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THE INFLUENCE OF STORAGE TEMPERATURE ON OXIDATIVE STABILITY AND SHELF-LIFE OF PEANUTS

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Key words: Food Quality, Peanuts, Oxidative stability, Shelf-Life, Storage.

Abstract

The aim of this study was to evaluate the influence of storage temperature on oxidative processes and shelf-life of peanuts. Shelled roasted peanuts of two different origin, Argentina and Brazil, vacuumpacked in laminatepolyamide /polyethylene, were stored up to 6 months in practical (20 ± 1°C) and accelerated (28 ± 1°C) storage dark conditions. The measure of oxidative stability was peroxide value with proposed limiting value 20 meq O_2/kg of extracted oil and hexanal (proposed critical limit 3 ppm). The kinetic parameters from Arrhenius' equation were calculated. The temperature dependent oxidativeprocesses in peanuts from Argentina and Brazil do not occure xactly in the same way. Moreover, regardless of peanuts origin, there was higher temperature sensitivity for primary thansecondary oxidative changes observed. Uncontrolled increase of temperature from e.g. 20°C to 25°C would reduce shelf-life of peanuts by 20–30% which entails not only economic consequences but is also important because of nutritional value and food safety issues.

WPŁYW TEMPERATURY PRZECHOWYWANIA NA STABILNOŚĆ OKSYDACYJNĄ I TRWAŁOŚĆ ORZECHÓW ARACHIDOWYCH

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Abstrakt

Celem pracy była ocena wpływu temperatury przechowywania na przebieg procesów oksydacyjnych i trwałość orzechów arachidowych. Zapakowane próżniowo w laminat poliamid/polietylen orzechy arachidowe, pochodzące z Argentyny i Brazylii, przechowywano przez 6 miesięcy bez dostępu światła w warunkach praktycznego składowania (20 ± 1°C) oraz przyspieszonego starzenia (28 ± 1°C). Jako limity krytyczne wyróżników stabilności oksydacyjnej badanych orzechów przyjęto zawartość nadtlenków na poziomie 20 meq O_2/kg wyekstrahowanego tłuszczu i zawartość heksanalu na poziomie 3 mg/kg orzechów. Na podstawie równania Arrheniusa wyznaczono parametry kinetyczne procesów utleniania. Mimo, iż temperaturowa zależność procesów oksydacyjnych nie była jednakowa w przypadku próbek z Argentyny i Brazylii, w obu rodzajach wykazano większą zależność od temperatury zmian pierwotnych niż wtórnych. Kontrolowanie i przestrzeganie założonej temperatury podczas przechowywania orzechów ma ogromne znaczenie dla wartości odżywczej i bezpieczeństwa produktu. Wykazano, że niekontrolowany wzrost temperatury przykładowo z 20°C do 25°C skraca trwałość orzechów o 20–30%.

Introduction

Oxidative processes of lipid fraction during processing and storage contribute food quality. They may change nutritional value of food because of impact on essential fatty acids, proteins and vitamins (Chun et al. 2005, HĘŚ and KORCZAK 2007). Some of the arising products of oxidation such as free radicals or oxysterols have been described to have negative or even toxic health effect (GUILLEN and GOICOECHEA 2008). Degradation of the unstable primary oxidation products, hydroperoxides, leads to the formation of a variety of volatile compounds, such as aldehydes, ketones, hydrocarbons, alcohols, acid compounds and furans. Formed secondary products with low threshold values are responsible for the off-flavors development (MIN and BOFF 2002, OLMEDO 2012).

Several internal and external factors may have an impact on storage stability of peanuts. The works on influence of storage conditions on oxidative stability of different nuts proved that the most important factor influencing shelf-life was temperature which had the accelerating effect on the deteriorative processes (VANHANEN and SAVAGE 2006, MEXIS et al. 2009, WAMBURA et al. 2012, WILKIN et al. 2014).

The effect of temperature on the rate of reaction can be described by the Arrhenius equation (SCHMIDL and LABUZA 2000):

$$k = k_a \exp(-E_a / RT) \quad (1)$$

where:
k – the rate constant,
k_a – the pre-exponential constant,

E_a – the activation energy (kJ/mole),
R – the gas constant (8,315 J/mol·K),
T – the absolute temperature (K).

The activation energy can be used as the measure of temperature dependence of processes – the higher the E_a, the faster the reaction as temperature increases.The increase of temperature has various impacts on different kinds of changes in food. The chemical reactions are usually highly temperature dependent (MAN 2011).

