Forecasting and quality control of confectionery products with the use of "water activity" indicator

I V Plotnikova¹, I M Zharkova¹, G O Magomedov¹, M G Magomedov¹, A A Khvostov² and E N Miroshnichenko¹

¹Voronezh State University of Engineering Technologies, 19, Revolution Ave., Voronezh, 394036, Russian Federation
²MESC AF «N.E. Zhukovsky and Y.A. Gagarin Air Force Academy», 54A, Starykh Bolshevikov St., Voronezh, 394064, Russian Federation

E-mail: plotnikova_2506@mail.ru

Abstract. For confectionery products, the value of water activity is mainly determined by their moisture and sugar content in a recipe. Along with the preserving effect, sugar is involved in the formation of organoleptic, functional and technological products properties; it also regulates their acidity, lowers water activity, which increases water binding energy in material and reduces probability of microorganisms’ development. To reduce sugar content in products, white cane sugar is replaced by other sugars, sugar substitutes, or “new generation” sweeteners, which differ in their chemical nature, sweetness degree and technological properties (including water-binding ability). To obtain a specific confectionery product with specified consumer properties, it is necessary to make a technologically justified choice of the most suitable raw materials and semi-finished products (you need to know the chemical composition, humidity and water activity amount). The purpose of the study is the generalization and systematization of the information available in the scientific and technical literature on the value of the water activity indicator of raw materials, semi-finished products and confectionery products; obtaining new experimental data on the value of the water activity index in a number of “new generation” sweeteners sold in the Russian market. By controlling the moisture content and Aw indicator value of the products, it is possible to forecast the intensity of various physicochemical, biochemical and microbiological processes during products storage, to create “Stability maps of confectionery products depending on water activity” and to produce products with the required shelf life.

1. Introduction

One of the most important tasks manufacturers of confectionery products are facing nowadays is to ensure quality and safety of the products throughout the declared shelf life specified in regulatory or technical documents [1].

The moisture content of a product affects significantly the development of microorganisms in it, the binding of chemical compounds, which changes products consistency and structure. The reproduction rate of microorganisms decreases with the product moisture content diminution. However, for the microorganism’s development, not the absolute value of humidity is of greater importance, but its availability for a number of biochemical processes and microorganisms’ development [2, 3].
Since confectionery products are multiphase concentrated systems which are characterized by certain indicators (dispersion, shape and structure of solid phase particles, uniform distribution of components), control and processes forecasting (including physico-chemical and biochemical ones) are of primary importance for ensuring their storage stability connected with moisture migration (Figure 1) [3].

A reliable tool for the quantitative assessment of these processes for forecasting and regulating the stability of food is the “water activity” indicator (Eng. water activity $\text{aw}$), which has a thermodynamic nature [4, 5]. This indicator is included in the ISO 9000 system of standards, it is monitored when analyzing risks at critical control points (the Hazard Analysis of Critical Control Points). The definition of $\text{aw}$ is obligatory in the countries of the European Union and the United States, when examining a number of products [6]. $\text{aw}$ measurement is carried out on the most famous modern Swiss equipment with a function of water activity measuring - Rotronic hygrometer modification "HygroPalm Aw" and Decagon modification "AquaLab" [7].

Water activity is associated with the equilibrium relative humidity of food products (ERH, %) which is equal to $\text{aw} \cdot 100$, when a product does not absorb and does not lose moisture to the atmosphere. The reason for the moisture migration between a product and environment is the difference between the equilibrium relative humidity of the product and the relative humidity (RH) of the environment during the storage period. $\text{aw}$ is expressed in dimensionless units of a scale from 0 to 1 and it is calculated as the ratio of the vapor pressure above the product $P_s$ to the vapor pressure above pure water $P_w$ at the same temperature according to the formula [1]:

$$\text{aw} = \frac{P_s}{P_w} = \frac{\text{RH}}{100},$$

where $P_s$ is the pressure of water vapor in the system above the product; $P_w$ is the vapor pressure above pure water.

