on the material they are made from. For this reason a considerable amount of effort was spent training the panel how to scale oxidized flavor. At four months there were significant differences between the products stored in glass versus the same product stored in each of the plastic containers. Of interest here is that there was no significant difference by the descriptive analysis panel between the fresh dill chips packed in the monolayer PET containers with the two types of lids (high and low barrier properties for oxygen).

Off-Flavor

Off-flavor and oxidized flavor could be considered to be the same attribute. For this study, because we did not know what flavors might be impacted by the packaging, we defined the off-flavor attribute to encompass flavors that would not normally associate with fresh pack pickles other than oxidized. Panelists rated the product packaged in plastic as being significantly different ($P < 0.01$) from that in glass after four months of storage for this attribute (Figure 22).

2.7 Conclusions

Food packaging companies continue to pursue innovation as the demand for conveniently-packaged, quality products increases. Plastic packaging has become common in the food sector, but would be a novelty for the pasteurized fresh pack pickle market.

This study revealed differences in the perception of pasteurized fresh pack dill chips packaged in traditional glass jars and several variations of plastic bottles and lids using both the scaling of fourteen critical attributes by a trained descriptive analysis panel and the liking scores of an untrained consumer panel.

In a reasonable shelf life period (seven months); glass, monolayer PET with a high oxygen barrier lid and monolayer PET with a low oxygen barrier lid and added turmeric were preferred by the consumer panel. The turmeric imparts a flavor to the end product that is quite variable in liking and through time degrades such that it was the least preferred product by twelve months.

Descriptive sensory analysis revealed degradation in overall appearance, crunchiness, firmness and fresh flavor and increases in cured appearance, oxidized and total off-flavor within four months of storage for all products packed in plastic compared to glass containers.

The producers of pasteurized fresh pack pickles generally have a unique flavor profile they hope to maintain in their products. Results of sensory studies involving both consumer and descriptive analysis panels can often be associated with changes in chemical components. Knowledge about what chemicals are actually changing while helping explain changes in perception and liking might also lead to developing alternative processing techniques that can improve future products.

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Acceptability Test
Fresh Kosher Dill Chips

Check the box that best describes your overall opinion of each sample.

	Dislike Extremely	Dislike Very Much	Dislike Modestly	Dislike Slightly	Neither Like Nor Dislike	Like Slightly	Like Modestly	Like Very Much	Like Extremely	*Comments*
Sample # 1	☐	☐	☐	☐	☐	☐	☐	☐	☐	
Sample # 2	☐	☐	☐	☐	☐	☐	☐	☐	☐	
Sample # 3	☐	☐	☐	☐	☐	☐	☐	☐	☐	
Sample # 4	☐	☐	☐	☐	☐	☐	☐	☐	☐	
Sample # 5	☐	☐	☐	☐	☐	☐	☐	☐	☐	
Sample # 6	☐	☐	☐	☐	☐	☐	☐	☐	☐	

Figure 4. Consumer Panel Evaluation Form.

North Carolina State University

INFORMED CONSENT FORM for RESEARCH

The Effects of Plastic Packaging on Pickle Flavor

Principal Investigator: Lisa Moeller Faculty Sponsor: Dr. Roger McFeeters

What are some general things you should know about research studies? You are being asked to take part in a research study. Your participation in this study is voluntary. You have the right to be a part of this study, to choose not to participate or to stop participating at any time without penalty. The purpose of research studies is to gain a better understanding of a certain topic or issue. You are not guaranteed any personal benefits from being in a study. Research studies also may pose risks to those that participate. In this consent form you will find specific details about the research in which you are being asked to participate. If you do not understand something in this form it is your right to ask the researcher for clarification or more information. A copy of this consent form will be provided to you. If at any time you have questions about your participation, do not hesitate to contact the researcher(s) named above.

What is the purpose of this study? The purpose of this study is to evaluate the effects of various packaging materials on the flavor of fresh pack dill pickles.

What will happen if you take part in the study? If you agree to participate in this study, you will be asked to taste six pickle samples and fill out an evaluation form. The evaluation should take between 15 and 30 minutes, and will be completed in single sessions.

Risks All products have been prepared using food grade materials with ingredients that are FDA approved and are similar in composition to those already being used commercially in the pickle industry. Products contain FD&C Yellow #5. Individuals whom are sensitive to this ingredient should not participate in this study.

Benefits This research is aimed at helping the pickle industry better evaluate the potential for plastic packaging.

Confidentiality The information in the study records will be kept confidential. No reference will be made in oral or written reports which could link you to the study.

Compensation For participating in this study you will receive a food treat.

What if you have questions about this study? If you have questions at any time about the study or the procedures, you may contact the researcher, Lisa Moeller, or (919-513-7782).

What if you have questions about your rights as a research participant? If you feel you have not been treated according to the descriptions in this form, or your rights as a participant in research have been violated during the course of this project, you may contact Deb Paxton, Regulatory Compliance Administrator, Box 7514, NCSU Campus (919/515-4514).

Consent to Participate "I have read and understand the above information. I have received a copy of this form. I agree to participate in this study with the understanding that I may choose not to participate or to stop participating at any time without loss of benefits to which I am otherwise entitled."

Figure 5. Informed Consent Form for Research.

CONSUMER PANEL

1. Gender ☐ Female ☐ Male

2. Age
   - ☐ 18
   - ☐ 19-24
   - ☐ 25-44
   - ☐ 45-59
   - ☐ >60

3. How often do you consume Fresh Kosher Dill Pickles?
   - ☐ Never
   - ☐ A few times per year
   - ☐ Once per month
   - ☐ Once per week
   - ☐ Two or more times per week

4. How often do you visit the grocery store?
   - ☐ Never
   - ☐ A few times per year
   - ☐ Once per month
   - ☐ Once per week
   - ☐ Two or more times per week

Figure 6. Brief Consumer Survey.

Attribute/Intensity	2	5	10	15
Sweet (Sucrose, g/l)	20	50	100	160
Salty (NaCl, g/l)	1.6	3.5	5.5	7.0
Sour (Citric acid, g/l)	0.5	0.8	1.5	2.0
Bitter (Caffeine, g/l)	0.5	0.8	1.5	-
Vinegar (20% Acetic Acid ml/l)	1.3	2.6	11.6	-
Astringency (Alum, ml/l)	0.5	1.1	2.2	3.0
Polish Dill (Polish Dill Emulsion, ml/l)	0.01	0.02	0.20.	0.50

Figure 7. Solutions for training descriptive analysis panel.

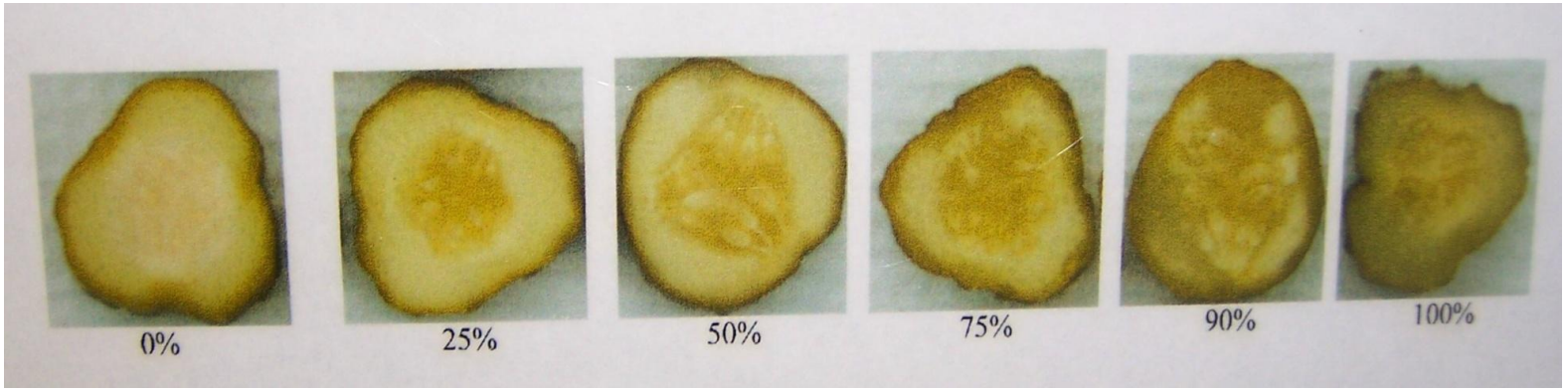

Figure 8. Cure Diagram. (Showing Percentage Cure for Fresh Pack Chips).

Taste Panel

Panelist #: _____
Date: _____
Sample #:_____

APPEARANCE EVALUATION:

Cure (% surface area)			R													
	[0]	[10]	[20]	[30]	[40]	[50]	[60]	[70]	[80]	[90]	[100]					
Overall appearance (difference from reference)																
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															extreme

TEXTURE EVALUATION:

Firmness												R				
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	very soft															very firm
Crunchiness														R		
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	not crunchy															very crunchy

TASTE EVALUATION:

Sweet Taste		R														
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Sour Taste									R							
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Salty Taste									R							
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Polish Dill Pickle Flavor									R							
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Vinegar Flavor									R							
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Astringency				R												
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Bitter Taste	R															
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong
Oxidized	R															
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very strong

OVERALL EVALUATION:

Freshness													R			
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															very fresh
Off-Flavor	R															
	[0]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
	none															extreme

Figure 9. Trained descriptive analysis panel worksheet with “R” over intensities assigned for the reference samples.

Lot Number	Tukey Grouping	Number	Mean Liking Score
1	A	1150	4.88
2	A	1157	4.97

Figure 10. Comparison of Consumer “Liking Scores” by Lot.

Gender	Tukey Grouping	Number	Mean Liking Score
Male	A	1481	4.89
Female	A	826	4.99

Figure 11. Comparison of Consumer “Liking Scores” by Gender.

Age	Tukey Grouping	Number	Mean Liking Score
18	A	30	4.83
19-24	A	1768	4.91
25-44	A	270	4.84
45-59	A	209	5.18
>60	A	10	4.70

Figure 12. Comparison of Consumer “Liking Scores” by Age Groups.

Consumption	Tukey Grouping	Number	Mean Liking Score
Two or more times per week	A	240	5.25
Once per week	A	528	5.00
Once per month	A	802	4.91
A few times per year	A	647	4.77
Never	A	90	4.80

Figure 13. Comparison of Consumer “Liking Scores” by Consumption.

Shopping Behavior	Tukey Grouping	Number	Mean Liking Score
Two or more times per week	A	328	4.80
Once per week	A	900	5.00
Once per month	A	905	4.83
A few times per year	A	130	5.16
Never	A	30	5.93

Figure 14. Comparison of Consumer “Liking Scores” by Shopping Frequency.

Table 2. Cover Solution Formulas for Dill Chips.

Formula 1: (with FD&C Yellow #5)

Per liter:

Ingredient	Weight (gm)
Morton's Pickling Salt	54.16
Anhydrous Calcium Chloride	3.97
200 Grain Vinegar	74.16
FD & C Yellow #5	0.51
Polish Dill Flavor Concentrate	0.83
Benzoate with Coloring Mixture	5.50
Antifoam C Mixture	0.92
Water	896.67

Formula 2: (with Turmeric)

Per liter:

Ingredient	Weight (gm)
Morton's Pickling Salt	54.16
Anhydrous Calcium Chloride	3.97
200 Grain Vinegar	74.16
Turmeric Mixture (*)	0.60
Polish Dill Flavor Concentrate	0.83
Clear Benzoate	5.50
Antifoam C Mixture	0.92
Water	896.67

(* this results in an equilibrated curcumin level of 250 ppm)

Table 3. Experimental Treatments.

Container	Lid	Additions	Storage Temperature (C^o)
Monolayer PET	Fresh Seal II™	None	30^oC
Monolayer PET	OptiSeal™	None	30^oC
Glass	Metal	None	30^oC
Glass	Metal	None	5^oC
Monolayer PET	OptiSeal™	Turmeric	30^oC
CPTX-312	Fresh Seal II™	None	30^oC

Note: OptiSeal™ is a plastic lid with good sealing characteristics but with low gas barrier properties. Fresh Seal II™ on the other hand was designed to provide a barrier to gases such as oxygen.

Table 4. Data set variables.

Variable - Class	Levels	Values Measured
Treatments	Six	CPTX, G30, G5, Mono B, Mono NB, Turmeric
Lot	Two	1,2
Storage Time at 30^{o}C	Two	7 month, 12 month
Gender	Two	Male, Female
Age	Five	18, 19-24, 25-44, 45-59, 60 or over
Pickle Consumption	Five	Never, A few times per year, Once per month, Once per week, Two or more times per week
Grocery Shopping Frequency	Five	Never, A few times per year, Once per month, Once per week, Two or more times per week

Table 5. One-way Analysis of Variance of Consumer Liking Scores for Dill Chips Packaged in Glass or Pasteurizable Plastic Containers.

Mean consumer liking scores from a nine-point hedonic scale*

Packaging Type	Seven Months	Twelve Months
Reference**	5.77 ± 2.17[a†]	6.03 ± 2.11[a]
Glass	5.75 ± 2.09[a]	5.19 ± 2.27[b]
Mono Barrier (Fresh Seal II™)	5.26 ± 2.07 [a,b]	4.59 ± 2.07[b,c]
Mono No Barrier (OptiSeal™)	4.46 ± 2.21[c]	4.35 ± 2.16[c]
CPTX 312	4.52 ± 2.13[c]	4.77 ± 2.23[b,c]
Turmeric	4.75 ± 2.18[b,c]	3.67 ± 2.13[d]

* Values are expressed as mean ± standard deviation.

** Reference pickles were packed in glass and stored at 5^{o} C.

† a, b, c, d, means within the same column followed by different letters are significantly different ($P < 0.05$).

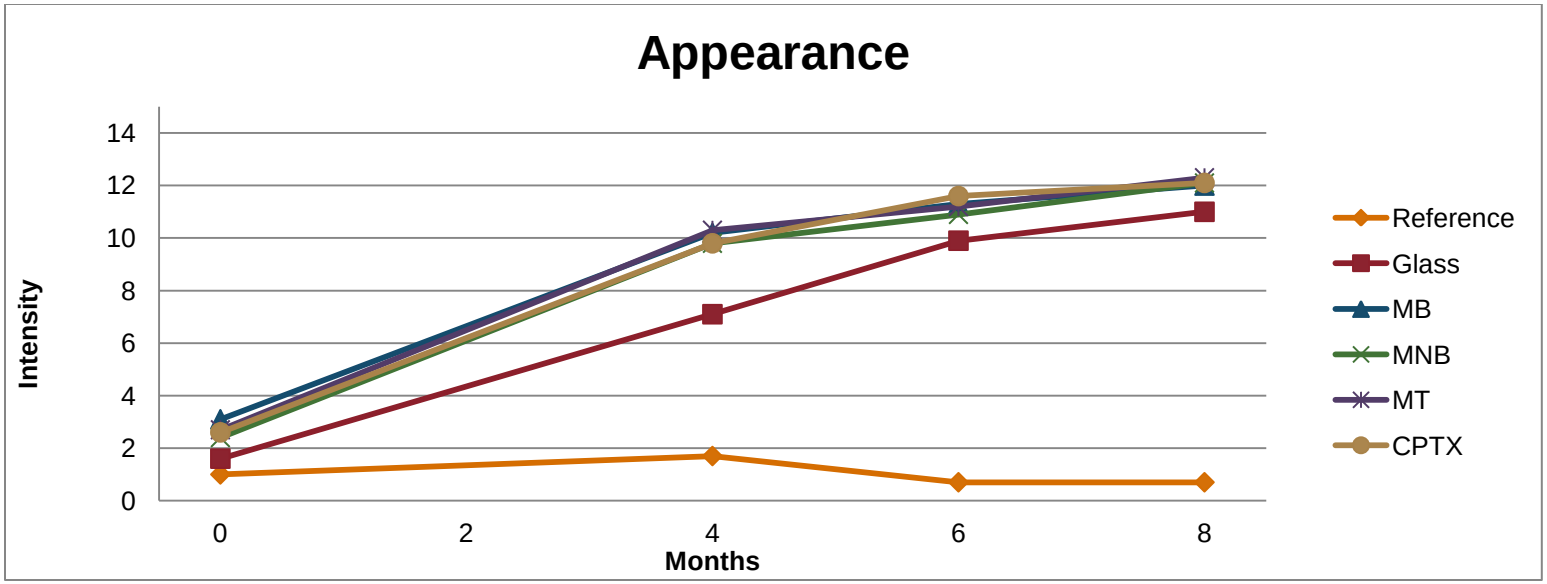

Figure 15: Difference in appearance of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months as compared to a "reference."

