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EVALUATION OF THE STABILITY OF THE STORAGE OF SELECTED FRUIT AND VEGETABLES FREEZE-DRIED POWDER BASED ON THE CHARACTERISTICS OF THE SORPTION PROPERTIES

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Abstract: The aim of the study was the analysis of the storage stability of selected freeze-dried vegetables and fruit powders based on the characteristics of sorption properties. Analysis of the evaluation of sorption properties was done with static-desiccation method and determining the sorption isotherms in a wide range of environmental water activity a_w = 0.07–0.93. A BET equation was used to mathematically interpret the course of water vapor sorption isotherms. Sorption isotherms of tested samples of lyophilisates in powder were characterized by a sigmoidal shape typical of porous surfaces, on which multilayer adsorption leading to capillary condensation occurs. On the basis of the conducted tests, it was found that the product IV – lyophilisate of blueberry was characterized by a higher storage stability.

Keywords: fruit and vegetables freeze-dried powders, sorption isotherm, BET, storage stability.

1. INTRODUCTION

Examples of products that should be consumed daily by man are fruits and vegetables. They contain essential nutrients that improve functioning of the body, but also have taste and aesthetic values. Due to their specificity, fresh fruits and vegetables have low storage stability. During the vegetation period as well as during storage, physiological processes occur which lead to spoilage of the product. However, the progressive development of food preservation technology allows obtaining an alternative form of vegetables and fruits, which are offered on the food market in the form of freeze-dried products. Freeze-dried fruits and vegetables available in the market are offered in the form of freeze-dried vegetables and fruits as a whole or in the form of freeze-dried powder. Considering the interest of consumers in lyophilized products, powder freeze-dried products are more popular, especially among people actively practicing sports as well as among people who care about proper balancing of the diet. Lyophilized vegetables can be added to various types of cocktails, cereals, drinks or meals, and the freeze-dried fruit powder can also be added to cocktails, juices, fruit cocktails, yogurts, ice cream, thus increasing the content of micro and macro elements in prepared food.The essence of freeze-drying is to remove water from the foods, so that the operating conditions allow obtaining freeze-dried product, where in the nutritional properties will be retained and biological, but the product has not got the same properties as natural raw material. Dehydrated, freeze-dried are characterized by high quality, practically intact structure, and their water content is between 1.5% to 4.0% with a water activity of 0.20–0.35.The low water content promotes long-term storage of freeze-dried food [Kondratowicz, Burczyk and Janiak 2009], provided that they are stored in a dry and cool place. The material obtained in the lyophilize-tion process contains about 98% of dry matter, thus it is characterized by high hygroscopicity determined by low water content as well as by the powder structure itself.

The state of water in the material is an important issue determining the physical, chemical or biological properties of food. The water sorption isotherms are used to assess the state of water in food [Pałacha 2008].They determine the equilibrium relationship between the amount of adsorbed water by the weight of the food and the water activity in a constant temperature and at constant total pressure. Therefore, the aim of the study was to assess the sorption properties of selected vegetables and freeze-dried fruits in powders by determining the vapor sorption isotherms in a wide range of water activity a_w = 0.07–0.93. Aim of the study is based on the following research hypothesis: the storage conditions of freeze-dried powders affect storage stability.

2. MATERIAL AND METHODS

The selected research material was vegetables and fruit freeze-dried powder. Lyophilized vegetables – beet LIO Shake (I) and spinach LIO Shake (II) have been produced by Foods to Ann, and freeze-dried fruits – chokeberry (III), blueberries (IV), elderberry (V) and rosehips (VI) produced by Premium Rosa. The selection of the research material was conditioned by the growing popularity of using vegetable and fruit freeze-dried by consumers who care about their health while being physically active.

Water content was determined by drying the samples (ca. 2 g ±0.0001 g) at a temperature of 105°C for 1 h [Krełowska-Kułas 1993]. Water activity was determined in the AquaLab apparatus, with an accuracy of ±0.003 (Series 3 model TE, Decagon Devices USA) at a temperature of 25 ±1ºC.

