ABSTRACT

MCDANIEL, KRISTIN ALICIA. Effects of Different Time/ Temperature Roast Combinations on Peanut Flavor, Mechanical and Nutritional Properties. (Under the direction of Dr. Jack P. Davis.)

Peanuts in North America and Europe are primarily consumed after dry roasting. Standard industry practice is to roast peanuts to a specific surface color (Hunter L-value) for a given application; however, equivalent surface colors can be attained using different roast temperature/time combinations. Accordingly, a single lot of runner peanuts was roasted using five temperatures (147 ºC, 157 ºC, 167 ºC, 177 ºC, and 187 ºC) and various roast times to obtain 3 degrees of roast colors corresponding to L-values of 53±1, 48.5±1, and 43±1, for light, medium and dark roasts, respectively.

Moisture content (MC), mechanical textural properties, hydrophilic oxygen radical adsorption capacity (H-ORAC), tocopherol content, sugar content, flavor and other characteristics were determined across the roast matrix. MC ranged from 0.41% for the 147 ºC dark roast to 1.70% for the 187 ºC light roast peanuts. At the same roast temperature, MC decreased as peanuts became darker; however, for a given color, MC decreased with decreasing roast temperature due to longer roast times required for specified color formation. Peak force at compression data, derived from a Kramer shear cell compression test, positively correlated (R^2=0.64) with MC. Total tocopherol contents ranged from 140 to 470 µg/g oil and decreasing MC correlated (R^2=-0.67) with increased total tocopherols. Total sugar contents of completely defatted flours ranged from approximately 7.4 to 8.6 g /100 g. Glucose and fructose were significantly ($p<0.05$) influenced by roast color and temperature.

Pasted samples were evaluated in duplicate by a trained sensory panel using a 15-point universal scale for 17 flavor attributes. Descriptive sensory analysis (DSA) was compared to volatile data collected from the same samples using various Electronic Nose instruments (E-Nose – Gemini/Fox/Heracles) in triplicate. As expected, samples roasted to different colors were differentiated ($p<0.05$) using DSA terms including, roasted peanutty, sweet aromatic, dark roast, raw beany, bitter, and ashy. Dark roast, bitter, ashy and raw beany attributes were correlated with E-NOSE sensor data ($R^2 >0.70$). Principal component analyses of E-Nose data revealed a clear distinction for volatiles among peanuts roasted at 147 °C, 157 °C, 167 °C, 177 °C and 187 °C, whereas the sensory panel only noted clear differences between 147 °C and 187°C. GC analyses (Heracles) suggested the majority of discriminatory volatiles were Maillard products such as pyrazines and dimethyl pyrazine. Hexanal was another important discriminatory compound identified most prominently in light roasted peanuts and especially those seed which were roasted at lower temperatures/longer times. Low temperature long time roasting may accelerate peanut oil oxidation leading to changes in hexanal concentrations. Generally, DSA panel found that for peanuts roasted to an equivalent surface color, those peanuts roasted at higher temperatures/shorter times had decreased intensities ($p<0.05$) for attributes, such as ashy and bitter, which are typically associated with negative peanut flavor. Hunter L-value data was also compared to E-eye data and a Global Statistical Quality Control Model was developed to evaluate degree of roast. The variation in characteristics related to method of roasting is sufficient to suggest influences on final product shelf life and consumer acceptability.

Effects of Different Time/ Temperature Roast Combinations on Peanut Flavor, Mechanical and Nutritional Properties

by
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DEDICATION

This work is dedicated to my family for their unfailing support throughout all of my life's many adventures. Mom, Dad, Wes, Anna and Will without your love and support I would not be the person I am today. Words could never fully express my gratitude and love for each of you.

BIOGRAPHY

Kristin McDaniel, better known as Ali, grew up in Alpharetta, Georgia with her parents Burton and Judy McDaniel and siblings Wes, Anna and Will. Growing up Ali was very active in school serving as her high school class president from her sophomore to senior year. Along with being active in school, Ali spent much of her time growing up traveling around the country with her family showing Santa Gertrudis cattle. She has been a member of the National Santa Gertrudis Association since she was 8 years of age and has served as treasurer on the National Junior Board of Directors.

Upon completion of high school, Ali attended the University of Georgia (UGA). In 2008, Ali graduated from UGA with honors and received her B.S.A. in food science and was recognized as a UGA College of Agricultural and Environmental Sciences Outstanding Senior (CAES). She served as a CAES Ambassador, the UGA Food Science Club Co-President, and was a member of Zeta Tau Alpha, Phi Tau Sigma, and Alpha Zeta. Following graduation from UGA, Ali participated in a semester long foreign exchange program at Universität Hohenheim in Stuttgart, Germany. While at the Universität Hohenheim Ali attended courses in Organic Food Chain Management and worked in a Food Chemistry laboratory earning her a certificate of International Agriculture. In the summer following, Ali worked at Chick-fil-A, Inc. as a Brand Development Intern.

In 2009 Ali began her Master's program in food science at North Carolina State University. Along with working as a Graduate Research Assistant in the USDA-ARS peanut lab, Ali also worked with the Center for Student Leadership, Ethics & Public Service as the

Executive Director of the Service Leadership Team. Upon graduation, Ali will begin working with the USA Dry Pea & Lentil Council as the Food Marketing Manager in Moscow, Idaho.

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CHAPTER 1:

Literature Review

1.1 The Peanut

Peanuts, *Arachis hypogaea,* have been an important crop around the world for many centuries. The earliest documentation of peanuts is found in Peru in 1502; however, there is much debate over the original domestication location. A native crop of South America, the most significant hypothesis is that peanuts were originally cultivated in the southern Bolivia-northwestern Argentina area. This is suggested due to the presence the subspecies *hypogaea* and several natural hybridizations, along with the extensive variety of uses for the crop. (Peanut Science and Technology 1982 Ch. 1)

Although commonly thought of as nuts, peanuts are legumes. Following pollination, pegs grow down into the ground where they develop into peanut pods. The peanut plant is self-pollinating and best suited for growth in warm climates with loose sandy soil, making the southern U.S. a primary growing location (**Table 1.1**). There are four main varieties of peanuts that are grown: Runner, Virginia, Spanish and Valencia representing 80%, 15%, 4% and 1% of U.S. production respectively (National Peanut Board 2011).

Table 1.1 Breakdown of percentage of U.S. peanut crop grown in each state (American Peanut Council Feb. 2011).

State	Percentage of U.S. Crop (%)
Georgia	41
Texas	24
Alabama	10
North Carolina	9
Florida	6
Virginia	5
Oklahoma	5

The Runner variety tends to produce a high yield and is mainly used in the production of peanut butter. Smaller kernels with reddish-brown skins characterize the Spanish variety that is used extensively in the candy and confectionary industry. Virginia peanuts have larger kernels and a good overall appearance. For this reason, Virginia peanuts are often used for whole kernel in-shell processes. The Valencia variety often has three kernels and is very sweet, making it useful for whole peanut consumption or boiled peanuts. (American Peanut Council 2011).

1.2 History of Processing

Processing of peanuts creates the diverse range of products and adds value to the crop. In the early 1800's, peanuts began to be extensively imported into Europe due to shortages of other oil crops. In America there was also an increase in importation; however, instead of oil production the main use was for roasting. During the Civil War, production of peanuts increased further in America as oil sources became scarce. Following the Civil War the growth region of peanuts expanded from small gardens to larger regions in the southeast. Until this time cotton had been the major cash crop in the south; however, the destruction of cotton crops in the early 1900's by the boll weevil led to further increase in production of peanut crops (Peanut Science and Technology 1982 Ch.1). The recognition of peanuts as an essential oil crop in 1941 by the United States government led to an increase in breeding programs and technology for peanut production (Peanut Science and Technology 1982 Ch.1).

Currently, peanuts represent the 12th largest cash crop in the United States (American Peanut Council 2011). There are several forms in which peanuts are consumed including whole kernels, peanut butter, and oil along with many further processed items such as

candies and confectionaries. Peanut butter represents the largest portion of the U.S. total market accounting for approximately 50% (American Peanut Council 2011). Whole kernels, candies, and confectionaries represent about 35% of U.S. consumption, with oil consumption falling at approximately 15% (American Peanut Council 2011).

1.3 Peanut Nutritional Composition

Peanuts are living organisms, therefore the nutritional composition will vary due to variety, growing location, climate conditions, maturity, curing as well as storage conditions (Basha and others 1976, Sanders 1980, Sanders and others 1982). Peanuts are considered a nutrient rich food source because they are a good source of proteins, have a desirable lipid profile, and are an excellent source of phosphorous, B vitamins, magnesium, tocopherols, phytosterols, and antioxidants (Ahmed and Young 1982, Hoffpauir 1953). By weight, peanuts are approximately 54% oil, 21-36% protein and 25% carbohydrates and ash (Hoffpauir 1953).

Peanut oil consists of palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), eicosenoic (20:0), arachidic (20:4), behenic (22:0), and lignoceric (24:0) fatty acids, with oleic and linoleic fatty acids making up more than 80% of the total oil profile (Bolton and Sanders 2002). Peanuts are a rich source of monounsaturated fatty acids (MUFA acids) and low in saturated fatty acids (Bolton and Sanders 2002, Mercer 1990), and the consumption of peanuts, and oilseeds with similar fatty acid profiles, has been shown to reduce the risk of coronary heart disease by decreasing total and low-density lipoproteins (Baker and others 2003, Kris-Etherton and others 2001, Kris-Etherton and others 2008, Pelkman and others 2000).

Peanuts are high in total amount of protein as compared to other oilseeds. Peanuts contain 18 amino acids, 9 of which are essential (**Table 1.2**). In order to measure the nutritional value of a protein source, protein digestibility-corrected amino acid scores (PCDAAS) are used. PCDAAS is a measurement that accounts for the amount and types of amino acids in a food as well as the digestibility. A complete protein has a PCDAAS of 1.0. Peanuts have a PCDAAS of 0.52, making them a better protein source than many other tree nuts.

Table 1.2 Typical amino acid profile of peanuts (Monteiro and Prakash 1994).

Amino Acid	**Quantity (g/100 g protein)**
Glutamic acid	23.01
Aspartic acid	12.91
Arginine	12.43
Leucine	6.25
Phenylalanine	5.41
Serine	5.22
Glycine	5.15
Proline	5.01
Tyrosine	4.12
Alanine	3.74
Valine	3.65
Lysine	3.12
Isoleucine	2.83
Threonine	2.50
Histidine	2.22
Tryptophan	1.59
Methionine	0.52
Cysteine	0.33

The carbohydrate component of peanuts consists of sugar, starch, pectin and cellulose (Hoffpauir 1953). The predominate sugar in peanuts is sucrose followed by stachyose and

raffinose (Hoffpauir 1953). Immature peanuts have higher levels of sugars than mature peanuts (Sanders and others 1989).

1.4 Roasting

A critical step of processing peanuts for snack nuts, confectionaries and peanut butter is roasting. Dry roasting represents the most significant form of processing in the U.S., followed by oil roasting, and a very small percentage of peanuts are processed using techniques such as water blanching and boiling (American Peanut Council 2011). Roasting is important for increasing food safety by eliminating pathogens and enhancing quality parameters by creating a more desirable flavor and textural profile to the consumer (van Boekel and others 2010). Roasting can also provide an increased bioavailability and functionality of certain nutritional components (van Boekel and others 2010).

Understanding of the roasting process is of interest because roasting is a critical processing step not only for peanuts, but many other food products such as coffee, cocoa, grains and other tree nuts. Roasting is central to the development of color, flavor and textural development through chemical reactions, heat transfer and drying which occur during roasting (Chiou and others 1991, Newell and others 1967, Saklar and others 2001, Simsek 2007). Color development is generally used as a way of measuring degree of roast because it's a quick, easy and nondestructive testing method (Manzocco and others 2000), as well as being an indicator of final peanut flavor (Smyth and others 1998). Coffee producers also use roast color as an indicator of final product quality (Baggenstoss and others 2008). The development of color is mainly a function of nonenzymatic browning, and more specifically the Maillard Browning Reaction (MBR) (Newell and others 1967, Saklar and others 2001).

In order for the MBR to occur in peanuts, roasting temperatures need to be at least approximately 150 °C (Davidson and others 1999). Color development depends on the initial composition of sugars and amino acids, as well as roasting time and temperature (Newell and others 1967, Rodriguez and others 1989).

The initial phase of roasting is characterized by a rapid lowering of the moisture content (MC) and A_w of the peanuts (Adams and De Kimpe 2009, deMan 1999, Liu and others 2011). MC significantly decreases during the first 5-10 minutes of roasting, and components such as total carbohydrates and glucose content have been found to dependent on MC during this time (Chiou and others 1991). The presence of these components will have an effect on the reactions that occur in subsequent roasting stages. After the initial rapid drying stage, color development has been reported to occur rapidly (Saklar and others 2001). Baggenstoss and others reported that the majority of aroma compounds being formed during coffee roasting also occur during medium dehydration (2008). However, during the time that the majority of flavor compounds are being produced MC has been reported to have little change (Smyth and others 1998).

The rate at which reactions occur during roasting will be affected by the roasting temperature as well as airflow through the roasting bed (Saklar and others 2001). These conditions in turn effect the reaction kinetics of roasting which are important to understanding the overall roasting process (Davidson and others 1999). During roasting, other factors which influence the rate of the MBR are A_w, temperature, the types of sugars and amino acids present, and pH (deMan 1999).

1.5 Maillard Browning Reaction

There are 4 main types of non-enzymatic browning reactions that occur in food: MBR, degradation of ascorbic acid, lipid peroxidation and caramelization (Davies and Labuza 1997). In peanuts, the main nonenzymatic browning occurs in the form of MBR. The MBR is also the main form of non-enzymatic browning during roasting of products such as tree nuts, coffee, cocoa and grains (Saklar and others 2001).

MBR is a complex series of reactions (**Figure 1.1**) needing both reducing sugars and amino acids to occur. The first step of the MBR is a condensation reaction between the carbonyl group from the sugar and the amine group from the protein. As the product loses water a Schiff base is formed which is then converted into an aldosylamine. The next step is the Amadori rearrangement, which can follow three major pathways: the formation of a diketosamine, enolization, or Strecker degradation. The final step is polymerization, which creates melanoidins and heterocyclic compounds which make up the majority of the flavor and aroma compounds. Flavor compounds are also formed during the Strecker degradation process; however, these flavors are often thought of as off-flavors. (Davies and Labuza 1997)

Melanoidins produced by the polymerization reaction are characteristic of the brown color and increase in molecular weight as browning increases. High molecular weight Maillard Browning products (MBP) have been associated with darker roasted coffee (Liu and others 2011) and darker beer (Hofmann 1998). Differences in color are perceived due to the unique absorbance of the melanoidins produced. Flavor compounds formed from the MBR consist of volatile heterocyclic such as pyrazines, pyrroles, pyridines, oxazoles, and oxalines (Schirack and others 2006). These heterocyclic compounds are formed during final steps of

the MBR and the production depends on several things such as the type and amount of sugars and amino acids present, the ratio of sugars to amino acids, temperature, time, and pH (Hofmann 1998, Manzocco and others 2000, Yilmaz and Toledo 2005).

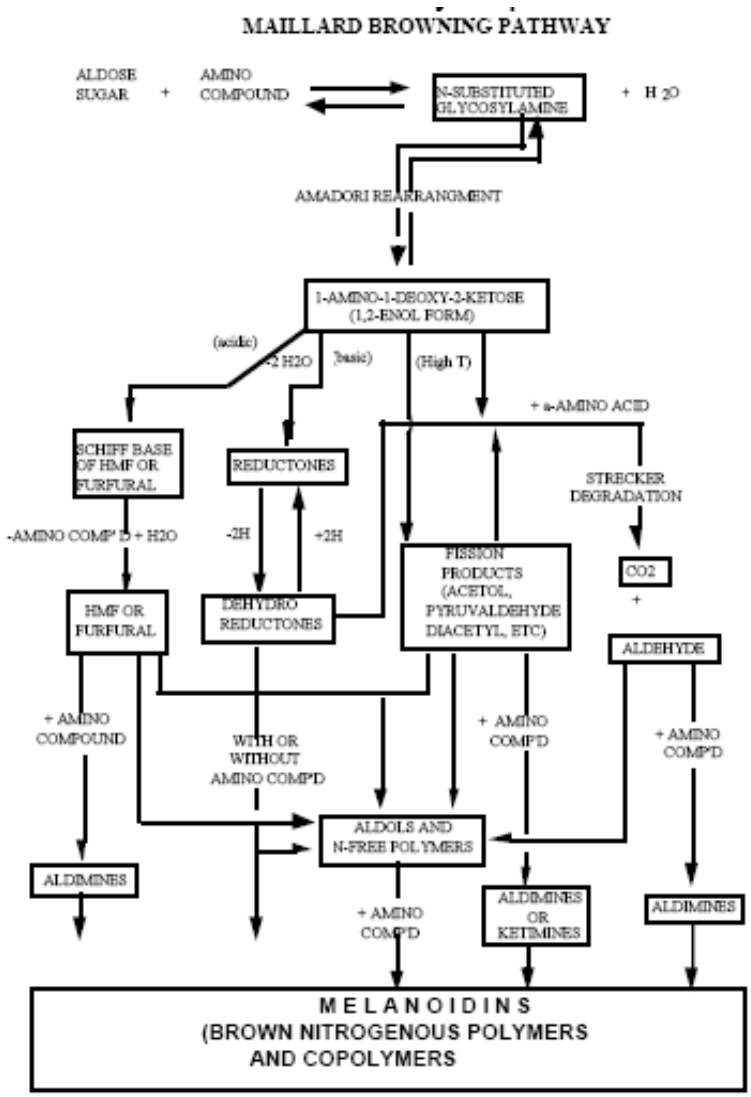

Figure 1.1 Schematic for nonenzymatic Maillard Browning Reaction (Davies and Labuza 1997).

1.6 Roasted Peanut Flavor

Human perception of flavor represents a combination of tongue and olfactory receptor responses interpreted simultaneously in the brain, which then produce a classification or judgment perceived as flavor (Baldwin and others 2011). The olfactory systems is comprised of 10-100 million unique receptors (Deisingh and others 2004). Each of these receptors can bind odor molecules, some at levels as small as parts per trillion (Breer 2003). The olfactory system is even further complicated because some odors can bind with multiple receptors and vice versa as well as combinations of odor compounds binding simultaneously to create a whole new perception in the brain (Baldwin and others 2011). Once odor compounds bind to a receptor, signals are sent via neural pathways to the brain to stimulate recognition (Baldwin and others 2011). The interpretation of these signals can be based on previous experiences, chemical and physical factors (Baldwin and others 2011). This complexity of human flavor perception can make flavor determination of food products difficult. Flavor characterization of food products can be done through traditional human sensory panels, instrumental analysis of volatile compounds, and more recently through technologies such as electronic-noses (E-Nose).

Descriptive sensory analysis (DSA) panels utilize a group of humans to make up a panel, which in turn functions as a single instrument (Meilgaard and others 1999). The typical size of DSA panel is 8-12 participants; all having good palate discrimination and the willingness to participate. DSA panels typically operate using Quantitative Descriptive Analysis (QDA) or the Spectrum ® method. There are several differences between QDA and the Spectrum ® method; however, one of the most important is the type of scale used. QDA

utilizes a product specific scale, whereas the Spectrum ® method utilizes a universal scale. For either type of panel, a lexicon must be developed in order to evaluate the product. Established peanut lexicon was developed by Johnsen and others and is still used as the current terminology for roasted peanut flavor (Johnsen and others 1988). DSA provides information about how the product rates on a set scale using defined lexicon. DSA will not give information about consumer preference or quantification of specific volatile compounds in the product. In order to identify and quantify specific volatile compounds found in a sample, instrumental analysis must be used. Gas chromatography (GC), GC- mass spectrophotometry (GC-MS), solid-phase microextraction (SPME), and GC-olfactometry (GC-O) have been utilized to identity volatile aromatic compounds of peanuts (Adams and De Kimpe 2009, Baker and others 2003, Buckholz and others 1980, Liu and others 2011, Schirack and others 2006). Information collected from these analytical methods can then be correlated with DSA to determine which volatile compounds are responsible for flavor.