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 1.4)

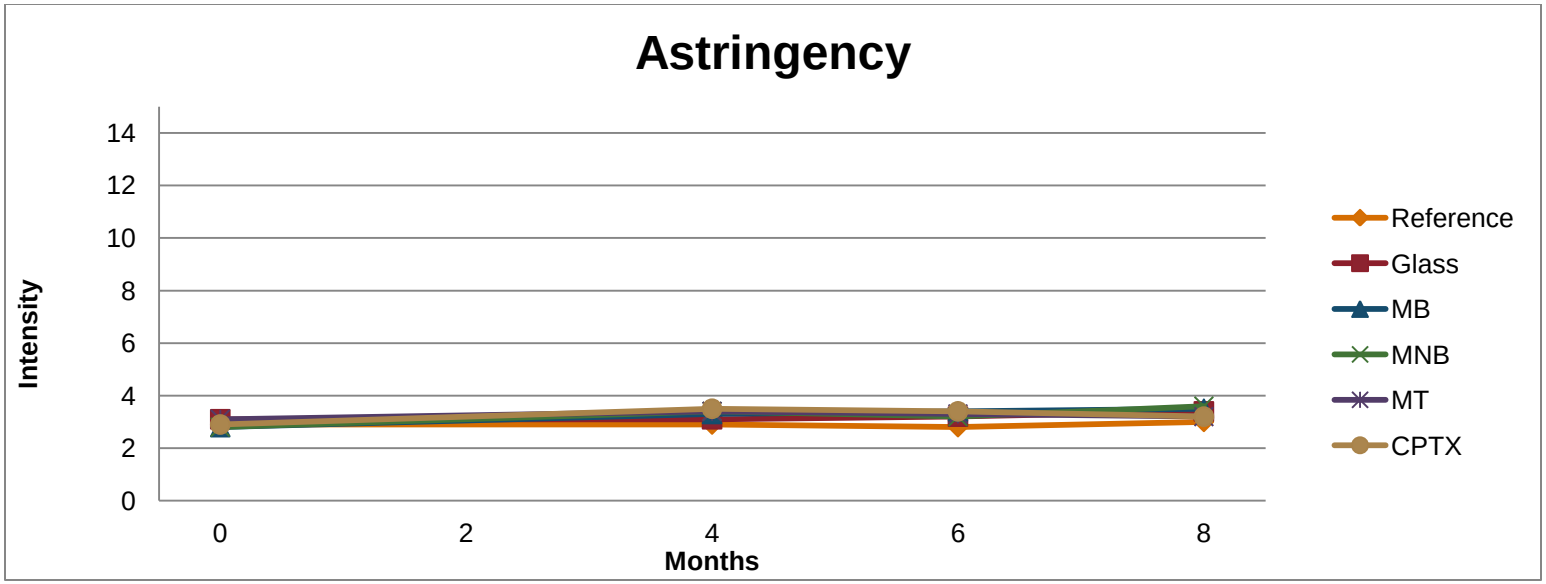

Figure 16: Difference in the intensity for the attribute "astringency" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX = CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.3)

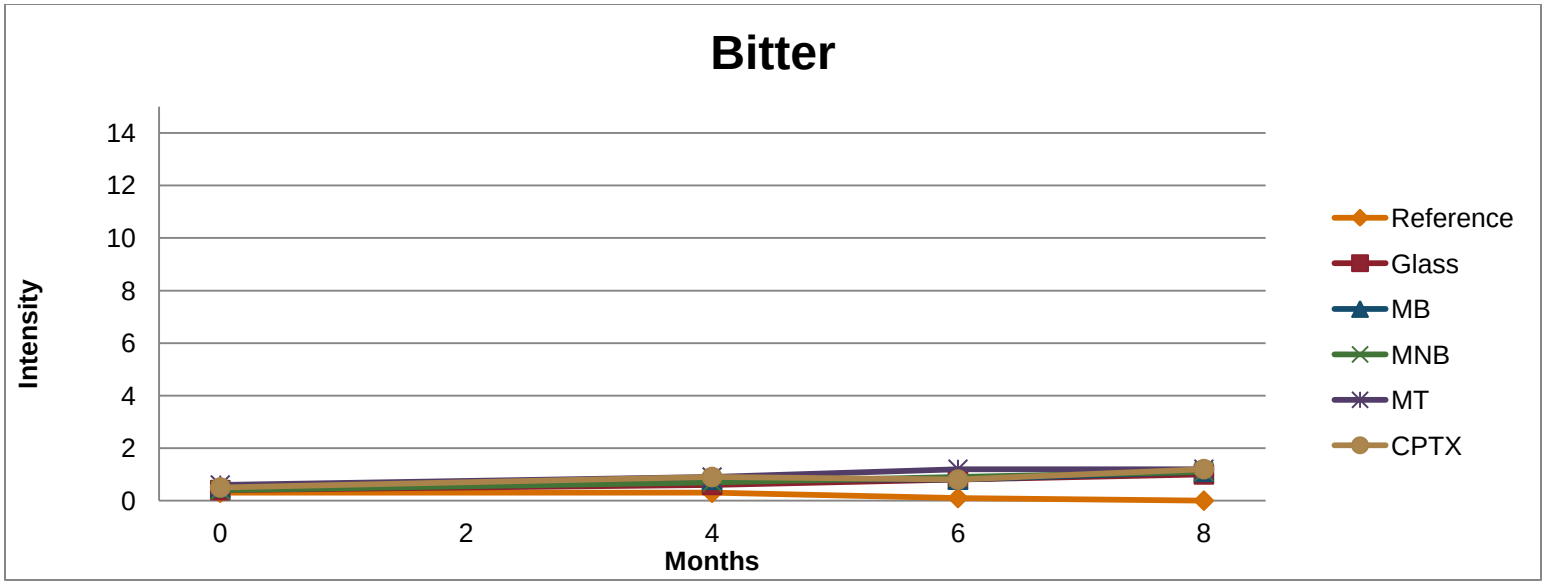

Figure 17: Difference in intensity for the attribute "bitter" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.3)

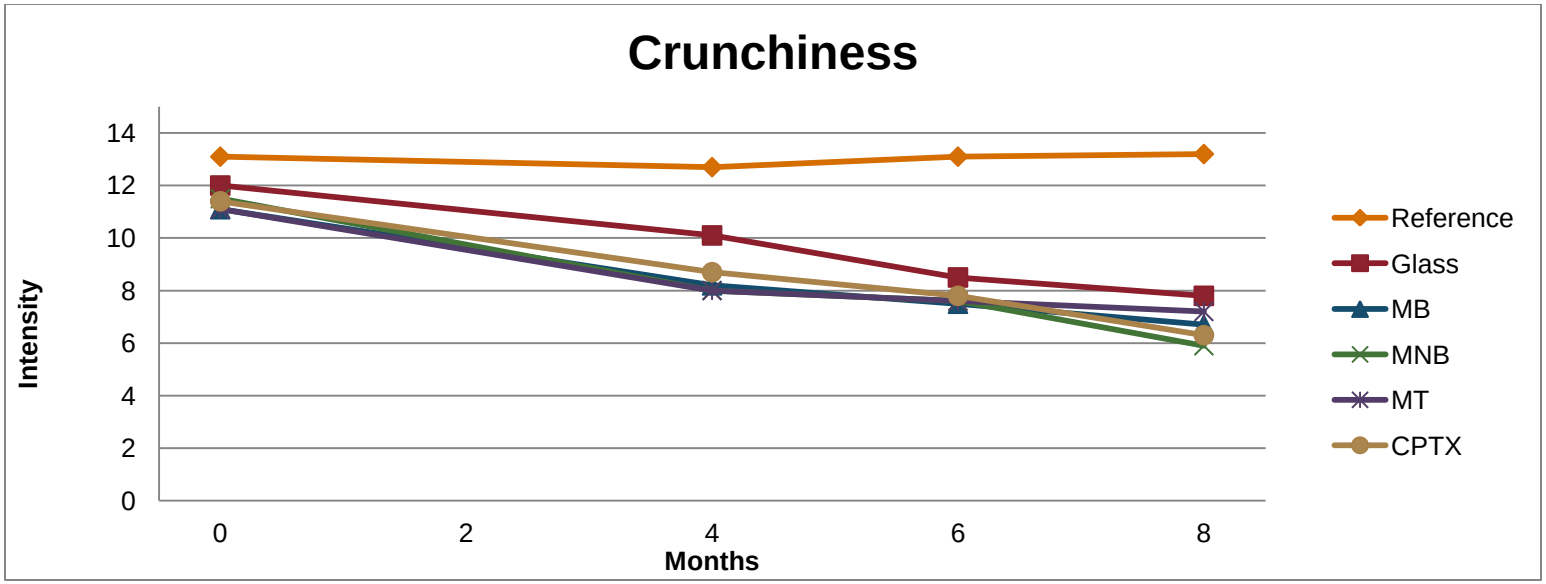

Figure 18: Difference in the crunchiness of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 1.4)

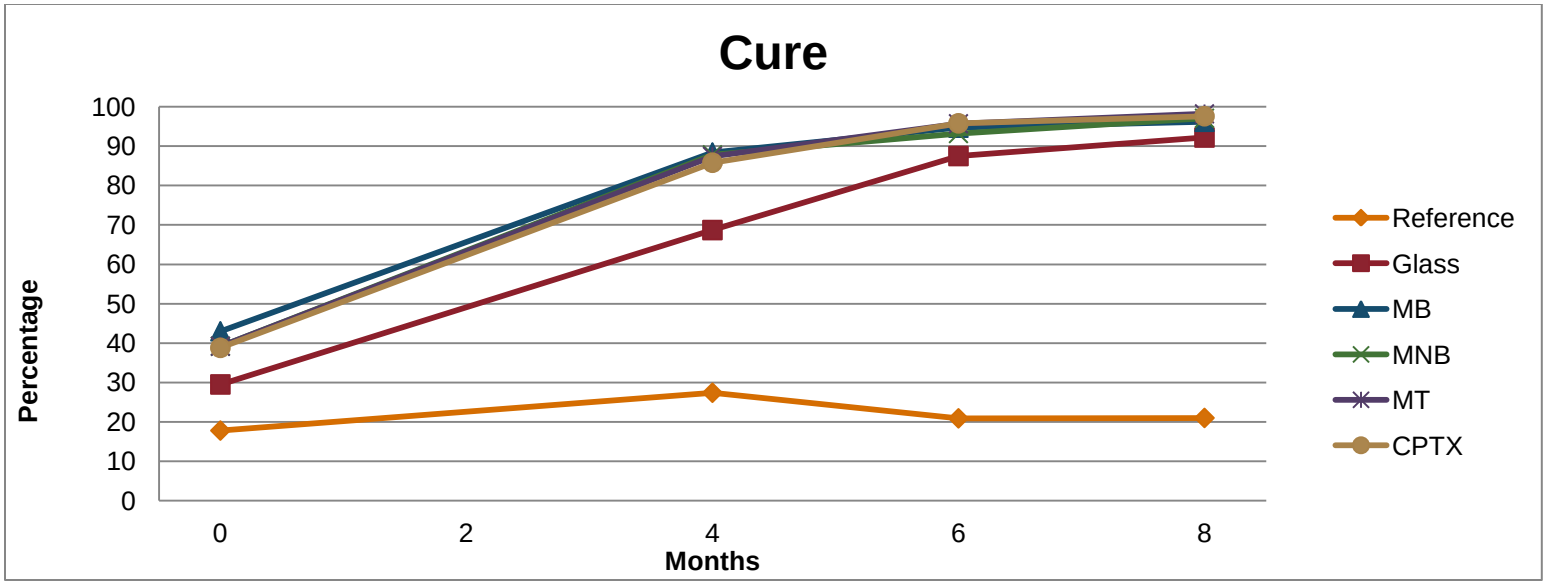

Figure 19: Difference in the degree of curing of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 9.6)

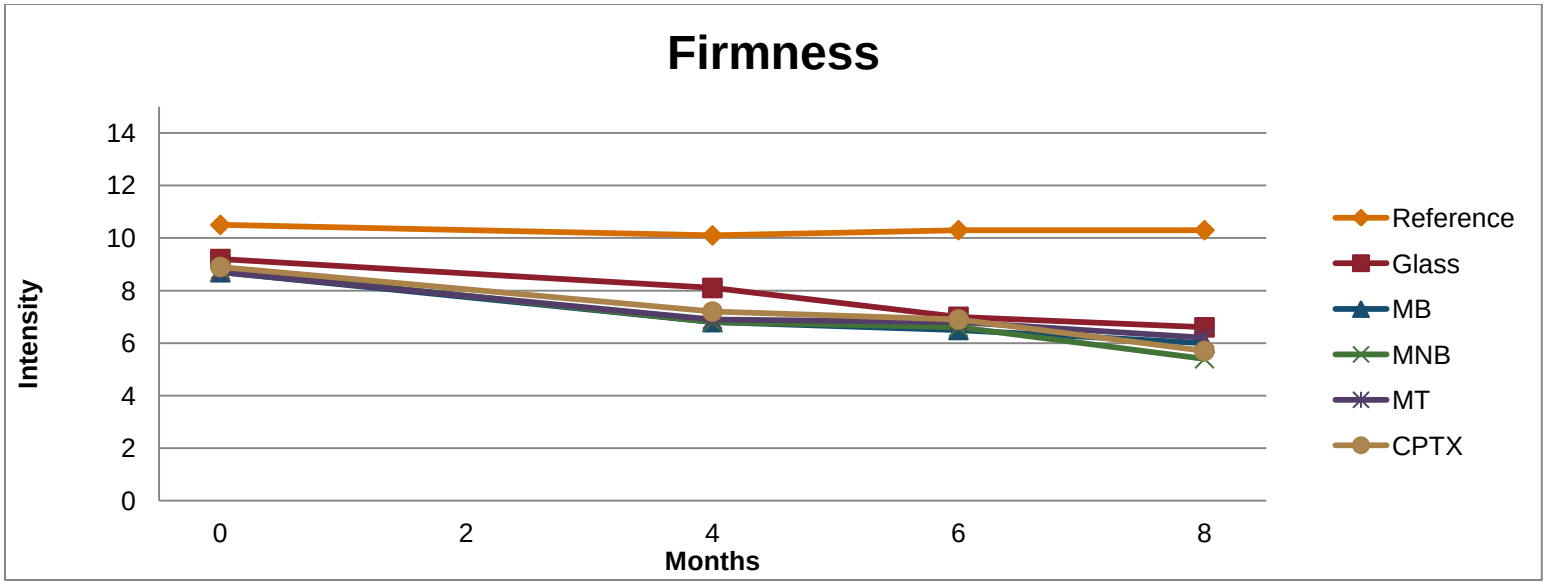

Figure 20: Difference in the firmness of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.9)

