Spectral Properties and Effect of Drying Temperature on Almonds with Concealed Damage

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The feasibility of using near infrared light transmission, obtained after drying, to predict if an almond would develop concealed damage after roasting was studied. It was observed that, after drying, nuts with concealed damage have less absorbance in the oil absorption band at 930 nm and increased absorbance in the region between 700 and 750 nm. From near infrared transmission spectra obtained after drying, discriminant analysis was used to classify nuts as concealed damaged or undamaged; validation classification error rates as low as 12.4% were obtained. The effect of drying temperature, and moisture exposure, on the incidence of almonds with concealed damage was also studied. The use of a lower temperature drying treatment can reduce the incidence of concealed damage. The incidence of concealed damage for nuts receiving the same moisture treatment was 44.4 and 1.2% when dried at 110 and 55 °C, respectively.

Keywords: almond; Maillard; near infrared; detection; browning

Introduction

Concealed damage in almonds is defined by the industry as a browning of the kernel interior after moderate to high heat processing, such as cooking or roasting (1). Bitter flavors are developed in extreme cases of concealed damage after roasting or cooking (1). **Figure 1** shows an example of an undamaged almond and an almond with concealed damage after cooking. There are no visible indications of concealed damage on the exterior of the kernel before or after cooking or roasting. There are no visible indications of concealed damage on the interior of the kernel after drying but before cooking. Since concealed damage is not visible from the kernel exterior, this type of damage does not fall into any of the USDA defect categories for almonds (2).

The concealed damage disorder is apparently initiated when nut kernels are exposed to a warm and moist environment (1, 3). Nuts are most likely to encounter conditions favorable for the development of concealed damage when rain occurs during harvest. It is hypothesized by the almond industry that the Maillard reaction causes the browning in almonds (4). It has been shown that almonds exposed to moisture for long periods of time start to produce reducing sugars (3), and lipids may oxidize (5). In soybeans, lipid oxidation can form aldehydes that serve as reactants in the Maillard browning reaction (6). Further research (5) showed that reducing sugars in almonds formed during exposure to moisture will disappear during drying; presumably, because these sugars bind to proteins during the initial stage of the Maillard reaction.

The incidence of concealed damage is very sporadic from year to year. It becomes a significant problem every 3–5 yr, when a heavy rain occurs during harvest. Mission variety almonds are most susceptible to concealed damage, possibly due to a late harvest time when exposure to rain is more probable (4). Almonds containing more than 60 g/kg moisture are dried upon delivery to the processor. Nuts may be dried in bins at approximately 54 °C, or on a continuous belt between 93 and 121 °C (7). During a wet harvest season, the quantity of almonds requiring drying upon delivery to the processor may exceed 20% of the total harvest and exceed the drying capacity of most almond producers. This creates an increased time period when almonds are held at a high moisture content which further increases the incidence of concealed damage. Properly dried nut shipments are essentially free of concealed damage while the wet shipments that are dried immediately upon delivery to the processor typically contain 1–10% or more concealed damaged nuts (4).

Detection of nuts with concealed damage would ideally be performed after the drying process, when nuts are removed from storage for final processing. Most almonds are used as ingredients in foods and are impossible to inspect after cooking. However, no browning is present after drying. It has been found that properties such as kernel volume, thickness, post-dry moisture, and moisture loss during drying have very low

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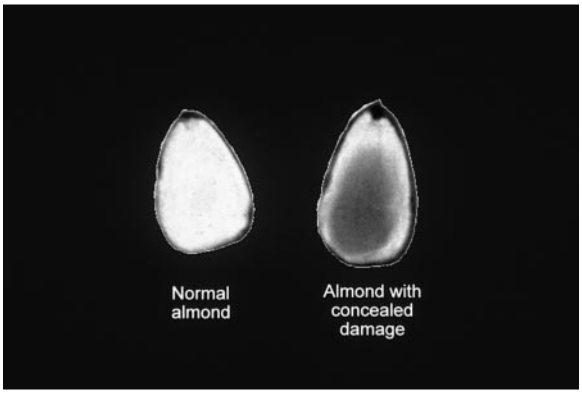

Fig. 1 Undamaged almond and almond with concealed damage

correlations with the extent of browning associated with concealed damage (5). This study investigates the effect of drying temperature on the incidence of almonds with concealed damage and the feasibility of a near infrared (NIR) detection system for almonds with concealed damage after drying but before roasting. It is hypothesized that the NIR transmission could detect changes in sugars, oil oxidation levels, or early Maillard reaction products after drying which would facilitate the prediction of concealed damaged after roasting.

