Quantification of Color Change Resulting from Pheophytinization and Nonenzymatic Browning Reactions in Thermally Processed Green Peas†

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The visual green color degradation, as represented by the change of the $-a$ value measured by a tristimulus colorimeter, was found to be caused by not only pheophytinization but also by nonenzymatic browning reactions in green peas at 100, 110, and 120 °C. Mathematical models were developed for predicting the change in the $-a$ value as a function of time and temperature by knowing the kinetic parameters (rate constant and activation energy) of each mechanism. The rate of disappearance of greenness via pheophytinization followed a first-order kinetic model, while the rate of color loss due to nonenzymatic browning reactions followed a zeroth-order kinetic model after an initial lag period. The activation energies for pheophytinization and nonenzymatic browning were 20.4 and 22.3 kcal/mol, respectively.

Keywords: *Kinetics; visual green color; browning; colorimetry*

INTRODUCTION

The final quality of thermally processed green vegetables can be immediately judged from their color. It has been noted that color may be the most important sensory attribute of food and therefore holds a preeminent position in overall food quality (Clydesdale, 1991). Tristimulus colorimeters objectively characterize food color based on the tristimulus method which measures the light reflected from an object using three sensors filtered to have the same sensitivity as the human eye (anonymous, 1993). The tristimulus values can be converted to the L, a, and b color scale with L representing lightness. The a and b are color directions, where $+a$ is the red direction, $-a$ is the green direction, $+b$ is the yellow direction, and $-b$ is the blue direction. LaBorde (1993) reported that sensory panel scores for green color and overall product acceptance of thermally processed peas were linearly related to the $-a$ value, and therefore, it was possible to use the $-a$ value as a quality indicator.

The kinetic parameters for chlorophyll a, chlorophyll b, and visual green color degradation have been determined in pureed green peas at 70, 80, and 90 °C by high-performance liquid chromatography and tristimulus colorimetry (Steet, 1995). In that work, the $-a$ value was used as the physical parameter for characterizing the extent of the color degradation, and a technique based on the physical parameter for characterizing the extent of the color degradation, and a technique based on fractional conversion was developed in the determination of kinetic parameters of visual green color loss in peas. The degradation of chlorophyll a, chlorophyll b, and greenness followed a first-order reaction, and the temperature dependence of the degradation rate was adequately modeled by the Arrhenius relationship with activation energies of 19.5, 17.1, and 18.2 kcal/mol, respectively. Mathematical models that successfully predicted the changes in concentrations of chlorophyll a and chlorophyll b as well as green color ($-a$ value) as a function of time and temperature were presented. It was concluded by the author that pheophytinization, the conversion of chlorophylls into pheophytins, was solely responsible for the loss of visual green color. This conclusion was drawn by observing that the $-a$ value remained at a constant equilibrium value when all chlorophylls had disappeared, and the equilibrium value was independent of reaction temperature.

However, concern has been raised as to whether the kinetic parameters previously determined (Steet, 1995) at temperatures below 90 °C are able to be extrapolated to higher temperatures, so that the change in color during thermal processing can be predicted. Furthermore, there have been indications that pheophytinization may not be the only reaction that is responsible for color change in thermally processed green vegetables. Westcott et al. (1955) studied the nonenzymatic discoloration of green bean puree during thermal processing using a photovolt reflection meter supplemented by visual observations. The colored constituents of green bean puree were removed by acetone extraction to study browning without masking the effect of natural pigments. They found that the decolorized tissue underwent a browning during thermal processing and continued to darken during storage. Several theories were presented by the authors to explain the browning reactions. Preliminary work conducted in our laboratory also showed that the $-a$ value of pureed green peas heated for long periods of time at 120 °C did not level off at an equilibrium value as expected. The continued change of the $-a$ value after all chlorophylls were gone, as heating time was increased, indicated the existence of additional chemical reactions other than the conversion of chlorophylls to pheophytins.

The objectives of this research were 3-fold. The first objective was to develop a technique to determine the reaction kinetics of color change due to nonenzymatic browning reactions through tristimulus colorimetry, using the $-a$ value as the physical property at 100, 110,

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and 120 °C. The second objective was to determine the kinetics of visual green color loss via pheophytinization using the procedure developed (Steet, 1995) and to determine the kinetics of chlorophyll *a* and chlorophyll *b* degradation in peas via high-performance liquid chromatography at 100, 110, and 120 °C. The third objective was to develop mathematical models for predicting the overall color change (or the $-a$ value) as a function of time and temperature. This model would combine the effects of both pheophytinization and any additional browning reactions that change the $-a$ value during heating.