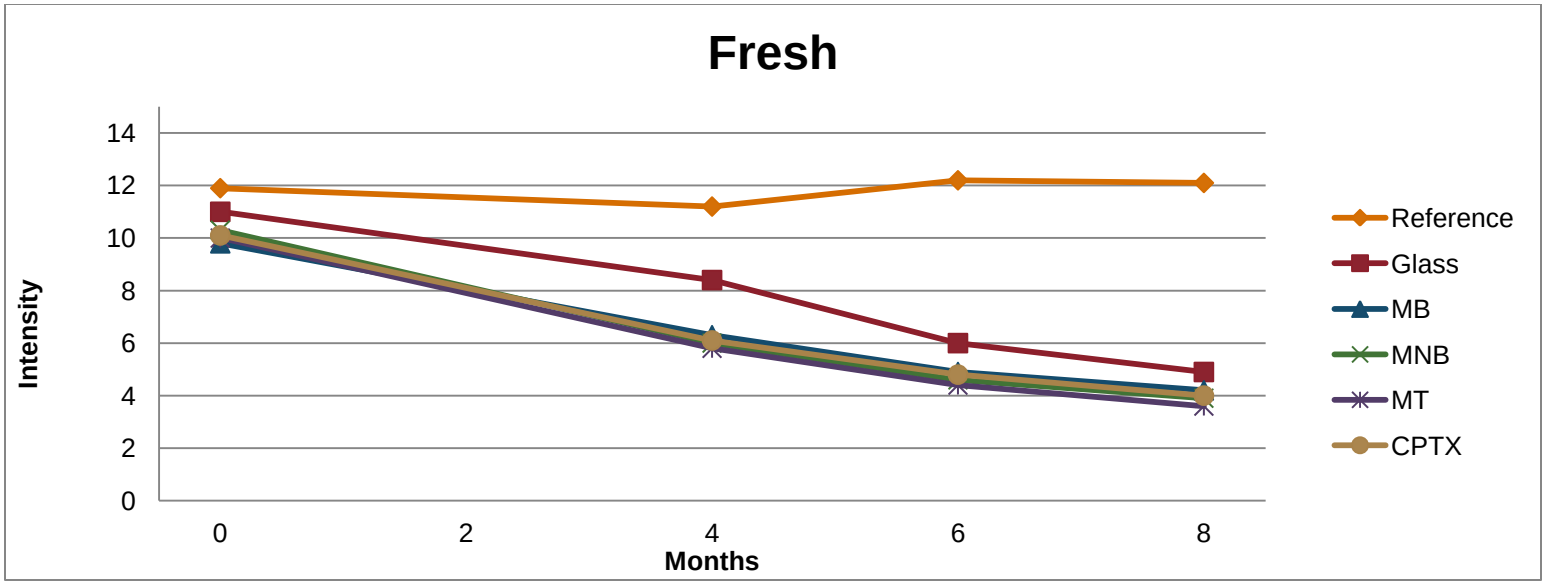

Figure 21: Difference in the intensity for the attribute "fresh" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 1.0)

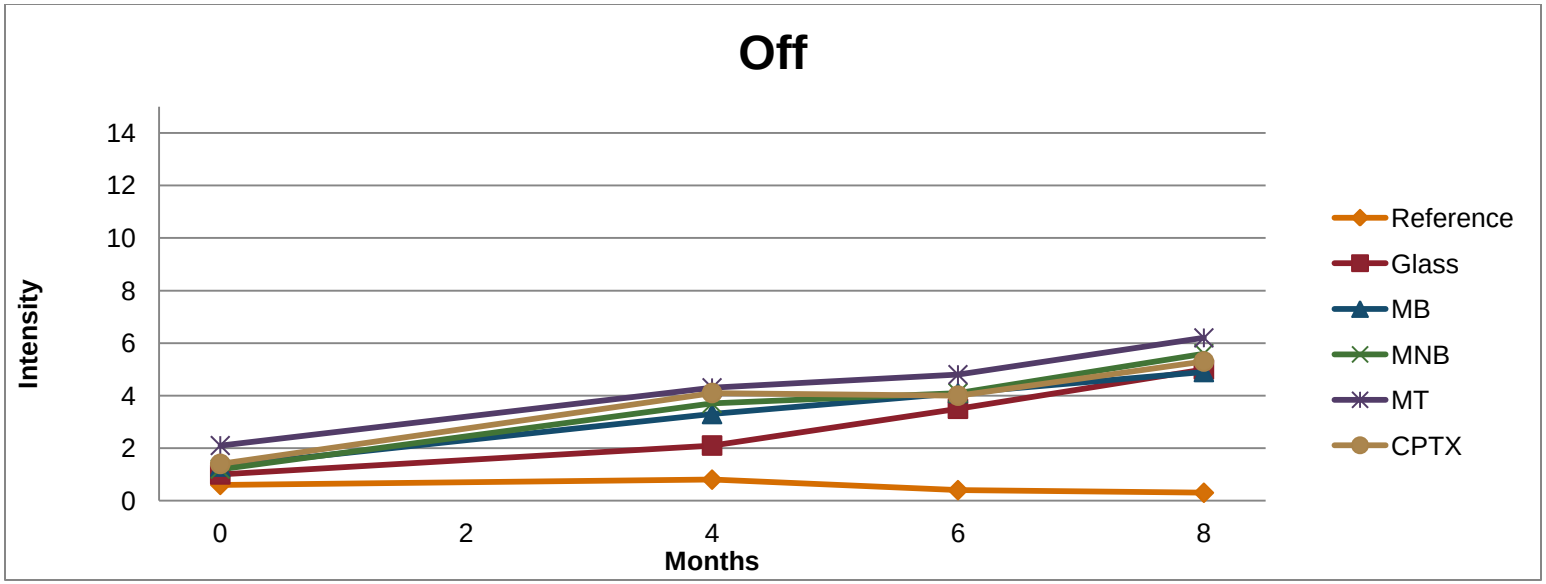

Figure 22: Difference in the intensity for the attribute "off-flavor" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.9)

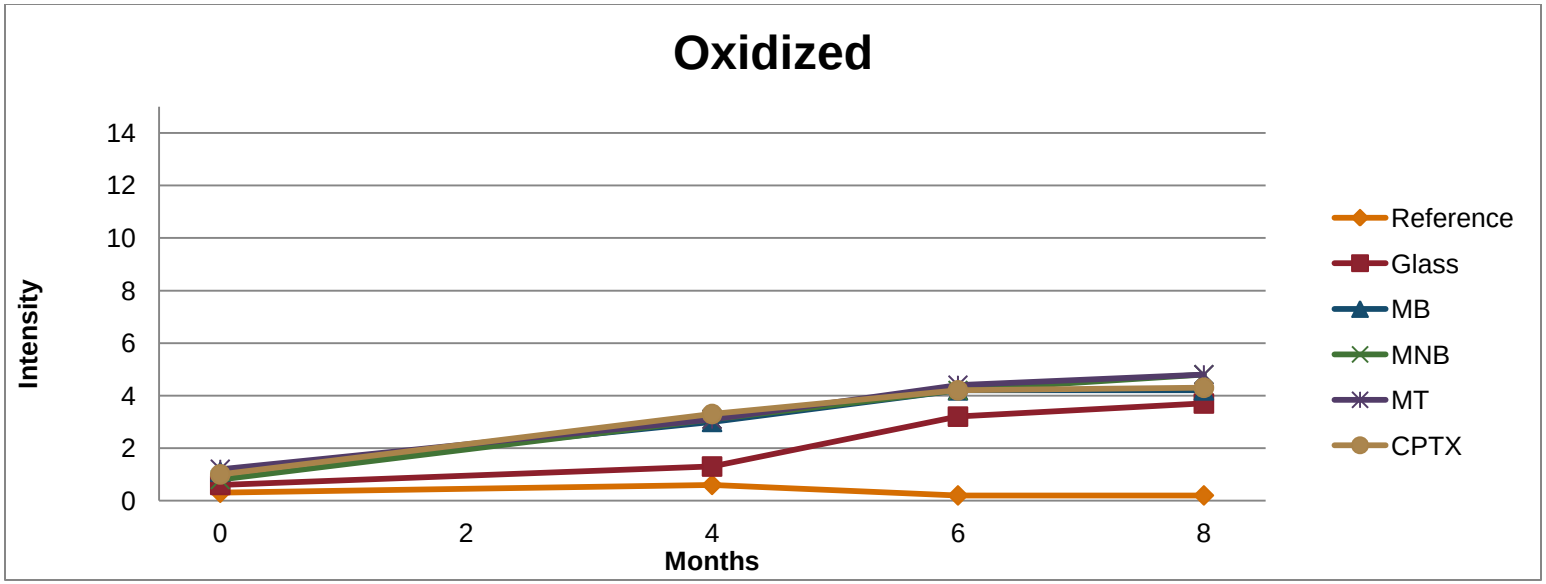

Figure 23: Difference in the intensity for the attribute "oxidized" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.9)

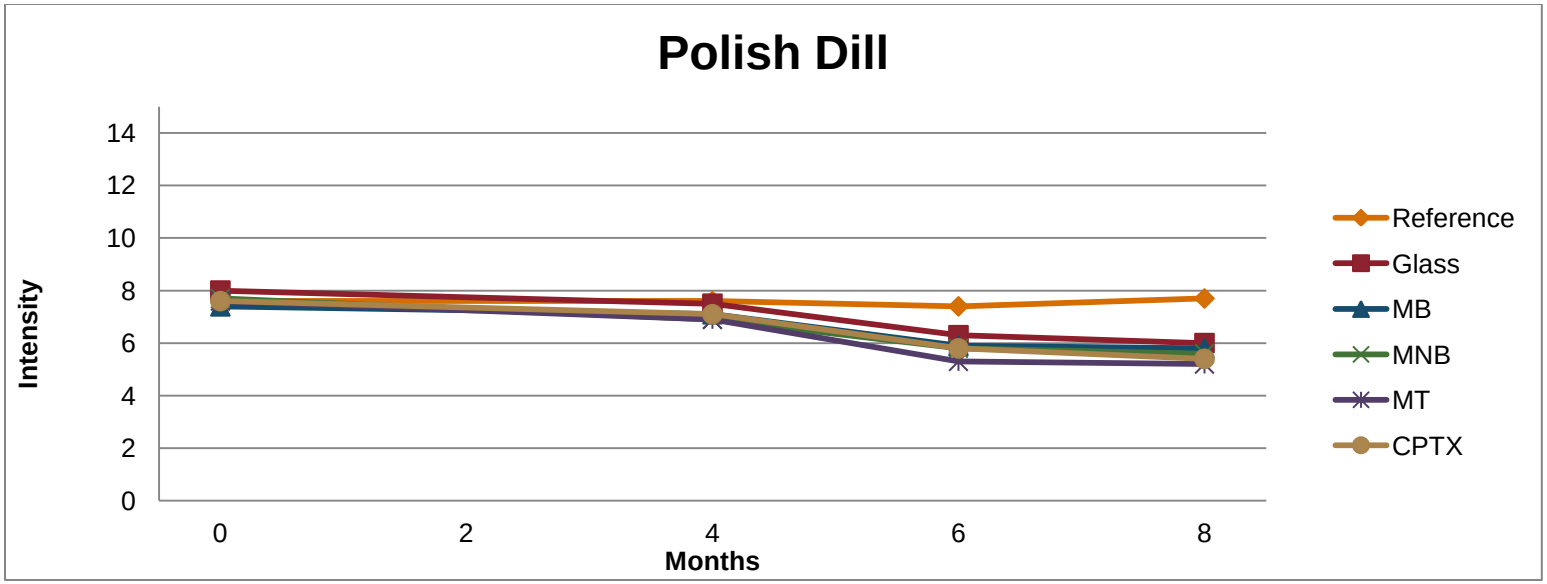

Figure 24: Difference in the intensity for the attribute "polish dill" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.6)

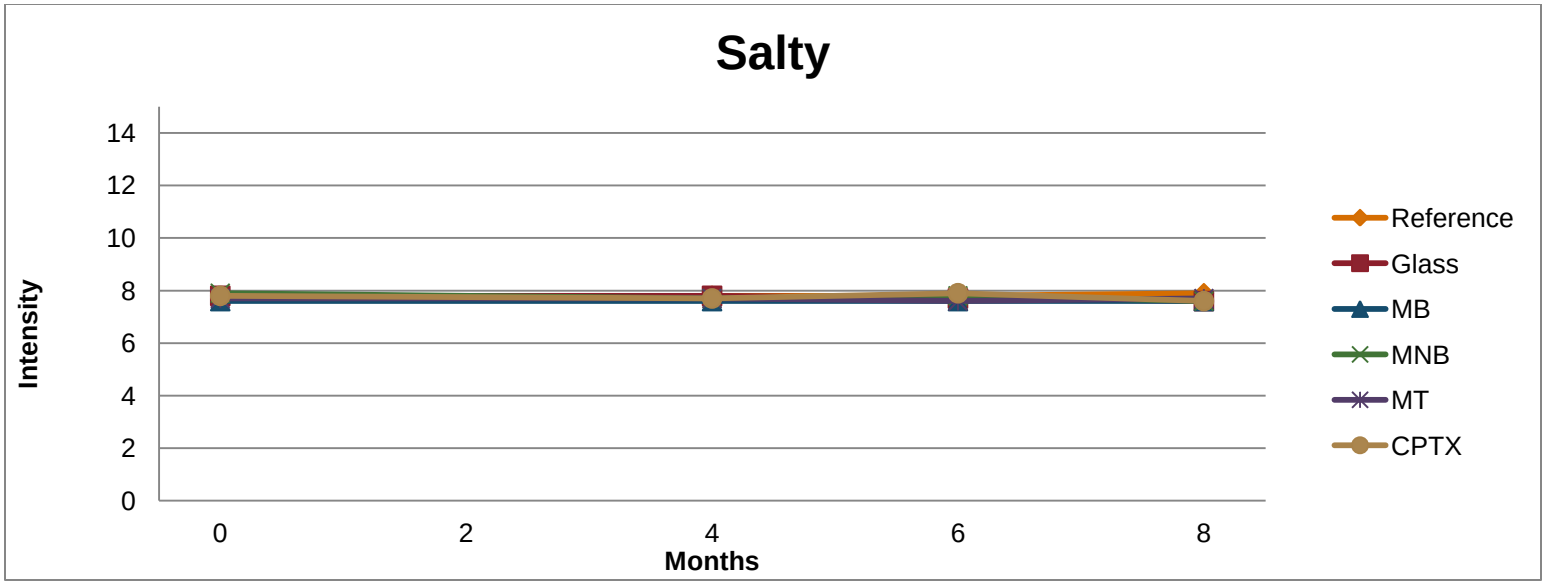

Figure 25: Difference in the intensity for the attribute "salty" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

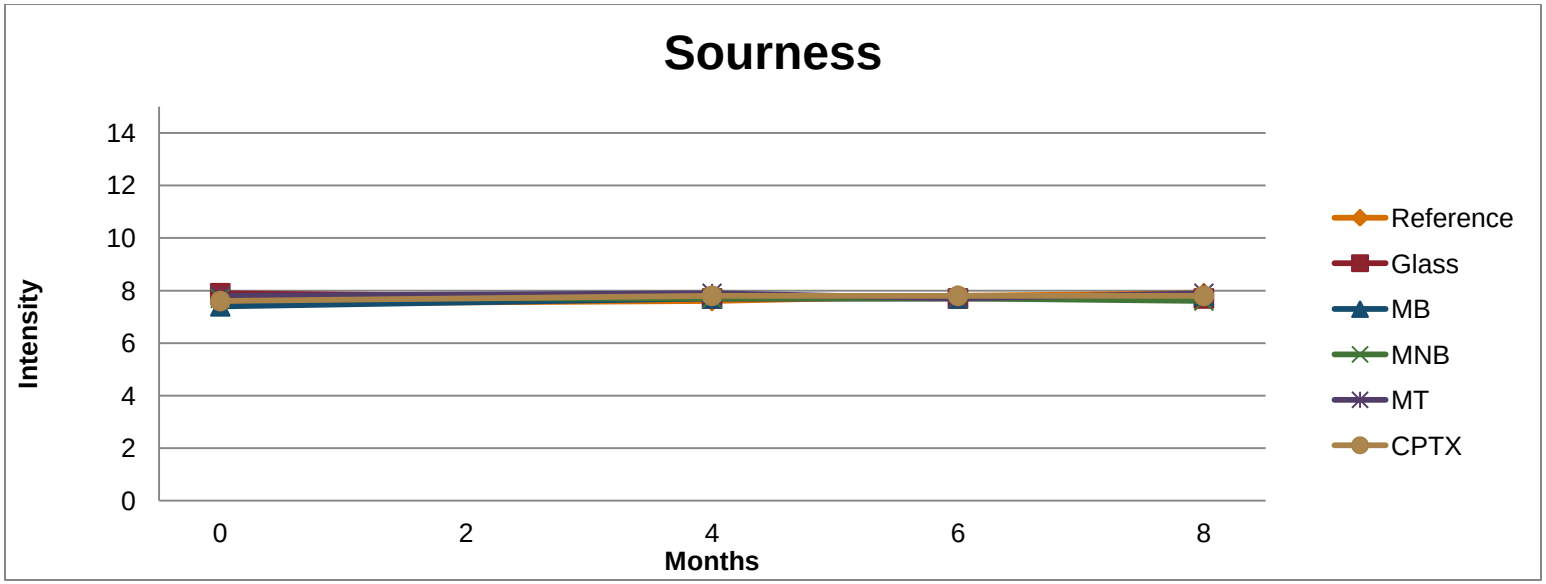

Figure 26: Difference in the intensity for the attribute "sour" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

