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Effect of visible light on the process of accelerated oxidation of dye contained in red paprika powder

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Abstract: *Effect of visible light on the process of accelerated oxidation of dye contained in red paprika powder.* The effect of temperature and visible light intensity on changes in ground paprika colour was investigated. In determination of changes in colour parameters there were used the colour space L^*. a^*, b^*, the total colour change TCD and sample whiteness index WI. Investigations were carried out at three lighting intensity levels of D65 light (6000, 4500, 0 lx) at storage temperature (30º, 40º, 50ºC). The DOE model for investigation planning included in Statistica Program was used in investigations. The validation investigations were carried out to verify the model. Colour changes in the investigated samples were connected, first of all, with their lighting intensity and less so with storage temperature. A two-stage process of colour changes in the samples illuminated with the light of intensity 6000 lx was found. The carried out investigations can be used in predicting the time of changes in colour parameters of ground paprika exposed to intense radiation in the range of visible light.

Key words: accelerated oxidation, red paprika powder, visible light.

INTRODUCTION

Dry red paprika in the form of powder is one of most commonly used dyes in food industry. It is commonly used for the change in colour and aroma of soups, dressings and other products. In respect to high content of antioxidants, the red paprika powder is used as a natural additive to many food products of so called healthy food category.

The colour change during paprika storage, its processing and further storage is a serious problem for the producers. The colour of raw paprika depends on carotenoids created during ripening. However, the change in ground paprika colour depends on many other factors: moisture content, temperature and light. During traditional drying process, due to prolonged time of exposition of material subjected to drying to the heat, light and oxygen, 20–30% of initial carotenoid content is destroyed, thus, the initial colour of paprika is changed, while the red colour intensity is a basic criterion for dried material quality on the market [De Guevara et al. 2002].

During storage of both the raw and dry paprika as well as its round form, the colour is changed mainly due to degradation of carotenoids and non-enzymatic getting brown. These processes speed up in the case of storage at increased temperature [Shin et al. 1995].

There is little investigations in the world references that present the effect of selective (D65) sunlight on changes in colour of sweet paprika powder. Practically, during storage of dried paprika in open packages it is subjected to sunlight operation of lowered emission in the range of UV radiation.

The changes in paprika colour were measured with the use of colorimeters [Carbonell et al. 1986]. However, changes in colour on the surface of paprika are not uniform, due to non-uniform overcolourings that occur in random places and result from different exposition of the product to radiation. The industrial colorimeters are used in measurements on very small areas from 2 to 5 cm^2; it is limitation for the measurements on surfaces of heterogeneous changes in colour. This measurement limitation is often bypassed by measuring the mean value of a measuring series executed for the entire sample; sometimes, the sample is mixed in order to obtain an uniform colour distribution on its surface. The measurements carried out by this method often cause omission of very useful information on colour distribution. Measurements with the use of colorimeter can be useful in checking the quality of samples of more or less same colour, but they do not fit for engineering measurements on colour distribution on the surface. Therefore, in this work there is proposed application of image analysis system to evaluate the colour changes kinetics in the ground dried red paprika.

AIM OF WORK

The work aimed at investigating the effect of exposure to visible light within the spectrum of daily radiation D65 on changes in colour parameters of paprika extract described with variables L^*, a^*, b^*, total colour change (TCD) and change in whiteness index (WI).

METHODICS

The research material was red paprika powder of trade name the extract of paprika, purchased on local market. To homogenize the fractal composition, the powder was sieved through a sieve of hole diameter 100 μm. The sieved fraction was placed on a Petri dish, maintaining the uniform layer thickness equal to about 5 mm. Initial moisture content of powder, measured by drying-weighing method, amounted to 12%. The three parallel samples (A, B and C) of the same paprika mass and layer thickness were prepared for measurements.

– Sample A (reference) – was covered with a glass (other part of Petri dish) and placed inside a black container that protected against the visible radiation effect, but allowed for free air flow around the dish.

– Sample B was covered with a transparent cover made of the lead glass. The cover transparency was measured with the use of spectrum transmittance meter LS102 (Shenzen Linshang Technology Co. Ltd). Transmittance of waves in the length range 200–380 nm amounted to 15%, in the range 760–2500 nm to 88%, and in the visible light range (380––760 nm) to 70.1%.

