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WATER ACTIVITY AS A STRUCTURING PARAMETER OF THE HYSTERESIS CYCLE AND ITS ROLE IN FOOD STABILITY

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Abstract

In food science, water sorption isotherms are often used to understand the stability of food preserved in different conditions. Water activity is defined as the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water (po) at the same temperature. In food, water activity (a_w) explains how water affects the rate of microbial growth and many other chemical reactions. The paper aimed to study aw as an indicator of structuring the hysteresis cycle, its role in the changes that occur in several dried fruits in the Albanian market and to reach the hysteresis cycle through the determination of aw values in adequate conditions. Referring to physico-chemical indicators as protein, fat, and acidity, they were found to be within the limits allowed by law. So, there was no visible impact on the change of these indicators during the storage period. From the results obtained for walnuts as a specific case, it was observed that due to the dependence of moisture content on aw, the adsorption/desorption isotherms do not overlap, which refers precisely to the hysteresis cycle. It was possible to obtain a second-order desorption isotherm, with a very good approximation.

***Key words**: food safety, hysteresis cycle, moisture, water activity, Water Activity (aw) Meters.*

INTRODUCTION

Food preservation involves the action taken to maintain the nature of a selected food and/or its desired properties, with the aim of keeping it fresh and safe to the consumer within a certain period of time. A stable food product can be developed by applying different processing techniques and by keeping it in appropriate conditions. Food stability determination from a scientific basis rather than empiricism is a challenge to food scientists and engineers (Sandulachi et al., 2012).

Water is a very important component in foods. For a long time, the industry has known how important it is to check the free water. Water activity (a_w) measurement forms the basis of this and provides important information about the safety and quality of a product. Finally, it provides information regarding the possibility of microbiological growth on the surface. Studies for the evaluation of water activity in food products and their conclusions, are part of the scientific research on the preservation, stability and shelf life of food products. Water activity (a_w), combined with temperature and pH have a significant effect in microbial growth in food (Peleg et al., 2021).

In order for a food to have an appropriate shelf life without relying on refrigerated storage, it is necessary to control either its acidity level (pH), the level of water activity (a_w) or a suitable combination of the two. This can effectively increase the product's stability and make it possible to predict its shelf life under known environmental storage conditions. (Sandulachi et al., 2012).

The water activity (a_w) of a food is the ratio between the vapor pressure of the food itself, when in a completely undisturbed balance with the surrounding air media, and the vapor pressure of distilled water under identical conditions $a_w = (p/p_o)$ T. Aw also defined as the ratio of the “the sum of the partial pressures that the water vapors coming out of the components of a food product, exert on the product itself and the vapor pressure of distilled water under identical conditions”. The term “water activity” (aw) was developed to reflect the intensity with which water associates with various nonaqueous constituents. Relative vapor pressure-RVP is related to the percentage of relative humidity in equilibrium conditions (% ERH) of the product environment as follows: RVP = (p/po) T = % ERH/100. Relative vapor pressure (RVP) is the name for (p/p_0) T (Damodaran et al., 2007).

The recognition of a_w as a storage and stability factor for dried fruit-nuts, was an incentive for the experimental work presented in this publication.

Nuts have water activities that are generally less than 0.7. This group are usually described as dry fruits with an edible seed and a hard shell, with cashews (*Anacardium occidentale*), walnuts (*Juglans regia*), almonds (*Prunus dulcis*), chestnuts (*Castanea sativa*), pistachios (*Pistacia vera*), and hazelnuts (*Corylus avellana*) as the ones with higher production worldwide. It is known that nuts are a good source of many nutrients, including monounsaturated and polyunsaturated fatty acid profiles, vitamins E and K, selected minerals such as magnesium, copper, potassium, and selenium, dietary fibers, carotenoids, and phytosterols with potential antioxidant properties (De Souza et al., 2017). Nuts are a rich source of proteins and essential amino acids (Gonçalves et al., 2023). It is important to mention the beneficial effects of walnuts due to the fatty acid profile found in walnut oil, in particular the presence of ω-3 and ω-6 PUFA that are essential dietary fatty acids. These are the nonaqueous constituents that the value of a_w depends on (Boaghi et al., 2019). Our study was focused on the experimental determination of the physicochemical characteristics of dried fruits. Hysteresis can have a significant effect on the chemical reactions in food (Zomorodian et al., 2007). In this research we have considered the study of the hysteresis cycle specifically for walnuts.