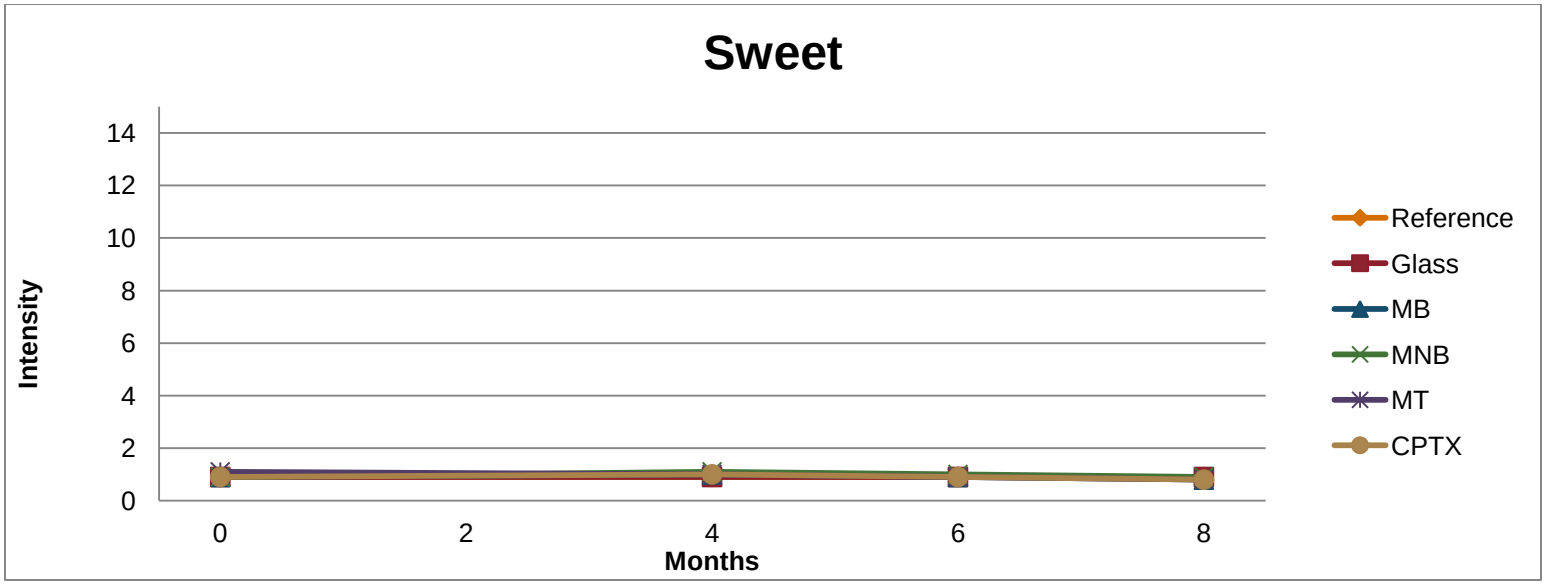

Figure 27: Difference in the intensity for the attribute "sweet" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner(OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

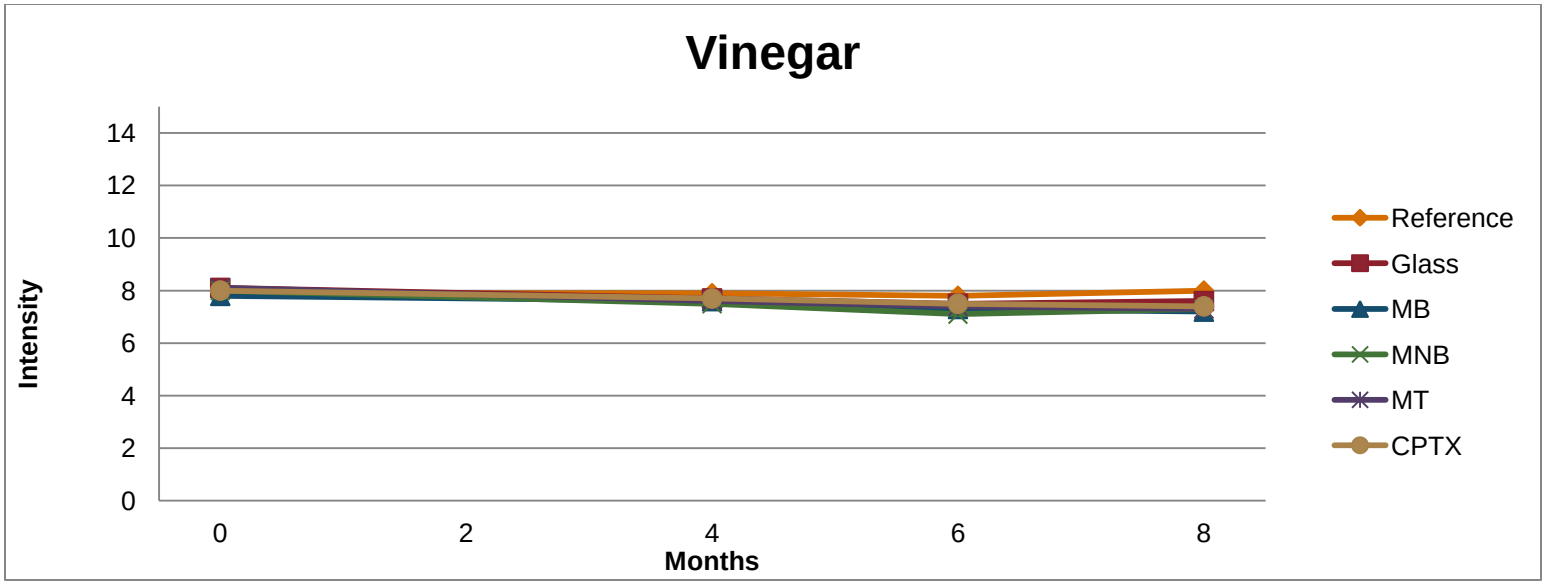

Figure 28: Difference in the intensity for the attribute "vinegar" of fresh pack dill chips stored in glass and pasteurizable plastic containers at 0, 4, 6 and 8 months.

(Reference = glass stored at 5^{o}C, Glass = glass stored at 30^{o}C, MB = monolayer polyethylene terephthalate with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C, MNB = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C, MT = monolayer polyethylene terephthalate with a lid without an oxygen barrier liner (OptiSeal™) stored at 30^{o}C and added turmeric, and CPTX =CPTX-312 plastic container with an oxygen barrier lined lid (Fresh Seal II™) stored at 30^{o}C.)

Least Significant Difference (LSD = 0.4)

CHAPTER 3: VOLATILE ANALYSIS OF FRESH PACK DILL CHIPS IN PLASTIC AND GLASS CONTAINERS USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY WITH TIME-OF-FLIGHT MASS SPECTROMETRY

3.1 Abstract

Innovation is a process that creates and delivers additional value in the marketplace. Consumers identify products by both the packaging and the quality of the food product they contain. The selection of proper packaging materials that are compatible with pickled products while maintaining quality during processing and storage is critical to proposing a change from traditional glass containers to plastic packaging. Solid-phase microextraction (SPME) coupled with two-dimensional gas chromatography time-of-flight mass spectrometry (GC x GC ToFMS) was used to evaluate differences among fresh pack pickles processed and stored in traditional glass jars compared to three polyethylene tererphthalate (PET) packages. Volatile analysis of samples after six months of storage revealed over 500 peaks using GC x GC ToFMS. Of these, 81 compounds were found to be significantly different among treatments due to packaging ($P < 0.001$). Hierarchial clustering analysis heat maps separated these compounds into four distinct groups for comparison: 24 compounds higher in CPTX-312, 12 compounds higher in monolayer PET, 32 compounds higher in glass and 13 compounds lower in CPTX-312. Identification of these components and consideration of classes of compounds helped facilitate comparisons of the treatments. Oxidation and scalping were considered to be the most probable causes for the differences in volatile components detected and the differences in perception of key attributes among treatments. The volatile compound data and sensory analysis data combined indicate that dill chips packed in monolayer PET with a barrier lid are more comparable to product packed in glass than other

packaging variations in this study.

3.2 Introduction

It is interesting to note that even though it has been reported that eighty percent of the food products we consume have come in contact with polymeric packaging (Ackerman et al., 2009) there are no commercially available pasteurized fresh pack pickles in plastic containers. Fresh pack product is subjected to high temperatures during processing. Storage in glass jars after processing results in a shelf life of at least 18 months. High temperature processing and an expectation of a long shelf life present a challenge to produce this product in plastic packaging. To determine if conversion to plastic packaging is feasible, this project was designed to compare the changes that take place in fresh pack dill chips preserved in glass jars to changes that occur in pasteurizeable plastic containers based upon sensory and chemical analysis.

The role of a sensory evaluation is to provide critical data about the acceptability of a food product, to understand how to target consumers and identify and quantify the intensity of important product attributes. The overall flavor profile of a food is determined by volatile and non-volatile components. The human nose has enormous discriminatory power and allows individuals to detect thousands of different aromas often with 10- or 100-fold more sensitivity than the best laboratory equipment (Meilgaard et al., 2007). Using this capability, human subjects can score products for their desirability in the case of a consumer panel or score the intensity

of product attributes with a trained sensory panel. However, detection, identification and determination of differences in the concentrations of the combinations of chemical compounds that may contribute to the flavor of a food require the use of instrumental analysis in combination with the appropriate sensory techniques.

As consumers look for better taste of packaged foods, the food industry will continue to develop new packaging options to meet the needs. Interactions between aroma compounds and packaging can result in dynamic and time-dependent changes in food quality during shelf life. Berry Plastics, Crown Cork & Seal, Amcor and Graham Packaging are just a few of the companies that have been investigating plastic packaging for pasteurized pickle products. Their expertise in development of superior packaging for fruit juice, wine and aseptic foods it is hoped will result in suitable packaging for the pickle industry.

There are several ingredients that give dill pickles their distinct flavor profile. Garlic (*Allium sativum L*.) oil is one ingredient that is often added. The intensity of the garlic is directly related to its volatile components. Changes in flavor intensity can occur quickly with this oil due to the instability of compounds responsible for garlic flavor (Ma et al., 2011). In addition to garlic oil, dill oil is also commonly added to flavor fresh pack dill pickles. Anethofuran, α-phellandrene, limonene and carvone are often found in pure dill oil. The amounts of each constituent differs based on the growing area of the dill plants (Ahmad et al., 1990) and the amount of leaves, stems and seeds used in the processing of the oil (Rădulescu et al, 2010).

The characterization of complex volatile profiles requires the use of powerful

separation techniques. Barley coffee (Bianchi et al., 2007) essential oils (Babushok and Zenkevich, 2009), and “green leaf odor” (Ruther 2000) are examples of products recently studied by scientists in the Netherlands, Russia and Germany respectively to better understand individual components. The information from their work can be used as building blocks for others interested in optimizing extraction techniques and conditions. Their data also provides complimentary information such as retention index values to be used as comparisons in future food analysis studies (Bianchi et al., 2007).

In complex food systems that are susceptible to subtle changes in flavor a discovery-based approach can be enlightening. Advanced spectrometry equipment and procedures provides a powerful way to separate complex mixtures and allow the detection of differences in an array of compounds. Using non-targeted profiling can lead to the discovery of previously misunderstood or unknown relationships among compounds that affect the perception of the end product.

Zhou and McFeeters (1998) identified volatile components in fermented cucumbers using a purge and trap sampler in combination with gas-chromatography mass spectrometry (GC-MS). They accounted for over 100 peaks and 37 identifiable compounds. Marsili and Miller (2000) were the first to publish data identifying key odor chemicals in fermented cucumber brines using solid-phase micro-extraction (SPME) with GC-olfactory experiments as well as GC-MS analysis.

In recent years, research at North Carolina State University that related the sensory scores for the intensity of oxidized odors in fermented pickles to actual

compounds (Zhou et al., 2000, Cleary and McFeeters, 2006) has proved useful to the pickle industry. In addition, Johanningsmeier and McFeeters (2011) have developed a non-targeted comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry method to detect volatiles from fermented and fresh pack pickles.

The objective of this investigation was to use SPME in combination with GC x GC ToFMS to detect the volatile compounds in the various packaging treatments and then make comparisons between the analytical results and the data collected from the sensory panels.

3.3 Materials and Methods

3.3.1 Sample Preparation

Two-dimensional gas chromatography time-of-flight mass spectrometry analysis of volatile compounds was conducted using a modified version of procedures developed by Johanningsmeier and McFeeters (2011). Samples from the various treatments were stored at -80^{o} C until analysis. Samples included six replicates of each of the six treatments stored for six months.

Screw-cap (10 ml) headspace vials (Microliter Analytical Supplies, Inc., Suwannee, Ga., U.S.A.) were prepared by adding 0.40 grams of sodium chloride to each. This is a common practice to increase the concentration of volatile compounds in the headspace.

Frozen samples were thawed and then diluted (1 part sample: 9 parts deionized water) immediately before preparation for analysis. This dilution in previous trials was shown to minimize column overloading. 100 µl of the sample was added to the vial, as well as 886 µl of deionized water, 4 µl of 3N H_2SO_4, and 10 µl of internal standard. The internal standard was 100 ppm deuterated hexanoic acid (ISOTEC™, Miamisburg, Ohio, CAS# 953-48-44-0). It was added to the vials to check the reproducibility of the analysis.

Samples to be analyzed were randomized by PROC PLAN (version 9.1.3 SAS® software, SAS Institute, Cary, NC) and placed in this order in the refrigerated tray (2^oC). Auto-sampling was performed using a CombiPal auto sampler (Model CTC Analytics, LEAP Technologies, Carrboro, NC). A sample was moved to the heater/shaker on the auto-sampler and heated to 40^o C while shaking for 15 minutes with 500 rpm of agitation (5s on and 2s off) prior to extraction.

Volatile compounds were collected by insertion of a 1 cm, 50/30 µm DVB/Carboxen™/PDMS StableFlex SPME fiber (Supelco, Bellefonte, PA) into the headspace above the sample for 30 min at 40^o C with 100 rpm agitation (5 sec on and 2 sec off). Extracted volatile compounds were desorbed from the SPME fiber in the GC inlet at 250^o C for 30 min. A blank sample (996 µl of deionized water and 4 µl of 3N H_2SO_4) was run between each sample to reduce carryover of compounds on the SPME fiber.

A LECO® Pegasus III® time-of-flight mass spectrometer (ToFMS) instrument (Model # 614-100-700, LECO Corporation, St. Joseph, MI) was connected to an

Agilent GC (Model# 6890N, Agilent Technologies, Santa Clara, CA) fitted with a secondary oven and cryogenic modulator. The two-dimensional separation was achieved using a SolGel-Wax™, 28.15 m x 0.25 mm ID x 0.25 µm film thickness (SGE, Austin, TX), polyethylene glycol 1^{rst} dimension column in the primary oven and an RTX 17-01, 0.9 m x 0.1 mm ID x 0.1 µm film thickness (Restek, Bellefonte, PA), 14% cyanopropyphenyl – 86% dimethyl polysiloxane 2nd dimension column in the secondary oven.

A 0.75-mm-ID-Siltek deactivated SPME liner (Restek, Bellefonte, PA) was used in the inlet. Columns were conditioned according to manufacturer recommendations prior to use. The inlet temperature was set at 250^{o} C and operated in a pulsed spit less mode with a pulse pressure of 37 psi for 1 minute. The split vent was opened 2 minutes following injection, and the GC was operated in constant flow mode with 1.3 ml/min helium gas. The primary oven temperature was maintained at 40^{o} C for 2 min and then increased at 3^{o} C/min to 140^{o} C. The temperature ramp was increase to 10^{o} C/min to 250^{o} C and the temperature was held at 250^{o} C for 3 minutes.

The secondary oven followed the same temperature program except the temperature was maintained at 10^{o} C higher than the main oven until reaching a maximum temperature of 250^{o} C. The transfer temperature was also maintained at 250^{o} C. The modulator offset was +30^{o} C with a 2.75 sec 2nd dimension separation time and 0.80 sec hot pulse. Compressed air (30 psi) was used for the hot pulses, and liquid nitrogen-cooled nitrogen gas (18 psi) was used for the cold pulses. The

mass spectrometer was operated with -70 eV and an ion source temperature of 200^{o} C. The detector voltage was set at 1600 V and massed 26-500 were collected at 200 spectra per second. No solvent delay was employed.

