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EVALUATION OF THE QUALITY AND STABILITY OF THE STORAGE OF MARJORAM (*ORIGANUM MAJORANA L.*) BASED ON THE CHARACTERISTICS OF THE SORPTION PROPERTIES

OCENA JAKOŚCI I STABILNOŚCI PRZECHOWALNICZEJ MAJERANKU (*ORIGANUM MAJORANA L.*) NA PODSTAWIE WŁAŚCIWOŚCI SORPCYJNYCH

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Abstract: The aim of the study was to assess the quality and stability of the marjoram (*Origanum majorana L.*) storage using the characteristics of the sorption properties. In the studied products, evaluation of the sorption properties was done by static and dynamic method based on the kinetics and rate of adsorption of water vapor. For mathematical interpretation of running of water vapor sorption isotherms, the BET equation was used, and also the usefulness of GAB, Peleg and Oswin models was shown to describe the obtained adsorption isotherms, basing on the coefficient of determination (R^2). On the grounds of the survey, it was found that the national product, more expensive – marjoram I, was characterized by higher quality and storage stability.

Keywords: marjoram, sorption kinetics of water vapor, sorption isotherm, BET, storage stability.

Streszczenie: Celem pracy była ocena jakości i stabilności przechowalniczej majeranku (*Origanum majorana L.*) z wykorzystaniem charakterystyki właściwości sorpcyjnych. W badanych produktach oceny właściwości sorpcyjnych dokonano metodą statyczną oraz metodą dynamiczną na podstawie przebiegu kinetyki i szybkości procesu adsorpcji pary wodnej. Do matematycznej interpretacji przebiegu izoterm sorpcji pary wodnej zastosowano równanie BET oraz przedstawiono przydatność modeli GAB, Pelega i Oswina do opisu uzyskanych izoterm adsorpcji, opierając się na współczynniku determinacji (R^2). Na podstawie przeprowadzonych badań stwierdzono, że wyższą jakością i stabilnością przechowalniczą charakteryzował się produkt krajowy, droższy – majeranek I.

Słowa kluczowe: majeranek, kinetyka sorpcji pary wodnej, izoterma sorpcji, BET, stabilność przechowalnicza.

1. INTRODUCTION

Spices are food ingredients that can be used in food products, because of their flavouring properties – taste, flavor, aroma and color. Marjoram [*Origanum majorana L.*] is the most popular, traditional domestic spice used in food products because of its sensory attractiveness. The use of spices is versatile and the most important factor determining their quality is above all essential oil and water content.

Sorption properties of spices play an important role in the process of manufacture and storage. The instrument for determining these properties are: the determination of adsorption isotherms of water, and accurate analysis using mathematical models. Spices sensitivity to moisture and degree of absorbency of putting water through product and anticipated changes that may occur in the material during storage can be defined through the prescribed isoterms. Characteristics of hygroscopic properties of spices are an important element in the production process and to determine the storage stability of those products.

The aim of this study was to assess the impact of the brand on the hygroscopic properties of marjoram (*Origanum majorana L.*) the most popular spice brand in Poland (I) and cheaper private label (II), purchased in Poland.

Marjoram is a herbaceous plant native in Europe and in the Mediterranean. Marjoram belongs to family *Lamiaceae*, formerly *Labiatae*. Marjoram has often been mistaken with oregano in botanical description. For many years both marjoram and oregano were known as *Origanum majorana L*. Now marjoram is identified as *Majorana hortensis* as a member of the mint family. Distinguishing marjoram from oregano is possible during flowering, mainly due to the characteristically different inflorescences [Senderski 2004].

Marjoram is characterized by light gray- green color, has a strong, aromatic smell and a bitter, spicy taste. Marjoram commercially often occurs as rubbed twigs, much less in the form of whole twigs. Marjoram owes its popularity to characteristic aroma, widely used in cookery [Newerli-Guz 2012].

Aside from seasoning use, the healing properties of marjoram are also used. Marjoram herb is used as an anti-inflammatory and carminative, it enhances the gastric secretion and limits excessive fermentation. It is used as a medicament to facilitate the digestion, resulting in gastric acid secretion. Obtained from herb marjoram oil has antiseptic, anti-inflammatory and anti-acne activity. The effectiveness of antimicrobial activity equals in action cinnamon and cloves essential oils [Góra and Lis 2007].

2. MATERIAL AND METHODS

Dried marjoram spices samples, were obtained from the Tricity market and investigated. Five packaging of all investigated spices in triplicate were taken from market according to PN-ISO 948 [PN-EN ISO 948:2009].

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 and with the dynamic method by assaying water vapor sorption kinetics. Sorption isotherms of steam were determined at 25°C by the static desiccator method. 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 there was designated capacity of adsorption monolayers using the BET equation.

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

where:

a – adsorption [g/g],
v_m – monolayer water content [g/g],
c – constant energy [kJ·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].