The control of $\text{aw}$ indicator allows one to forecast the processes which occur during storage period of the products. So, for example, products with ERH exceeding RH environment (for example, fondant and marzipan) will dry out during storage, and products with ERH below RH environment (for example, candy caramel, cookies, wafers), on the contrary, will absorb moisture from the air. Moisture migration occurs when the ERH of individual components in the composite products is different or between the ERH of the product and the environmental RH, which is more than 2%. With different ERH, moisture can also migrate inside a product, what is often observed in multicomponent products (for example, in chocolate glazed cookies with water-based filling). The greater the

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**Figure 1.** The sequence of actions for the implementation and prediction of the processes associated with moisture migration.
difference in ERH between adjacent components (for example, between cookies and filling), the stronger the moisture migration and the shorter the shelf life is [8].

Sorption and desorption processes during storage period of products depend on many factors: temperature and relative humidity of the ambient air, chemical structure of raw materials and products, changes in Aw. Confectionery products can either absorb or release moisture, depending on environmental conditions [9]. For some products, sorption plays a positive role, for others it is negative, the same applies to moisture desorption. So, for example, for pastille-marmalade products, fondant, milk, liquor sweets, gingerbread cookies, etc., the process of moisture desorption during their storage period plays a negative role in connection with the processes of moisture migration, crystallization of sucrose and product hardening. To prevent these processes, moisture-retaining components or additives are introduced into the recipe (for example, the enzyme invertase agent, sugars — fructose, xylitol, sorbitol, invertible additives — dry beer and baker's yeast containing invertase enzyme), which enhance hydration properties and have an invertible ability, and also it is recommended to use polypropylene and metallized polypropylene films for products packaging [10-11].

The value of AW for confectionery products is largely determined by their moisture and sugar content in the recipe [12]. Along with the preserving effect, sugar is involved in the formation of organoleptic and functional technological properties of products, regulates their acidity, lowers Aw, which helps to increase the binding energy of water in the material and reduce the probability of microorganisms’ development [13]. To reduce sugar intensity of products, white cane sugar is replaced with other sugars, sugar substitutes, or “new generation” sweeteners [14-18], which differ in their chemical nature, degree of sweetness, and technological properties (including water-binding ability). As a result, confectionery with sweeteners behave differently during storage period. For example, in the paper [16] it was shown that replacing cane sugar in cereal bars, producing from grains, nuts and dried fruits with a combination of sorbitol and maltitol or sorbitol and nutriose, allows to obtain a more stable product. This is due to the fact that the resulting product with sweeteners is characterized by an equilibrium value of relative humidity closer to normal environmental conditions than sugar bars.

To obtain a specific confectionery product with specified consumer properties, it is necessary to make a technologically justified choice of the most suitable raw materials and semi-finished products (you need to know the chemical composition, humidity and Aw value). In connection with the foregoing, we formulated the purpose of the study.

2. The purpose of the study
The purpose of the study is the generalization and systematization of the information available in the scientific and technical literature on the value of the water activity indicator of raw materials, semi-finished products and confectionery products; obtaining new experimental data on the value of the water activity index of “new generation” sweeteners sold in Russian market.

3. The object of the study
Papers were searched in the PubMed database using the following keywords: “water activity (Aw) in food”, “water activity”, as well as in the electronic scientific library https://elibrary.ru. The objects of the experimental study were samples of sugars (beet sugar, glucose, fructose), sweeteners (isomaltitol, maltitol, erythritol, xylitol, sorbitol, stevioside) and sugar substitutes (maltodextrin, inulin).

4. Materials and methods
In accordance with the purpose of the study, the materials used were sugars (beet white sugar in accordance with State Standard Specification №33222-2015 Russia); food glucose (Dextrose monohydrate) in accordance with State Standard Specification №975-88 Russia; fructose in accordance with Technical Conditions №9197-010-72315488-2011 Russia; sweeteners (maltitol) in accordance with Technical Conditions №20.14.23-037-60381327-2018 (SHANDONG LUJIAN
BIOLOGICAL TECHNOLOGY CO., LTD, China), erythritol according to Technical Conditions № 24.14.23-021-94446794 (Cargill Deutschland GmbH, Germany), Isomalt according to Technical Conditions № 9111-073-00334675 (Cargill Deutschland GmbH, Germany), xylitol according to Technical Conditions № 9197-009-72315488-2011 (LLC "Sweet World" Company, Russia), sorbitol according to Technical Conditions № 9197-008-72315488-2010 (LLC "Sweet World" Company, Russia), stevioside according to Technical Conditions № 9199-003-90836854-13 (“ PURE CIRCLE Sdn. Bhd.”, Malaysia) and maltodextrin sweeteners according to Technical Conditions № 9199-005-50876759-15 (DONG XIAO, China) and inulin (BIONOVA, Belgium).

