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DETERMINATION OF THE PHYSICAL CHARACTERISTICS OF FOOD RAW MATERIALS BY SPECTROPHOTOMETRY – THE EXAMPLE OF HONEY

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K e y w o r d s: honey, color, $L^*a^*b^*$, storage, discrimination.

A b s t r a c t

The paper presents changes in the color of 10 selected types of honey during storage. The measurements were performed using a MiniScan XE Plus spectrophotometer (HunterLab). The color of honey was described based on $L^*a^*b^*$ coordinates. The values of hue h^* and chroma C^* were also calculated. Until day 14 of storage. no statistically significant ($p = 0.01$) changes in the color of crystallized oilseed rape honey, liquid multifloral honey and crystallized multifloral honey were noted. The color of the remaining seven honey types started to change on the first day of storage.

IDENTYFIKACJA FIZYCZYCH CECH SUROWCÓW SPOŻYWCZYCH METODĄ SPEKTROFOTOMETRYCZNĄ NA PRZYKŁADZIE MIODÓW

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S ł o w a k l u c z o w e: miody, barwa, $L^*a^*b^*$, przechowywanie, dyskryminacja.

A b s t r a k t

W pracy przedstawiono zmianę barwy dziesięciu wybranych typów miodów w czasie ich przechowywania. Pomiar wykonano z wykorzystaniem spektrofotometru MiniScan XE Plus firmy HunterLab. Barwę opisano modelem $L^*a^*b^*$. Zostały także wyliczone indeksy odcienia barwy h^* oraz

nasycenia C^*. W czasie przechowywania nie zauważono istotnie statystycznych (p = 0,01) zmian w barwie do 14 dnia przechowywania dla miodów rzepakowego skrystalizowanego, wielokwiatu płynnego oraz wielokwiatu skrystalizowanego. Barwa pozostałych siedmiu typów zmieniała się od pierwszego dnia przechowywania.

Introduction

Color is one of the key quality attributes and physical characteristics of food raw materials and products, which considerably affects their evaluation. Color provides information about the chemical composition, processing suitability and storage life of food products. Color may be described by two methods. The first method involves organoleptic evaluation, and the other – instrumental measurement. Both approaches have their advantages and disadvantages. Standardized instrumental techniques show high reproducibility and accuracy, whereas organoleptic assessment methods support color description corresponding to human visual perception. Instrumental measurements require the use of spectrophotometers and colorimeters. Based on the composition of the spectrum of radiation reflected by the studied object, a computer program calculates color coordinates in the XYZ space for a specified observer (field of view of 10^o and 2^o) and illuminant (e.g. D65. C. A).

Color is one of the most variable features of honey, owing to its floral origin, the applied technological process and the temperature and time of storage (SALA et al. 1993). TERRAB et al. (2004) assessed the color of 23 samples of thyme (*Thymus mastichina* and *Thymus capitatus*) honey and 13 samples of avocado (*Persea Americana)* honey, collected in Spain between 2002 and 2003. A discriminant analysis was employed to distinguish between the two types of honey. The two analyzed honey types were better characterized when lightness L^*, chroma C^* and hue angle h* were used as variables (94% accuracy). LAZARIDOU et al. (2004) determined the color of honey with the use of a Metertech UV/VIS SP8001 spectrophotometer and a Minolta Dimage 5 digital camera. A total of 33 types of honey of different botanical origin from different geographical regions of Greece were analyzed. Honey samples were assayed for sugar composition, water content, water activity values and thermal properties. Color was measured at a wavelength of 420 nm, following honey sample dilution with distilled water at a 1:5 ratio (BATH, SINGH 1999). The images of honey samples were taken using a digital camera and a proper illumination system, according to the procedure proposed by PAPADAKIS et al. (2000). POPEK (2002) attempted to develop a new method for honey identification relying on a discriminant analysis. The author examined the physicochemical properties, quality attributes and color components of 73 honey samples, but the obtained results were unsatisfactory – the applied

procedure did not enable to classify all honey types. GONZALES et al. (1999) studied changes in honey color during storage in relation to honey composition and initial color. Samples of 16 floral honeys, collected in different geographical plain regions of temperate climate in Argentina. were analyzed. Honey color was measured using a Hunterlab 5100 spectrophotometer. The illuminated area had a diameter of 4.7 mm. The values of color attributes, reflecting brown pigment formation in honey, were calculated as described by BUERA et al. (1985) and BUERA (1989).