A plot of water content (expressed as a mass of water per unit mass of dry material) of a food vs. (p/p_0) T is known as a Moisture Sorption Isotherm (MSI) (Damodaran et al., 2007*)*. However, not all of the products resulted in the same curve type. The classification of the curve type could explain the properties of that product. Moisture sorption isotherms exhibit a variety of shapes, many of which are amenable to at least qualitative interpretation (Andrade et al., 2011). Sorption isotherms classified according to their shape and processes, establish five different types (Blahovec & Stavros, 2009).

In food science, isotherms are primarily used to understand the effects of drying, processing and storage on the quality of food products (Nollet et al., 2008; Bell & Labuza, 2000; Hay et al., 2022). In particular, by fitting a theoretical model such as the Brunauer-Emmett-Teller (BET) (Staudt et al., 2013) or Gugenheim-Anderson-de Boer (GAB), they are often used to determine what is known as "the water in monomolecular layer" (M_m). In theory, as moisture content increases above M_m, more and more water become available to act as a solvent and thereby facilitate the change reactions of food products. According to theoretical data (Damodaran et al., 2007), the experimental curves follow the same path in sorption and desorption, regardless of the deviations that depend on the type of food product or raw materials and the processes to which they are subjected.

Water activity, unlike water content, can determine a food's shelf stability. The microorganisms are potential sources of contamination and spoilage in different values of water activity (Majumdar et al., 2018; Macri et al., 2020). Hence several preservation processes are used to extend the stability of foods by reducing the moisture content to levels below those required by micro-organisms for survival and reproduction (Liu et al., 2022; Racchi et al., 2020). Even at low pH values and low a_w, certain yeasts and molds species might pose a risk to the stability of Intermediate Moisture Foods (IMF) (Vermeulen et al., 2015). There are different approaches to conservation and stability of fresh fruit products or dried fruits. On the other hand, the stability of shelf-stable products (SSP) is achieved with a combination of factors, (including a_w) and with good production and distribution practices, (including the selection of packaging).

MATERIALS AND METHODS

The experimental work was structured in the selection and preparation of the samples, sensorial and physicochemical characterization, and finally the construction of the sorption/desorption isotherms of linearized hysteresis cycle. Several types of dried fruits, with a wide use in Albanian market were selected. The samples of almonds, hazelnuts, pistachios, walnuts, salted peanuts vacuum packaging, old walnuts and unsalted peanuts were evaluated. First, a sensorial assessment of all samples was carried out. Products were considered safe, at first sight, in terms of texture, color, aroma, and taste. Each sample was cut first, thus preparing for physico-chemical evaluation and determination of water activity. Physicochemical characterization included determination of moisture, fat using the Soxhlet extraction method, determination of nitrogenous substances and proteins using improved Kjeldahl method (Sáez-Plaza et al., 2013) and titratable acidity (expressed in oleic acid) of grinded samples based in the formula below (Nielsen et al., 2010):

$$\% \, acid \left(\frac{wt}{wt}\right) = \frac{N \, x \, V \, x \, Eq \, wt}{W \, x \, 1000} x \, 100$$

Where:
N = normality of titrant, usually NaOH (mEq/ml)
V = volume of titrant (ml)
Eq. wt. = equivalent weight of predominant acid (mg/mEq)
W = mass of sample (g)
1000 = factor relating mg to grams (mg/g) (1/10 = 100/1000).

The determination of water activity was performed using the NOVASINA AG, CH-8853-Lachen. Labstart-aw device.

The determined water activity values were accompanied by the determination of moisture under the same conditions for each sample. Moisture was determined by the classic method, with drying in a thermostat until constant weight, at a temperature of 105°C. In order to study the hysteresis cycle and to evaluate the stability of the sample, a walnut sample was used by building a work package with sorption and desorption of water from the sample cut in small pieces, for a period of time of 1, 3 and 6 hours. The sample was previously dried and the moisture and water activity were measured periodically. Then it was moistened again with 25 ml water and the periodic increase in humidity and the respective water activity were measured in order to observe the trend of water sorption isotherms.

RESULTS AND DISCUSSIONS

The values of average moisture for all samples are presented in the Figure 1 and Table 1.

It is observed that walnuts have the highest percentage of the moisture. Old walnuts have a moisture reduction of 12.63% compared to fresh walnuts. This decrease is understandable referring to the long storage time. The old walnuts have been stored for 2 years in a dried place and this reduction has influenced the inhibition of the visible development of microbial loads. Salted peanuts in vacuum resulted in an increase in the moisture by 50% of the value, while it was expected that the salt would play the role of protector by changing the osmotic pressure. Apparently, opening the package, stimulates immediate absorption of water. Another factor could be the use of very dry storage places for unsalted peanuts. This situation should be evaluated with a future experimental work, intended only for this type of product, its storage and packaging forms.

Data obtained from the analysis of the titratable acidity, fat and protein content in dried fruits are presented in Table 2 and Figure 2.