– Sample C was left without cover.

All the three kinds of dishes were placed in a light chamber equipped with lighting system that emitted light D65 of colour temperature 6500 K [Ekielski

2011], in the range of visible light wave length. Illumination at surface of samples was measured with the use of luxmeter LX1108 (Volcraft make); it amounted to L = 6000 lx. The illumination was additionally measured with the use of lunometer probe LX1108 under the glass cover of sample B and under the darkened package of sample A. The illumination values amounted to L_B = 4500 lx and L_A = 3, respectively, (actually 0) lx; it confirmed the predicted results of illumination (for sample B), calculated during measurement of light transparency coefficient.

In planning of investigations and results elaboration there was used a research plan for three-value quantities included in the DOE module of Statistica 10 Program. According to assumed plan the samples were stored in the light chamber at temperature 30°, 40° and 50°C. The photographs of investigated samples were taken at intervals from 1 to 10 hours. The covers of samples A and B were removed during taking photos, then replaced. The colour of sample surfaces were measured with the use of colour space RGB, which was then converted to space CIE XYZ and recalculated to colour system CIE $L^*a^*b^*$. In calculations there were used the algorithms written in C++ language and implemented to the National Instruments visional system [Ekielski et al. 2012]. Photos were taken with the camera of resolution 6 MPx equipped with lens of set diaphragm 1 : 8; they were then recorded in TIFF format with 24-bit colour depth in RGB standard. Prior to every measurement, the camera processing unit was calibrated with the use of calibration plate of white reference standard Minolta (for light D65: L^* = 98.23, a^* = 0.05, b^* = 1.21). At the same time, in each colour sample measurement the white reference standard was photographed. Then, deviation of the obtained colour from reference standard was calculated and correction coefficients were marked on the photos made under these conditions. The area obtained as a result of segmentation was analyzed as average value with standard deviation of colour space parameters CIE $L^*a^*b^*$.

Whiteness index (WI) was calculated with equation:

$$WI = 100 + - \sqrt{\left((100 - L^*)^2 + (a^*)^2 + (b^*)^2\right)} \qquad (1)$$

There were also measured the total change in colour of samples (TCD) described with equation:

$$TCD = = \sqrt{\left((L_o^* - L^*)^2 + (a_o^* - a^*)^2 + (b_o^* - b^*)^2\right)} \qquad (2)$$

where L_o^*, a_o^*, b_o^* are the initial value of corresponding colour parameters.

IMAGE SEGMENTATION

Separation of image from the background was executed by transformation of colour image into monochromatic one (grey) and application of the Gauss low-pass filter, that enable to remove noise from the image. The limits of measuring area were obtained by calculation of the threshold value with the method given by Fan [2012]. The segmentation algorithm was written in C++ language and used in the Matlab 7.1 Program. Then, the area

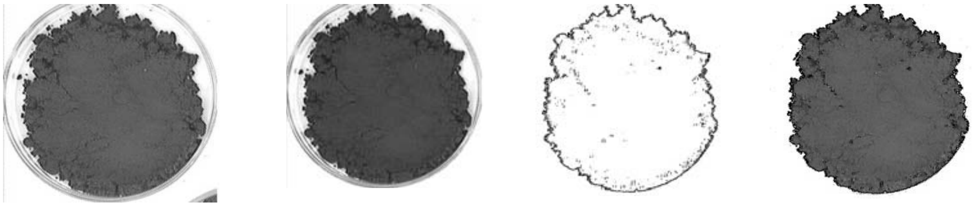

FIGURE 1. Phases of photo processing: A – photo of Petri dish placed in light chamber, B – image conversion into greyness space $R \in <0.255>$, C – determination of sample edge, D – removing of colour image background outside area determined with limits

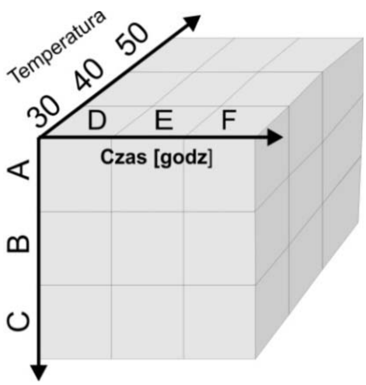

FIGURE 2. OLAP block of independent variables levels of experiment: A, B, C – illumination, $L \in \{0, 4500, 6000\}$ [lx], respectively; D, E, F – storage time, 0, 46, 90 hours, respectively; storage temperature (30°, 40°, 50°C)

determined as a result of segmentation was automatically marked on the colour photo of sample. All the areas outside the sample limits were removed. The image processed in that way was subjected to further investigations.