Electronic systems seek to mimic the human response to sensory perception through using a combination of DSA and analytical evaluation. E-Noses utilize sensors that mimic odor receptors (Baldwin and others 2011). The main types of electronic sensors utilized in E-Nose systems for food products include organic polymers, metal oxides, quartz crystal microbalance and GC (Baldwin and others 2011). The most commonly used E-Nose sensors are the metal oxide semiconductor sensors (MOS), conducting polymer and surface acoustic wave sensors (Deisingh and others 2004, Ghasemi-Varnamkhasti and others 2009). MOS produce unique, dynamic responses to volatile compounds which are then correlated with sensory characteristics of the sample (Baldwin and others 2011). Electronic sensors have

been used to distinguish and identify volatile odor compounds in cheese, bread, oil and several other foods (Gursoy and others 2009, Mildner-Szkudlarz and Jelen 2010, Ponzoni and others 2008). However, E-Nose systems must be "trained" and calibrated to recognize patterns from the volatile profiles (Baldwin and others 2011). E-Noses are sensitive to temperature, relative humidity and sensor drift, making the use of these technologies (Baldwin and others 2011). These factors along with the complexity of the human olfactory system can make correlation of human sensory data and electronic sensors challenging (Baldwin and others 2011).

Peanut flavor is mainly developed during roasting, and factors such as variety, growing, harvesting, maturity, curing and storage conditions all have been shown to influence roasted peanut flavor (Rodriguez and others 1989, Sanders and others 1989). Immature peanuts of the same size and variety will roast to a darker color more rapidly than mature peanuts due to higher sugar contents in the less mature peanuts (Sanders and others 1989). Larger kernel size within the same variety is typically associated with maturity. Mature peanuts have been found to have higher amounts of proteins which can break down into free amino acids during roasting, allowing for greater development of typical peanut flavor (Rodriguez and others 1989). Color development is mainly a product of MBR, which utilizes sugars and amino acids found in peanuts. Sucrose is the most abundant sugar in peanuts, and it's inversion to glucose and fructose has been reported to aid in the development of roasted peanut flavor through the development of MBP (Newell and others 1967, Rodriguez and others 1989). The amino acids aspartic acid, glutamic acid, glutamine, histidine, asparagine, and phenylalanine have been reported to contribute to typical roasted

peanut flavor (Newell and others 1967). The denaturation of proteins and the breakdown of the polypeptide bonds during roasting allow free amino acids to participate in the MBR (Rodriguez and others 1989, Smyth and others 1998).

As roasting time increases the formation of volatile compounds increases. The most predominate MBP formed are the heterocyclic nitrogen compounds, followed by the heterocyclic oxygen compounds and then the non-heterocyclic compounds (Liu and others 2011). These non-heterocyclic compounds are mainly aldehydes, alcohols, ketones and esters and are associated with lipid degradation (Buckholz and others 1980, Liu and others 2011). Aldehydes are described as producing off-flavors in oils such as painty, green, beany or rancid (Liu and others 2011). One of the more predominate aldehydes is hexanal, which is often used as a marker for oxidative damage in oils. Hexanal is produced through the degradation of linoleate.

Pyrazines are heterocyclic nitrogen compounds and are thought to be primary compounds responsible for peanut flavor (Buckholz and others 1980, Liu and others 2011, Warner and others 1996). Several pyrazine compounds have been identified as contributing to peanut flavor, such as methylpyrazine, dimethylpyrazine, and methylethylpyrazine (Smyth and others 1998, Warner and others 1996). Other products of the MBR which will affect peanut flavor include melanoidins, pyrroles, furans and additional low molecular weight compounds (Schirack and others 2006).

The formation of these pyrazines is attributed to the self-condensation of α-aminoketones from the Strecker dehydration (Liu and others 2011). Roasting peanuts more than 30 minutes at a constant temperature has been reported to be associated with increased

furan derivatives, which are associated with having caramel like and fruity aromas (Liu and others 2011). High levels of pyrazines have also been correlated with dark roast and in excess amounts with bitter sensory attributes (Smyth and others 1998). Even though several compounds have been identified that are associated with peanut flavor, the simple combination of these compounds does not create peanut flavor, suggesting the system is very complex (Smyth and others 1998).

1.7 Texture

Along with flavor, texture is a key component in determining product acceptance. Food texture is a combination of the force required during mastication along with auditory responses perceived during mastication (Roudaut and others , Vickers 1984). Terms such as crispness and crunchiness are accepted as representing key auditory responses (Sandoval and others 2008). Both terms, crispy and crunchy have been reported to describe the texture of roasted oil seeds (Varela and others 2008).

In peanuts, MC plays an important role in the development of texture. MC decreases during roasting which alters the internal microstructure of the seed (Smyth and others 1998). This change in the microstructure helps to create the desired crunchiness of roasted peanuts and may have potential as a marker for textural properties (Smyth and others 1998) and has been shown to decreases the force required to compress peanuts after roasting (Kumar and others 2009). Similar results have been observed in other oilseeds such as almonds, hazelnuts, and cashews, which indicate that long roasting times decreases MC and increases crunchiness (Saklar and others 1999, Varela and others 2009, Wanlapa and Jindal 2006). High roasting temperatures have also been reported to decrease the amount of force needed

to compress nuts (Kumar and others 2009). However, if MC becomes too low an undesirable brittleness or crumbling effect has been observed (Kumar and others 2009).

Whole peanuts lack uniformity of individual kernels which causes difficulties for mechanical and acoustical texture analysis methods (Sandoval and others 2008). Bulk testing methods, in which multiple units are tested simultaneously, have been used in cereals and other oilseeds, and this approach minimizes variation due to lack of uniformity within the sample (Hung and Chinnan 1989, Sandoval and others 2008, Wanlapa and Jindal 2006). The use of a Kramer shear cell (KSC) for bulk testing allows for the compression responses of multiple seeds to be recorded simultaneously. This form of bulk testing has been used to analyze cereal texture as well as almonds, cashews, hazelnuts and peanuts (Sandoval and others 2008). Mechanical parameters from the KSC are derived from the resulting force vs. displacement curves, including the maximum force at compression. Max force has been reported to have good association with texture sensory terms (Wanlapa and Jindal 2006).

1.8 Oxidation in Peanuts

Oxidation in food products leads to decreased quality and shelf-life. Factors such as environmental stresses from harvesting or cutting, exposure to light, heat and air can all cause different forms of oxidation (Burton and Ingold 1986). Lipid oxidation in food is one of the main causes of off-flavors as well as loss of nutritional components (Warner and others 1996). Even under refrigerated conditions foods can undergo both autoxidation and lipid peroxidation (Burton and Ingold 1986). **Figure 1.2** depicts the main steps in radical chain oxidation reactions: initiation, propagation and termination (Burton and Ingold 1986).

Initiation

Production of $R\cdot$ (Rate= R_i) (1)

Propagation

$R\cdot + O_2 \rightarrow ROO\cdot$ (2)

$ROO\cdot + RH \rightarrow ROOH + R\cdot$ (3)

Termination

$ROO\cdot + ROO\cdot \rightarrow$ molecular products (4)

Figure 1.2 Steps of oxidation free radical chain reaction, where RH = lipid molecule and $R\cdot$ = carbon centered radical (Burton and Ingold 1986).

Since peanuts consist of approximately 50% oil, implementing strategies to minimize oil degradation is extremely important to the peanut industry. The fatty acid profile affects the rate of oxidation since degree of saturation has an effect on oxidation (Chandrasekara and Shahidi 2011). Typically oleic (18:1) acid accounts for about 50% of the lipid profile; however, high oleic varieties have been developed which increase the amount of oleic acid to approximately 80% of the lipid profile (Talcott and others 2005). Oleic acid is a monounsaturated acid and it is less prone to oxidation than linoleic (18:2) acid. High oleic peanut varieties contain higher ratios of oleic acid to linoleic acid. The oil from high oleic peanuts oxidizes at a slower rate than traditional peanut oil which increases the shelf life of high oleic peanuts (Baker and others 2002, Bolton and Sanders 2002, Norden and others 1987, Riveros and others 2010, Talcott and others 2005).

Primary oxidation products of lipids are hydroperoxides, which can be further broken down into secondary oxidation products such as alcohols and carbonyl compounds

(Chandrasekara and Shahidi 2011). A primary marker for oxidation in many food products is hexanal (deMan 1999). Hexanal is formed in peanuts as they oxidize, and it therefore used as a marker for peanut oxidation. Smyth and others demonstrated that high oleic cultivars had low amounts of hexanal production even after 80 days under accelerated storage conditions of 64 °C compared to normal oleic peanuts reaching high levels of hexanal production after only 20 days (1998).

In addition to the chemical markers of oxidation, sensory panels can discriminate off-flavors such as cardboard/stale and painty which are associated with lipid oxidation (Riveros and others 2010). Flavor attributes associated with oxidized flavors have been shown to be positively correlated with analyses such as peroxide value (PV), conjugated diene test, and p-anisidine values, which are used to measure oxidation products (Riveros and others 2010). The off-flavors ashy and stale/floral were reported to be associated with the compounds phenylacetaldehyde, guaiacol, and 2,6-dimethlypyrazine (Schirack and others 2006)

Other factors which can affect oxidation are A_w, MC, storage time and storage conditions. Roasted peanuts with $A_w > 0.44$ have been reported to have higher levels of oxidation (Baker and others 2002). Storing samples under vacuum conditions has been found to slow the rate of oxidation for both raw and roasted samples over time (Chun and others 2005). Roasted peanuts experienced greater tocopherol loss than raw peanuts making them more prone to oxidation (Chun and others 2005). However, modifying the roasting times and temperatures could affect the oxidation rate. Davis and others reported that at the same roast temperature, peanuts roasted to a darker color had less tocopherol loss under accelerated storage conditions than peanuts roasted to lighter colors (2010).

1.9 Antioxidant Activity in Peanuts

Many plant food sources contain natural antioxidants that aid in the preservation of the quality of nutrients, flavor and shelf life of the product. However, antioxidants are also often added to food products to increase the shelf-life and extend the quality of the products. Antioxidants are compounds that help to quench free radicals by reducing the rate at which oxidation occurs or by halting the chain reactions of oxidation. These two classes of antioxidants are termed preventative and chain-breaking antioxidants, respectively (Burton and Ingold 1986). Additionally compounds can act as antioxidants by chelating transition metals. Antioxidants are generally thought of as beneficial compounds; however, having high concentrations of antioxidants can cause pro-oxidant qualities to be exhibited.

In peanuts the main oil soluble antioxidant compounds are tocopherols, which are more commonly known as Vitamin E (Hashim and others 1993). Vitamin E is combination of α, β, γ, and δ-tocopherols (Ball and Ratcliff 1978) and act as chain-breaking antioxidants (Burton and Ingold 1986). α-tocopherol has been reported to have the greatest antioxidant capacity (Burton and Ingold 1986, Hashim and others 1993). β,γ and δ-tocopherols can potentially convert to α-tocopherol within peanuts, which increases their biological activity (Hashim and others 1993). Runner varieties of peanuts have been reported to contain the highest tocopherol levels for α,γ, and δ-tocopherols when compared to 3 different Virginia varieties (Hashim and others 1993).

During roasting tocopherols help to prevent oxidation of peanuts by halting free radical chain reactions. With increasing time and heat, tocopherol content is expected to

decrease as it is utilized as an antioxidant. However, it has been reported that antioxidant capacity of roasted peanuts is significantly higher than raw peanuts (Davis and others 2010, Talcott and others 2005). Cashew nuts roasted at a high temperature of 130 °C for a constant time of 33 minutes have also demonstrated significantly higher oxidative stability than cashew nuts roasted at low temperatures of 70 °C for 6 hours(Chandrasekara and Shahidi 2011). This increased oxidative stability was attributed to additional antioxidants compounds such melanoidins and phenolic compounds created through the MBR during roasting (Acar and others 2009, Chandrasekara and Shahidi 2011, Davis and others 2010, Talcott and others 2005). Antioxidant properties of MBP have been shown in model systems such as coffee, breads, and fermented foods (Amarowicz 2009, Manzocco and others 2000). p-coumaric acid has a high antioxidant potential and has been reported to significantly increase in peanuts with roasting due to its release from the native esterified form (Talcott and others 2005).

Melanoidins, which contribute to the characteristic brown color of many roasted products, have been reported to scavenge free radicals and chelate metals (Manzocco and others 2000, Yilmaz and Toledo 2005). The types of potential antioxidant properties generated by the MBP depends on the types and amounts of initial reactants (**Table 1.3**). Having different methods of antioxidant activity in food products allows for better protection against oxidation. The main sugars that react in the MBR in peanuts are fructose and glucose. Lysine, which is found in peanuts, has a readily available amine group that makes it extremely reactive in the MBR (deMan 1999). Therefore, some potential methods of

antioxidant protection created during the MBR could be copper chelating, DPPH radical scavenging, peroxyl radical scavenging, and hydroxyl radical scavenging (**Table 1.3**).

Table 1.3 Antioxidant properties of Maillard Browning Products reported from model systems (Yilmaz and Toledo 2005).

Model System Sugar- Amino Acid	**Mode of antioxidant properties**
Glu-His	Copper chelator Oxygen radical scavenger Peroxyl radical scavenger
Glu-Lys	Copper chelator DPPH radical scavenger Peroxyl radical scavenger Hydroxyl radical scavenger
Glu-Gly	Copper chelator Peroxyl radical scavenger Hydroxyl radical scavenger Fe^{2+} radical scavenger
Fru-Lys	Copper chelator Hydroxyl radical scavenger

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CHAPTER 2

Effect of Different Time/ Temperature Roast Combinations on Nutritional and Mechanical Properties of Peanuts

2.1 Abstract

Peanuts in North America and Europe are primarily consumed after dry roasting. Standard industry practice is to roast peanuts to a specific surface color (Hunter L-value) for a given application; however, equivalent surface colors can be attained using different roast temperature/time combinations. Accordingly, a single lot of runner peanuts was roasted using five roast temperatures (147 ºC, 157 ºC, 167 ºC, 177 ºC, and 187 ºC) and various roast times to obtain 3 degrees of roast corresponding to L-values of 53±1, 48.5±1, and 43±1, for light, medium and dark roasts, respectively.

Moisture content (MC), mechanical textural properties, hydrophilic oxygen radical adsorption capacity (H-ORAC), tocopherol content, sugar content, and other characteristics were determined across the roast matrix. MC ranged from 0.41% for the 147 ºC dark roast to 1.70% for the 187 ºC light roast peanuts. At the same roast temperature, MC decreased as peanuts became darker; however, for a given color, MC decreased with decreasing roast temperature due to longer roast times required for specified color formation. Peak force at compression as measured by a Kramer shear cell positively correlated (R^2=0.64) with MC. Total tocopherol contents ranged from 140 to 470 μg/g oil and decreasing MC correlated (R^2=-0.67) with increased total tocopherols. Total sugar contents of completely defatted flours ranged from approximately 7.4 to 8.6 g /100 g. Glucose and fructose were significantly ($p<0.05$) influenced by roast color and temperature. The variation in characteristics related to method of roasting is sufficient to suggest influences on final product shelf life and consumer acceptability.

2.2 Introduction

The majority of peanuts in North America and Europe are consumed dry roasted, making the sensory and nutritional properties of these materials of valuable interest to the peanut industry. Proper roasting is critical to flavor and texture development as well as antioxidant and polyphenolic content of the final product. Standard industry practice is to roast peanuts to a specific color (L-value). As color develops during roasting, Maillard browning reactions (MBR) create various volatiles, including pyrazines, pyrroles, and furans, which are major contributors to roasted peanut flavor (Newell and others 1967, Warner and others 1996). Roasting also reduces moisture content and modifies the internal microstructure of peanuts to create the characteristic crunchy and crispy textures of roasted peanuts (Lee and Resurreccion 2006).

Raw peanuts contain an initial level of inherent antioxidants. During roasting some antioxidants are lost due to heat instability, while others will be formed via chemical reactions such as Maillard browning (Acar and others 2009). Maillard reaction products (MRP) have shown substantial antioxidant capacities in various model systems and roasted foods, including coffee, oilseeds, baked goods, etc (Manzocco and others 2000, Yilmaz and Toledo 2005). Roasting also increases polyphenolic content in peanuts and other foods by releasing compounds such as p-coumaric acid and hydroxybenzoic compounds which can serve as antioxidants (Talcott and others 2005b). Vitamin E is an important class of lipid soluble antioxidants in peanuts (Burton and Ingold 1986). During storage of peanuts under atmospheric conditions, degradation of Vitamin E occurs more rapidly in moderately roasted peanuts as compared to raw peanuts (Chun and others 2005). Recent research indicated that

under accelerated storage conditions, Vitamin E in darker roasted peanuts was higher than that measured in moderately roasted, or even raw, peanuts (Davis and others 2010). Increased antioxidants resulting from the roasting process are thought to protect Vitamin E in the darker roasted peanuts (Davis and others 2010) .

While the industry typically roasts to a specific color for a given application, peanuts can be roasted to the same color using different time/temperature combinations (**Figure 2.1**). The kinetics of browning reactions contribute to, and are expected to correlate with, other key reactions in peanuts associated with flavor, texture, antioxidant capacity, etc. Accordingly, the objective of this research was to evaluate the nutritional characteristics of roasted peanuts systematically prepared using a range of time/temperature combinations. Peanuts were dry roasted to color values typically associated with "light", "medium" and "dark" intensities using 5 different time/temperature combinations for each of the three colors. Roasted peanuts were evaluated for textural and nutritional characteristics. Correlations among texture, and nutritional properties as related to color development and roasting conditions were determined. This research should result in a more comprehensive understanding of key reactions contributing to roasted peanut texture and nutritional composition and in turn allow these properties to be optimized during industrial roasting.

2.3 Materials and Methods

2.3.1 Materials

A representative sample of medium-grade size Georgia Green runner peanuts (*Arachis hypogaea*) were obtained from a single harvested lot. According to normal practices the

peanuts had been harvested, cured, shelled and stored prior to delivery to North Carolina State University.

2.3.2 Peanut Roasting

Peanuts were brought to room temperature and roasted in a lab scale oven (Despatch, Minneapolis, MN) to 3 roast colors as determined by a Hunter colorimeter (Light 53±1, Medium 48.5±1, and Dark 43±1) at 5 different temperatures (147 ºC, 157 ºC, 167 ºC, 177 ºC, and 187 ºC). Roasting times were dependent on the roast color and temperature and were determined using linear regression on the preliminary roast curves shown in **Figure 2.1**. The resulting roast times are provided in **Table 2.1**. Following roasting, samples were placed onto a forced air blower, manually blanched, placed into 8 oz glass mason jars, flushed with nitrogen and stored in cold storage until further analysis. Samples of blanched peanut skins were placed into labeled zip lock bags and stored in refrigerated storage for subsequent analysis.