Objective and Scope of the Study

The objective of this study was to determine changes in the color of selected types of honey during storage. A discriminant analysis was performed to find out whether honey types can be classified based on color components. A method for color measurement was developed, and the obtained results were subjected to a statistical analysis.

Experimental Material

The measurements were performed on 10 types of honey (Tab. 1). Samples of liquid and crystallized honey were collected in 2004. Prior to color measurement. honey samples were placed in a thermostat (40°C 24 hours) for liquefaction.

Table 1

Types of honey subjected to evaluation

Honey type	Name
Honey – 1	liquid oilseed rape honey
Honey – 2	liquid buckwheat honey
Honey – 3	crystallized coniferous honeydew honey
Honey – 4	crystallized oilseed rape honey
Honey – 5	liquid multifloral honey
Honey – 6	pine honey
Honey – 7	crystallized multifloral honey
Honey – 8	liquid honeydew honey
Honey – 9	crystallized buckwheat honey
Honey – 10	mixed honey composed of honey 5 and honey 9 at a 50/50 ratio 9

Measurement Method

The color of honey was measured in reflected light, using a MiniScan™ XE Plus spectrophotometer (HunterLab) connected to a computer. Color coordinates were determined in the CIE $L^* a^* b^*$ space for the 10° standard observer and the D65 standard illuminant. The color of each honey type was measured in 30 replications, over a period of 38 days, at two-day intervals. Honey samples were placed in cube-shaped plastic containers (5x5 cm), and color was measured on each side (in five replications), at each vertex and in the middle of each side. Means were compared by a one-way analysis of variance at a significance level of $p = 0.01$ (Duncan's test). The results were verified statistically using Statistica 8.0 software. The values of whiteness index (WI E313) and yellowness index (YI E313) were calculated using Universal Software ver. 3.80 provided with the spectrophotometer. The MS Exel application was used to calculate the values of chroma C^* and hue h^*. A discriminant analysis was performed to determine whether the studied honey types could be distinguished from one another. The applied method was selected for the study since the values of the variables had a normal distribution and the variance matrix for variables in groups was homogeneous. Due to the nature of the variables, there was a minimal risk of the matrix not fulfilling the redundancy condition. The values of chroma C^*_{ab} and hue h^*_{ab} were calculated as follows:

$$C^*_{ab} = \sqrt{a^{*2} + b^{*2}} \tag{1}$$

$$h^*_{ab} = \arctan\left(\frac{b^*}{a^*}\right) \tag{2}$$

where:
a^* – redness component
b^* – yellowness component

Results and Discussion

Honey samples were divided into two groups based on the mean values of color lightness L^* (Fig. 1).

Honey 1 honey 5 and honey 4 were classified into the first group, while the second group comprised the remaining honey types. In group one, there were significant differences between honey 1 and honeys 5 and 4 while in group two – between honey 8 and honeys 7 and 10. Not all types of honey could be distinguished based on the values of color component L^*. The greatest difference in lightness was noted between oilseed rape honey and honeydew

honey. Significant differences were also observed between liquid and crystallized oilseed rape honey, and between liquid and crystallized multifloral honey.