RESULTS OF INVESTIGATIONS

The results obtained during experiment are presented in Table 1. Basing on these results there was carried out analysis of the effect of particular input variables on the change in colour parameters $L^*a^*b^*$, whiteness index (WI), total colour change (TCD) and magnitude that describes the change in red to yellow ratio:

$$S = \frac{b^*}{a^*} \tag{3}$$

where a^* – describes colour change from red to green, b^* – describes colour change from yellow to blue.

A nonlinear model with interactions was assumed in elaboration and statistical analysis. The analysis of variables significance showed insignificant effect of temperature on colour change dynamics. Figures 3, 4, 5, 6 and 7 present the models for changes in parameters L^*, a^*, b^*, TDC and WI depending on illumination and time of sample exposition to light radiation. In respect to insignificant effect of storage temperature (at significance level $p < 0.05$) within the measuring ranges, the diagrams were made for temperature 40°C.

The model for changes in L^* (brightness) presented in Figure 1 enables to find two areas of variability. The sample brightness for illumination up to 3500 lx did not change within the investigated period. In the case of increased illumination above 3500 lx, time of exposition up to 40 hours did not affect the changes in brightness. However, prolongation of exposition time above 40 hours caused acceleration of

TABLE 1. Results of colour changes obtained at various illumination degrees

No	Illumination [lx]	Exposition time [hour]	Temperature [°C]	L^*	a^*	b^*	WI	TDC	$\overline{E}$
1	6000 (C)	0	30	38.74	56.74	41.76	6.64	0	
2	4500 (B)	0	30	38.74	56.74	41.76	6.64	0	0
3	0 (A)	0	30	38.74	56.74	41.76	6.64	0	
4	6000 (C)	46	30	46.93	54.83	40.10	13.80	8.57	
5	4500 (B)	46	30	41.00	56.68	42.30	7.90	2.32	
6	0 (A)	46	30	40.39	56.68	42.30	7.51	1.74	
7	6000 (C)	90	30	79.58	16.01	12.30	71.28	64.77	
8	4500 (B)	90	30	45.87	55.34	42.80	11.54	7.34	
9	0 (A)	90	30	41.24	56.73	42.64	7.86	2.65	
10	6000 (C)	0	40	38.74	56.74	41.76	6.64	0	
11	4500 (B)	0	40	38.74	56.74	41.76	6.64	0	
12	0 (A)	0	40	38.74	56.74	41.76	6.64	0	
13	6000 (C)	46	40	46.94	54.85	40.11	13.79	8.58	
14	4500 (B)	46	40	41.05	56.67	42.31	7.93	2.38	
15	0 (A)	46	40	40.40	56.65	42.32	7.52	1.75	
16	6000 (C)	90	40	79.59	16.03	12.33	71.27	64.75	
17	4500 (B)	90	40	45.89	55.32	42.79	11.57	7.36	
18	0 (A)	90	40	41.23	56.72	42.65	7.86	2.64	
19	6000 (C)	0	50	38.74	56.74	41.76	6.64	0	
20	4500 (B)	0	50	38.74	56.74	41.76	6.64	0	
21	0 (A)	0	50	38.74	56.74	41.76	6.64	0	
22	6000 (C)	46	50	46.94	54.84	40.12	13.79	8.58	
23	4500 (B)	46	50	41.01	56.69	42.32	7.89	2.34	
24	0 (A)	46	50	40.38	56.67	42.33	7.49	1.74	
25	6000 (C)	90	50	79.59	16.03	12.31	71.28	64.76	
26	4500 (B)	90	50	45.89	55.36	42.81	11.54	7.36	
27	0 (A)	90	50	41.22	56.76	42.63	7.84	2.63	

Source: own elaboration.

brightness changes dynamics. Coefficient L^* quickly increased at the end of period to the value L^* = 100 % (shade close to white).

