Agronomy Research **15**(S2), 1386–1398, 2017

A study of the forms of bound water in bread and bakery products using differential thermal analysis

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Abstract. The objective is to study the forms of bound water in bread and bakery products using differential thermal analysis, changes to these forms corresponding to different recipe components, and changes occurring during storage. The subject of this research are bread and bakery products made of wheat flour (with gluten content of 28.5%, and ash content of 0.55%): without added fat; with tap water or activated water used for dough mixing; with varying fat content (4 and 14%); protein-enriched with cedar nut flour (5%); and dietary (food) fiber-enriched with red-fruited mountain ash and sea buckthorn powder (5%). The reference samples of bread and bakery products were stored in plastic film bags at 20 ± 2 °C for a period of 72 hours. The freshness was monitored by changes in the physical-chemical parameters (moisture content, swelling capacity, friability). The various forms of bound water were determined using the method of differential thermal analysis on a simultaneous TGA-DTA/DSC thermogravimetric analyzer, with a programmable temperature regime. Based on the obtained digital data on thermogram (TG) change, using Pearson's criterion, a mathematical model has been created to identify the linear sections with a different inclination angle which are characterized by a constant rate of water removal. For all studied samples of bakery products, 6 linear sections were identified, but statistically significant results were obtained for sections III, IV and V, with the exception of section III for bakery products with cedar flour. Use of activated water, fat, and additives of cedar flour, powders of red-fruited mountain ash and sea-buckthorn in the production of bread and bakery products leads to redistribution of water forms, which is confirmed by changes in the boundaries of the linear sections, both for freshly made products and for products after storage. As a result, these products stay fresh longer.

Key words: bread, bakery products, activated water, powder, bound water, storage

INTRODUCTION

One of the main problems of the bread-baking industry is the limited storage time of the products, i.e. of bread and bakery products. Despite the fact that bread and bakery products are usually packed individually, its usual storage time is still less than 72 hours, due to the desiccation and staling of the products. For more than 160 years, scholars have investigated the processes of staling, but no universally recognized theory has been generated so far. Most scholars consider starch retrogradation to be the main cause of staling. Over time, the starch, gelatinized in baking, releases the water that it has absorbed, and thus the liberated hydroxyl groups of glucose residue are bound with their hydrogen bonds. Partial transition of the starch into its crystalline state occurs there, accompanied by its structural densification. This is what is a cause of changes in friability and swelling capacity of the crumb of the bread and bakery produce during storage (Goryacheva et al., 1983; Schiraldi et al., 1996; Karim et al., 2000; Haros et al., 2002; Xie et al., 2004; Cocchi et al., 2005). Slowing-down of the process of retrogradation is facilitated by both physical factors (kneading of dough, temperature pattern of baking, storage conditions and freezing of partially baked bread) and other factors which enable the separation of starch grains and prevent starch aggregation. (Rasmussen & Hansen, 2001; Fessas & Schiraldi, 2001; Bárcenas et al., 2003; Azizi & Rao, 2005; Fessas & Schiraldi, 2005; Le-Bail et al., 2011; Bosmans et al., 2013; Eckardt et al., 2013; Fadda et al., 2014; Al-Hajji et al., 2016). As the quantity of proteins and other biopolymers grows the process of staling starts to slow down (Goryacheva et al., 1983; Xie et al., 2004; Pashchenko & Zharkova, 2006**)**. The reason is believed to be the complicated redistribution of water depending on the bonds between the biopolymers of bread. This question remains unexplored and controversial.

In bread and bakery products, water is present in free and bound forms (Goryacheva et al., 1983; Pashchenko & Zharkova, 2006; Palyvoda et al., 2013). The amount of easily removable water in these products cannot be high because of the predominance of biopolymers - proteins and starch, and non-starch polysaccharides. Part of the water can easily penetrate into micro pores in the protein and be retained by a macromolecular matrix (Damodaran et al., 2007; Nechayev, 2015); some authors refer to this form of water as physic-mechanically bound (Yurchak et al., 1988). Low energy binding is characteristic of osmotically retained water. Adsorbed water (water of polymolecular and monomolecular layer) and organically bound water is considered as bound water. Adsorption is accompanied by a thermal effect, and removal of this water requires a large amount of energy. The stronger the bond, the greater the energy required to break it (Duckworth, 1980; Yurchak et al., 1988; Damodaran et al., 2007; Nechayev, 2015).