Table 2

Mean values of color components and indices

Types of honey	L^*	a^*	b^*	WI E313	YI E313	C^*	h
	[-]	[-]	[-]	[-]	[-]	[-]	[-]
Honey – 1	24.30^{a}	0.13^{cd}	1.38^{cd}	-13.02^{a}	7.48^{d}	1.40^{bc}	84.73^{a}
Honey – 2	25.87^{cd}	0.17^{d}	1.49^{d}	-13.24^{a}	7.87^{d}	1.51^{c}	83.35^{a}
Honey – 3	25.90^{cd}	-0.37^{a}	0.92^{b}	-6.43^{c}	3.93^{a}	1.01^{a}	111.74^{e}
Honey – 4	24.78^{b}	0.10^{cd}	1.38^{cd}	-12.75^{a}	7.37^{d}	1.41^{bc}	85.73^{a}
Honey – 5	24.56^{b}	0.13^{cd}	1.50^{d}	-14.30^{a}	8.05^{d}	1.52^{c}	84.90^{a}
Honey – 6	26.06^{cd}	0.06^{cd}	0.90^{b}	-6.03^{c}	4.69^{ab}	0.93^{a}	86.00^{b}
Honey – 7	25.82^{c}	0.54^{e}	0.67^{a}	-3.36^{d}	4.54^{ab}	0.90^{a}	51.27^{c}
Honey – 8	26.09^{d}	-0.01^{c}	0.84^{ab}	-5.23^{cd}	4.21^{ab}	0.86^{a}	90.38^{d}
Honey – 9	26.02^{cd}	-0.20^{b}	1.25^{c}	-10.29^{b}	5.89^{c}	1.28^{b}	98.94^{d}
Honey – 10	25.82^{c}	0.21^{d}	0.92^{b}	-6.36^{c}	5.09^{bc}	0.96^{a}	77.28^{a}

Mean values (determined on day 1) in columns followed by different superscript letters are significantly different at $p = 0.01$.

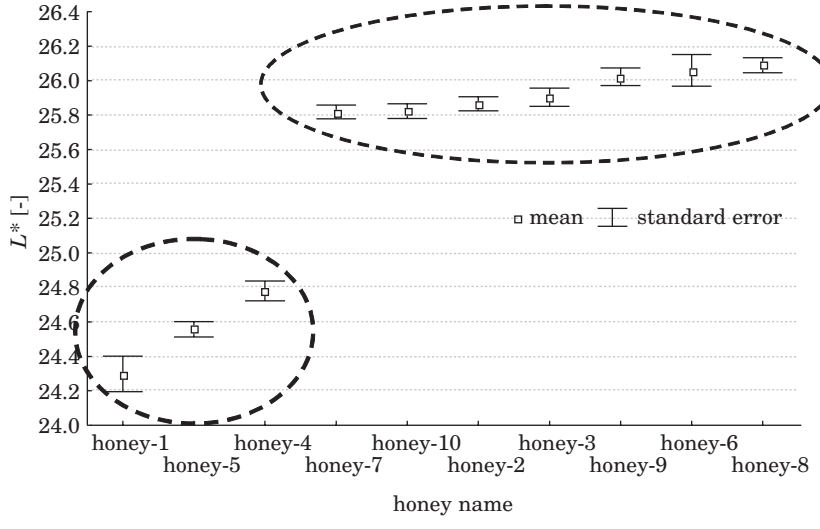

Fig. 1. Mean values of color component L^* (lightness) for each honey type on the first day of measurement

Based on the mean values of color redness a^*, the analyzed honeys were divided into four groups (Fig. 2). Honeys 3, 9 and 7 formed separate groups, while group four comprised the remaining honey types.

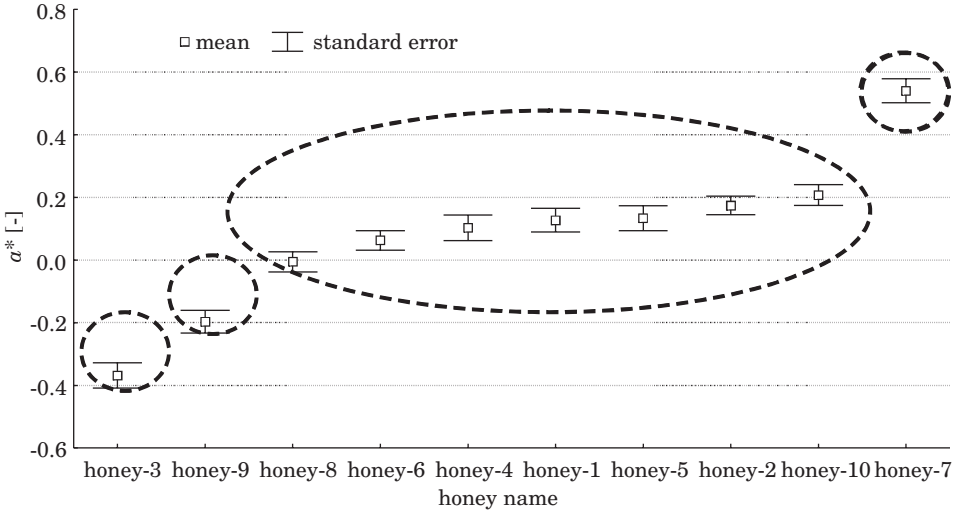

Fig. 2. Mean values of color component a^* (redness) for each honey type on the first day of measurement

