

‘GAB’ Generalised Equation as a Basis for Sorption Spectral Analysis

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Abstract

BLAHOVEC J., YANNIOTIS S. (2010): ‘GAB’ generalised equation as a basis for sorption spectral analysis. Czech J. Food Sci., **28**: 345–354.

The transformed sorption isotherm (represented by the ratio of water activity and moisture content (d.b.) versus water activity) was approximated by polynomials of 2nd–6th order. It is shown that the relative derivative of the transformed equation expresses the deviation of the sorption isotherm from the linear relationship between the moisture content and water activity either to the sorption isotherm of the Lagmuir’s type (the positive relative derivative) or to the sorption isotherm of the solution type (the negative relative derivative). The relative derivative plotted versus water activity then serves as a spectral indicator of the prevailing sorption mechanism. Spectral analysis is applied to sorption isotherms of potato and wheat starches and some fruits and vegetables. For starches, the differences in the spectral indicator between resorption and desorption as well as the effect of starch processing (gelatinisation and hydrolysis) on spectral analysis are discussed. The role of spectral analysis in the assessment of the prevailing sorption mechanism (surface vs solution sorption) is demonstrated for fruits and vegetables.

Keywords: sorption; isotherm; GAB; food; approximation; polynomial; water; activity; spectrum

Water in moist materials has an activity, which can reach the highest value of one. This water in equilibrium with the surrounding water vapour determines the sorption isotherms of the materials, i.e. the dependence between the moisture content (usually d.b.) and water activity at constant temperature.

The sorption isotherms of biological and food materials are mostly of sigmoid shape, type II of Brunauer’s classification (BRUNAUER 1943; BLAHOVEC & YANNIOTIS 2009). The sigmoidal sorption isotherms can be approximated by many sorption models. The ‘GAB’ (Guggenheim, Anderson, and de Boer) model is considered one of the most useful ones which in many simple sorption

cases can be used for the approximation of the experimental data at water activity of up to 0.9 (VAN DEN BERG 1984). ‘GAB’ equation is usually presented in the form:

$$w = \frac{w_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where:

w – moisture content (d.b.)

a_w – water activity

w_m, K, C – three free sorption parameters characterising the sorption properties of the material

Parameter w_m denotes the moisture content corresponding to the monomolecular layer on the whole free surface of the material; parameters K

and C depend on the temperature by Arrhenius type equations (VAN DEN BERG 1981, 1984) with the corresponding molar sorption enthalpies. BLAHOVEC (2004) showed that parameters K and C have to fulfil the following relations: $0 < K \leq 1$, whereas C should be higher than 0. For $C \geq 2$ the 'GAB' equation gives a sigmoidal shape curve with a point of inflection (II type of Brunauer's classification), but for $0 < C < 2$ the isotherm is of type III only.

The 'GAB' parameters w_m , K and C can be obtained easily after the transformation of equation (1) to equation (2) (HAILWOOD & HORROBIN 1946) in the following manner:

$$a_w/w = a + b_1 a_w + b_2 a_w^2 \quad (2)$$

K is the solution of the quadratic equation:

$$aK^2 + b_1 K + b_2 = 0 \quad (2a)$$

and then

$$C = (b_1/aK) + 2 \quad (2b)$$

$$w_m = 1/(b_1 + 2Ka) \quad (2c)$$

The 'GAB' equation has been successful in many cases (VAN DEN BERG 1984), however, there are also cases where the 'GAB' equation fails to describe some sorption isotherms, especially at higher water activities. This observation motivated TIMMERMAN and CHIRIFE (1991) to study the so-called third stage of sorption using the experimental data on starch. It seems that the 'GAB' rigidity causes problems with the approximation of some sorption data (BLAHOVEC 2004; BLAHOVEC & YANNIOTIS 2008, 2009), especially in such cases where sorption has more sources (different substances aggregated in one product, etc.). Formulas (2a), (2b), and (2c) give then unreasonable values for w_m , C , and K which, in some cases, are in conflict with the above mentioned limits. In a previous paper, we showed that the standard 'GAB' formula can be generalised either by adding new terms of higher order to the polynomial of the second order on the right side of Eq. (2) (BLAHOVEC & YANNIOTIS 2008) or by modification of HAILWOOD and HORROBIN'S (1946) expression for the moisture content (the generalised HH isotherms (BLAHOVEC & YANNIOTIS 2009)).