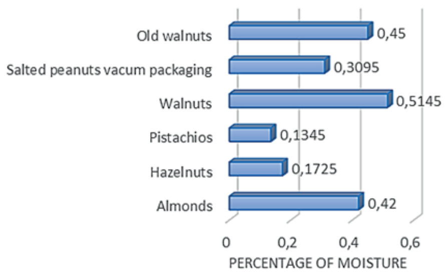

Figure 1. Moisture values in % for different types of dried fruits

Table 1. Moisture values in % for different types of dried fruits

No.	Samples	Moisture, %
1	Almonds	4.652
2	Hazelnuts	2.697
3	Pistachios	1.7105
4	Walnuts	5.232
5	Salted peanuts vacum packaging	2.6825
6	Old walnuts	4.2065

The acidity values presented in Table 2 and it is observed a very low acidity for all samples, so in reality acidity does not represent an important indicator for their physicochemical changes. The selected samples are neutral to slightly alkaline. This also explains the fact that many of them, for example pistachios are used as satisfactory choices for the people with acid reflux, or with problems in the digestive tract (Mandalari et al., 2022). The samples show also high percentages of fat. They are considered as fatty woody fruits. The highest percentage of fat it is observed in walnuts and this an expected result referring to the theoretical values of triglycerides in dry woody fruits (average value 65.21%). A result under discussion is that of the fat in a local product hazelnut, which after verification and repetition, comes out again with this value. Even the protein values for all samples are within the expected range.

Table 2. The determination of acidity, fat and proteins in the selected samples

No.	Samples	Acidity, %	Fat, %	Proteins, %
1	Almonds	0.2794	47	21.86
2	Hazelnuts	0.1397	28.9	21.97
3	Pistachios	0.4224	50.41	22.36
4	Walnuts	0.2808	64.76	20.04
5	Salted peanuts vacum packaging	0.0823	56.28	20.63
6	Old walnuts	0.2220	59.62	17.20

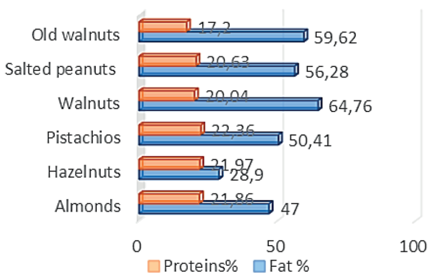

Figure 2. Fat and proteins in the selected samples

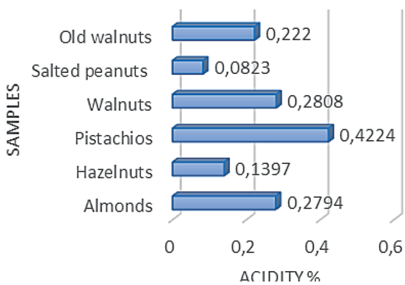

Figure 3. The percentages of acidity of the selected samples

Water activity was determined using the NOVASINA AG. Device.

For each measurement, the temperature was controlled. The experiments were performed in an area with a controlled temperature of 22-25°C. Water activity was measured three times for the same sample and the average values are presented in Table 3 and the Figure 4.

Table 3. Values for water activity

Nr.	Samples	Aw
1	Almonds	0.58
2	Hazelnuts	0.52
3	Pistachios	0.47
4	Walnuts	0.70
5	Salted peanuts	0.50
6	Old walnuts	0.57

Almonds, hazelnuts, pistachios, salted peanuts and old walnuts have the values of aw at the levels of the lower limit of mould development (a_w = 0.5-0.6). These are expected values and explain the contamination of these products by these microorganisms, especially *Aspergillus* sp. as an aflatoxin-producer in long time preserved woody fruits, in high humidity conditions.

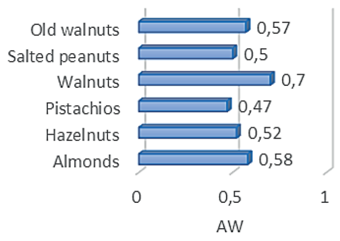

Figure 4. Water activity values for the selected samples (results of Table 3)

Walnuts have a higher value of water activity and unsalted peanuts have a very low value, slightly higher than that of the monomolecular layer. There are no values that correspond to the development of yeasts or bacteria (respectively a_w >0.8 and a_w >0.9). In fact, the low values of aw in this group, make them resistant to the presence of endemic microorganisms, while the presence of some identified pathogens, such as *Salmonella*, *Clostridium, Listeria*, etc. (Brar et al., 2018), is related to the lack of hygiene in collection, processing, distribution as well as consumption.