In group four, there was a significant difference between honey 10 and honeys 8 and 6. Crystallization affected the values of color component a^* in the following honey pairs: honey 3 (crystallized coniferous honeydew honey) and honey 8 (liquid honeydew honey), honey 5 (liquid multifloral honey) and honey 7 (crystallized multifloral honey), honey 2 (liquid buckwheat honey) and honey 9 (crystallized buckwheat honey). The above honey types differed significantly with respect to the mean values of a^*.

The mean values of color component b^* (yellowness) supported the division of the investigated honey types into two groups (Fig. 3). The first group covered honeys 7, 8, 6, 10 and 3, and the second group – honeys 9, 1, 4, 2 and 5. There were statistically significant differences in b^* values within each of the groups. In group one, a significant difference was found between honey 7 and honey 10, while in group two – between honey 9 and honeys 5 and 2.

Similarly as in the case of redness a^*, also the values of color component b^* were affected by crystallization in the following honey pairs: honey 5 (liquid multifloral honey) and honey 7 (crystallized multifloral honey), honey 2 (liquid buckwheat honey) and honey 9 (crystallized buckwheat honey). The above honey types differed significantly with respect to the mean values of b^*.

Honey samples were divided into three groups based on the mean values of WI E313 (Fig. 4). The first group covered honeys 5, 2, 1 and 4, honey 9 formed the second group, and honeys 3, 10, 6, 8 and 7 were included in the third group. In group three, there were significant differences in WI E313 values between

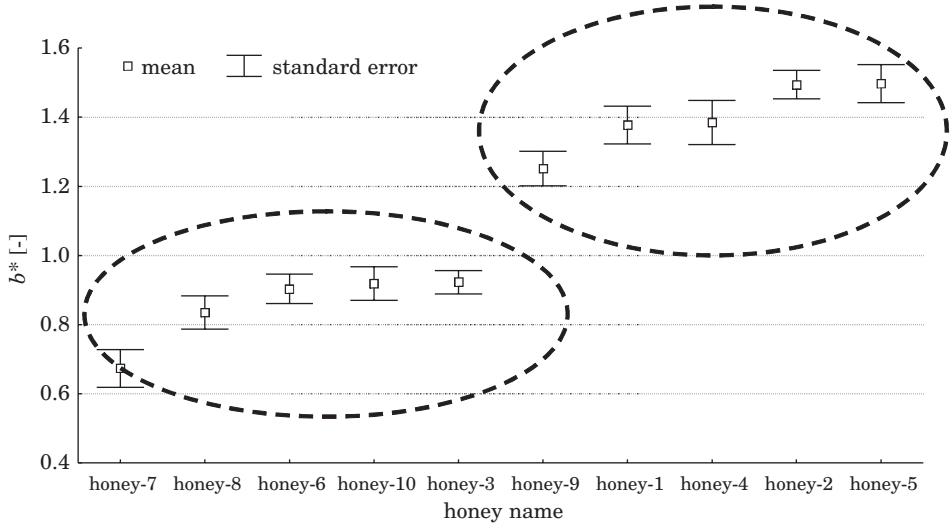

Fig. 3. Mean values of color component b^* (yellowness) for each honey type on the first day of measurement

