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COMMODITY ANALYSIS OF QUALITY CHANGES IN FROZEN STRAWBERRY CAUSED BY TEMPERATURE FLUCTUATIONS

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Key words: strawberry, frozen fruits, temperature fluctuation, quality changes.

Abstract

The objective of the studies was to evaluate the level of quality changes in frozen strawberry stored at fluctuating temperatures and to verify H_0: the levels of the tested parameters within time occurred as the arithmetic mean of the levels of these traits recorded under extreme conditions. The studies were carried out with frozen strawberries stored at constant temperatures of –18°C and –25°C and at variable temperatures of –18°C/–25°C in a 48-hour exchange cycle. The fruits were tested for the content of anthocyans and vitamin C, total and active acidity, and thawing spill before storage and at 4-week cycles for the total of 24-week storing period. Although verification of H_0 demonstrated that the values of the examined traits were not equal to the levels recorded under extreme conditions, they were slightly divergent from the assumed hypothetical values. For the majority of the analysed parameters, the temperature fluctuations caused a slightly lower degree of changes than it would appear from the arithmetic mean at extreme temperatures.

TOWAROZNAWCZA OCENA ZMIAN JAKOŚCI MROŻONYCH TRUSKAWEK WYWOŁANYCH FLUKTUACJĄ TEMPERATURY

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Słowa kluczowe: truskawki, mrożone owoce, fluktuacja temperatur, zmiany jakości.

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Abstrakt

Celem badań była ocena poziomu zmian jakości mrożonych truskawek składowanych w warunkach fluktuacji temperatury oraz weryfikacja H_0. Poziomy badanych cech w czasie kształtowały się jako średnia arytmetyczna poziomów tych cech uzyskiwanych w warunkach skrajnych. Materiał badawczy stanowiły mrożone truskawki przechowywane w temperaturze stałej –18°C i –25°C oraz zmiennej –18°C/–25°C z 48-godzinnym cyklem zmiany. Oznaczono w nich zawartość antocyjanów i witaminy C, kwasowość czynną i ogólną oraz wyciek rozmrażalniczy przed przechowywaniem i w cyklach czterotygodniowych przez 24 tygodnie składowania. Weryfikacja H_0 wykazała, że wartości badanych cech nie były równe wypadkowej poziomów uzyskiwanych w warunkach skrajnych, choć w niewielkim stopniu odbiegały od założonych wartości hipotetycznych. Fluktuacja temperatury powodowała w przypadku większości analizowanych cech nieznacznie niższy poziom zmian niż wynikałoby to ze średniej arytmetycznej w temperaturach skrajnych.

Introduction

Strawberries are most often consumed as fresh fruit and processed products, such as jams, juices and frozen fruit. A large scale production of frozen strawberries is due to the seasonality of supply of these fruits, the short period of shelf life of fresh fruits and very diverse use, as a frozen product.

Freezing, which is one of the best methods for protecting strawberries before lowering their quality during long-term storage, is a time-limited. The main factors affecting the quality changes are frozen fruit storage time, temperature and its fluctuations. These factors may affect the texture, flavor, appearance, color and nutrients stored, frozen strawberries. Temperature fluctuations may result from different causes. In the case of frozen fruits, they may be a result of cold chain impact, particularly during transport and distribution and storage conditions before consumption (CRUZ et al. 2013, ABD-ELHADY 2014).

According to the recommendations by the Minister of Agriculture and Rural Development of 19th September 2003 and the standard *Wiśnie zamrożone...* PN-A-78653:1997, deep-frozen agricultural and food products should be transported and stored at constant temperature not higher than –18°C. The regulation issued by the Minister allows, however, for an increase in the temperature of frozen food by up to 3°C only for loading and unloading during transport. It is thus concluded that the aforementioned regulation does not permit temperature fluctuations during storage of frozen food. Such fluctuation is allowed, yet only at the level of ±1°C, by the standard *Towary żywnościowe...* PN-83/A-07005/Az7:1999 (KRALA et al. 2010).

