## Influence of Different Packaging Systems on Stability of Raw Dried Pistachio Nuts at Various Conditions

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#### Abstract

The influence of packaging system on stability during storage of raw dried pistachio nuts was studied. The pistachio nuts were packed in plastic multilayer pouches (PS/EVOH/PE) at different conditions (atmosphere, vacuum and oxygen scavenger). Accelerated Shelf Life Testing (ASLT) method was used for evaluation the storage of pistachio at 20, 35 and 50 °C. Samples were analyzed at 4, 8, 12 weeks by using of split-plot design. To follow the oxidation profile, the formation of volatile oxidized products (Hexanal) was determined by GC-MS. Results showed that the formation of hexanal under all conditions was significant (p<0.05) and the oxidative process could be quantitatively controlled by decreasing the oxygen concentration surrounding raw dried pistachio nuts by the using of packaging systems. Pistachio nuts stored in oxygen scavenger system had a lower hexanal amount than both of vacuum and atmospheric systems.

Keywords: Pistachio nuts, Packaging, Stability, Hexanal, Oxygen scavenger

#### **INTRODUCTION**

Pistachio is the edible seed of the pistachio tree (*pistacia vera L.*). It is one of the favourite tree nuts of the world and is widely cultivated in dry and hot areas of the Middle East, Mediteranean countries and the USA. (Garcia, and Streif ,1992). A special feature of pistachios is its split shell. The moisture content of pistachios vary between 34-40 % (wet basis) after dehulling and separation processes, it must be reduced to 5% (wet basis) for safe storage and further processing (Hsu, Mannapperuma and Singh, 1991). Pistachio nuts

dried to 4-6% moisture are very stable and could be held for up to 12 months at temperatures as high as 20 °C without significant losses in quality attributes (Kader et al. 1982).

The kernels are a rich source of oil (50 - 60 %) and contain linolenic and linoleic fatty acids, essential for human diet and oleic acid (Maskan and Karatas, 1998). It contains around 23% protein, 19% carbohydrate and 5% moisture. Pistachio nut also contains high amounts of K and P, and various amounts of Ca, Mg and Fe. The fatty acid composition of the nut is 54.4–71.8% oleic acid, 16.7–35.3% linoleic acid, 7.2–10.5% palmitic acid, 0.9–2.5% stearic acid and less than 2 % linolenic acid (Gamily and Hayoglu 2007). Oxidative rancidity, a major cause of food deterioration, is due to the oxidation of lipids. The oxidative deterioration of food involves primarily auto

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oxidative reactions. These are further accompanied by various secondary reactions. Unsaturated fatty acids are most susceptible to oxidative attack. (Adhikari et al. 2003).

One of the factors that affect the autoxidation of common food fats is the total number of unsaturated linkages in the sample. However, the total amount of unsaturation may not be as important as the degree of unsaturation within a given molecule. A fat high in linoleic or linolenic acid would be more susceptible to oxidation than one containing a similar amount of oleic acid. Oxygen is necessary for auto oxidation of fats. Therefore, the removal of atmospheric oxygen from a fat or food product exerts a protective effect (Aurand and woods 1973). Oxidative deterioration has often been quantified in terms of the peroxide value or the content of volatile secondary lipid oxidation products, such as hexanal. The common polyunsaturated fatty acid, linoleic acid, is very susceptible to oxidation and during this process, hexanal is produced (Jensen and Risbo 2006). It is formed during the oxidation of linoleic acid via the 13-hydroperoxide and it has an odour described as "grassy" which contributes to off-flavour. In the last few years hexanal has been determined in food matrixes, using many different sample preparation methods and detection techniques (e.g. gas chromatography, liquid chromatography, spectrophotometry) . (Sanches et al. 2005). Hexanal is a good indicator of the degree of oxidation and has along with other volatiles been applied in various products to follow the quality deterioration (Berenzon and Saguy 1998, Jensen and Risbo 2006).

