Shelf-life kinetic model for freeze-dried oranges using sensory analysis and luminance determination

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Abstract Physical (luminance) and sensory variables (color and taste) were used to analyze the aging of freeze-dried oranges slices, determining the influence of temperature and time on aging and evaluating the shelf-life. The highest value in the luminance distribution curve, especially useful when the color of the food products is not uniform, and the color and taste scores obtained in sensory analysis were used to evaluate the shelf-life. Different kinetics models were probed to explain the experimental results but only third-order kinetic model correlated the luminance as a function of time and temperature. This kinetic constant obtained depended on the temperature following an Arrhenius model, giving an activation energy equal to 208 kJ/mol ($R^2 = 0.9959$). The correlation between physical (luminance) and sensory variables (color and taste) may be used to evaluate the shelf life of the orange slices, finding revealed that at 28 °C the shelf life may expected to be 10 years.

Keywords Shelf life · Freeze-drying · Orange · Luminance · Sensory analysis · Kinetic model

Introduction

The marketing of processed fruits has continually expanded due to the improved quality of these products, the convenience of ready-to-serve products, and the need for

products year round. This has led to increased processing to enhance product life. Dehydrated fruits have received special attention because they are easily obtained, retaining the characteristics of natural products, reducing the transportation cost, and avoiding the fruit deterioration (Hough et al. 2006). Freeze drying is a process in which the product is first frozen and then, while still in a frozen state, the majority of the water is reduced by sublimation and desorption so as to limit biological and chemical reactions at the designated storage temperature (Koroishi et al. 2009). Compared with other drying methods, freeze drying is one of the best ways to retain the bioactivity of the phytochemicals and nutrients, color, structure, and flavor of foods. It can also be achieved good rehydration capability for porous structures. As a result, the market share of freeze-dried products is increasing (Duan et al. 2012). Freeze drying has been employed mainly in the dehydration of materials with high commercial value such as mushrooms, carrots, peppers, strawberries (Hough et al. 2006), coffee, spices or meat, and food ingredients, being a valuable alternative for preserving foods (Ratti 2001).

Shelf life is the period of time in which all of the food's primary characteristics remain acceptable for consumption. Shelf-life determination for products which have a relatively low water activity, where quality changes are the deciding factors, is an unacceptably slow process in the commercial environment (12 months or longer) (Corrigan et al. 2012). Accelerated shelf-life tests are methods to speed up aging in order to evaluate the food behavior quickly under extreme conditions. The most common way to make a rapid shelf-life determination is to store the product at high temperatures. Different parameters, such as bacterial contamination or chemical composition, are usually used to evaluate the shelf life of food products. Because of the importance of the visual aspect of a product,

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many articles have been based on characterizing optical changes over time. Therefore, optical parameters have been studied to relate the loss of quality of foods, such as cabbage (Arce-Lopera et al. 2013), frozen spinach (Dermesonluoglu et al. 2015), meat (Iqbal et al. 2010), fish (Murakoshi et al. 2013), dehydrated apples (Nowak and Lewicki 2005), fresh mushrooms (Mohapatra et al. 2010; Oliveira et al. 2012), and dried apple-cluster snack (Saavedra et al. 2013). Those studies reveal that temperature significantly determines color and texture degradation. Thus, for example, Oliveira et al. (2012) determined the shelf life of fresh mushrooms using the browning index (BI) for measuring color parameters, as reported by Masikan (2001). Mohapatra et al. (2010) also used BI to evaluate the color degradation of mushrooms and reported a linear dependence of the final BI with temperature and an Arrhenius-type relationship between temperature (0–15 °C) and storage time (1–7.5 days). Others authors, such as Dermesonluoglu et al. (2015), have also used the Hunter color parameters “L, a, b” to calculate the total color E. Also, the Weibull model has shown notable potential for describing degradation kinetics because of its flexible shape and ability to model a wide range of degradation kinetics. The model considers the scale parameter (a) as a reaction-rate constant and the shape parameter (b) as a behavior index (Cunha et al. 1998).

Several authors, studying different food products and reference compounds, have found that the deterioration rate follows a first-order reaction kinetic. Thus, Saavedra et al. (2013) studied color variations in an accelerated shelf-life testing of a dried-apple cereal-like snack. In this case, best fit for CIE-Lab color variations was found using pseudo-first-order kinetics, although the model had low correlation coefficients. In another study, Pace et al. (2011) evaluated the visual appearance to assess the quality of fresh-cut nectarines using a conventional colorimeter and a computer vision system (CVS). The results showed that the CVS ($R^2 = 0.76$) was more effective than the colorimetric method ($R^2 = 0.57$) in a correlation of the visual-appearance score (consumer evaluation) with color parameters. Also, researchers have found that the Arrhenius equation can explain the temperature sensitivity of the rate constant (Bunkar et al. 2014). For example, Dermesonluoglu et al. (2015), testing spinach, found activation energies of 70.3 ± 11.3 and 132.0 ± 5.8 kJ/mol for the loss of chlorophyll and vitamin C, respectively.