3.3.2 Data Analysis

ChromaTOF® software (version 4.33, LECO Corporation, St. Joseph, Michigan) data processing methods were used to detect and quantify peaks based on unique masses as determined by the deconvolution algorithm. Chemical names were assigned to peaks that had a minimal mass spectral similarity ≥ 800 (1000 is an exact match). The NIST/EPA/NIH Mass Spectral Library (National Institute of Standards and Technology (NIST) Gaithersburg, Maryland, 2005). The unique mass (U) for each peak, as assigned by ChromaTOF® deconvolution algorithm, was used for peak area calculations. Table 6 shows the data processing parameters. Alignment of chromatograms was accomplished using StatCompare®.

ANOVA followed by hierarchial clustering of standardized LS means was accomplished using JMP Genomics version 4.1 (SAS Institute, Cary, NC). Significance was established at $P < 0.001$. The chromatograms for compounds from the heat maps originally contained 91 compounds. Manually reviewing the data reduced the number to 81 significantly different peaks. The ten compounds that were removed from the analysis were determined to be associated with column bleed or insufficient data points.

Peak tables from all samples were exported to Excel® 2007 (Microsoft Corp.,

Redmond, Wash., U.S.A.) for analysis. Peak area data were compared several ways: by making glass 100%, and relating the other treatments to these levels, by chemical formulas and structures.

3.4 Results and Discussion

Characterization of volatile compounds was performed to better understand the relationship between chemical changes taking place in the different packages compared to the sensory data. The volatile components in the different packaging treatments may have been affected by scalping, oxidation and permeation to different degrees. The ranking of acceptance scores by two independent consumer panels after seven months of storage (n=189) were as follows: glass > monolayer PET with high oxygen barrier lid > CPTX-312 > monolayer PET with low oxygen barrier lid ($P < 0.05$) (Chapter 2, section 2.4.1). Descriptive analysis panel scaling revealed significantly different scores for the key attributes: off, oxidized and fresh, between the glass and plastic packaging at four and six months. The data from both sensory panels indicates that there were differences in the chemical changes that occurred among the different packaging treatments that humans could detect.

Two-dimensional gas chromatography time-of-flight mass spectrometry detected over 500 peaks among the four treatments that were analyzed in this study at S/N > 250. Analysis of variance (ANOVA) and hierarchial cluster analysis (HCA) identified 81 peaks that were significantly different among treatments ($P < 0.001$). The compounds represented by these peaks were separated into four distinct

categories based on the HCA heat map (Appendix 14):

1. Red: Higher in CPTX
2. Blue: Higher in monolayer PET
3. Green: Higher in glass
4. Orange: Lower in CPTX

Tables 7-10 contain lists of compounds found to be significantly different ($P < 0.001$) among the treatments for each one of these categories. Tables 12-15 show the compounds separated into the same four same categories, but these tables include percentage peak area as compared to glass and the chemical class for each compound. This was done to make comparisons easier as literature stated that the polarity, chain length, chain branching and hydophobicity of the food material helped determine how easily it was attracted to the plastic (Dury-Brun et al., 2007, Ducruet et al., 2007, Sajilata et al., 2007). A comparison of treatments by the number of compounds in each class and chemical group, as well as the number of carbon atoms in each compound is included (Table 11).

Interestingly, there were 24 compounds that were significantly higher in CPTX-312 than any of the other packages. CPTX-312 is a multilayer package consisting of a layer of nylon containing cobalt between two layers of monolayer PET. The group of compounds that was found to be significantly higher in the CPTX-312 eluted sooner on the column than did the compounds that were higher in glass. The retention indices for the compounds higher in CPTX-312 ranged from 640 to 1350 (Table 7) while glass ranged from 942 to 2154 (Table 9). The unique

mass assigned to the compounds for CPTX-312 ranged from 33 to 98 and averaged 54 (Table 7) while in glass the range was 45 to 121 and averaged 74 (Table 9). Patel (1992) proposed that the cobalt added to the CPTX-312 works predominantly as a catalyst for free radical reactions that use oxygen. The lower average molecular weights of identified components in the CPTX-312 packaged fresh pack cucumbers may be the result of free radical degradation products of components from the package or the product. Of particular note is the fact that a number of ketones and alcohols were at much higher concentrations in the CPTX-312 than in the glass at 30^{o} C or in the monolayer PET jars with either low or high oxygen barrier lids.

The group of compounds lower in CPTX (Tables 10 and15) relative to the other treatments contained twelve compounds, but only four were assigned CAS Registry numbers. Of special interest to this study are nonanol and 2,6-nonadien-1-ol. These compounds are both alcohols possibly produced as a result of reduction reactions involving (*E,Z*) -2-6-nonadienal and (*E)*-2-nonenal. The aldehydes (*E,Z*) -2-6-nonadienal and (*E)*-2-nonenal are the major flavor impact components responsible for fresh cucumber flavor (Palma-Harris et al., 2001).

Of the 13 volatile compounds found to be higher in the monolayer PET than in the glass, 12 of the compounds were higher in the dill chips in the monolayer PET with the low oxygen barrier lid as compared to the dill chips stored in the monolayer PET with the high barrier lid (Table 13). There was speculation that the lid barrier properties might be as critical to the inherent quality of the product as the bottle

itself. There were significant differences in the liking by consumers between the two monolayer PET packages. The product packed in containers with high barrier lids performed significantly better (Chapter 2, section 2.4.1). Seven of the nine compounds higher in monolayer PET that were identifiable through the CAS Registry were hydrocarbons containing oxygen. The other two were a benzene derivative and a short chain chloroalkane.

Dill chips were specifically chosen for this study because of the subtle tastes imparted by the essential oils in the flavor emulsions added to this item. Several of the components of the dill and garlic oils including D-limonene, limonene, α-phellandrene, dimethyl sulfide and L-fenchone that were found to be significantly higher in glass containers ($P > 0.001$) than all of the plastic packages. These results show that these compounds are lost to a greater extent during processing and storage in plastic containers than in glass. In the case of each of these compounds, the relationship of the concentrations was monolayer PET with high oxygen barrier lid > monolayer PET with low oxygen barrier lid > CPTX-312 (Table 14). This relationship is similar to the ranking of the consumer panel liking scores (Table 5).

Twenty four of the 32 compounds higher in glass were found in the CAS Registry (Table 9). Six of the compounds contained only hydrogen and carbon, four of which were benzene derivatives. Fifteen had oxygen containing groups attached to the hydrocarbon and most contained ten carbons. Ayhan et al. (2001) in their packaging study of the effects of plastic packaging on flavor, vitamins and color compounds in orange juice noted a loss of primary aldehydes which they explained

by the absorption of flavor compounds into the packaging material, the acceleration of flavor degradation due to the initial oxygen concentrations and the transmission through the package. They noted that the absorption and degradation of flavor compounds was affected by storage temperatures. In this study product stored in glass at 30^{o} C was considered the control and product stored in glass at 5^{o} C was considered the reference. The glass wall of the container represents an inert barrier to the outside environment affected only by temperature and light.

Berlinet et al. (2005) found that through time many of the changes in aroma compounds in orange juice could be explained by acid catalyzed reactions irrespective of the package. They measured losses of 50% of such compounds as hexanal, octenal and nonanal and increases in various alcohols. In this study, the alcohols represented the largest group of chemicals that were significantly different among the treatments (Table 11). It can be noted that the alcohols present at higher levels in the glass were higher molecular weight compounds as compared to the plastic packaging.

3.5 Conclusions

Differences in the perception of dill chips among the various treatments were related to chemical and physical changes that took place. Both sensory and two-dimensional gas chromatography time-of-flight mass spectrometry testing were performed on the samples to help explain the changes through time. Volatile analysis data for fresh pack pickles in pasteurizable plastic and glass containers

after six months of storage revealed 81 compounds that could be divided into four distinct categories based on packaging types.

Fresh pack dill chips were chosen specifically for this study as this item was thought to be more sensitive than other commercially pickled items to the potential effects of plastic packaging. Inherent chemical reactions of the food matrix itself, storage temperatures, the flavor components added to make the products and the packaging material used to make the bottles and the lids are all critical to the quality of the end product.

Dill chips in CPTX-312 (considered a premium package for some food items) did not perform as well as monolayer PET or glass in the consumer evaluations after seven months of storage. 24 compounds were significantly higher and 12 compounds were revealed to be significantly lower in the CPTX-312 than the other treatments after six months of storage ($P < 0.001$).

There were significant differences in the consumer acceptability of the monolayer PET packages with either OptiSeal™ or Fresh Seal II™ lids ($P < 0.05$). OptiSeal™ does not offer as much protection against oxygen ingress and this proved to be a disadvantage to overall consumer liking. The volatile compounds revealed to be higher in glass that were related to the dill and garlic flavor added in the cover solution were in many cases lower in the samples from the PET containers with the OptiSeal™ lids as compared to the Fresh Seal II™ lids.

There were 32 compounds that were found to be significantly higher in the glass than any of the plastic packaging treatments. These compounds in many

cases are recognized to be important flavor components and are thought to contribute to scalping and oxidation issues in other food-plastic packaging relationships. The changes in the volatile components when taken collectively for the dill pickle chip samples represent a noticeable and consistent pattern that follows what was observed with the consumer and descriptive sensory analysis testing.

Table 6. Data processing parameters for GC x GC ToFMS analysis.

Data Step	Parameter*	Setpoint
Peak detection	Baseline offset	0.8
	Number of points for smoothing	Auto
	Peak width	0.1 sec
	Signal to noise (S/N)	250
	Number of apexing masses	2
GC x GC parameters	Match required to combine	600
	Overide (early and late)	0.05 sec
Quantification	Mass to use for area/height calculation	U (unique mass)
	Library selected	NIST (2005)
Analyte match criteria	Mass threshold	10
	Minimum similarity	600
	Maximum number of modulation periods apart	1
	Maximum retention time difference	4 sec
Searching for peaks not found by initial peak finding	Signal to noise ratio	20
Define analytes	Minimum number of samples that contain the analyte	5
	Minimum percent of samples in the class that contains analyte	66%

Table 7. Identification of compounds higher in CPTX containers.

Name	CAS[1] Registry Number	Method of Identification[2]	Similarity	RI[3]	tr_1	tr_2	Mass[4]
Unknown 20	n/a	MS	n/a	640	165.83	0.509	64
Butane, 2-chloro-	78-86-4	MS	856	766	190.00	0.665	56
Unknown 81	n/a	MS	n/a	912	275.34	0.704	33
Butyl methyl ketone	75-97-8	MS	806	942	309.80	0.915	57
Hexane, 2,2-dimethyl-	590-73-8	MS	880	958	327.44	3.110	57
Diisopropyl ketone	565-80-0	MS	881	995	369.93	1.148	43
Heptane, 2,2-dimethyl-	3074-71-3	MS	784	1000	374.60	2.344	57
Acetonitrile	75-05-8	MS	954	1000	377.82	0.609	41
Butyl methyl ketone	565-61-7	MS	888	1011	394.87	1.012	43
Methyl neopentyl ketone	590-50-1	MS	834	1014	401.82	1.092	43
Pentane, 2,2,3,3-tetramethyl-	7154-79-2	MS	925	1016	402.37	2.437	57
Ethoxyacetic acid	623-53-0	MS	882	1042	447.50	0.819	45
Ethyl propyl ketone	589-38-8	MS	890	1045	452.37	1.080	57
Isobutyl alcohol	78-83-1	MS	912	1096	538.85	0.706	41

Table 7. Continued

Diatol	105-58-8	MS	882	1104	552.37	0.962	45
Propanol	590-36-3	MS	853	1106	557.03	0.854	59
2-Pentanol	6032-29-7	MS	n/a	1121	592.37	0.783	45
3-Hexen-2-one	763-93-9	MS	813	1128	605.59	1.000	98
Isoamyl methyl ketone	110-12-3	MS	888	1136	625.07	1.229	43
3-Pentanol, 2-methyl-	565-67-3	MS	853	1153	666.84	0.888	59
Unknown 200	n/a	MS	n/a	1161	682.01	1.093	56
2-Hexanol, (R)-	26549-24-6	MS	816	1217	813.42	0.881	45
Hexanenitrile	628-73-9	MS	784	1289	988.45	1.096	54
Allyl Isothiocyanate	57-06-7	MS	872	1350	1144.32	0.919	99

[1]Chemical Abstracts Service registry number

[2]MS: identification based on mass spectral match to NIST 2005 library, RI: comparison with published retention indices on polyethylene glycol column phase.

[3]Retention indices based on first dimension retention of components on a SOL-GEL-WAX (polyethylene glycol) column using SPME GC x GC-ToFMS

[4]Mass selected by ChromaTOF® software during automated data processing to represent and interference free mass for each analyte; the unique mass for each component was used for calculation of peak areas.

Table 8. Identification of compounds higher in PET containers.

Name	CAS[1] Registry Number	Method of Identification[2]	Similarity	RI[3]	tr_1	tr_2	Mass[4]
Ethyl Chloride	75-00-3	MS	933	653	168.00	0.517	64
1-Penten-3-ol	616-25-1	MS	902	1156	671.97	0.736	57
2-Penten-1-ol, (Z)-	1576-95-0	MS	922	1313	1049.93	0.769	57
2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	n/a	MS	866	1382	1218.07	1.390	91
Isophorone	78-59-1	MS	n/a	1388	1235.71	1.351	82
p-Cymene	1195-32-0	MS, RI	950	1424	1325.26	1.228	117
2,4-Heptadienal, (E,E)-	5910-85-0	MS	874	1485	1473.61	1.051	81
Benzaldehyde	100-52-7	MS, RI	978	1508	1529.53	0.902	77
Crypton	500-02-7	MS	881	1650	1858.26	1.261	96
Unknown 405	n/a	MS	n/a	1654	1869.78	1.103	92
Ocimenol	5986-38-9	MS	811	1673	1911.32	1.019	93
Unknown 463	n/a	MS	n/a	1813	2202.50	0.905	105
4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)but-3-en-2-one	n/a	MS	885	1986	2412.88	0.745	43

Table 8. continued

[1]Chemical Abstracts Service registry number

[2]MS: identification based on mass spectral match to NIST 2005 library, RI: comparison with published retention indices on polyethylene glycol column phase.

[3]Retention indices based on first dimension retention of components on a SOL-GEL-WAX (polyethylene glycol) column using SPME GC x GC-ToFMS

[4]Mass selected by ChromaTOF® software during automated data processing to represent and interference free mass for each analyte; the unique mass for each component was used for calculation of peak areas

Table 9. Identification of compounds higher in glass containers.

Name	CAS[1] Registry Number	Method of Identification[2]	Similarity	RI[3]	tr_1	tr_2	Mass[4]
Dimethyl sulfide	75-18-3	MS	942	703	178.75	0.567	47
Unknown 26	n/a	MS	n/a	715	178.50	0.556	76
Pentane, 1-chloro-	543-59-9	MS	837	933	299.93	0.956	55
Unknown 101	n/a	MS	n/a	944	312.22	0.937	79
Crotonaldehyde	4170-30-3	MS	938	1036	438.92	0.777	70
Camphene	79-92-5	MS	872	1053	464.73	1.588	93
1-Propene, 3,3'-thiobis-	592-88-1	MS	875	1136	625.52	1.080	45
à-Phellandrene	99-83-2	MS, RI	861	1151	658.82	1.646	93
D-Limonene	5989-27-5	MS, RI	898	1185	737.05	1.657	68
Limonene	138-86-3	MS, RI	868	1192	752.94	1.610	68
á-Phellandrene	99-83-2	MS, RI	880	1194	757.22	1.666	93
Phenol, 4-ethyl-	123-07-9	MS	766	1211	798.86	1.124	107
1,7-Octadiene, 3,6-dimethylene-	n/a	MS	773	1265	930.68	1.339	79
Vinyl amyl ketone	4312-99-6	MS, RI	888	1294	1002.29	1.277	55
2-Heptenal, (Z)-	543-49-7	MS, RI	928	1316	1055.69	1.221	55

Table 9. Continued

Unknown 261	n/a	MS	n/a	1317	1059.05	1.183	59
6-Methylheptane-1,6-diol	n/a	MS	776	1363	1172.43	1.186	59
L-Fenchone	7787-20-4	MS	872	1380	1216.88	1.532	81
2-Hexen-1-ol, (E)-	928-95-0	MS	915	1398	1262.43	0.827	57
2-Octenal, (E)-	2548-87-0	MS	864	1420	1315.28	1.314	70
3-Furaldehyde	498-60-2	MS	912	1452	1395.07	0.780	96
α- Fenchyl alcohol	512-13-0	MS	921	1571	1677.43	1.099	81
Terpinen-4-ol	562-74-3	MS	880	1589	1719.93	1.182	71
Unknown 378	n/a	MS	n/a	1595	1735.21	1.308	93
Unknown 387	n/a	MS	n/a	1606	1760.17	1.231	68
Beta-terpineol	138-87-4	MS	828	1619	1789.79	1.075	71
2-Decenal, (Z)-	3913-71-1	MS	907	1634	1821.81	1.443	41
Benzene, 1-methoxy-2-(1-methylethenyl)-	10278-02-1	MS	867	1657	1874.93	1.162	105
Unknown 418	n/a	MS	n/a	1690	1950.50	1.018	121

Table 9. Continued

1-Undecanol	112-42-5	MS	919	1962	2387.44	0.721	55
Thymol	89-83-8	MS	864	2125	2554.93	0.599	135
Sabinene	3387-41-5	MS	n/a	2154	2585.00	0.713	93

[1]Chemical Abstracts Service registry number

[2]MS: identification based on mass spectral match to NIST 2005 library, RI: comparison with published retention indices on polyethylene glycol column phase.