Since the 1950s, widespread use of plastic packaging material has taken place in the food industry. A single polymer is often unable to provide a suitable barrier; thus most food packaging materials have multilayer constructions. In multilayer constructions, polymers with different plastic, barrier properties are combined, where at least one layer acts as an oxygen barrier and other layers act as water barriers and sealing properties. A commonly used converting method for multilayer polymers is lamination sachets (Pettersen et al. 2005). Some studies have recently been published on the pistachio such as quality and safety of pistachio nuts as influenced by post harvest handling procedures (Kader.and Labavitch, 1980), fatty acid oxidation of pistachio nuts stored under various atmospheric conditions and different temperatures (Maskan and Karatas 1998), studies related to the description and evaluation of pistachio nuts quality (Kader et al.1982), characterization of pistachio kernel oils from Iranian cultivars (Kamangar, Farrohi and Mehrn 1975), behavior of oil seeds under various storage conditions (Hadorn et al. 1995), chemical composition of the pistachio nuts of Kerman, Iran (Hosseini 1977), supercritical CO<sub>2</sub> extraction of lipids from roasted pistachio nuts (Palazoglu and Balaban 1998), and determination the shelf life of raw dried pistachio nuts (Sedaghat et al. 2005) The objectives of this investigation were prediction the stability of raw dried pistachio nuts by hexanal determination and study the effect of temperature, storage time and packaging systems on the quality of pistachio nuts

### METHODS AND MATERIALS

#### **Pistachio nuts**

The Ohadee variety of Iranian pistachio nuts (*Pistacia vera L.*) was obtained from Fizabad Pistachio Factory, Khorasan, Iran. The average moisture content of the nuts was determined to be  $3.8 \,\%$ , using the oven drying method (AOAC, 1975). The samples were placed in sealed plastic bags and held at 0 -1 °C until the day of experiments.

#### Packaging material

The packaging material used in the experiments was transparent plastic multilayer pouches (PE/PA/PE) with a thickness of 80  $\mu$ m, manufactured by Henklman (Hertogenbosch, The Netherlands),

#### **Sample preparation**

100 g raw dried pistachio nuts were dispensed into transparent plastic multilayer pouches ( $22 \times 17.5$  cm) .The plastic pouches were then sealed by sealing chamber vacuum machine (model 200 XL, Henkelman vacuum system) under three packaging systems ( atmosphere, vacuum and oxygen scavenger (AGELESS <sup>®</sup>). This oxygen scavenger has designed to be used with dehydrated or dried foods. All samples were prepared in triplicates for accelerated storage conditions.

#### **Accelerated storage conditions**

Plastic pouch samples were held in controlled temperatures at 20, 35 and 50 °C for 4, 8 and 12 weeks. Beginning of the storage period was assignated as time zero. Storage temperatures and time were selected based on dehydrated food shelf-life studies (Labuza and Schmidl 1985). The relative change in the level of hexanal of stored pistachio nuts monitored using the GC-MS method. The pistachio samples were taken from the storage chambers after 4,8 and 12 weeks storage interval and stored in freezer (-80 °C ) until the day of analysis.

#### **GC-MS** analysis

Volatile oxidation product (hexanal) was analyzed using a dynamic headspace sampling method, modified from Hall et al. (1985) Thirty grams of raw dried pistachio kernel were transferred to a 500 ml flask with a closed headspace adapter, which was then allowed to equilibrate at room temperature. The flask was equilibrated containing Chromosorb 102 by leading a helium gas stream (40 ml/min) through the cartridge. After reaching equilibrium, the volatile compounds were adsorbed onto an adsorption cartridge. The adsorption cartridges were then injected onto a fused-silica capillary column (60 m, i.d. 0.32 mm, and film thickness) coated with a DB1 phase (J&W Scientific Inc.) situated in an HP 5890 gas chromatograph. The gas chromatograph was equipped with split detection, where one part was led to a flame ionization detector and three parts to an Incos 50 mass spectrometer (Finnigan). The analysis was performed with the following parameters: helium flow 4.0 mL/min; temperature programming from 30 °C to 200 °C at a rate of 4 °C min; holding time at 200 °C, 20 min. The results are given as ng/L. An HP 3550 laboratory data system was used to collect data and calculate peak areas of volatiles from the FID responses. Figure 1 shows a sample plot that was obtained .The amount of volatiles was calculated using externally-determined calibration values (Lennersten and Lingnert 1998).