The sorption properties of these products were determined with the static method based on the evaluation of water vapor sorption isotherms. Sorption isotherms of steam were determined at 25°C. The time necessary to reach system equilibrium reached 45 days. Crystalline thymol was introduced into the exsiccators with water activity above 0.7 to prevent microflora growth in the samples. The initial weight of the product and changes in water content enabled calculating the equilibrium water content and plotting sorption isotherms with the use of EXCEL program.

The empirical data were subjected with the use of the Brunauer, Emmett and Teller equation BET (1) in a water activity range of $0.07 \leq a_w \leq 0.33$ [Ościk 1983]. The fitting of empirical data to the BET equation was characterized based on determination coefficient (R^2) and standard error of estimation (FitStdErr) and the F statistic value, as determined using the Jandel-Table Curve 2D v 5.01.

Based on the equilibrium moisture content of the products designated capacity of adsorption monolayers BET surface area and sorption.

$$a = \frac{v_m c a_w}{(1-a_w)[1+(c-1)a_w]} \tag{1}$$

where:

a – adsorption (g/g),
v_m – monolayer water content (g/g),
c – constant energy ($kJ \cdot mol^{-1}$),
a_w – water activity(-).

On the basis of water content estimated in the monolayer adsorbed at a temperature lower than the boiling temperature and the so-called "water cross-section", the specific surface area of adsorbent was calculated according to the equation (2) [Paderewski 1999]:

$$a_{sp} = \omega \frac{v_m}{M} N \tag{2}$$

where:

a_{sp} – surface area of sorption (m^2/g),
N – Avogadro number ($6{,}023 \cdot 10^{23}$ molecules/mol),
ω – water setting surface ($1{,}05 \cdot 10^{-19}$ m^2/molecule),
M – water molecular mass (18,015 g/mol).

3. ANALYSIS OF THE RESULTS

The nutritional value of the tested products is presented in Table 1. The vegetable freeze-dried were significantly different in terms of nutritional value. The freeze-dried of beet powder was characterized by a lower content of fat, fiber and protein, in comparison with the freeze-dried spinach (II). In the case of the nutritional profile of fruit freeze-dried powder, it was found that the lowest calorific value was distinguished by freeze-dried rosehip fruit (VI), with the highest content of fiber as well as protein in the group of fruit lyophilisates evaluated (Table 1).

Table 1. The nutritional value of products tested (100 g of the product), as declared by the producer on the wrapping

Product	Energy value [kJ/kcal]	Fat [g]	Carbohydrates [g]	Fiber [g]	Protein [g]
I	1338/318	0.5	58.0	21.5	9.5
II	1240/296	3.6	17.1	30.5	33.7
III	1361/325	2.3	57.3	30.1	3.6
IV	1482/352	5.0	64.0	19.0	3.6
V	1303/311	2.3	53.0	33.0	3.1
VI	1067/258	2.9	28.0	52.0	4.0

Source: own study.

The water contained in food products is one of the main factors affecting the intensity of all processes occurring in the product. The proper amount of water in the product also affects the sensory attributes and determines the susceptibility of the product on corruption. Most ways of preserving food consist in reducing the amount of water in the product and reducing its activity [Sikorski 2007; Ocieczek, Skotnicka and Baranowska 2017].

Table 2 shows the average water content and the activity of the tested products. The evaluation of the initial content and water activity of the freeze-dried vegetables tested, showed that the highest value of the evaluated parameters and the product was characterized by the beet lyophilized to give a water content of about 4.93 g/100 g d. m. and water activity $a_w = 0.256$ (Table 2). In the group of freeze-dried fruit powder, the highest content and water activity of the product characterized the freeze-dried of wild rose (VI). The lowest content and activity of water, however, was characterized by freeze-dried chokeberry (III). In addition, it was found that the water activity level of the tested lyophilisates provided them with microbiological safety and storage stability.

Table 2. The content and water activity of the tested products

Product	Water content [g/100 g d. m.]	SD	Water activity [-]	SD
I	4.9270	0.124	0.265	0.019
II	3.2338	0.175	0.127	0.005
III	1.5363	0.029	0.160	0.009
IV	5.1374	0.163	0.255	0.027
V	5.2273	0.089	0.233	0.018
VI	9.2682	0.089	0.532	0.012

Source: own study.