MATERIALS AND METHODS

Sample Preparation. Frozen green peas obtained from the supermarket were freeze-dried in a Stokes commercial freeze-dryer (F. J. Stokes Machine Co., Philadelphia, PA). The dried peas were ground into a fine powder with a Fitzmill Model D comminuting machine (W. J. Fitzpatrick Co., Chicago, IL) using the 1A screen. The pea powder was sealed in Ball home canning jars and stored at −20 °C until use.

Before each heating experiment pea puree was prepared by mixing 400 g of distilled water with 100 g of freeze-dried pea powder. This ratio was chosen because it represented the moisture content of fresh green peas. The pea puree sample was covered and placed in the refrigerator for at least 2 h in order to ensure complete hydration of the pea powder.

To determine the kinetic parameters of the nonenzymatic browning reactions alone without any influence from chlorophyll *a* and *b* degradation, a pea puree model system which had all chlorophylls converted to pheophytins by hydrochloric acid was used. High-performance liquid chromatography was used to verify that no chlorophylls remained in the acid-treated pea puree. The puree was prepared so that the final moisture content was also 80%. First, 10 g of 12.1 N hydrochloric acid (Fisher Scientific, Springfield, NJ) was mixed with 370 g of distilled water. Then 100 g of freeze-dried pea powder was added to the acid solution and thoroughly mixed. The color instantly converted from bright green to olive-brown. The puree was covered and hydrated for at least 2 h. Finally, 20 mL of aqueous sodium hydroxide was added to the puree to neutralize the pH to 6.8, which is the pH of freshly prepared pea puree.

Kinetic Apparatus. The apparatus consisted of two major components: a microwave oven with a feedback temperature control system and the microwave kinetics reactor (MWKR). A detailed description of the design and operating characteristics of the MWKR was provided by Welt et al. (1993). As a review, the MWKR is a completely sealed microwavable pressure vessel made from ULTEM 1000 (GE Plastics, Pittsfield, MA). The vessel was designed with the following features: (1) capability to provide uniform heating over a wide sample viscosity; (2) capability to provide a short and uniform come-up time for a relatively large sample size, (3) ability to withstand high temperatures and pressures, (4) sampling port which provides a convenient sampling method, (5) transparency to microwave energy, and (6) drive shaft for continuous mixing. The apparatus was able to maintain the sample temperature within ±0.3 °C of the desired point.

Kinetic Studies. Before each experiment the optical fiber temperature probe (Luxtron Corp., Santa Clara, CA) which measured temperature in the MWKR was calibrated at 100 °C with boiling distilled water. After sufficient hydration time, the pea puree (either freshly prepared or acid treated) was placed into the reaction vessel and completely sealed. The mechanical stirrer (Model 14-505-1, Fisher Scientific, Springfield, NJ) was adjusted to give maximum rotation. The microwave oven was turned on, and after the entire sample reached the desired temperature, the first sample was taken. During each run, samples (approximately 15 g) were taken at predetermined time intervals and cooled immediately with agitation in an ice bath. The samples were sealed in amber vials and refrigerated until further color and chlorophyll analysis. Kinetic studies were performed in duplicate at 100, 110, and 120 °C.

Color Analysis. The color analysis of the samples taken from the kinetic experiments involved freshly prepared pea puree and the acid-treated pea puree. The *L*, *a*, and *b* values for each sample were measured by a tristimulus colorimeter (Model CR 210, Minolta Corp., Ramsey, NJ). The colorimeter was calibrated with a standard white plate ($L = 97.79$, $a = -0.53$, $b = +2.28$) before color measurements were taken. The granular-materials attachment (Model CR-A50, Minolta Corp., Ramsey, NJ) was filled with the sample and covered with glass. Care was taken to assure that no air bubbles were present between the glass and the puree. Color measurements were taken in duplicate.

Pigment Extraction. The following technique for pigment extraction applied only to the freshly prepared pea puree. After color measurements the pigments were extracted from the pureed peas with acetone following a modified method described by Schwartz and von Elbe (1983). The chlorophylls were extracted by adding 20 mL of acetone to 5 g of puree and blending with a Tekmar tissumizer (Cincinnati, OH) for 2 min. The mixture was then filtered under vacuum through Whatman No. 42 filter paper (Fisher Scientific, Springfield, NJ). An additional 5 mL of acetone was used to wash the filter paper. The filtrate was transferred to a 50 mL volumetric flask and brought to volume with acetone. Prior to injection into the HPLC column, the sample was filtered through 0.22 μm filter paper (Fisher Scientific, Springfield, NJ).

