CONTROL OF OXIDATIVE ODORS THROUGH ACTIVE PACKAGING ODOR SCAVENGERS

by

HEATHER J. OLIVER

(Under the Direction of Aaron L. Brody)

ABSTRACT

Peanut butter HooAH!™ bars are formulated with high levels of lipids to meet the unique requirements for the Armed Forces. Unfortunately, this high level of lipids makes the product more susceptible to oxidation and the reaction products associated with the process, such as hexanal, lead to off-odors. Odor removing materials, such as activated carbon, were incorporated into the packages to reduce the levels of malodors. Sensory analysis was conducted to gain qualitative and quantitative information on the effects of the odor-scavenging material. Instrumental and chemical analysis was conducted to quantitatively determine the effects of the odor-scavenging material. Activated carbon was effective in reducing both characteristic and malodors within the product container. The addition of the activated carbon to a package structure would allow for a wider application of the technology.

INDEX WORDS: Active packaging, odor scavenger, activated carbon, sensory studies, Peroxide Value, Solid Phase Microextraction, lipids, lipid oxidation, oxidative rancidity, odor control

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DEDICATION

To mom, dad, Paul and Jason, I could not have made it this far without you.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Natick Laboratories

The Department of Defense (DoD) Combat Feeding Program was established in 1970 and is located in Natick, Massachusetts, at the United States. Army Soldier and Biological Chemical Command, Natick Soldier Center. The Combat Feeding Program is responsible for the research, development, integration, testing and engineering that supports military combat rations, as well as field food-service equipment technology and combat feeding systems for all military forces. Seven teams that work together to meet each military service's unique combat feeding requirements: Individual combat Rations; Energy and Equipment Technologies; Group Rations; Systems Equipment and Engineering; Advanced Processing/Packaging; Food Engineering Services; and Performance Enhancement/Food Safety. The Combat Feeding Program continuously collaborates with industry, academia, and other government agencies to develop cutting edge technologies, which meet the stringent needs of the military (www.natick.army.mil/programs/food/index.htm).

Meal, Ready-to-Eat

The Individual Meal, Ready-to-Eat (MRE) is the standard military field ration, which replaced the C Ration in the early 1980's and was developed to support the individual soldier in all the Armed Forces (www.natick.army.mil/products/food/index.htm). Military shelf-life standards are much higher than those of the food industry for consumer products (Shaw et al., 1997). The MRE must meet the following standard requirements: maintain high quality for three years at 80°F and for six months at 100°F; must be highly accepted by the soldiers; meet

the Office of the Surgeon General's nutritional requirements; and the packaging must meet stringent durability requirements- including resistance to airdrop, rough handling and temperature extremes (www.natick.army.mil/products/food/mre.htm). If there is not a war-time situation in progress, the stored rations are periodically inspected for quality and safety and, if approved for consumption, the rations are rotated out and consumed during military training exercises (Shaw et al., 1997). Therefore, longer storage time of the rations is more cost effective for the military.

HooAH! Bar

The HooAH!™ bar is a nutrient-dense ambient temperature shelf stable portable food developed in 1996 by the joint-service efforts of the U.S. Army Soldier Systems Center and M&M Mars, Inc. HooAH!™ bars fell under the Performance Enhancing Ration Components project, which designed the HooAH!™ bar to increase energy and improve performance of soldiers during intense military operations. In addition, to being a vehicle for essential nutrients, the HooAH!™ bar must be able to perform under all climactic extremes, be sufficiently stable to withstand long-term storage, be packaged to withstand logistical rigors and be appealing enough to military personnel. The goals of the HooAH!™ bar are accomplished through the combination of simple sugars, complex carbohydrates and most importantly fat. The lipids are essential due to their properties that enhance mouthfeel, flavor and increase energy. The main ingredients of a HooAH!™ bar are corn syrup and rice crisp blended with corn for texture and carbohydrates. Cottonseed or soybean oil is used for fat. Sterling Foods, Inc. in San Antonio, Texas is currently producing the HooAH!™ bar for the military. The

HooAH!™ bars come in a variety of flavors, such as apple-cinnamon, chocolate, cranraspberry, peanut butter and raspberry (Biberdorf, 2000).

Throughout shelf life studies during the developmental stage, the Peanut Butter flavored HooAH!™ bar repeatedly received lower sensory ratings. One such study at Natick Laboratories gave the following results. Samples of the Peanut Butter HooAH!™ bar were stored for two weeks at 40°F and 120°F then evaluated by a sensory panel using a 9-point hedonic scale. The Peanut Butter HooAH!™ bars stored at 40°F produced the following sensory results based on a 9-point scale: Appearance = 5.92; Odor = 5.58; Flavor 5.33; Texture = 6.17; and overall = 5.42. The Peanut Butter HooAH!™ bars stored at 120°F produced the following sensory results based on a 9-point scale: Appearance = 5.00; Odor = 5.58; Flavor 4.50; Texture = 5.50; and overall = 4.63 (Natick Lab Results, 2000). Because of the low scores, Natick removed the Peanut Butter flavored HooAH!™ bar from the menu to optimize the product formulation. Further studies included removing the off odors believed to be from lipid oxidation.

Chemical and Biochemical Reactions:

The shelf life of a food product may be defined as the time from production and packaging of the product to the point at which it becomes unacceptable to target consumers under defined environmental conditions. Over time, one or more quality attributes of a food may reach an undesirable state during the shelf life of the product. Once a food product has reached the end of its shelf life, the product may be considered unsafe or undesirable for consumption. During the shelf life of a product, deterioration can take place by means of physical, chemical and/or microbiological changes. The

reaction mechanisms leading to these changes may be triggered and/or accelerated by environmental factors such as temperature, humidity, oxygen and light (Man et al., 2000).

Chemical reactions involve the internal food components and the external environmental factors, which can lead to food deterioration and reduced shelf life. The rate of these reactions is determined by the change in concentration over time. The rate of a chemical reaction can be calculated with the following equation:

$$-\frac{dC}{dt} = kC^n$$

where the change in concentration, C, of chemical compound (or quality factor) during the chemical reaction at time, t, is defined by the initial concentration, the reaction rate constant, k , and the order of the reaction, n (Roos, 2001). Less specifically, the most important modes of chemical deterioration in food products are associated with enzymatic action, oxidative reactions (particularly lipid oxidation), and non-enzymatic browning (Man et al., 2000).

As indicated above, environmental factors can also accelerate quality degradation within a food product. One of the most important external factors is temperature. The temperature effect on reaction rates can be defined by the Arrhenius relationship:

$$k = k_0 e^{\frac{-E_a}{RT}}$$

where k is the rate constant, k_0 is the frequency factor, E_a is activation energy, R is the gas constant, and T is the absolute temperature. The ratio of reaction rates in relation to temperature is defined as the Q_{10} value, which states that a 10°C increase in temperature increases the rate by the Q_{10} factor (Roos, 2001). Therefore, increases in temperature will accelerate the degradation process of food products.

Another important factor determining the rates of reaction in foods is water activity. Water activity can influence the rate of enzyme-catalyzed reactions, lipid oxidation, and non-enzymatic browning. The rate of most reactions decreases when the water activity is below a value of 0.75 (Nawar, 1996). In addition, oxygen and pH can induce changes in foods when catalyzed by enzymes.

Overall, the deterioration of food usually consists of a series of events, which result in altered quality attributes, such as off-odors. Through reaction mechanisms, flavor precursors are converted to odorous volatiles (Man et al., 2000). Since odor is the focal point of this paper, lipid oxidation reactions, which lead to volatile odor compounds, are further discussed.

Lipid Oxidation:

The presence of oxygen is a major factor in many deterioration mechanisms of food products, which can lead to many adverse effects when found in a food package. Off-flavors and off-odors from oxidative rancidity result in quality deterioration and shortened shelf life of products stored at ambient temperatures (Man et al., 2000; Brody et al., 2001)

Oxidative reactions utilize the oxygen from the package headspace, oxygen that is trapped within the product, permeates into the package, or free radical oxygen released by thermal treatment (Man et al., 2000). When oxygen is present, unsaturated fatty acids become the source of rancidity development during storage of the food product (Rossell, 1986). Unsaturated fatty acids absorb the oxygen from peroxides that break into short chain compounds such as, esters, acids, aldehydes, ketones, and fatty acids (Brody et al.,

2001). Oxidative rancidity is associated with an unpleasant odor and flavor as a result of free radicals generated during the oxidation, or autocatalytic process (Nawar, 1996). The first product of oxidation is an intermediate, hydroperoxide, which is odorless, eventually breaks into aldehydes and ketones, as well as other breakdown products. (Rossell, 1986; Rossell, 1989; Ulberth, 1998). Oxidative rancid flavors and odors are chemically complex, since they are derived from one or all of the unsaturated fatty acids originally present in the lipid, which can each oxidize through several different mechanisms making it very difficult to identify in a food product. For example, oxidation of lipids may involve triacylglycerols in one food or phospholipids in another (Nawar, 1996). However, through research, it has been established that most aldehydes are ultimately derived from linoleic or linolenic acids (Hamilton, 1989). For example, linoleic acid, which is a major unsaturated fatty acid in many food products, can be oxidized to hexanal, octanal, and 2,4-decadienal (Koelsch et al., 1991).

The basic lipid oxidation reaction can be summed up in the following reaction:

$RH + O_2 \rightarrow ROOH \rightarrow$ Secondary Products = rancidity or end of shelf life

Where: RH = polyunsaturated lipids; O_2 = oxygen; and ROOH = lipid hydroperoxide (primary product) (Ragnarsson et al., 1977). More specifically, lipid oxidation is caused by a free radical chain reaction that can be broken down into three steps: initiation, propagation, and termination (Hamilton, 1989; Ragnarsson et al., 1977).