Other sensorial parameters such as taste are fundamental because these parameters can be correlated with the consumer acceptance. However, sensory acceptability limits based on hedonic scores require a cut-off score, which is sometimes selected in an arbitrary manner. Shelf-life limits determined this way do not always accurately reflect consumer behavior in deciding whether to accept or reject a

product for consumption, and may give little information on what consumers would normally do when faced with the product (Corrigan et al. 2012).

The objective of this work is to develop a process and determine a model that relates a physical property (color) with the sensory properties of a freeze-dried product, and calculate the shelf life of this product.

Materials and methods

Materials

Thermo-sealed packages of 30 g freeze-dried oranges slices were supplied by Terra Pau C.A. company (Benialfaquí, Alicante, Spain). The samples were vacuum packed in plastic heat-sealed bags. The oranges weight in each bag was 30 g. Control samples were kept in a refrigerator at 5 °C.

Procedure for the accelerated shelf-life tests

Accelerated shelf-life tests were applied to the freeze-dried oranges samples. The tests consisted of placing the vacuum-packed samples in a dry oven at several constant temperatures (35, 45, 50 and 55 °C) for 1, 2, 3, and 4 weeks. The samples removed from the oven were stored in the refrigerator at 5 °C until the end of the experiment (maximum 4 weeks).

The sensory analysis and the luminance measurement were made jointly when the accelerated shelf-life tests were finished. The analysis was made at room temperature.

Sensory analysis

Participants

Twenty-three individuals (57% women, mean age = 30.8 years and 43% men, mean age = 28.3) participated in the study. They were volunteers from the University of Granada (Spain) and gave their written agreement by signing a consent form to participate to the surveys.

Questionnaires

The color and taste were evaluated following a questionnaire. The scale was rated from 1 to 5: 1 = dislike a lot, 2 = dislike, 3 = acceptable, 4 = like, 5 = like a lot, where 1 was the total absence of the parameter and 5 was the highest score for the sample. After making the color and taste estimation, the participants were questioned about if they would consume the product under these conditions.

Procedure

Each sample obtained at different temperature and time was tested. Sensory analyses of the samples obtained in the accelerated shelf-life tests were conducted to evaluate the quality of the product. Two sensory parameters, color and taste, were analyzed by the participants using the questionnaires indicated in “Questionnaires” section. The samples analyzed were tested at room temperature.

The product and the scored system were indicated to the participants before the sensory analysis was carried out, but not about the researching to not interfere in the analysis. The participants tasted three freeze-dried oranges slices that had undergone the accelerated shelf-life tests. They rated them immediately after tasting. Responses were analyzed individually for both color and taste.

Luminance measurement

The luminance of the samples that have undergone accelerated shelf-life tests was measured. This measurement was made before the sensory analysis was done. The samples analyzed were tested at room temperature and the measurement was made by triplicate. The control samples are samples that have not undergone accelerated test.

To evaluate the luminance of the samples, they were photographed (Cannon iR2270, Spain; photograph was made at a distance of 10 cm at 25 °C, distance between the light source and the bottom plate was 10 cm, angle between the light source and the bottom plate 45° approx.). The images were processed and the luminance (L) and its distribution curves were calculated using the software Techné Imalab v.2.0 (Techné, Knowledge and Product Engineering Research Group, University of Granada, Spain). The scale of the luminance thus calculated goes from 0 (black) to 255 (white) and is proportional to the photometric luminance defined as the light intensity per unit area (cd/m^2). The analysis was performed considering 10 areas of each photograph ($0.5 \text{ cm} \times 0.5 \text{ cm}$), homogeneously distributed within the areas containing pulp and containing no skin or ribs. For each area, only the greatest value in the luminance distribution curve was used in the analysis. The maximum luminance of a sample under the test conditions (L_{max}) was defined as the arithmetic average of the luminance of the 10 areas of each image.