Another method of expressing the temperature dependence of reaction is the Q_{10} (temperature quotient) approach. Q_{10} can be defined as the reaction rate at one temperature compared to that at a temperature 10°C lower (SCHMIDL and LABUZA 2000):

$$Q_{10} = k_{(T+10)}/k_T \quad (2)$$

where:
Q_{10} – the temperature quotient,
T – the absolute temperature (K).

The relationship of Q_{10} and Ea can be described by the means of the following equation:

$$\ln (Q_{10}) = 10E_a/RT(T+10) \quad (3)$$

where:
Q_{10} – the temperature quotient,
E_a – the activation energy (kJ/mole),
R – the gas constant (8,315 J/mol·K),
T – the absolute temperature (K).

The most important mechanism of lipid oxidation is chemical process of autoxidation. It is influenced by temperature (KERRIHARD et al. 2015). Inappropriate storage conditions, such as temperature abuse, would increase the rate of oxidation in peanuts. Taking into consideration high temperature dependence of oxidative processes, it is important to recognize the way the changes of storage temperature influence peanuts' shelf-life. The aim of this study was to evaluate the influence of storage temperature on oxidative processes and shelf-life of peanuts.

Materials and Methods

Materials

Shelled roasted peanuts of two different origins sample A – from Argentina, and sample B – from Brazil, were supplied by a local importer. The samples were vacuum packed in plastic laminate PA (polyamide) / PE (polyethylene). The total fat was 52,7% (sample A) and 53,1% (sample B) and the moisture content 1,9% (A) and 1,4% (B), as determined using AOAC Official Methods (948.22, 925.40).

The samples were stored in closed 100 g packages up to 6 months in practical (20°C ± 1°C) and accelerated (28°C ± 1°C) storage dark conditions. After and at the end of each month the samples were withdrawn to perform the analysis of hydroperoxides and after every two months for hexanal measurements. The experiment was repeated twice.

Lipid extraction

Lipids were extracted from peanuts according to the method described by FOLCHET et al. (1957) with modifications. About 10 g milled peanuts were homogenized twice with 50 ml chloroform/methanol mixture (2:1 vol/vol). The obtained mixture was filtered and combined into a separatory funnel. The extract was then diluted with distilled water and the lower phase was collected and passed through anhydrous sodium sulfate. Solvent was removed in a rotary vacuum evaporator (BüchiLabortechnik, Flawil, Switzerland). The extracted lipids were used forhydroperoxides evaluation.

Peroxide value

PV (peroxide value) in extracted lipids was determined by iodometric method according to Polish Standard (PN-EN ISO 3960:2009) and expressed in meq O_2/kg of extracted oil.

Hexanal analysis

Hexanal measurements in peanuts were performed with the use of the SHS-GC (static headspace gas chromatography). The analyses were carried on the Varian 3800 gas chromatograph (Varian Inc., Lake Forest, CA, USA)

equipped with an autosampler Tekmar 7000 (Tekmar-Dohrmann, Cincinnati, USA).

Sample preparation

A standard stock solution containing hexanal in the concentration around 2 mg/ml of freshly refined rapeseed oil (Z.T. Kruszwica S.A., Kruszwica, Poland) was used to prepare subsequent solutions. The hexanal has not been detected in rapeseed oil as measured by SHS-GC. Then, a standard addition method was applied: 4 g ± 0.2 g of peanuts were placed in glass vials (22 mL) and 0.5 mL of rapeseed oil without any standard (zero sample) or 0.5 mL of rapeseed oil containing increasing concentration of hexanal was added (KOLB and ETTRE 2006). Vials were closed with the use of septum and left in darkness overnight to equilibrate.

Static headspace conditions

Samples were agitated for 30 min at 50°C to reach equilibrium. The headspace conditions were as follows: vial pressurization 34.5 kPa, pressurize time 0.5 min, sample equilibration 0.1 min, loop fill 0.6 min, loop equilibration, 0.1 min, injection 0.1 min, loop temperature 110°C, transfer line temperature 120°C, vial needle flow 55 mL/min. The gas phase (the headspace) was introduced into the carrier gas stream- helium (Linde, Kraków, Poland) and carried into the column.

Gas chromatography

A gas chromatograph Varian 3800 was equipped with a flame ionization detector and a capillary column CP Sil 8CB (30 m x 0.53 mm x 1.5 μm; Varian Inc., Lake Forest, CA, USA). The initial column temperature was 40°C (2 min), then it was raised to 100°C (8°C/min) and to 200°C (20°C/min), then held 5,5 min (SAMOTYJA and MAŁECKA 2010). Hexanal was determined by comparison of retention time with that of a known hexanal standard.

