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Sorption isotherms for osmo-convectively-dried and osmo-freeze-dried apple, sour cherry, and blackcurrant

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SUMMARY

The aim of our work was to measure sorption isotherms on freeze-dried and convectively-dried fruits (apple cv. Idared; sour cherry cv. English Morello; blackcurrant cv. Tiben), previously osmotically dehydrated in fructo-oligosaccharide solution, or concentrated apple juice. Isotherms were fitted using the Guggenheim-Anderson-de Boer Model. In none of the cases studied was isotherm non-continuity in the vicinity of the initial value of a_w observed. All isotherms, classified as type III, demonstrated an increase in the equilibrium water content, along with an increase in water activity. A higher water content was observed in lyophilised material compared to material dried by convection. The water content in the monolayer (100 g^{-1} dry matter) ranged from 12.0 g for dried apple, to 17.0 g for dried sour cherry. These values can be considered as optimal in order to ensure safe storage conditions. The dried fruits should therefore be kept in a water activity range of 0.45 – 0.54 for lyophilised, and 0.46 – 0.63 for convectively-dried material.

Osmotic dewatering is a mass transfer process which leads to many changes in the chemical composition and physical properties of food (Torreggiani and Bertolo, 2001; Sablani *et al.*, 2002; Lewicki and Porzecka-Pawlak, 2005). One of these properties is water sorption. The level of moisture affects the physical and rheological characteristics of food, and its stability (Lewicki, 2004).

Water activity (a_w) is defined as the ratio of the vapour pressure of water in the food to the vapour pressure of pure water at the same temperature (McLaughlin and Magee, 1998). Water activity indicates how tightly the water is bound in the food, from a structural and chemical point of view, and hence describes the availability of the water to participate in chemical and biochemical reactions. For example, non-enzymatic browning is most intense at a_w values in the range of 0.6 – 0.7 (Fontana, 1998). In addition, it is known that the microbial stability of food is strongly dependent on its water activity. Different microorganisms require different levels of a_w for their growth. No microbial proliferation occurred when the a_w was $\leq$ 0.5, but it was assumed that microbiological safety was ensured when the a_w value was $\leq$ 0.6 (Beuchart, 1981; Prothon and Ahrne, 2004).

A common way of presenting the relationship between a_w and water content is a sorption isotherm (Falade *et al.*, 2003; Kaymak-Ertekin and Gedik, 2004; Gondek and Lewicki, 2005); however, there is no direct relationship between these two parameters. The shape of the curve depends, above all, on the composition and structure of the material, temperature, and pressure (Mayor *et al.*, 2005).

Many mathematical models to describe the water sorption behaviour of foods can be found in the literature (see Kaymak-Ertekin and Gedik, 2004; Mayor *et al.*, 2005, Moraga *et al.*, 2006). The Guggenheim-Anderson-de Boer (GAB) Model is considered to be the most versatile and the best one for fitting the sorption data for the majority of food products in a water activity range of 0 – 0.85 (Lomauro *et al.*, 1985; Prothon and Ahrne, 2004; Mayor *et al.*, 2005).

Knowledge of water sorption characteristics is important for shelf-life predictions and determinations of the critical moisture for the acceptability of products that lose quality mainly by moisture absorption. The ability to predict water content during storage can lower the cost of product development, and shorten the time for shelf-life estimations (Siripatrawan and Jantawat, 2006).

This approach was chosen as one tool to support the development of new dried fruit products undertaken within the ISAFRUIT Project. Among the osmotic agents investigated and anticipated to have a positive health impact (Konopacka *et al.*, unpublished), fructo-oligosacharide syrup (with prebiotic potential impact) and concentrated apple juice (building sweetness using natural fruit sugars) were selected for this study on sorption properties, due to their ability to create the desired sensory properties of osmo-dried fruit. The aim of our work was to measure the sorption isotherms for newly-designed dried fruit products formulated with a promising osmotic agent using the Dehydration-Impregnation by Soaking (DIS) technique, then freeze-dried or convectively-dried.