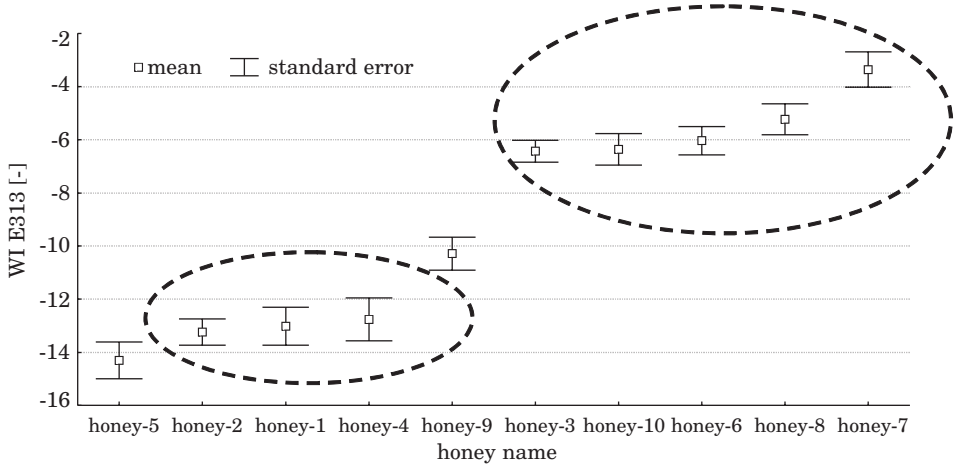

Fig. 4. Mean values of whiteness index (WI E313) for each honey type on the first day of measurement

honey 7 and the remaining honey types. Crystallization affected WI E313 values in the following honey pairs: honey 5 (liquid multifloral honey) and honey 7 (crystallized multifloral honey), honey 2 (liquid buckwheat honey) and honey 9 (crystallized buckwheat honey). Differences in WI E313 values were also noted between honey 10 (mixed honey composed of honey 5 and honey 9 at a 50/50 ratio) and honeys 5 and 9, which enabled to differentiate between mixed honey and the two honeys it was composed of.

The studied honey types differed significantly with regard to the values of yellowness index (YI E313) (Fig. 5). Coniferous honeydew honey was characterized by the lowest value of this index. whereas liquid multifloral honey and liquid buckwheat honey showed the highest YI E313 values.

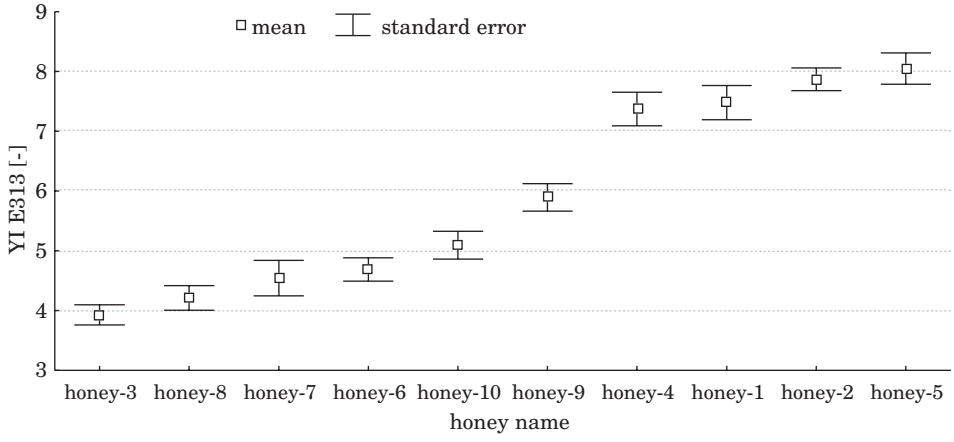

Fig. 5. Mean values of yellowness index (YI E313) for each honey type on the first day of measurement

The yellowness index allowed to discriminate between crystallized and liquid honey of the same type, including after the liquefaction of crystallized samples, which suggests that this index may be used for detecting prior crystallization.

Changes in the color of honey during storage

Figure 6 illustrates changes in the color lightness of selected honey types during 38 days of storage, and Figure 7 shows honeys 4, 5, 7 characterized by a different pattern of lightness changes. The values of color lightness decreased over storage. A rapid drop in lightness noted between day 3 a 4 in all honey types was followed by an increase and a further decrease on consecutive days until the final measurement when lightness oscillated around 24 units.