#### **Statistical analysis**

Results were compared by multifactor analysis of variance (multifactor ANOVA) to test for significant differences. Means of the groups were compared using the least significant difference (LSD) multiple range test by using a Statgraphics statistical packet (Statgraphics plus, 2000). Sigma Plot 2001 (SPSS Inc., Chicago, USA) and SlideWrite Plus Version 6 soft ware used for drawing plots and differences among samples. Means were reported to be significant when p<0.05.

#### **RESULTS AND DISCUSSION**

#### a) Effect of temperature

Figure 2A shows the effect of different temperature on the hexanal during storage. The results showed that significant (p < 0.05) difference was obtained between 20 and 50 °C. At 35 °C hexanal level was increased but it was no significant (p $\geq$ 0.05). The higher the storage the higher the hexanal level. The increase in hexanal values could be attributed to the oxidation of fats in pistachio nuts . Increase in storage temperature

causes oxidation of fats, which produces alkyl peroxides. Hexanal is formed during both autoxidation and photo synthesized oxidation of linoleate (Lennersten and Lingnert 1998). Lipoxygenases catalyze the hydroperoxidation of polyunsaturated fatty acids, such as linoleic and linolenic acids which are abundantly accumulated in the nut kernels, with consequent production of 9- or 13- hydro peroxides. These molecules are

very unstable and are rapidly converted to an array of other compounds such as short-chain aldehydes. These volatile aldehydes are important constituents of the flavour and aroma of many fruits and vegetables. However, not all  $C_6$  aldehydes are perceived as pleasant. In the case of pistachio nuts, hexanal is the principle responsible of the unpleasant "grassy - beany" flavour (Piccirillo et al. 2005)

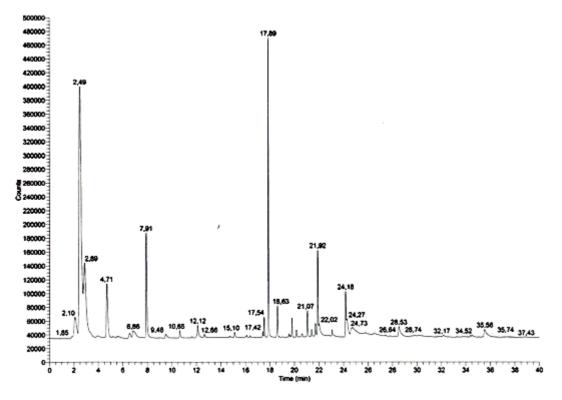


Figure 1: Typically plot of hexane's samples during storage by effect of treatments (temperatures, packaging systems and storage times) from GC- MS

#### b) Effect of packaging systems

Hexanal level showed significant (p<0.05) decrease with changing of packaging systems from atmospheric to vacuum and to oxygen scavenger respectively (Figure 2B). Data shown that packaging systems had a significant effect on the quality of pistachio nuts. As a comparison, the hexanal reduction samples stored in a system with oxygen scavenger was 2.25 to 2.48 times lower

than both of atmosphere and vacuum respectively. The application of oxygen scavenger in packaging confections, rice cakes, biscuits and crackers, seafood, oily products, cake mixes and coffee has been studied by other workers. It has also been used to prevent oxidative rancidity or to prevent flavour and colour defects in high-fat foods (e.g. nuts, potato chips, beef jerky),. (Berenzon and Saguy 1998). Analysis of the data revealed that there was significant interaction of the factors on hexanal ( $p \ge 0.05$ ) and Figure 3 shows the interaction effects on hexanal. Increasing the storage temperature from 20 to 35 °C, the hexanal concentration increased significantly, while the hexanal concentration decreased at 50 °C (Figure 3A). This reduction in hexanal level could be due to its further breakdown and participation in maillard type reactions at the higher storage temperature, (Adhikari et al. 2003, Berenzon and Saguy 1998).