Chemicals

Hexanal (98% GC) was from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Other chemicals were of reagent quality grade and were provided by POCh (Gliwice, Poland).

Estimation of shelf-life

The kinetic parameters were calculated for measured primary and secondary oxidative processes. The loss of food quality can be represented by the kinetic equation:

$$dC/dt = kC^n \tag{4}$$

where:
C – the quality factor measured,
t – time,
k – the rate constant,
n – the reaction order.

The rate constant $k$of each temperature was determined separately for hydroperoxides and hexanalby plotting ln C versus time. Then, the rate constant – temperature dependence was established on the basis ofconverted Arrhenius equation:

$$lnk = lnk_0\text{-}(E_a/RT) \tag{5}$$

Subsequently, the activation energy was determined (Gallagher et al. 2011). The temperature quotient Q_{10} was calculated from the Eq. (3) (MAN 2011).

The shelf-life of peanuts was estimated by plotting the linear relation between the log of end-point and the tested temperatures. The results were presented as the shelf-life linearcurves directly showing the end-point of oxidative stability versus temperature (°C).

Statistical analysis

All analyses were done in duplicate and the results were expressed as average values. The data were fitted to the mathematical models and the regression analyses were carried out. The calculations were performed using Statistica 8.0 software (StatSoft, Inc., Tulsa, USA).

Results and Discussion

Oxidative stability

The course of oxidative changes in peanuts is presented in Figure 1. The lower stability of lipid fraction, the higher is the extent of primary and secondary oxidative processes as measured by PV and hexanal concentration (respectively).

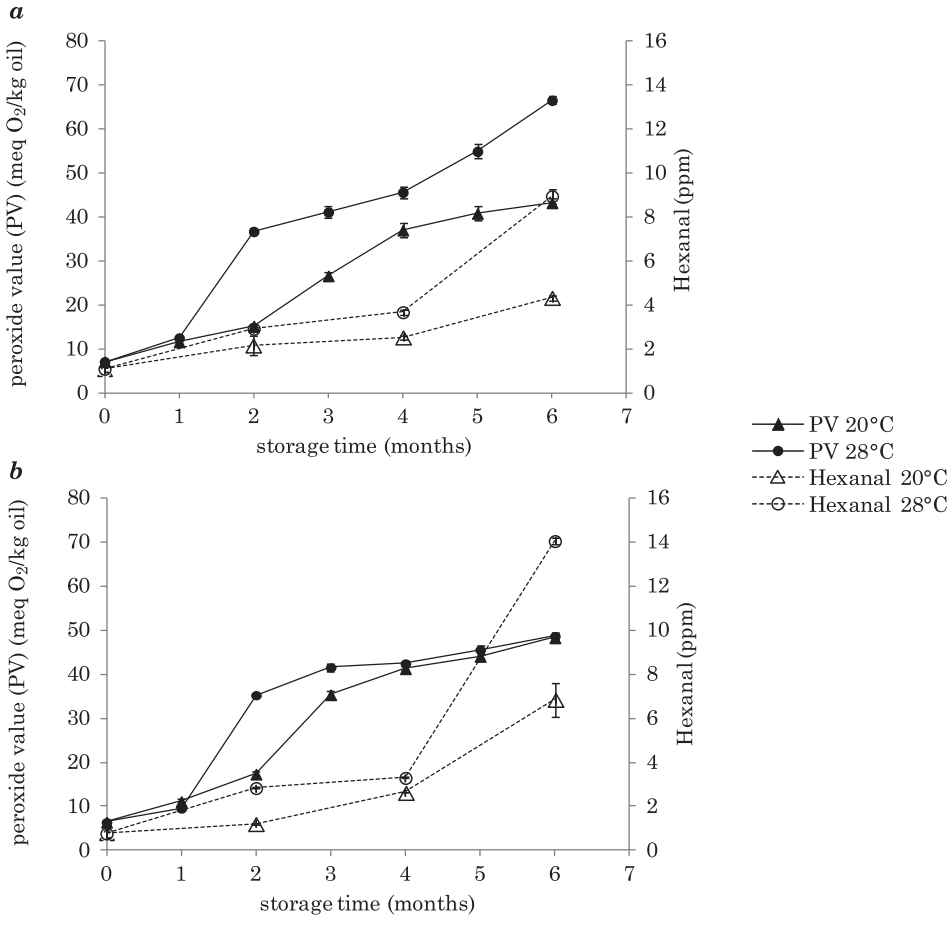

Fig. 1. The extent of primary and secondary oxidative changes in peanuts during 6-months storage at 20°C and 28°C. A – sample A, B – sample B