The initial color lightness of honeys 4, 5 and 7 was 25 units, and it remained unchanged until day 8 of storage. On day 8 the value of lightness started to increase, to reach 35 – 46 units on day 38. The increase in the lightness of honeys 4, 5 and 7 could be due a faster rate of crystallization accompanied by a shift in color towards whitish yellow.

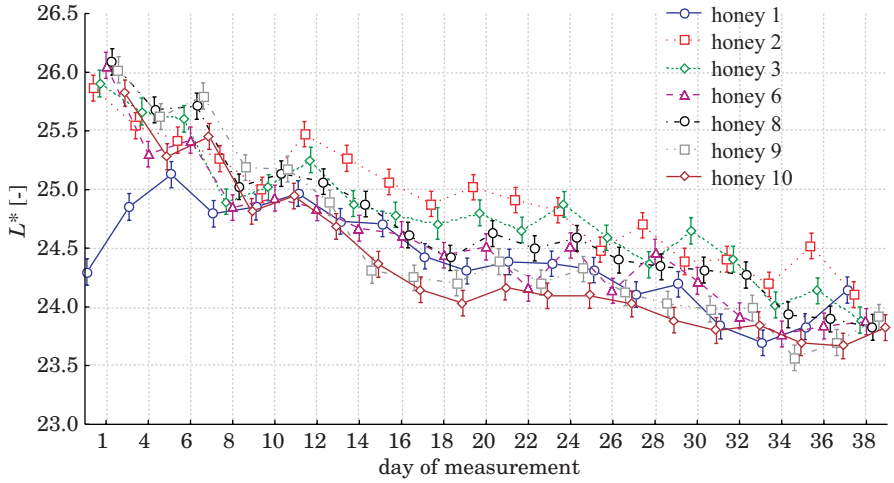

Fig. 6. Changes in the mean values of color component L^* (lightness) in selected honey types on successive days of measurement

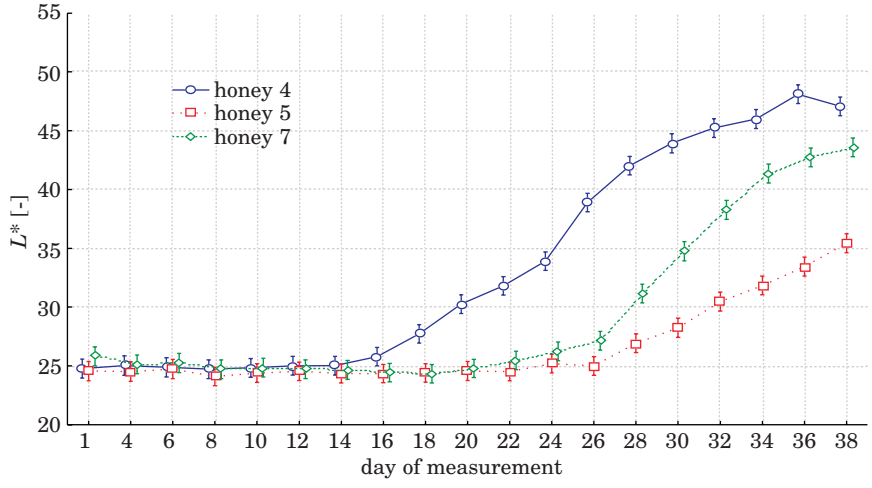

Fig. 7. Changes in the mean values of color component L^* (lightness) in honeys 4, 5 and 7 on successive days of measurement

The patterns of changes in color component a^* (redness) (Figs. 8, 9) were different in particular honey types. In the majority of cases, the value of redness was similar on the first and on the last day of measurement. An initial decrease in redness was followed by an increase in its contribution.

In honeys 4, 5 and 7, the mean value of a^* oscillated around 0.3 until day 14 of storage, and it started to increase on day 15, to reach 1 on the last day of measurement.