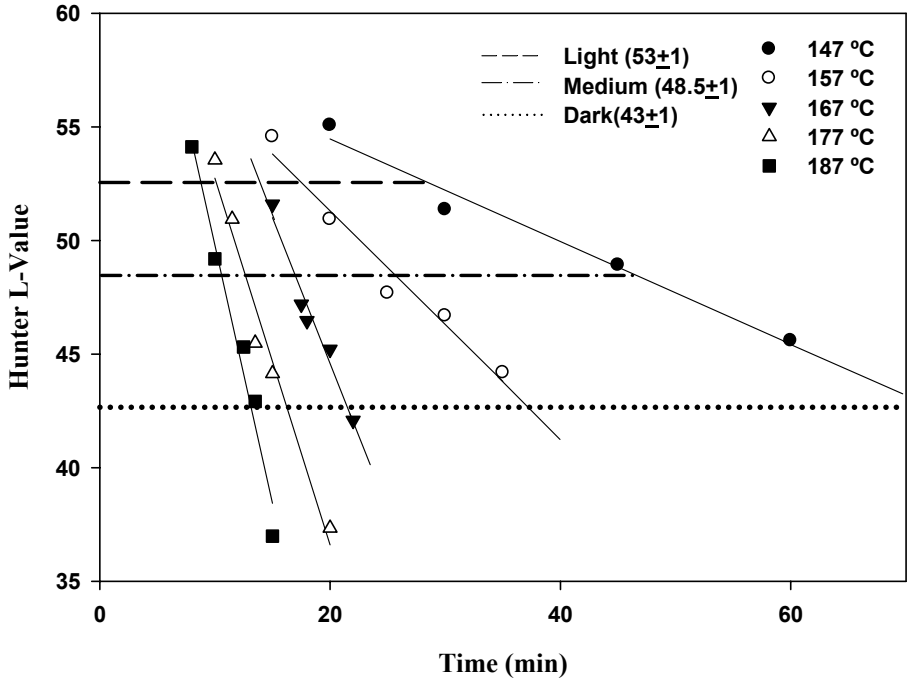

Figure 2.1 Color (Hunter L-Value) development of peanuts roasted at different temperatures. Solid, straight lines represent best linear fits of data. Dashed, horizontal lines represent Hunter L-Values associated with roast colors (Light = 53±1, Medium = 48.5±1, Dark = 43±1).

Table 2.1 Average roasting times for all roast color and temperature combinations.

	147 ºC	157 ºC	167 ºC	177 ºC	187 ºC
Roast Color (L-Value)	Time (minutes)				
Light (53±1)	26.5	16.6	13.5	10.0	8.6
Medium (48.5±1)	46.4	25.6	17.0	12.2	10.6
Dark (43±1)	70.8	36.6	21.2	15.4	12.3

2.3.3 Statistical Analysis

A complete randomized split plot block design was used. This design eliminates variation due to day or oven equilibration concerns with varying temperature. A block was defined as one week containing all 15 roast time/temperature combinations. Plots were represented by a day, which contained all roast colors for a given temperature. Within plots roast colors were randomly assigned to obtain a balanced distribution for each temperature. Data was analyzed by analysis of variance (ANOVA) using SAS® Ver. 9.0 (Cary, NC, U.S.A.). Means were separated using Duncan's multiple range test when a significant F-value was obtained. Linear correlations between attributes were made using averages of the three roasts that distinguished each time/temperature combination.

2.3.4 Water Activity (A_w)

Water activity was measured using a bench-top Decagon Aqua Lab water activity meter (Pullman, WA). Whole seed roasted samples were brought to room temperature and ground into a coarse powder using a coffee grinder. Powder was then placed into Aqua Lab sampling containers to approximately half full and the vapor allowed to equilibrate for approximately 3 minutes prior to a water activity measurement. All samples were measured in triplicate at the instrument.

2.3.5 Moisture Content (MC)

Whole peanut seeds from each time/temperature roast combination were placed in triplicate into aluminum pans, weighed and transferred into an oven at 130 ºC for 6 hours. Peanuts were then cooled to ambient temperature, weighed and MC calculated using the formula below:

$$MC = \frac{(\text{wet mass} - \text{dry mass})}{\text{dry mass}} \times 100\%$$

2.3.6 Sugar Content

Sugars were analyzed by high pressure liquid chromatography (HPLC) (Pattee and others 2000). The column was a CarboPac^{TM} PA-1 (Dionex Cat. No. 035391), 4 mm i.d. fitted with a CarboPac^{TM} PA-1 guard column (Dionex Cat. No. 043096) and the mobile phase was 200 mM NaOH used at an isocratic flow rate of 1.0 mL/min. After mechanical oil expression, peanut flour was defatted using a Soxhlet apparatus with hexane as the extraction solvent. Defatted samples were air dried and then 0.09-0.10 g were dissolved into 15 mL of 60:25:15 methanol: chloroform: deionized water (DI) water extraction solvent. Samples were then vortexed and sonicated for 20 minutes, centrifuged and the solvent decanted and evaporated overnight. Internal standards of lactose (Aldrich Cat No. 25,971-3) and cellobiose (Fluka, Cat No. 221050) were then added and swirled until residue was removed from the beaker. Fifty µL of sample solution were then brought to 2 mL with DI water, vortexed and decanted to a syringe fitted with a Dionex OnGuard ® II H Filter (Dionex Cat. No. 057085). The first mL was discarded and the second collected in an HPLC autosampler vial and analyzed via HPLC. A standard made up of 9.5 mL DI water, 50 µL of internal standard and 50 µL of standard solution consisting of 5 mg of myo-inositol (Sigma Cat No. I-5125), 10 mg of glucose (Sigma Cat No. G-5250), 15 mg of fructose (Fisher Cat No. L-95), 50 mg of sucrose (Fisher Cat No. S-5), 20 mg of raffinose (Aldrich Cat No. 20,667-9) and 20 mg of stachyose (Sigma Cat No. S-4001) diluted to 50 mL with DI water. Identification of sugars was done through comparison of retention times of unknown samples

to know standards. Quantification was completed by measuring peak areas and comparing to total peak areas.

2.3.7 Amino Acid Assay

A 6N hydrochloric acid (HCl) with 1% Phenol was prepared as the extraction solvent. A National Institute of Standards and Technology (NIST) peanut butter standard was used as a reference. Samples and reference were prepared by adding 0.05 g of defatted peanut meal or NIST reference into a CEM hydrolysis vial with the addition of 4 mL 6N HCl w/ 1% Phenol. The CEM vial was then sealed and heated for 10 minutes at 165 ºC. Following extraction, samples were brought to 25 mL with 0.02N HCl. Dilutions of 1:10 and 1:5 in 0.02N HCl were placed into AA split cap vials for defatted peanut meal and NIST reference, respectively. The hydrolysates were analyzed with a Hitachi L-8900 Amino Acid Analyzer (Hitachi High Technologies, Inc.) according to the operation manual. In this method, after samples are hydrolyzed, free amino acids are separated with an ion exchange column and the amino acids are then derivatized with ninhydrin for detection at 570 and 440 nm. Data analysis was performed with EZChrom Elite software for the Hitachi Amino Acid Analyzer.

2.3.8 Tocopherol Analyses

Tocopherols were analyzed by HPLC using a Luna silica column 5µ, 250 mm length, 4.60 mm i.d. (Phenomenex, Torrance, CA, Cat No. 00G-4274-EO). A mobile phase of 1% isopropanol in hexane was used at a flow rate of 1.2 mL/min (Hashim, Koehler, Eitenmiller, & Kvien, 1993). Roasted samples were ground in a coffee grinder, wrapped in two layers of cheesecloth and mechanically pressed using a Carver press to obtain expressed oils. Approximately 0.18-0.20 g expressed oil was diluted into the 0.8 mL 1% isopropanol in

hexane solvent. Twenty μL of diluted samples were injected onto the column and measured using a Waters 2487 Dual Wavelength Absorbance Detector set to 294 nm. Internal standards of α, β, γ, and δ tocopherols were diluted into the 1% isopropanol in hexane solvent and used to identify tocopherol concentrations in the samples. Beer's Law and UV maxima of the solutions were used to calculate the concentration of the standards. To calculate the unknown tocopherol contents in the samples, peak areas of the standards and samples were compared.

2.3.9 Peroxide Value Analysis

Peroxide values (PV) were analyzed using the A.O.C.S Official Method Cd 8-53. Oil from each roasted samples in the amount of 15 mL was placed in an open glass petri dish at accelerated storage conditions of 85 $\pm$ 3 ºC. After 7 days, 5.00 g $\pm$ 0.05 g of each sample was weighed and 30 mL of 3:2 acetic acid: chloroform solution was added to dissolve the oil. Saturated potassium iodine solution was added in the amount of 0.5 mL and the mixture allowed to stand for exactly 1 minute. After the time elapsed, 30 mL of DI water were added and the mixture titrated with 10 N sodium thiosulfate. The titration is complete when the color changes from reddish-brown or orange to white. Peroxide value was then calculated using the following formula.

$$\text{Peroxide Value (milliequivalents peroxide/1000 g sample)} = \frac{(S - B) \times N \times 1000}{\text{mass (g) of sample}}$$

Where: B = titration of the blank, mL
S = titration of the sample, mL
N = normality of the sodium thiosulfate solution

2.3.10 Extraction of Roasted Peanuts and Corresponding Blanched Skins for Antioxidant Analysis

A Dionex (Sunnyvale, CA) ASE® 200 Accelerated Solvent Extractor was used to extract raw and roasted peanuts as well as corresponding skins (Wu and others 2004). Hydrophilic extraction was performed using the degassed solvent 70:29.5:0.5 Acetone/Water/ Acetic Acid (AWA) with a static phase of 5 minutes, 60% flush, 60 second purge and temperature setting of 80 ºC. Whole seed peanut samples were finely ground into a powder using a coffee grinder. Powders from whole seed samples and skins in the amount of 1.0 g and 0.5 g respectively were mixed with the 25 g of sand and placed in the extraction cell. Upon completion of the cycle extracts were brought up to 50 mL with AWA.

2.3.11 Hydrophilic-Oxygen Radical Absorbance Capacity (H-ORAC) assay

H-ORAC was measured using an adapted procedure (Prior and others 2003). Fluorescence was measured using a SAFIRE^2 microplate reader with Magellan (v. 6.1) reader software (Tecan USA, Raleigh, NC). Costar polystyrene flat-bottom black 96 microwell plates (Corning; Acton, Massachusetts) were used to contain the assay reagents. Sample dilutions of 1:100 were prepared from the hydrophilic extractions of the whole peanuts and 1:1000 of the hydrophilic extractions of skins in 75mM phosphate buffer pH 7.4. A Trolox (Aldrich; Milwaukee, WI) standard curve was created using standards of 50 μM, 25 μM, 12.5 μM, 6.25 μM, and 3.12 μM Trolox in phosphate buffer. A solution of 70 nM Fluorescein (Reidel-deHaen; Seelze, Germany) in 75mM phosphate buffer was prepared daily. A 153 mM solution 2,2'-azobiz (2-amidino-propane) dihydrochloride (AAPH) (Wako; Richmond, VA) in 75mM phosphate buffer was prepared daily and immediately prior to use.

130 μL of sample or Trolox dilutions for the standard curve were added to the microwell plate in triplicate, followed by the addition of 60 μL of FL to each microwell using a multi-channel pipette. The plate was then incubated in the SAFIRE^2 for 15 minutes and allowed to equilibrate to 37 ºC. Following equilibration, 60 μL of AAPH solution were added to each well using a multi-channel pipette. Fluorescence readings (Excitation wavelength =483 $\pm$ 8 nm, Emission wavelength =525 $\pm$ 12 nm) were collected over 90 min. Kinetic cycles were set at 1 min with medium intense orbital shaking every 5 sec. Data was presented as relative fluorescence units ranging from 0 to 60,000 relative fluorescence units. Resulting data was then exported to Excel for subsequent analysis. The net area under the curve was correlated to Trolox concentrations using a linear model standard curve to determine the Trolox equivalent (TE) of the roasted samples.

2.3.12 Kramer shear cell (KSC) compression analysis

An Instron universal materials testing machine (model 5565; Instron, Norwood, MA) mounted with a 10 plate KSC and 5 kN load cell was used to analyze multi-seed mechanical properties during compression. The Instron was lowered at a crosshead speed of 100 mm/min onto 15 g of whole peanut kernels from each sample evenly distributed with no overlapping in the KSC (internal dimensions of 70 x 80 x 55 mm). Analysis was performed in triplicate for each roasted sample. A diagram of the Kramer shear cell is shown in **Figure 2.2**. Multiple data points were collected from the resulting Force vs. Displacement curves, including the curve peak, which corresponds to maximum force at fracture. Data was exported to Excel for further analysis.

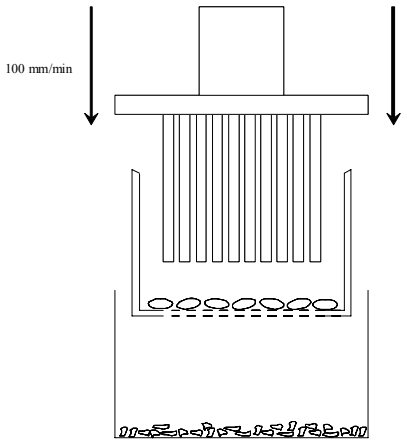

Figure 2.2 Diagram of Kramer Shear Cell for oilseed textural analysis.

2. 4 Results and Discussion

Table 2.2 Correlation coefficients (R^2) for analysis of peanuts roasted to a variety of time temperature combinations. Numbers in bold represent significant correlations ($p<0.001$).

	Roasting Time	Temperature	Surface L-Value	Surface a-Value	Surface b-Value	PV	Lysine Content	Total AA Content	Arginine Content	Max Force
Roasting Time	**1.00**	**-0.77**	-0.34	0.21	-0.12	-0.38	-0.29	-0.25	-0.26	-0.47
Temperature		**1.00**	-0.03	-0.02	-0.31	0.36	-0.07	0.16	0.10	0.38
Surface L-Value			**1.00**	-0.77	**0.92**	0.18	**0.93**	0.07	0.18	0.49
Surface a-Value				**1.00**	**-0.73**	-0.05	**-0.70**	-0.21	-0.28	-0.35
Surface b-Value					**1.00**	0.13	**0.84**	-0.01	0.12	0.30
PV						**1.00**	0.07	-0.09	-0.08	0.33
Lysine Content							**1.00**	0.34	0.44	0.45
Total AA Content								**1.00**	**0.98**	0.08
Arginine Content									**1.00**	0.14
Max Force										**1.00**

Table 2.2 Continued

	H-ORAC	Total Sugar Content	Glucose Content	Sucrose Content	Fructose Content	Tocopherol Content	Alpha Tocopherol	Beta Tocopherol	Gamma Tocopherol	Delta Tocopherol	MC	A_w	H-ORAC Skins
Roasting Time	-0.07	-0.37	0.44	-0.34	**-0.62**	**0.65**	**0.74**	-0.08	0.51	-0.04	**-0.71**	-0.52	-0.08
Temperature	0.08	0.24	-0.09	0.23	**0.72**	**-0.59**	**-0.64**	-0.06	-0.52	0.12	0.47	0.36	-0.13
Surface L-Value	-0.23	0.43	**-0.78**	0.41	-0.11	-0.50	-0.56	-0.39	-0.36	-0.39	**0.80**	0.49	0.13
Surface a-Value	0.11	-0.20	**0.57**	-0.19	0.08	0.45	0.48	0.39	0.35	0.25	**-0.59**	-0.42	-0.04
Surface b-Value	-0.29	0.37	**-0.68**	0.37	-0.33	-0.22	-0.28	-0.24	-0.11	-0.34	**0.58**	0.25	0.10
PV	-0.25	0.41	-0.09	0.43	0.22	**-0.82**	**-0.75**	-0.50	**-0.86**	-0.19	0.33	-0.12	0.00
Lysine Content	-0.14	0.31	**-0.69**	0.27	-0.06	-0.50	-0.53	-0.38	-0.39	-0.53	**-0.69**	0.50	0.05
Total AA Content	0.25	-0.16	0.00	-0.19	0.25	-0.26	-0.22	-0.03	-0.30	-0.27	0.02	0.21	-0.19
Arginine Content	0.24	-0.12	-0.06	-0.16	0.21	-0.26	-0.23	-0.05	-0.28	-0.32	0.11	0.26	-0.17
Max Force	-0.02	0.10	-0.41	0.07	0.12	-0.58	-0.58	-0.43	-0.50	-0.39	**0.64**	0.48	-0.12
H-ORAC	**1.00**	-0.35	0.16	-0.41	0.04	-0.01	0.05	0.12	-0.05	0.10	-0.14	0.26	-0.03
Total Sugar Content		**1.00**	-0.23	**0.99**	0.42	-0.25	-0.32	-0.04	-0.17	0.25	0.49	0.07	-0.06
Glucose Content			**1.00**	-0.23	0.25	0.51	0.57	0.24	0.38	0.37	**-0.68**	-0.39	-0.30
Sucrose Content				**1.00**	0.38	-0.22	-0.28	-0.02	-0.14	0.26	0.46	-0.01	-0.07
Fructose Content					**1.00**	-0.41	-0.48	0.11	-0.34	0.34	0.29	0.30	-0.16

Table 2.2 Continued

	Tocopherol	Alpha Tocopherol	Beta Tocopherol	Gamma Tocopherol	Delta Tocopherol	MC	A_w	H-ORAC Skins
Tocopherol	**1.00**	**0.97**	0.48	**0.96**	0.24	**-0.67**	**-0.60**	-0.23
Alpha		**1.00**	0.35	**0.87**	0.15	**-0.75**	**-0.64**	-0.26
Beta			**1.00**	0.53	0.47	-0.18	-0.19	0.03
Gamma				**1.00**	0.28	-0.49	-0.50	-0.19
Delta					**1.00**	-0.21	-0.16	0.14
MC						**1.00**	**0.61**	0.05
A_w							**1.00**	0.13
H-ORAC Skins								**1.00**

2.4.1 Moisture Content

Moisture content (MC) is a critical factor affecting the flavor, texture and shelf life of most foods, as MC generally influences the rate of numerous reactions important to food quality (deMan 1999). As peanuts are roasted, moisture is released into the atmosphere. The rate at which the moisture is released will depend on both the roast temperature and the amount of time that the samples are roasted. Regardless of roast temperature, MC decreased in a curvilinear fashion with increasing roast time (**Figure 2.3**). The sample with a MC between 5-6% was the raw, unroasted control. When not considering data for the raw sample, the plot of MC vs. roasting time displayed a more linear trend (R^2=-0.71). As discussed below, MC of the roasted samples seemed to critically affect and/or predict measurements of numerous other chemical and physical attributes of the seed known to be important to final product quality. Surface darkness, as quantified by the Hunter L value, strongly correlated with MC (R^2=0.80). Since color development is known to be largely due to the MBR and the formation of MBP, this correlation indicates that MC is important to the rates and extent of this reaction.