The amount of hydroperoxides increased from starting point to the end of experiment. PV increased from the initial level of 7.1 meq O_2/kg to 15.2 meq O_2/kg (sample A) and from 6.5 meq O_2/kg to 17.4 meq O_2/kg (sample B) in the two first months of storage at 20°C. After this period there wasa sudden change in PV observed. During the third month of the test at 20°C PV of peanuts reached the level of 26.6 meq O_2/kg (A) and 35.4 meq O_2/kg (B). Storage at elevated temperature resulted in higher degree of primary oxidation products formation. The analyses showed rapid increase of PV during second month of storage at 28°C to the values 36.7 meq O_2/kg (A) and 35.3 meq O_2/kg(B).

Initial concentrations of hexanal were 1.1 ppm (sample A) and 0.8 ppm (sample B). Hexanal concentration increased slowly till the end of fourth month of storage, and then rapidly increased to 4.3 ppm (A) and 6.8 ppm (B) at ambient conditions and to 8.9 ppm (A) and 14.0 ppm (B) at 28°C as measured at the end of storage.

Shelf-life considerations

The shelf-life limiting value (end-point) of PV was established on the level of 20 meq O_2/kg. There is no standard critical limit of hydroperoxides in peanuts and in literature different values are assumed, but usually they are within the range of 20–30 meq O_2/kg (EVRANUZ 1993). Taking into consideration the course of oxidative processes, the established critical limit corresponds to the propagation phase excerpt of the PV curves.

Rapid decomposition of primary products, yielding sharp increase of hexanal was observed after fourth month of samples storage and corresponded to the avera gealdehyde contents of about 3 ppm – this value was used as the critical limit during further considerations in this study. For comparison, MEXIS et al.(2009) who studied the effects of storage conditions on the quality of walnuts, proposed limit for PV close to 10 meq O_2/kg of walnut oil with respective values for hexanal 1–2 ppm. ROBARDS et al.(1988) correlated hexanal concentration with flavor score of corn chips and found out that samples unacceptable according to the hedonic scale corresponded to concentration of hexanal exceeding 5 ppm. Nepote et al. (2006) found out that the end point of consumer acceptance of rancid flavor in peanuts corresponded values over 80 meq O_2/kg, what was much beyond the accepted limit of hydroperoxides. The difficulty for arbitrary assignation of a limiting value of a given quality criterion in shelf-life studies is a result of complexity of deteriorative changes in food. The kind, amount and the rate of secondary oxidation products formation depend on the rate of their precursors' decomposition which in turn depend on food composition and mechanism of deterioration.

From adjustments of experimental data to different kinetic models the first order reaction model was selected to describe the oxidative changes in peanuts during storage. The kinetic parameters (the rate constant k and the activation energy E_a) are presented in Table 1.

Table 1

Rate constant (k) for hydroperoxides and hexanal formation, the activation energy (E_a) and temperature quotients Q_{10}

Criterion of shelf-life	Sample	Temperature (°C)	Rate constant [a]k (1/month)	Coefficient of determination (R^2)	Activation energy E_a (kJ/mol)	Temperature quotient Q_{10}
Hydroperoxides formation	A	20	0.413 ± 0.023	0.991	63.0	2.4
		28	0.821 ± 0.148	0.969		
	B	20	0.553 ± 0.037	0.991	39.1	1.7
		28	0.846 ± 0.263	0.912		
Hexanal formation	A	20	0.232 ± 0.042	0.940	36.2	1.6
		28	0.345 ± 0.057	0.949		
	B	20	0.364 ± 0.040	0.977	17.6	1.3
		28	0.441 ± 0.087	0.928		

Explanation to Table 1: [a]k ± confidence intervalat 95%

Increasing rate constant with rising temperatures confirms temperature dependence of measured processes. Regardless of the sample origin, there was higher temperature dependence for PV than hexanal observed. It means that increase in temperature would result in higher degree ofhydroperoxidesformation than hexanal. On the contrary, a reduction in temperature would have greater impact on inhibition of hydroperoxides formation.