Sorption properties of freeze-dried fruit and vegetable powder fulfil an important role in their preparation and storage. An effective tool for the study of these properties is the determination and analysis of sorption isotherms.Knowledge of the shape of the isotherm allows to evaluate the mechanism of the process of determining the water binding in the product, identify the sensitivity of the product to moisture and to predict changes during storage of the product [Andrade, Lemus, and Pérez 2011; Ocieczek, Skotnicka and Baranowska 2017].

The shape of water vapor sorption isotherms was related to the occurrence of monolayer sorption in low water content ($a_w < 0.25$), multilayer sorption ($0.25 < a_w > 0.7$) and capillary condensation ($a_w > 0.7$). Assessing the shape of the limited adsorption isotherms of the tested products, it was found that they are characterized by continuity waveform (Fig. 1). Thus determined sorption isotherms reflect the process of physical adsorption taking place on the bodies of porous. As a result of this process, the shape had characteristic curves for isotherm type II (Fig. 1). In terms of water activity a_w = 0.07–0.75, higher sorption (hygroscopic) characterized product IV – the blueberry freeze-dried powder. In contrast the a_w = 0.75–0.93 covering the range of capillary condensation occurred reversal higher sorptivity showed the freeze-dried product V – the freeze-dried elderberry (Fig. 1).

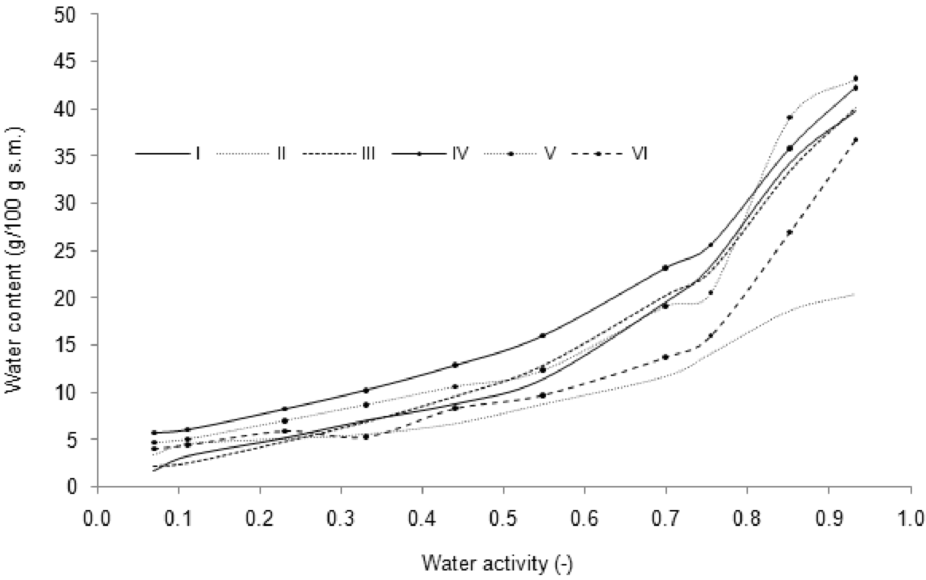

Fig. 1. Sorption isotherms of tested products

Source: own study.

The sorption isotherms abruptly swung upwards, which probably indicated to initiate the swelling process of products I-VI. According to the literature on the course of sorption isotherms could probably affect both diverse chemical composition of the products, but above all the structure of the products I–VI and resulting from the freeze drying process used (Fig. 1). Ciurzyńska and Lenart [2009], when assessing the sorptive properties of lyophilized strawberries, found that they have a sigmoidal shape characteristic of most food products, corresponding in type II isotherms. Also, Moraga, Martinez-Navarrete and Chiralt [2004] for freeze-dried strawberries obtained a sorption isotherm course typical for products with high sugar content. This is connected with the slow changes in equilibrium water contents at low water activity and rapid increase above water activity 0.5. At that water activity level interactions between solvent (water) and soluble solid are connected with sugar dissolution.

The course of sorption isotherms in the water activity range of $a_w = 0.07–0.33$ enabled determining parameters of the BET equation (v_m, c_e) by assaying the degree of its fit (R^2, FitStdErr) to empirical data.

Respective results were presented in Table 3.