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MATERIALS AND METHODS

Production of osmo-dried fruit

Dried fruit products were produced from apple (‘Idared’), sour cherry (‘English Morello’), or blackcurrant (‘Tiben’) harvested in Poland in 2006. The apples were cut into 1 cm cubes before freezing. The sour cherries were stoned. The blackcurrants were frozen, without pre-treatment but, on the day of processing, the frozen berries were scratched in the carborundum drum of kitchen food processor (Talent 881.0; Zelmer, Rzeszów, Poland). Blackcurrant fruit were abraded in 200 g portions on the lowest machine speed for 60 s. Each sample of frozen blackcurrant material (approx. 500 g) was dipped into an osmotic solution [4:1 (w/w) syrup:fruit ratio] placed in a container. The containers were then placed in a shaking water bath (SW 22; Julabo, Seelbach, Germany) at 100 rpm and an amplitude of 20 mm, at 40°C.

Two hypertonic solutions 60° Brix were used for osmotic dehydration: (i) a fructo-oligosaccharide (FOS) preparation containing 51.7% (w/w) dry weight (DW) FOS, 12.1% (w/w) sucrose, 33.6% (w/w) glucose, and 2.6% (w/w) fructose for sour cherry and blackcurrant; or (ii) an apple concentrate containing 20.5% (w/w) sucrose, 17.8% (w/w) glucose, 58.2% (w/w) fructose, 3.5% (w/w) sorbitol, and 3% titratable acids (as malic acid) for apple.

Osmotic dehydration was carried out for 60 min at 40°C. The fruits were then drained and rinsed with cold distilled water, and gently blotted on filter paper (Stanlab, Lublin, Poland). Each fruit sample was then split into two portions. The first was subjected to convective drying (sour cherry, 8 h at 60°C; blackcurrant, 10 h at 60°C; apple, 4 h at 60°C). The other portion of each sample was freeze-dried (–30°C for 24 h and 50°C for 2 h).

Determination of sorption isotherms

Samples of whole dried fruits of known weight [two samples of each product: convectively-dried apple (2.43 ± 0.22 g), freeze-dried apple (1.94 ± 0.16 g), convectively-dried sour cherry (5.00 ± 0.49 g), freeze-dried sour cherry (3.20 ± 0.20 g), convectively-dried blackcurrant (4.84 ± 0.56 g), and freeze-dried blackcurrant (3.53 ± 0.30 g)] were placed in desiccators containing ten different saturated salt solutions: LiCl ($a_w = 0.113$), H_2SO_4 (1,495 g l^{-1}, $a_w = 0.157$), potassium acetate ($a_w = 0.225$), $MgCl_2$ ($a_w = 0.329$), K_2CO_3 ($a_w = 0.438$), $Mg(NO_3)_2$ ($a_w = 0.529$), $NaNO_2$ ($a_w = 0.648$), NaCl ($a_w = 0.753$), $(NH_4)_2SO_4$ ($a_w = 0.810$), or $BaCl_2$ ($a_w = 0.903$). Thymol was placed in the desiccators containing NaCl, $(NH_4)_2SO_4$, and $BaCl_2$ in order to prevent the growth of mould. After 3-months storage at 25° ± 1°C, the samples were weighted (Gondek and Lewicki, 2005). The water content sorption isotherms were then fitted using the Guggenheim-Anderson-De Boer (GAB) Model, as follows:

$$M = M_m \times C \times k \times a_w / [(1 - k \times a_w)(1 - k \times a_w + C \times K \times a_w)]$$

where, M is the moisture content [g 100 g^{-1} dry matter (DM)], a_w is the water activity, and M_m, k, and C are GAB constants.