Studies on the changes in the quality of frozen strawberries, resulting from undesirable conditions in the cold chain, are an important element in determining the storage stability under conditions of temperature fluctuation (CRUZ et al. 2013).

The objective of the studies was to determine the level of quality changes in frozen fruits stored under conditions of fluctuating temperature and to verify the null hypothesis, assuming that the quality changes in products stored at fluctuating temperatures is not equal to hypothetical changes constituting the arithmetic mean of the changes in products stored at constant temperatures representing the extreme values of temperature fluctuations.

Materials and Methods

The studies were carried out on a strawberry Senga-Sengana. One hundred pounds of strawberries were frozen at –38°C in a fluidized bed tunnel Unidex TZF-3A UDS, in a sharp freezer operation situated in Gronowo Górne near Elbląg. The frozen fruits were transported in the transport packages, i.e. in three-layer paper bags lined with polyethylene film, to the laboratory at Gdynia Maritime University. Transportation of frozen fruits held in a van cooled eutectic plates and lasted for about eighty minutes. In the laboratory strawberry were put into polyethylene bags (commonly used in retail sales) that contained approximately 500 g of the product. The weighing, packaging and welding of the retail packages were performed at room temperature and lasted approx. 3 minutes. The material was divided into three parts, representing the following storage variants: *A* – material stored in a chamber freezer Zanussi ZV130R at constant temperature of –18°C; *B* – material stored in a chamber freezer Zanussi ZV130R at constant temperature of –25°C; and *C* – material stored in a chamber freezer Zanussi ZV130R at variable temperature –18°C/–25°C with a 48-hour exchange cycle.

The material was stored for 24 weeks and submitted for the physical and chemical analyses before storage and at 4-week cycles during storage.

Before the analyses and except for thawing spill, strawberries were thawed at room temperature.

The physical and chemical analyses of frozen strawberries were performed by determining the content of anthocyan pigments with the method by Fuleky and Francis (*Technologia chłodnictwa...* 1995), active acidity according to *Przetwory owocowe i warzywne...* PN-90/A-75101/06, total acidity according to *Przetwory owocowe i warzywne...* PN-90/A-75101/04, volume of thawing spill (JARCZYK et al. 1986), and the content of vitamin C with the spectrophotometric method according to *Produkty spożywcze...* PN-A-04019:1998. All measurements and markings were performed in nine replications.

While developing an indicator that would describe the changes provoked by storage temperature fluctuations, it was assumed that the quality changes in stored products at fluctuating temperatures were not equal to hypothetic changes constituting the arithmetic mean of changes that occur in products stored at constant temperatures representing the extreme fluctuation temperatures. The model that would allow for a verification of the assumption on the average increment in a quality change (P%) caused by temperature fluctuations was established based on a relation described with the following equation (PUKSZTA 2014):

$$P\% = \frac{1}{n}\sum_{i=1}^{n} R \tag{1}$$

where:
$P\%$ – indicator of the level of changes induced by fluctuation; it determines the average increment of quality change,
R – relative difference between the real and hypothetical value of trait [%].

$$R = 100 - \left(\frac{Z}{M} \cdot 100\right) \tag{2}$$

where:
Z – real level of trait for variable temperature,
M – hypothetical level of trait for variable temperature.

$$M = 0.5 \cdot (C_W + C_N) \tag{3}$$

where:
C_W – level of trait at higher temperature,
C_N – level of trait at lower temperature.

Results and Discussion

Freezing and storage of frozen strawberries induce transformations that result in:

– a reduction of the sensory value due to a partial degradation of anthocyan pigment, browning and changes in taste and smell substances,

– texture changes in the products that cause a decrease in water retention capacity,

– changes in the nutritional value due to a reduction in vitamin C content.

The rate of these transformations is determined, among others, by time and a constant product storage temperature (PUKSZTA and PALICH 2006).