Differential thermal analysis makes it possible to define physical and chemical changes of substance using a programmed temperature increase. In the course of the analysis, a gradual break of water molecules bonds with biopolymers of bread and bakery products takes place, accompanied by a change in mass of the sample. Previously, differential thermal analysis could define only the total amount of free and bound water (Schiraldi et al., 1996); now, bound water is considered as aggregate of water forms having different binding energy. In the works (Antipov et al., 2010; Ostrikov & Napolskikh, 2012; Palyvoda et al., 2013; Kazantseva, 2015) researchers were able to determine up to 5 sections of stepwise behavior of water in food systems with different binding energy by using differential thermal analysis. Thermogravimetric analyzers equipped with analog-to-digital converters simplify the process of inflection points defining and identification of linear sections of stepwise water removal from food systems, corresponding to different forms of water binding.

The objective is to study the forms of bound water in bread and bakery products using differential thermal analysis, and to study their changes depending on the formula components and during storage.

MATERIALS AND METHODS

Bread ingredients

The materials to make bread and bakery products:

- Wheat flour (28.5% of gluten, and 0.55% ash content) made by Kombinat khleboproductov imeni Grigorovicha, OAO (A.F. Grigorovich Bread and Bakery Plant OJSC), Chelyabinsk, Russia;
- Activated water (catholyte) obtained by electrolysis (processing time 30 minutes at 200 V) using AP-1 device made by *Aquapribor* Research and Development Company in the Republic of Belarus. Electrochemical activation of water leads to the rupture of hydrogen bonds in the $[H_2O]_x$ associates and to the increased concentration of H_2O monomolecules (Naumenko, 2014);
- *Sloboda* refined deodorized sunflower oil, produced by *Efko* OAO (OJSC), Russia;
- Cedar nut flour containing 34% proteins (Nilova et al., 2013), produced by *Spetsialist* OOO (*Specialist* LLC), Russia;
- The powders of red-fruited mountain ash (domestic sp.) and sea buckthorn (*Vitaminnaya* breed) were obtained from squeezed berries, dried at 50 to 55 °C (to a moisture level of 6%) and milled into powder.

Bread and bakery products were made using the formulas shown in Table 1 (Nilova, 2012). For products using activated water, traditional bread making recipes were used.

Table 1. Dough recipes

Ingredient, g	Bread	Bakery products with additives				
		4% fat	14% fat	cedar nut flour	red-fruited mountain ash powder	sea buckthorn powder
Flour	1,000	1,000	1,000	950	950	950
Cedar nut flour	-	-	-	50	-	-
Red-fruited mountain ash powder	-	-	-	-	50	-
Sea buckthorn powder	-	-	-	-	-	50
Vegetable oil	-	40	140	40	140	140
Sugar	-	50	140	50	140	140
Salt	15	15	15	15	15	15
Yeast	20	20	20	20	20	20

Bread making

All reference samples were produced using a straight dough method. The experimental laboratory baking of the 300 g bread loaves and 100 g bakery products was done at 220 °C (Nilova et al., 2013; Naumenko, 2014; Kalinina, 2014).

Then the reference samples were cooled for 3 hours, and packed in plastic film bags and stored at a temperature of 20 ± 2 °C for 72 hours. The tests were performed 3 and 72 hours after baking.

Research Methods

The freshness condition was assessed based on changes in the physical and chemical properties, such as the moisture content, swelling capacity and friability.

Moisture content was determined by drying the reference samples at 130 °C for 40 minutes; the swelling capacity of the crumb was determined by the quantity of water absorbed by the crumb in 5 minutes (as milliliters per 1g of dry matter) within 5 minutes; the friability was determined according to the quantity of crumbs formed in 15 minutes as a result of hanging and shaking crumb pieces at 190–250 rpm (as percentage of crumbs formed relative to the remaining soft part).

Forms of water binding in bread and bakery products were determined by means of differential thermal analysis using a MOM manufactured simultaneous TG-DTA / DSC thermogravimetric analyzer, a Paulik Erdey system model, made in Hungary. Studies were carried out in quartz crucibles with sample weight of 1g. Al_2O_3 calcinated at temperature of 1,800 °C was used as a reference substance. The oven heating temperature variation rate was 2.5 °C min^{-1}, and the maximum heating temperature was 220 °C. Using the analog-to-digital converter, we obtained curves in digital form. In order to determine the temperature ranges in relation to water evaporation in various forms of binding, we used the TG curve, reflecting the change in sample weight in relation to temperature or time. In order to identify forms of water binding we used the piecewise-linear approximation method. To define temperature intervals corresponding to water evaporation for various bound forms of water molecules, TG curves characterizing sample mass change versus temperature were used. Using Pearson's criteria, a piecewise-line approximation model for identification of water molecules bound forms was created.