The figure also shows a large difference in production of hexanal between samples stored in the atmosphere, vacuum and oxygen scavenger. As can be seen from the differences in hexanal production, there was a large difference in oxidation rate between the oxygen scavenger with vacuum and atmosphere packaging systems for raw dried pistachio nuts. The higher the oxygen concentration, the higher the production of theoretically, lower hexanal. at oxygen concentrations the lipid oxidation should be more strongly influenced by differences in oxygen concentrations. An explanation could be that the reactions producing secondary oxidation products were influenced by the oxygen concentration.

Oxygen scavenger is effective in lowering oxidation rates due to a lower oxygen concentration, and results suggest that oxygen scavenger packaging was an ideal packaging system for raw dried pistachio nuts . Berenzon and Saguy (1998) showed that oxygen scavenger was effective in reducing the oxidative formation of hexanal in both sunflower seeds and corn chips during accelerated storage tests. It is seen from Figure 3B, with increasing the time of storage in vacuum, hexanal increased but in atmosphere hexanal increased at 35 °C and decreased at 50 °C. We found that hexanal of pistachio nuts increased with extending the storage time under all examined temperatures (20, 35, 50 °C) and the minimum hexanal accumulation was observed at 20 °C for all treatments (data not shown).

#### C) Effect of storage time

The longer storage time resulted in the higher of hexanal level in all package systems at all conditions significantly (p<0.05) (Figure 2C). Jensen and Risbo (2006) showed that the development of lipid oxidation (measured by hexanal content) in oatmeal and peanuts increased linearly with time. Goode and Soutar (1995) showed that as oxygen of head space of package nut would begin to oxidize and hexanal would be formed by looking at the rates of increase in hexanal vs. time at accelerated exposure.

The following second order polynomial equation was chosen in order to determine the effect of time and temperature on the hexanal

$$z = a_0 + a_1 x + a_2 y + a_3 x y + a_4 x^2 + a_5 y^2$$

Where z = amount of hexanal ,  $a_0$  is constant ,  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$  and  $a_5$  are the coefficients of the polynomial . x is time and y is temperature. Figure 4 shows the amount of hexanal in response surface design .The following second- degree polynomial equation was found to explain the amount of hexanal ( $r^2 = 0.86$ )

# $Z = 11.4048 - 0.07414X - 1.1883Y + 0.01591XY - 0.0001X^{2} + 0.09927Y^{2}$

The model found a linear relationship between hexanal concentration and time, whereas temperature represents the quadratic effect on the response . As can be seen from Figure 4, hexanal concentration increase linearly with an increase in time. Mate et al. (1996) showed that hexanal concentration was followed to monitor the oxidative rancidity process and quality of pistachio nuts

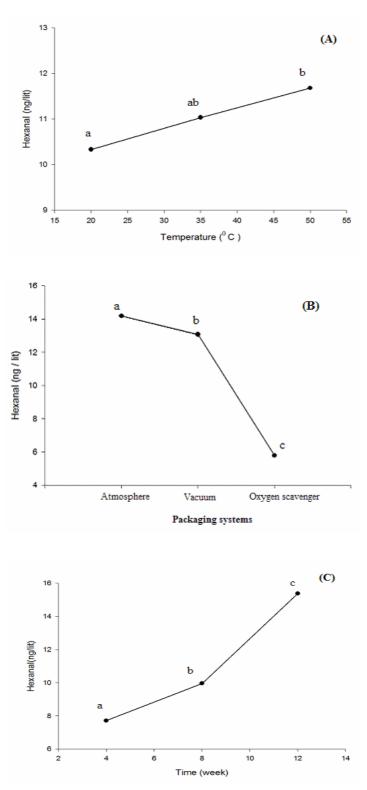


Fig 2: Effect of (A) temperature, (B) Packaging systems and (C) storage time, on Hexanal concentration (ng/L) of raw dried pistachio nuts, points with common letter are not significantly different by LSD test (p < 0.05).