In this paper, we apply the generalised 'GAB' formula to sorption isotherms of the basic types of Brunauer's classification to explain the differ-

ences between the types as well as the basic special isotherm properties. The differences between the real types are expressed via the sorption spectra evaluating the presence of different kinds of sorption.

Basic property of the reciprocal secant-slope transformation (RSS-transformation)

The left side of Eq. (2) represents a special type of moisture content transformation. We will term it RSS-transformation denoted as $[w]$ and defined as:

$$[w] = a_w/w \quad (3)$$

that can be rearranged into the following form:

$$[w]w = a_w \quad (3a)$$

The first and second derivatives of this formula give:

$$([w]w)' = [w]'w + [w]w' = 1 \quad (4)$$

$$([w]'/[w]) + (w'/w) = 1/([w]w) = 1/a_w \quad (4a)$$

$$([w]w)'' = 0 = [w]''w + 2[w]w' + [w]w'' \quad (5)$$

$$([w]'/[w]) + (w'/w) = 1/([w]w) = 1/a_w \quad (5a)$$

where quotes express derivatives versus a_w

More information on the properties of RSS transformation will be published elsewhere (BLAHOVEC – unpublished).

Generalised 'GAB' model

The generalised 'GAB' equation can be expressed in the following form (BLAHOVEC & YANNIOTIS 2008):

$$[w] = a + \sum_{i=1}^n b_i a_w^i \quad (6)$$

where:

n – order of the polynomial
 $a, b_i (i = 1, n)$ – polynomial coefficients

For $n = 2$, Eq. (3) is the standard 'GAB' equation with coefficients:

$$a = 1/w_m KC \quad (6a)$$

$$b_1 = (1/Cw_m)(C - 2) \quad (6b)$$

$$b_2 = (K/Cw_m)(1 - C) \quad (6c)$$

These coefficients are very important also for the generalised 'GAB' because they determine the initial point of $[w] - a_w$ plot:

$$[w]_0 = a \quad (7a)$$

$$[w]'_0 = b_1 \quad (7b)$$

$$[w]''_0 = 2b_2 \quad (7c)$$

where: subscript 0 denotes that it corresponds to $a_w = 0$

In the standard 'GAB' theory, $[w]$ is a parabolic function of a_w and $[w]'$ decreases linearly in most cases (C is higher than 1 and b_2 is negative in this case – BLAHOVEC (2004)) up to the final value $b_1 + 2b_2$ at $a_w = 1$. The second derivative $[w]''$ is independent of water activity and equals $2b_2$. It means that:

$$[w]'_1 = [w]'_0 + [w]''_0 \quad (7d)$$

The derivatives of $[w]$ higher than the second one are zero in this case. The 'GAB' generalisation in Eq. (6) can be then understood as the acceptance of the existence of the nonzero higher $[w]$ derivatives leading to Eq. (6) as a part of the Taylor set for $f(a_w) = [w]$ at the point $a_w = 0$:

$$f(a_w) = f(0) + \sum_{i=1}^{\infty} \frac{f^{(i)}(0)}{i!} a_w^i \quad (8)$$

where:

$$f^{(i)}(0) \equiv [w]^{(i)}_0 - i^{\text{th}} \text{ derivative of the function } f \text{ at the point } a_w = 0$$

The polynomial expression for $[w]$ in Eq. (6) allows to calculate directly the derivatives of $[w]$ for $a_w = 0$. dw/da_w at this point can be also calculated. This is a rather harmful process in which l'Hospital rule has to be used repeatedly. The first four derivatives were calculated and are given in Table 1. The results are in agreement with simpler formulas given in a previous paper (BLAHOVEC 2004). In the generalised 'GAB' theory, the expressions like those in Table 1 are more complicated than those for the standard 'GAB' because in the standard theory the terms containing b_3 and/or coefficients given by $[w]$ derivatives of the order higher than 2 are zero.