HPLC Analysis. The chlorophyll assay was performed in accordance with the high-performance liquid chromatography procedure described by Schwartz and von Elbe (1983). The HPLC system consisted of the following components, all manufactured by Waters Associates (Milford, MA): a Nova-Pak C_{18} radial-pak cartridge, a Model U6K injector, a Model 600 multisolvent delivery system, and a Model 481 variable wavelength detector set at 658 nm. The chromatograms were recorded and integrated with a Model 730 data module.

The mobile phase used for chlorophyll analysis was an isocratic solution consisting of ethyl acetate:methanol:water (50:37.5:12.5, v/v/v). The mobile phase was sparged from time to time with helium to remove any dissolved gases. The flow rate was set at 1.5 mL/min. An aliquot of 15 μL of the extracted solution was injected in duplicate into the column. The area under the chlorophyll peaks was recorded for each injection and compared to standard chlorophyll *a* and chlorophyll *b* calibration curves. These calibration curves were constructed by injecting known concentrations of solutions of pure chlorophyll *a* and pure chlorophyll *b* (Sigma Chemical Co., St. Louis, MO) in butanol and recording the resulting peak area. Peak area vs chlorophyll (*a* and *b*) concentration was linear throughout the concentration range studied.

RESULTS AND DISCUSSION

Normalized concentration curves (C/C_0), where C is the concentration of chlorophyll *a* or chlorophyll *b* at a given time and C_0 is the initial concentration, for the degradation of chlorophyll *a* and chlorophyll *b* in pea puree heated at 100, 110, and 120 °C are shown in Figures 1 and 2, respectively. The quantification of chlorophyll *a* and chlorophyll *b* concentrations included the C-10 epimers a′ and b′ which have similar spectral properties to their parent compounds (Katz et al., 1968). The degradation of chlorophyll *a* and chlorophyll *b* in pea puree followed a first-order reaction as shown by the linearity of the data on the semilog plots. The reaction rate constants, *k*, were determined from the slopes of the normalized curves and are tabulated in Table 1. The r^2 values obtained from the linear regression performed on each replicate were always greater than 0.99. It is noteworthy to mention that the experiments were designed to allow enough heating time so that the concentrations of chlorophyll *a* and chlorophyll *b* would have changed by at least 1 log cycle, which was

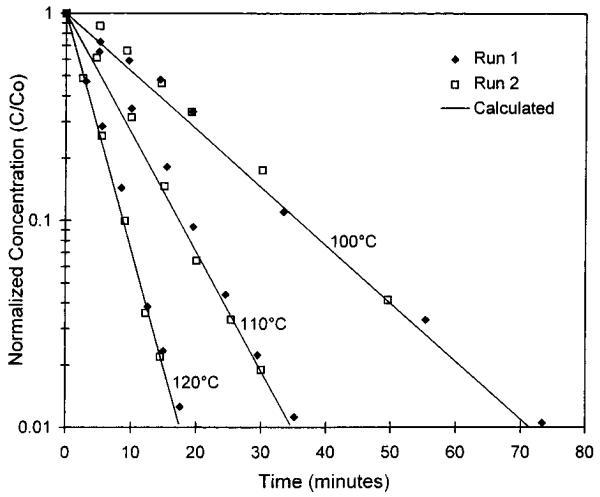

Figure 1. Normalized concentration curves for the degradation of chlorophyll *a* in pureed green peas at 100, 110, and 120 °C.

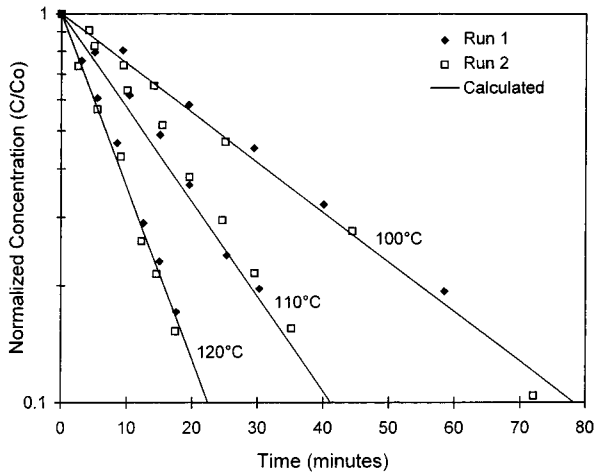

Figure 2. Normalized concentration curves for the degradation of chlorophyll *b* is pureed green peas at 100, 110, and 120 °C.