Materials and methods

Moisture and drying treatments

Whole almond kernels were treated with one of three moisture treatments (none, short or long) and one of two drying treatments. The long moisture treatment comprised soaking the nuts in water for 60 min, then transferring them to a 95% relative humidity environment for 60 h. The short moisture treatment comprised soaking the nuts in water for 30 min then transferring them to a 95% relative humidity environment for 30 h. The following seven moisture-drying treatment combinations were used:

(1) long moisture and 110 °C convection drying,
(2) long moisture and 55 °C convection drying,
(3) short moisture and 110 °C convection drying,
(4) short moisture and 55 °C convection drying,
(5) no moisture treatment and no drying,
(6) no moisture treatment and 110 °C convection drying,
(7) no moisture treatment and 55 °C convection drying.

The nuts that were dried but received no moisture treatment were dried for the same length of time as the short moisture treatment nuts. For this entire experiment, Mission variety almonds were used as this variety usually has the highest incidences of concealed damage. Eighty-one whole almond kernels, 1996 harvest, were exposed to each moisture and drying treatment combination.

Light transmission spectra measurement

Whole kernel transmission spectra from 700–1000 nm were measured before treatment, and transmission spectra from 700–1400 nm were measured after drying. Two different fiber optic spectrometers were used. A silicon photodiode array sensor based spectrometer (Ocean Optics, Dunedin, FL, U.S.A., #PC1000) was used to obtain the spectrum from 700–1000 nm in approximately 0.48 nm intervals, and an InGaAs photodiode array spectrometer (Control Development, South Bend, IN, U.S.A., #OSC/256L-1.7T1-250A/0.9-1.7/3.2) was used to measure the spectrum from 950–1400 nm in 3.2 nm intervals. Each spectrometer sampled ten complete transmission spectra and stored the average. The integration time of each photodiode element on the silicon spectrometer and InGaAs spectrometer was 0.5 and 1.0 s, respectively. The integration times and number of samples to average were obtained by trial and error. Approximately 15 s were required to acquire spectra for one nut with these parameters.

The light source was a 100 W quartz tungsten halogen lamp (Oriel, Stratford, CT, U.S.A., #77501). The time that the nut was exposed to the light source had to be minimized. If the nut was exposed to the light source for more than one minute, heating and scorching would sometimes begin, due to the intense radiation from the light source. The light transmission spectra of each nut was measured at approximately the thickest point perpendicular to the sature plane. The transmitted light through the nut was split and directed to each of the two spectrometers through fiber optic cables. This facilitated the acquisition of spectra by both spectrometers at the same time. A light standard and dark standard were obtained between sampling each nut. The dark standard was obtained by blocking the light source with a steel shutter. The light standard was obtained by placing a glass neutral density filter with a transmission of 0.1% (Ealing, Holliston, MA, U.S.A., #35-5941) in place of the sample.

After the acquisition of all spectra, each spectrum was smoothed by a 19 point Savitzky–Golay 2nd order filtering operation (8). To correct for wide variations in skin quality, nut thickness, and nut shape, absorbance values were normalized by dividing each absorbance value by the mean of all values in the sampled spectrum. This data treatment helped to cancel out the effect of nut thickness, skin chips, and skin condition. Absorbance values from the Ocean Optics spectrometer were not equally spaced between 700 and 975 nm. Equally spaced data in 5 nm increments was computed by 19 point interpolation. First derivative spectra were computed using the central difference method with a 5 nm gap. Second derivative spectra were computed using the central difference method with a 10 nm gap (8).