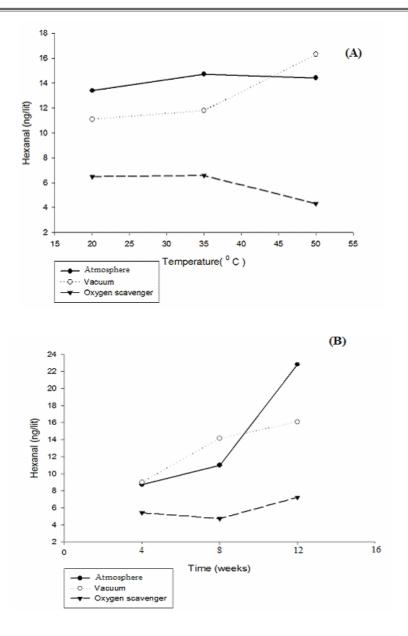


Fig 3: Multiple Rang Test for effect of (A) packaging and temperature, (B) packaging and time on Hexanal concentration (ng/L) of raw dried pistachio nuts.

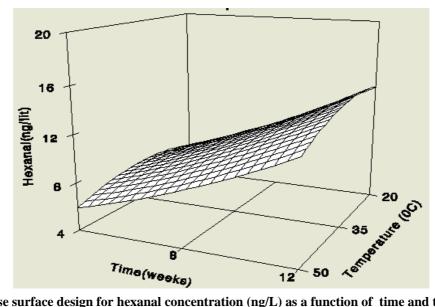


Figure 4: Response surface design for hexanal concentration (ng/L) as a function of time and temperature.

#### **CONCLUSION**

In conclusion, the data suggested that the oxidative process could be quantitatively controlled by decreasing the oxygen concentration surrounding raw dried pistachio nuts . There is potential application for either vacuum and oxygen scavenger packaging to eliminate the oxygen content within this nut and therefore retarding the The oxygen scavenger was more oxidation. important in the stability of raw dried pistachio nuts . The GC-MS method developed could be used as a tool for the rapid detection of lipid oxidation .Its advantages include rapid testing, and its reliability makes it a good tool for routine quality screening analysis of stored pistachio nuts. Data From storage study indicated that level of the hexanal was increased significantly under various conditions.

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## تاثیر انواع مختلف سیستم های بسته بندی بر پایداری پسته خشک خام در شرایط مختلف

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#### چکیدہ

تاثیر انواع مختلف سیستم های بسته بندی بر پایداری پسته خشک خام طی نگهداری در شرایط مختلف مورد مطالعه قرار گرفت . پسته ها در کیسههای چند لایه پلاستیکی ( PE / EVOH PS ) بسته بندی گردید و در شرایط مختلف ( اتمسفر ، خلاء و حضور جاذب اکسیژن ) نگهـداری شـدند . جهـت ارزیابی پسته نگهداری شده در ۲۰ ، ۳۵ و ۵۰ درجه سانتی گراد از روش آزمون تعیین زمان ماندگاری تسریع شده ( ASLT ) استفاده شد . نمونه هایی از پسته نگهداری شده در شرایط مختلف پس از ۴ ، ۸ . ۱۲ هفته با استفاده از طرح آماری split – piot مـورد ارزیـابی قـرار گرفت. بـرای پیگیری روند اکسایشی محصول ، میزان تولید مواد فرار حاصل از اکسیداسیون ( هگزانال ) با استفاده از دستگاه MS – 200 تعیین مقدار گرفت. بـرای نشان داد که تولید هگزانال تحت کلیه شرایط نگهداری معنی دار بود ( ۲۰/۵ P ) و فرآیند اکسایشی را می تـوان بـا کـاهش غلظت اکـسیژن محیط سیستم بسته بندی بطور کمی کنترل نمود . پسته نگهداری شده در سیستم بسته بندی دارای جاذب اکسیژن دارای کمترین میزان هگزانال نسبت بـه دو نوع سیستم بسته بندی دیگر یعنی خلاء و شرایط اتمسفر بود.

کلمات کلیدی : پسته خشک ، بسته بندی ، پایداری ، هگزانال ، جاذب اکسیژن

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