Table 1. Reaction Rate Constants for the Thermal Degradation of Chlorophylll *a*, Chlorophyll *b*, and Visual Green Color at 100, 110, and 120 °C

		rate constants (min^{-1})		
replicate	temp (°C)	chlorophyll *a*	chlorophyll *b*	greenness
1	100	0.0630	0.0284	0.0381
2	100	0.0652	0.0311	0.0383
1	110	0.1324	0.0557	0.0766
2	110	0.1370	0.0537	0.0774
1	120	0.2536	0.1007	0.1547
2	120	0.2672	0.1070	0.1540

necessary to distinguish a first-order reaction from a zeroth- or second-order reaction (Lund, 1977).

The change in the visual green color as represented by the $-a$ value of thermally processed green peas as a function of time at 100, 110, and 120 °C is shown in Figure 3. The initial $-a$ value, a_0, was measured after the sample reached the desired temperature. In the previous work (Steet, 1995) where degradation kinetic studies were performed at 70, 80, and 90 °C, the $-a_0$ was independent of temperature and equal to 24. Due to higher temperatures and longer come-up times in this study, there was a change in the $-a$ value during the come-up period so that the $-a_0$ was temperature dependent. In the same work the author also discovered

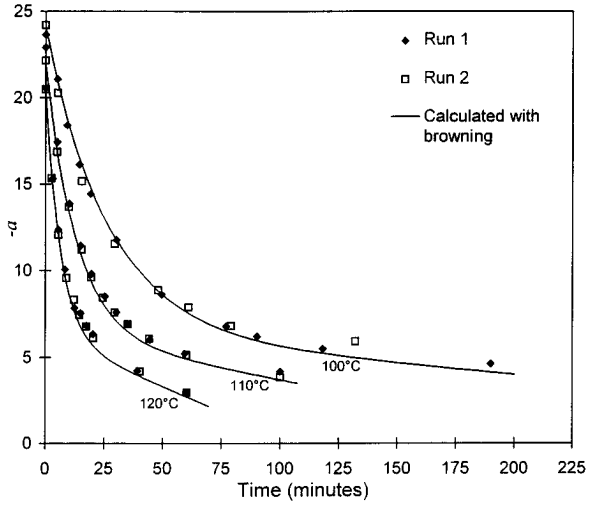

Figure 3. Color change as represented by the $-a$ value in pureed green peas heated at 100, 110, and 120 °C.

that the $-a$ remained constant at 6.0 ($-a_\infty$) when all chlorophylls were converted to pheophytins, regardless of reaction temperature. However, it can be seen in Figure 3 that the $-a$ value continued to decrease below 6.0 indicating the existence of additional reactions.

The additional change in the $-a$ value could have been attributed to (1) further conversion of the pheophytin *a* and pheophytin *b* into breakdown compounds and/or (2) nonenzymatic browning reactions. Schwartz and von Elbe (1983) found that pheophytin *a* and pheophytin *b* further converted to pyropheophytin *a* and pyropheophytin *b*, which were the major chlorophyll degradation products found in commercially canned spinach puree heated at temperatures ranging from 116 to 126 °C. However, due to the similarity in spectral characteristics of pyropheophytins and pheophytins, this further conversion should not have changed the $-a$ value significantly. Furthermore, the $-a_\infty$ value would not have remained constant if the formation of pyropheophytins had affected the color ($-a$) of the pea puree heated at 70, 80, and 90 °C through the combinations of lower temperatures and longer heating times. Therefore, it was concluded that the further decrease in the $-a$ value was a result of additional nonenzymatic browning reactions. Due to the complexity of nonenzymatic browning reactions, it was not the intention of this work to determine what these browning reactions were but only to develop a technique to quantify and predict the rate of the nonenzymatic browning reactions through tristimulus colorimetry.