Q_{10} values for reactions in peanuts A and B were found to be different. These values were also differentiated in relation to primary and secondaryoxidation products formation. Increase of temperature of 10°C would cause increase of hydroperoxides formation 2,4 – fold in peanuts A and 1,7 – fold in sample B, whereas hexanal would be formed 1,6 and 1,3 times faster (in peanuts A and B, respectively).

Higher values of E_a and Q_{10} for peanuts A mean that with increase of temperature their shelf-life would be reduced more than that of B samples.

Similarly, the temperature decrease would prolong shelf-life of peanuts A more than peanuts B.

On the basis of storage trials the shelf-life can be estimated at any temperature range in which the mechanism of reactions does not change. The influence of temperature on the predicted time to reach PV = 20 meq O_2/kg and 3 ppm of hexanal is presented in Figure 2. This period is exponentially reduced with increasing temperature and indicates quality deterioration resulting reduction of shelf-life.

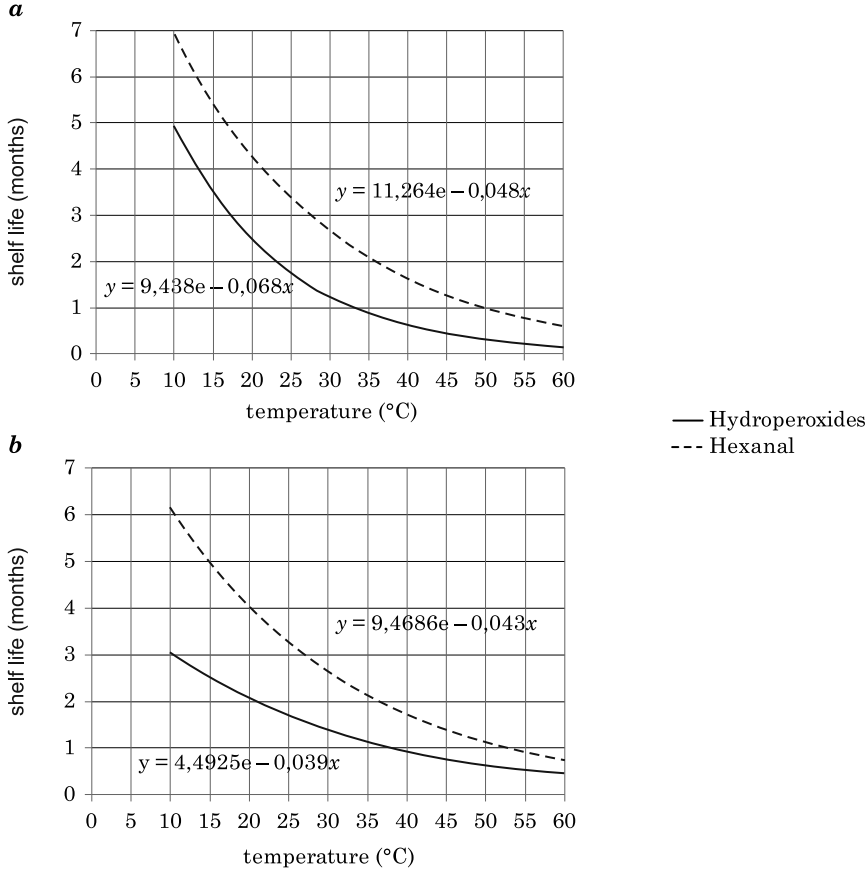

Fig. 2. Predicted shelf-life of peanuts as a function of temperature. A – sample A, B – sample B

Presented shelf-life curves show that oxidative stability of peanuts according to storage temperature does not change exactly in the same way and depends on the origin of the product. Moreover, during chain of distribution

and storage, some additional factors (such as temperature fluctuations through time) can influence the shelf-life and therefore they also should be taken into consideration.

Conclusions

The storage temperature influences oxidative processes in peanuts and thus decrease their shelf-life. Uncontrolled increase of temperature from e.g. 20°C to 25°C would reduce shelf-life of peanuts by 20–30% which entails not only economic consequences but is also important because of nutritional value and food safety issues. It can be assumed that the retailers are not always aware of this fact, the peanuts are often stored in unsuitable conditions and, finally, lose their quality before they reach the consumer.

The temperature dependent oxidative processes in peanuts do not change in the same way. Different activation energies mean that increase of temperature would have different impact on samples which have the same state of oxidation after production (packaging). Q_{10} values available in literature should be used only for approximation or experiment design purposes as there is no universal value for a certain kind of food.

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