Effects of the principal ingredients of biscuits upon water activity

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Summary

Water activity of biscuits was determined at various temperatures within the interval 20–30 °C. For the majority of the products tested, the values of a_w increased with the increasing temperature. Linear regression analysis revealed that the value of a_w for biscuits is significantly influenced by moisture and total protein contents. A linear regression formula could be set up to describe the relationships between water activity, temperature and the contents of the principal ingredients of biscuits. Using this formula it could be demonstrated that the relationship between water activity and temperature is significantly influenced by moisture content only.

Keywords

water activity; moisture content; biscuits

In the Czech Republic, long shelf-life bakery products are referred to as „biscuits“. These are mostly small products of flat shape, with pronouncedly sweet taste. The principal characteristic by which these products differ from other bakery products is the low moisture content (5 % max.). The main ingredients most frequently include wheat flour, sugar and fat. Water is added to make the dough for the biscuits, nevertheless it is not among the major ingredients present in the final product. Unbound water evaporates rather easily during the baking process at high temperatures (as high as 230 °C). Water bound to some functional groups of the molecules of substances present in the bakery products may also get partly released at such high temperatures, and this helps the colouring of the surface of the final products [1]. Water activity (a_w) and moisture content are always important parameters influencing stability of biscuits during storage, in particular the resistance against microbes and rheological properties of the products.

Typical of biscuits is not only low moisture content but also a rather low value of a_w. Foods with an a_w <0.60 are considered as microbiologically stable, although some of their constituents may undergo chemical reactions. For foods with a_w <0.20 this mainly includes enhanced lipid oxidisation [2] accompanied by pronounced alterations of their sensory qualities during storage [3]. Being products with a long shelf life, biscuits are usually not stored at constant temperatures, they are mostly kept at „room temperature“ only, which however may be rather variable depending on climatic conditions (21–28 °C).

The aim of this paper has been to determine water activity in selected biscuit products at various temperatures and to study the degree of the dependence of this relationship on the contents of the principal ingredients of biscuits.

MATERIALS AND METHODS

Biscuits

The samples tested (manufacturers: Opavia LU, Prague, Czech Republic and Václav & Ježo, Ilava, Slovak Republic) were purchased in the market hall and stored in air-tight polyethylene bags at laboratory temperature and in a dark room. Samples for measurements were obtained by homogenising the same type of product obtained from at least two different localities. The samples mostly originated from different product lots. In this way, it could be secured that these measurement results represented long-term average values.

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Water activity determination

Water activity was determined at the temperatures of 20, 25 and 30 °C using a Thermoconstanter TH 500 device (Novasina, Axair, Switzerland). Prior to the measurement, the sample was carefully homogenised (for 5–10 s) in a mortar. The values of a_w represent the arithmetic means of at least three independent determinations at each temperature.

Humidity content determination

Humidity content was determined after drying of the sample at the temperature of 102 °C to give a constant weight, using moisture analyser MLB50-3 (KERN & Sohn, Balingen, Germany). The test principle consists in the drying of a sample placed on the scales (scale sensitivity upon drying ±0.02 g) at a constant temperature produced by 2 halogen lamps placed above the sample.

Determination of the contents of nutrients

Protein content was determined by the method according to Kjeldahl, and fat content was determined following acid hydrolysis and extraction using the Soxhlet apparatus. The values of saccharide content were taken from the manufacturer's data indicated on the package, and used for approximate comparisons of the products studied.

RESULTS AND DISCUSSION

The values of water activity of samples tested at various temperatures ranged within the interval of a_w between 0.10 and 0.23 (Tab. 1). Higher values of a_w of 0.46–0.53 were measured for two samples (sweet biscuits for children and confectioner's biscuits). These products also contained more moisture (6–7 %). In the other samples of biscuits, moisture contents ranged within 2–4 %. All the samples tested contained significant amounts of saccharides and fats within relatively wide ranges (60–76 % and 3–25 %, respectively), the protein content oscillated between 5–13 %. The concentrations of the basic nutrients and moisture in biscuits influences mainly the rheological properties of the final product [4, 5] as well as the organoleptic qualities [6]. The influence of the contents of the basic ingredients of biscuits on their water activity at various temperatures has not yet been studied.

Water activity increased with the temperature increasing within the interval 20–30 °C in the majority of the products ($p < 0.05$). This relationship was characterised by a positive slope of the linear regression curve, and the determination coefficient ranged within the interval between 0.80 and 0.99. An inverse relationship was observed in three samples, i. e. water activity decreased

Tab. 1. Water activity of biscuits at different temperatures and statistical parameters of the linear regression of the temperature dependence of a_w.