In the determination of the kinetics of the nonenzymatic browning reactions, the pea puree was treated with concentrated hydrochloric acid to convert the chlorophylls into pheophytins. Then the pea puree was neutralized with sodium hydroxide to bring the pH of the puree to its original value. The acid-treated pea puree with an initial $-a$ value of 6.0 was used as the model food system in the study of browning kinetics. Care was taken to assure that the acid-treated pea puree had the same moisture content (80%) as the freshly prepared pea puree.

Figure 4 shows the rate of browning, expressed as the rate of change of $\Delta -a$, in acid-treated pea puree at 100, 110, and 120 °C. The $\Delta -a$ was defined as

$$\Delta -a = -a_0 - (-a_b) \qquad (1)$$

where $-a_b$ is the $-a$ value due to the nonenzymatic

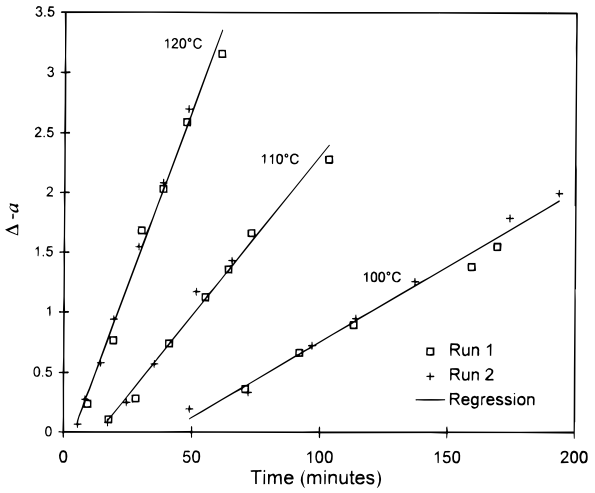

Figure 4. Change in the $-a$ value as a result of browning at 100, 110, and 120 °C.

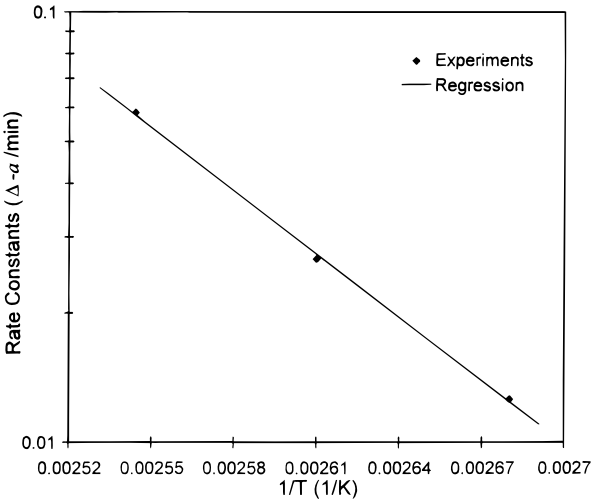

Figure 5. Logarithm of the lag times for browning reactions vs temperature (°C).

browning reactions at time t and the $-a_0$ is the $-a$ value at time 0 ($-a_0 = 6.0$). A lag period, where there was no significant change in $\Delta-a$, was observed for each temperature, and the duration of the period decreased as the temperature was increased.

The nonenzymatic browning reactions in pea puree followed a zeroth-order reaction after the initial lag period, as shown by the linearity of the $\Delta-a$ versus time data on a linear−linear plot. The rate constants, k, with a unit of $\Delta-a$/min, were determined by linear regression on the slopes of the lines. The nonenzymatic browning reactions have also been shown to follow a zeroth-order reaction model with a lag period in various liquid, semisolid, and solid food systems (Mizrahi et al., 1970; Waletzko and Labuza, 1976; Peterson et al., 1994). The rate constants for browning reactions in the literature are normally expressed in the unit of OD/min since the extent of browning is normally measured by a spectrophotometer at a wavelength of 420 nm.

The rate constants of the nonenzymatic browning reactions at 100, 110, and 120 °C were used to construct the Arrhenius plot shown in Figure 5. The linearity of the data indicated that the temperature dependence of the reactions obeyed the Arrhenius relationship with an activation energy, E_a, of 22.3 kcal/mol. The E_a fell in the range of 16−30 kcal/mol reported by Labuza and Baiser (1992) for nonenzymatic browning in various food products.