Based on the obtained R^2 values, it was found that the BET model ($a_w = 0.07–0.33$) was characterized by a good fit.In the area of 90–99% explained the relationship between the content and the water activity in freeze-dried powders of fruit and vegetables.

Table 3. The BET equation parameters

Product	**v_m [g/100 g d.m.]**	**c_e**	**R^2**	**FitStdErr**
I	6.870	4.69	0.909	0.291
II	3.870	21.23	0.992	0.449
III	6.149	5.277	0.924	0.311
IV	7.249	27.81	0.996	0.396
V	6.235	24.61	0.996	0.312
VI	3.675	79.83	0.961	0.705

Where: v_m – monolayer capacity; C_e – constant energy; R^2 – determination coefficient; FitStdErr – standard error.

Source: own study.

Monolayer capacity (v_m) is determined on the basis of the BET equation, corresponds to a single layer of molecules adsorbed water vapor and is referred to as an indicator of the availability of a polar water vapor independently, which component is a source of hydrophilic groups [Mathlouthi 2001; Ocieczek 2012]. Theoretically the water content of the layer corresponds with the optimum amount of water in the product and indicates the quality of the storage stability.

Own study showed that the highest value of the monolayer was characterized by product IV (Table 3). This suggests that the resulting value of the surface area of the sorption may be influenced kind of raw materials or process parameters which contribute to a greater extent to expose the functional group capable of adsorbing water molecules.

Constant energy reflects the difference between the enthalpy of desorption monolayer and the enthalpy of vaporization of the liquid adsorbent. The results of the constant c_e ($c_e \geq 2$) confirm the sigmoidal shape of the curve of adsorption and suggest that in the tested products occurred only a process of physical adsorption (Table 3).

Based on the obtained value of the monolayer capacity v_m surface of sorption was determined. The obtained results (Table 4) showed that a greater surface area of the sorption was characterized by product IV.

Thus, it is possible to assume that the highest stability and storage stability determined by the value of the monomolecular layer, was characterized to product IV, freeze-dried blueberry powder.

Table 4. Microstructural characteristics of the tested products

Product	Specific surface of sorption a_{sp} [m^2/g]	Total capacity of capillaries [mm^3/100 g]	Size of capillaries at a_w = 0.75 [nm]
I	241.386	97.633	4.949
II	135.976	53.332	2.994
III	216.05	96.166	4.110
IV	254.70	103.621	5.406
V	219.06	102.857	4.338
VI	129.10	79.655	3.376

Source: own study.

The volume of the capillary of the tested material was calculated as the sum of the volume of water adsorbed by the material in the water activity range from 0.75 to 0.93. Determination of the total volume of the capillaries in the area of capillary condensation, based on the progression of sorption isotherms at a_w = 0.75 (Table 4) showed that the highest values of the rated parameter characterized product IV. It can be assumed that the chemical composition of the raw material determines the differentiation capacity of the capillaries. Resolution of the most likely radius of the capillary in the tested products I–VI was located in the region from 2.994 to about 5.406 nm.

4. CONCLUSIONS

1. On the basis of the assessment of the initial water activity, it was found that all investigated vegetables and fruit freeze-dried in powder were characterized by water activity below $a_w < 0.6$, which indicated the microbiological stability of the tested products.
2. The water vapor sorption isotherms of vegetables and fruit freeze-dried in powder were characterized by a course consistent with the second type of sorption isotherms according to the classification of Brunauer. The shape of the sorption isotherm was related to the presence of monomolecular sorption at water activity $a_w < 0.3$, the range of multilayer sorption in water activity $a_w = 0.34–0.75$ and the capillary condensation at the water activity $a_w > 0.76$.
3. The size of the monolayer capacity (v_m) determined on the basis of the bet equation, which determines the sorptive capacity of the adsorbents and the availability of a polar water vapor showed that the product I – the freeze-dried beet powder and blueberries powder (IV) showed the highest stability and storage stability.
4. The product IV was characterized by the highest specific surface area of sorption, which suggests that the obtained value of sorption specific surface was probably influenced by the type of raw material or parameters of the technological process used, which contributed to the disclosure of functional groups capable of adsorbing water molecules.
5. Based on the survey, it was found that the storage conditions of studied fruit and vegetables in the freeze-dried powders determined the storage stability of products.

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