All TG curves obtained for the samples of bread and bakery products show similar behavior (Fig. 1), but size of the temperature zones corresponding to evaporation of water having different bonds energy were different. In order to construct a model for the TG curves, conversion values α were calculated and curves -lgα versus 1,000 T^{-1} were plotted using a piecewise-linear approximation Y = F (X). For each of the curves obtained, 6 linear sections with different inclination angles to the horizontal axis were identified (Fig. 2). The model is described by the linear function $Y_i=A_i \cdot x+B_i$ and $X_i< x \leq X_{i+1}$, defining their definition domains. The model parameters subject to identification are the coefficients Ai, Bi, i = 1 ... N and section areas Xi, i = 1 ... N-1, where N is the number of linear sections.

Rate of weight change α was calculated as a ratio of weight to total amount of water contained in the product which was defined by TG curve at the end of dehydration process. The form of the resulted curve reflects complicated nature of water and dry matter interaction in the products and assumes difference in the rate of water release for the different sections of this curve.

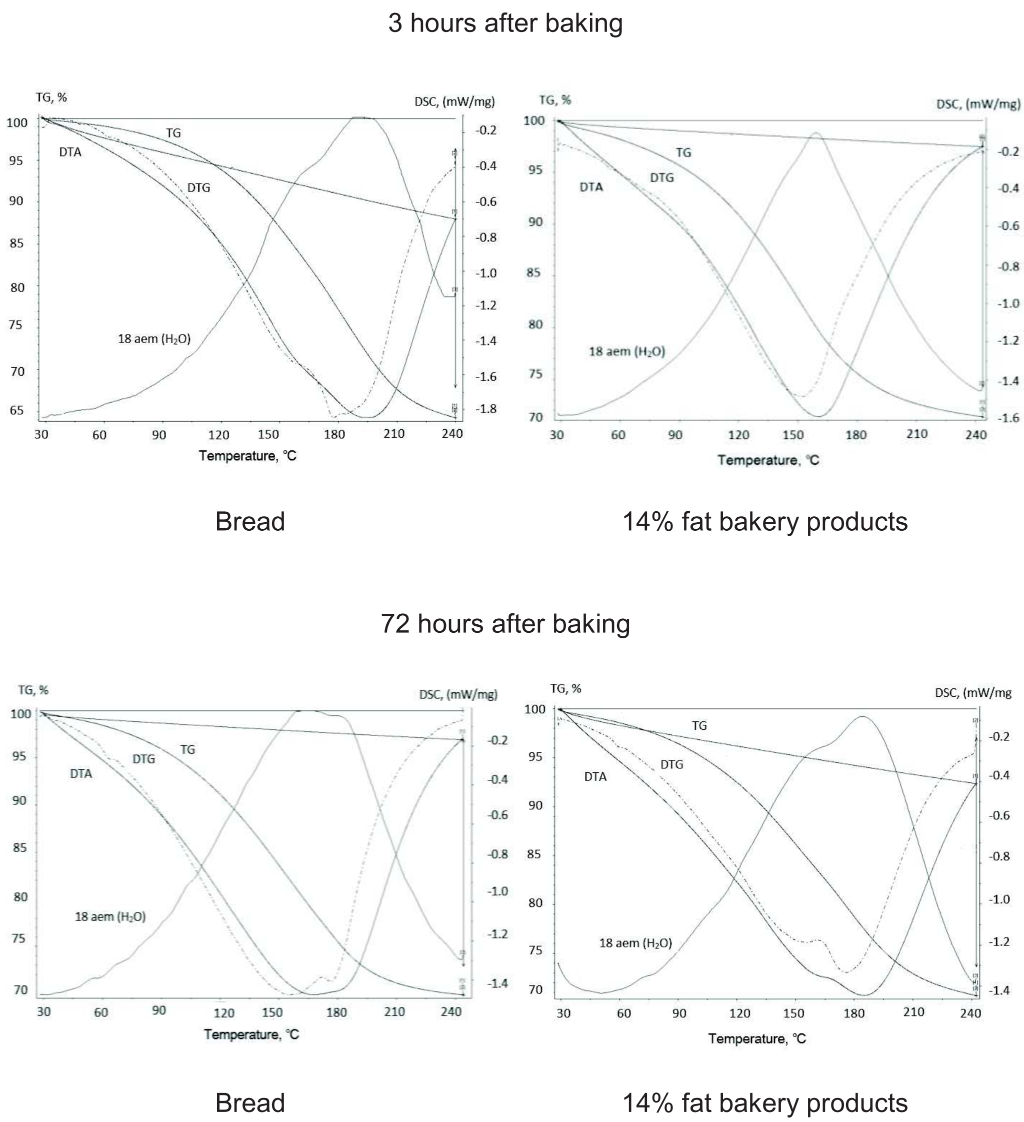

Figure 1. Thermogram of the reference samples of bread and bakery products, 3 (above) and 72 (below) hours after baking: TG – sample mass, DTA – temperature change rate, DTG – weight change rate.

Therefore, curves of the matter transformation ratio versus temperature allow studying of various, kinetically unequal forms of moisture bounding and reflects difference in dehydration rate (Ostrikov & Napolskikh, 2012).

To obtain dehumidification mechanism data on the basis of the obtained curves, to define temperature range and amount of moisture desorbed with approximately equal rate, this curve in coordinates (-lgα; 1,000/T) was used.