[3]Retention indices based on first dimension retention of components on a SOL-GEL-WAX (polyethylene glycol) column using SPME GC x GC-ToFMS

[4]Mass selected by ChromaTOF® software during automated data processing to represent and interference free mass for each analyte; the unique mass for each component was used for calculation of peak areas

Table 10. Identification of compounds lower in CPTX containers.

Name	CAS[1] Registry Number	Method of Identification[2]	Similarity	RI[3]	tr_1	tr_2	Mass[4]
Unknown 106	n/a	MS	n/a	964	335.70	0.739	46
Bicyclo[3.2.1]oct-2-ene, 3-methyl-4-methylene-	n/a	MS	828	1235	858.68	1.465	91
Unknown 292	n/a	MS	n/a	1411	1292.59	1.464	43
1-Octen-3-ol	3391-86-4	MS, RI	909	1444	1374.93	0.955	57
4-Acetyl-1-methylcyclohexene	n/a	MS	870	1538	1599.72	1.237	43
Unknown 370	n/a	MS	n/a	1574	1682.50	1.245	93
Tricyclo[3.2.1.0(1,5)]octane	n/a	MS	801	1580	1701.43	1.234	93
2-Octen-1-ol, (Z)-	n/a	MS	870	1606	1760.00	0.929	57
Methyl benzoate	93-58-3	MS	911	1606	1758.89	0.986	105
1-Nonanol	28473-21-4	MS	830	1655	1868.50	1.043	56
Unknown 441	n/a	MS	n/a	1723	2021.70	1.129	81
2,6-Nonadien-1-ol	7786-44-9	MS	848	1758	2096.04	0.790	41

[1]Chemical Abstracts Service registry number

Table 10 continued.

[2]MS: identification based on mass spectral match to NIST 2005 library, RI: comparison with published retention indices on polyethylene glycol column phase.

[3]Retention indices based on first dimension retention of components on a SOL-GEL-WAX (polyethylene glycol) column using SPME GC x GC-ToFMS

[4]Mass selected by ChromaTOF® software during automated data processing to represent and interference free mass for each analyte; the unique mass for each component was used for calculation of peak areas

Table 11. Comparison of treatments by the number of compounds in each chemical class and group.

Chemical Class	Group	High Glass	High CPTX	Low CPTX	High PET
Hydrocarbons	Alkane	1 (10[1])	3 (8,9,9)		
	Alkene	1 (10)			
	Benzene derivative	4 (10,10,10,10)			1 (10)
Groups containing oxygen	Alcohol	7 (6,8,10,10,10,10,11)	5 (4,5,6,6,6)	3 (8,9,9)	3(5,5,10)
	Ketone	3 (8,10,10)	7 (6,6,6,6,7,7,7)		2 (9,9)
	Aldehyde	5 (4,7,8,8,10)			2 (7,7)
	Carboxylic acid		2 (5,9)	1 (8)	
Groups containing nitrogen	Nitrile		2 (2,6)		
Groups containing chlorine	Chloroalkane	1 (5)	1 (4)		1 (2)
Groups containing sulfur	Thiocyanide	2 (2,6)	1 (4)		

[1]The number of carbon atoms in the compound

Table 12. Comparison of compounds higher in CPTX containers.

Name	CAS Registry Number	Peak Areas Relative to Glass (%) CPTX	G30	MB	MNB	Formula	Chemical Class
Unknown 20	n/a	520	100	0	239	n/a	
Butane, 2-chloro-	78-86-4	824	100	199	318	C_4H_9Cl	Chloroalkane
Unknown 81	n/a	170	100	31	52	n/a	
Butyl methyl ketone	75-97-8	707	100	102	112	$C_6H_{12}O$	Ketone
Hexane, 2,2-dimethyl-	590-73-8	142	100	90	124	C_8H_{18}	Alkane
Diisopropyl ketone	565-80-0	1121	100	179	228	$C_7H_{14}O$	Ketone
Heptane, 2,2-dimethyl-	3074-71-3	152	100	92	146	C_9H_{2O}	Alkane
Acetonitrile	75-05-8	735	100	214	207	C_2H_3N	Nitrile
Butyl methyl ketone	565-61-7	1115	100	211	274	$C_6H_{12}O$	Ketone
Methyl neopentyl ketone	590-50-1	963	100	106	92	$C_7H_{14}O$	Ketone
Pentane, 2,2,3,3-tetramethyl-	7154-79-2	188	100	80	174	C_9H_{2O}	Alkane
Ethoxyacetic acid	623-53-0	581	100	208	190	C_9H_2O	Carboxylic acid
Ethyl propyl ketone	589-38-8	533	100	163	167	$C_6H_{12}O$	Ketone
Isobutyl alcohol	78-83-1	332	100	140	157	$C_4H_{10}O$	Alcohol
Diatol	105-58-8	905	100	229	247	$C_5H_{10}O_3$	Carboxylic acid
Propanol	590-36-3	235	100	94	113	$C_6H_{14}O$	Alcohol
2-Pentanol	6032-29-7	724	100	161	146	$C_5H_{12}O$	Alcohol
3-Hexen-2-one	763-93-9	333	100	182	203	$C_6H_{10}O$	Ketone
Isoamyl methyl ketone	110-12-3	919	100	288	311	$C_7H_{14}O$	Ketone
3-Pentanol, 2-methyl-	565-67-3	2082	100	379	497	$C_6H_{14}O$	Alcohol
Unknown 200	n/a	1186	100	192	183	n/a	
2-Hexanol, (R)-	26549-24-6	867	100	287	260	$C_6H_{14}O$	Alcohol
Hexanenitrile	628-73-9	1546	100	401	211	$C_6H_{11}N$	Nitrile
Allyl Isothiocyanate	57-06-7	671	100	265	413	C_4H_5NS	Thiocyanate

Table 13. Comparison of compounds higher in PET containers.

Name	CAS Registry Number	Peak Areas Relative to Glass (%)				Formula	Chemical Class
		CPTX	G30	MB	MNB		
Ethyl Chloride	75-00-3	456	100	392	401	C_2H_5Cl	Chloroalkane
1-Penten-3-ol	616-25-1	409	100	456	631	$C_5H_{10}O$	Alcohol
2-Penten-1-ol, (Z)-	1576-95-0	103	100	859	879	$C_5H_{10}O$	Alcohol
2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	n/a	69	100	234	337	n/a	
Isophorone	78-59-1	195	100	481	565	$C_9H_{14}O$	Ketone
p-Cymene	1195-32-0	131	100	271	305	$C_{10}H_{12}$	Benzene derivative
2,4-Heptadienal, (E,E)-	5910-85-0	165	100	329	283	$C_7H_{10}O$	Aldehyde
Benzaldehyde	100-52-7	146	100	336	413	C_7H_6O	Aldehyde
Crypton	500-02-7	134	100	241	276	$C_9H_{14}O$	Ketone
Unknown 405	n/a	112	100	183	391	n/a	
Ocimenol	5986-38-9	184	100	171	195	$C_{10}H_{18}O$	Alcohol
Unknown 463	n/a	307	100	405	844	n/a	
4-(2,6,6-Trimethylcyclohexa-	n/a	433	100	643	942	n/a	

Table 14. Comparison of compounds higher in glass containers.

Name	CAS Registry Number	Peak Areas Relative to Glass (%)				Formula	Chemical Class
		CPTX	G30	MB	MNB		
Dimethyl sulfide	75-18-3	12	100	48	28	C_2H_6S	Sulfide
Unknown 26	n/a	4	100	17	4	n/a	
Pentane, 1-chloro-	543-59-9	17	100	27	27	$C_5H_{11}Cl$	Chloroalkane
Unknown 101	n/a	56	100	54	50	n/a	
Crotanaldehyde	4170-30-3	19	100	43	39	C_4H_6O	Aldehyde
Camphene	79-92-5	29	100	41	36	$C_{10}H_{16}$	Alkene
1-Propene, 3,3'-thiobis-	592-88-1	25	100	70	5	$C_6H_{10}S$	Sulfide
à-Phellandrene	99-83-2	12	100	26	19	$C_{10}H_{16}$	Benzene derivative
D-Limonene	5989-27-5	22	100	52	41	$C_{10}H_{16}$	Benzene derivative
Limonene	138-86-3	25	100	41	36	$C_{10}H_{16}$	Benzene derivative
á-Phellandrene	99-83-2	5	100	15	8	$C_{10}H_{16}$	Benzene derivative
Phenol, 4-ethyl-	123-07-9	11	100	12	11	$C_8H_{10}O$	Alcohol
1,7-Octadiene, 3,6-dimethylene-	n/a	21	100	18	30	n/a	
Vinyl amyl ketone	4312-99-6	13	100	32	24	$C_8H_{14}O$	Ketone
2-Heptenal, (Z)-	543-49-7	15	100	38	33	$C_7H_{16}O$	Aldehyde
Unknown 261	n/a	26	100	51	52	n/a	
6-Methylheptane-1,6-diol	n/a	24	100	47	47	n/a	
L-Fenchone	7787-20-4	32	100	64	54	$C_{10}H_{16}O$	Ketone
2-Hexen-1-ol, (E)-	928-95-0	53	100	107	97	$C_6H_{12}O$	Alcohol

Table 14. Continued.

2-Octenal, (E)-	2548-87-0	8	100	25	21	$C_8H_{14}O$	Aldehyde
3-Furaldehyde	498-60-2	56	100	73	94	$C_8H_{14}O$	Aldehyde
α- Fenchyl alcohol	512-13-0	44	100	80	69	$C_{10}H_{18}O$	Alcohol
Terpinen-4-ol	562-74-3	10	100	57	46	$C_{10}H_{18}O$	Alcohol
Unknown 378	n/a	51	100	103	81	n/a	
Unknown 387	n/a	5	100	11	9	n/a	
Beta-terpineol	138-87-4	5	100	14	12	$C_{10}H_{18}O$	Alcohol
2-Decenal, (Z)-	3913-71-1	5	100	34	22	$C_{10}H_{18}O$	Aldehyde
Benzene, 1-methoxy-2-(1-methylethenyl)-	10278-02-1	45	100	87	86	$C_{10}H_{12}O$	Ketone
Unknown 418	n/a	3	100	118	111	n/a	
1-Undecanol	112-42-5	22	100	24	22	$C_{11}H_{24}O$	Alcohol
Thymol	89-83-8	38	100	49	44	$C_{10}H_{14}O$	Alcohol
Sabinene	3387-41-5	20	100	34	32	$C_{10}H_{16}$	Alkane

Table 15. Comparison of compounds lower in CPTX containers.

Name	CAS Registry Number	Peak Areas Relative to Glass (%) CPTX	G30	MB	MNB	Formula	Chemical Class
Unknown 106	n/a	11	100	66	71	n/a	
Bicyclo[3.2.1]oct-2-ene, 3-methyl-4-methylene-	n/a	16	100	39	39	n/a	
Unknown 292	n/a	24	100	62	39	n/a	
1-Octen-3-ol	3391-86-4	48	100	3	109	$C_8H_{16}O$	Alcohol
4-Acetyl-1-methylcyclohexene	n/a	30	100	72	107	n/a	
Unknown 370	n/a	30	100	86	88	n/a	
Tricyclo[3.2.1.0(1,5)]octane	n/a	37	100	94	88	n/a	
2-Octen-1-ol, (Z)-	n/a	16	100	75	79	n/a	
Methyl benzoate	93-58-3	48	100	178	133	$C_8H_8O_2$	Carboxylic Acid
1-Nonanol	28473-21-4	35	100	97	127	$C_9H_{20}O$	Alcohol
Unknown 441	n/a	0	100	123	0	n/a	
2,6-Nonadien-1-ol	7786-44-9	39	100	135	107	$C_9H_{16}O$	Alcohol

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CHAPTER 4: FUTURE STUDIES

The pickled vegetable industry has used glass jars exclusively for fresh pack products that require a thermal process. New markets and increasing consumer demands indicate the growing importance of research on the effects of different types of plastic packaging on fresh pack pickled products. A multidisciplinary approach was used in this project to discover the differences and similarities between glass and plastic packaging, as well as to better determine possible causes of any differences identified.

Dill chips were specifically chosen for this study. They are commercially the most important fresh pack item and were considered to be more sensitive to sensory changes due packing material and storage. It was thought the emulsions in the dill category would be more apt to oxidize and scalp in plastic containers than the flavorings for other products. Dill brines also have a lower viscosity and less sugar than the second most common type of fresh pack (bread & butter pickles).

Cut products were used to more readily assess any changes in overall appearance and cure. Also using chips made it easier to serve to panelists in the sensory evaluations. All products were produced similarly to what is traditionally done to prepare product when packing in glass jars. Unlike the glass jars that remained rigid, the plastic containers built up pressure, expanded and vented. When the plastic containers cooled they developed a vacuum that contributed to a rapidly cured appearance.

Flavoring issues were identified with the plastic containers by both the consumer and descriptive analysis sensory panels. The product with the greatest

plastic packaging challenges was selected in order to identify significant changes due to packaging and identify ways to adjust for any differences in product quality and other attributes. Once concerns are identified it should be possible to modify packaging and/or processing to ensure the desired outcomes. This suggests the need for future studies and work on other fresh pack items.

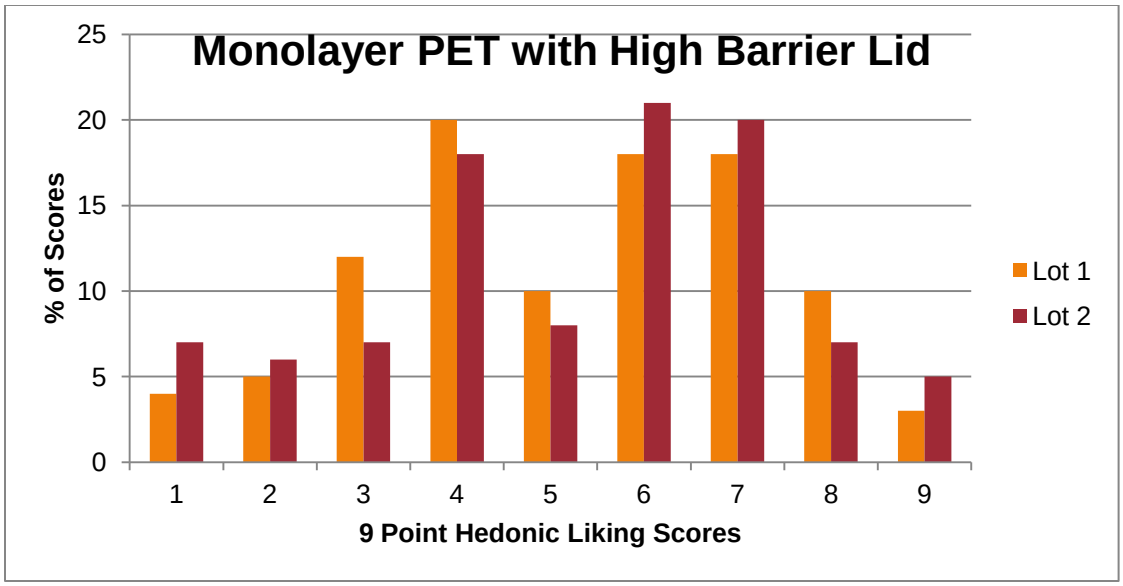
The major issues identified by this project were the rapid development of detectable oxidized flavor in product processed in plastic containers, more rapid increases in off-flavors in plastic, and development of cured appearance immediately after heat processing. The following types of questions indicate the types of data that once collected can be used to more successfully utilize plastic containers for pasteurized pickled vegetable products:

- In what ways can processing procedures be changed to minimize the development of vacuum in plastic containers? One example might be to close jars after the contents are heated rather than closing cold jars.
- What range of container sizes and shapes will be compatible with any modified processing procedures?
- Do the amounts or formulation of flavoring emulsions need to be modified to account for any scalping of flavor components by the plastic containers?
- Shelf-life evaluations at three or more storage temperatures would make it possible to do reasonable shelf life projections for real life product distribution conditions.