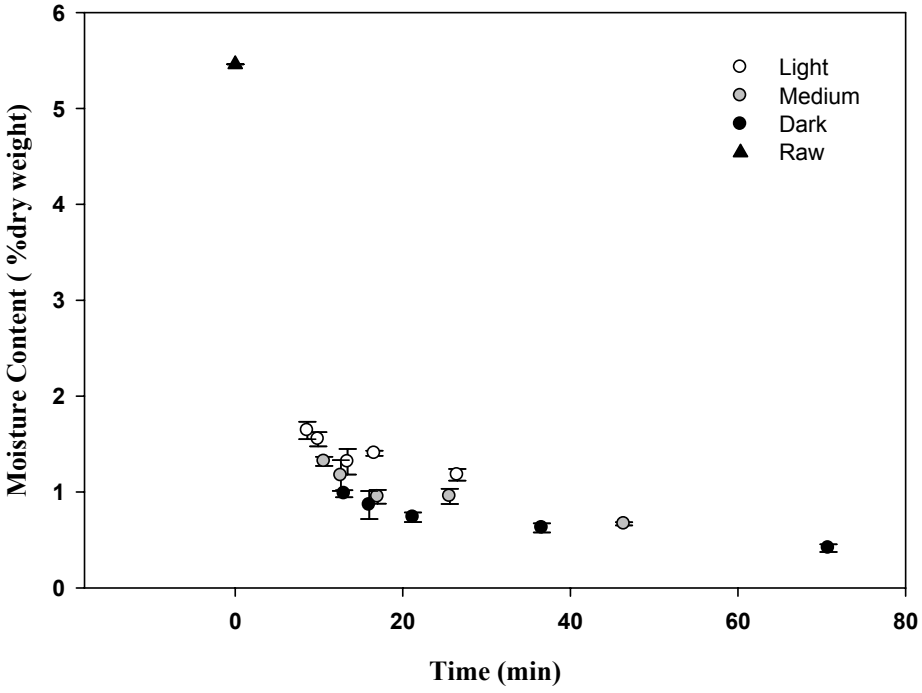

Figure 2.3 Moisture content vs. roast time (min) of raw peanuts and peanuts roasted to a variety of different time/temperature combinations.

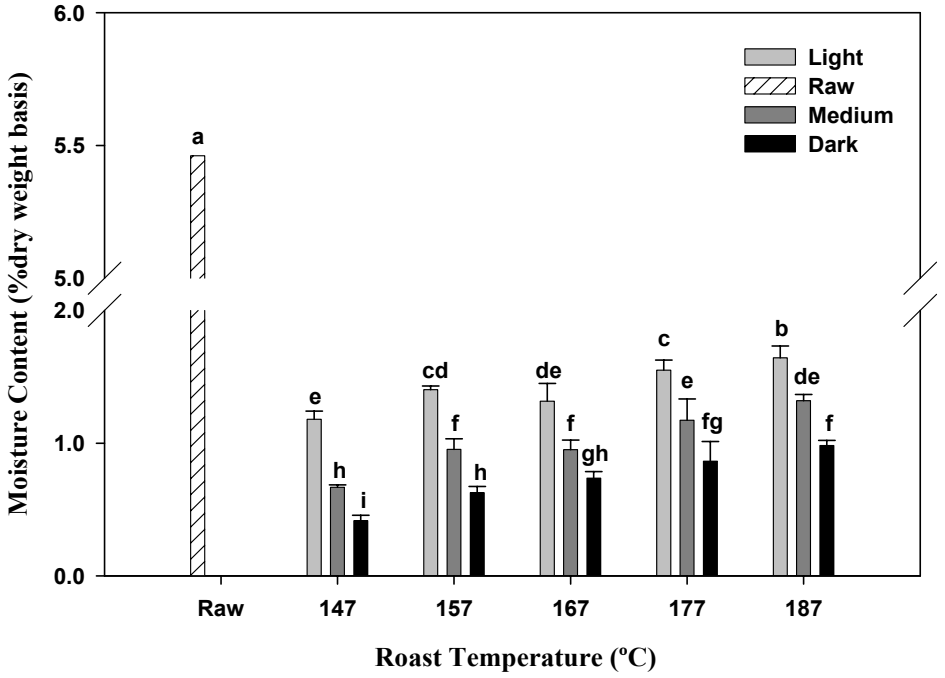

Figure 2.4 Moisture content of raw peanuts and peanuts roasted to a variety of different time/temperature combinations.

MC data for all 15 time/temperature treatments and the raw-blanched peanut seed is presented in terms of dry weight percentage in **Figure 2.4**. All roasted samples have lower ($p<0.05$) MC than the raw-blanched sample. At a given roast temperature, the dark roast samples had the lowest MC followed by the medium and light roasted samples. At a given roast temperature, the longer times in the oven necessary for darker color formation in turn decreased MC (**Figure 2.3**).

2.4.2 Water Activity (A_w)

A_w is another factor known to be important for determining the rates at which reactions critical to food quality occur (Labuza and others 1970). A_w is a measurement of the amount of free water available within the food matrix to participate in reactions. An A_w of 0.3-0.8 is conducive for lipid oxidation as well as nonenzymatic browning (deMan 1999). MC and A_w were moderately linearly correlated (R^2= 0.61) (**Table 2.2**) and A_w displayed similar trends across roast temperature and colors (**Figure 2.5)** as observed for MC (**Figure 2.4**). Despite these similarities, A_w was not significantly correlated with surface colors, which suggest that MC more strongly influences color development. However, A_w did show a strong negative correlation across roasting with total tocopherols and α- tocopherol (**Table 2.2**), meaning samples with lower A_w tended to have higher tocopherols. A_w was measured approximately 6 months after moisture measurements, and this additional storage time and this time in storage could affect measured A_w.

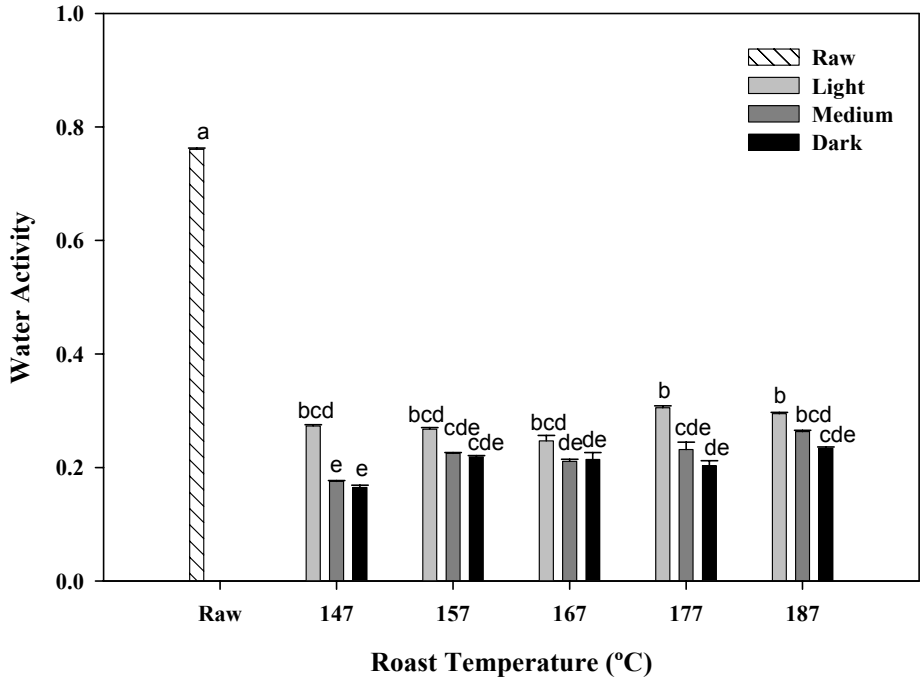

Figure 2.5 Water Activity of raw peanuts and peanuts roasted to a variety of different time/temperature combinations.

2.4.3 Sugar Analyses

Sugar content of peanuts is critical to the development of peanut color and flavor as these compounds are central in the MBR (Mason and others 1969, Newell and others 1967). Total sugar content for peanuts is a combined measure of glucose, fructose, sucrose, raffinose, and stachyose. Sucrose is the most abundant sugar found in peanuts, yet as a non-reducing sugar it does not participate in the MBR; however, heat can cause some sucrose to be converted into glucose and fructose- both of which are reducing sugars (Reyes and others1982, Mascon and others1969). Peanuts also have a small, baseline level of these

monosaccharides naturally present. These monosaccharides participate in the MBR ultimately resulting in the formation of certain phenolic compounds which are largely characteristic of peanut flavor (Newell and others 1967). Total sugar contents and sucrose contents were strongly correlated R^2=0.99 (**Table 2.2**) as sucrose was the predominate sugar detected in these samples.

Fructose content was found to have a strong correlation with both time and temperature, R^2=-0.62 and 0.72, respectively (**Table 2.2**). Overall, fructose content appeared to be more roast temperature dependent than color dependent. Averaged across all roast colors at a given roast temperature, fructose content generally decreased with decreasing roast temperature (**Figure 2.6**). Beyond the baseline level of fructose naturally present in the peanuts, factors influencing detectable fructose levels with roasting include consumption of this sugar in the MBR and inversion of sucrose to yield additional fructose (and glucose). Increased roasting temperatures at equivalent roast times, or increasing roast temperatures at equivalent roast times are hypothesized to decrease this sugar, as both of these conditions likely favor increased Maillard browning; however, higher roast temperatures and/or longer roast times should also favor sucrose inversion which could increase levels of free fructose. As such, levels detected in these samples likely represent a balance of these competing reactions. It is noted that detectable sucrose levels across all roast samples were not statistically different; however, sucrose is present at much higher levels than fructose (or glucose) and hence minor chances in sucrose content could strongly influence detectable fructose.

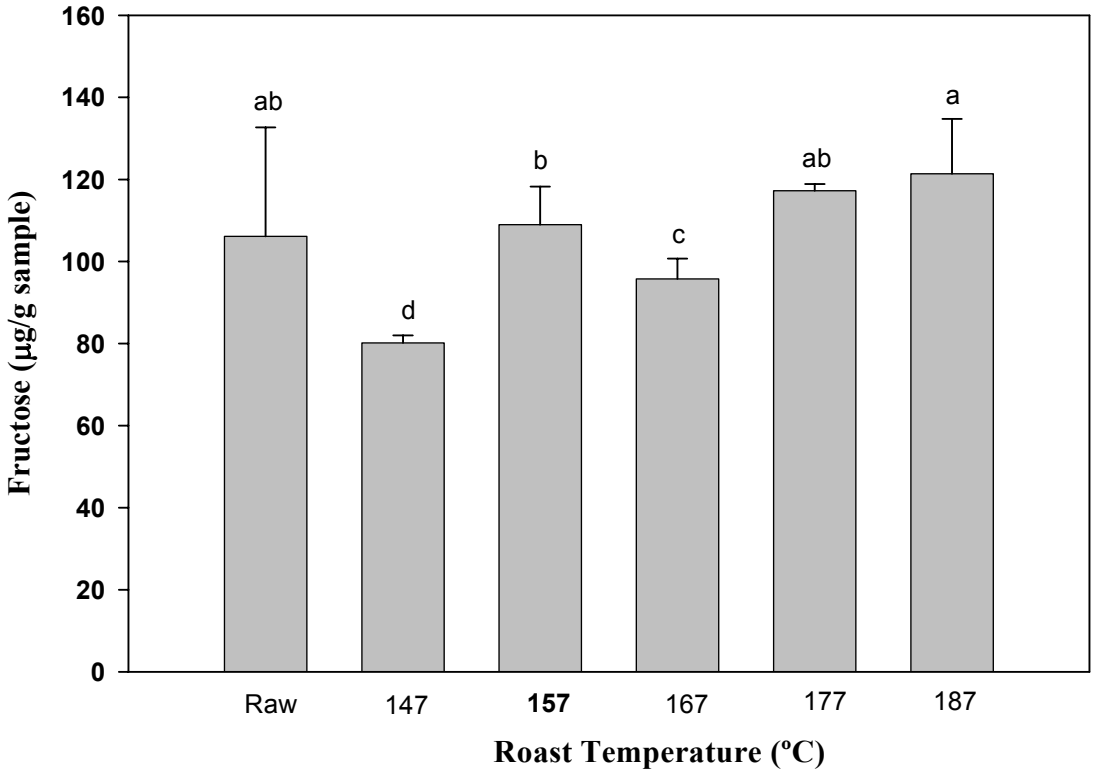

Figure 2.6 Fructose content of raw peanuts and peanuts roasted to different colors at varying temperatures.

Glucose content increased from light to dark roast within each roast temperature; however, at equivalent roast colors, glucose was minimally affected by roast temperature, suggesting that glucose content is more dependent on roast color than roast temperature and detectable levels of this sugar are summarized accordingly in **Figure 2.7**. Glucose content and surface L-value of peanuts were significantly correlated ($p<0.001$) (**Table 2.2).** As glucose is a primary substrate for the MBR, and this reaction is expected to decrease

detectable glucose levels, the overall increase in detectable glucose with darker color formation suggests more glucose is being generated, than consumed, with darkening roast colors. Sources of this free glucose could be inverted sucrose or release of glucose or breakdown of raffinose and stachyose, both of which decreased with darkening roast color (data not shown). Further work and analyses would be needed to better understand these potential hypotheses.

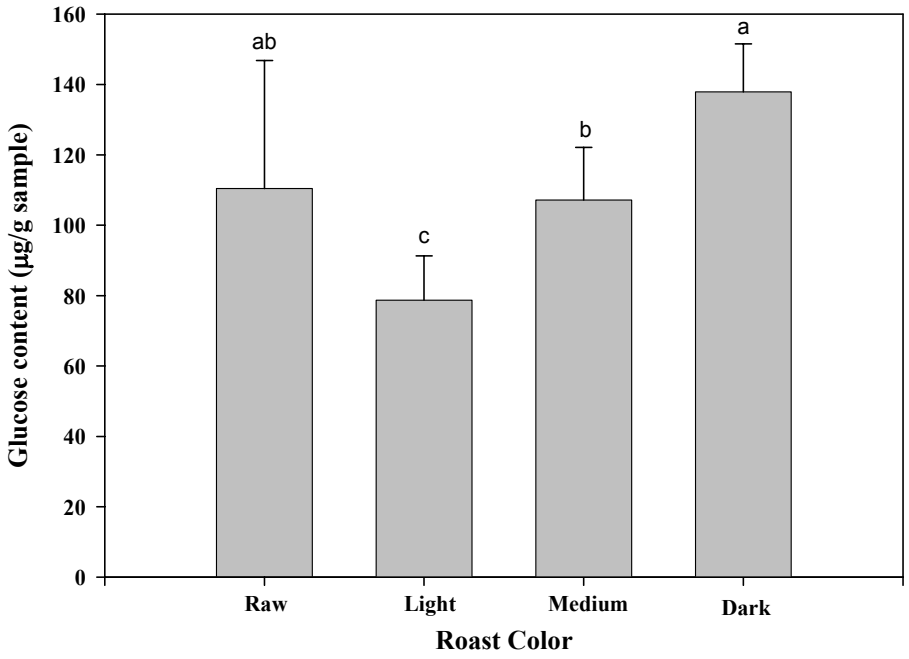

Figure 2.7 Glucose content of raw peanuts and peanuts roasted to different colors at varying temperatures.

2.4.4 Amino Acid Analysis

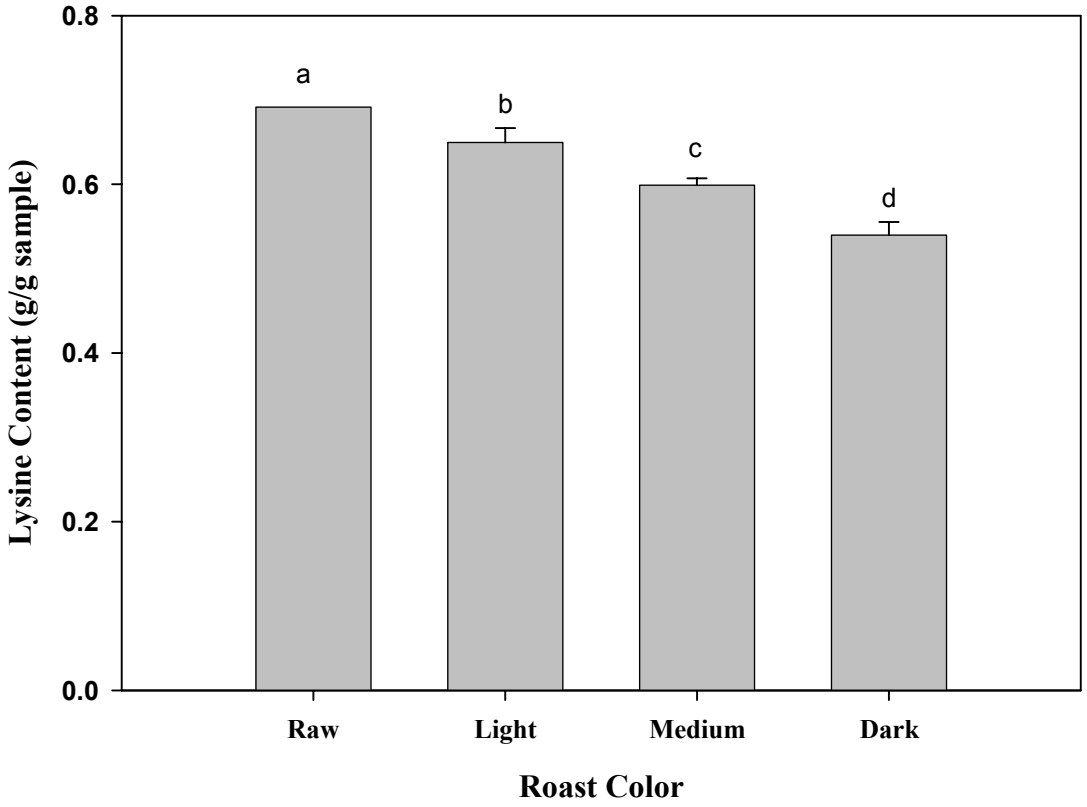

Figure 2.8 Lysine content of raw peanuts and peanuts roasted to different colors averaged over 5 temperatures (147-187 ºC).

Along with sugar contents, amino acid content of peanuts can also be used as an indicator of the MBR. Lysine is a highly reactive AA due to its free ε-amino group and therefore is readily available to participate in the MBR (deMan 1999 Chapter 3). For each roast temperature, lysine content decreased significantly from light to dark roast and the data is summarized across all roast temperatures in **Figure 2.8**. At equivalent roast colors, no

significant differences were found in lysine content at different roast temperatures. Differences among roast colors were significant regardless of roast temperature, indicating that lysine content was more dependent on final roast color than roast temperature.

2.4.5 Tocopherol Analyses

Peanuts naturally contain α, β, γ, and δ tocopherols (Peanut Science and Technology Ch.17 1982). After oil extraction by mechanical pressing, total tocopherols for the raw and roasted samples are presented in terms of μg/g oil in **Figure 2.9**. Tocopherol content of raw peanuts was measured at approximately 400 μg/g sample oil. The 147 ºC and 157 ºC medium and dark roasts have higher tocopherol contents than the raw sample. A potential explanation for this increase is that oil extractability is increased by roasting due to protein denaturation (Yoshida and Kajimoto 1994) and/or damage to cell membranes (Lee and others 2004) and this newly released oil has higher tocopherol contents.