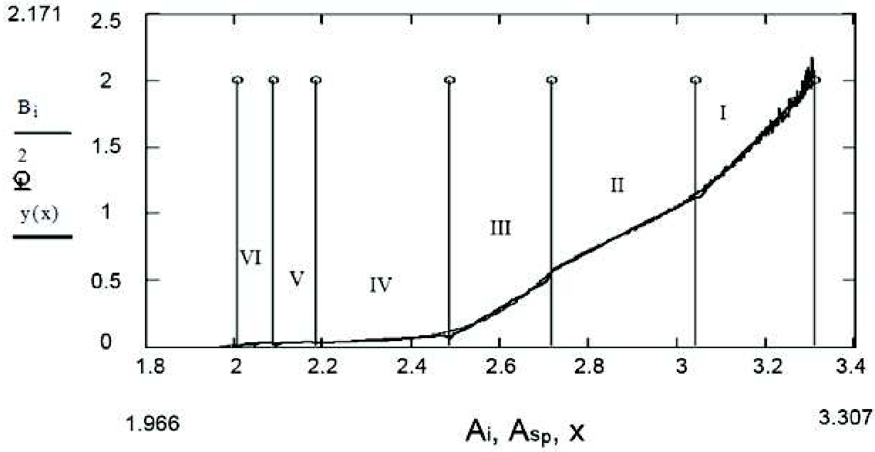

Figure 2. The -lgα to 1,000 T^{-1} ratio piecewise-linear approximation model.

The baking of the bread and bakery products using various recipes, and the study of each sample were carried out three times. The mathematical results were calculating using conventional statistics methods, and were expressed as arithmetic mean (M) and standard deviation (m). In order to identify statistically significant differences between two compared groups, the Mann-Whitney criteria (U) was used. Differences were considered significant where $p < 0.05$.

RESULTS AND DISCUSSION

To assess the role of water in the bread staling process, samples were baked in which the dough mixing was carried out first using tap water (control) and then using activated water (catholyte). After cooling the bread to room temperature (3 hours), the reference samples had almost the same moisture content values, but different swelling and friability values (Table 2). The friability of the bread with activated water was 0.7% less than that of control sample, and its swelling capacity was higher by 0.8 ml per 1 g of dry weight. Differences between the parameters of the control samples and the bread made with activated water could be associated with the redistribution of the bound water forms in the bread (Fig. 3).

Bread sample thermograms showed similar behavior, but by creating a piecewise-linear approximation model and using Pearson's criterion, it was possible to identify 6 linear sections with a different inclination angle. The curves for bread (reference sample) and for bread with activated water have different linear sections boundaries and only the boundaries of sections II, III, IV, and V are statistically significant. This makes it possible to expect a quantitative difference in the content of different forms of water (Fig. 3).