Biscuits	Water activity a_w			Slope of the straight line $a_w = a.x(T) + b$ (R^2)
	20 °C	25 °C	30 °C	
flavourless, flat	^{a}0.110	^{b}0.129 ± 0.003	^{c}0.161 ± 0.004	0.0065 (0.96)
with honey and hazelnuts	^{a}0.121 ± 0.005	^{b}0.170 ± 0.001	^{c}0.205 ± 0.002	0.0084 (0.98)
cocoa-flavoured	^{a}0.180 ± 0.002	^{b}0.194 ± 0.003	^{c}0.206 ± 0.002	0.0026 (0.97)
for children	^{a}0.106 ± 0.001	^{b}0.122 ± 0.002	^{c}0.160 ± 0.002	0.0054 (0.95)
with cereals and fruit	^{a}0.268 ± 0.006	^{b}0.255 ± 0.006	^{c}0.232 ± 0.001	–0.0036 (0.92)
with cereals and milk	0.108	^{b}0.127 ± 0.002	^{c}0.169 ± 0.002	0.0084 (0.99)
coconut flavoured*	^{a}0.205 ± 0.003	^{a}0.210 ± 0.002	^{b}0.232 ± 0.001	0.0027 (0.85)
with milk*	^{a}0.231 ± 0.007	^{b}0.218 ± 0.001	^{a}0.239 ± 0.001	0.0007 (0.11)
cookies	^{a}0.168 ± 0.001	^{b}0.186 ± 0.001	^{c}0.208 ± 0.001	0.004 (0.99)
sweet biscuits for children*	^{a}0.467 ± 0.003	^{b}0.461 ± 0.002	^{c}0.408 ± 0.003	–0.006 (0.83)
confectioner's sweet biscuits	^{a}0.530 ± 0.001	^{b}0.459 ± 0.008	^{c}0.379 ± 0.009	–0.015 (0.99)
yolk cream rings	^{a}0.184 ± 0.001	^{b}0.201 ± 0.001	^{c}0.228 ± 0.001	0.0044 (0.98)
meringues	0.106	^{a}0.120 ± 0.002	^{b}0.160 ± 0.005	0.0081 (0.98)
cinnamon cookies	^{a}0.119 ± 0.001	^{b}0.150 ± 0.002	^{c}0.181 ± 0.001	0.0062 (0.99)
cocoa cream rings	^{a}0.201 ± 0.002	^{b}0.214 ± 0.001	^{c}0.232 ± 0.001	0.0032 (0.98)
snack	^{a}0.116 ± 0.003	^{a}0.121 ± 0.002	^{b}0.158 ± 0.009	0.0042 (0.80)
rational	^{a}0.221 ± 0.002	^{a}0.228 ± 0.004	^{a}0.229 ± 0.005	0.0008 (0.39)

The different superscripts indicate statistically significant differences between temperature-dependent water activities, e.g. a a a – no difference, a b c – differences at every temperature, a a b – different value of a_w at the third temperature, $p < 0.05$. * – marks samples in respect of which the temperature dependence of a_w is better fit by a 2nd degree polynomial equation, $x(T)$ – temperature as independent variable, R^2 – determination coefficient.

Tab. 2. Statistical parameters of the linear regression of the temperature dependence of water activity $a_w(T)$ on protein, fat and moisture content in biscuits.

	$a_w(T) = f$(protein content)			$a_w(T) = f$(fat content)		$a_w(T) = f$(moisture content)		
	Linear regression equation $y = ax + b$							
	A***	B**	C***	A**	B**	A***	B***	C***
Correlation coefficient r	–0.789	–0.811	–0.738	0.629	0.621	–0.938	–0.938	–0.870
Determination coefficient R^2	0.622	0.656	0.545	0.396	0.386	0.880	0.880	0.750
Standard deviation	0.004	0.004	0.004	0.005	0.005	0.002	0.002	0.003
	Linear equation $y = ax^2 + bx + c$							
	A***	B***	C***	A**	B**	A***	B***	C***
Determination coefficient R^2	0.731	0.731	0.731	0.588	0.587	0.890	0.860	0.860
Standard deviation	0.003	0.003	0.003	0.004	0.004	0.002	0.002	0.002

A – [g/100 g sample], B – [g/100 g dry solids], C – [g/100 g fat-free dry solids]. *** – $p < 0.001$, ** – $p < 0.01$, * – $p < 0.05$.