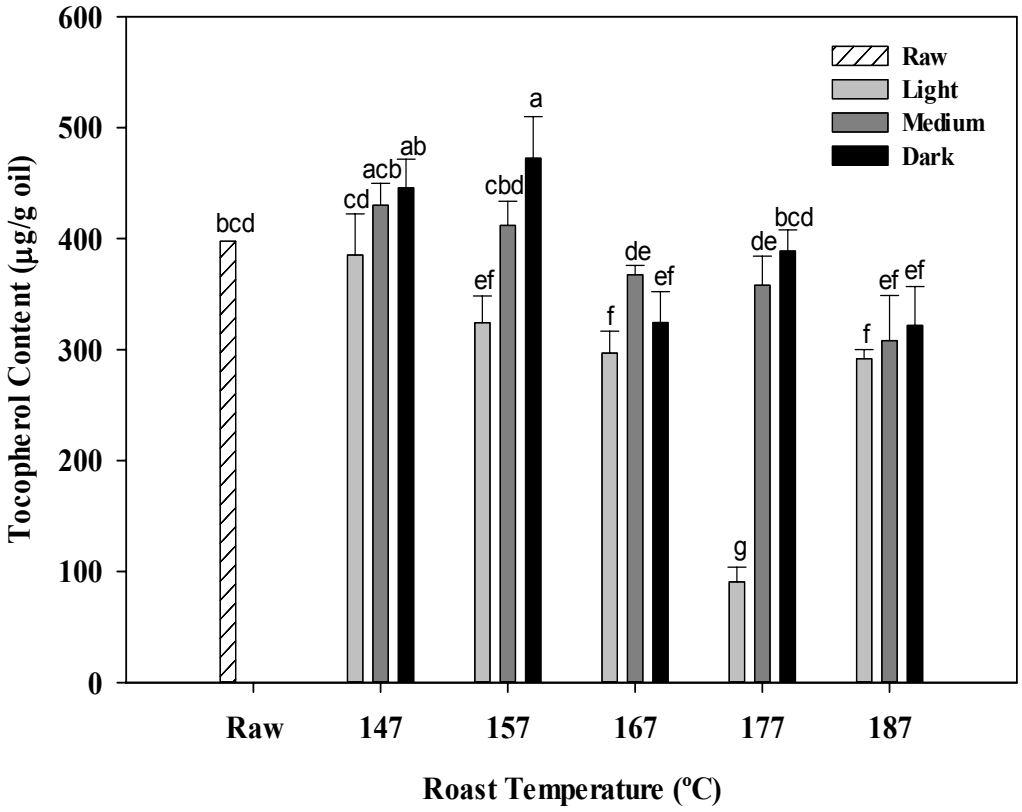

Figure 2.9 Total tocopherol content of oil from raw peanuts and peanuts roasted to different colors at varying temperatures.

Tocopherols act as antioxidants by trapping free radicals and preventing oxidation (Burton and Ingold 1986). Even though roasting may improve oil extraction and hence increase total tocopherols, tocopherol content is also expected to decline with roasting as the heat enhances oxidation (deMan 1999 Chapter 9). It is hypothesized that at equivalent roast temperatures, tocopherol content would decrease with longer heating times. Furthermore, it is hypothesized that at equivalent roast times, tocopherol content would

decrease with increasing roast temperature. Countering this loss of tocopherols with roasting, is the generation of MBP's during roasting, and these MBP's have inherent antioxidant activity and hence the potential to protect the tocopherols. The antioxidant capacity of roasted peanuts is significantly higher than raw peanuts (Davis and others 2010, Talcott and others 2005a). Antioxidant properties of MBP's have been shown in model systems such as coffee, breads, and fermented foods (Amarowicz 2009, Manzocco and others 2000). In general, when samples were roasted at equivalent roast temperatures, those samples roasted to darker colors had increased tocopherol contents (**Figure 2.9**), which supports the hypothesis that the increased concentrations of MBP's are protecting the tocopherols from oxidation. Total tocopherols of samples tended to decrease with increasing roast temperature (**Figure 2.9**). This suggests that the increased temperatures more effectively degraded tocopherols. Expressed oils from the dark roasted seed were darker in color than oil from light or medium roasted seed, meaning MBP's are transferring with the expressed oils. Oil from cashew nuts roasted to darker colors at high temperature short time (130 ºC for 33 min) had significantly darker color than oil from cashews roasted to low temperature long time (70 ºC for 6 h), which was attributed the presence of MBP (Chandrasekara and Shahidi 2011).

MC and tocopherol content was also found to be significantly correlated (R^2 = -0.67), and samples with decreased MC tended to have increased levels of tocopherols (**Figure 2.10**). Note that data for peanuts roasted at 177°C were not included in this analysis or graph. The presence of water enhances oxidation potential within a food which could be a direct mechanism for this relationship, in addition to MC tending to decrease in samples

roasted to darker colors which in turn had increased concentrations of antioxidative MRP's. The decreased MC, increased MBP's and higher tocopherol contents could promote increased shelf life in darker roasted peanuts.

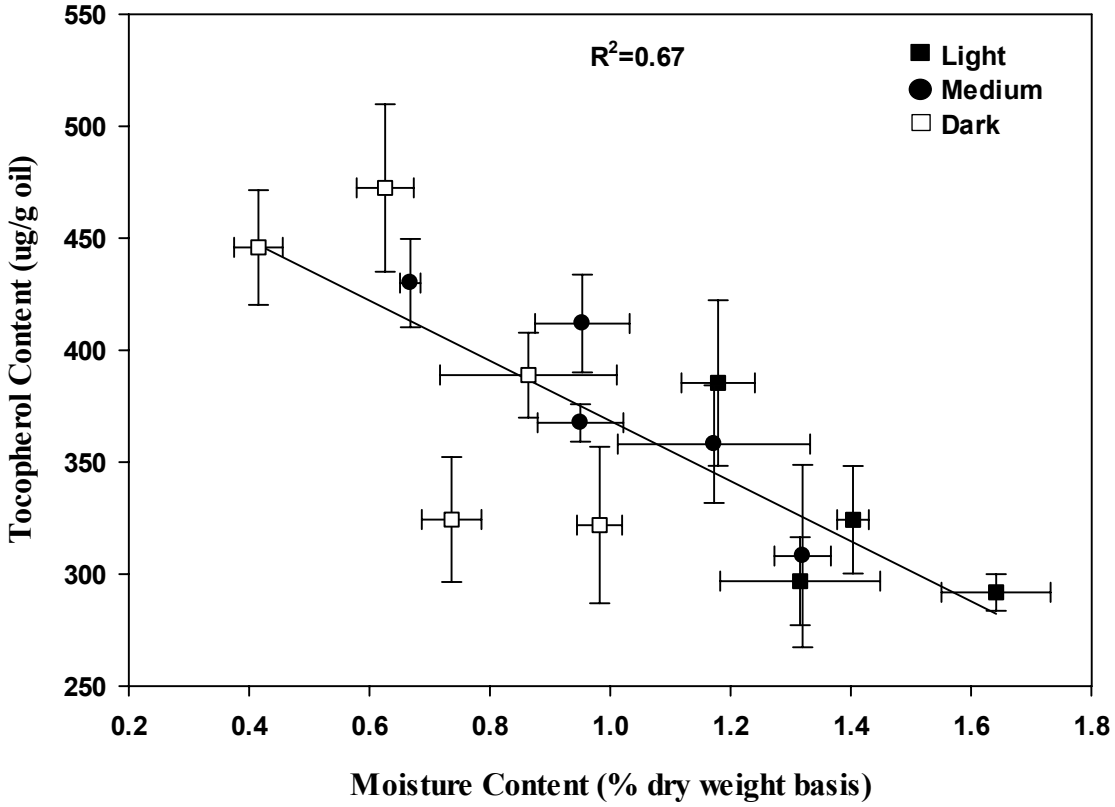

Figure 2.10 Tocopherol content versus moisture content of peanuts roasted 3 colors (light, medium and dark with L-Values 53±1, 48.5±1, 53±1, respectively) at 5 temperatures (147-187 ºC).

To further determine the stability of the roasted oil samples, oil from each time/temperature combination was placed into accelerated oxidative conditions modified

from Davis and others (2010). It was previously observed that tocopherol content of oils derived from darker roasted peanuts had increased stability as compared to oils extracted from raw or light colored peanuts (all samples roasted at an equivalent temperature) (Davis and others 2010). For the current study, samples were collected after 1, 2 and 3 days in the oven and analyzed for tocopherol content. Degradation of tocopherols under accelerated storage conditions after 3 days indicated that, oils derived from dark colored samples roasted at lower temperatures had the lowest percentage of tocopherol degradation (**Table 2.3**). This suggests MBP's with antioxidant activity were transferred into the oils and protected the tocopherols from degradation.

Peroxide value (PV) is a measurement of primary and secondary oxidation products (deMan 1999), Increased PV values are indicative of increased oxidation and the pattern of PV with roast temperatures and roast colors after 7 days of accelerated oxidative conditions is presented in **Figure 2.11**. These trends complement that which was observed for tocopherol degradation (**Table 2.3**). That is, samples with increased tocopherol retention tended to have lower PV values. However, oxidation products go through formation, stabilization, and decomposition phases (deMan 1999). So although a sample may have a lower PV score, if it is in the decomposition phase it is further oxidized than a sample with a higher PV still in the formation phase. As PV data was only collected after 7 days due to logistical considerations, the data must be interpreted with this caveat (potential for decomposition) in mind.

Table 2.3 Percent decrease in tocopherols over 3 days at accelerated storage conditions of 85 ± 3 ºC.

		% Decrease over 3 days Accelerated Storage				
Roast Color		Roast Temperature (ºC)				
	Raw	147	157	167	177	187
Raw	26.4					
Light		24.9	23.6	18.9	31.0	24.0
Medium		17.7	24.0	13.3	38.0	25.3
Dark		12.4	12.2	27.1	33.9	26.9

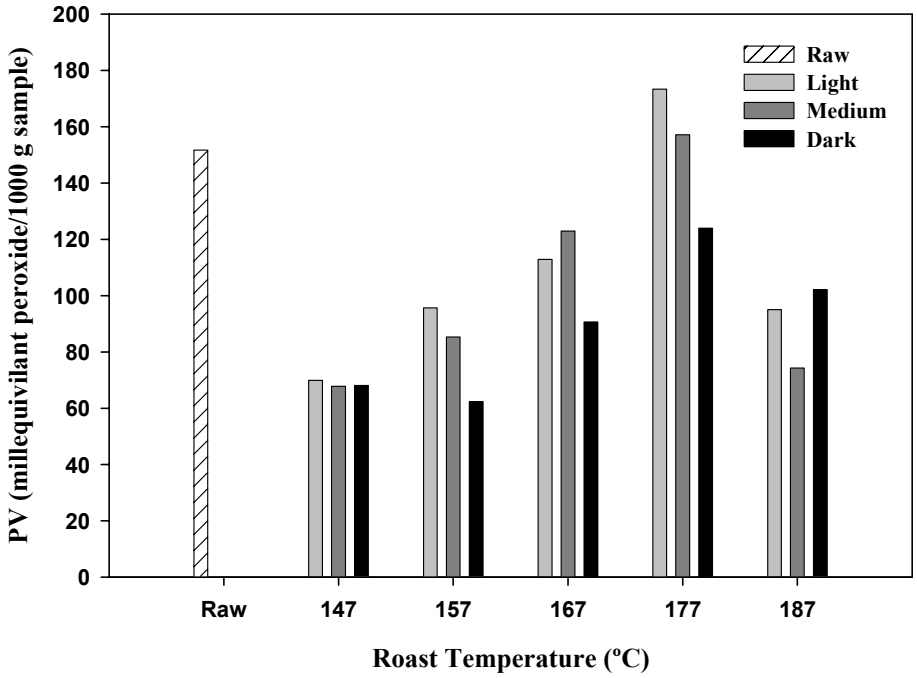

Figure 2.11 Peroxide Values of peanut oil from peanuts roasted to a variety of time/temperature combinations after 7 days at accelerated storage conditions (85 ± 3 ºC). (Values are based on single analysis due to sample quantity limitations.)

2.4.6 Hydrophilic-Oxygen Radical Absorbance Capacity

Roasting increases the amount of hydrophilic antioxidants present due to the formation of MBP (Oliviero and others 2009) and the release of phenolic compounds previously bound within the cellular structure of peanuts (Talcott and others 2005). MBP have been found to increase antioxidant capacity in model systems during heating of glucose solutions containing various amino acids (Manzocco and others 2000). Even short roasting times of 10 min at 175 °C have been shown to increase H-ORAC in peanuts by approximately 22% (Talcott and others 2005). H-ORAC data of raw and roasted samples is presented in terms of μmol Trolox equivalents (TE)/ 100g (**Figure 2.12**). Trolox is used as the standard for this assay and is a water soluble Vitamin E analog. All roasted samples exhibited significantly higher H-ORAC values than the raw sample representing an average increase of 42 % from raw to roasted samples (**Figure 2.12**). The increase in H-ORAC from raw to roasted samples agrees with previous studies that roasting increases antioxidant capacity (Davis and others 2010, Talcott and others 2005). No differences were observed in H-ORAC for peanuts roasted to different colors or at different roast temperatures, although trends did suggest increasing H-ORAC with darkening color.

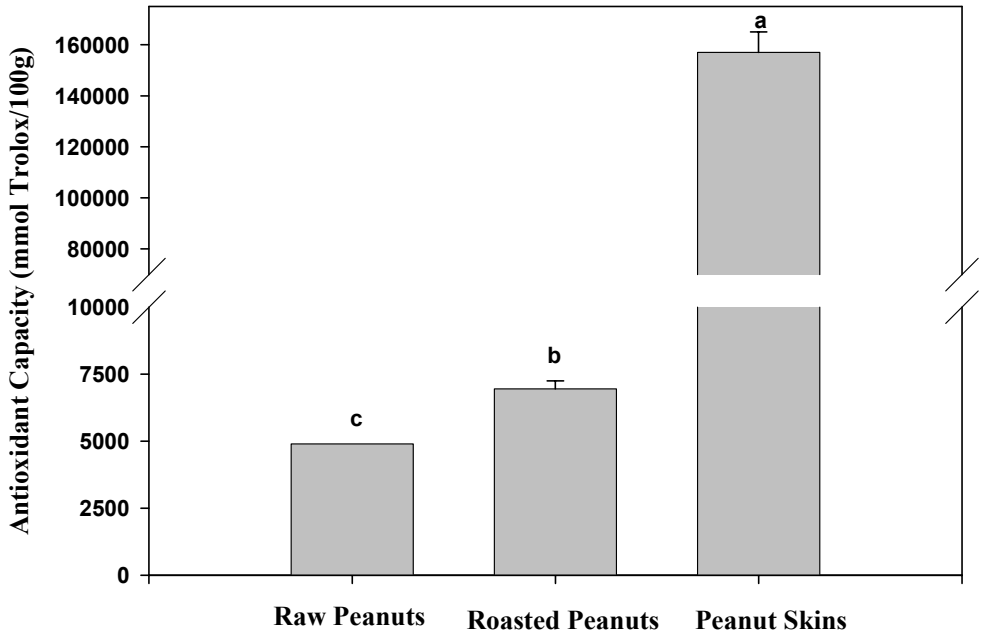

Figure 2.12 H-ORAC of raw peanuts, roasted peanuts averaged across all time/temperature combinations, and blanched peanut skins collected after roasting at all time/temperature combinations.

Peanut skins are the protective outer layer of the peanut seed. During roasting, peanut skins are often removed as waste products and sold at low cost for use in animal feed (Sobolev and Cole 2004). Approximately 750,000 tons of peanut skins are produced annually on a worldwide basis (Sobolev and Cole 2004). Unlike the peanut seed which darkens due to the MBR, the darkening of peanut skins with roasting is more likely a function of phenolic polymerization since peanut skins do not contain high levels of sugar (Davis and others 2010).

Peanut skins contained significantly ($p<0.05$) more antioxidants than both raw and roasted samples, representing a 32 fold increase from raw peanuts and a 22 fold increase from roasted samples (**Figure 2.12**). These high H-ORAC values are due to the naturally high polyphenolic content of peanut skins, and this data supports recent work indicating the excellent potential of peanut skins, a current by-product of the peanut industry, to serve as a natural source of antioxidants and/or other neutraceutical compounds (Nepote and others 2005, O'Keefe and Wang 2006, Yu and others 2006, Yu and others 2005).

2.4.7 Kramer Shear Analysis

Roasting changes the internal microstructure of the peanut resulting in a texture that is more brittle, crispy and crunchy (Varela and others 2008). Mechanical properties of the roasted seeds have been used to correlate to human textural perception. Due to the non-uniform peanut size, previous work has shown that bulk (multiple seed) compression testing produce results more similar to human textual perception than single seed compression testing. Therefore, a multiple seed compression test was used to create force vs. displacement curves for the current roasted samples, which in turn was used to make inferences on roasted peanut texture.

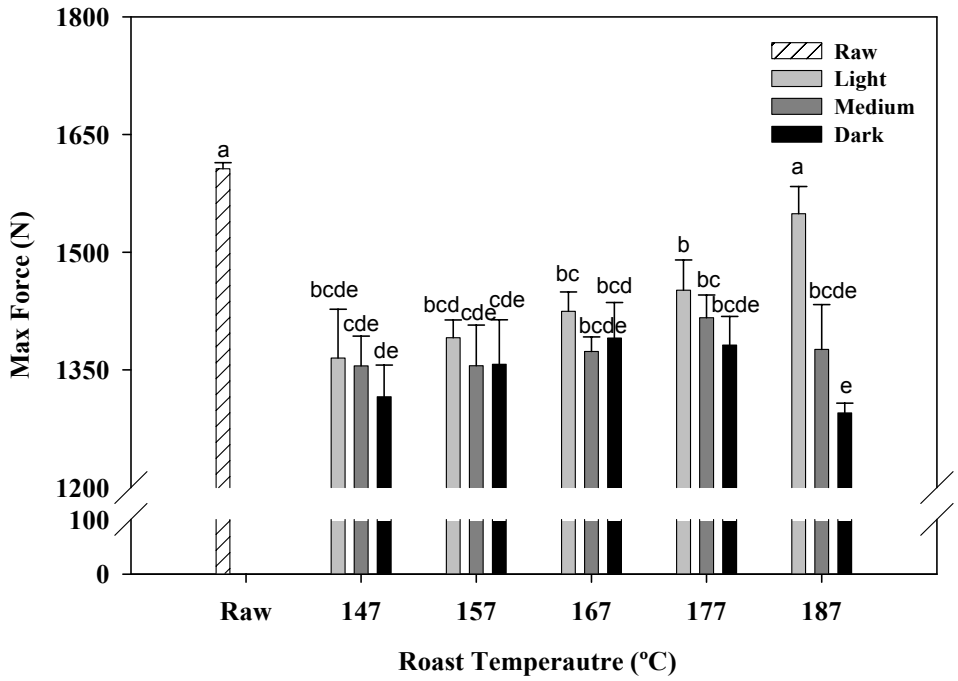

Figure 2.13 KSC max force of raw peanuts and peanuts roasted to different colors at varying roast temperatures.

The peak value from max force vs. displacement has been shown to be a relevant measure to sensory perception (Wanlapa and Jindal 2006). All roasted samples except the 187 ºC light roast had significantly lower max force at fracture than the raw blanched sample (**Figure 2.13**). The 187 ºC light roast, which was the sample roasted for the least amount of time, had the highest max force of the roasted samples. For all light roasted samples, max force increases from 147 ºC to 187 ºC. Medium roasted samples indicate an increased max force up to 177 ºC, and dark roasted samples increase up to 167 ºC after which point increasing the roasting temperature appears to decrease the max force needed

to fracture the samples. Roasting for a longer time at equivalent roast temperatures allows peanut seed to be broken down more easily during mastication.