Table 2. Changes in the physical and chemical parameters of the bread and bakery product samples during storage *

Reference samples	Moisture content, %		Friability, %		Swelling ml g^{-1} (of d.m.)	
	after 3 hours	after 72 hours	after 3 hours	after 72 hours	after 3 hours	after 72 hours
Bread						
Reference sample	42.0 ± 0.3	40.5 ± 0.4	5.5 ± 0.2	17.4 ± 0.2	6.7 ± 0.2	3.2 ± 0.1
Sample with activated water (catholyte)	42.5 ± 0.2	41.3 ± 0.3	4.8 ± 0.1	13.6 ± 0.3	7.5 ± 0.1	4.2 ± 0.1
Bakery products						
4% fat	39.2 ± 0.4	38.3 ± 0.2	4.3 ± 0.1	12.5 ± 0.3	7.7 ± 0.1	5.1 ± 0.1
With cedar nut flour	39.8 ± 0.1	39.2 ± 0.2	3.7 ± 0.1	9.7 ± 0.1	8.7 ± 0.1	6.9 ± 0.1
14% fat	35.5 ± 0.2	34.8 ± 0.1	4.0 ± 0.1	11.2 ± 0.2	8.5 ± 0.1	6.1 ± 0.1
With red-fruited mountain ash powder	34.7 ± 0.1	34.2 ± 0.1	3.1 ± 0.1	8.1 ± 0.1	9.3 ± 0.1	7.5 ± 0.1
With sea buckthorn powder	34.5 ± 0.1	34.0 ± 0.1	2.8 ± 0.1	6.7 ± 0.1	8.8 ± 0.1	6.7 ± 0.1

*Results were obtained using generally accepted methods of statistical analysis and expressed as an arithmetical average and its standard deviation. Statistically significant by Mann-Whitney criterion $p < 0.05$.

For bread (reference sample) the first dehydration stage (linear section I) was observed at the temperature range of 26.2–56.1 °C, apparently caused by the removal of free water, of which there was a small amount. In linear section II (56.1–91.3 °C) there was maximal water loss – almost half of all the water removed in the course of differential thermal analysis (DTA). This could be caused by the beginning of the gelatinization of the starch, elimination of water contained in the macromolecular matrix, and water bound with the starch hydration centers (Goryacheva et al., 1983, Pashchenko & Zharkova, 2006, Palyvoda et al., 2013, Kazantseva, 2015). In the linear section III (91.3–125.8 °C) the amount of removed water decreased in comparison with linear section II – by 38.3%, but was significant – 31.1% of the total amount of water removed at DTA. Perhaps the complete gelatinization of the starch contributed to the release of the hydration shell of hydrophilic groups of the starch polymer and polypeptide chains (Pashchenko & Zharkova, 2006). The further temperature rise in linear section IV (125.8–180.6 °C) could result in denaturation of the protein molecules and release of the bound water portion contained in the closed cells of protein micelles (Goryacheva et al., 1983, Palyvoda et al., 2013, Kazantseva 2015). However, since the protein content of the bread is less than that in starch, the proportion of water removed in this section was only 7.4%. The last two linear sections – V (180.6–201.2 °C) and VI (201.2–225 °C) - are probably showing the difficult-to-remove, tightly bound water – a 'monolayer' strongly interacting with hydrophilic groups of nonaqueous biopolymers), as well as crystalline hydrates (Nechayev, 2015). But the amount of water removed in these sections differed by 1.5x. Thus, statistically significant values were obtained only for curve section V.