Initiation:	$RH + O_2 \rightarrow R^{\bullet} + {}^{\bullet}OOH$
	$RH \rightarrow R^{\bullet} + {}^{\bullet}H$
Propagation:	$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$
	$RO_2^{\bullet} + RH \rightarrow RO2H + R^{\bullet}$
Termination:	$R^{\bullet} + R^{\bullet} \rightarrow R - R$
	$RO_2^{\bullet} + R^{\bullet} \rightarrow RO_2R$

The initiation step produces free radicals $R^{\bullet}$ from lipid molecules RH by their interaction with oxygen in the presence of a catalyst. The catalyst can be an external energy sources such as heat, light, or high-energy radiation or transition metal ions (Hamilton, 1989; Man et al., 2000). In turn, the free radical $R^{\bullet}$ produced in the initiation step reacts to form a lipid peroxy radical $ROO^{\bullet}$ which can react further to give the hydroperoxide, ROOH. The free radical chain can be stopped by termination reactions, where two radicals combine to give products, which do not feed the propagation reactions (Hamilton, 1989). The flavor and odor of the oil begins to change at the start of the second phase, which is also known as the threshold point (Koelsch et al., 1991). Pentane and hexanal are important compounds that can indicate the degree of rancidity and overall quality of a product susceptible to oxidation (Ulberth, 1998)

Lipid Oxidation of Peanuts and Peanut Butter

Lipid oxidation is the main cause of flavor deterioration, off-flavor and off-odor formation in peanuts and peanut products. As mentioned above, this process can be accelerated by moisture, light, oxygen, or high temperatures (Man et al., 2000; Reed et al., 2002). Although these factors are important to the overall stability of peanuts and peanut products, the main component affecting oxidation is the fatty acid composition of the peanut (Braddock et al., 1995; Pattee et al., 1982). Peanut oil contains 55-65% monounsaturated fatty acids, 26-28% polyunsaturated fatty acids, and 17-18% saturated fatty acids (Mugendi et al., 1998; Ory et al., 1992). Peanuts produce characteristic volatile flavor compounds that are derived from non-enzymatic browning and off-odors from lipid oxidation reactions (Warner et al., 1996). Therefore, generation of volatile

compounds during processing and storage can result in the unique aroma and flavor of roasted peanuts but are also responsible for degradation and rancidity. Therefore, it is important to understand the difference between the formation of desirable aromas and the objectionable odors.

Free amino compounds and sugars are considered to be precursors of roasted peanut flavor, which is identified by the pyrazine compound (Warner et al., 1996), while off-flavors and off-odors can be induced by the breakdown of fatty acids by means of oxidation (Basha et al., 1996). Peanut oil is approximately 30% linoleic acid, which can be degraded to aldehydes, mainly hexanal, and ketones that are the by-products of oxidation that cause the off odors (St. Angelo, 1996, Grosso et al., 2002; Basha, 1993). The volatile compounds associated to the peanut's characteristic aroma and off-odor have been extensively evaluated through sensory, chemical and instrumental analysis.

Sensory Analysis

Sensory testing is effective in understanding which chemical compound is causing off notes through sight, taste, touch and smell. Sensory testing can also determine the effectiveness of different package materials in order to find the one that meets the performance needs. A package should be considered a system, because the package affects the product, which means the product is not independent of the package (Pierce, 2002). Peanut and peanut butter properties are commonly analyzed by sensory techniques to determine differences between treatments and overall quality of peanut products (El-Shimi, 1992). The most common methods of sensory analysis to evaluate package performance are descriptive and consumer tests.

Descriptive analysis depends on trained panelists to detect the sensory attributes of a food product and provide both qualitative and quantitative responses. Descriptive tests are commonly used to determine the aroma, flavor, and/or texture of food products when developing a new product, understanding the shelf life or packaging of a product or relating perceived attributes to instrumental and chemical results. The commonly used descriptive methods are: flavor profile method; texture profile method; quantitative descriptive method (QDA®); Spectrum™; time intensity and free choice profiling methods (Meilgaard et al., 1999). Examples of descriptive terms for oxidation end-products produced by an oil or a fat include rancid, painty, beany, green, metallic, and stale (Hamilton, 1989).

Affective tests are those that assess acceptance, preference, pleasure, or liking for the samples (Cardello, 1997; Meilgaard et al., 1999). Affective tests are also called consumer tests and usually require 100-500 untrained panelists. The affective tests are important for product maintenance, development and optimization. Qualitative information can be gained about a product through focus groups and interviews (Meilgaard et al., 1999). Quantitative information on how a representative group feels about a product can be collected by determining their degree of liking/preferring the sensory attributes. The most widely used scale for assessing food liking or disliking is the 9-point hedonic scale, which was developed by Peryam and Giraridot in 1952 (Peryam et al, 1952). The word hedonic means “having to do with pleasure” (Cardello, 1997).

Gills et al. (2000) compared the acceptability of unstabilized peanut butter and peanut butter stabilized with palm oil using sensory Texture Profile Analysis to quantify

the results from the eight panelists in regards to the description of the textural attributes of both peanut samples. Texture Profile Analysis (TPA) evaluates the quantitative description of the textural attributes of a product based on mechanical, geometrical, and fat and moisture characteristics from first bite through completion (Dubost, 2003; Szczesniak, 1963). No significant differences were found between the treatments in the flavor attributes, but there was a significant difference between treatments in the textural attributes. The result for the consumer panel indicated that there were significant differences only between the hydrogenated vegetable oil, unstabilized peanut butter and the peanut butter stabilized with palm oil in texture, oiliness, spreadability and overall liking. Overall, differences existed in the sensory profiles of the peanut butter stabilized with palm oil, unstabilized peanut butter and hydrogenated vegetable oil (Gills, 2000).

A study conducted by Dubost et al. (2003) determined the ideal soy protein levels for existing peanut spreads. This relationship was evaluated through sensory analysis and consumer tests. Consumers evaluated acceptability using a three-point acceptability scale (3=tastes great, 2=acceptable, 1=unacceptable) (Shewfelt et al., 1997) instead of a nine-point scale. The results indicated that the lowest level of soy protein was significantly different from commercial peanut butter in aroma and mouthcoating. The mid-level soy protein showed a significant difference in textural attributes as compared to commercial peanut butter; whereas, the highest level of soy protein was significantly different from the commercial peanut butter in all attributes except color. Consumers scored the commercial peanut butter as most desirable, found low to intermediate levels of soy protein to be acceptable and rejected the commercial soy product.

Chemical Analysis

Lipid oxidation leads to oxidative rancidity, which in turn is the most common cause of deterioration of oil quality (Rossell, 1986). Oxidative rancidity can be measured by the following: Peroxide Value (PV), Anisidine Value (AnV), Totox Value, Thiobarbituric Acid (TBA) Test, Kreis Test (Rancidity Index) and other chemical methods as well as physical methods and chromatographic methods (Rossell, 1989). Peroxide Value is the most common method of analysis, which is reported in milli-equivalents of oxygen per kilogram of fat. Measuring the quality of a fat by the Peroxide Value is a good guide since a Peroxide Value less than 1 unit is considered a fresh and high quality product. Whereas, Peroxide Values up to 10 units are considered a low quality product and may indicate the start of off flavor and odors due to rancidity (Rossell et al., 1986; Rossell, 1989). Peroxides themselves do not produce a flavor; however, they do lead to the production of aldehydes and ketones, which may have pronounced off-flavors. (Rossell, 1986; Rossell, 1989). The Peroxide Value test is commonly used in the evaluation of peanuts and peanut products.

Adebiyi et al. (2002) compared the effects of five different processing conditions and four different packaging structures at three different relative humidities for three months. After three months of storage Peroxide Values were slightly elevated, which was an effect of the degradation of the oil during roasting.

Mugendi et al. (1998) employed chemical analysis to compare the stability of two high-oleic peanut lines and one normal-oleic peanut line over a ten week time period. The peroxide method was used to determine the degree of oxidation the peanut oil during storage. After ten weeks of storage the normal-oleic peanut oxidized at a much faster rate

than the high-oleic peanut. It was concluded that the rates of oxidation varied due to the difference in the polyunsaturated fatty acid levels.

Evranuz (1993) used peroxide values to determine the effect of temperature and moisture on fat oxidation in unblanched salted roasted peanuts. The level of peroxides increased during storage at each temperature; however, the rate of oxidation at high temperatures appeared to increase at a greater rate than the lower temperatures. The samples stored at the lowest and highest percent moisture content appeared to oxidize at a much greater rate than the intermediate moisture levels. The results indicated that the storage stability of the peanuts was dependent on moisture and temperature.

Chromatographic Analysis

Headspace analysis involves the direct analysis of the volatile compounds above a contained sample; therefore, highly volatile compounds are best suited for this form of analysis. The headspace analysis techniques are simple to perform since there is usually no sample preparation. A gas chromatogram is most commonly used to quantify and identify the volatiles collected. Multiple samples can be taken without disrupting the integrity of the sample. Techniques for the analysis of headspace have traditionally been limited to the collection of volatiles under either dynamic or static conditions. A relatively new technique, Solid Phase Microextraction, was developed by J. Pawliszyn to allow simple, rapid and relatively inexpensive collection of more volatile compounds than the more traditional techniques (Rouseff et al., 2001).

Solid Phase Microextraction (SPME) uses a modified syringe that is fitted with a thin, solid rod of fused silica that is coated with an absorbent polymer (Kataoka et al.,

2000). The silica fiber is typically 1 cm in length and 0.11mm in diameter. The SPME technique has a two-part process. The first stage is absorption of the analytes from the sample onto the fiber coating for a predetermined amount of time. The second stage is desorbing the analytes from the fiber in the injection port of the GC (Rouseff et al., 2001; Wercinski, 1999). The collection technique can take place through headspace or direct immersion. The headspace collection is exposure of the SPME fiber in the vapor phase above a gaseous, liquid, or solid sample. The direct immersion technique is the direct injection of the fiber into the liquid sample (Kataoka et al., 2000). For the analysis of volatile compounds, the headspace technique is more appropriate than the alternative. SPME and other headspace analysis methods have successful identified peanut and peanut butter characteristic aroma compounds as well as compounds that are associated to off-odors of peanuts and peanut products.