During preservation and storage of strawberries, anthocyan pigments undergo degradation.

The results of the studies on the changes in the concentration of anthocyan pigments in frozen strawberries stored at different temperatures are presented in Table 1.

Table 1

Content of anthocyans in frozen strawberries in relation to time and temperature of storage

Storage time [weeks]	Contente of anthocyans [mg/100 g]											
	storage temperature											
	–18°C			–25°C			–18°C/–25°C					
	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	*M*	*R*	*P%*
	content of antocyans befor storage 8.10 mg/100 g											
4	7.58	6.4	0.99	7.95	1.9	0.88	7.18	11.4	0.94	7.77	7.53	11.84
8	7.06	12.8	0.96	7.15	11.7	0.93	6.25	22.8	0.70	7.11	12.03	
12	6.25	22.8	0.85	6.55	19.1	0.52	5.70	29.6	0.70	6.40	10.94	
16	5.60	30.9	0.31	5.90	27.2	0.54	5.02	38.0	0.25	5.75	12.70	
20	4.85	40.1	0.43	5.57	31.2	0.55	4.55	43.0	0.62	5.21	12.67	
24	4.25	47.5	0.28	5.30	34.6	0.52	4.05	50.0	0.23	4.78	15.18	

$\bar{Y}$ – arithmetic mean $n = 9$, Δ% – percentage change in the level of examined trait in relation to the initial level, Se(*Y*) – standard deviation, *M* – hypothetical average level of trait for variable temperature, *R* – relative difference between the real and hypothetical value of trait [%], *P%* – indicator of the level of changes induced by fluctuation; it determines the average increment of quality change.

In all the tests carried out during the storage of the test material was observed lowering of the anthocyanin content. The rate of degradation of anthocyanins was different in relation to the storage temperature.

Irreversible transformations of anthocyan pigments may result from oxidative polymerization, which causes a change from the red, natural colour of fruits to ared-russet colour which is typical of long-stored products. The activity of phenoloxidase enzymes that are found in fruits may also be a factor which induces degradation of anthocyans. Anthocyans are not direct and proper substrates for phenoloxidases which may be oxidized indirectly by quinones generated by an enzymatic oxidation of chlorogenic acid or catechin. Further stages of oxidation and polymerization may occur without enzymes. The lack of enzymes or their inactivation as observed in frozen food causes a process of pigment degradation to occur mainly as the oxidation of vitamin C. Ascorbic acid may reduce quinones and inhibit the process of oxidative polymerization of anthocyans. However, in products rich in vitamin C, degradation of anthocyan pigments is a more rapid process. The main role is attributed to a hydroperoxide which is produced in the process ofnon enzymatic oxidation of ascorbic acid to dehydroascorbic acid, particularly with the presence of copper ions, or as a result of an interaction of anthocyans with the products of ascorbic acid degradation. These processes are substantially accelerated at fluctuating storage temperatures (HORUBAŁA 1975, *Technologia chłodnictwa...* 1995).

According to WROLSTAD et al. (1970) and SOKOŁOWSKA et al. (1969), anthocyan pigment destruction is impacted by copper and iron ions, light, ascorbic acid and some products of sugar degradation. The impact of temperature on this process could be indirect by changing the quantity of free water, pH, and sublimation of ice or the concentration of l-ascorbic acid.

Table 2

Active acidity of frozen strawberries in relation to time and storage temperature

Storage time [weeks]	Active acidity [pH]											
	storage temperature											
	–18°C			–25°C			–18°C/–25°C					
	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	*M*	*R*	*P*%
	active acidity before storage 3.65											
4	3.63	0.5	0.02	3.63	0.5	0.02	3.61	1.1	0.03	3.63	0.55	
8	3.62	0.8	0.02	3.63	0.5	0.02	3.58	1.9	0.04	3.62	0.97	
12	3.60	1.4	0.04	3.62	0.8	0.01	3.56	2.5	0.03	3.61	1.39	1.26
16	3.58	1.9	0.03	3.61	1.1	0.02	3.55	2.7	0.02	3.60	1.25	
20	3.55	2.7	0.04	3.59	1.6	0.02	3.51	3.8	0.03	3.56	1.40	
24	3.49	4.4	0.05	3.57	2.2	0.02	3.46	5.2	0.04	3.53	1.98	