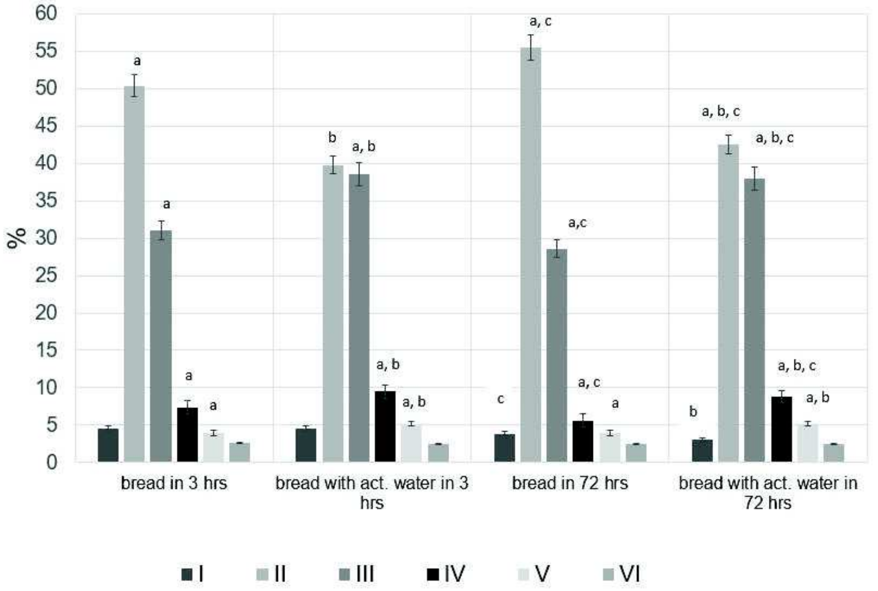

Figure 3. Changes in the forms of bound water in the studied samples of bread during storage. Statistically significant by Mann-Whitney criterion ($p < 0.05$) differences between the line sections: a – in bread samples; b – in bread with activated water in comparison with reference sample; c – in bread samples during storage.

For bread with activated water, statistically significant lengths were identified for linear curve sections III, IV and V. A statistically significant widening of these sections and a narrowing of section III were observed. Redistribution of the forms of bound water may be associated with the fuller swelling of the proteins as a result of the penetration of activated water into its structure in the form of monomolecules (Yurchak et al., 1988, Naumenko, 2014).

After 72 hours of storage, water redistribution occurred in all bread samples. The general trends in the changes to the linear sections were similar irrespective of the kind of water used for bread making, but the linear sections typical for the removed water differed in size. After storage, a statistically significant widening was observed only for linear curve section II: for reference sample - by 5.1%; for bread with activated water - by 2.7%. The amount of removed water for sections III and IV showed a statistically significantly decrease of 2.5 and 1.8%, respectively, in comparison with the reference sample, and by 0.5 and 0.7%, respectively, in comparison with the bread with activated water. The boundaries of linear sections V and VI remained unchanged. Only in the reference sample was there a significant decrease in linear section I. Changes in the forms of bound water in bread during storage could be associated with aging of biopolymers. The result is that they become denser, forming cracks between the starch and protein, which leads to increased friability of the bread and reduces its swelling capacity (Table 2). As a result, the removed water content in the bread increases in linear section II, and it decreases in section I due to the shrinkage/desiccation of the products that is confirmed by the changes in the moisture content values. In the bread with activated water the process is slower - the moisture content after 72 hours is 0.8% less in comparison to the control sample.

When fats and sugar are used in the recipes of the bakery products, less water is required for the dough mixing, so the initial moisture content of the products is lower in comparison to the bread. Fats facilitate the plasticization of the dough, adsorbing the hydrophobic part of the molecule on the surface of the starch grains, and increase the quantity of hydrophilic parts (Goryacheva et al., 1983). Therefore, the swelling capacity of bakery products depends on the amount of added fat: buns with 14% fat have a higher value than buns with 4% fat (Table 2). Increasing the elasticity of the dough by enveloping the starch grains with fats reduces the friability of bakery products when cooled to room temperature for 3 hours. But increasing the amount of fat from 4 to 14% has no significant effect on friability values, which change only by 0.3%. The quantity of added fats in the recipes of bakery products also had no significant effect on the redistribution of forms of bound water (Figs 4 and 5)., Bakery products with 4 and 14% fat content showed statistically significant differences in the sizes of linear sections II, III and IV.. Linear sections III and IV had statistically significant increases in size - by 0.5% and 1.2%, respectively. And linear section II decreased by 1.7%. In comparison with reference sample (bread), the addition of fat to the recipe caused statistically significant changes in the sizes of sections II, III, V, and for bakery products with 14% of fat, in the size of section IV.