Table 1. Equations for a_w derivatives of w ($a_w = 0$) calculated from parameters of Eq. (3)

Derivative	Formula
First	$1/a$
Second	$-2b_1/a^2$
Third	$\frac{6}{a^2} \left(\frac{b_1^2}{a} - b_2 \right)$
Fourth	$\frac{18}{a^2} \left(\frac{2b_1b_2}{a} - \frac{b_1^3}{a} - b_3 \right)$

It is not difficult to calculate a_w derivatives of $[w]$ for special values of a_w ; their values at $a_w = 1$ can be calculated easily as shown below for their lower degrees:

$$[w]_1 = a + \sum_{i=1}^n b_i \quad (9a)$$

$$[w]'_1 = \sum_{i=1}^n i b_i \quad (9b)$$

$$[w]''_1 = \sum_{i=2}^n i(i-1) b_i \quad (9c)$$

where: subscript 1 denotes $a_w = 1$

The generalised 'GAB' theory gives results that differ from the standard theory: in the case of $[w]$ vs a_w plot, the difference is expressed as non-parabolicity of the plot. These deviations are difficult to rationalise. It could be done more easily for a_w plots of the $[w]$ first derivative, because in this case the standard 'GAB' theory gives a simple linear plot.

Brunauer's types of sorption isotherms

The Brunauer's types of sorption isotherms are given in the usual form in Figure 1. The most different types in this classification are types I and III: the first one exhibits a sharp increase in w at low water activity values but the slope decreases over the whole water activity range whereas in the second case, the small initial slope of the water content to water activity plot increases over the whole water activity range. Type II can be understood as a combination of types I and III; type I at lower water activities and type III at higher water activities. Types IV and V are modifications of types II and III, respectively. The modifications consist in mechanisms similar to those in type I superimposed on the modified mechanisms at high water activities.

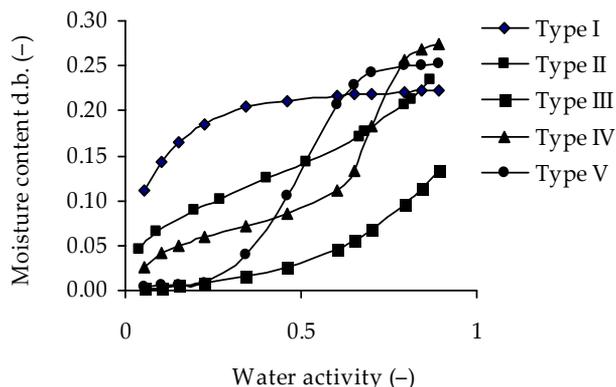


Figure 1. The basic sorption isotherm types of Brunauer’s classification (BRUNAUER 1943)

Figure 2 contains the sorption data from Figure 1 recalculated into the $[w] - a_w$ plot. The data from class I isotherm lead to the increasing, nearly linear, $[w] - a_w$ plot. In the case of the most important representative of this class, the Langmuir’s isotherm (ADAMSON 1976), Eq. (6) reduces to the following simple form:

$$[w] = a + b_1 a_w \tag{10a}$$

Equation (10a) with only two parameters a and b_1 represents a good approximation for experimental isotherms of this type in many cases. The isotherm of the III-rd type is represented by a decreasing function in the $[w]$ vs a_w plot, and in the special case of generalised Raoult’s law for solutions it can be expressed in the following linear form:

$$[w]_0 = a - b_1 a_w \tag{10b}$$

Usually, an increase of the polynomial degree on the right sides of Eqs. (10a) and (10b) does not lead to a much better approximation of the

Table 2. Coefficients of determination for the generalised ‘GAB’ approximation (Eq. (6)) to data plotted in Figure 2b

Brunauer’s class (n)	IV	V
2	0.8909	0.8429
3	0.8983	0.8429
4	0.9613	0.9025
5	0.9804	0.9514
6	0.9805	0.9695

experimental data for classes I and III. The sorption isotherms of type II are well approximated by the ‘GAB’ theory via Eq. (2).

The sorption isotherms of the IV-th and V-th type should be approximated by Eq. (6) with polynomials of an order higher than the 2nd on the right side. The coefficients of determination obtained for different polynomial orders for the data of Figure 2b are given in Table 2. It is clear that with increasing polynomial order the coefficient of determination increases for both the IV-th and the V-th Brunauer’s classes.