The kinetics and rate of water vapor sorption were determined in the environment with relative humidity of – a_w = 0.44, 0.64, 0.86, within 24 h. Interpretation of sorption kinetics were kinetic curves and rate curves. Kinetic curves represented graphic description of changes in the quantity of water (g/100 g d.m.) adsorbed in time. While rate curves reflected the steam adsorption rate changes in time (g H20/(100 g s.s.$\cdot$min^{-1})) and were the differential of kinetic curves. Closed-circuit Deryng apparatus was used in essential oil determination of marjoram samples. They were distillated with water, about 10 grams of the product were quantitatively transferred to a flask and 200 ml water was added, several porous glasses or porcelain pieces and mixed thoroughly. The flask was connected with a Deryng apparatus then receptacle filled with water to start cooling and to perform distillation for 3 h, calculating from the start of the reflux the contents of the flask. After finishing the distillation process the volume of oil is determined and its content in the raw material calculated in percent [Farmakopea Polska 2002].

3. ANALYSIS OF THE RESULTS

Table 1 shows the average essential oil and water content and the activity of the tested products.

The content of essential oil in marjoram according to Polish Pharmacopeia VIII [Farmakopea Polska 2002] should not be lower than 0.5%, and all of the tested samples meet these requirements. Many factors could affect the low essential oil content. Bad storage conditions (temperature and relative humidity) usually cause oil loss by evaporation. Very important is also physical condition of the spice, mainly connected with moisture content.

The essential oil content in dried marjoram can vary from 0.5 to 3.5% [Góra and Lis 2007]. In Seidler-Łożykowska study it significantly depended on weather conditions in particular years of research from 1.51 to 2.08% [Seidler-Łożykowska 2007].

Product I was characterized by higher content and water activity and had higher retail price. Comparing the obtained values of the designated parameter content and water activity to a study conducted by Pałacha and Malczewska [Pałacha and Malczewska 2010] it should be stated that investigated marjoram I and II were characterized by low values of parameters evaluated in comparison to e.g. cumin (8.22 g/100 g d.m.) or peppers (7.42 g/100 g d.m.). At the same time Pałacha and

Malczewska [Pałacha and Malczewska 2010] found no simple relationship between water content and its activity.

Table 1. The content and water activity of the tested products

Tabela 1. Zawartość i aktywność wody badanych produktów

Product	Essential oil content [%]	Water content [g /100 g d. m.]	SD	Water activity (-)	SD
I	0.55	8.99	0.203	0.439	0.006
II	0.90	7.19	0.186	0.351	0.004

Source: own study.

Assessing the shape of the limited adsorption isotherms of the tested products, it was found that they were 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 was characteristic of curves for isotherm type II. In terms of water activity a_w = 0.07–0.75, higher sorption (hygroscopic) characterized product I – more expensive. In contrast, the a_w = 0.75–0.93 covering the range of capillary condensation, the reversal occurred and higher sorptivity showed product II (Fig. 1). The sorption isotherms abruptly swung upwards, which probably indicated to initiate the swelling process of products I and II. 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 and II and the species and geographical origin of the assessed marjoram I and II.

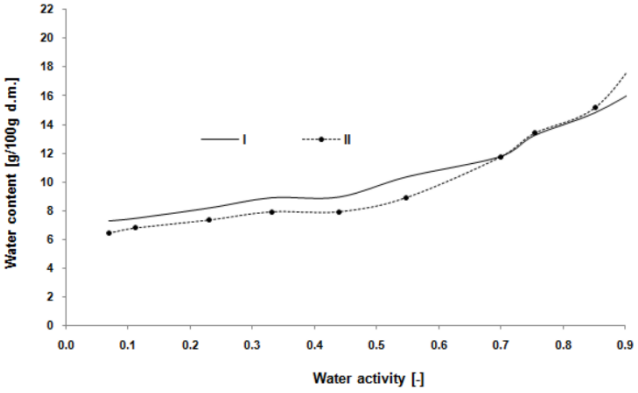

Fig. 1. Sorption isotherms of tested products

Rys. 1. Izoterma sorpcji badanych produktów

Source: own study.

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 2.

Table 2. The BET equation parameters

Tabela 2. Parametry równania BET

Product	v_m	c_e	R^2	FitStdErr
I	5.86	74.64	0.993	0.435
II	5.22	69.78	0.832	1.430

Where: R^2 – determination coefficient, V_m – monolayer capacity, C_e – constant energy, 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 product I was characterized by the higher value of the monolayer (Tab. 2). 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 (Tab. 2).

Table 3. Microstructural characteristics of the tested products

Tabela 3. Charakterystyka mikrostruktury badanych produktów

Product	Specific surface of sorption a_{sp} [m^2/g]	Total capacity of capillaries [mm^3/100 g]	Size of capillaries at a_w = 0.70 [nm]
I	207	44.72	2.79
II	184	47.81	2.83

Source: own study.