It has been known for many years that pyrazines and aldehydes appear to be the most important flavor volatiles in the development of peanut odors. The following pyrazines and aldehydes were identified and quantified by Warner (1996) using an automatic headspace sampler combined with GC/MS: 2-methyl pyrazine, 2,6-dimethyl pyrazine, 2,3,5-trimethyl pyrazine, 2-ethyl-5-methyl or 6-methyl pyrazine, pentanal, hexanal, heptanal, octanal and nonanal. The 2-ethyl-methyl pyrazine represents the roasted or nutty flavor/aroma of peanuts; therefore, indicating these compounds to be beneficial flavor compounds. On the other hand, the concentrations of hexanal, heptanal, octanal and nonanal increased as the storage time increased, which create a cardboard or oxidized flavor/odor. Hexanal proved to be the predominant compound (Basha, 1996; Warner, 1996). Warner (1996) indicated that a flavor fade mechanism occurred over

time. Flavor fade is when the characteristic odors of a product are masked by more influential compounds, such as the development of low-molecular weight aldehydes from lipid oxidation. The flavor-fade in peanuts occurred because as aldehydes increase during storage, pyrazines decrease, which leads to a decrease in flavor and an increase in off-odors.

Chung (1993) identified ninety-nine volatile compounds by headspace analysis of heated peanut oil, which included 42 hydrocarbons, 22 aldehydes, 11 fatty acids, 8 alcohols, 8 ketones, 4 furans, 2 esters and 2 lactones. Further identification included that of formaldehyde, acetone, acetaldehyde, propanal, 2-pentanone, butanal, and 2-hexanone in the same headspace analysis. Specific identification of the hydrocarbons were 18 n-alkenes, 7 n-alkanes, 5 n-alkylbenzenes, 3 alkadienes, 2 cycloalkenes, 2 n-alkylcycloalkenes, 2 monoterpene hydrocarbons, 1 bicycloalkane, 1 cycloalkane, and 1 alkyne. The hydrocarbons were identified as the most abundant class of identified compound. However, they were followed by aldehydes, which were identified as 6 n-alkanals 11 n-alkenals 4 n-alkadienals, and 1 aromatic aldehyde. These aldehydes, along with free fatty acids, were formed by the thermal oxidation and hydrolysis of triglycerides.

Grosso et al. (2002) measured hexanal levels in roasted and cracker-coated peanuts by the solid phase microextraction (SPME) method. A 100µm polydimethylsiloxane fiber was used to absorb the headspace volatile with a collection time of thirty minutes. The hexanal content increased for both samples during storage at 40°C. The hexanal levels of the cracker-coated peanuts increased only slightly before

day 42 then spiked afterwards, but the roasted peanuts increase at a much more steady and slightly more rapid rate.

Peanut products have been extensively evaluated using sensory analysis alone and in combination with instrumental and chemical analysis. A study conducted by Reed et al. (2002) combined sensory, chemical and instrumental analysis to analyze the peanut products. They used a descriptive sensory test to evaluate the peanut characteristics, Peroxide Value to determine the degree of rancidity and SPME-GC to determine the volatile compounds associated with the peanut flavor. Dubost et al. (2003) study on peanut soy spreads combined the quantitative and qualitative methods of sensory analysis, consumer study and instrumental analysis in order to establish a relationship between the three.

Active Packaging

Active packaging materials are intended to sense internal or external environmental changes and to respond by offsetting the change in an otherwise suitable package (Brody et al., 1997; Brody et al., 2001). Active package materials have also been referred to as "smart" and "functional" packaging. Active packaging, in conjunction with other food processing and packaging technologies, is able to enhance the quality and safety of the food and beverage products. The active component may be a part of the packaging material or an insert into the package, such as a desiccant sachet (Brody et al., 1997). Desiccants started the active packaging era with their addition into dry product packages to adsorb moisture. Desiccants can be contained in a moisture-permeable sachet, pouch, patch, coupon, label, etc. The desiccant sachet is incorporated

into the package to absorb water vapor from the contained product and from the package headspace, as well as any water vapor that enters by permeation or transmission through the package structure (Brody et al., 2001).

Moisture sorption is no longer the only form of active packaging. The mechanism of deterioration of the packaged product can be slowed or eliminated by new technologies in active packaging, as well as enhancing the final presentation of the product. Some of the existing technologies include microwave susceptors that brown and crisp food products in the microwave, extreme temperature integrators that indicate temperature abuse, and time-temperature indicators that signal potential loss of shelf life during distribution (Labuza, 1996). The technologies that have recently enhanced food and beverage products include oxygen scavengers, antimicrobial films, carbon dioxide emitters, aroma emitters, and odor absorbers.

Oxygen scavengers are produced to reduce the oxidative effects of the product by removing the oxygen from the sealed package environment. During packaging, the excess oxygen is removed from the headspace of the package; however there are still residual oxygen levels left within the package (Brody et al., 1997). A gas-permeable, flexible sachet containing reduced iron can be inserted into the package to remove any oxygen trapped in the product or that permeates into the package through the package walls. There has been limited success of incorporating oxygen-removing materials directly into a package structure. However, several beer and juice companies have benefited from the addition of oxygen scavengers directly into the bottles (Brody et al., 2001). In addition, antioxidants, such as tocopherols (vitamin E), are being incorporated into plastic packages to reduce the odors generated in plastic processing (Laermer et al.,

1994). Oxygen scavengers and antioxidants have different roles in active packaging. Oxygen scavengers react with oxygen to form new compounds while antioxidants react with free radicals and peroxides to slow or block the actual oxidation reactions (Brody et al., 2001).

Antimicrobial packaging materials are able to retard or eliminate the growth of mold and pathogens. The antimicrobial agent works on the surface of a food product. Ethanol and sulfur dioxide volatilize, which can control growth just as an edible film can. Edible films coat the product, usually fresh fruits and vegetables, to prevent microbial invasion (Labuza, 1996).

Carbon dioxide and ethylene scavengers have been used in conjunction with modified-atmosphere (MA) food preservation in large bulk shipments of fresh fruits and vegetables. Carbon dioxide emitters are utilized to suppress microbiological growth and have limited success in modified-atmosphere packaging (MAP). Ethylene scavengers have proven quite successful in the fresh-fruit bulk shipment category (Brody et al., 2001).

Malodors generated or captured within closed food packages are undesirable; therefore, odor removers incorporated into packaging are increasingly important in some classes of food packaging. Aroma emitters are able to mask unpleasant odors or react with the odors to neutralize them. Currently, aroma emitters can be illustrated by the fragrance incorporated in plastic garbage and trash bin liners. However, most food products generate off-odors due to the deterioration of the food product during storage. With a food product that is susceptible to lipid oxidation, the more desirable action would

be to incorporate a material that would eliminate the odor from the headspace instead of masking the odors (Brody et al., 2001).

Aldehyde scavengers are an example of a system that successfully removes aldehydes, such as hexanal and heptanal, from the headspace of an oxidized product. These aldehydes commonly cause off-flavors and impart a rancid odor and taste to foods (Brody et al., 2001). DuPont has been awarded patents for the incorporation of aldehyde scavengers into flexible packaging structures (Brodie and Visioli, 1994) based on the supposition that food products such as snacks, crackers, cookies, and cereals can benefit from the addition of an aldehyde scavenger. Studies conducted at DuPont on the addition of aldehyde scavengers to the lid of peanut butter packages, potato chip and coffee packages determined that hexanal levels in all three packages were significantly reduced by the end of the shelf life.

ColorMatrix, located in Cleveland, OH, has conducted research on an acetaldehyde scavenger for PET beverage bottles. Acetalydehyde is a low molecular weight aldehyde that is commonly found in fruits and is a result of the melting process of PET and inparts off-flavor to the contained product. The acetaldehyde remains trapped in the solidified polymer and can migrate into the food/beverage during storage. The scavenger reacts with the aldehyde and becomes a highly stable six-ring compound that is unable to migrate from the bottle wall to the food/beverage due to its bulky size. The scavenger proved to be the most successful aldehyde scavenger in the market for carbonated beverages and the future holds expanded product lines to include more active compounds and film and sheet applications (Standish, 2003).

Cyclodextrin

Cyclodextrins have been studied as packaging components for many years, but they have not been incorporated into commercial use until the last decade. In the late 1990's, manufacturing of the three most common cyclodextrins (alpha, beta, and gamma) was optimized and possible to create at an industrial level (Trinh, 2001; Wood, 2001). Dextrins are a group of homologous cyclic oligosacharides, obtained from starch by the action of cyclodextrin glycosyltransferase (CGTase) (Horikoshi, 1979; Wood, 2000). Cyclodextrines are homogeneous cyclic molecules consisting of six or more α-(1,4)-D-glucopyranose links, which results in the lack of a reducing end-group or a non-reducing end-group due to the cyclic arrangement (Horikoshi, 1979). The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units (Brunner, 1998; Trinh 2001).

The most stable 3D molecular configuration for these oligosaccharides takes the form of a torus shape with the smaller and larger opening of the toroid presenting primary and secondary hydroxyl groups. The cyclodextrin has a rigid, truncated conical molecular structure with a hollow interior of a specific volume due to the specific coupling of the glucose monomers (Trinh, 2000; Wood 2000; Wood, 2001). Hydrogen atoms and glucosidic oxygen-bridge atoms form the interior lining of the cavity, which forms an electron rich non-polar environment. The internal cavity, which is lipophilic and hydrophobic, is attractive to organic materials, such as aromatics, alcohols, halides, and hydrogen halides, carboxylic acids and their esters, etc (Wood, 2000). The physical-chemical properties of cyclodextrin enable it to include organic and inorganic molecules, which are called an inclusion complex (Trinh, 1998). The complexed molecule that enters

the cyclodextrin's interior is considered a "guest" molecule, which is "complexed" without the formation of covalent bonds (Figure2) (Wood, 2001).