The DM content was determined by drying samples in a vacuum oven at 70°C (Gondek and Lewicki, 2005). The experimental data were fitted to the Model using a non-linear regression (STATISTICA Version 5; StatSoft, Inc., Tulsa, OK, USA). In order to evaluate the goodness-of-fit of each equation to the experimentally determined isotherms, mean relative percentage deviation modules (RMS) were calculatedas follows:

$$RMS = 100 \times \left(\Sigma\ [(u_e - u_o) / u_e]^2 / N\right)^{0.5}$$

where N is the number of data, u_e is the experimental value for the moisture content, and u_o is the predicted value for the water content.

TABLE I

Water activity and dry matter (DM) content of dried fruit

Fruit	Water activity (a_w)	Dry matter content [% (w/w)]
Osmo-convectively-dried apple	0.542	92.4
Osmo-freeze-dried apple	0.219	99.6
Osmo-convectively-dried sour cherry	0.699	71.8
Osmo-freeze-dried sour cherry	0.294	97.8
Osmo-convectively-dried blackcurrant	0.633	88.3
Osmo-freeze-dried blackcurrant	0.267	97.2

RESULTS AND DISCUSSION

Among the fruits prepared for the present investigation, blackcurrants were characterised by having the highest water activities (0.699 for convectively-dried fruit and 0.294 for freeze-dried fruit; Table I). The lowest a_w values were observed for convectively- and freeze-dried apples, being 0.542 and 0.219, respectively. The corresponding DM contents for each product are also presented in Table I. The parts of the isotherms (shown in Figures 1 – 3) situated on the left-side of the initial a_w values illustrate the desorption process. Parts of the curves situated on the right-side of the points illustrate the adsorption process. In none of the cases studied was an isotherm non-continuity observed in the vicinity of the initial value of a_w. This may illustrate a lack of hysteresis in the measurements of a_w. A similar behaviour in sorption isotherms has been observed for osmotically-dehydrated raisin, apricot, mango, and pineapple (Gondek and Lewicki, 2005). Roman *et al.* (1982) linked the lack of hysteresis with dissolving and crystallisation of sugars. Bolin (1980), Tsami *et al.* (1990), Lahsasni *et al.* (2004), and Moraga *et al.* (2004) reported the presence of hystereses in the isotherms for different fresh and processed fruit (e.g., raisin, pear, strawberry).

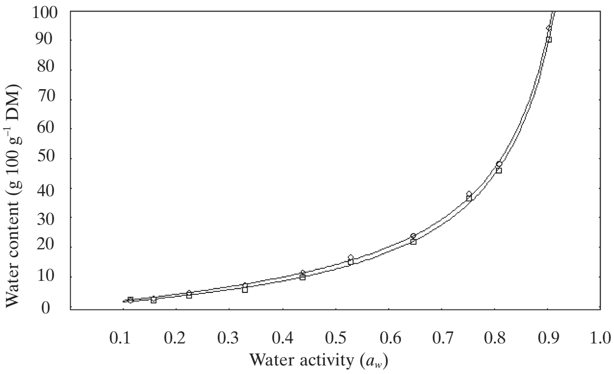

FIG. 1

Sorption isotherms of osmo-convectively-dried apple (□) and osmo-freeze-dried apple (○).

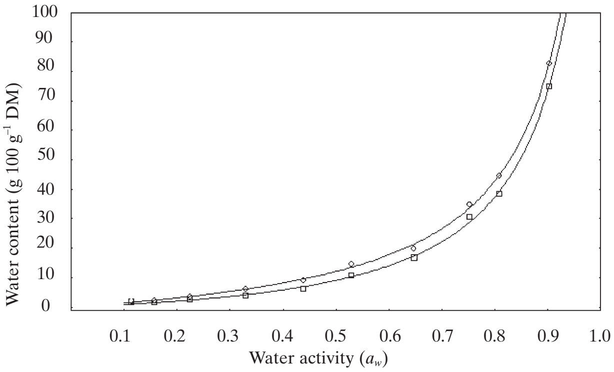

FIG. 2
Sorption isotherms of osmo-convectively-dried blackcurrant (□) and osmo-freeze-dried blackcurrant (○).