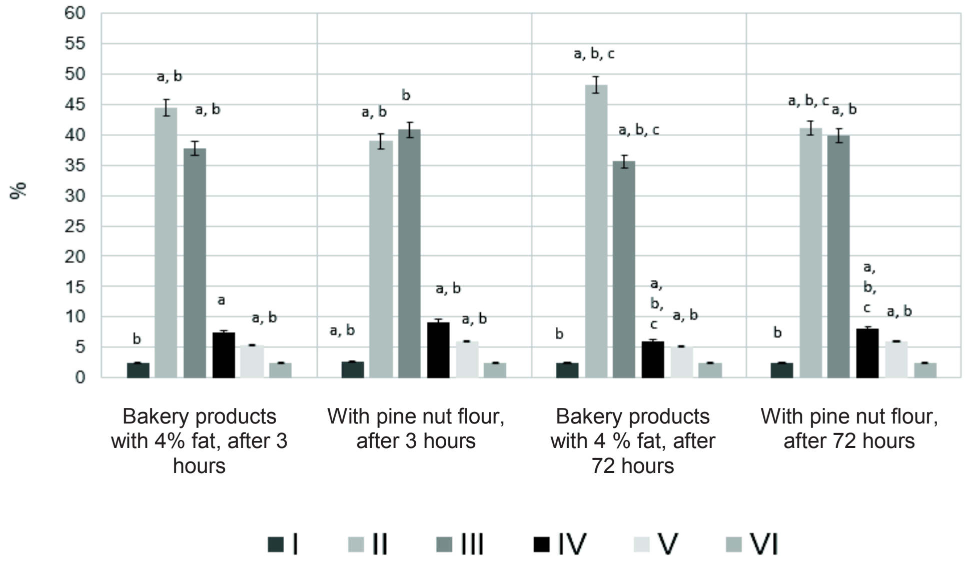

Figure 4. Changes in the forms of bound water in the studied samples of bakery products with 4% fat during storage. Statistically significant by Mann-Whitney criterion ($p < 0.05$) differences between the line sections: a – in bakery product samples; b – in bakery product in comparison with reference sample; c – in bakery product samples during storage.

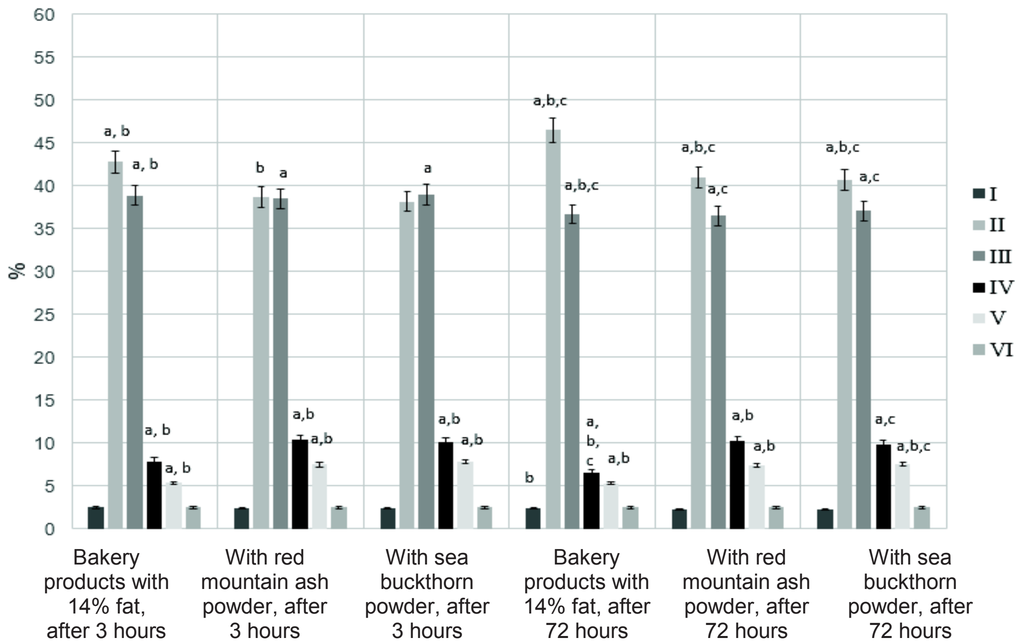

Figure 5. Changes in the forms of bound water in the studied samples of bakery products with 14% fat during storage. Statistically significant by Mann-Whitney criterion ($p < 0.05$) differences between the line sections: a – in bakery product samples; b – in bakery product in comparison with reference sample; c – in bakery product samples during storage.

Such a change in the size of linear sections for the bakery products in comparison with the bread was caused by the staling processes, despite a 3 time difference in mass. And if the crumb swelling capacity after 72 hours decreased by 2 times, then swelling capacity of the bakery products with 4% fat decreased by 1.5 times and bakery products with 14% fat - by 1.4%. A reverse behavior was observed in the changes of the crumb friability values. After 72 hours the bread friability increased by 3.1 times, and bakery products friability – by 2.9 times and friability of products with 4% and 14% fat – by 2.8 times, respectively. Such changes may be associated with the blocking with fats of crumb starch aggregation during storage, enveloping with thin films not only the starch but also the protein. As a result, they released water more slowly as compared to bread, thus preventing their densifying and formation of air layers. The amount of water in linear section III decreased by 5.6% and 5.7%, and in section IV by 17.6% and 16.5%, respectively for bakery products with 4% and 14% fat (Figs 4 and 5).