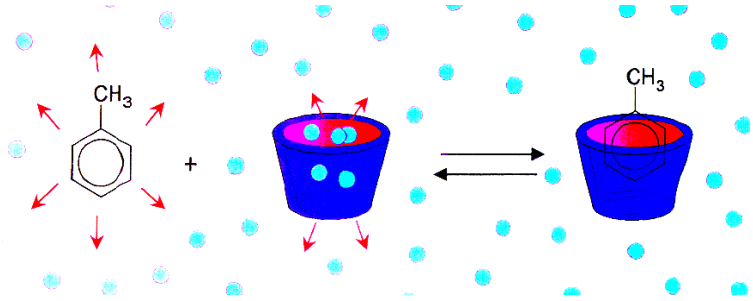

FIGURE 2. Representation of an inclusion complex formation between cyclodextrin and toluene (Wood, 2001).

The difference in cyclodextrin cavity sizes provides a basis for selectivity so that different size molecules may be complexed, which will allow for the specific off-odors to be adsorbed from the headspace of our packaged food product.

β-Cyclodextrin has proven to be a versatile molecule. For example, it can act in foods as a stabilizer of flavors and pigments, anti-oxidants and emulsions. The suggested use of cyclodextrins and cyclodextrin mixtures, which pertain to odor removal packaging are deodorizing of foods along with protection of the food from oxidation and UV-degradation during storage or processing (Horikoshi, 1979). In addition, cyclodextrin has shown to reduce residual organic volatile contaminants in package materials (Wood, 2001). The main advantage of β-cyclodextrin is their ability to protect aroma compounds against thermal or chemical degradation and especially against oxidation.

Cyclodextrins have been shown to improve barrier properties of package materials, which results in improved sensory properties of the product. A package design with the capabilities of an aroma barrier with the inclusion of cyclodextrin has been

developed by Wood (2001). Two examples were presented to test the effectiveness of cyclodextrin for retarding the transport of organic vapors: (1) HDPE monolayer blown films containing triacetyl alpha and triacetyl beta cyclodextrin and non-cyclodextrin films and (2) recycled paperboard folding carton with a starch-based backside coating containing a mixture of alpha and gamma cyclodextrin. The study indicated that a membrane containing cyclodextrin reduces organic vapor transport by increasing the lag time, reducing permeation and reducing the volatile sorption by the packaged food product.

Delarue and Giampaoli (2000) described the interaction between aroma compounds and carbohydrate matrixes focusing on the mechanism involved in retaining and encapsulating high amounts of volatile mixtures by β-cyclodextrins. The study found that the successful retention of the flavor compounds was the result of polar or hydrophilic interactions involving hydroxyl groups from the carbohydrate matrix.

Most articles have focused on the flavor encapsulation and barrier properties of cyclodextrin; however, due to cyclodextrins selective binding properties, the future for odor adsorption within packages is promising. For example, the literature has suggested that a mixture of cyclodextrins would be beneficial to vary the size of the cavities, which would accommodate the wide range of odors produced (Dodd, 2002).

Molecular Sieves

In 1932, J.W. McBain originated the term "molecular sieve" to describe a class of porous solid materials that had been purged of adsorbed water and exhibited selective adsorption properties (Breck, 1974; Szostack, 1989). McBain also stated that for a material to be considered a molecular sieve, it must exhibit shape and size selectivity

among a mixture of components (Szostack, 1989). Structurally, the molecular sieve is a crystalline aluminosilicate, or synthetically produced zeolites (Breck, 1974; Szostack, 1989; www.thomasregister.com/olc/adcoa/molecula.htm). The words zeolite and molecular sieve are interchangeable and only slightly different in structure and application. Thus, molecular sieve will be used in this thesis. The framework of the molecular sieve is based on an extensive three-dimensional network composed of silicon and aluminum tetrahedral which are bound to one another by oxygen (Barrer, 1978; Breck, 1974; Szostack, 1989). Molecular sieves are naturally and synthetically formed from the following elements: sodium, potassium, magnesium, calcium, strontium, and barium (Breck, 1974). The dehydrated crystalline structure that is formed from the previously mentioned elements has a large internal surface area available for adsorption.

Cation-exchange properties of molecular sieves allow the material to reversibly sorb and desorb guest molecules that are small enough to enter the zeolite pores or channels. The molecular sieves are highly selective because the crystalline pores will completely exclude molecules which are larger than their diameter (Breck, 1974; www.thomasregister.com/olc/adcoa/molecula.htm). When the molecular sieve is exposed to a gas or a liquid, the pores and channels of the crystalline structure fill until they are saturated with the gas or liquid, which allows for no more adsorption (Breck, 1974). The molecular sieve will adsorb a considerable amount of liquid or gas when aided by strong ionic forces due to the presence of cations such as sodium, calcium and potassium (www.thomasregister.com/olc/adcoa/molecula.htm).

Molecular sieves have three important properties for industrial purposes. The properties are: (1) the capacities to adsorb gases, vapors and liquids; (2) to catalyze

reactions; and (3) to act as cation exchangers (Barrer, 1978). Molecular sieves are commercially available in four different grades: 3A, 4A, 5A and 13A. Type 3A Molecular Sieve is the potassium form that will adsorb molecules, which have a critical diameter of less than three angstroms (e.g. helium, hydrogen and carbon monoxide). Type 4A Molecular Sieve is the sodium form that adsorbs molecules with a critical diameter of less than four angstroms (e.g. ammonia). Type 5A Molecular Sieve is the calcium form adsorbing molecules having a critical diameter of less than five angstroms (e.g. methanol, ethane, propane). Type l3X is a modified form of the sodium zeolite with a pore diameter of ten angstroms, which can adsorb molecules of chloroform, carbon tetrachloride and benzene. Type 13X is used commercially for general gas drying, air plant feed purification, liquid hydrocarbon and natural gas sweetening. In addition, 13X is successful in adsorbing aromatics and hydrocarbons (www.thomasregister.com/olc/adcoa/molecula.htm).

DuPont in Wilmington, GE and Capital Specialty Plastics in Auburn, AL. have each commercialized the incorporation of molecular sieves into polymer blends for the adsorption of moisture malodors that have accumulated within a package. UOP Corporation in Des Plaines, IL has developed a technology that incorporates molecular sieves called, “Smellrite”/ “Abscents.” The adsorptive capacity of the material lowers the odor concentration in the air to a level below the olfactory threshold (Brody et al., 2001). In addition to odor and moisture removal from food packages, UOP’s molecular sieves can be used as an odor-adsorbing material in incontinence and feminine hygiene products (Marcus, 1990). Molecular sieves have also been successfully incorporated into the diaper industry for odor and moisture control (Brody et al., 2001).

Activated Carbon

The general term for activated carbon includes a wide range of carbon-based materials, which are treated to exhibit a high degree of porosity and continuous internal surface area. Activated carbons are classified on the basis of their particle size and particle shapes as well as whether they are in the powdered, granulated, spherical, or pelleted form. The most common forms of activated carbon material are granular and powder. The granular form is characterized by a large internal surface area and small pores, whereas the powdered form is associated with larger pore diameters but a smaller internal surface (Bansal et al., 1988). The surface area of activated carbon typically ranges from 500-1400 m^2/g; however, in some cases of the powder form, the internal surface area may be as high as 2500 m^2/g (Bansal et al., 1988; Cheremisinoff et al., 1978). Any material that has a high carbon content and is low in inorganics, can be used as a raw material for the production of activated carbon, such as wood, coal, lignite, coconut shell, peat, and others (Bansal et al., 1988). The coconut shell material is preferred for applications with gas adsorption (Mattson et al., 1971).

Activated carbons are excellent adsorbents because of their porous surface area, universal adsorption effect and capacity, and high degree of surface reactivity. Active carbons have a strong adsorption capacity, which can be as high as 0.6-0.8 cm^3/g. The adsorption process occurs mostly in cavities identified as micropores, which are mostly slit-shaped spaces between crosslinked flat aromatic sheets (Bansal et al., 1988). Generally, the pore size and surface area of the material as well as the chemical reactivity of the surface determine the active carbon's degree of adsorption. The physical parameters mentioned, can be controlled to some degree to produce carbons that can be

selective and useful for specific applications. In addition, the chemical nature or polarity of each carbon material varies, which also varies the molecular influences between molecules (Mattson et al., 1971). Due to the nature of the product, the selectivity of the final product can be influenced by the properties of the raw material as well as the parameters of the activation process.

The nature of the manufacturing processes used in the production of activated carbons remains a closely guarded secret within the industry; however, it is known that the raw material undergoes a two-part process (Bansal et al., 1988; Cheremisinoff et al., 1978; Mattson et al., 1971). The first step is carbonization, which is accomplished by heating the raw carbon material, in the absence of oxygen, to a temperature below 800°C that will dry and volatilize substances in the carbon (Bansal et al., 1988; Cheremisinoff et al., 1978). The second step of the process is to increase the surface area where the carbon is "activated" by the action of oxidizing agents. Activating agents can be steam, air, carbon dioxide at elevated temperatures or chemical agents such as phosphoric acid, zinc chloride, and sulfuric acid (Bansal et al., 1988; Cheremisinoff et al., 1978; Mattson et al., 1971).