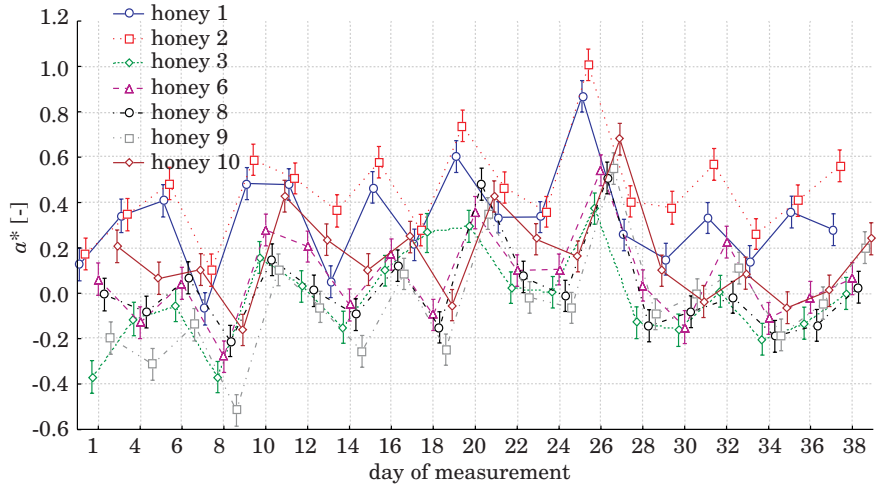

Fig. 8. Changes in the mean values of color component a^* (redness) in selected honey types on successive days of measurement

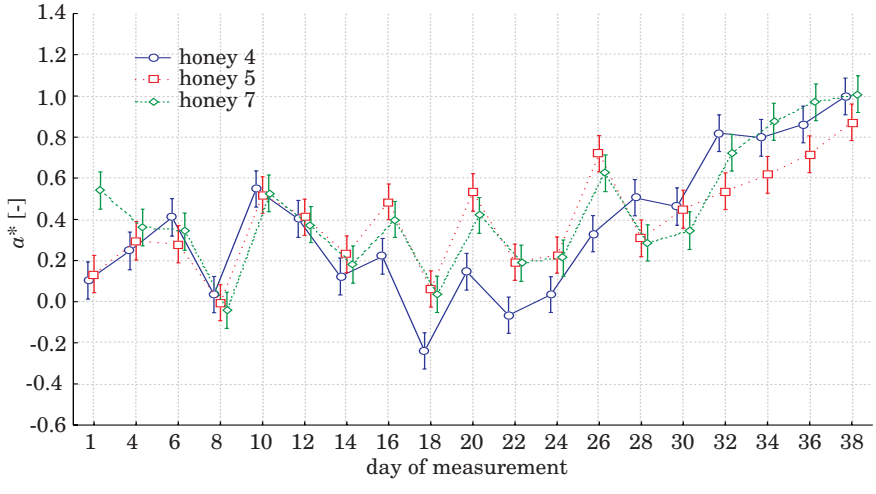

Fig. 9. Changes in the mean values of color component a^* (redness) in honeys 4, 5 and 7 on successive days of measurement

Changes in color component b^* (*yellowness*) (Figs. 10, 11) were similar to those observed in coordinate a^* – a decrease was followed by an increase. On the last day of storage, b^* values decreased in all honey types, ranging from 0 to 0.6 unit.

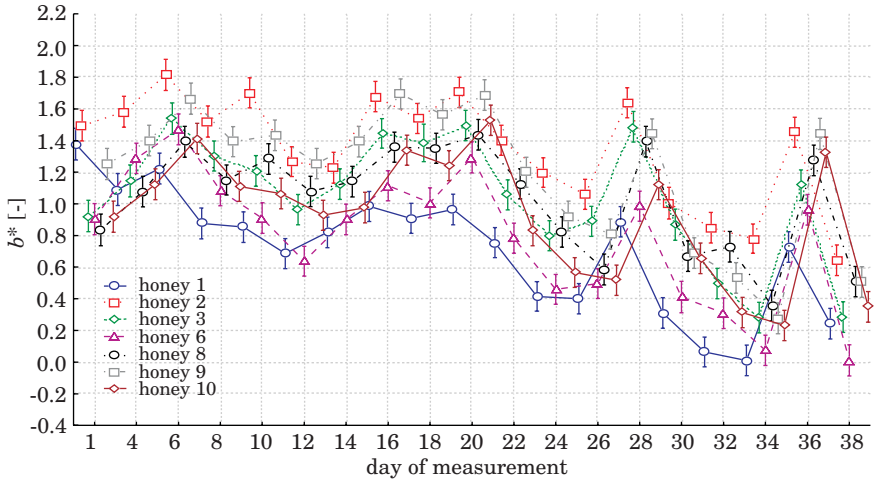

Fig. 10. Changes in the mean values of color component b^* (yellowness) in selected honey types on successive days of measurement

In crystallized oilseed rape honey, liquid multifloral honey and crystallized multifloral honey, b^* values remained unchanged until day 8 of storage in honey 4 and until day 12 in honeys 5 and 7. The final value of yellowness was 8 units in honey 4 and 12 units in honeys 5 and 7.