Texture of food is related to the MC (deMan 1999 Chapter 1). Moisture loss is thought to be critical factor in developing texture during roasting (deMan 1999, Ozdemir and others 2001). There was good correlation between max force and MC of roasted samples (R^2= 0.64, **Figure 2.13**). Decreasing MC, which is related to roasting time, has been reported to increase crunchiness of almonds (Varela and others 2009), cashews (Wanlapa and Jindal 2006) and hazelnuts (Saklar and others 1999). Light roasts tend to have higher MC along with higher max force followed by the medium and dark roast respectively. This strong linear correlation between MC and max force indicates that MC could be used as a marker for determination of the texture of roasted peanuts (**Figure 2.14).**

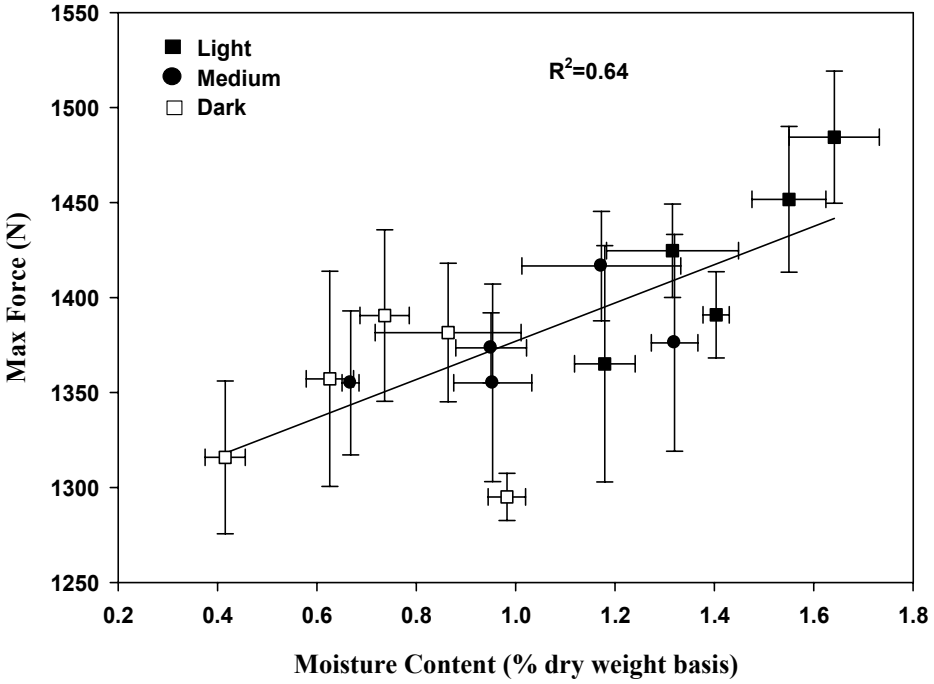

Figure 2.14 Maximum force during compression from Kramer Shear cell testing versus moisture content of roasted peanuts.

2.5 Conclusions

Roasting significantly effects the final composition and quality of peanuts. Surface color (L-value) of peanuts which is often used for the determination of final product quality was found to be negatively correlated with glucose content, positively correlated with lysine content and positively correlated with MC, with R^2 values of -0.78, 0.93, and 0.80, respectively. Both glucose and lysine are reactants in the MBR which is the primary reaction contributing to the color development of roasted peanuts. MC appears to be central to many aspects of the final product. MC was significantly correlated with roasting time, surface

color, lysine content, glucose content, max force, and initial tocopherol content and tocopherol content during storage, with R^2 values of -0.71, 0.80, -0.69, -0.68, 0.64, -0.67 and -0.71, respectively). As MBR occurs during roasting hydrophilic antioxidants are formed which act in conjunction with tocopherols to prevent against oxidative degradation. Tocopherol content generally decreased with increasing roast temperature; however, within a given temperature darker roast had higher tocopherol contents. This indicates that antioxidants from MBR are potentially protecting tocopherols in darker roasted samples. An accelerated storage study indicated that oils from dark samples roasted at lower temperatures had the least amount of tocopherol degradation over time. Data from this study can be considered holistically to optimize peanut roasting to improve various aspects of product quality.

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CHAPTER 3

Effect of Different Time/ Temperature Roast Combinations on Peanut Flavor - Descriptive Sensory, Electronic Nose and Electronic Eye Characterizations

3.1 Abstract

Roasting is of central importance to peanut flavor. Standard industry practice is to roast peanuts to a specific surface color (Hunter L-value) for a given application; however, equivalent surface colors can be generated using different temperature/time roast combinations. To better understand the effects of roast temperature and product color on peanut flavor, a standard lot of runner peanuts was roasted using 5 roast temperatures to 3 post-blanch surface colors corresponding to light, medium and dark. Samples were roasted in triplicate and evaluated in duplicate by a trained sensory panel using a 15-point universal scale for 17 attributes. Descriptive sensory analysis (DSA) was compared to volatile data collected from the same samples using various Electronic Nose instruments (E-Nose – Gemini/Fox/Heracles) in triplicate. As expected, samples roasted to different colors were differentiated ($p<0.05$) using DSA terms including, roasted peanutty, sweet aromatic, dark roast, raw beany, bitter, and ashy. Dark roast, bitter, ashy and raw beany attributes were correlated with E-NOSE sensor data ($R^2 >0.70$). Principal component analyses of E-Nose data revealed a clear distinction for volatiles among peanuts roasted at 147 °C, 157 °C, 167 °C, 177 °C and 187 °C, whereas the sensory panel only noted clear differences between 147 °C and 187°C. GC analyses (Heracles) suggested the majority of discriminatory volatiles were Maillard products such as pyrazines and dimethyl pyrazine. Hexanal was another important discriminatory compound identified most prominently in light roasted peanuts and especially those seed which were roasted at lower temperatures/longer times. Low temperature long time roasting may accelerate peanut oil oxidation leading to changes in hexanal concentrations. Generally, DSA panel found that for peanuts roasted to an equivalent

surface color, those peanuts roasted at higher temperatures/shorter times had decreased intensities ($p<0.05$) for attributes, such as ashy and bitter, which are typically associated with negative peanut flavor. Hunter L-value data was also compared to E-eye data and a Global Statistical Quality Control Model was developed to evaluate degree of roast.

3.2 Introduction

The majority of peanuts consumed in the United States are dry roasted and this process is critical for proper color and flavor development (Reyes and others 1982). Peanuts are dry roasted for whole seed consumption, peanut butter, and for use in certain candies and confectionaries (American Peanut Council 2011). Typically, peanuts are roasted to a specific surface color which is often measured by a Hunter colorimeter and reported in terms of L-Value. Measurement of surface color is the primary method for determining final product quality in many commercial roasting processes (Baggenstoss and others 2008, Manzocco and others 2000, Simsek 2007) as color measurements are quick, easy and nondestructive (Manzocco and others 2000). Measurements of surface color also strongly correlate with flavor development (Baggenstoss and others 2008, Smyth and others 1998). However, as illustrated in **Figure 3.1**, equivalent surface colors can be produced by modifying the roasting time/temperature conditions; therefore, the flavor development at different roast time/temperatures combinations is of fundamental interest to the peanut industry as this information could allow for roast optimization.

Determination of peanut flavor has traditionally been assessed using descriptive sensory analyses and various gas chromatography (GC) based techniques for identification of volatile flavor compounds (Schirack and others 2006b). Volatile flavor compounds produced

during roasting are mainly Maillard browning products (MBP) formed during the Maillard browning reaction (MBR) (Newell and others 1967, Warner and others 1996). During the MBR, reducing sugars and amino acids react to create MBP's such as pyrazines, pyrroles and furans (Schirack and others 2006a). The initial composition of peanuts is effected by the cultivar, growing, harvesting and storage conditions (Basha and others 1976, Rodriguez and others 1989, Sanders 1980, Sanders and others 1982, Sanders and others 1989) which in turn affects the amount and composition of amino acids and sugars available for the MBR and hence final color and flavor.

Flavor development of peanuts is affected by the sugars and amino acids available for the MBR as well as off-flavors produced during later stage MBR. The main sugar found in peanuts is sucrose (Hoffpauir 1953) which must be converted through inversion to glucose and fructose in order to participate in the MBR (Reyes and others 1982, Rodriguez and others 1989). Peanuts also have small, baseline levels of glucose and fructose as available substrates for the MBR. Immature peanuts contain higher levels of sugar than mature peanuts (Sanders and others 1989). Amino acid content will also affect the flavor development of peanuts through the MBR and aspartic acid, glutamic acid, glutamine, histadine, asparagine and phenylanine are thought important substrates for this reaction (Newell and others 1967). Oil roasting has been found to decrease the molecular weight of polypeptides and was thought to be the result of MBR (Basha and Young 1985, Newell and others 1967). Off-flavors can also be produced through the end stage MBR and/or oxidation reactions (Warner and others 1996). Lipid degradation will affect peanut flavor. Non-heterocyclic compounds such as aldehydes, alcohols, esters and ketones are produced during

lipid degradation (Liu and others 2011). Another prominent lipid oxidation product is hexanal, which is a secondary lipid oxidation product that produces off-flavors associated with rancidity (Liu and others 2011). It is the combination of these many different reactions that produce the final peanut flavor.

Another approach for characterizing the sensory properties of foods is through the use of electronic systems which mimic human sensory responses to foods. In the case of flavor, such instruments are typically referred to as electronic-noses (E-Nose). A typical E-Nose system is composed of a sensor, a recording device and a computer to analyze the data. The human olfactory system is comprised of 10-100 million unique receptors (Deisingh and others 2004), which makes the correlation of human sensory data and electronic sensors difficult (Baldwin and others 2011). In the human brain the multitude of unique combinations and patterns with which these receptors can be perceived makes mimicking that response extremely difficult. E-systems are also sensitive to external factors such as temperature, humidity and the level of calibration (Baldwin and others 2011). The main types of electronic sensors utilized in E-Nose systems include organic polymers, metal oxides, quartz crystal microbalances and GC based systems (Baldwin and others 2011). Metal oxide semiconductor sensors (MOS), conducting polymer sensors, and surface acoustic wave sensors are the most commonly used E-Nose sensors (Deisingh and others 2004, Ghasemi-Varnamkhasti and others 2009). MOS's display unique responses to volatile compounds with time (Baldwin and others 2011), and these dynamic responses can be used to distinguish and identify volatile odor compounds in beverages, eggs, oils, grains, nuts, meat and fish, just to name a few (Gursoy and others 2009, Mildner-Szkudlarz and Jelen

2010, Ponzoni and others 2008). However, E-Nose systems must be "trained" and calibrated to recognize patterns from the volatile profiles (Baldwin and others 2011).

The use of electronic systems has potential to aid in making faster and more accurate analyses of sensory characteristics as compared to traditional sensory panels (Baldwin and others 2011). There has been little use of electronic systems for characterizing peanut flavor; therefore, the goal of the this research was to assess sensory attributes of peanut samples roasted to three different colors (light, medium and dark) as defined by a Hunter colorimeter at 5 different temperatures ranging from 157-187 ºC using a trained sensory panel, and to relate this sensory information to data collected using a range of E-nose systems. Sensory data is important for these roasted samples, as there is no published information regarding the flavor profile of peanuts systematically dry roasted to equivalent colors at various roast temperature/time combinations. Such flavor data could provide fundamental information on peanut roasting and the development of peanut flavor as related to the kinetics of color development. Furthermore, by relating the DSA data collected for these sample to complementary data from the various e-Nose systems, the potential of these e-Nose systems to predict and discriminate peanut flavor can be better understood.

3.3 Materials and Methods

3.3.1 Materials

A representative sample of medium-grade size Georgia Green runner peanuts (*Arachis hypogaea*) were obtained from a single harvested lot. The peanuts were harvested, cured, shelled and stored prior to delivery to North Carolina State University according to standard industry practices.

3.3.2 Peanut Roasting

Peanuts were brought to room temperature and roasted in a lab scale oven (Despatch, Minneapolis, MN) to 3 roast colors as defined by a Hunter Colorimeter (light 53±1, medium 48.5±1, and dark 43±1) at 5 different temperatures (147 ºC, 157 ºC, 167 ºC, 177 ºC, and 187 ºC). Roasting times were dependent on the defined roast color and temperature and these times were determined using linear regression on the preliminary roast curves shown in **Figure 3.1**. These resulting times are shown in **Table 3.1**. Following roasting, samples were placed onto a forced air blower, manually blanched, placed into 8 oz glass mason jars, flushed with nitrogen and stored in cold storage until further analysis. One set of samples was sent via overnight delivery to collaborators at α-MOS in Hanover MD for E-Eye and E-Nose measurements and a second identical set of samples was prepared for descriptive sensory analysis. Both sets are described in more detail below.

Table 3.1 Average Roasting times for all roast color and temperature combinations.

	147 ºC	157 ºC	167 ºC	177 ºC	187 ºC
Roast Color (L-Value)	Time (minutes)				
Light (53±1)	26.5	16.6	13.5	10.0	8.6
Medium (48.5±1)	46.4	25.6	17.0	12.2	10.6
Dark (43±1)	70.8	36.6	21.2	15.4	12.3

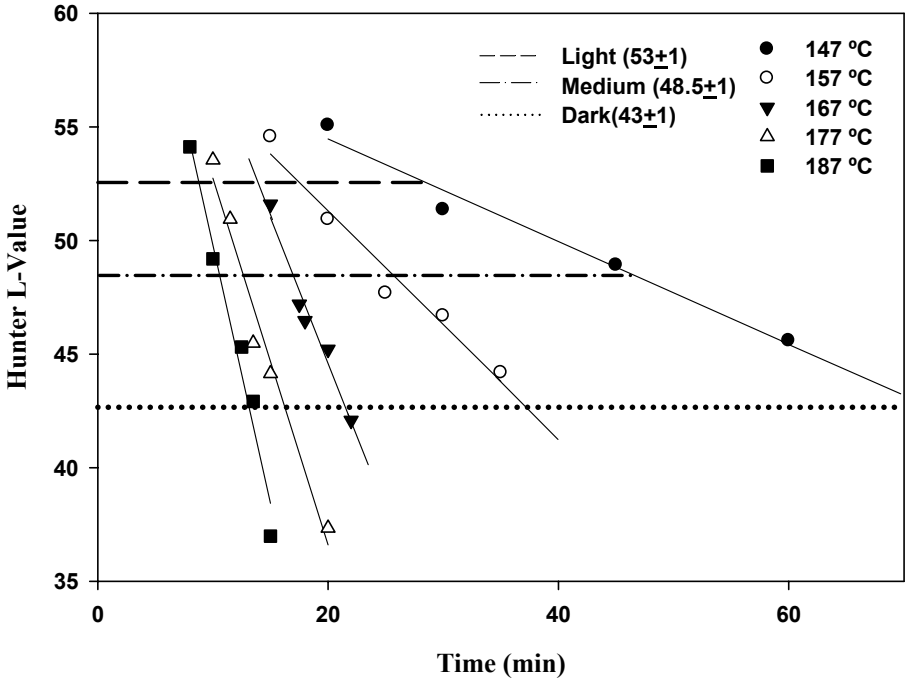

Figure 3.1 Color (Hunter L-Value) development of peanuts roasted at different temperatures. Solid, straight lines represent best linear fits of data. Dashed, horizontal lines represent Hunter L-Values associated with roast colors (Light = 53±1, Medium = 48.5±1, Dark = 43±1).

3.3.3 Statistical Analysis

A complete randomized split plot block design was used. This design eliminates variation due to day or oven equilibration concerns with varying temperature. A block was defined as one week containing all 15 roasts time/temperature combinations. Plots were represented by a day which contained all roast colors for a given temperature. Within plots roast colors were randomly assigned to obtain a balanced distribution for each temperature.

Data was analyzed by analysis of variance (ANOVA) using SAS® Ver. 9.0 (Cary, NC, U.S.A.). Principle Component Analysis (PCA) plots were obtained using Excel Stat

3.3.4 Descriptive Sensory Analyses

Following roasting, peanuts were ground into a paste using a Hobart mixer. Pasted samples were placed into glass jars, flushed with nitrogen and stored at -4 ºC. Prior to sensory evaluation samples were brought to room temperature. All 45 roasted samples were evaluated in duplicate. Using a random number generator, all samples were evaluated once, randomized again, and then evaluated a second time. Peanut pastes were analyzed for 18 different attributes (**Table 3.2**) using a descriptive sensory analysis panel of 12 panelists. Each panelist had received training on all attributes and participated in a minimum of 100 hours in the evaluation of peanuts samples.

Table 3.2 Lexicon for peanut flavor (Johnsen and others 1988).

Attribute	Description
Roast Peanutty (RP)	Aroma associated with medium-roasted peanuts
Dark Roast (DR)	Aroma associated with dark-roasted peanuts
Raw Beany (RB)	Aroma associated with light-roasted peanuts
Sweet Aromatic	Aroma associated with sweet material such as caramel, vanilla and molasses
Woody/Hull/Skins	Aroma associated with base peanut character (dry wood, peanut hulls, skins)
Bitter	Taste on tongue associated with bitter agents (caffeine, quinine)
Astringency	The chemical feeling factor on the tongue associated with tannins and alum; causing puckering or dry mouth sensations
Ashy	Aroma associated with very dark roast (espresso)
Cardboardy/Stale	Aroma associated with oxidized fats and oils
Painty	Aroma associated with linseed oil, oil based paint
Earthy	Aroma associated with wet dirt and mulch
Plastic Chemical	Aroma associated with burnt plastics
Fruity Fermented	Aroma associated with floral, fermented, rotten garbage
Metallic	The chemical feeling factor on the tongue associated with iron and copper
Tongue and Throat Burn (TTB)	Burning sensation on back of tongue or throat immediately following ingestion or expectoration
Sour	Basic taste associated with acids
Sweet	Basic taste associated with sugars
Total Off-notes	Combination of all off-notes perceived (does not necessarily add up to scores from all other off-notes)

3.3.5 Electronic Eye Color Determination

Sample color was evaluated with an Iris E-Eye system (Alpha M.O.S., Hanover, MD) using a high resolution CCD camera (4096 colors) to take a snapshot of the surface of the peanuts after eliminating color from the background. Color maps were generated to determine statistical differences among samples. Data is presented in terms of pixels, rather than an average color. E-Eye data was collected by collaborators at α-MOS and the analyzed data was returned via a confidential report.

3.3.6 Electronic Noses (E-Nose) Analysis

3.3.6.1 α Fox and Gemini E-Noses (MOS E-Nose Systems)

The α Fox 4000 consist of 18 MOS's split between 3 chambers. The Gemini consists of 6 MOS. For both the α Fox and Gemini, 20 g of whole seed roasted samples were placed into a 100 mL vial and incubated in a Peltier heating tray to 40 °C. The autosampler HS100 injects 2.5 mL of air from the headspace at a rate of 2.5 m/s. Each MOS sensor responds uniquely to the sample injection and produces a graphic response, which was then analyzed with the software Alphasoft V12.3. MOS E-Nose data was collected by collaborators at α-MOS and the analyzed data was returned via a confidential report.

3.3.6.2 Heracles E-Nose (GC E-Nose System)

The Heracles E-Nose is different from the α Fox and Gemini E-Nose in that instead of MOS's, the Heracles E-Nose is equipped with 2 columns used to perform GC analyses. GC data was collected from the headspace of samples using two capillary columns (2m length and 100 μL diameter) with different polarities (non-polar DB05 and slightly polar DB1701)

at 280°C. 20 g of roasted peanut samples were placed in to 100 mL glass vials and heated to 40°C in a Peltier tray. Data was analyzed using the software Alphasoft V12.3. An alkane solution (n-hexane to n-hexadecane) was used for calibrations. Retention times were compared with Kovats indices to identify the volatile compounds using AroChemBase. GC E-Nose data was collected by collaborators at α-MOS and the analyzed data was returned via a confidential report.

3.4 Results and Discussion

Table 3.3 Mean values of descriptive sensory analysis attributes for peanuts based on a 15 point sensory Spectrum ® scale.