Activated carbons have been utilized for many decades and have a broad range of applications. Activated carbons are extensively used in the treatment of domestic and industrial wastewater treatment to remove color and odor, purify, dechlorinate, and detoxicate potable waters (Bansal et al., 1988). Activated carbon is used in the food, chemical, pharmaceutical, paper and pulp, and petroleum industries for solvent recovery, air purification, removal of color from various types of sugar syrup, purification of many

chemical, pharmaceutical, and food products, and a variety of gas phase applications (Bansal et al., 1988; Cheremisinoff et al., 1978).

A U.S. patent assigned to Westvaco (Parks, 1996) describes a paperboard product that is coated with low-density polyethylene (LDPE). The inner layer contains an odor absorbing material, such as activated carbon. The coated paperboard is used to form folding cartons for packaging food products that emit "significant" odors or aromas. The coating, which is in contact with the odor-emitting product, is capable of absorbing such odors (Brody et al., 2001; Parks, 1996).

Polyethyleneimine (PEI)

Polyethyleneimine (PEI) is a water-soluble polymer, with a branched structure that has amino groups built in the main chain. The polymer is very rich in reactivity and has the highest cation density among existing materials. According to Salamone, "PEI is prepared by ring opening polymerization of ethyleneimine monomer using acid catalyst (Salamone, 1991; Salamone, 1999). The branching structure of PEI is caused by the high reactivity, which means the polymer is not perfectly linear. However, when produced by ethyloxazoline it can have a linear chain structure. PEI is known to react with aldehydes and ketones (Salamone, 1996).

PEI's unique characteristics make it useful as a water-treating agent, enzyme fixing agent, chelating agent, adhesive fiber treating agent in many industrial fields. The industries that PEI has impacted are the paper, adhesives, ink and photography, textiles, medical and cosmetics industries (Salamone, 1996 and Salamone, 1999).

Objectives

The primary objective of this research was to develop an active packaging odor scavenger that removes off-odors from the interior of HooAH!™ packages. Based on adsorptive properties and selectivity four odor-removing materials were selected to evaluated, activated carbon, molecular sieve, PEI and cyclodextrin. A series of sensory descriptive tests were conducted to determine which of the four materials had a perceived effect on the headspace odor. The second objective was to determine through sensory acceptance tests that the product itself was not being altered with the addition of the chosen odor-removing material. The third objective was to determine through sensory difference tests if a difference could be perceived between the control and treated samples. The Peroxide Value test was conducted to chemically determine if the product was being altered by the addition of the odor-removing material. The SPME-GC/MS analysis of the container headspace was to instrumentally determine if the odor-removing material was effective at reducing the hexanal levels present.

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CHAPTER 2

SENSORY ANALYSIS OF PEANUT BUTTER HOOAH!Ô BARS TREATED WITH ACTIVE PACKAGING ODOR SCAVENGERS[1]

[1] Oliver, H.J., A.L. Brody, R.L. Shewfelt, and L.R. Kline. To be submitted to *Journal of Food Quality*.

ABSTRACT

The peanut butter HooAH!™ bar (MRE) received low sensory scores during shelf-life tests due to off-odors. Off-flavors and off-odors from oxidative rancidity result in quality deterioration and shortened shelf life of products stored at ambient temperatures. Sensory testing is effective in understanding which chemical compound is causing the off note through sight, taste, touch and smell. Activated carbon, molecular sieve, cyclodextrin and PEI are all odor-removing materials and this study determines through sensory methods, which is the most effective at removing off odors. Descriptive tests indicated that PEI was more successful at reducing the odor levels of all reference standards except the rancid oil, which activated carbon was by far the most effective at removing. The acceptance test responses determined there was not a significant effect by storage temperature or by packaging treatment. Of the 28 panelists who participated in the difference test, 85.7% correctly identified the odd sample.

INTRODUCTION

The Individual Meal, Ready-to-Eat (MRE) is the standard military field ration, which replaced the C Ration in the early 1980's and was developed to support the individual soldier in all Armed Forces (www.natick.army.mil/products/food/mre.htm). The HooAH!™ bar is a MRE component that is a nutrient-dense food developed in 1996 to meet the unique requirements of the Armed Forces. Lipids are essential to the performance of the HooAH!™ bar due to their properties that enhance texture, taste and energy. The HooAH!™ bars come in a variety of flavors including apple-cinnamon, chocolate, cranraspberry, peanut butter and raspberry (Biberdorf 2000). The peanut butter HooAH!™ bar has received low sensory scores during shelf-life tests due to off-odors. Off-flavors from oxidative rancidity result in quality deterioration and shortened shelf life of products stored at ambient temperatures (Man et al., 2000; Brody et al., 2001).

Sensory testing is effective in understanding which chemical compounds are causing off notes through sight, taste, touch and smell. Sensory testing can also determine the effectiveness of different package materials in order to identify the one that meets the performance needs. A package product should be considered a system, because the package affects the product, which means the product is not independent of the package (Pierce, 2002). The most common methods of sensory analysis to evaluate package performance are descriptive and consumer tests. Descriptive analysis depends on trained panelists to detect the sensory attributes of a food product and provide both qualitative and quantitative responses (Meilgaard et al., 1999). Affective tests are those

that assess acceptance, preference, pleasure, or liking for the samples (Cardello, 1997; Meilgaard et al., 1999).

Odor adsorbing materials that have been used for commercial applications of odor-removal due to their excellent odor adsorbing and binding properties include activated carbon (Bansal et al., 1988; Cheremisinoff et al., 1978; Brody et al., 2001; Parks, 1996); molecular sieve (Brody et al., 2001); cyclodextrins (Trinh, 2001; Wood 2000; Wood, 2001); and polyethyleneimine (Salamone, 1996; Salamone, 1999). The primary purpose of this study was to determine which material successfully reduces the off-odors of the HooAH!™ bar. The second objective is to determine the acceptability of the control samples compared to the samples packaged with activated carbon. The final objective was to determine if a perceived odor difference could be detected between the control and treated samples.

MATERIALS AND METHODS

Test samples

Peanut Butter flavored HooAH!™ Bars were manufactured by Sterling Foods, Inc., San Antonio, Texas and shipped to The University of Georgia from the Natick Soldier Center, where the bars were stored under room temperature conditions until utilized for analysis.

The 1 gm Minipax sachets containing either activated carbon, molecular sieve, polyethyleneimine, and cyclodextrin were produced by Multisorb Technologies, Inc., Buffalo, NY.

Storage Conditions

Descriptive Test: One Peanut Butter HooAH!™ bar was placed in a 150x75mm Pyrex Crystallizing Dish with a custom fit glass cover. There were fourteen containers per storage temperature: 3°C, 10°C, 25°C, 31°C and 37°C. At each temperature, there was one set of control and one set of each odor-removing material: activated carbon; molecular sieve; polyethyleneimine; α-cyclodextrin; β-cyclodextrin ; α/β-cyclodextrin mix. A set consisted of two identical samples. Each group was tested for approximately four months.

Acceptance Test: Six Peanut Butter flavored HooAH!™ Bars were placed in a 170x90mm Pyrex Crystallizing Dish with a custom fit glass cover. There were twelve containers total and four containers per storage temperature: 3°C, 25°C, and 37°C. At each temperature half of the samples were control and half were exposed to activated carbon. The samples were placed in their respective containers and temperature chambers three weeks prior to the test date.

Difference Test: One-third of a bar was placed in a 100x50mm Pyrex Crystallizing Dish with a custom fit glass cover. There were thirty-six containers, each containing one-third of a bar. There were twelve containers per storage temperature: 3°C, 25°C, and 37°C. At each temperature half of the samples were control and half were exposed to activated carbon. The samples were placed in their respective containers and temperature chambers three weeks prior to the test date.

Sensory Panel

Descriptive Test: Four panelists were recruited for the odor descriptive test of whom three had previously participated in sensory descriptive analysis tests. The

recruitment criteria included that the panelists were: (1) between the ages of 18 and 55, (2) not allergic to peanut products, (3) able to detect the trace characteristic and off-odors of the peanut product, (4) available and willing to participate during training and long-term testing sessions.

The four panelists met for a one-hour initial session to determine the characteristic and off-odors of the Peanut Butter HooAH!™ bar. Initial standards were determined from the initial session and evaluated over the next three one-hour training sessions. A final list of reference standards that represented the characteristic and off-odors of the HooAH!™ Bar, were retained after consensus by panel members. The intensities of the reference standards were based on a 150-mm unstructured line scale. The reference standards and their intensities were determined collectively by the panel members to assure that judgments of each panelist were in the same range as those of the other panelists (Table 1).

Acceptance Test: A total of 107 panelists were recruited for the consumer acceptance test at The University of Georgia, Athens campus. The recruitment criteria included that the panelists were: (1) between the ages of 18 and 55, (2) not allergic to peanut products, (3) available and willing to participate during the designated test session.

Difference Test: A total of 28 panelists were recruited for the difference test at the University of Georgia, Athens campus. The recruitment criteria included that the panelists were: (1) between the ages of 18 and 55, (2) not allergic to peanut products, (3) available and willing to participate during the designated test session.

Sensory Method

Descriptive Test: Odor attributes of Peanut Butter HooAH!™ Bar samples were evaluated using a modified Spectrum™ technique for descriptive analysis (Meilgaard et al., 1999) where panelists were calibrated based on reference standards (Table 1) using 150-mm line scale instead of 15 point line scale. The anchor points for the 150-mm line scale are 12.5, which indicates a weak degree of intensity and the opposite anchor is 137.5, which indicates the strong degree of intensity.

Acceptance Test: Overall consumer acceptance of the Peanut Butter HooAH!™ Bar was evaluated using a 9-point Hedonic scale (9=like extremely; 1=dislike extremely) (Meilgaard et al.,1999).

Difference Test: Any perceived differences between the control and activated carbon samples were evaluated using a Triangle test to determine if the overall difference between the two samples is significant (Meilgaard et al., 1999).