with the increasing temperature, characterised by negative slope of the curve, with an average determination coefficient value of 0.95 (Tab. 1). The decrease of the value a_W with the increasing temperature is typical of some low-molecular substances such as crystalline sugar or salt or foods containing large amounts of dissolved substances (such as dried fruits) [7]. Such an inverse effect may be explained by partial evaporation of crystalline water at higher temperatures, and by the saturation of the solution with low-molecular substances at lower values of a_W (30 °C) compared with water activity measured at 20 °C. At a constant value of a_W and higher temperatures, larger amounts of water get adsorbed. The sweet biscuit products differed from the other product samples by not only their higher moisture content but also by higher contents of saccharides ($p < 0.001$), proteins ($p < 0.001$), and lower concentrations of fats ($p < 0.01$). A sample of cereals and fruit-containing biscuits which also showed values of a_W decreasing with the increasing temperature, also contained more moisture than the other samples ($p < 0.01$). The differences in the behaviour of water activity with the increasing temperature observed in sweet biscuits may have been due to higher contents of simple saccharides. Confectioner's biscuits even had visible sugar crystals on their surface, and they may have become more hygroscopic at the temperature of 30 °C than they were at 20 °C. Since the contents of the different saccharide groups were not studied, we may but speculate that the sugar content may play an important role in temperature-dependent water activity changes. The results suggest that the temperature dependence of biscuits, $a_{W,}$ may be solely connected with the moisture content in the final product. As a matter of fact, the temperature dependence of a_W is described by complex empirical models consisting of several parameters [8]. For the purposes of this study and based on regression characteristics obtained it may be assumed that there is a linear relationship between a_W and temperature within the temperature interval 20–30 °C. Smaller values of the standard deviations and larger values of the determination coefficients suggested 2nd degree polynomial as a more appropriate model for 4 samples to describe the temperature dependence of a_W (Tab. 1). In biscuits for rational nutrition, water activity did not change within the temperature interval tested ($p < 0.05$).

Additionally, we studied the degree to which the temperature dependence of a_W may be influenced by the contents of the principal ingredients of the product. This relationship will be further referred to as slope $a_W(T)$. Using linear regression, the relationship was studied between the dependent variable represented by the slopes of the straight line $a_W = a.x(T) + b$ shown in Tab. 1, where $x(T)$ stands for the temperature of measurement, and the contents of moisture, fats and proteins (independent variables). The results are presented in Tab. 2.

A negative correlation was found for the set of 17 different biscuit samples tested between the slope describing $a_W(T)$ and the moisture content, with the correlation coefficient $r = -0.94$ ($p < 0.001$). A significant correlation at the same probability level was found between the slopes of the straight line $a_W = a.x(T) + b$ and the protein content ($r = -0.789$, $p < 0.001$) expressed in terms of weight per 100 g product (Tab. 2). The magnitude of the slope $a_W(T)$ was also dependent on the saccharide content (correlation coefficient $r = -0.54$). Since the values obtained were rather approximate, this characteristic was burdened by a bigger statistical error as compared to the other independent variables. It is recognised that, with the knowledge

Tab. 3. Linear regression equation ($y = ax_1 + b$) describing effect of moisture content upon temperature dependence of water activity $a_w(T)$.

x_1 expressed in terms of	a	b	Determination coefficient (R^2)	Probability level
g/100 g sample	–0.004	0.014	0.882	p <0.001
g/100 g dry solids	–0.003	0.013	0.884	p <0.001
g/100 g fat-free dry solids	–0.003	0.017	0.749	p <0.001

y – slope $a_w(T)$ as a dependent variable, x_1 – moisture content as an independent variable, a, b – linear regression parameters.

of the contents of some substances in foods and with that of the parameters of the corresponding regression curves, water activity values may be successfully predicted, most frequently at a constant temperature [9-11]. The fat contents had an inverse effect, with the correlation coefficient $r = +0.63$. The best results were obtained when the independent variables were expressed in terms of weight in the dry solids. Attempts to express the independent variables in terms of weight in the fat-free dry solids resulted in a marked worsening of the regression parameters (Tab. 2). This is in contradiction to reports by other authors who found statistically significant improvements of regression parameters [11].

A linear regression equation was constructed to describe the relationship between water activity, temperature and the contents of the principal ingredients of biscuits. Using statistical analysis of independent variables (variable analysis, DataFit, Oakdale Engineering. Oakdale, USA) we could show that it is the moisture content parameter only which is suitable as the input into the regression equation describing the temperature-water activity relationship. The parameters of the linear regression equation are shown in Tab. 3. The magnitude of the changes in the value of a_w with the increasing temperature is thus dependent solely on the moisture content in biscuits.

CONCLUSION

Water activity of biscuits increased significantly with the temperature increasing within the interval 20–30 °C. A statistical analysis of independent variables confirmed our previous assumptions that it is the moisture content that is the sole and major factor determining the magnitude of temperature-dependent changes in a_w of the products tested. Based on this theoretical relationship described by a linear function, the moisture content may be adjusted during the production process so as to minimise changes in the value of a_w during the storage. Using regression parameters, the moisture content was set at 4.3 g in 100 g dry solids. The influence of the contents of the other ingredients of the biscuits tested is viewed as insignificant.

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