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Analytical Methods

The change of fatty acids composition of Polish biscuits during storage

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ABSTRACT

Commercially available Polish biscuits were stored for 10 months under different storage conditions i.e. in temperatures of 5 °C and 20 °C. The chemical quality alteration caused by chemical reactions occurring within biscuits were studied in terms of change of composition of fat extracted from studied samples in one-month intervals. Correlation of data from standard methods e.g. gas chromatography or classic titration with FT-IR spectroscopy, was followed by calculation of four statistical models that accurately predicted peroxide value, oxidative stability, polar fraction content and unsaturated trans fatty acid content in any samples. On the basis of data obtained, scheme of chemical reactions involved in oxidation process was suggested. A critical time of storage was proposed as an indicator of the period of the highest rate of chemical changes. Among factors considered to influence oxidative stability, the following had the greatest impact: initial water content, initial fat content, and time of storage.

1. Introduction

Monitoring changes that may occur during storage is essential for the overall quality, functionality and economic value of the product. In bakery products, the parameter that summarizes the quality of biscuits is the composition of fat characterized by peroxide value (PV), oxidative stability (OS), polar fraction (PF), composition of free fatty acids (FFA) and trans fatty acid content (TFA). Fat oxidation process (starting typically with C=C reaction with oxygen) may occur in different pathways. The oxidation mechanism is interesting from a scientific point of view, while commercially it decides on important product feature, the shelf life.

The content of peroxides in alimentary fats, reflected in peroxide value (PV), refers to the degree of primary oxidation of fat and thus its tendency to go rancid. Unsaturated fatty acids, commonly present in fats, react with oxygen forming peroxides which are precursors of a series of chain reactions forming volatile substances with the unpleasant rancid smell. These reactions are accelerated by high temperature and exposure to light and oxygen (Yildiz, Wehling, & Cuppett, 2002). The lower peroxide value, the higher oxidative stability and the better quality of alimentary fats.

Peroxide value (PV) is a primary parameter describing product quality. Although technically simple, the traditional procedure of PV determination is time-consuming and costly. It requires potentially hazardous solvents, glassware and is dependent on a visual detection of endpoint (Van der Voort, Sedman, Yaylayan, & Saint-Laurent, 2003). Recently, determination of PV in commercial products (e.g. oils) has been achieved using modern methods, e.g. Fourier Transformed Infrared Spectroscopy (FT-IR) (Yildiz et al., 2002). It can also be applied in determination of other parameters important for foodstuffs quality. The theoretical principles and sample applications of FT-IR have been reported in previous papers (Koczoń, Dobrowolski, Lewandowski, & Mazurek, 2003; Koczoń, Lewandowski, Lipińska, & Sobczak, 2001; Koczoń, Piekut, Borawska, Świsłocka, & Lewandowski, 2006). It has been used in analysis of fresh vegetables, e.g. carrots (Quilitzsch, Barańska, Schulz, & Hoberg, 2005), live fish (Solberg, Saugen, Swenson, Bruun, & Isaksson, 2003), genetically modified barley seeds (Jacobsena, Søndergaardb, Møllera, Deslerc, & Muncka, 2005), oils (Chippie, Jamieson, Golt, Hsu, & Lo, 2002; Guillen & Cabo, 2002; Tay, Singh, Krishnan, & Gore, 2002) or water in food (Buning-Pfaue, 2003). In all above-mentioned papers, authors developed statistical models involving spectral and reference data used for determination of content of the studied components e.g. α-caroten, or β-caroten (Quilitzsch et al., 2005) or β-glucan (Jacobsena et al., 2005).

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There are fewer papers, however, that concentrate on monitoring chemical changes occurring in foods (Quilitzsch et al., 2005).

The resistance of fats to oxidation (oxidative stability) can be evaluated with dynamic tests such as Rancimat based on the measurement of the induction time. Induction time is time from experiment onset to radical increase in amount of products of oxidation process e.g. short chain carboxylic acids (Candeia et al., 2011).

Polar fraction (PF) represents the content of monoacylogliceroles, diacylogliceroles, and free fatty acids that strongly influence the initial rate of oxidation. Hydroperoxides are interim chemicals formed during oxidation. They may accumulate or break down to form low molecular weight compounds, such as alcohols, aldehydes, ketones, and free fatty acids. This process is known as autooxidative rancidity. Regardless of their rate, all chemical reactions occurring inside the product during storage usually cause product deterioration.

Free fatty acids content (FFA), including unsaturated trans fatty acids content (TFA), was the last parameter measured in current study. TFA is especially important due to its contribution to product nutritional value (de Roos, Schouten, & Katan, 2001; Dlouhý et al., 2003).

In this paper, we assessed PV, OS (Rancimat), PF, FFA and TFA in the studied biscuits in one-month intervals during 10 months of storage at 5 °C or 20 °C by conventional methods and FT-IR spectroscopy. Influence of time of storage, free fatty acids content and temperature on peroxide value, PV was evaluated. Critical time of storage (CTS) at room temperature was defined and evaluated. The aim of this study was to develop statistical models correlating several measured parameters of biscuits (PV, OS, PF, and TFA) with IR spectral data to establish a reliable procedure for rapid measurement of these parameters representing chemical changes. Dependent variables, e.g. water content (W), initial fat content (IFC), ratio W/IFC, free fatty acid content (FFA), were measured against independent variables e.g. time of storage (t) and temperature of storage (T) in order to detect most influential factor.