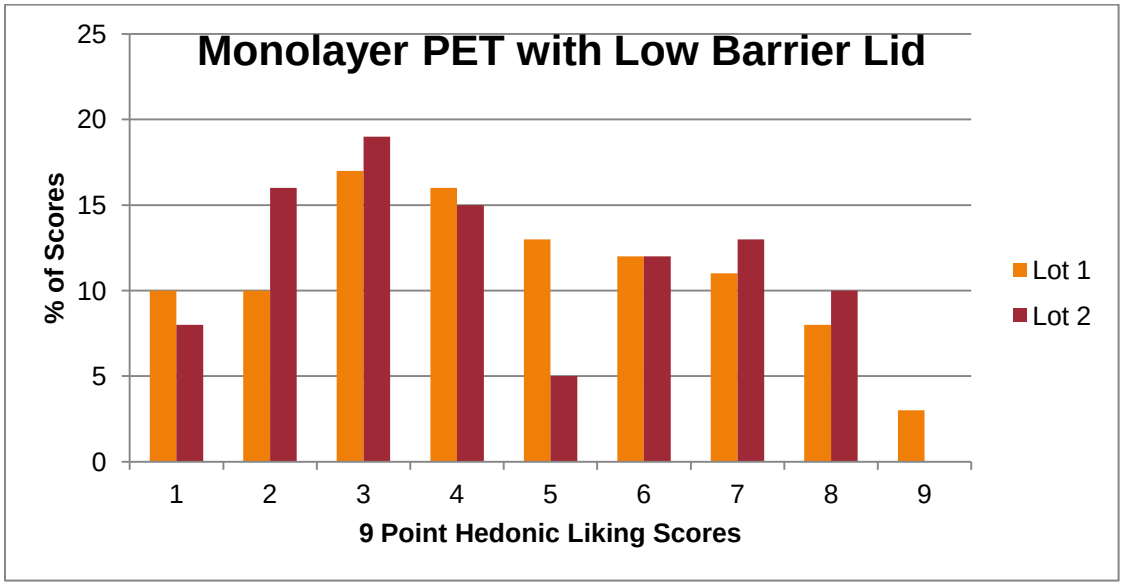
- If reasonable shelf life cannot be achieved with standard monolayer containers with a barrier lid, what other types of containers might be better suited to provide adequate product shelf life.

Pickles are considered by many to be a traditional food so changes in packaging that may work well for certain products may not benefit this category to the same extent. Future research will make the inevitable transition to plastic packaging for those that venture that direction a greater success.

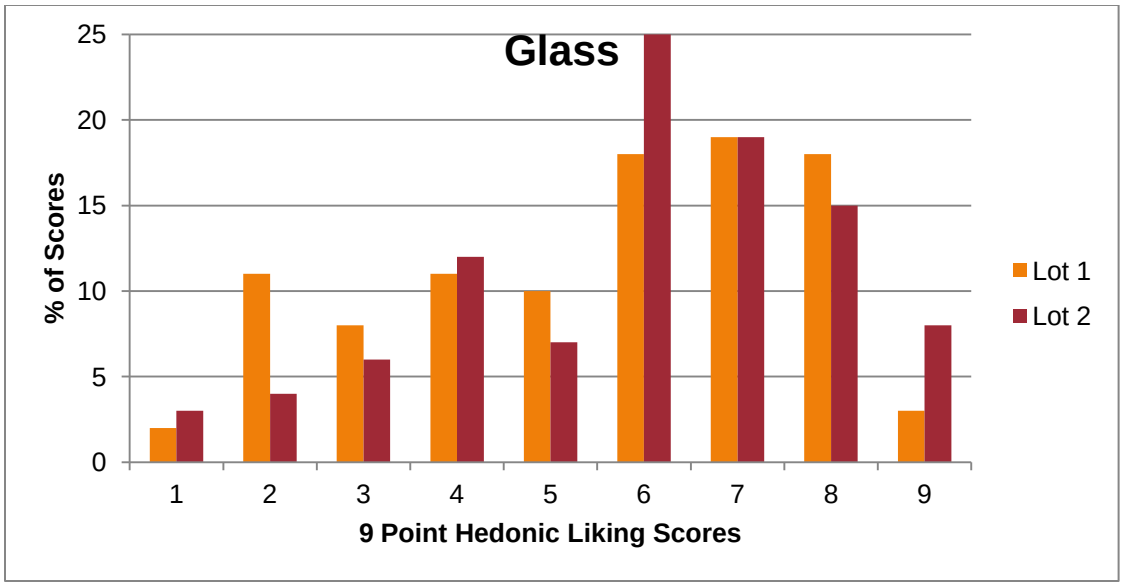
APPENDIX



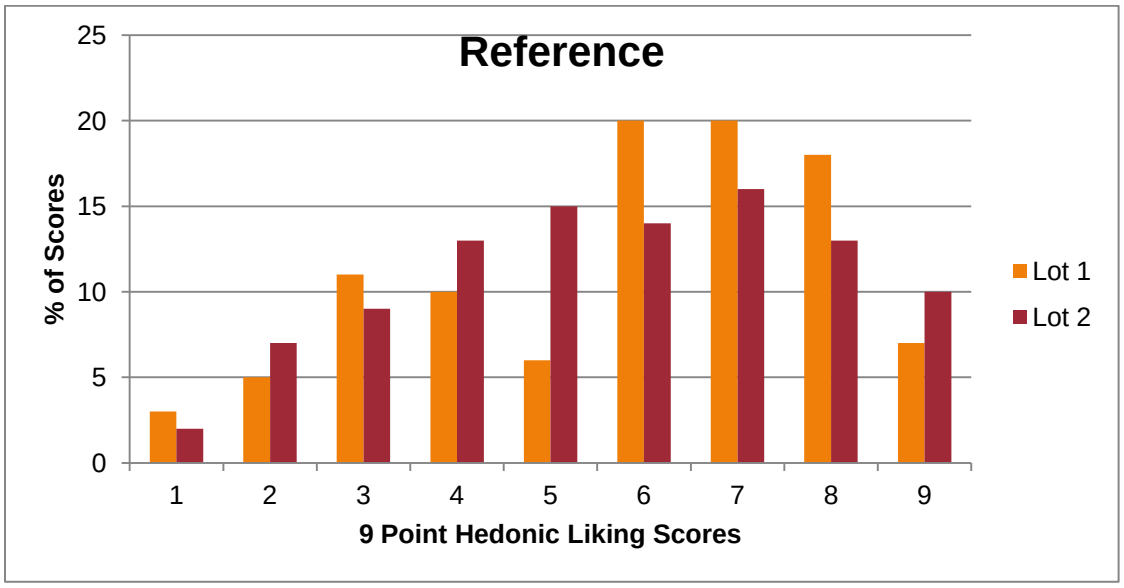
A 1. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Monolayer PET with High Oxygen Barrier Lids (FreshSeal II™) at 30°C after Seven Months of Storage (n=189)



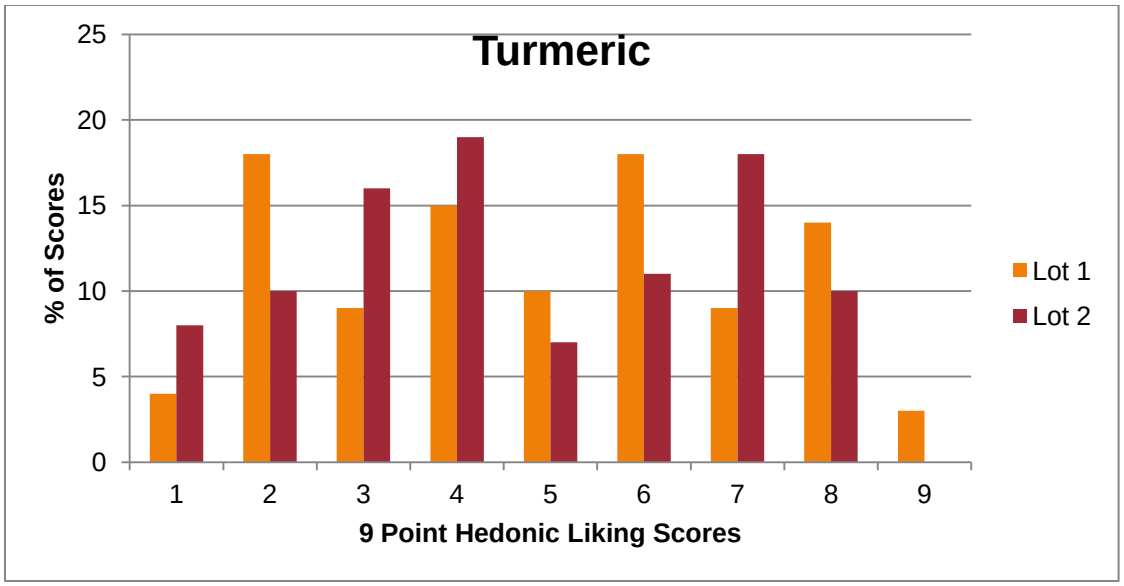
A 2. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Monolayer PET with Low Oxygen Barrier Lids (OptiSeal™) at 30°C after Seven Months of Storage (n=189)



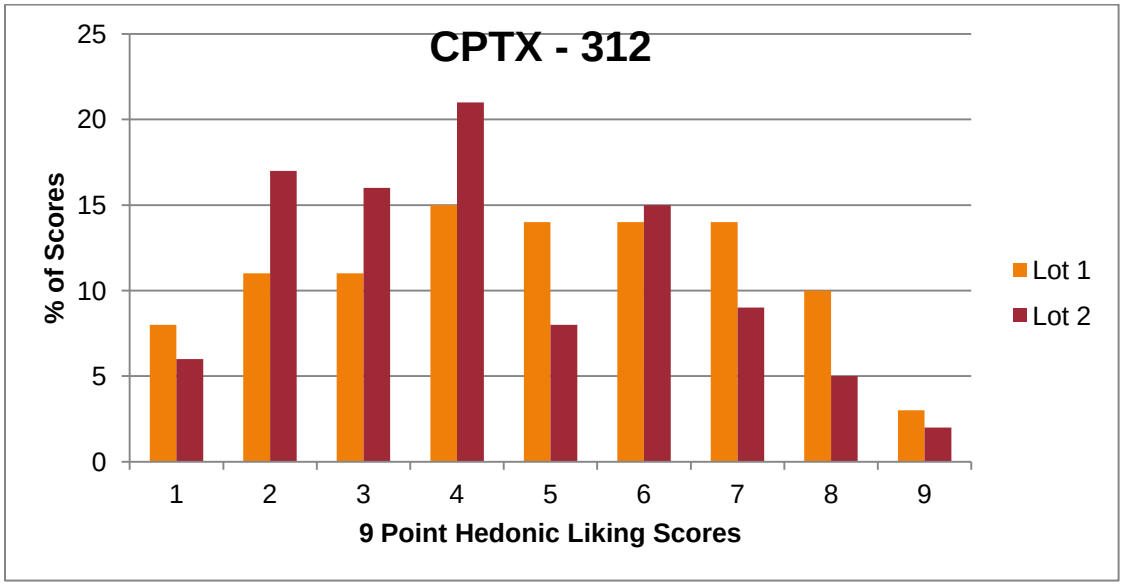
A 3. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Glass at 30°C after Seven Months of Storage (n=189)



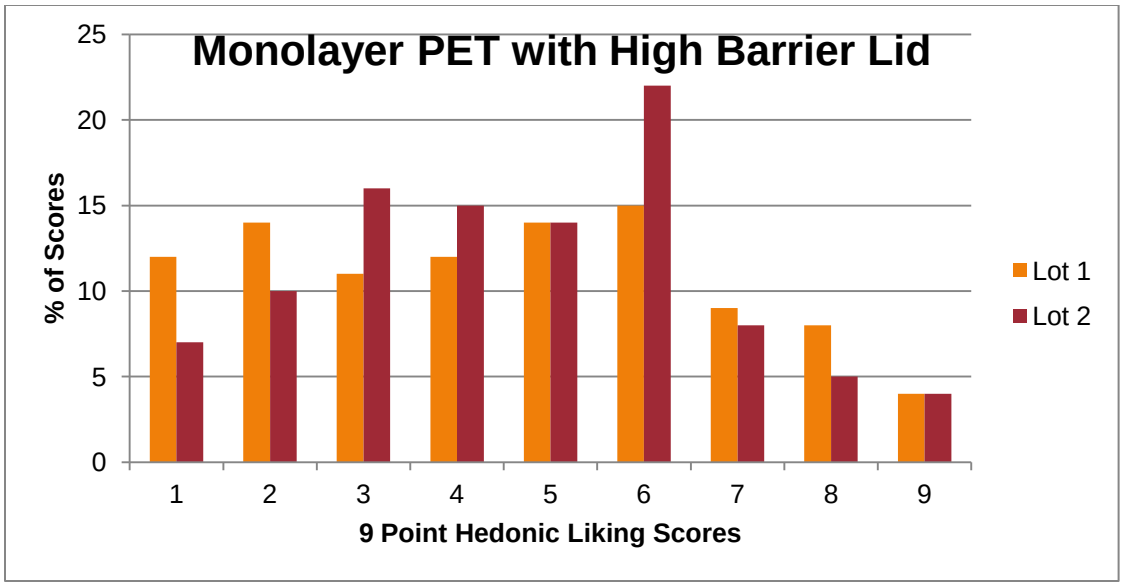
A 4. Distribution of Liking Scores for Fresh Pack Dill Chips Created as the Reference Sample (Stored at 5°C) after Seven Months of Storage (n=189)



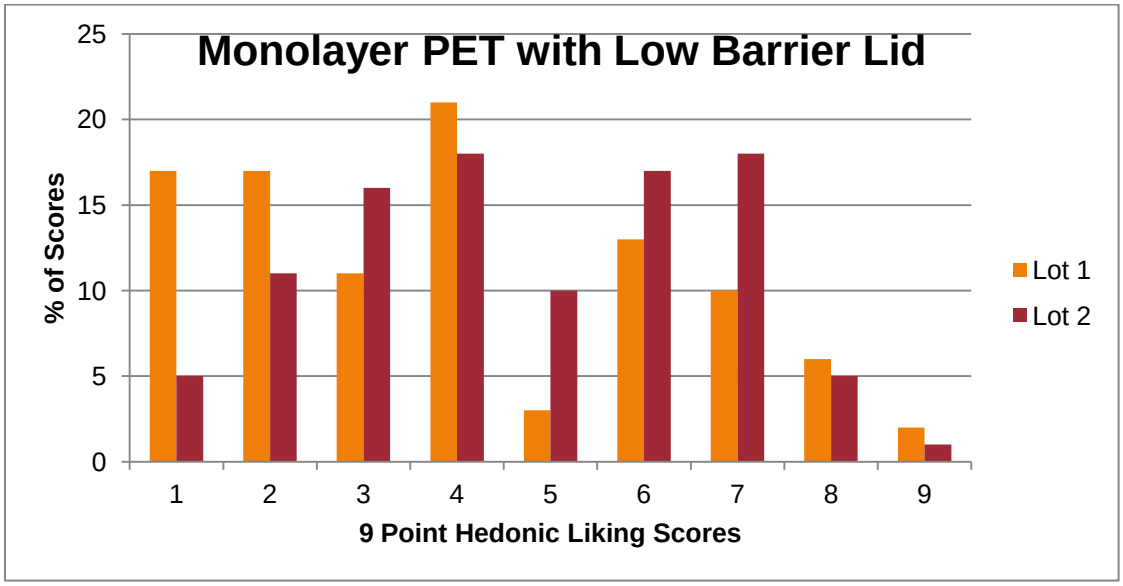
A 5. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Monolayer PET with Low Oxygen Barrier Lids (OptiSeal™) at 30°C with Added Turmeric after Seven Months of Storage (n=189)