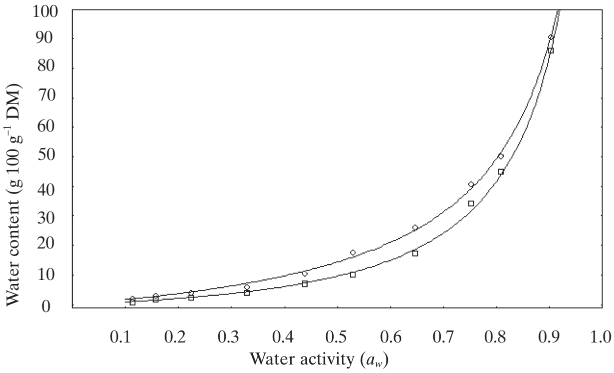

FIG.3
Sorption isotherms of osmo-convectively-dried sour cherry (□) and osmo-freeze-dried sour cherry (○).

All the isotherms presented demonstrated an increase in the equilibrium water content along with an increase in a_w. In addition, for each fruit, a higher water content was observed in the lyophilised material after 3-months storage compared with material dried by convection. These differences were smallest for apple (Figure 1), more pronounced for blackcurrant (Figure 2), and greatest for sour cherry (Figure 3). This recurrent dependence may result from considerable changes in the structure of fruit subjected to high temperatures during convective-drying, compared to freeze-drying, in which the structure remains virtually unchanged. Shrinkage of fruit during convective-drying causes the water-holding sites to come sufficiently close to one another to interact and to form a metastable state. Consequently, the water binding capability of such material is lower. Maskan and Göğüş (1998) pointed to this theory as one that can also explain the phenomenon of hysteresis.

Apples subjected to convective-drying or lyophilisation demonstrated a higher equilibrium water content over the whole range of a_w (Figure 1) than blackcurrants (Figure 2). Lyophilised sour cherries (Figure 3) contained the highest quantity of water among all the products tested for a_w in the range from 0.5 – 0.85, as opposed to convectively-dried sour cherries, which contained less water than dried apples and lyophilised blackcurrants. The equilibrium water content in blackcurrants dried by convection was the lowest among all the products tested over the whole water activity range, in particular for a_w values ≥ 0.5.

All the isotherms obtained had a similar shape, one characteristic of material containing considerable quantities of sugars (Maskan and Göğüş, 1998; Moraga *et al.*, 2004). They showed a relatively slow increase in water content for a_w values ≤ 0.5, a faster increase for average values of a_w ≥ 0.5, and a rapid increase for a_w ≥ 0.85. The low values of the energy constant (*C*), from 0.47 to 1.56 (Table II), indicated that all were type III isotherms (Roskar and Kmetec, 2005). Published data give a number of examples of processed fruits and vegetables (e.g., grape, apple, blueberry, pineapple, mango, apricot, and papaya) for which this type of sorption isotherm have been determined (Bolin, 1980; Lim *et al.*, 1995; Vazquez *et al.*, 1999; Konopacka *et al.*, 2002; Proton and Ahrne, 2004; Gondek and Lewicki, 2005). Mayor *et al.* (2005) placed the sorption isotherm for osmotically dehydrated papaya between a type II and a type III. Moraga *et al.* (2006), in turn, qualified the isotherms for kiwifruit processed in different ways as type II (the value of *C* was ≥ 2). This type of isotherm was also obtained in the case of fresh mulberry (Maskan and Göğüş, 1998).