Cedar nut flour (Table 1) was used to enrich the bakery products with proteins by replacing 5% of the wheat flour in the recipes with 4% fat. Bakery products with 4% fat served as a reference sample. Already 3 hours after baking, the freshness parameters of the bakery products with cedar nut flour differed from those of the reference sample: swelling capacity was 11.5% higher, and the friability was 16% lower (Table 2). The protein in the cedar nut flour influenced the forms of bound water that mainly led to increase in the amount of water removed in linear section III in comparison to the reference sample. Changes in the amount of water removed in sections IV and V also increased, but these additions were less appreciable. The increased amount of bound water slowed down the staling processes. After 72 hours, bakery products with cedar flour had lower values of friability and swelling capacity. Redistribution of forms of bound water in the crumb of the bakery products was slower, especially in section III. This is reflected in the smaller loss of moisture content in the product after storage. It should be noted that there were no changes in the amount of removed water in linear sections V and VI.

Pomace of red-fruited mountain ash and sea-buckthorn powders were used in the recipes of bakery products with 14% fat by replacing 5% of the wheat flour. As these products comparison, bakery products with 14% fat without additives were used as a reference sample. After 3 hours the bakery products with the powders had lower values of moisture content than the reference sample, likely due to the strong water binding in linear section V formed on the surface of the fiber and pectin with a high degree of esterification (Nilova, 2012). Also, the amount of removed water for linear section IV showed a statistically significant increase, and to a greater degree than for linear section III. Change in boundaries of linear section III were not statistically significant for bakery products with powder in comparison with the reference sample. Nevertheless, bakery products with powder had a lower friability value and greater swelling capacity in comparison with the reference sample. Water redistribution during storage of the bakery products with powder was insignificant, particularly for linear sections IV and V, which is confirmed by the absence of statistically significant changes. Only for bakery products with sea-buckthorn did changes in the boundaries of linear section V during storage reach statistically significant values. The amount of removed water for linear section III increased to a greater degree – by 5%, irrespective of the kind of powder, which insignificantly increased the water ratio for linear section II. The change in these boundaries during storage was statistically significant. As a result, after 72 hours the bakery products with powder were absolutely fresh, as confirmed by measurements of their physical and chemical parameters.

CONCLUSIONS

Based on results of differential thermal analysis carried out using a Simultaneous TGA-DTA/DSC thermogravimetric analyzer, Paulik Erdey system model with analog to digital converter, which is able to define the sample mass change versus temperature (TG) in digital form, and using Pearson's criterion, a mathematical model was created to identify the linear sections with a different inclination angle which are characterized by a constant rate of water removal. For all studied samples of bakery products, 6 linear sections were identified, but statistically significant results were obtained for sections III, IV and V sections, with the exception of section III for bakery products with cedar flour. In order to find correspondence between the identified sections and different forms of bound water, it is necessary to continue this study using other physical methods.

The importance of water in the bread staling process is confirmed by the results of activated water use for dough mixing. Activation of water, which causes an increased concentration of H_2O monomolecules, leads to deeper penetration of water molecules into the structure and a fuller swelling of the biopolymer. In freshly baked bread with activated water there is a statistically significantly increase in the boundaries of linear sections III, IV and V. As a result, bread with activated water loses water slower, which is confirmed by statistically significant changes in the sizes of linear sections II. III. IV during storage in comparison with the reference sample.

The use of various ingredients (fat, cedar flour, powders of red-fruited mountain ash and sea-buckthorn) in the manufacture of bakery products leads to redistribution of water forms both in freshly made products, and in products after storage. Linear sections statistically significantly increase for in freshly baked products, there is a statistically significant increase in linear section III when using fat and cedar flour, and in sections IV and V when using powders of red-fruited mountain ash and sea-buckthorn. As a result, less water is lost from these products, and the staling process is slowed, which is confirmed by the results of the study of the mass moisture ratio, friability and swelling capacity of the bakery products.

ACKNOWLEDGEMENTS. This article was written with support from the Government of the RF (Resolution №211 of 16.03.2013), Agreement № 02.A03.21.0011 and subsidies for the fulfillment of a fundamental part of a state order, project №40.8095.2017/BCh. The work was supported by Act 211 Government of the Russian Federation, contract № 02.A03.21.0011.

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