The analysis of $[w] - a_w$ plots of different sorption isotherms shows that we can determine the two most important basic types of sorption isotherms: Langmuir’s type (Brunauer’s type I) with increasing $[w] - a_w$ plot, and Rault’s type (Brunauer’s type III) with decreasing $[w] - a_w$ plot. The third very important type is the Brunauer’s type II represented by a parabolic $[w] - a_w$ plot. It is represented by the classical ‘GAB’ equation, which approximates well a great part of the isotherm for many different materials. It can be used also for the estimation of the materials free surfaces. On the other hand, the Brunauer’s classes IV and V represent only a small part of real

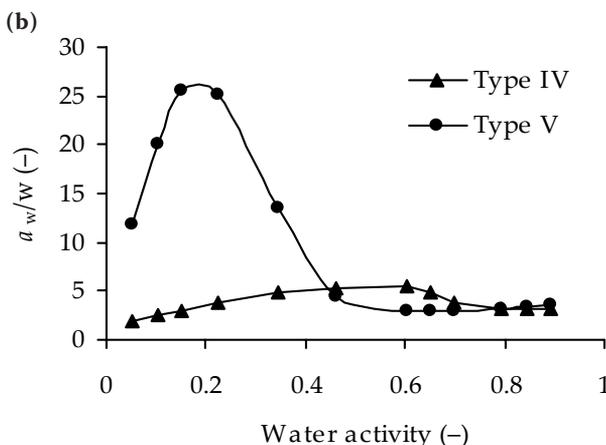
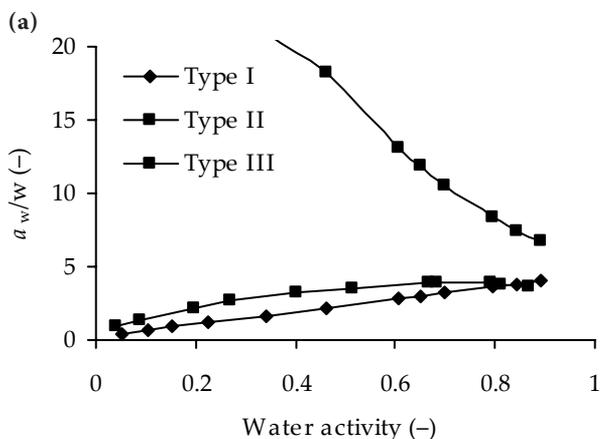


Figure 2. Sorption isotherms of Brunauer’s classes from Figure 1 as $[w] - a_w$ plots: (a) Basic classes (I, II, and III), (b) Modified classes (IV and V)

Table 3. Coefficients of the polynomials ($a, b_i, i = 1, 6$) obtained for native potato starch resorption (R) and desorption (D) (data VAN DEN BERG 1981)

Polynomial degree	A	b_1	b_2	b_3	b_4	b_5	b_6	R^2
R_2 (GAB)	0.634	9.452	-7.66					0.992
R_6	0.332	16.8908	-64.48	204.0	-375.0	339.0	-118.6	0.997
D_2 (GAB)	0.536	7.119	-5.40					0.979
D_6	0.311	12.675	-43.86	123.6	-219.4	204.8	-76.3	0.998

sorption isotherms as products of combination of the basic isotherm classes that varies with the water activity level. Detailed analysis of real sorption isotherms using the generalised HH sorption isotherm was done in a previous paper (BLAHOVEC & YANNIOTIS 2009). It was shown that, in most cases, the classification and isotherm approximation were carried out successfully by combining the surface and solution sorption phenomena (YANNIOTIS & BLAHOVEC 2009).

'GAB' sorption spectral analysis

Spectral analysis of sorption isotherms is based on Eq. (4a) according to which the relative moisture content w'/w is expressed as:

$$\frac{w'}{w} = \frac{1}{a_w} - \frac{[w]'}{[w]} \quad (11)$$

When $[w]'/[w]$ equals zero, then $w' = w/a_w$. The solution of this simple differential equation is

$w = ka_w$, where k is an arbitrary constant. The term $[w]'/[w]$ is then a measure of the deviation from the proportional relation between w and a_w . The deviation is positive when $[w]'/[w]$ is less than 0 and vice versa. The zero point of $[w]'/[w]$ corresponds to the zero point of $[w]'$ and, consequently, to the maximum of $[w] - a_w$ plot. The positive $[w]'/[w]$ corresponds more to "Langmuir's" surface sorption, whereas the opposite sign of $[w]'/[w]$ corresponds more to Raoult's solution sorption. The absolute value of the ratio $[w]'/[w]$ is then a measure of the prevalence of the dominating source of sorption. The domination of the source of sorption is a_w -dependent and it has to be expressed in a spectral plot versus a_w . The whole spectrum of $[w]'/[w]$ can then be evaluated by its mean value.