Sample Evaluation

Descriptive Test: The set of samples were taken from the temperature chambers thirty minutes prior to testing for each panelist. Each sample was labeled with a three-digit code and randomly presented to the panelist. The testing was conducted on a random basis over a four-month period. The panelists were asked to smell the headspace of each sample from left to right and rate the samples relative to intensity ratings of standard references developed during training on the handout provided. A candy treat was provided for participation.

Table 1. Reference Standards and Intensity Ratings Used To Evaluate Headspace Odor of Peanut Butter Flavored HooAH!™ Bars

Reference Standard	Intensity
Diluted Molasses	75
Jif® Peanut Butter	150
Caramel	150
Peanuts	150
Melba Cracker	75
Rancid Oil	25 and 150
Brown Sugar	150

Intensity ratings based on 150-mm unstructured line scales anchored with the descriptors weak = 12.5 and strong = 137.5

Acceptance Test: All samples were removed from the temperature chamber one hour prior to testing in order to equilibrate to room temperature. The HooAH!™ samples were broken into six pieces and placed in 3.25 oz. Sweetheart Plastic Portion cups and capped with lids. Panelists were presented with three randomly coded samples and instructed to taste each sample and rate the degree of like to dislike on the provided handout. Palates were cleared with unsalted crackers and distilled water between samples. A candy treat was provided for participation.

Difference Test: The samples were removed from the temperature chambers to be brought to room temperature thirty minutes prior to the test. The samples were coded with three-digit random numbers and set-up in random order for the panelists prior to the test. Panelists were instructed to smell the headspace of the samples from left to right

and indicate on the worksheet which sample was unlike the other two. A candy treat was provided for participation.

Analysis and Interpretation of Results

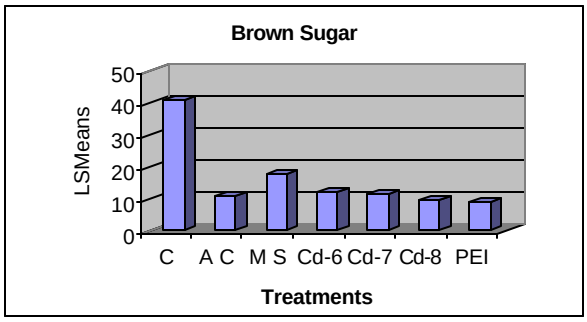
All data was analyzed using SAS statistical package v. 8.1 (SAS Institute Inc., Cary, NC). The Descriptive Test was analyzed by PROC REG and the acceptance test was analyzed by the LOGISTIC Procedure.

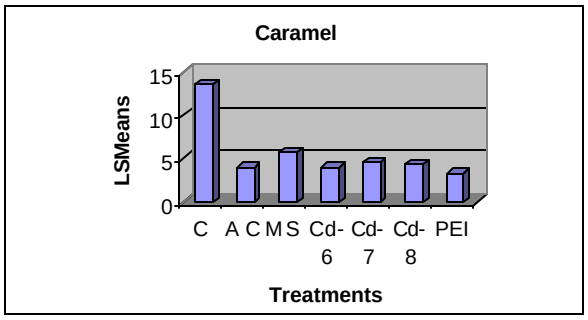
RESULTS AND DISCUSSION

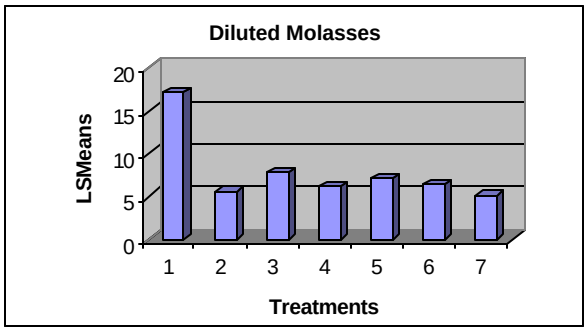
Descriptive Test

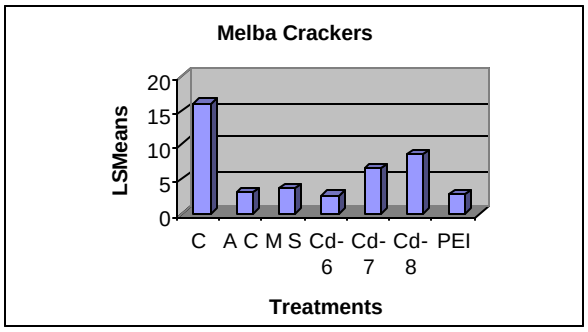
The four odor scavenging materials were chosen because of their odor adsorbing and binding characteristics. No interaction effects between temperature and packaging treatment were observed, but a significant main effect for storage temperature was observed for the 'rancid oil' and the 'brown sugar' descriptors ($P<0.05$). At each reference standard (brown sugar, caramel, diluted molasses, melba crackers, peanuts, peanut butter and rancid oil), there was a statistically significant difference between the treatments. PEI was more successful at reducing the odor levels of all reference standards except the rancid oil (Fig. 1). Activated carbon was by far the most effective odor adsorbing material for the off odors of the rancid oil. The overall goal of the odor adsorbing material was to adsorb the off-odors of the HooAH!™ bar. Since rancid oil standard represented the oxidative odors that were of greatest concern in HooAH!™ bar storage, activated carbon was chosen as the material to conduct further studies.

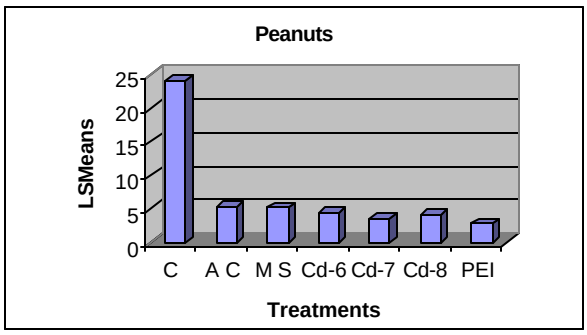
FIGURE 1.
EFFECTS OF THE TREATMENT CONDITIONS AS RELATED TO THE REFERENCE STANDARDS (C = CONTROL; AC = ACTIVATED CARBON; MS = MOLECULAR SIEVE; CD = CYCLODEXTRIN; PEI = POLYETHEYLENEIMINE).

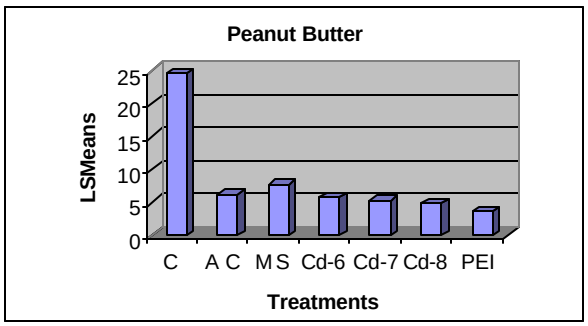


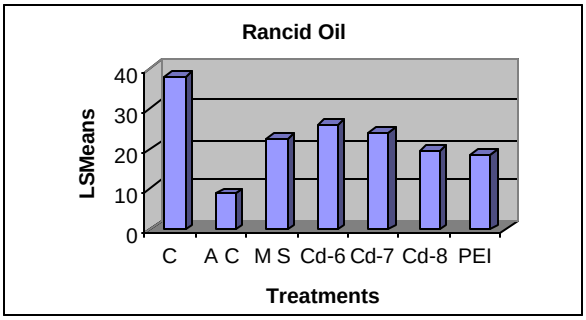












Acceptance Test

The majority of the responses for the overall acceptability of the HooAH!™ bar were “like moderately” (7) and “like slightly” (6) (Table 2), with over half the responses rating them at “neither like/dislike” (5) or below. No interaction effects between temperature and packaging treatment were observed ($P>0.05$). Likewise, there was not a significant effect by storage temperature or by packaging treatment (Table 3). Since the consumer acceptance test found no noticeable difference between the taste of the control sample and the treated sample, the addition of activated carbon does not lead to improved product quality.

TABLE 2.
PERCENTAGE OF RESPONSES PER DEGREE OF ACCEPTABILITY FOR THE CONTROL AND SAMPLES PACKAGED WITH ACTIVATED CARBON

Response	Percent %
9 Like Extremely	0.9
8 Like Very Much	8.1
7 Like Moderately	21.2
6 Like Slightly	19.0
5 Neither Like/Dislike	15.9
4 Dislike Slightly	14.6
3 Dislike Moderately	10.6
2 Dislike Very Much	8.1
1 Dislike Extremely	1.6

TABLE 3.
PERCENTAGE OF RESPONSES PER TREATMENT

Hedonic Score	9	8	7	6	5	4	3	2	1
Activated Carbon	1	15	32	30	26	22	19	13	2
Control	2	11	36	31	25	25	15	13	3

Difference Test

Of the 28 panelists who participated in the difference test, 85.7% correctly identified the odd sample. The results illustrate that the panelists were able to perceive a difference in the headspace odor between the control and treated samples. The total correct answers resulted in an a-risk below 0.1% (<0.001), which provides statistical evidence that an apparent difference exists between the control and treated samples (Meilgaard et.al., 1999). In addition, a few panelists commented on favoring the "low" to "no" odor of the treated samples. The difference test was able to determine that the activated carbon treatment was effective in lowering the off-odor levels perceived by the panelists.

CONCLUSIONS

Activated carbon was effective at reducing all odor notes both oxidative (rancid oil) and desirable (brown sugar, caramel, diluted molasses, melba crackers, peanuts and peanut butter) as determined by both the descriptive and difference tests. The odor scavenging activity did not prevent peroxide formation, but dramatically reduced the presence of hexanal in the package headspace, presumably preventing formation of further degradation products (Oliver et al., 2003). The odor scavenging properties of

activated carbon, however, were not sufficient to lead to a noticeable improvement in product quality during storage for 3 weeks at temperatures ranging from 3-37°C. The odor-scavenging effect of activated carbon may lead to aroma improvement at extended storage time by removal of hexanal and other oxidative products, but may also lead to decreased quality due to the adsorption of desirable odors.