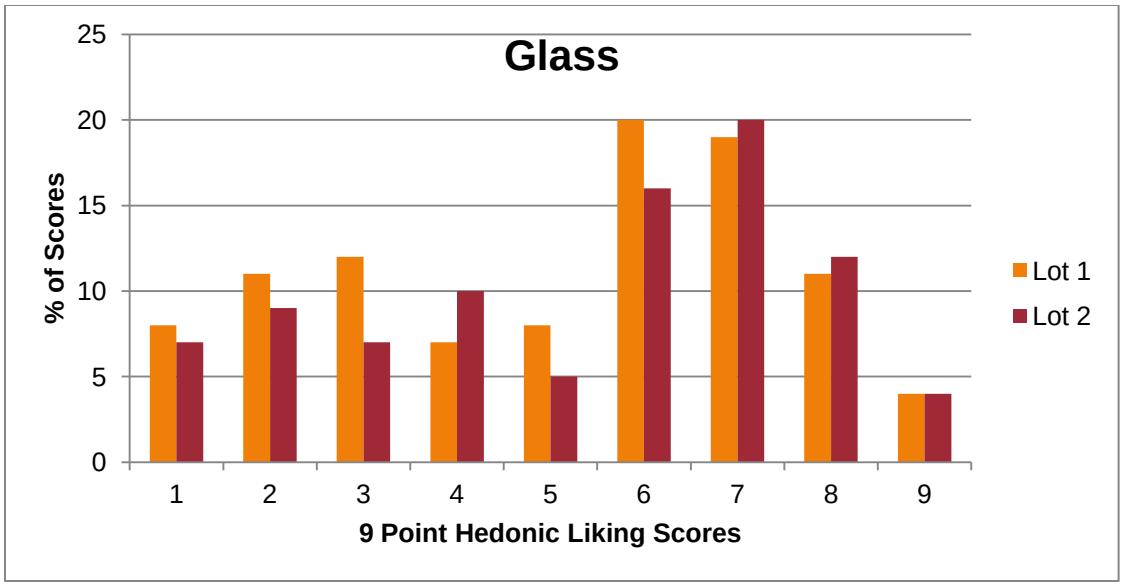
A 6. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in CPTX-312 with High Oxygen Barrier Lids (Fresh Seal II™) at 30°C after Seven Months of Storage (n=189).



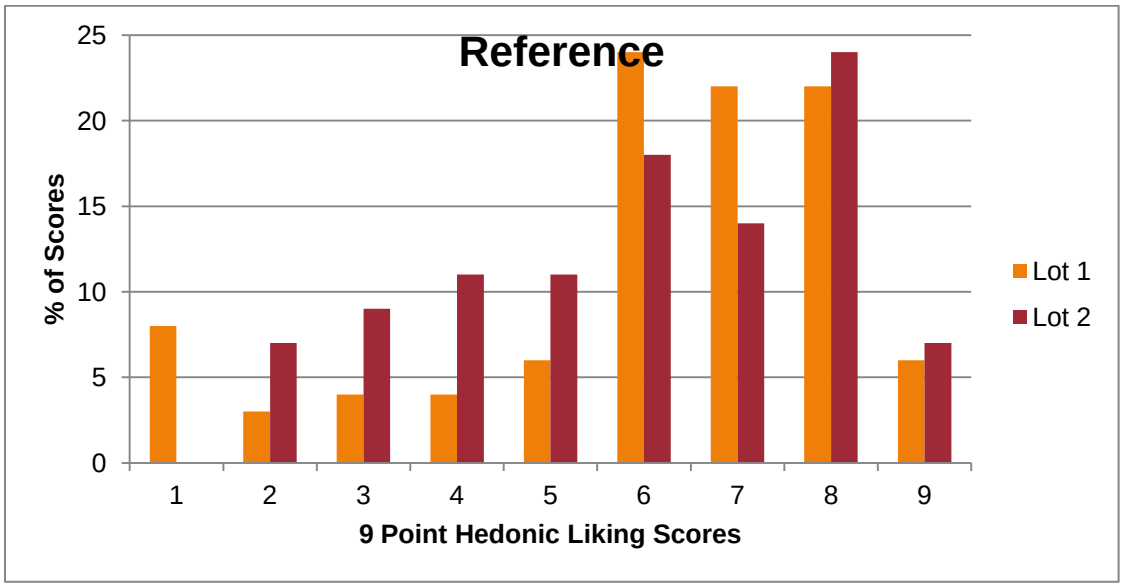
A 7. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Monolayer PET with High Oxygen Barrier Lids (Fresh Seal II™) at 30°C after Twelve Months of Storage (n=196)



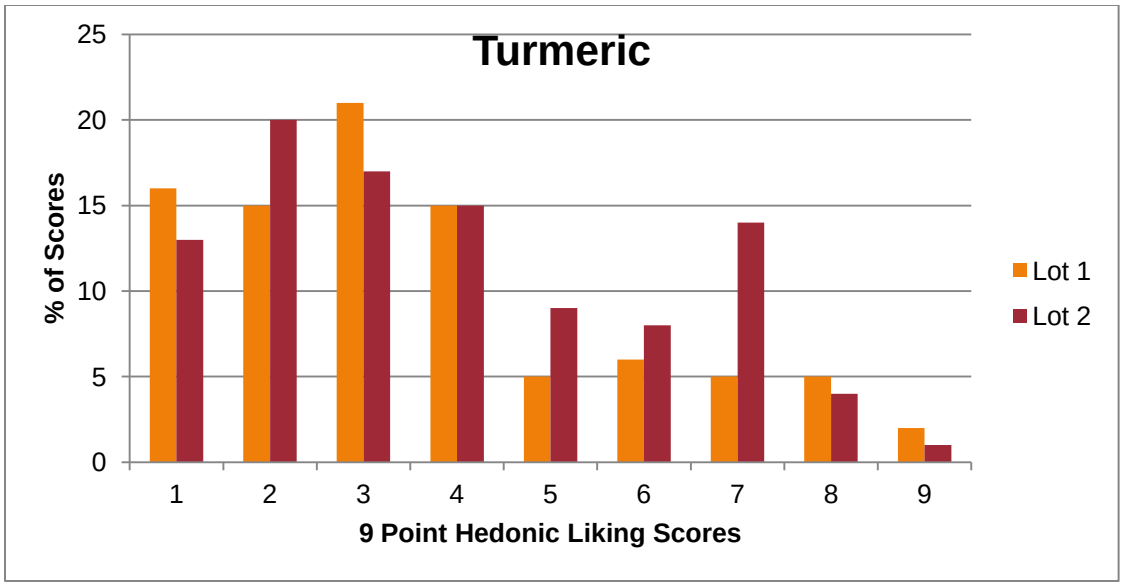
A 8. Distribution of Liking Scores for Fresh Pack Dill Chips Stored in Monolayer PET with Low Oxygen Barrier Lids (OptiSeal™) at 30°C after Twelve Months of Storage (n=196)



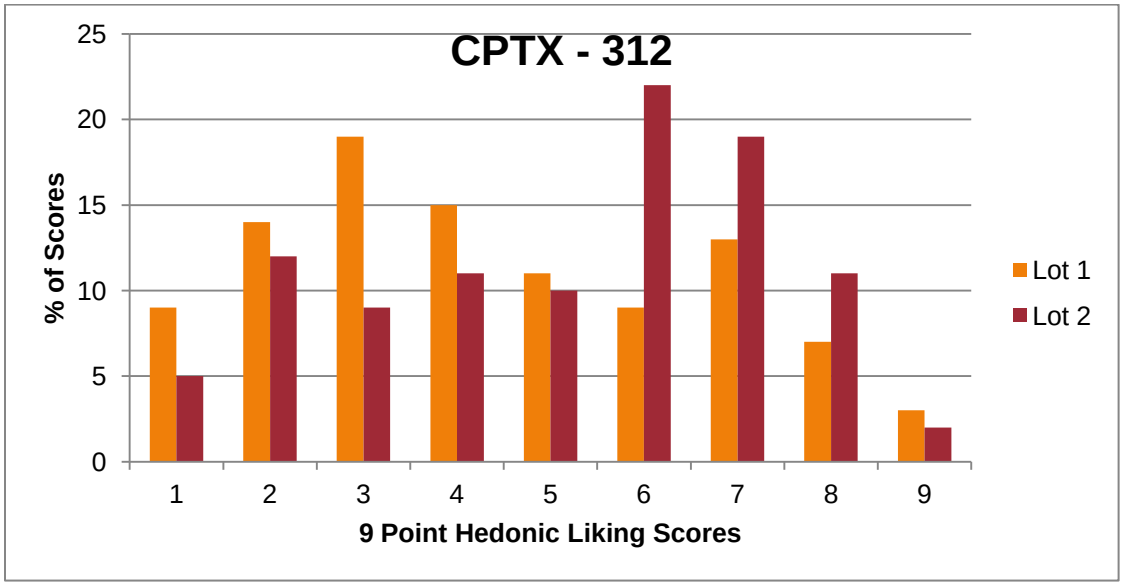
A 9. Distribution of Liking Scores for Dill Chips Stored in Glass at 30°C after Twelve Months of Storage (n=196)



A10. Distribution of Liking Scores for Dill Chips Created as the Reference (Stored at 5°C) after Twelve Months of Storage (n=196)



A11. Distribution of Liking Scores for Dill Chips Stored in Monolayer PET with Low Oxygen Barrier Lids (OptiSeal™) at 30°C with Added Turmeric after Twelve Months of Storage (n=196)



A12. Distribution of Liking Scores for Dill Chips Stored in CPTX-312 with High Oxygen Barrier Lids (Fresh Seal II™) at 30°C after Twelve Months of Storage (n=196).

Difference of Least Squares Means Compared to Glass Control for all 14 Attributes

Appearance

	0.5	4.0	6.0	8.0
MB	0.0409	<.0001	0.0436	0.0747
MNB	0.2633	<.0001	0.1034	0.0841
T	0.0691	<.0001	0.0418	0.0159
CPTX	0.1159	<.0001	0.0103	0.0600

Astringency

	0.5	4.0	6.0	8.0
MB	0.3276	0.3331	0.3007	0.9125
MNB	0.1572	0.2133	0.9332	0.7602
T	0.8614	0.1433	0.5442	0.2830
CPTX	0.4164	0.0890	0.2926	0.7721

Crunchiness

	0.5	4.0	6.0	8.0
MB	0.0480	<0.0001	0.0071	0.0045
MNB	0.2634	<0.0001	0.0148	<0.0001
T	0.0457	<0.0001	0.0206	0.1373
CPTX	0.1766	0.0004	0.0590	0.0002

Bitter

	0.5	4.0	6.0	8.0
MB	0.7768	0.3631	0.9642	0.5433
MNB	0.9915	0.8115	0.7433	0.5331
T	0.4268	0.1869	0.0858	0.1954
CPTX	0.5652	0.1992	0.8840	0.4020

Cure

	0.5	4.0	6.0	8.0
MB	<.0001	<.0001	0.0014	0.1061
MNB	<.0001	<.0001	0.0114	0.0222
T	<.0001	<.0001	0.0003	0.0049
CPTX	<.0001	<.0001	0.0002	0.0153

Salty

	0.5	4.0	6.0	8.0
MB	0.2990	0.4789	0.7789	0.9688
MNB	0.7507	0.6420	0.6478	0.9210
T	0.3429	0.5655	0.9955	0.7036
CPTX	0.4923	0.7188	0.3085	0.8014

Firmness

	0.5	4.0	6.0	8.0
MB	0.0667	<.0001	0.0512	0.0365
MNB	0.1517	<.0001	0.1707	<.0001
T	0.1264	<.0001	0.3456	0.1489
CPTX	0.2764	0.0007	0.7859	0.0022

Sour

	0.5	4.0	6.0	8.0
MB	0.1678	0.9600	0.8757	0.9652
MNB	0.5092	0.9873	0.8981	0.4327
T	0.5737	0.4124	0.8547	0.8756
CPTX	0.2061	0.7185	0.7061	0.8956

Fresh

	0.5	4.0	6.0	8.0
MB	0.0092	<.0001	0.0146	0.1748
MNB	0.0956	<.0001	0.0022	0.0434
T	0.0265	<.0001	0.0006	0.0095
CPTX	0.0313	<.0001	0.0084	0.0401

Sweet

	0.5	4.0	6.0	8.0
MB	0.9981	0.4116	0.9264	0.4140
MNB	0.9518	0.2873	0.3904	0.8656
T	0.1948	0.5056	0.6591	0.8628
CPTX	0.8812	0.4180	0.7393	0.8544

Off

	0.5	4.0	6.0	8.0
MB	0.5858	0.0300	0.2880	0.7517
MNB	0.6721	0.0019	0.1637	0.2271
T	0.0289	<.0001	0.0078	0.0318
CPTX	0.4330	0.0001	0.2807	0.3279

Vinegar

	0.5	4.0	6.0	8.0
MB	0.4156	0.8471	0.6760	0.2655
MNB	0.6272	0.6713	0.2963	0.2855
T	0.8696	0.7624	0.5845	0.2465
CPTX	0.5373	0.7924	0.7844	0.5703

Oxidized

	0.5	4.0	6.0	8.0
MB	0.4291	0.0040	0.1073	0.2764
MNB	0.7275	0.0016	0.1299	0.0177
T	0.4035	0.0025	0.0515	0.0561
CPTX	0.5120	0.0008	0.1438	0.0593

Key:

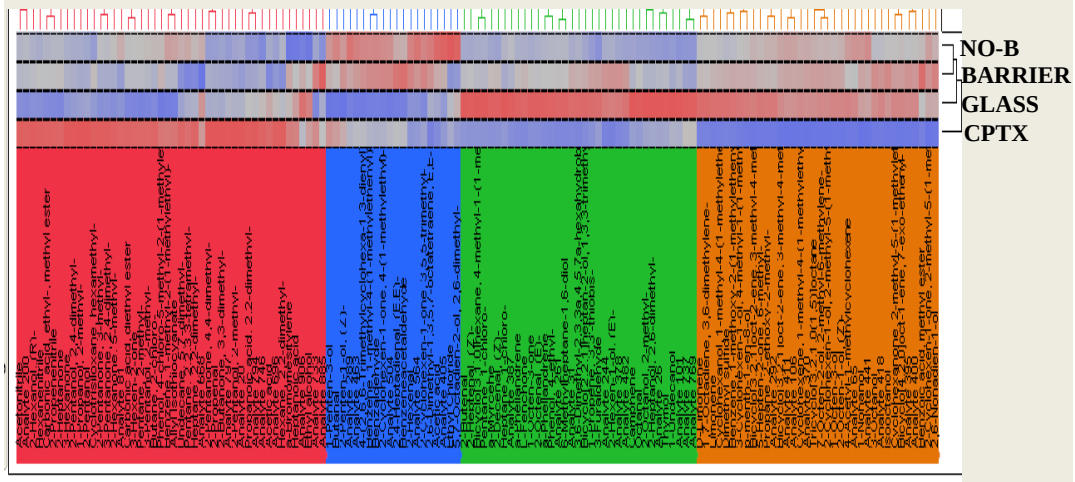
	<0.01
	0.01-0.05
	0.05-0.10

Pr > [t] if # is less than 0.05, one may reject the hypothesis of no difference @ 95% C.I.

Polish Dill

	0.5	4.0	6.0	8.0
MB	0.1276	0.6313	0.5012	0.3107
MNB	0.4260	0.3080	0.3131	0.1695
T	0.3246	0.3093	0.0314	0.3049
CPTX	0.2437	0.6352	0.3778	0.1283

A.13 Difference of Least Squares Means Compared to Glass Control for All 14 Attributes.



RED=higher concentration **BLUE=lower concentration**

A.14 Hierarchial clustering of volatile compounds that changed significantly among treatments (P<0.001).