Theoretical model

In photometry, the relative luminance is often defined relative to a reference luminance, usually white. In this work, the relative luminance (L_r) has been defined as a function of the highest luminance of the control samples ($L_{\text{max}0}$) according to the expression:

$$L_r = L_{\text{max}} / L_{\text{max}0} \quad (1)$$

A general kinetic model relating the decrease of the L_r with time is proposed (Eq. 2) to explain the luminance results obtained for the freeze-dried oranges samples that have undergone the accelerated shelf-life tests:

$$dL_r/dt = -K_L L_r^n \quad (2)$$

where K_L is the reaction kinetic constant, t is time, and n is the reaction order. Integrating Eq. (2) gives:

$$L_r^{1-n} / (1-n) = L_{r0}^{1-n} / (1-n) - K_L t \quad (3)$$

Different orders have been applied to the experimental results. The third-order model ($n = 3$), corresponding to Eq. (4), is the model that shows the best fit:

$$1/L_r^2 = 1/L_{r0}^2 + 2K_L t \quad (4)$$

Considering that L_r of the control sample (L_{r0}) is equal to 1, the model equation is:

$$1/L_r^2 = 1 + 2K_L t \quad (5)$$

The regression analysis method used to fit the experimental data to the mathematical model proposed was the method of least squares using Microsoft Excel® 2007.

Results and discussion

The luminance measurement was made from the photographs of the samples. As an example, for samples tested at 55 °C as a function of time (Fig. 1, photographs), it shows that the samples darken when the time increases. In the same Fig. 1 (graph), it shows that the value of the highest luminance diminished with time. Figure 2 shows the L_r of the samples as a function of time and temperature. As can be seen, the L_r values decreased with time and temperature.

Following the procedure of the sensory analysis, color and taste were determined by the participants as a function of time and temperature. The mean value of color and taste versus L_r value obtained for each sample by all participants is shown in Fig. 3. The participants in the sensory analysis indicated that they would be willing to consume the freeze-dried orange slices when the scores were above 3, both color and taste.

Validation of the theoretical model for the luminance measurement

The dependence between luminance values with time and temperature are consistent for those found by other researchers (Nowak and Lewicki 2005; Cortés et al. 2009; Mohapatra et al. 2010; Oliveira et al. 2012; Saavedra et al.

Fig. 1 Photographs and luminance analysis of samples at 55 °C

Fig. 2 L_r versus time at different temperatures (filled circle, 35 °C; open circle, 45 °C; filled square, 50 °C; open square, 55 °C) (solid line, model proposed)

2013). Previous works (Saavedra et al. 2013) have tried to fit zero-order variations of color CIE-Lab (L , a and b) of a dried-apple cereal-like snack. Low determination

Fig. 3 Sensory-analysis parameters versus L_r (filled circle, Color; open circle, Taste)

coefficients were found: 0.3991 at 18 °C, 0.7589 at 25 °C and 0.4075 at 35 °C. In other studies, it was assumed that the color loss corresponded to a first-order kinetic model (Hough et al. 2006; Palazón et al. 2009). It is not always possible to fit the color change in foods to first-order

kinetics due to the complexity of the reactions underlying these phenomena (Ibarz et al. 1999).

Figure 4 shows the fitting of the model, Eq. (5), to the experimental data indicated in Fig. 2. Table 1 shows the K_L value as a function of temperature. In the range analyzed, the experimental data recorded between 45 and 55 °C are fitted adequately with the proposed kinetic model with r^2 between 0.87 and 0.99. The experimental data corresponding to 35 °C show an almost linear dependence with time with a slope value close to 0, so that longer times would be necessary to get an accurate value of K_L at this temperature. Experiments made with temperatures higher than 55 °C should permit to obtain conclusions at shorter times. However, very high temperatures could trigger aging or degradation by other mechanisms than those that act within the range analyzed in this work and therefore would not be recommended.

For the experimental results found, the Arrhenius equation can explain the dependence between K_L and temperature applying:

$$\ln K_L = \ln K_{L0} - E_a/RT \quad (6)$$

where T is temperature (K), the pre-exponential factor value, K_{L0} , is $4.99 \times 10^{30} \text{ h}^{-1}$; and the activation energy, E_a , is 208 kJ/mol. The fit has a good correlation ($R^2 = 0.9959$) as is reflected in Fig. 5.

The L_r values at different times and temperatures can be recalculated considering the model proposed, Eq. (5), and using the pre-exponential factor value and the activation energy calculated following Eq. (6). Figure 2 lines show the L_r values that the proposed model provides at different temperatures and times. As can be seen, the model acceptably fits the experimental results.