Changes in parameters a^* and b^* had similar course. For illumination below 3500 lx the value of parameters a^* i b^* initially did not change (up to 30 hours), then medium illumination caused a slow increase in parameters values. In the case of illumination above 3000 lx, after 35 hours of exposition a quick decrease in the value of a^* and b^* occurred. An intensive illumination of samples led to a decrease in both parameters, to the value close to 0. In the case of illumination up to 3500 lx parameter a^* was more stable than parameter b^*. The a^* parameter increased from 60 to 80 units, while b^* parameter increased only from 40 to 60 units, which proved the bigger relative change in parameter b^* than a^*.

The whiteness index (WI) and total colour change index (TDC) showed a similar trend of changes. Observations on changes in WI index enabled to determine dynamics of product colour value decline to the white colour. The index TDC presented total change in colour when compared to initial colour. At intensive illumination the values of both components that describe the colour (TDC and WI) quickly increased towards white. Prediction diagram of changes in colour parameters at illumination about 3000 lx presents the phenomenon of sample darkening. The initial stabilization of WI and TDC parameters after 35 hours of exposition got the inverse course than expected. The occurrence of sample darkening was small, but detectable by measuring equipment. It was connected with an increase in a* and b* parameter values. The similar phenomenon was found during prolonged storage of paprika powder in a darkened room [Topuz et al. 2009]. In these investigations the authors found more intensive

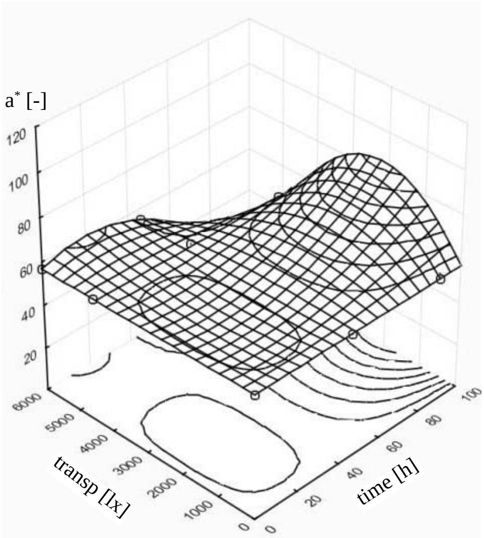

FIGURE 4. Response surface of a* parameter depending on illumination and time of sample exposition to light D65 at temperature 40°C

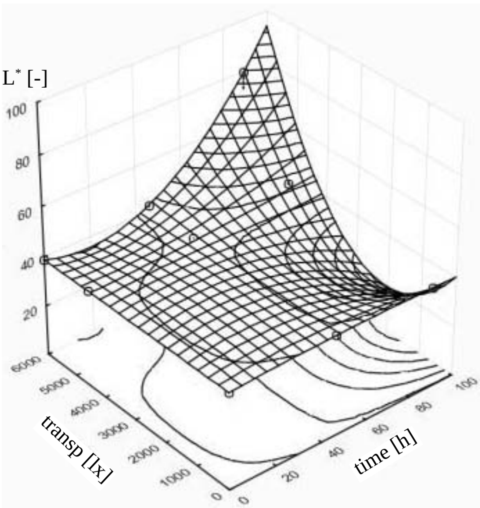

FIGURE 3. Response surface of L* parameter depending on illumination and time of sample exposition to light D65 at temperature 40°C

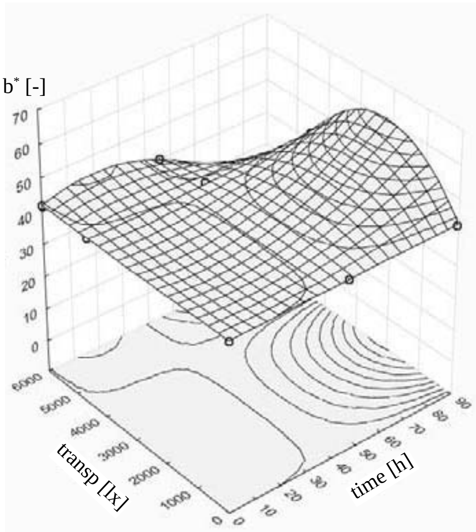

FIGURE 5. Response surface of b* parameter depending on illumination and time of sample exposition to light D65 at temperature 40°C