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CHAPTER 3

INSTRUMENTAL AND CHEMICAL ANALYSIS OF PEANUT BUTTER HOOAH!Ô BARS TREATED WITH ACTIVE PACKAGING ODOR SCAVENGERS[2]

[2] Oliver, H.J, A.L. Brody, R.L. Shewfelt, and L.R. Kline. To be submitted to *Journal of Food Processing and Preservation.*

ABSTRACT

The peanut butter HooAH!™ bar (MRE) received low sensory scores for the odor during shelf-life tests, possibly due to the high level of lipids in the product. SPME-GC/MS analysis was conducted for samples stored at 3°C, 25°C and 37°C. There was an overall decrease in the levels of all compounds when treated with activated carbon. A significant difference ($P<0.05$) was observed between the control samples and the samples treated with activated carbon at all storage temperatures. Peroxide Values (PV) were determined for samples stored at 3°C, 25°C, and 37°C. The effect on PV was significant for storage time ($P<0.05$), but it was not significant for activated carbon. Together, these results indicate that the activated carbon is an effective material for reducing the off-odors from the HooAH!™ bar without interfering with the composition of the product.

INTRODUCTION

The Individual Meal, Ready-to-Eat (MRE) is the standard military ration that was developed to support the individual soldier in all the Armed Forces. The peanut butter flavored HooAH!™ bar is a MRE that was designed to increase energy and improve performance of soldiers during intense military operations while performing under all climactic extremes and being sufficiently stable to withstand long-term storage (www.natick.army.mil/products/food/mre.htm). The goals of the HooAH!™ bar are accomplished through the combination of simple sugars, complex carbohydrates and most importantly fat (Biberdorf, 2000). The peanut butter HooAH!™ bar received low odor sensory scores during shelf life tests, possibly due to the oxidation of lipids in the product.

The presence of oxygen is a major factor in many deterioration mechanisms of food products, which can lead to many adverse effects when found in the headspace of a food package (Man et al., 2000; Brody et al., 2001). When oxygen is present, unsaturated fatty acids become the source of rancidity development during storage of the food product (Rossell, 1986). Unsaturated fatty acids or other unsaturated hydrocarbons such as, aldehydes and ketones, absorb the oxygen during the oxidative reactions (Brody et al., 2001). It has been established that most aldehydes are ultimately derived from linoleic or linolenic acids (Hamilton, 1989). For example, linoleic acid, which is a major unsaturated fatty acid in many food products, can be oxidized to hexanal, octanal, and 2,4-decadienal (Koelsch et al., 1991). Hexanal is an important compound that indicates the degree of rancidity and overall quality of a product susceptible to oxidation (Ulberth, 1998)

Malodors generated or captured within closed food packages are undesirable; therefore, odor removers incorporated into packaging are increasingly important in some classes of food packaging. Activated carbon has been commercially used to reduce odor levels due to its unique adsorbing and binding properties (Bansal et al., 1988; Cheremisinoff et al., 1978; Brody et al., 2001; Parks, 1996). The first objective of this study was to determine through instrumental analysis the effects of activated carbon on the reduction of hexanal levels. The second objective of this study was to ensure that the properties of the product itself were not being altered by the addition of the activated carbon.

MATERIALS AND METHODS

Test samples

Peanut Butter flavored HooAH!™ bars were manufactured by Sterling Foods, Inc., San Antonio, Texas and shipped to The University of Georgia, Athens, GA from Natick Soldier Center, Natick, Mass., where the bars were stored under room temperature conditions until utilized for analysis

The 1 mg Minipax sachets with Activated Carbon were provided by Mulitsorb Technologies, Inc., Buffalo, NY.

Storage Conditions

Gas Chromatography-Mass Spectrometry: Twelve 125x65mm Pyrex Crystallizing Dishes contained one bar each, which was broken into thirds. The container

was fit with a custom glass cover with a rubber septum to allow headspace sampling without interrupting the integrity of the container. There were four containers per storage temperature: 3°C, 25°C, and 37°C. At each temperature half of the samples were the control and half were packaged with activated carbon sachets.

Peroxide Value: Eight 170x90mm Pyrex Crystallizing Dishes each contained five whole bars. The container was fit with a custom glass cover. There were four containers per storage temperature: 3 °C and 37°C. At each temperature half of the samples were the control and half were packaged with activated carbon sachets.

Gas Chromatography-Mass Spectrometry

Extraction Procedure: An SPME fiber holder for manual sampling with a 1 cm long 65 µm poly(dimethylsiloxane)/divinylbenzene-coated fiber (Supelco, Bellefonte, PA) was used for headspace analysis. The fiber was conditioned in the GC injector port at 260°C for 30 min.

GC/MS Analysis Conditions: Gas chromatographic analysis was performed using a Hewlett Packard 5890 Gas Chromatogram and a Hewlett Packard 5970 Series Mass Selective Detector (MSD). The computer program used with the GC/MS was the G1034C Version C.03.00 from Hewlett Packard (1989-1994). A fused silica capillary column SPB™-5 (0.25 µm) with column dimensions of 30m x 0.25mm was used to separate the desorbed compounds.

The compounds were desorbed from the fiber at 250°C for 3 minutes in the injection port of the GC. The column was maintained at 35°C for 3 minutes, then increased 20°C/min to 40°C, further increased 6°C/min to 130°C, and finally increased

25°C/min to 200°C and held for 1 min. The gas chromatogram was programmed for splitless conditions with the pressure set at 12 psi.

Peroxide Value

Sample Preparation: One bar from each container was removed and cut into very small pieces (≈20g). The samples were placed in aluminum weigh trays and then put into a Precision Thelco convection oven at 100°C for 18 h. Once dried the pieces were cooled in a desiccator until used for extraction.

Soxhlet Extraction: The AOAC 963.15 (1995) Soxhlet extraction method was used to extract the fat from the product. Approximately 27 grams of dried product was used for each extraction procedure. The extraction time for each sample was eight hours.

Peroxide Value Analysis: The AOCS method (Cd 8-53) was used to determine the peroxide values of all samples.

Statistical Analysis

All data was analyzed using PROC GLM method on the SAS statistical package v. 8.1 (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

Gas Chromatography-Mass Spectrometry

Hexanal was identified by GC/MS in trial runs and was used as the marker for oxidation as it is known that hexanal is a by-product of lipid oxidation that causes off-odors (Basha, 1996; Warner 1996). Gas chromatograms for two SPME extractions from

the HooAH!™ containers are shown in Figures 1 (37°C-Control) and 2 (37°C-Activated Carbon). There was an overall decrease in the levels of all compounds when treated by activated carbon. A significant difference ($P<0.05$) was observed between the control samples and the samples treated with activated carbon at all storage temperatures (Fig. 3). Hexanal levels declined by the third week suggesting that it was being further degraded into other oxidative products as described by Nawar (1996). These results suggest that activated carbon is adsorbing hexanal, an oxidative intermediate, as it is being formed. Such action would slow the formation of further breakdown products and would be expected to decrease the formation of off-odors and flavors (Brody et al., 2001; Nawar, 1996).

FIGURE 1.
SPME-GC/MS RESULT OF THE CONTROL HOOAH!™ BAR STORED AT 37°C DURING WEEK 1. HEXANAL AT 7.73 MIN. IS THE IDENTIFIED COMPOUND OF INTEREST.

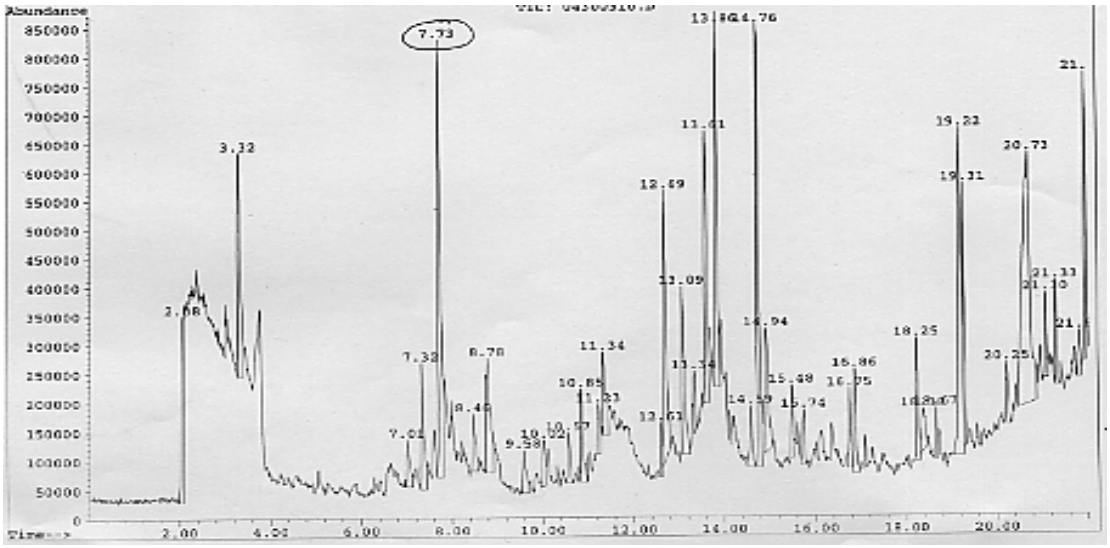


FIGURE 2.
SPME-GC/MS RESULT OF THE HOOAH!™ BAR TREATED WITH ACTIVATED CARBON AND STORED AT 37°C DURING WEEK 1. HEXANAL AT 7.30 MIN. IS THE IDENTIFIED COMPOUND OF INTEREST.