Aw measurements were performed with the use of Rotronic HigroPalm HP23-AW-Set portable hygrometer. A sample of the test product was placed in a sealed measuring chamber, where the air temperature was controlled, and held until equilibrium was established. The stabilization process is controlled by measuring air humidity over the surface of the product sample using a relative humidity sensor (% RH = 100 · Aw). All measurements were performed in standard mode with 7-fold repetition, the results were processed by methods of mathematical statistics using the standard Microsoft Excel program.

5. Discussion of the results
There is a single concept of dividing food ingredients and products by shelf life into three groups depending on Aw and active acidity (pH): short-lived products, perishable and resistant to long-term storage products. Data on the humidity and Aw influence on the growth of microorganisms in various raw materials, semi-finished products, and confectionery products are presented in table 1 [6, 10, 17-28].

| The name of raw materials, semi-finished products, confectionery products | The name of the indicators | Microorganisms capable of growth (at the lower edge of Aw range, the growth rate is minimal) |
|---|---|---|
| **Short-lived products (with high humidity and risk degree): 0.98>Aw>0.87** | Moisture content (W), % | Water activity (Aw) |
| - whole cow's milk | 95-85 | 0.98-0.95 |
| - cream | 95-85 | 0.98-0.95 |
| - sour cream with fat mass fraction of 25% | 95-85 | 0.98-0.95 |
| - fresh fruits | 95-85 | 0.98-0.95 |
| - reconstituted juices and purees | 95-85 | 0.98-0.95 |
| - fresh melange | 95-85 | 0.98-0.95 |
| - eggs | 95-85 | 0.98-0.95 |

| **Perishable products (with intermediate humidity and medium risk degree): 0.87>Aw>0.50** | | |
|---|---|---|
| - condensed milk with sugar | 40 and less | 0.87-0.80 |
| - juice concentrates | 40 and less | 0.87-0.80 |
| - jams, preserved fruits, marmalade | 40 and less | 0.87-0.80 |
| - syrups (fruit, chocolate) | 40 and less | 0.87-0.80 |
| - butter sponge-cake, impregnated with syrup | 40 and less | 0.87-0.80 |
| - whipping products W = 15-17% | 40 and less | 0.87-0.80 |
| - fruit muffins | 40 and less | 0.87-0.80 |
| - fondant sweets | 40 and less | 0.87-0.80 |
| - fruit cakes and pastries | 40 and less | 0.87-0.80 |
| - butter cream, cream frosting | 40 and less | 0.87-0.80 |
| - prickly pear (Opuntia spp.) | 40 and less | 0.87-0.80 |

Pseudomonas; Escherichia; Proteus; Shigella, Klebsiella; Bacillus; Clostridium perfingens; some yeast

Many mushrooms (mycotoxic Penicillia); Staphylococcus Aureus; most Saccharomyces; Debaryomyces
| Table 1. Ending |
|----------------|
| - frozen fruits | - fruit jams and toppings thermostable | 35 and less | 0.80-0.75 |
| - marmalade | - fruit glaze | - fruit candies | - pastille |
| - wheat flour | - starch syrup | - molasses | - nuts |
| - raisins, dry fruits | - marzipan | - marshmallows on egg white | - zephyr |
| - cupcakes | - dried fruits | - toffee candies | - iris |
| - gingerbread cookies | - crusts | - semi-finished baked puff | - semi-finished baked shortbread |
| - cereal bar | | | |

**Persistent products (with low humidity and risk degree): 0.50 > A_r > 0.10**

| - egg powder W = 5% | - sunflower oil | - marshmallows on gelatin base | - biscuits on dry mixes |
| - chocolate sweets with filling | - cocoa powder | - whole milk powder W = 4-6% | - chocolate, chocolate products without filling |
| - soft caramel | - halva | - dragee | - chewing gum |
| - sugar cookies, short-dough biscuits | - hard-dough biscuits | - crackers W = 3-5% | - crisp biscuits |
| - waffle sheet | - turmeric | - beet sugar | - whole milk powder W = 2-3% |
| - candy caramel | - solid cookies | - crackers W = 2-3% | - cereal flakes W = 5% |
| - halva tahini (tahini) | | | |

| 8 and less | 0.30-0.10 |

**Absence of microorganism growth**
As it can be seen from table 1, Aw can be in a wide range from 0.98 to 0.1 depending on the composition and physico-chemical characteristics of raw materials, semi-finished products and finished products. All confectionery products are divided into three groups: I - products with low humidity (from 1 to 11%) and AW below 0.5; II - products with intermediate humidity (from 11 to 40%) and 0.87 > Aw > 0.50; III - products with high humidity (more than 40%) and AW more than 0.87 [10, 18-20].