* key cf. the Table 1

Table 3

Total acidity of frozen strawberries in relation to time and temperature of storage

Storage time [weeks]	Total acidity [g citric acid/100g product]											
	storage temperature											
	–18°C			–25°C			–18°C/–25°C					
	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	$\bar{Y}$	Δ%	Se(*Y*)	*M*	*R*	*P*%
	total adcidity before storage 0,9387 g/100g											
4	1.0240	9.1	0.0006	0.9600	2.3	0.0004	1.0371	10.5	0.0007	0.9920	-4.55	
8	1.0835	15.4	0.0009	1.0415	11.0	0.0005	1.1262	20.0	0.0008	1.0861	-3.69	
12	1.1429	21.8	0.0007	1.1080	18.0	0.0007	1.1600	23.6	0.0008	1.1533	-0.59	-3.58
16	1.1887	26.6	0.0008	1.1745	25.1	0.0004	1.2131	29.2	0.0007	1.1771	-3.06	
20	1.2016	36.2	0.0007	1.2112	29.0	0.0005	1.3156	40.2	0.0005	1.2064	-3.22	
24	1.3881	47.9	0.0009	1.2785	36.2	0.0005	1.4181	51.1	0.0009	1.3333	-6.36	

* key cf. the Table 1

Acidity of food products is one of the most important criteria used to evaluate their quality. It may be determined as a quantity of acid compounds produced with electrolytic dissociation and neutralized by titration with base or ph-metrically as the concentration of hydrogen ions. For the evaluation of strawberries, changes in total acidity and in pH may be an indicator of their quality (*Technologia chłodnictwa*... 1995).

The course of changes in active and total acidity during storage of frozen strawberries is presented in Table 2 and Table 3.

Analysis of the results showed a reduction in pH values and an increase in the total acidity of the fruit stored at a variable temperature and constant –18°C and –25°C.

The changes in acidity during the storage of strawberries are related to an increase in the concentration of organic and inorganic salts in unfrozen water. These salts may precipitate changes, thus affecting the acidity of environment. Organic acids and their salts constitute natural buffer solutions. When specific salts precipitate, a buffer solution may decrease its volume and lose, partially or totally, its buffer capacity.

A partial hydrolysis of pectins and release of the active groups of galacturonic acid (the basic components of these polysaccharides) may have occurred under the influence of organic acids. Although at low temperatures these processes are limited, they may have contributed to an increase in the acidity of the stored products (*Chemia żywności*... 2000, HORUBAŁA 1975).

During storage of frozen strawberries, their cellular and tissue structure is affected, leading to a spill during thawing.

The volumes of thawing spill from frozen strawberries in relation to time and storage temperature are presented in Table 4.

Table 4

Thawing spill from frozen strawberries in relation to time and storage temperature

Storage time [weeks]	Thawing spill [cm^3/100 g]											
	storage temperature											
	–18°C			–25°C			–18°C/–25°C					
	$\bar{Y}$	Δ%	Se(Y)	$\bar{Y}$	Δ%	Se(Y)	$\bar{Y}$	Δ%	Se(Y)	M	R	P%
	thawing spill before storage 18.50 cm^3/100 g											
4	18.63	0.5	0.61	18.80	1.6	0.35	20.00	8.1	0.44	18.70	-6.95	-16.23
8	19.60	5.9	0.52	18.90	2.2	0.46	21.80	17.8	0.56	19.25	-13.25	
12	21.20	14.6	1.22	19.50	5.4	0.56	23.50	27.0	0.62	20.35	-10.07	
16	23.20	25.4	0.76	20.40	10.3	1.04	25.80	39.5	0.95	21.80	-5.50	
20	25.60	38.4	0.85	20.50	10.8	0.46	29.20	57.8	1.35	23.05	-26.68	
24	28.20	52.4	0.82	21.90	18.4	0.61	33.80	82.7	1.22	25.05	-34.93	

* key cf. the Table 1

The results indicate a steady increase in the size of the thawing spill with storage time. The greatest rate of growth thawing spill characterized by strawberries stored under conditions of temperature fluctuations, the smallest and at constant -25°C.