Roast Color	Roast Temperature	Attribute									
		Roast Peanutty	Dark Roast	Raw Beany	Sweet Aromatic	Woody/ Hull/Skins	Sweet	Bitter	Astringency	Ashy	Total off-notes
Light	147	5.03^{cd}	2.57^{e}	2.52^{ab}	3.10^{abc}	3.08^{b}	3.05^{a}	2.11^{d}	1.00^{c}	0.04^{e}	0.21^{bcd}
(53±1)	157	4.98^{cd}	2.41^{e}	2.73^{a}	2.99^{bc}	3.10^{b}	2.52^{b}	2.11^{d}	1.01^{c}	0.03^{e}	0.07^{d}
	167	5.44^{ab}	2.86^{cd}	2.29^{bc}	3.26^{a}	3.07^{b}	2.50^{b}	2.04^{d}	1.00^{c}	0.05^{e}	0.05^{d}
	177	4.97^{cd}	2.48^{e}	2.59^{ab}	3.09^{abc}	3.13^{b}	2.58^{b}	2.04^{d}	1.00^{c}	0.04^{e}	0.14^{cd}
	187	5.24^{abc}	2.59^{de}	2.46^{ab}	3.11^{abc}	3.05^{b}	2.54^{b}	2.05^{d}	1.02^{bc}	0.03^{e}	0.05^{d}
Medium	147	4.83^{de}	3.24^{b}	2.04^{cd}	2.88^{cd}	3.36^{a}	2.19^{b}	2.57^{bc}	1.03^{abc}	0.53^{c}	1.10^{a}
(48.5±1)	157	5.49^{a}	3.17^{b}	1.99^{cde}	3.27^{a}	3.14^{b}	2.44^{b}	2.17^{d}	1.00^{c}	0.21^{e}	0.25^{bcd}
	167	5.45^{ab}	3.19^{b}	1.93^{de}	3.27^{a}	3.18^{b}	2.43^{b}	2.18^{d}	1.00^{c}	0.22^{e}	0.11^{d}
	177	5.46^{ab}	3.14^{bc}	2.02^{cd}	3.21^{ab}	3.14^{b}	2.50^{b}	2.16^{d}	1.01^{bc}	0.29^{de}	0.26^{bcd}
	187	5.50^{a}	3.07^{bc}	2.11^{cd}	3.26^{a}	3.09^{b}	2.58^{b}	2.10^{d}	1.01^{bc}	0.17^{e}	0.04^{d}
Dark	147	4.55^{e}	3.77^{a}	1.71^{ef}	2.77^{d}	3.42^{a}	2.14^{b}	2.68^{ab}	1.06^{ab}	0.86^{ab}	1.41^{a}
(43±1)	157	4.54^{e}	3.95^{a}	1.46^{f}	2.69^{d}	3.43^{a}	2.13^{b}	2.74^{a}	1.07^{a}	0.91^{a}	1.25^{a}
	167	5.06^{cd}	3.68^{a}	1.52^{f}	2.99^{bc}	3.34^{a}	2.28^{b}	2.47^{c}	1.05^{abc}	0.63^{bc}	0.53^{b}
	177	5.09^{abc}	3.70^{a}	1.51^{f}	3.09^{abc}	3.32^{a}	2.33^{b}	2.41^{c}	1.00^{c}	0.72^{abc}	0.55^{b}
	187	5.03^{cd}	3.84^{a}	1.45^{f}	3.06^{abc}	3.41^{a}	2.26^{b}	2.46^{c}	1.03^{abc}	0.52^{cd}	0.46^{bc}

*Means within a column followed by the same letter are not significantly different (Duncan's multiple range test $p<0.005$).

3.4.1 Descriptive Sensory Analysis

ANOVA was performed on sensory attributes for roasted peanut samples. **Table 3.3** lists the 10 sensory attributes evaluated (**Table 3.2**) that demonstrated significance ($p<0.05$) as distinguished by Duncan's test. Each attribute was evaluated using the Spectrum ® method which consists of a universal scale ranging from 0-15 (Meilgaard and others 1999). Using the universal scale, attributes are ranked in the same manner across all products (Meilgaard and others 1999). The scale is not product specific, but rather intensity specific with references to mark points throughout the scale (Meilgaard and others 1999).

A medium roast at 167 °C was used as the reference peanut sample in accordance to standard practices within the USDA ARS MQRU lab (Raleigh, NC). The results for the medium roast at 167 °C shown in **Table 3.3** represent the experimental control, and this experimental sample was equivalent to the reference roasted peanut in both roasting time/temperature conditions as well as storage and handling conditions. As such, comparisons to the control will be made throughout this study as a point of reference.

Roast color is a nondestructive method of determining completion of roasting (Manzocco and others 2000) and has been found to be associated with MBR (Saklar and others 2001). MBPs are associated with flavor development in peanuts and other roasted products. Roast color is a good indicator of peanut flavor (Smyth and others 1998), and final roast color of coffee has also been used as an indicator for final quality (Baggenstoss and others 2008). Roast peanutty is one of the most important flavor components of roasted peanuts and has been reported to be associated with MBP's such as pyrazines (Smyth and others 1998, Warner and others 1996). Regardless of roast temperature, the panel effectively

distinguished samples according to roast color. For a given roast color, DSA attributes were ranked more similarly across all roast temperatures, indicating that roast color had more of an affect than roast temperature when assessing sensory attributes.

For medium roasted samples, the sweet aromatic attribute progressively increased ($p<0.05$) with increasing roast temperature, while bitter, ashy and total off notes progressively decreased ($p<0.05$) with increasing roast temperature. Furthermore, roast peanutty scores was lowest for the samples roasted at 147 ºC compared across all medium roast samples. Increased roast peanutty and sweet aromatic scores coupled with decreased bitter, ashy and total off note scores collectively suggest that low temperature/long time roasting negatively impacts overall peanut flavor while high temperature/short time roasting has the potential to positively impact peanut flavor. Similar trends were observed in dark roasted peanut samples, that is sweet aromatic and roasted peanutty scores progressively increased ($p<0.05$) with increasing roast temperatures, while scores for bitter, ashy and total off notes decreased ($p<0.05$). Again, these trends collectively suggest that higher temperature/shorter time roasting could positively impact peanut flavor when preparing samples roasted to a dark color. When roasting to a light color, roast temperature minimally impacted any of the measured attributes.

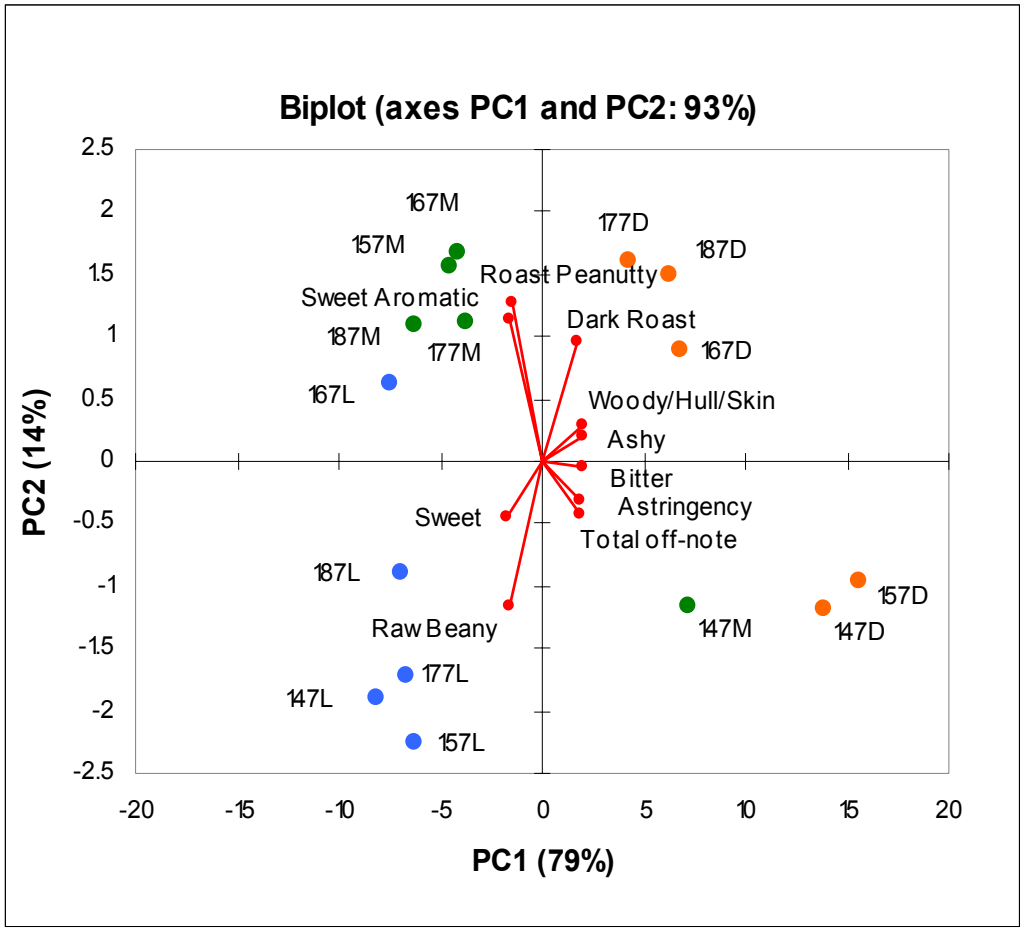

Figure 3.2 Principle Component Analysis of descriptive sensory analysis panel attributes showing significance ($p<0.05$).

Principle component analysis (PCA) was performed using the 10 DSA attributes that showed significance using Duncan's test (**Figure 3.2**). Principle components (PC) 1 and 2 cover 93% of the variability, with PC1 accounting for 79% and PC2 accounting for 14%. In order to determine the components which make up each PC further analysis is required; however, associations can be made based on the proximity of samples to the attributes vectors. Light roasted samples were mainly associated with the attributes raw beany and sweet flavor attributes. Medium roasts were associated with roast peanutty and sweet aromatic flavor attributes. Dark roasts were associated with dark roast, ashy and woody/hull/skins flavor attributes. The samples that most associated with bitter, astringency and total off-notes were the 147 ºC medium and dark roasts and the 157 ºC dark roast, which had roasting times of 46.4, 70.8, and 36.6 minutes respectively, which were the three longest roasting times of all 15 treatments (**Table 3.1**). Longer roasting times at the same temperature have been associated with the formation of pyrazines, which in high concentration have been associated with negative sensory attributes including bitter and dark roast (Smyth and others 1998). Therefore, the longer roasting times of the 147 ºC medium and dark roasts and the 157 ºC dark roast were thought to contribute to the negative flavor attributes associated with these samples.

3.4.2 Electronic Eye

Each of the 15 roast treatments prepared in triplicate were assigned a code (**Table 3.4**), which was used during the analysis of the Iris E-Eye and E-Nose systems. For evaluation of color using the E-Eye system, a snapshot of whole peanut kernels from each roast was used to produce color maps. Color maps for the 167 ºC light, medium and dark

samples illustrate differences observed among measured colors for samples roasted to different roast colors (**Figure 3.3**). Of the 4096 colors evaluated, six were determined to be sufficient to evaluate color differences among roasted samples. A PCA bi-plot using these 6 most discriminate colors was created, with PC1 and PC2 accounting for 81% and 12% of the variation, respectively (**Figure 3.4**). Roasted samples were distributed along PC1 based on roast color as initially defined by Hunter L-values. Within samples roasted to the light, medium or dark colors, no discernable trend was observed for E-eye data and roast temperature (**Figure 3.4**). Therefore, both the E-Eye and Hunter colorimeter produced good discrimination among roast color and the E-Eye instrument generally discriminated samples as well as the Hunter L-value data.

Table 3.4 Roasted peanut samples codes, time, temperature, surface and paste colors (Hunter L-Value).

Code	**Roast Color**	**Time (min)**	**Temperature (ºC)**	**Surface average color**			**Paste Color**		
				L	a	b	L	a	b
L1a	Light	26.5	147	52.6	6.8	21.2	56.0	8.7	24.4
L1b	Light	26.5	147	52.9	6.3	21.0	56.3	7.9	25.0
L1c	Light	26.5	147	51.2	7.1	20.7	55.9	8.5	24.9
L2a	Light	16.5	157	53.8	6.5	21.1	57.5	7.8	24.7
L2b	Light	16.5	157	53.1	6.9	20.6	57.8	7.7	24.5
L2c	Light	16.5	157	51.9	7.0	20.6	56.7	8.0	24.8
L3a	Light	13.5	167	52.1	7.4	20.7	54.2	8.8	24.8
L3b	Light	13.5	167	51.3	6.4	20.3	54.4	9.4	24.3
L3c	Light	13.5	167	50.6	7.8	20.0	53.8	9.7	24.4
L4a	Light	10	177	52.7	5.6	20.2	56.7	7.9	24.0
L4b	Light	10	177	52.0	6.7	20.4	55.2	8.5	24.6
L4c	Light	10	177	53.8	6.4	20.3	56.1	8.5	24.4
L5a	Light	8.5	187	52.7	5.9	20.0	57.7	7.3	24.5
L5b	Light	8.5	187	51.2	6.1	19.7	54.8	9.0	23.8

Table 3.4 Continued

L5c	Light	8.5	187	52.8	6.7	19.9	54.8	8.3	24.1
M1a	Medium	46.5	147	48.6	7.6	20.4	49.2	10.5	23.6
M1b	Medium	46.5	147	47.3	7.8	19.8	50.3	10.7	24.5
M1c	Medium	46.5	147	47.6	8.5	19.6	49.5	10.4	24.1
M2a	Medium	25.5	157	47.9	8.0	20.0	49.8	10.8	23.9
M2b	Medium	25.5	157	47.3	7.9	19.9	48.2	10.5	23.4
M2c	Medium	25.5	157	48.7	7.1	20.0	48.2	11.6	23.7
M3a	Medium	17	167	47.6	8.1	19.8	50.5	10.6	24.3
M3b	Medium	17	167	47.9	8.8	19.5	48.3	11.4	23.7
M3c	Medium	17	167	47.1	8.0	19.7	48.6	11.4	23.6
M4a	Medium	12.5	177	48.5	8.3	20.1	49.6	10.6	23.5
M4b	Medium	11.5	177	48.3	8.2	19.7	50.5	10.3	23.9
M4c	Medium	12.5	177	47.4	8.3	19.4	47.5	11.8	23.0
M5a	Medium	10.5	187	48.7	7.3	19.6	48.7	10.5	23.7
M5b	Medium	9.5	187	48.7	7.6	19.3	49.4	10.4	23.1
M5c	Medium	9.5	187	48.4	7.2	19.5	52.4	9.7	24.3
D1a	Dark	71	147	44.8	8.5	19.2	45.1	12.3	22.9
D1b	Dark	71	147	44.0	8.7	18.7	44.3	11.7	22.3
D1c	Dark	71	147	43.2	8.7	18.3	44.6	7.3	22.9
D2a	Dark	36.5	157	43.2	9.3	18.4	44.8	12.6	22.8
D2b	Dark	36.5	157	43.6	8.9	18.4	43.1	12.7	22.2
D2c	Dark	36.5	157	42.9	8.7	18.2	43.2	12.3	22.5
D3a	Dark	21.25	167	42.6	9.1	18.7	43.8	12.4	22.1
D3b	Dark	21.25	167	42.5	10.0	18.0	42.8	12.5	21.0
D3c	Dark	21.25	167	43.1	7.8	18.1	42.6	12.6	22.0
D4a	Dark	16	177	42.1	9.4	18.0	40.7	12.5	19.6
D4b	Dark	14.25	177	42.8	14.0	17.1	46.1	11.8	22.8
D4c	Dark	16	177	42.5	8.3	17.6	41.4	12.8	21.7
D5a	Dark	12	187	42.0	8.8	17.4	40.7	12.1	20.7
D5b	Dark	12	187	42.0	9.3	17.3	41.0	13.2	20.9
D5c	Dark	12	187	42.8	7.9	17.6	42.7	12.0	21.7

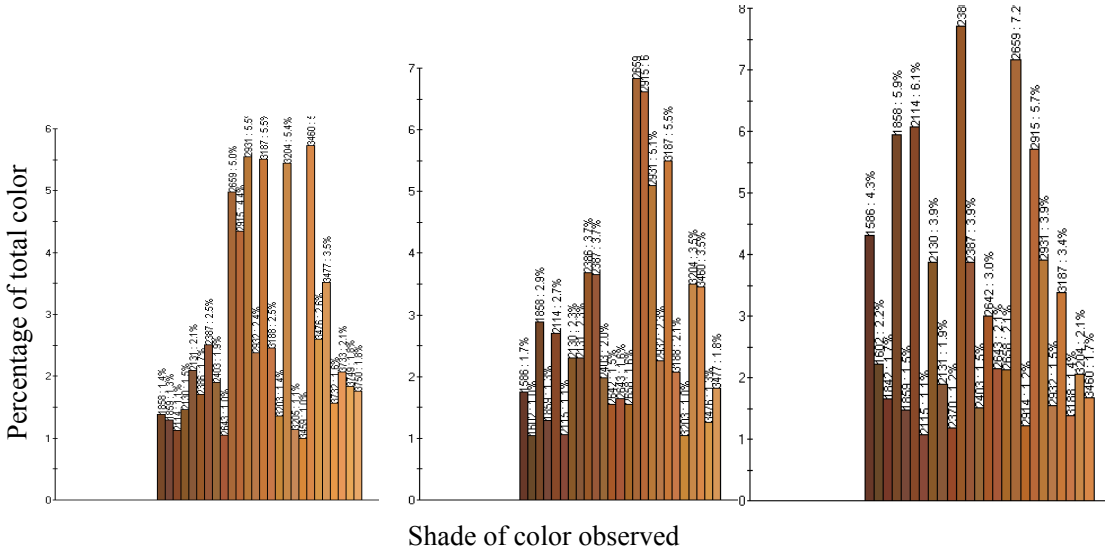

Figure 3.3 Iris E-Eye colors maps of 167 ºC light, medium and dark roast- left, middle and right respectively.

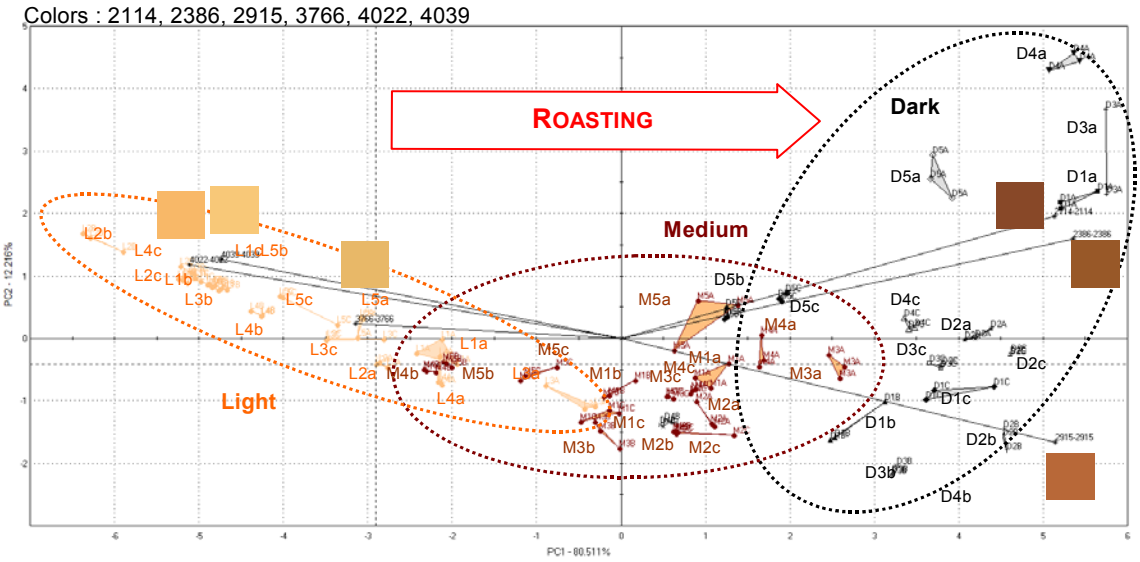

Figure 3.4 Principal component analysis (PCA) of 6 most discriminate colors of roasted peanuts on Iris E-Eye system.