The construction of the specific hysteresis cycle based on aw-moisture relationship was considered for walnut samples (Table 4).

Table 4. A_w-moisture dependence for walnuts in the conditions of adsorption and desorption of the aqueous phase

	Aw	Moisture (humidity) %	
Absorption values	0,54	2,93	
	0,96	16,99	
	0,95	17,8	
	0,96	19,65	
	0,95	22,006	
	0,95	8,88	Desorption values
	0,89	6,147	
	0,83	4,105	
	0,51	2,76	

The cycle provided an adsorption process that approximately responded to a first-degree equation, while the desorption, a real deviation and responded to a typical second-degree equation $y = kx^2+bx+c$. In the case of adsorption, the graphical approximation is clear with the line of linearity.

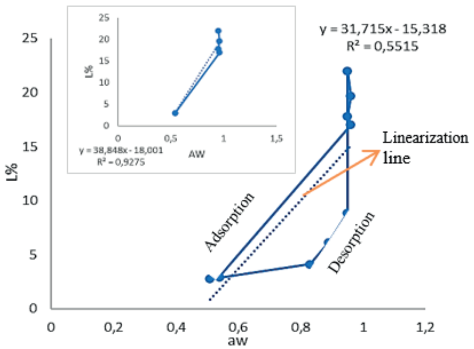

Figure 5. The adsorption/ desorption cycle obtained for walnuts (Inner graph - the adsorption isotherm only)

Walnuts are often consumed in a period of time, away from their collection and processing. So, in the risk of microbiological and physicochemical pollution, desorption is of particular interest, since their storage in an open environment can be done under different conditions of working practices. For this reason, desorption process was used for a test sample, and it was studied without changing the water absorption conditions, to verify the shape of the desorption lines. The results are presented in the Table 5 and Figure 6. Differences in the values of water activity are related with the tissue structure and porosity of the selected sample.

Table 5. Aw-moisture dependence of walnuts in the conditions of the desorption study

	Aw	L%	
The adsorption of the existing sample	0,54	2,93	
	0,96	16,99	
	0,95	17,8	
	0,96	19,65	
	0,95	22,006	
	0,95	18,97	Desorption of a new sample
	0,95	12,41	
	0,83	4,8	
	0,56	3,1	

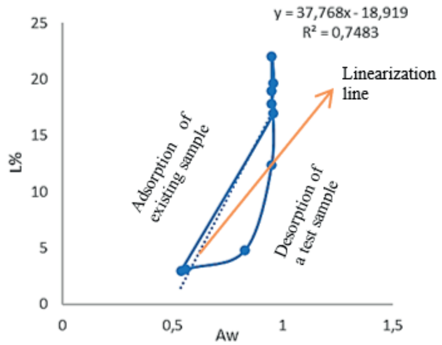

Figure 6. The cycle of adsorption-desorption for walnuts

Comparison of the Figures 5 and 6 clearly represents and verifies the same shape of desorption line, so this cycle can be used in any case for walnut samples, also for the linearization of the desorption curve, using B.ET. Equation (Damodaran et al., 2007) as below:

$$\frac{a_w}{m\,(1-a_w)} = \frac{1}{m_1 c} + \frac{c-1}{m_1 c}\, a_w$$

Where:
m - moisture, g H_2O/g dry matter
a_W - water activity
m_1 - BET monolayer value
c - a constant.

CONCLUSIONS

The evaluation of water activity is a very convenient method to observe the condition of dried fruits in water sorption and desorption processes, so their drying processes can be evaluated both by determining the moisture and the a_w values. Theoretical and experimental study of water activity concept, allows evaluating the choice of method of preserving food.

The evaluation of the physicochemical parameters of dried fruits in conservation, it was found to be within the limits allowed by law. This shows that for the samples in this study, there was no visible impact on the change of these parameters during the storage period. However, water activity, pH, temperature, and other parameters, have a direct impact on the microbial growth, thus a_w and pH are two of the most important parameters taken into consideration.

The high content of proteins, fats and dry matter brings the respective value of a_w below 0.6-0.7. During the study of the hysteresis cycle for walnuts, it was possible to obtain a second-order desorption curve and a straight line of the type y = kx+b for the adsorption process, with the best possible approximation ($R^2 = 0.9275$).

From the results presented also graphically, an experimental study extended in time for walnuts in storage is suggested. A comparison of a_w values is proposed to be evaluated, in order to observe if there have been created conditions to develop harmful microorganisms, mainly aflatoxin-producing moulds taking into consideration also pH as a very important indicator. It is also suggested that the evaluation of a_w can be accompanied by respective microbiological tests, in order to analyse the microbial growth in the same samples under study and to isolate and identify the specific strains of interest in this field.

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