A thawing spill is generated by a transformation of the crystal arrangement that is caused by sublimation of smaller ice crystals and flow of water vapour towards bigger crystals stimulated by a difference in partial pressures. This induces an increase in the average crystal size, leading to a decrease in the quality of the stored products. The constant increase in the size of ice crystals results in an ongoing destruction of the cell walls and in an increase in the volume of thawing spill. The process of re-crystallization is intensified by temperature fluctuations during storage. Re-crystallization occurs even in products stored at a relatively constant temperature, although its magnitude is minor and depends on the time and temperature of storage (PUKSZTA and PALICH 2006).

Krala et al. also pointed to the influence of temperature fluctuations on the size of the thawing spill fruit. In a study of the sensitivity of cherries on storage temperature fluctuation, they found that significant temperature fluctuations storage of frozen cherries promote recrystallization of ice and increase the damage to their texture, thereby increasing the thawing spill (KRALA et al. 2010).

Changes in the nutritional value due to a decrease in the content of vitamin C are one of the pathways leading to a reduction of the quality of frozen food products. This vitamin plays an important role in human nutrition and is assumed to be an indicator of the behaviour of other micronutrients in fruit and vegetable products during storage (HORUBAŁA 1975, SOKOŁOWSKA et al. 1969).

The changes in the content of vitamin C in frozen strawberries are presented in Table 5.

Table 5

Content of vitamin C in frozen strawberries in relation to time and temperature of storage

Storage time [weeks]	Content of vitamin C [mg/100 g]											
	storage temperature											
	–18°C			–25°C			–18°C/–25°C					
	$\bar{Y}$	Δ%	Se(Y)	$\bar{Y}$	Δ%	Se(Y)	$\bar{Y}$	Δ%	Se(Y)	M	R	P%
	content of vitamin C before storage 61.23 mg/100 g											
4	59.20	3.3	4.03	60.70	0.9	2.98	59.60	2.7	3.92	59.95	0.58	2.42
8	59.00	3.6	3.83	60.10	1.8	3.52	59.30	3.2	3.81	59.55	0.42	
12	57.40	6.3	3.92	59.50	2.8	3.28	57.9	5.4	2.98	58.45	0.94	
16	56.30	8.1	3.14	58.61	4.3	3.47	55.72	9.0	3.52	57.46	3.02	
20	55.92	8.7	2.92	57.98	5.3	3.22	55.11	10.0	3.20	56.95	3.23	
24	53.88	12.0	3.41	57.25	6.5	3.93	52.05	15.0	4.13	55.57	6.33	

* key cf. the Table 1

During storage, the test products in all variants the temperature found a steady decline of the contents of vitamin C. The dynamics of this ratio varied depending on the storage option. Highest growth rate of the content of L-ascorbic acid showed strawberries stored in a variable temperature conditions.

The changes in the content of vitamin C during frozen storage of fruits and also indicates Skupień and Ancos et al. In blueberries stored for one year at temperature –25°C, Skupień state vitamin C losses of up to 72%, while de ANCOS et al., loss of vitamin after a year of storage at –20°C varieties of raspberry tagged at up to 55% (MICHALCZYK and KUCZEWSKI 2012).