3.4.3 Electronic Nose Systems

Differences among roasted samples were detected using all 3 E-Nose systems, including differences attributed to roast color and roast temperatures. Analysis of data from the Heracles E-Nose, which uses a GC based detection system, indicated clear differences among roasted samples (**Figure 3.5**). A PCA bi-plot of data collected from the Heracles E-Nose accounted for 97% of the variability, with PC1 and PC2 representing 64 % and 34 %, respectively (**Figure 3.5**). Roast color was distributed along PC1 and roast temperature along PC2.

Although the Heracles E-Nose produced the most discriminate PCA bi-plot, both the α Fox and Gemini E-Nose systems detected differences among roasted samples. The α Fox and the Gemini were used to produce odor maps, which represent dynamic responses of the MOS's to sample headspace. A typical signal map as generated by the 18 MOS's within the α Fox E-Nose is presented in **Figure 3.6**. Such dynamic sensor data was in turn used to generate a PCA bi-plot of all roasted samples measured via the α Fox (**Figure 3.7**). Samples were distinguished by roast color along PC1 which represented 48% of the variation and by temperature along PC2 which represented 44% of the variation. The information obtained by the α Fox provided similar information to that of the Heracles.

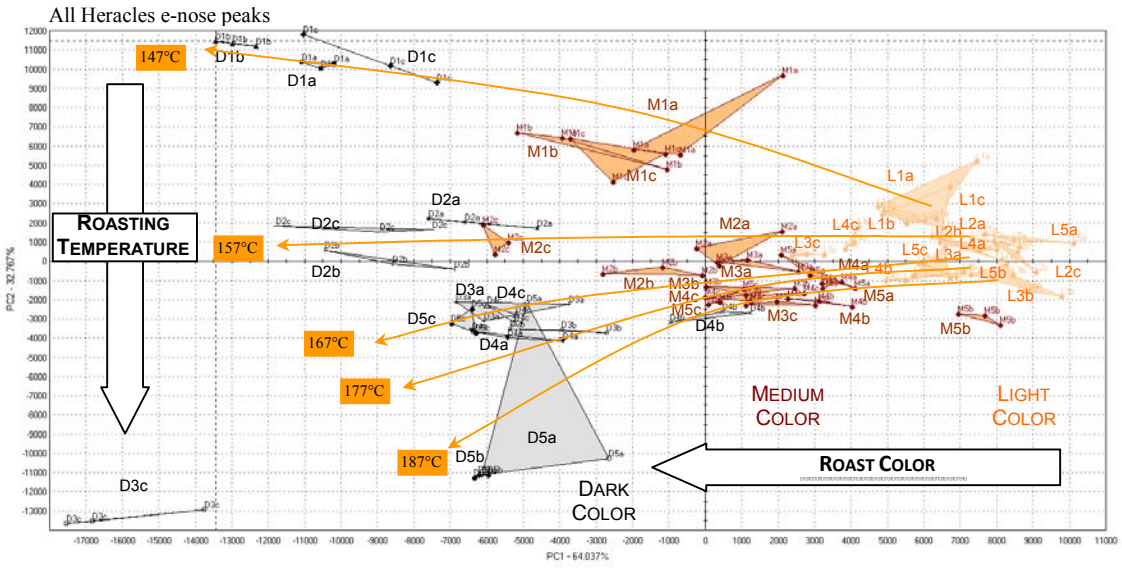

Figure 3.5 Global volatile map for peanuts roasted to varying time/temperature combinations using all peaks from Heracles E-Nose.

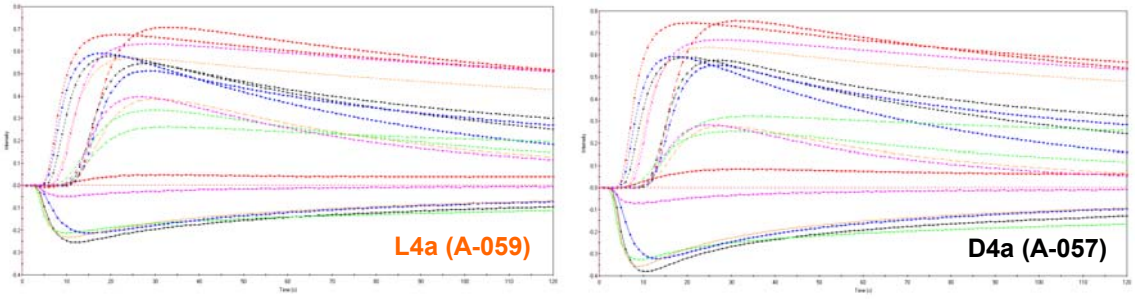

Figure 3.6. Signal maps of 18 α Fox E-Nose sensors obtained on 177 ºC light (left) and dark (right) roasts. Plotted as time versus odor units observed.

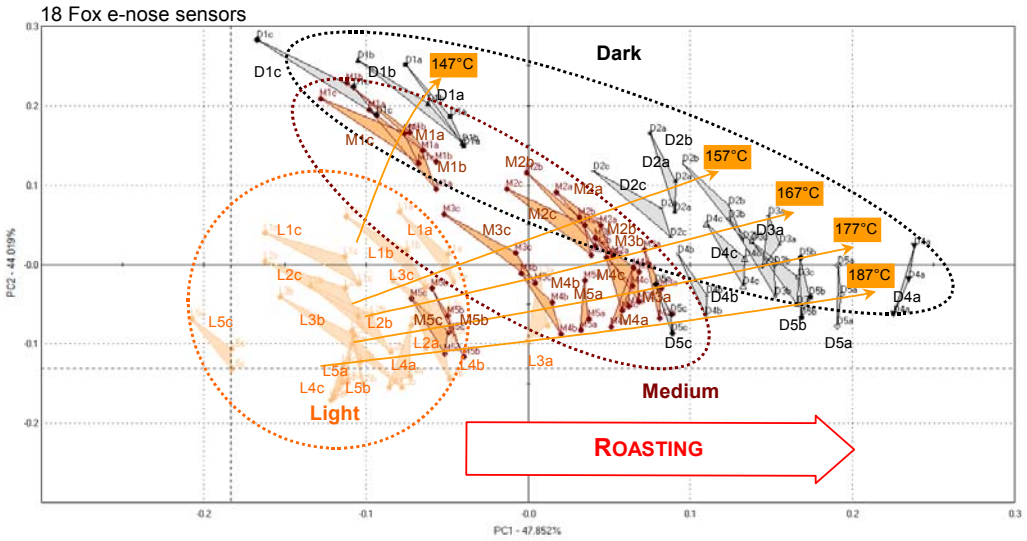

Figure 3.7 Principal component analysis of all roasted peanut samples evaluated on the α Fox E-Nose sensors.

A PCA bi-plot generated from data collected using the Gemini E-Nose which only has 6 MOS's (**Figure 3.8**) produced similar trends as those observed for the α Fox and the Heracles E-Nose systems. In the PCA plot with data from the Gemini E-Nose, roasted samples were more condensed spatially than in PCA plots obtained from data collected with the α Fox and Heracles E-Nose systems (**Figures 3.5 and 3.7**), indicating somewhat poorer discrimination of roasted samples as compared to data from the more advanced α Fox and the Heracles E-Nose systems. However, the PCA plot generated from the Gemini E-Nose data still accounted for 97% of variation among roasted samples, with PC1 and PC2 accounting for 67% and 30%, respectively. Again, roast color was distributed along PC1 and roast temperature was distributed along PC2.

Since both the α Fox and the Gemini were able to distinguish between samples similar to results produced by the more sophisticated Heracles, the two less sophisticated

models could be sufficient for determining differences among roasted samples if no volatile identification was needed. An advantage to using the Heracles E-Nose over the α Fox and Gemini E-Nose systems is that the Heracles E-Nose is able to potentially identify volatile compounds associated with each roasted sample and this information can help better explain differences among samples.

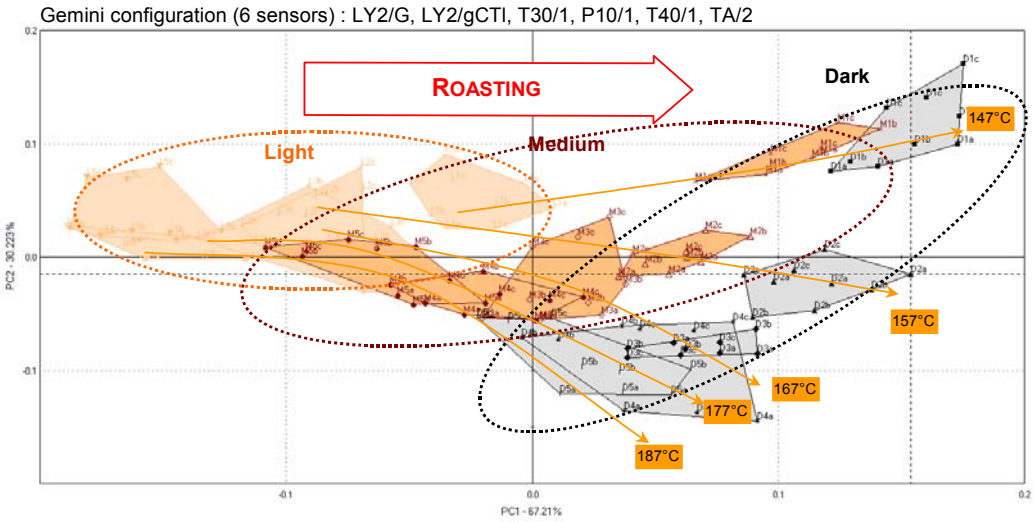

Figure 3.8 Principal component analysis of all roasted peanut samples evaluated on the Gemini E-Nose sensors.

Using Kovats indices, several compounds were potentially identified based on retention times of volatile compounds observed in the headspace of roasted samples using the Heracles E-Nose (**Table 3.5**). Potential volatile matches were then correlated with data from the DSA panel (**Table 3.6**). Regardless of roast temperature, high molecular weight pyrazine compounds were detected in greater quantities in dark roasted samples (**Table 3.6**) Highly volatile compounds were more concentrated in samples roasted at lower temperatures and

compounds with low volatility were more concentrated in samples roasted at higher temperatures (**Table 3.5**).

Another compound that was identified in the samples using the Heracles E-Nose was hexanal. Hexanal is often used as a marker for rancidity of products (Chandrasekara and Shahidi 2011). The Heracles E-Nose detected higher concentrations of hexanal in samples roasted to the light color and the 187 ºC medium roast. Peanuts roasted to a lighter color tended to have higher moisture contents and lower tocopherol contents (Chapter 2), and these data suggest that oxidation could be more favorable in the lighter roasted peanuts as compared to darker roasted samples. Data from the DSA panel did not specifically indicate rancidity for any of the roasted samples; however, total off-note scores of the 147 ºC and 157 ºC roasts were significantly higher than other roast temperatures. This finding indicates that the Heracles E-Nose system could have potential in identifying samples that may become rancid before the rancidity is detectable by the panel. The ability to quickly and easily determine potential rancidity would be a benefit to the peanut industry.

Strong correlations ($R^2 > 0.70$) were identified among some of the detected volatile compounds and many of the sensory attributes (**Table 3.6**). Several of the MBP volatile compounds identified on using the Heracles E-Nose were highly positively correlated with attributes such as dark roast, woody/hull/skins, bitter and ashy and strongly negatively correlated with attributes such as raw beany and sweet taste. Others have noted that MBP were found in higher concentration in peanuts roasted to darker colors and were associated with the sensory attributes dark roast, bitter and ashy (Smyth and others 1998). The strong correlation of volatile compounds identified by the Heracles E-Nose with the attributes such

as dark roasts suggest the potential of E-nose systems to rapidly characterize sensory properties of roasted peanut samples.

Table 3.5 Potential volatile compounds identified in the headspace of roasted peanuts by Heracles E-Nose using Kovats indices for references of volatiles.

t DB5	t DB1701	K DB5	K DB1701	Possible matches
4.1	3.8	489	511	furan
4.5	5	510	618	-
6.1	7.2	656	733	-
8.2	10.1	735	832	pyrazine
10.3	11.8	797	882	hexanal
11.3	13.1	818	914	2-methyl pyridine
14.7	16.2	906	995	2,5-dimethyl pyrazine

Table 3.6 Correlation coefficients among volatile compounds detected on Heracles E-Nose system and sensory attributes from DSA panel. Data shown in red indicates a strong correlation.

Kovats Column	**736-1**	**831-2**	**906-1**	**995-2**	**651-1**	**506-1**	**736-2**	**618-2**	**912-2**
	pyrazine	**pyrazine**	**2,5-DM pyrazine**	**2,5-DM pyrazine**	**-**	**furan**	**-**	**-**	**2-me pyridine**
Identification									
Roasted Peanutty	-0.55	-0.56	-0.24	-0.22	-0.29	-0.55	-0.22	-0.19	-0.29
Sweet Aromatic	-0.59	-0.60	-0.27	-0.25	-0.32	-0.58	-0.25	-0.23	-0.31
Dark Roast	**0.88**	**0.84**	**0.84**	**0.83**	**0.85**	**0.78**	**0.83**	**0.80**	**0.80**
Raw Beany	**-0.82**	**-0.80**	**-0.85**	**-0.85**	**-0.84**	**-0.71**	**-0.84**	**-0.82**	**-0.81**
Woody Hulls Skins	**0.87**	**0.85**	**0.73**	**0.72**	**0.75**	**0.81**	**0.71**	0.67	**0.73**
Cardboardy Stale	-0.02	0.01	-0.30	-0.31	-0.19	0.14	-0.24	-0.30	-0.30
Earthy	0.42	0.47	0.16	0.15	0.24	0.47	0.18	0.13	0.16
Painty	-0.01	-0.05	-0.14	-0.16	-0.05	0.12	-0.10	-0.13	-0.14
Plastic Chemical	0.43	0.49	0.07	0.08	0.16	0.52	0.10	0.05	0.10
Metalic	0.28	0.29	0.04	0.03	0.18	0.40	0.13	0.09	0.03
Sweet	**-0.86**	**-0.86**	-0.59	-0.57	-0.65	**-0.83**	-0.60	-0.55	-0.58
Bitter	**0.88**	**0.88**	0.65	0.63	0.69	**0.84**	0.64	0.58	0.64
Atringency	0.58	0.53	0.46	0.42	0.45	0.54	0.41	0.43	0.45
TTB	0.32	0.32	0.30	0.29	0.28	0.28	0.26	0.21	0.26
Ashy	**0.90**	**0.87**	**0.72**	**0.70**	**0.77**	**0.83**	**0.72**	0.64	**0.70**
Total Offnotes	**0.79**	**0.80**	0.43	0.41	0.53	0.83	0.45	0.35	0.43

Another benefit that information derived from the Heracles E-Nose system could provide to the peanut industry is the creation of quality control models. Using 177 ºC medium roast sample as a reference, a statistical quality control model was developed (**Figure 3.9**). This model utilizes information derived from the DSA panel along with information collected from the Heracles E-Nose to create a quality control model with an acceptable range that the volatile profile from the headspace of roasted samples must fall within to achieve acceptable sensory scores. Based on the global statistical model for all roast colors at177 ºC it was determined that the majority of medium roasts at 157 ºC , 167 ºC and 177 ºC along with light roasts at 147 ºC and 177 ºC and dark roasts at 177 ºC fall within the acceptable range. Roasted samples which fall outside of the acceptable range would therefore not be considered acceptable. With the collection of sensory data, a large database could be created to further develop the acceptable range. Once a sufficient amount of data is collected, this model could be used for a quick and easy method of determining peanut quality immediately after roasting.

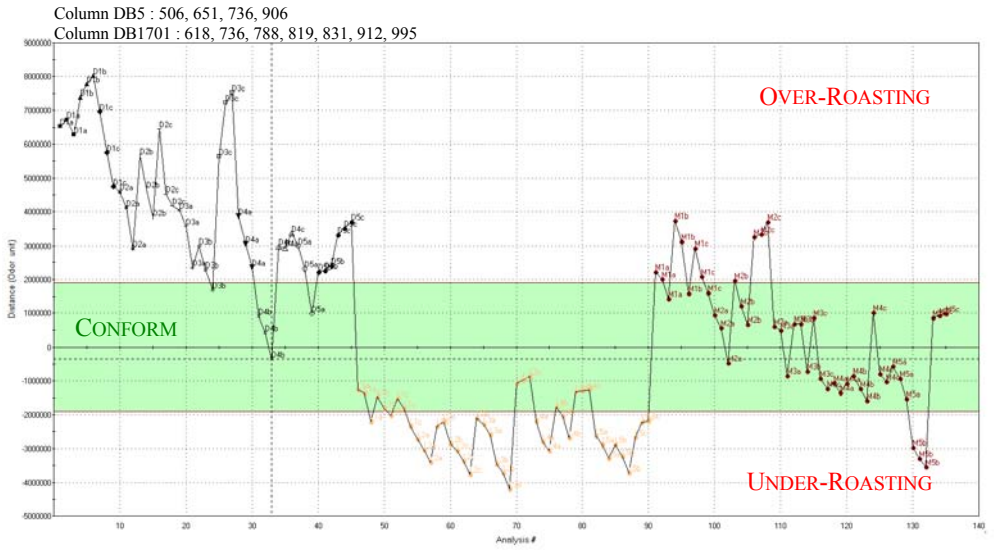

Figure 3.9 Statistical Quality Control (SQC) model based on the 177 °C medium roast as the reference using the Heracles E-Nose system.

3. 5 Conclusions

DSA panel indicated that across all roast temperatures roasted peanut flavor for all attributes was not significantly different for medium roasts between 157- 187 °C. Medium roasts were associated with more desirable attributes such as roast peanutty, and sweet aromatic, while light roast were associated with raw beany and sweet attributes and dark roast were associated with dark roast, bitter and woody/hulls/skin attributes. Roasting for an extended time at low temperatures produced undesirable flavors such as bitter, astringency and higher total off notes ($p<0.05$). Hexanal was detected using the Heracles E-Nose, and was identified in higher amounts among samples roasted at low temperature/light color combinations. This detection of hexanal by the Heracles E-Nose could provide earlier detection of samples that may become rancid.

The Iris E-Eye identified 6 colors out of 4096, which were sufficient for differentiating color differences among roasted samples. All E-Nose systems evaluated in this study could distinguish differences among samples due to roast color and roast temperature. The Heracles E-Nose was able to identity differences in volatile profiles of samples. The majority of volatile compounds identified corresponded to MBR products and were more concentrated in darker roasted samples. Dark roast, woody/hull/skins, and ashy sensory attributes had strong positive correlation with the pyrazine and furan compounds identified using the E-Nose, while raw beany had a strong negative correlation with these attributes.

Using a statistical quality control algorithm, the Heracles E-Nose system could be used to establish quality control parameters to determine over and under roasting. In conjunction with quality sensory data, the E-Nose systems demonstrated potential for use in processing operations for faster detection of roasted samples with positive sensory attributes. The electronic systems have potential; however, there is still a need for sensory data. Without effective sensory data, the instruments would not be properly "trained" to human perception.

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