Classification of nuts as concealed damaged or undamaged

After the spectra were obtained, browning was induced by cooking all nuts at 135 °C for 90 min in a gravity convection oven (Lab-Line Instruments, Inc., Melros Park, IL, U.S.A., Imperial IV). After cooking, the nuts were split at the suture and photographed (Eastman

Kodak Co., Rochester, NY., U.S.A., ASA 200, Ektachrome). Two paint chips, rawhide brown and almond color (Behr Process Corp., Santa Ana, CA, U.S.A.), were included in each image as standard colors. The rawhide paint chip approximated the darkest brown that may appear in concealed damaged almonds, while the almond color paint chip approximated the lightest color of undamaged almond kernels. The slides were digitized with a 35 mm film scanner (Nikon, Shinagawa-ku, Japan, LS-1000). The resolution of the digital images was 1296 × 1944 pixels which corresponded to approximately 150 pixels per inch in real space. The digital color intensity resolution was 24 bit (8 bits per RGB channel).

The digital images were further processed with a shareware software package (Image PC, Scion Corp, Frederick, MD, U.S.A.). Firstly, they were converted to grayscale, then linearly histogram stretched so that the mean intensity of the rawhide and almond paint chips were 10 and 245, respectively. This assured that the intensity scales of all images were consistent. Most almond images had a dark edge around the perimeter of the nut, caused by the brown skin and shadows adjacent to the nut. These areas were manually set to zero intensity with an eraser tool. About 10% of the almonds had cracks in the middle of the kernel, giving a darker appearance than the surrounding kernel tissue. The cracked areas were also manually set to zero intensity. Using these segmented images the mean pixel intensity, not including pixels with zero intensity, of each individual kernel was computed.

The almond industry defines a nut as concealed damaged if at least 50% of its kernel area appears 'dark' brown. The definition of dark brown varies among processors and the classification of concealed damage is usually performed by visual inspection. For this study, kernels with a measured mean image gray level less than 160 were classified as concealed damaged. This method produced classification results consistent with one California almond processor's definition of concealed damage.

Prediction of almonds with concealed damage from post-dry spectra

Principal component analysis was performed on the entire normalized absorbance, first derivative, and second derivative spectra from 700–1300 nm, from 700–975 nm, and from 1000–1300 nm. Statistical analysis was performed with the SAS statistical package (9, 10) to perform a two way classification based on the mean image gray level of the cooked almond kernel. Stepwise discriminant variable selection (sle = 0.05, sls = 0.05) of the principal components was then used to choose a relatively small set of variables to be used in the discriminant function. Discriminant analysis in SAS was trained with the selected principal components on half of the data (odd numbered samples) and validated with the other half (even numbered samples). The pool = test option was used to determine the equivalence of covariance matrices. The model selected by the stepwise selection procedure was checked for over fitting on the validation set. For each model, a plot was constructed of the number of variables in the model, in the order selected, versus the validation set classification error rate. The variables corresponding to the minimum error rate were recorded.

Table 1 Incidence of concealed damage for each treatment combination

Moisture treatment	Drying treatment	Percent of concealed damaged
Long	110 °C	44.4%
Long	55 °C	1.2%
Short	110 °C	60.5%
Short	55 °C	13.9%
None	110 °C	1.2%
None	55 °C	0.0%
None	None	0.0%

Results and Discussion

Effect of moisture and drying treatments

Using data from the moisture and drying treatments an ANOVA was performed with the drying method (none, low temperature, high temperature) and moisture exposure (none, short, long) as independent variables, and mean gray level as the dependent variable. Drying, moisture exposure, and the interaction between drying and moisture treatments are all significant at the 0.001 level.

Table 1 shows the fraction of nuts for each moisture/drying treatment classified as concealed damaged. For the long moisture treated nuts dried at 110 °C, 44.4% of the nuts were classified as concealed damaged. In contrast, of the long moisture treated nuts dried at 55 °C, only 1.2% were classified as concealed damaged. A reduction in concealed damage incidence was also obtained for the short moisture treated nuts. There was very little difference in the incidence of concealed damage between the control nuts (no moisture treatment and no drying) and nuts that were not exposed to moisture but dried. Similarly, a study of the reduction of internal browning in macadamia nuts, due to moisture exposure at harvest, has been accomplished with lower drying temperatures (11).