Fig. 4 Fitting of the third-order kinetic model, Eq. (5), to the experimental data

Table 1 K_L values calculated applying the model, Eq. (5)

T (°C)	K_L (h^{-1})	R^2
45	2.90×10^{-4}	0.87
50	8.60×10^{-4}	0.96
55	3.21×10^{-3}	0.99

Fig. 5 Fitting of the Arrhenius model, Eq. (6)

The color variation following Arrhenius dependence could be due to the fact that the enzymes are responsible of the reaction that occurs during aging of a food. However, sometimes it is difficult to compare the E_a values reported by different authors with various properties in different food products because the aging can affect properties (e.g. composition, texture or color) differently and the food composition is not similar. Thus, for example, Dermesonluoglu et al. (2015) used different parameters to study the quality loss of frozen spinach in the cold chain. The activation energy E_a for the different sensory attributes of frozen spinach analyzed was calculated from 29.21 (aroma) to 65.65 (freshness) KJ/mol. For other attributes, such as composition, they found a first-order reaction model for vitamin C and chlorophyll, giving E_a values equal to 132.0 ± 5.8 kJ/mol and 70.3 ± 11.3 kJ/mol, respectively.

Palazón et al. (2009), studying apple compote between 23 and 37 °C, used zero- and first-order reactions, considering an Arrhenius type relationship between temperature and constant rates found for different parameters. These authors determined the E_a for different parameters such as brightness, consistency, taste, bitterness, rancidity, and acidity, considering first-order reactions. These were between 37 and 76 kJ/mol, with R^2 from 0.8216 to 0.8977. For syneresis, texture and odor, the E_a values calculated considering zero-order reactions were between 18 and 57 kJ/mol with R^2 from 0.8471 to 0.8996. The E_a found for color, using a first-order reaction, was 75 kJ/mol ($R^2 = 0.8879$). Also Ibarz et al. (1999), studying the color changes caused by thermal treatments of pear puree at

temperatures from 80 to 98 °C, considered zero-order and first-order kinetic models to evaluate the appearance of non-enzymatic browning in the puree, considering an Arrhenius-type relationship between temperature and constant rates found for lightness. The best results corresponded to a first-order kinetic model with the E_a value of 76.4 kJ/mol ($R^2 = 0.964$). The color difference was calculated using the Hunter–Scotfield equation, which considers the Hunter color parameters L^* , a^* and b^* . Similar treatment was applied by these authors to different color parameters. When a^* parameter was used, the E_a value was 102.06 kJ/mol ($R^2 = 0.987$), similar to the results of Ibarz et al. (2000), who found an $E_a = 109.7$ kJ/mol for similar products. When absorbance (420 nm) was used as a color parameter, the E_a value was 62.8 kJ/mol ($R^2 = 0.650$), considering a zero-order kinetic model, notably lower than the ones reported by Ibarz et al. (2000), who calculated E_a values of 116 and 183.5 kJ/mol. Both Ibarz et al. (1999) and Palazón et al. (2009) found similar E_a values when a first-order reaction was applied to the color variation determined with similar food products, such as compote or puree.

Analysis of the sensory analysis: Shelf-life estimation

Figure 3 shows the color and taste scores obtained for the samples as a function of their L_r values. The participants in the sensory analysis indicated that they would be willing to consume the freeze-dried orange slices when the scores were above 3. Therefore, it can be considered that the shelf life would correspond to sensory-analysis values above 3. Figure 3 shows that these taste and color scores correspond to L_r values above 0.80.

Considering K_L expression, Eq. (6), in Eq. (5) and assuming that the minimum L_r value that a sample might have to be accepted by the consumer is 0.80, an expression that calculates shelf life (θ) as a function of temperature can be calculated as:

$$\ln \theta = 25094/T - 77.8 \quad (7)$$

This plot, presented in Fig. 6, enables us to estimate the shelf life of the product under storage conditions differing from those used in this study. So, the shelf life of this product at 28 °C would be 3629 days (10 years), comparable to the shelf life of other lyophilized products.

Frequently, in shelf-life evaluations of food products such as purees, compotes, or sauces, color analysis is used to estimate an average color to characterize the sample. However, when the color of the food product is not uniform, as for example freeze-dried orange slices, it is not as clear, easy or desirable to consider an average color. The model proposed could be a good alternative validated experimentally in this work.

Fig. 6 Estimation of shelf life for freeze-dried orange slices stored at different temperatures

Conclusion

Kinetic models have been proposed to explain the results obtained in accelerated shelf-life tests made to freeze-dried oranges. A third-order kinetic model has been proposed to correlate the luminance variation of the samples as a function of temperature and time. The activation energy found was 208 kJ/mol. The fit is adequately and has a good correlation ($R^2 = 0.99$). Luminance and sensory properties, color and taste, have been used together to evaluate the shelf life of freeze-dried oranges slices. Considering the preferences of the participants and the kinetic model proposed to explain the luminance variation as a function of temperature and time. An equation was computed that let us to evaluate the shelf-life of the product. At 28 °C, the shelf-life of the freeze-dried oranges may be expected to be 10 years.

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