The processes of oxidation and destructive impact of specific enzymes are the major pathways of vitamin C transformation. The impact of both factors is substantially intensified with a fluctuating storage temperature, which was confirmed by the present study. In addition, it was found that the fluctuation of temperature during the storage of frozen products significantly increased their loss-in-weight. This was most probably due to superficial ice sublimation that, because of a limited migration of water in the products, led to an extremely dehydrated layer with a porous structure. Sublimated ice is replaced by air, which – with a well-developed porous layer – may inevitably result in an intensification of oxidation processes, for instance, of L-ascorbic acid (PUKSZTA 2009). The increase in temperature from –25°C to –18°C which strawberries stored at fluctuating temperature were exposed to, contributed to an increase in the speed of enzymatic reactions and caused vitamin C degradation. According to MUÑOZ-DELGADO (1978), an increase of temperature by 10°C (from –20°C to –10°C) results in a 3.5–4-fold acceleration of enzymatic reactions responsible for vitamin C degradation. This thesis was reflected in a reduction of the content of L-ascorbic acid detected in strawberries stored at variable temperature and in a significantly lower reduction of vitamin C concentration at constant temperature, particularly at -25°C. Thus, reduction of storage temperature has a direct impact on a deceleration of enzymatic reactions (KLIMCZAK and IRZYNIEC 1997).

The studies also demonstrated that, from a quality perspective, it was more beneficial to store the product at extremely higher constant temperature of -18°C than at a fluctuating temperature of –18°C/–25°C. The level of transformations in strawberries stored at –18°C was lower than in the fruits stored at a variable temperature of –18°C/–25°C. (Tables 1, 2, 3, 4, and 5).

Cruz et al. in research on the effects of temperature fluctuation on the quality of frozen strawberries also found that it is preferable to store strawberries in a constant temperature than under temperature fluctuations (CRUZ et al. 2013).

The impact of temperature fluctuations on the direction and range of the examined quality traits was analysed based on the values and marks of the indicator of changes caused by fluctuation *P%*. The null hypothesis assumed that the quality changes of strawberries stored at a fluctuating temperature were not equal to the hypothetical changes which constituted the arithmetical mean of changes in the product stored at a constant temperature representing the extreme values of temperature fluctuations. With these assumptions, the indicator *P%* had large numerical values ($P>10$) when the difference between the hypothetical and real values was large. The mark of *P%* indicator depended on the deviation of real values from hypothetical values. If real values deviate towards a higher extreme parameter, the indicator of changes caused by fluctuation *P%* has a minus character.

The verification of the null hypothesis demonstrated that the values of the examined traits (Tables 1–5) were not equal to the resultant of the levels recorded under extreme conditions, though for the majority of the analysed quality parameters they slightly diverged from the assumed hypothetical values. The exception was the level *P%* for the changes in the volume of thawing spill and the content of anthocyans, showing that the temperature fluctuations caused a substantial intensification of these processes in stored strawberries (Table 1 and Table 4). In the case of active acidity, total acidity and vitamin C concentration, it was found that the deviations of the real values from the hypothetical ones were minor, which indicated a negative impact of temperature fluctuations on the changes in these quality parameters (Table 2, Table 3, and Table 5). In addition, a negative character of *P%* indicator for the changes in total acidity and volume of thawing spill indicates a deviation of the real values recorded at fluctuating temperature towards the values recorded during storage of strawberries at extremely higher temperature, i.e. -18^{o}C (Table 3 and Table 4).

The inclusion of the fluctuation of parameters in the analysed kinetic arrangement and, therefore, the application of a statistical model, allowed for a positive verification of the null hypothesis assuming a lack of negative impact of temperature fluctuations on the storage life and nutritional quality of frozen strawberries.

Conclusions

1. The changes in the quality of frozen strawberries stored at fluctuating temperature are not equal to the hypothetical changes constituting the arithmetic mean of the transformations occurring in products stored at constant temperatures representing the extreme values of temperature fluctuations.

2. Assuming the quality of frozen strawberries, it is more beneficial to store them at an extremely higher temperature, i.e. -18°C, than at a variable temperature of-18°C/-25°C.

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