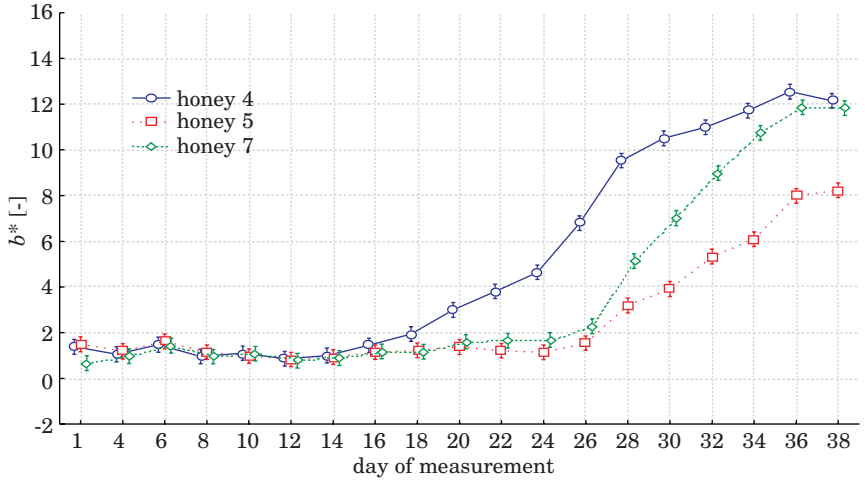

Fig. 11. Changes in the mean values of color component b^* (yellowness) in honeys 4, 5 and 7 on successive days of measurement

Results of a discriminant analysis

Table 3 presents the results of a stepwise discriminant analysis based on the values of L^*, a^*, b^*, WI 313 and YI 313, with five variables introduced successively into the model. The value of Wilks; Lambda and the F-statistic was 0.039813 and 45.13. respectively. Classification accuracy ranged from 18.8% to 84.8%. A high accuracy of classification based on color variables was obtained for liquid buckwheat honey (84.8%), crystallized multifloral honey and crystallized coniferous honeydew honey. As regards honey 5, ten samples were incorrectly classified as honey 1 and another ten samples – as honey 4, thus pointing to a high contribution of rapeseed pollen in this type of honey. The results obtained for honey 1 suggest that it is difficult to distinguish between liquid buckwheat honey and crystallized buckwheat honey based on their color, which was accomplished in buckwheat honeys. The lowest classification accuracy was reported for pine honey whose samples were erroneously classified as honeys 8, 9 and 10.

Table 3

Classification matrix for 10 honey types

Honey type	Classification accuracy [%]	1	2	3	4	5	6	7	8	9	10
1	61.3	19			10	2					
2	84.8		28							1	4
3	77.4			24	1				4	2	
4	62.5	5	1		20	4					2
5	37.5	10			10	12					
6	18.8	1		2	1		6	1	10	5	6
7	78.1		2	0				25			5
8	41.9			2			5	3	13	7	1
9	68.8		3	2			2		2	22	1
10	46.9		2				3	6	5	1	15

Conclusions

1. There exist homogenous groups of honey types that can be discriminated based on a single color component or index.

2. Crystallized honey may be distinguished from liquid honey with the use of a single color component or index.

3. The values of color component b^* (yellowness) and whiteness index

WI E313 enable to differentiate between mixed honey and the honeys it was composed of.

4. It was found. based on the values of color components L^*, a^* and b^*, that earlier crystallization affected the rate of later crystallization of honey.

5. Classification accuracy ranged from 18.8% to 84.8%. depending on honey type.

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