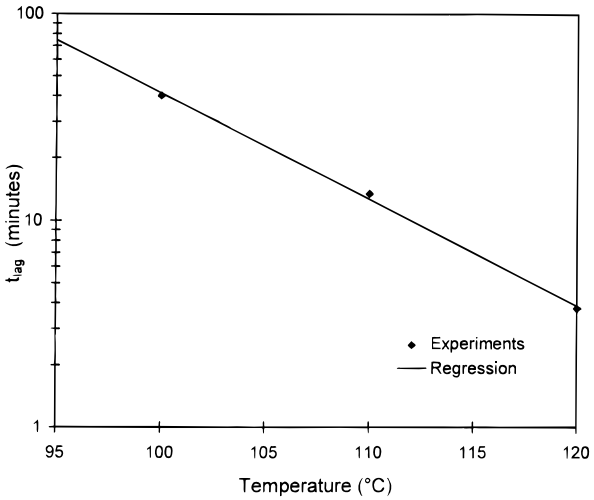

Figure 6. Arrhenius plot for the browning reactions at 100, 110, and 120 °C.

Table 2. Lag Times for Nonenzymatic Browning at 100, 110, and 120 °C

temp (°C)	t_{lag} (min)	temp (°C)	t_{lag} (min)
100	41.37	120	3.88
110	12.67		

The kinetic parameters for the nonenzymatic browning reactions are readily available in the literature. However, a model does not exist to predict the extent of browning taking into account both the kinetics and the lag time, t_{lag}. In this study the lag time at each temperature was determined by extrapolating the linear region of the data (Figure 4) to $\Delta-a = 0$. The lag times as a function of temperature are listed in Table 2. It was interesting to observe that a linear relationship was obtained when the logarithm of the t_{lag} was plotted against temperature in degree Celsius as shown in Figure 6. This graph is similar to a thermal death time (TDT) curve used in the determination of the z value (thermal resistance constant), the temperature change required to change the TDT curve by a factor of 10, of bacterial spores in thermal processing (Lund, 1975) when the t_{lag} is replaced by the decimal reduction time (D value). Therefore, the slope of the regression line in Figure 6 is defined here as z_{lag}, the temperature change in degree Celcius required to change the lag time by a factor of 10. It is not known how well the linear relationship would hold beyond the temperature range studied for estimating the lag times at other temperatures.

From this study and the earlier study (Steet, 1995), it was known that the $-a$ value of thermally processed green peas could have been altered through both pheophytinization and nonenzymatic browning reactions. However, because of the existence of a lag period for nonenzymatic browning, the change in visual green color (represented by the $-a$ value) at the early stage of heating was believed to occur completely via pheophytinization. Therefore, the procedure based on fractional conversion was then used to determine the kinetics of visual green color loss due to the conversion of chlorophylls to pheophytins, using the $-a$ value from the color meter as the physical parameter (Steet, 1995). Fractional conversion, f, is defined as

$$f = \frac{-a_0 - (-a_p)}{-a_0 - (-a_\infty)} \qquad (2)$$

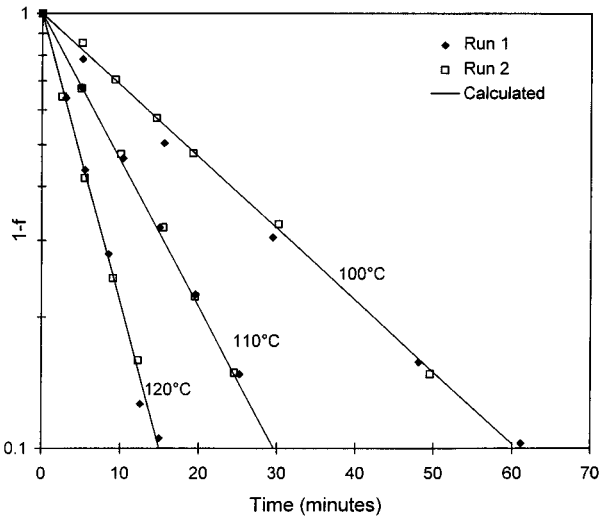

Figure 7. Green color degradation by pheophytinization in pureed green peas at 100, 110, and 120 °C.