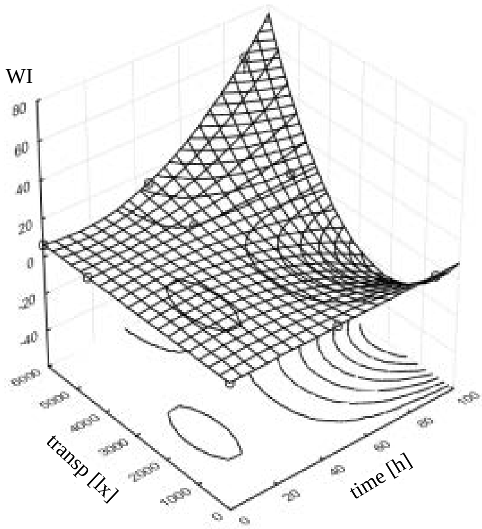

FIGURE 6. Response surface of whiteness index (WI) depending on illumination and time of sample exposition to light D65 at temperature 40°C

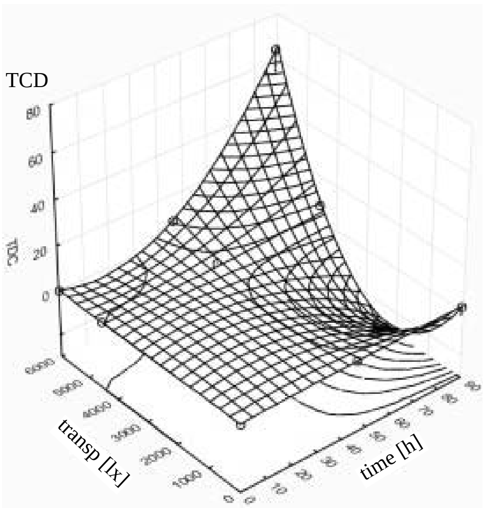

FIGURE 7. Response surface of relative colour change (TDC) depending on illumination and time of sample exposition to light D65 at temperature 40°C

dynamic of a* index changes than for b* index. The results were obtained at room temperature (20–23°C) and under isolated conditions. In experiment presented in the publication, the medium illumination (1500–3500 lx) and warm environment could lead to non-enzymatic decomposition of dyes that cause the sample darkening. The similar results were obtained in investigations on the effect of antioxidants on changes in paprika colour [Osuna-Garcia 1997; Park 2007]. However, these results were obtained during moderate illumination (scattered light) of dried paprika stored at room temperature (22–25°C).

CONCLUSIONS

Colour of red paprika extract is connected with the presence of yellow and red dyes. Therefore, the change in values of a* and b* parameters depended on changes in the product brightness (L*). An increase in intensity of paprika powder illumination led to quick changes in colour parameters. The light range from od 0 to 3000 lx did not affect colour of the investigated samples. Increase in illumination above 3500 lx resulted in dynamic phenomena of colour changes already after about 35–40 hours of sample exposition to light. Therefore, in such type of products one should avoid exposition to radiation of intensity above 2000 lx, even if this radiation is free from ultraviolet part of spectrum.

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Streszczenie: *Wpływ światła widzialnego na proces przyspieszonego utleniania barwnika zawartego w proszku z czerwonej papryki.* W pracy badano wpływ temperatury i natężenia światła widzialnego na zmiany barwy mielonej papryki. Do określenia zmian parametrów barwy wykorzystano przestrzeń barw L^*, a^*, b^* oraz całkowita zmianę barwy TCD, wskaźnik białości próbki WI. Badania przeprowadzono dla trzech poziomów intensywności oświetlenia światłem D65 (6000, 4500, 0 lx) w temperaturze przechowywania (30°, 40°, 50°C). W badaniach wykorzystano model planowania badań DOE zawarty w Programie Statistica. W celu weryfikacji modelu przeprowadzono badania walidacyjne. Zmiany barwy badanych próbek były związane przede wszystkim z intensywnością ich oświetlania, w mniejszym stopniu z temperaturą przechowywania. Zaobserwowano dwuetapowy proces zmiany barwy dla próbek oświetlonych światłem intensywności 6000 lx. Przeprowadzone badania mogą być wykorzystane do przewidywania czasu zmian parametrów barwy zmielonej papryki wystawionej na działanie intensywnego promieniowania w zakresie światła widzialnego.

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