As shown in **Table 1**, it appears that nuts exposed to the short moisture treatment will have a higher incidence of concealed damage. The mean gray level of almonds from the short moisture treatment experiments were found, at the 0.05 level, to be significantly lower (or browner) than from the long moisture treatment experiments. Tukeys Studentized Range (HSD) test was used for the comparison of means. One hypothesis for this result may be that higher moisture contents achieved with the long moisture treatment drives the initial stage of the browning reaction backwards (12). The long and short moisture treatments raised the moisture content of almonds to

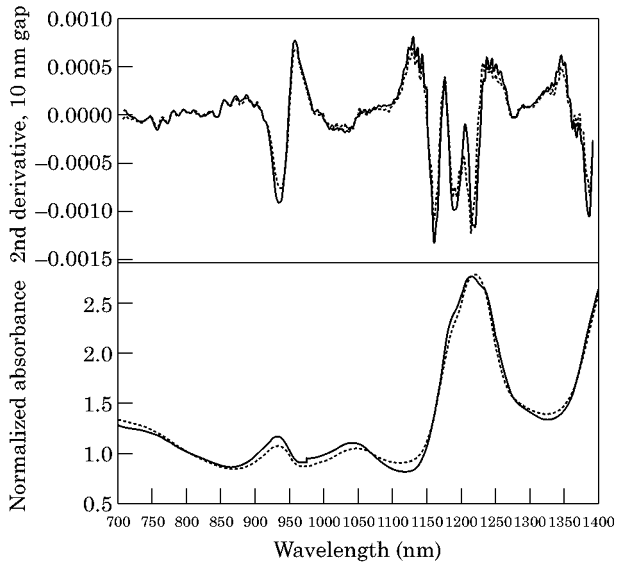

Fig. 2 Mean normalized absorbance spectra and second derivative spectra from 700–1400 nm of undamaged almonds and almonds with concealed damage. (——) normal almond; (· · ·) concealed damage

approximately 440 and 230 g/kg, respectively. The reducing sugar formation during moisture treatment was nearly identical for the long and short moisture treatments (5).

Spectral property results

The mean normalized transmission spectra and second derivative spectra from 700–1400 nm, obtained after drying but before cooking, for undamaged almonds and almonds with concealed damage are shown in **Fig. 2**. As can be seen from **Fig. 2**, the largest differences between means of the concealed damage groups are at 700 and 930 nm. The absorbance peak at 930 nm can be attributed to oil (13). Concealed damaged nuts have less absorbance in this area, possibly due to oxidation during moisture exposure (5). **Figure 3** shows the

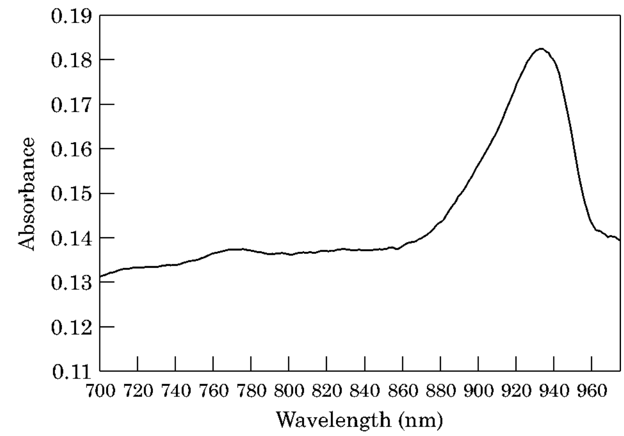

Fig. 3 Absorbance spectrum for pure almond oil

absorbance spectrum of pure almond oil having a peak at 930 nm.

Figure 4 shows the change in absorbance spectra of

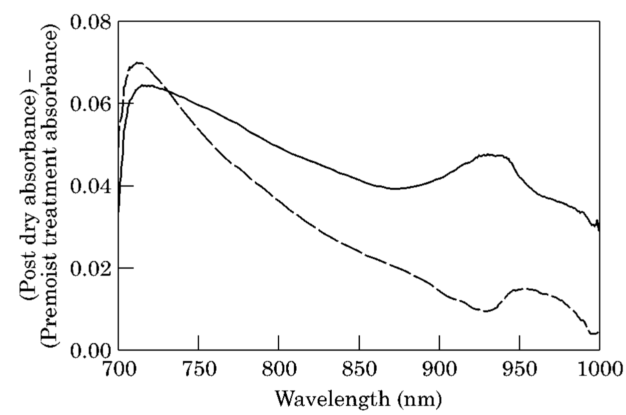

Fig. 4 Difference in mean absorbance spectra before and after moisture treatments and drying of concealed damaged nuts and undamaged nuts. (——) normal; (– – –) concealed damage