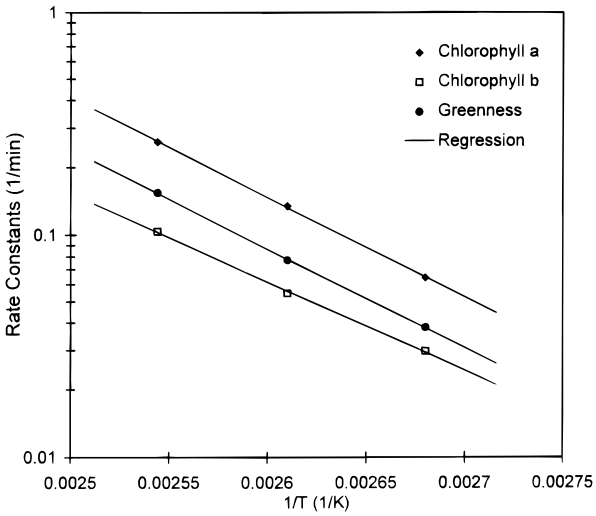

Figure 8. Arrhenius plot for the thermal degradation of chlorophyll *a*, chlorophyll *b*, and visual green color.

where $-a_0$ was the $-a$ value at the initial time t_0, $-a_p$ was the $-a$ value due to pheophytinization alone at any time t, and $-a_\infty$ was the $-a$ value at infinite time (t_∞) so that all the chlorophylls were converted to pheophytins. For a first-order reaction, a plot of the logarithm of $(1 - f)$ vs time would yield a straight line with a negative slope equal to the rate constant.

The loss of visual green color via pheophytinization in pea puree at 100, 110, and 120 °C is shown in Figure 7. The relationship was linear up to 1 log cycle change in $(1 - f)$ indicating that the degradation of visual green color followed a first-order reaction. The reaction rate constants were determined from the slopes of the lines and are tabulated in Table 1. Figure 7 was constructed with an $-a_0$ measured immediately after the come-up time and with an $-a_\infty = 6.0$. To calculate these rates, it was assumed that only chlorophylls were converted into pheophytins and no significant browning occurred.

The times required for 1 log cycle change in the visual green color were 66.7, 30, and 15 min at 100, 110, and 120 °C, respectively. It is necessary to point out that these time constants were longer than the lag periods of the nonenzymatic browning reactions suggesting that the determination of visual green color degradation kinetics through pheophytinization alone following the procedure of Steet (1995) might not have been valid. However, there was no difference found within the experimental error when only the first portion of the data (the corresponding heating time was shorter than the t_{lag}) and the whole range of data (see Figure 7) were used to calculate the rate constants by linear regression. Therefore, it was possible to isolate the change in the $-a$ value as a result of pheophytinization from the nonenzymatic browning reactions.

Figure 8 shows the Arrhenius plot for the degradation of chlorophyll *a*, chlorophyll *b*, and visual green color by pheophytinization. The linearity of the data on this graph indicates that the rate constant as a function of temperature all obeyed an Arrhenius relationship. The activation energies determined by linear regression for chlorophyll *a*, chlorophyll *b*, and visual green color were 20.4, 18.2, and 20.4 kcal/mol, respectively.

It has been shown by Steet (1995) that the rate constant for visual green color loss was nearly identical with that of chlorophyll *b* at 70 °C. It is interesting to observe in Figure 8, however, that the rate constant for visual green color further deviated away from that of chlorophyll *b* as the temperature was increased. The chemistry and overall perception of color change ($-a$ value) in green vegetables is a complicated phenomenon. The original attractive green color is due to the presence of both chlorophyll *a* and chlorophyll *b*. Chlorophyll *a* is different from chlorophyll *b* in both color and thermal stability (Tan and Francis, 1962; Canjura et al., 1991). Chlorophyll *a* is blue-green, and chlorophyll *b* is yellow-green (Belitz and Grosch, 1986). The resulting pheophytins also have different color perceptions, where pheophytin *a* is green-gray and pheophytin b is olive-green (Bennion, 1980). When pheophytinization occurs, the $-a$ value changes because of the loss of the green intensity which occurs as a result of chlorophyll loss, and at the same time, the $-a$ value is further changed by the addition of brown pigments into the mixture due to the formation of pheophytins. Therefore, the rate of color change in green peas is controlled not only by the concentrations of chlorophyll *a*, chlorophyll *b*, pheophytin *a*, and pheophytin *b* but also by the ratio of chlorophyll *a* to chlorophyll *b* and the ratio of pheophytin *a* to pheophytin *b*. It is hypothesized that the change in the ratio of chlorophyll *a* to chlorophyll *b* and pheophytin *a* to pheophytin *b* as a function of temperature, due to the difference in E_a, is responsible for the shift in the rate constants of visual green color change toward chlorophyll *a*.