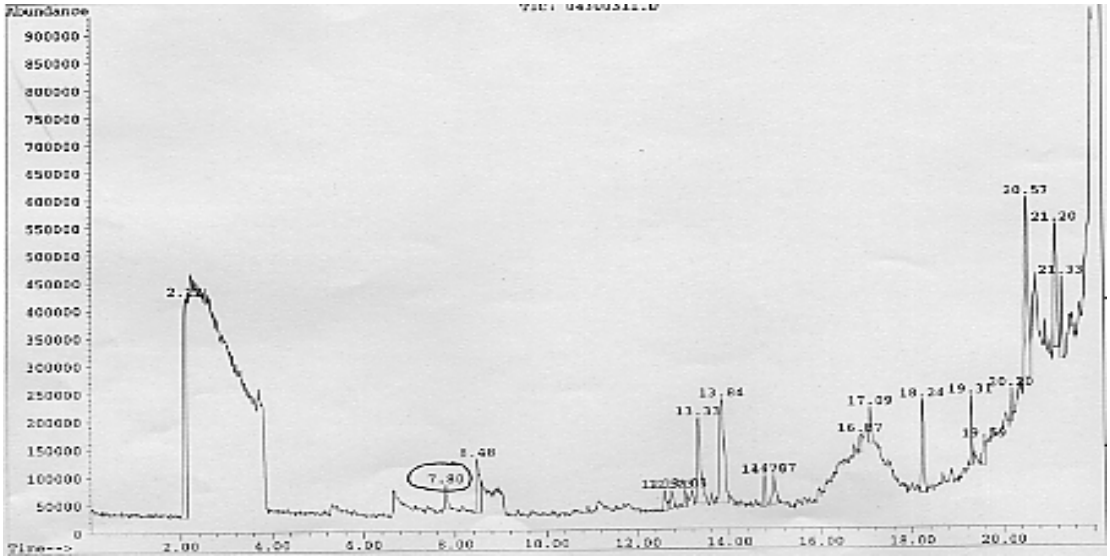
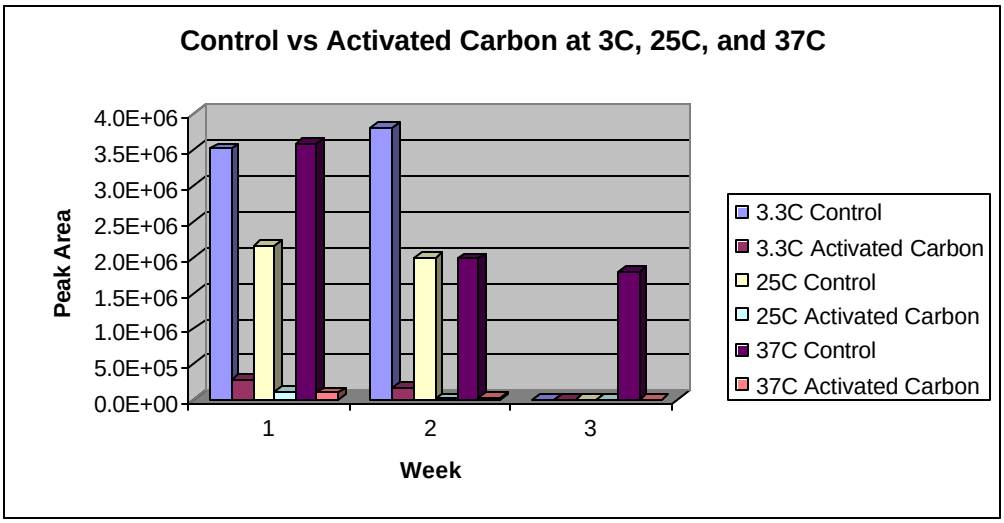


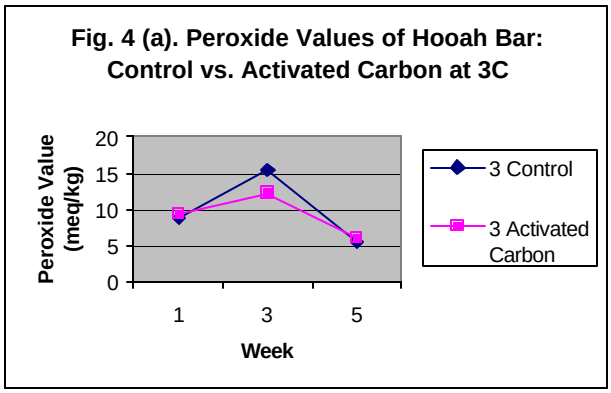
FIGURE 3.
EFFECT OF ACTIVATED CARBON AND STORAGE TEMPERATURE ON HEXANAL FROM THE HOOAH!™ BAR.

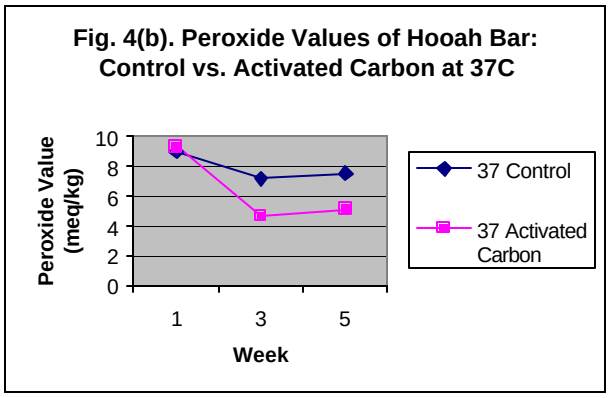


Peroxide Value

Peroxide Values increased slightly in both control and activated carbon samples at 3°C (Figure 4a) after 3 wk storage, but not at 37°C (Figure 4b). PV at 5 wk for both treatments declined between 3 and 5 wk during storage at 3°C and in the first 3 wk at 37°C. While the effect on PV was significant for storage time ($P<0.05$), it was not significant for activated carbon. The decline in PV suggests that peroxides formed were being broken down into smaller volatile compounds as described by Nawar (1996). Overall, the PV indicated that the composition of the HooAH!™ bar was not changed by the addition of the activated carbon.

FIGURE 4A AND 4B.
PEROXIDE VALUES OF HOOAH!™ BAR DURING STORAGE 3°C (A) AND 37°C (B) OVER A 5 WEEK STORAGE PERIOD.





CONCLUSIONS

The instrumental analysis was conducted to identify a representative volatile compound that was associated to lipid oxidation, then to determine if the compound could be reduced by the addition of activated carbon. Hexanal was identified within the headspace of the container and monitored throughout the study. The GC/MS results indicated that there was a significant difference between the control sample and the sample treated with activated carbon. Therefore, it is possible to conclude that activated carbon can effectively remove a significant level of hexanal present within the headspace of the container, decreasing the formation of off-odors. The Peroxide Values did not result in a significant difference between the control samples and the samples treated with activated carbon. These results indicate that the activated carbon did not alter the properties of the HooAH!™ bar. Together, these results indicate that the activated carbon

is an effective material for reducing the off-odors from the HooAH!™ bar without changing the composition of the product.

ACKNOWLEDGEMENTS

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CHAPTER 4

SUMMARY AND CONCLUSION

Peanut butter HooAH!™ bars were formulated with high levels of lipids to meet the unique requirements for the Armed Forces. Unfortunately, this high level of lipids made the product more susceptible to oxidation and the by-products associated with the process, such as hexanal, that leads to off-odors. It is well known that off-flavors and off-odors from oxidative rancidity result in quality deterioration and shortened shelf life of products stored at ambient temperatures (Man et al., 2000; Brody et al., 2001). Therefore, necessary measures must be taken to reduce the quality deterioration of the product. Advances in active packaging have made it possible to extend the shelf life of certain products. Odor removing materials, such as activated carbon, can be incorporated into a food packaging to reduce increased levels of malodors; therefore, increasing the quality and shelf life of the product.

In Chapter 2, we found that activated carbon was effective at adsorbing all odor notes both oxidative (rancid oil) and beneficial (brown sugar, caramel, diluted molasses, melba crackers, peanuts and peanut butter) as determined by both the descriptive and difference tests. The odor scavenging properties of activated carbon, however, were not sufficient to lead to a noticeable improvement in product quality during storage for 3 weeks at temperatures ranging from 3-37°C. The odor-scavenging effect of activated carbon may lead to quality improvement at extended storage time by removal of hexanal and other oxidative products, but may also lead to decreased quality due to the adsorption of desirable odors.

In Chapter 3, hexanal was identified within the headspace of the container and monitored throughout the study. The GC/MS results indicated that there was a significant difference between the control sample and the sample treated with activated

carbon. Therefore, it is possible to conclude that activated carbon can effectively remove a significant level of hexanal present within the headspace of the container. The Peroxide Values did not result in a significant difference between the control samples and the samples treated with activated carbon. These results indicate that the activated carbon did not alter the properties of the HooAH!™ bar. Together, these results indicate that the activated carbon is an effective material for reducing the off-odors from the HooAH!™ bar without interfering with the composition of the product.

The combination of sensory analysis with instrumental and chemical analysis is becoming more common and has been successful in research and development (Dubost et al., 2003; Reed et al., 2002). Utilizing both qualitative and quantitative analysis allows for a broad range of information. The sensory analysis can quantitatively (descriptive tests) and qualitatively (affective and difference tests) determine how the consumer perceives certain attributes of the product and how they feel about the product. In addition, chemical and instrumental analysis allows for qualitative data that a consumer might not be able to perceive. Together, sensory, chemical and instrumental analysis can provide a more complete understanding of a food product and its interactions with the surrounding environment. Future research should focus on incorporating the activated carbon material into a film material without reducing the exposed active surface area. Also, it would be interesting to determine the odor-removing effects activated carbon can have on other various products.