Table 2 Results of discriminant analysis using principal components of different portions on the spectra. Results are ordered from lowest error rate to highest

Spectra	Wavelength range (nm)	Percent of total error rate	Percent of false positives	Percent of false negatives	Number of principal components used
Absorbance and 1st derv. and 2nd derv.	1000–1300	12.4	1.4	11.1	8
First derivative	1000–1300	14.2	1.4	15.9	8
Absorbance and 1st derv. and 2nd derv.	700–975	15.0	5.4	11.1	5
Absorbance	1000–1300	15.4	1.4	12.7	10
First derivative	700–975	15.6	2.0	11.1	7
Absorbance	700–975	16.0	2.7	12.7	5
Absorbance and 1st derv. and 2nd derv.	700–1300	16.0	2.7	12.7	7
Absorbance	700–1300	16.6	4.1	12.7	8
Second derivative	1000–1300	18.3	0.7	11.5	8
First derivative	700–1300	18.6	1.4	20.6	7
Second derivative	700–1300	20.8	1.4	15.9	11
Second derivative	700–975	27.5	5.4	23.8	7

undamaged and concealed damaged nuts during the moisture and drying treatments. These plots were made by subtracting the normalized absorbance spectrum obtained before any treatment was applied to the nuts, from normalized absorbance spectrum obtained after drying. The curves in **Fig. 4** represent the mean of these differences in absorbance values for concealed damaged and undamaged nuts. The concealed damaged nuts show a higher increase in absorbance after drying around 700 nm than undamaged nuts. In contrast, undamaged nuts show a higher increase in absorbance after drying in the region around 930 nm than concealed damaged nuts.

Prediction of almonds with concealed damage from post-dry spectra

The results of the discriminant analysis using principal components of the normalized absorbance, first derivative, and second derivative spectra are tabulated in **Table 2**. The error rate is the percentage of nuts in the validation set incorrectly classified. The false positive error rate is defined as the percentage of undamaged nuts in the validation set being classified as concealed damaged. The false negative error rate is defined as the percentage of nuts with concealed damage in the validation set being classified as undamaged.

The lowest total error rate, 12.4%, obtained by this method was using principal components of the absorbance, first derivative, and second derivative spectra between 1000 and 1300 nm. This classification model had false positive and false negative error rates of 1.4 and 11.1%, respectively. Comparable false positive and false negative error rates are obtained using only first derivative spectra between 700 and 975 nm. This is an important result because silicon light detectors, sensitive between 700 and 970 nm, are less expensive, for a given signal to noise ratio, than detectors sensitive to light between 1000 and 1300 nm.

Development of a real time NIR system to detect almonds with concealed damage is discussed in (14).

Conclusions

For a given moisture treatment, the use of a lower temperature drying treatment can reduce the incidence of concealed damage. For the long moisture treated nuts dried at 110 °C, 44.4% of the nuts were classified as having concealed damage. In contrast, only 1.2% of the long moisture treated nuts dried at 55 °C were classified as having concealed damage. Similar results were obtained for the short moisture treated nuts.

Comparing the post-dry transmission spectra of concealed damaged and undamaged almonds, it was observed that nuts with concealed damage have less absorbance in the oil absorption band at 930 nm, and increased absorbance in the region between 700 and 750 nm. The difference between absorbance spectra, obtained before moisture treatment and after the drying of individual nuts, indicate that the changes in the absorbance occurs sometime during moisture treatment and/or drying.

Using NIR transmission spectra features, discriminant analysis was used to distinguish almonds with concealed damage from undamaged almonds before cooking. The lowest classification error rate on the validation set, 12.4%, was obtained using principal components of the absorbance, first derivative and second derivative spectra between 1000 and 1300 nm. The lowest classification error rate on the validation set, 15.0%, using spectra between 700 and 1000 nm was also obtained using principal components of the absorbance, first derivative and second derivative spectra.

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Mention of a specific product or vendor does not imply endorsement by USDA over other products which might be equally applicable.

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