Based on data obtained, a scheme for chemical reactions responsible for fat oxidation and therefore product deterioration occurring in biscuits during storage, was proposed.

2. Materials and methods

Biscuits were purchased from the local supermarkets in Warsaw (Poland). Expiration date of purchased biscuits was later than after 10 months. Five types of biscuits were studied: biscuits with oat flakes (indicated as A); biscuits with oat flakes, wheat flakes and dried fruits (indicated as B); biscuits with oat flakes and sunflower seeds (indicated as C); biscuits with oat flakes, sesame seeds and sunflower seeds (indicated as D) and biscuits with wheat flakes (indicated as E). Every of five biscuit types were divided into eighteen portions of equal weight. Nine portions were stored in a refrigerator (5 °C) and the remaining portions were stored at room temperature (20 °C). To avoid light effect, samples were wrapped in brown paper and placed in a dark place. For the scientific reasons, the long storage time and the two storage temperatures were applied, allowing to obtain some valuable data for the parameters of interest (see Table 1), which enabled to create a robust model for determination of desired parameters.

Sampling for reference methods as well as spectral measurements took place at every month of storage.

The experimental data for a given type of biscuit were obtained by five replicate measurements.

2.1. Analytical methods

2.1.1. Determination of fatty acid composition according to the Polish standard, PN-EN ISO 5508: 1996 (PN-EN ISO 5508, 1996)

The determination of fatty acid composition was carried out by gas chromatography (GC) analysis of fatty acid methyl esters using a Shimadzu GC 17 A chromatograph, a capillary column of 30 m in length, 0.22 mm inside diameter and film thickness of 0.25 μm was filled with stationary phase BPX 70. Nitrogen was used as carrier gas. The conditions for separation of methyl esters were: the starting temperature of 60 °C, the increase in temperature from 60 °C to 170 °C at the rate of 10 °C per minute, the increase in temperature from 170 °C to 230 °C at the rate of 3 °C per minute; the end temperature of 230 °C held for 15 min, the injector temperature 225 °C, the entire time of analysis was 47 min.

2.2. Analysis of the polar compounds according to the Polish standard PN-EN ISO 8420: 2008 (PN-EN ISO 8420, 2008)

The polar compounds of the extracted lipid fraction were analyzed according to the Polish standard procedure (PN-EN ISO 8420, 2008). The compounds were separated on the silica gel 60 (grains of 0.063–0.200 mm which is equal to 70–230 mesh STM) purchased from Merck (Poland). In the PF measurements the length of the column was 45 cm and its inside diameter was 2 cm.

2.3. Free fatty acids

Free fatty acids content was calculated based on acid values and the values of average molar masses of fatty acids determined by GC. Acid values were determined by titration of fat samples dissolved in the mixture of ethanol/diethyl ether (1:1, v/v) with 0.1 M ethanoic potassium hydroxide solution.

2.4. The Rancimat analysis according to the Polish standard, PN-EN ISO 6886: 2009 (PN-EN ISO 6886, 2009)

Antioxidant stability was evaluated by the Rancimat method. Temperature of measurement was 100 °C and air flow of 10 dm^3 per hour.

Table 1
Free fatty acid content (FFA), %), polar fraction content (PF, %), oxidative stability (OS, hours), and peroxide value (PV, mmol O_2 per kg) determined for the studied biscuits A, B, C, D and E, stored at 20 °C for 10 months.

Parameter	Type of the biscuits									
	A Time of storage		B Time of storage		C Time of storage		D Time of storage		E Time of storage	
	0	10	0	10	0	10	0	10	0	10
FFA (%)	3.8 ± 0.2	8.2 ± 0.3	1.1 ± 0.1	6.7 ± 0.3	1.0 ± 0.2	6.2 ± 0.5	1.0 ± 0.1	7.2 ± 0.3	4.1 ± 0.1	14.7 ± 0.4
PF (%)	5.9 ± 0.3	11.1 ± 0.5	3.1 ± 0.1	8.3 ± 0.4	3.5 ± 0.2	10.1 ± 0.2	1.4 ± 0.1	9.6 ± 0.3	3.9 ± 0.4	12.4 ± 0.5
Oxidative stability (h)	3.8 ± 0.3	0.2 ± 0.1	7.8 ± 0.3	2.1 ± 0.1	7.1 ± 0.4	2.1 ± 0.1	11.6 ± 0.5	3.6 ± 0.1	2.7 ± 0.2	0.2 ± 0.0
PV (mmol O_2 per kg)	4.2 ± 0.1	10.4 ± 0.4	0.8 ± 0.1	6.8 ± 0.4	1.1 ± 0.1	6.0 ± 0.4	0.4 ± 0.0	8.3 ± 0.3	0.8 ± 0.1	7.9 ± 0.3