The chlorophyll *a* and chlorophyll *b* concentrations as a function of time and temperature can be readily predicted after the kinetic parameters have been successfully determined. The concentrations of chlorophyll *a* and chlorophyll *b* as a function of time at a constant temperature for a first-order degradation kinetic model are

$$\ln(C/C_0) = -k_c t \qquad (3)$$

where C_0 is the initial chlorophyll concentration, k_c is the temperature dependent reaction rate constant (min^{-1}) for the change in chlorophyll concentration, and C is the chlorophyll concentration at any time t.

The rate constants as a function of temperature can be calculated by the Arrhenius equation knowing the pre-exponential constant (A_0) and the activation energy (E_a):

$$\ln k = \ln A_0 - \frac{E_a}{R}\frac{1}{T} \quad (4)$$

k is the rate constant at a temperature T in Kelvin and R is the gas constant (1.987 cal/mol K). The pre-exponential constants for chlorophyll *a* and chlorophyll *b* were 24.83 and 21.05, respectively. The predicted normalized concentrations as a function of heating time at 100, 110, and 120 °C are shown by the solid lines in Figures 1 and 2.

Prediction of the color change ($-a$ value) at 100, 110, and 120 °C was more involved since there were two independent reactions, pheophytinization and nonenzymatic browning, occurring simultaneously. These two reactions have different reaction orders, rate constants, and activation energies. The change of the $-a$ value due to pheophytinization at a constant temperature was related to heating time as

$$\ln(1 - f) = \ln\left[1 - \frac{-a_0 - (-a_p)}{-a_0 - (-a_\infty)}\right] = -k_p t \quad (5)$$

where k_p is the reaction rate constant for the color change due to pheophytinization and $-a_\infty$ is 6.0. Equation 5 was rearranged to have the following form:

$$-a_p = -a_\infty + [-a_0 - (-a_\infty)] \exp(-k_p t) \quad (6)$$

The color change due to the nonenzymatic browning reactions as a function of time was calculated by

$$\Delta -a_b = 0 \text{ when } t \le t_{lag} \quad (7)$$

$$\Delta -a_b = -k_b t \text{ when } t > t_{lag} \quad (8)$$

where k_b is the reaction rate constant for color change due to browning reactions. It is necessary to point out that the negative sign in eq 8 represents the loss of visual green color as a consequence of the formation of brown pigments. In eq 1 $\Delta -a$ was defined so that $\Delta -a \ge 0$ and increased as the heating time was increased which was a typical and more familiar phenomenon in studying browning reactions. However, the $-a$ value decreased as browning occurred and resulted in a negative $\Delta -a$.

The t_{lag} as a function of temperature is described as follows:

$$\log\left(\frac{t_{lag_T}}{t_{lag_{121C}}}\right) = (t_{lag_{121C}} - t_{lag_T})/z_{lag} \quad (9)$$

$t_{tag_{121C}} = 3.44$ min and $z_{lag} = 19.46$ °C. The temperature dependence of the rate constants for both pheophytinization and browning reactions can be calculated by eq 4, with the pre-exponential constants of 24.19 and 25.75, respectively.

Finally, the overall change in the $-a$ value is the summation of the change due to both pheophytinization and browning reactions:

$$-a = -a_p + \Delta -a_b \quad (10)$$

The predicted $-a$ values as a function of heating time in fresh puree at 100, 110, and 120 °C are also shown in Figure 3 by the solid curves. The excellent agreement between the predicted $-a$ value using the mathematical equations and the experimentally measured values indicates the adequacy of the procedure and the accuracy of the determined kinetic parameters for the color change due to both pheophytinization and nonenzymatic browning reactions.

CONCLUSIONS

(1) The change in the $-a$ value, measured by a tristimulus colorimeter, of thermally processed green peas was due to both the conversion of chlorophylls to pheophytins and the non-enzymatic browning reactions. (2) The change in the $-a$ value at short heating times was dictated by the conversion of chlorophyls to pheophytins. (3) Separate mathematical models were presented and kinetic parameters were determined to predict the change in the $-a$ value due to the both pheophytinization and the nonenzymatic browning reactions, respectively. (4) A mathematical model similar to the TDT plot was introduced to estimate the lag periods of nonenzymatic browning reactions as a function of temperature by knowing the z value of the lag time, z_{lag}. (5) The overall change in the $-a$ value was accurately predicted by the summation of the change due to the conversion of chlorophyll to pheophytin and the nonenzymatic browning reaction where $-a = -a_p + \Delta -a_b$.

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