Based on the obtained value of the monolayer capacity v_m surface of sorption was determined. The obtained results (Tab. 3) showed that a greater surface area of the sorption characterized product I. 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 $a_w = 0.75$ (Tab. 3) showed that the highest values of the rated parameter characterized the second product. 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 and II was located in the range from 2.79 to about 2.83 nm.

Table 4. Calculated parameters of the examined water sorption isotherms models of tested spices

Tabela 4. Obliczone parametry modeli izoterm sorpcji wody badanych przypraw

Model	Spices – sorption process	
	I	II
GAB	-	-
Vm	6.66	5.421
C	2.820e+14	2.095e+24
k	0.644	0.767
R^2	0.991	0.981
FitStdErr	0.345	0.667
F stat	396.60	181.22
Peleg	-	-
A	9.453	8.0248
B	3.081	0.465
D	9.186	8.025
E	0.089	0.627
R^2	0.996	0.752
FitStdErr	0.255	2.605
F stat	485.49	6.063
Oswin	-	-
h	10.367	9.739
z	0.183	0.251
R^2	0.972	0.959
FitStdErr	0.575	0.918
F stat	280.22	186.79

Source: own study.

To describe the sorption isotherms in studied marjoram samples GAB model, a two-parameter Oswin model, four paramenter Peleg were used [Pałacha and Malczewska 2010]. The compatibility of those models was expressed by the

coefficient of determination R^2 (Tab. 4). It was found that the phenomenon of water vapor adsorption of the tested product I was very well described by the Pelag and GAB equation, which are, according to the literature, the most useful to predict the optimal conditions of storage and the storage stability of food, particularly in anhydrous food [Pałacha and Malczewska 2010; Arslan and Togrul 2005].

In the case of a product II Oswin model accurately describes its water sorption isotherms.

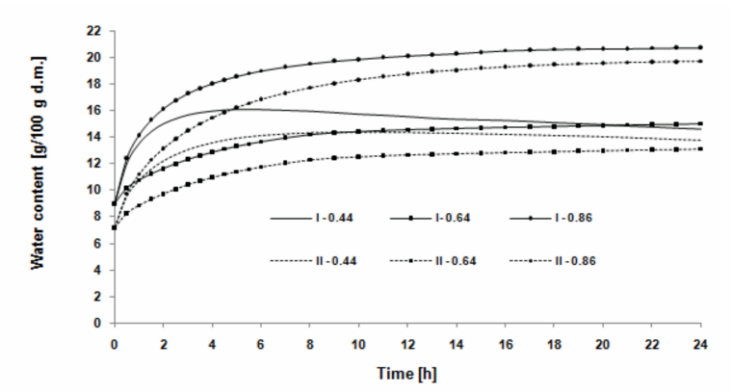

Fig. 2. The vapor sorption kinetics of tested products in an environment with a water activity of a_w = 0.44; 0.64; 0.86

Rys. 2. Kinetyka sorpcji wody badanych produktów w środowisku o aktywności wody a_w = 0,44; 0,64; 0,86

Source: own study.

It was found that the curves of the kinetics and the rate of adsorption of water vapor in products I and II look similar (Fig. 2 and 3). Based on the sorption kinetics and speed, it can be assumed that the initial water content plays the crucial role of sorption process of tested product. Differences in humidity of the product and its environment influenced poterntail difference of moisture and determined the driving force of studied processes [Ruszkowska, Ocieczek and Palich 2006].

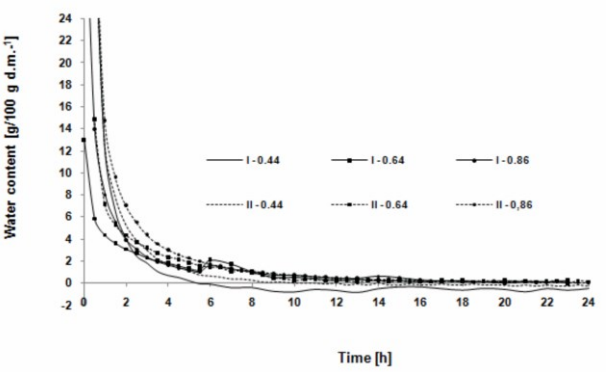

Fig. 3. The sorption rate of tested products in an environment a_w = 0.44; 0.64; 0.86

Rys. 3. Szybkość procesu sorpcji wody badanych produktów w środowisku a_w = 0,44; 0,64; 0,86

4. CONCLUSIONS

1. The essential oil content in investigated material varies, and all of the tested samples meet Pharmacopoeias requirements.
2. Adsorption isotherms of water vapor surveyed in marjoram I and II were characterized by a course consistent with the second type of adsorption isotherms according to the classification of Brunauer.
3. Product I – very popular spice brand is characterized by a higher sorption yield of monolayer capacity and a higher specific surface sorption, what probably indicates better product properties such as the quality and storage stability.

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