The water contents in the monolayers (M_m; in g 100 g^{-1} DM) ranged from 12.0 – 12.3 for lyophilised and convectively-dried apples, respectively, to 16.8 and 17.0 for convectively-dried and lyophilised sour cherries, and remained in the upper interval of published values, for different fruits. The values for osmo-freeze-dried apples was slightly lower than that (14.1) for freeze-dried apple (‘Gloster’) given by Irzyniec *et al.* (2003). Moraga *et al.* (2006) determined M_m to be 4.7 for lyophilised kiwifruit. Falade *et al.* (2003) gave values of 7.94 – 11.19 (measured at 20°C) for osmotically-dehydrated then dried plantain slices, being higher when a more concentrated sucrose solution was used for fruit dehydration. Ayranci *et al.* (1990) reported higher values of M_m (9.7, 11.7, 12.6, 14.0, and 17.3) for figs, apricots, prunes, raisins, and currants, respectively. The value of M_m (17.4) given by Lim *et al.* (1995) for lyophilised blueberries was close to the values obtained in our studies for convectively-dried and lyophilised sour cherries (17.0 and 16.8, respectively). A very similar M_m value (17.06) was obtained by Vullioud *et al.* (2004) for fresh sour cherries and cherries. M_m values obtained by Kaymak-Ertekin and Gedik (2004) for apple (‘Starking’) not subjected to preliminary processing prior to convective drying were 17.6 in the case of adsorption, and 22.0 in the case of desorption (for fresh apples).

It is important to know the monolayer capacity (M_m) because the corresponding water content of the material is considered optimal from the point of view of food stability, and allows proper storage conditions (a_w) to be selected (Falade *et al.*, 2003). With regard to the similar values of M_m for lyophilised fruits and those dried convectively (Table II), the corresponding water content values were also similar and amounted to 11.0% and 10.7% (w/w) for convectively-dried and lyophilised apples, respectively, 12.6% (w/w) and 11.6% (w/w) for blackcurrants, and 14.5% (w/w) and 14.4% (w/w) for sour cherries. The a_w values corresponding to the values determined for M_m were as follows: for lyophilised and convectively dried apples, 0.45 and 0.46, respectively; for blackcurrants, 0.52 and 0.61, respectively; and for sour cherries, 0.54 and 0.63, respectively. Thus, in order to ensure the optimal storage conditions for any dried fruit, it should be kept in an atmosphere of the above-mentioned water activity (a_w).

Table II

Parameters of the Guggenheim–Anderson–De Boer (GAB) Model applied to the sorption data (M_m*, k, C), correlation coefficient (R), and mean relative percentage deviation module (RMS)*

Product	M_m (g 100 g^{-1} DM)	*k*	*C*	*R*	*RMS* (%)
Osmo-convectively-dried apple	12.334	0.972	1.162	0.9996	11.8
Osmo-freeze-dried apple	12.036	0.976	1.562	0.9997	7.9
Osmo-convectively-dried blackcurrant	14.391	0.945	0.556	0.9993	13.4
Osmo-freeze-dried blackcurrant	13.078	0.956	1.016	0.9995	9.6
Osmo-convectively-dried sour cherry	17.019	0.946	0.470	0.9992	13.8
Osmo-freeze-dried sour cherry	16.800	0.935	0.951	0.9993	12.1

CONCLUSION

Sorption isotherms for osmo-convective and osmo-freeze-dried apples, sour cherries and blackcurrants were characterised by low values of *C* (≤ 2), and so should be classified as type III isotherms. In none of the cases studied here was there isotherm non-continuity in the vicinity of the initial value of a_w. Lyophilised fruit material exhibited a higher water content over the whole range of water activity (a_w) than material dried by convection. Water contents in the monolayer (Mm) amounted to 12.3 and 12.0 g 100 g^{-1} DM for convectively-dried and freeze-dried apples, 14.4 and 13.1 g 100 g^{-1} DM for correspondingly dried blackcurrants, and 17.0 and 16.8 g 100 g^{-1} DM for correspondingly dried sour cherries. The water activity values (a_w) corresponding to these values were 0.45 and 0.46 for convectively-dried and freeze-dried apples, 0.52 and 0.61 for convectively and freeze-dried blackcurrants, and 0.54 and 0.63 for convectively and freeze-dried sour cherries. These a_w values are recommended for storage of the products under optimal conditions.

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