Some types of baked semi-finished products for cakes and pastries – sponge cakes, trifles, have rather high values of Aw, but they have approximately the same humidity value (for example, Aw of semi-finished biscuit is 0.8, and trifles - 0.95 with humidity of 22.8 and 23.7% respectively). Puff and shortbread semi-finished products have Aw at the level typical for products with intermediate humidity (0.6-0.5) [9, 10].

However, it should be noted that not only the quantitative content of sugars, but also their qualitative composition is of primary importance. So, the semi-finished confectionery product - jam with a moisture content of 32.6% has a lower value of Aw = 0.83 than buttercream with a moisture content of 15.2% (Aw = 0.85). The presence of reducing sugars in fondant (fructose, glucose, maltose) leads to significant decrease of Aw level = 0.84 at a moisture content of 10-12% [10].

Confectionery with high humidity is highly susceptible to microbiological deterioration. At Aw = 0.87-0.98, the whole spectrum of microorganisms (bacteria and fungi) develops. Oxidative, microbiological, and enzymatic processes are possible in products with intermediate humidity; the development of yeasts, molds, and certain types of bacteria is most likely in them; they become stale during storage period. At Aw = 0.88-0.60, the development of microorganisms is limited. In products with low humidity, the microorganisms activity is suppressed, biological processes do not proceed in them, they retain their properties for a long time, however, during the storage period, processes of fats oxidation, loss of vitamins, enzymatic and non-enzymatic browning occur, such products are able to get wet during storage; at Aw <0.6 bacteria, molds and yeast practically do not develop [6]. However, some types of molds and osmophilic yeast are known to develop at Aw = 0.62 [1].

The significant effect on the microorganisms' growth is exerted by pH and the value of oxidation-reduction potential. Only lactic acid bacteria and certain types of yeast and mold can develop in products with low pH - less than 3.7. Products with pH from 5.0 to 7.0 are exposed to risks associated with the propagation of pathogenic microorganisms; at pH from 4.0 to 2.0, products are not exposed to risks [2, 9, 10].

Experimental data for the Aw determination of various sugars, sweeteners and a sugar substitutes are presented in table 2.

**Table 2.** The characteristic of water activity values (Aw) in experimental samples

| The name of the object of study | The name of the indicator | Water activity (Aw) | Temperature, °C |
|-------------------------------|--------------------------|---------------------|-----------------|
| Sugars:                       |                          |                     |                 |
| beet sugar                    |                          | 0,339±0,017         | 21,85±0,44      |
| glucose                       |                          | 0,331±0,014         | 21,74±0,52      |
| fructose                      |                          | 0,341±0,015         | 21,83±0,47      |
| Sweeteners:                   |                          |                     |                 |
| maltitoly                     |                          | 0,330±0,017         | 21,72±0,60      |
| isomatitlois                  |                          | 0,338±0,008         | 21,86±0,43      |
| erythritol                    |                          | 0,351±0,016         | 21,94±0,38      |
| xylitol                       |                          | 0,347±0,005         | 21,94±0,42      |
| sorbitol                      |                          | 0,320±0,003         | 21,69±0,56      |
| stevioside                    |                          | 0,335±0,004         | 22,01±0,49      |
6. Conclusion
The Aw indicator has the most important theoretical and applied value, it plays a significant role in storage, raw materials processing, producing of semi-finished products, the development of new innovative products with a given chemical composition, as well as in a storage period, which is consistent with the requirements of Technical Regulation of the Customs Union 021/2011 "On Food Safety". By controlling the moisture content of the products and Aw values, it is possible to predict the intensity of various physicochemical, biochemical and microbiological processes during the storage period of products, which will create “Stability maps of confectionery products depending on water activity” and create products with the required shelf life. This approach allows us to assess the impact of individual technological changes on products safety.

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