Starch data

The analysis here is based on Eq. (6) which serves as a basis for the calculation of the polynomial

Table 4. Characteristic mean spectral values of $[w]'/[w]$ for sorption of potato and wheat starch based on polynomials of 6-th order. Partial mean values of $[w]'/[w]$ over three ranges of a_w and mean values over the whole range of a_w are presented. The last column contains the a_w values which corresponds to the zero value of $[w]'/[w]$ (Original starch data at room temperature – VAN DEN BERG 1981)

	a_w	0.01–0.2	0.21–0.8	0.81–0.99	Total	a_{w_0}
Potato	resorption native	8.431	0.649	-2.270	1.678	0.612
	desorption native	7.829	0.799	-2.069	1.686	0.801
	resorption gelatinised	7.223	0.527	-4.292	0.964	0.724
	desorption gelatinised	8.744	0.911	-3.853	1.595	0.822
	resorption hydrolysed	6.043	0.634	-3.690	0.906	0.628
	desorption hydrolysed	5.384	0.798	-2.780	1.048	0.722
Wheat	resorption native	12.058	0.915	-2.907	2.458	0.793
	desorption native	12.910	1.056	-2.872	2.724	0.864
	resorption gelatinised	6.452	0.666	-4.005	0.948	0.671
	desorption gelatinised	9.025	0.999	-3.692	1.738	0.824

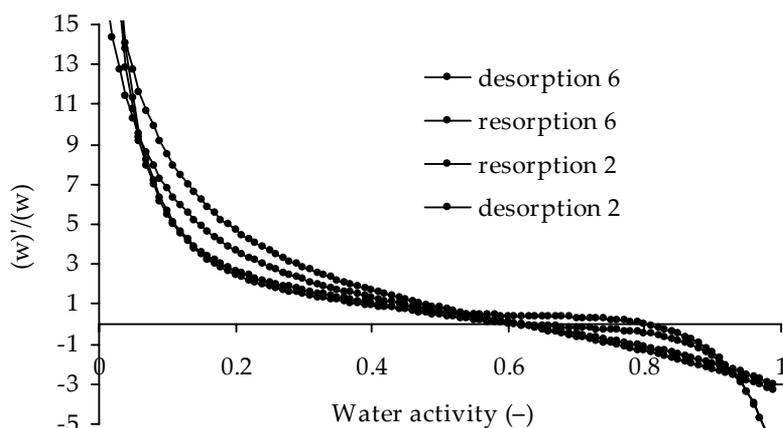


Figure 3. Spectral plot of the deviation of $[w]'/[w]$ vs a_w based on the data from VAN DEN BERG (1981) for potato starch. The data were used for the determination of parameters a and b_i in Eq. (6) (BLAHOVEC & YANNIOTIS 2008 – see example in Table 3). The number in the experimental regime (resorption or desorption) shows the degree of the polynomial used for the approximation of the data (2 means $i = 2$ (GAB equation), 6 means $i = 6$ in Eq. (6))

parameters a , and b_i ($i = 1 - 6$) from the experimental data (BLAHOVEC & YANNIOTIS 2008). The experimental data taken from VAN DEN BERG (1981) for potato and wheat starches are used here. Examples of the calculated polynomial parameters are given in Table 3. The corresponding spectra of $[w]'/[w]$ are plotted in Figure 3. Besides the curves based on the GAB equation, this figure contains the curves for Eq. (6) with $n = 6$. Comparing these curves, we can set two most important differences: (i) the shift of zero point to higher a_w values and (ii) systematic differences either at low a_w values (0.1–0.3) or at high a_w values (higher than 0.7). As to the sorption data approximated by a polynomial of 6-th order, we are able to distinguish between resorption and adsorption; the $[w]'/[w]$ plot lies a little higher for desorption than for adsorption, especially at higher water activities. Also, the shift

of zero point to higher water activities is higher at desorption than at adsorption.

The information on the spectral properties of different starch modifications studied by VAN DEN BERG (1981) is given in Table 4 and Figures 4–6. Figure 4 contains graphical information on the spectral aspects of the differences between native, gelatinised, and hydrolysed potato starch. This figure shows that at low water activities hydrolysed starch has lower values of $[w]'/[w]$ than native and gelatinised starches, indicating a softer surface adsorption with this modification of starch. On the other hand, the sharp decrease of $[w]'/[w]$ at high water activities indicates (Figure 4b) strong solution effects with hydrolysed starch at high water activities.

For further analysis, we can divide the whole scale of water activity into three parts: the part

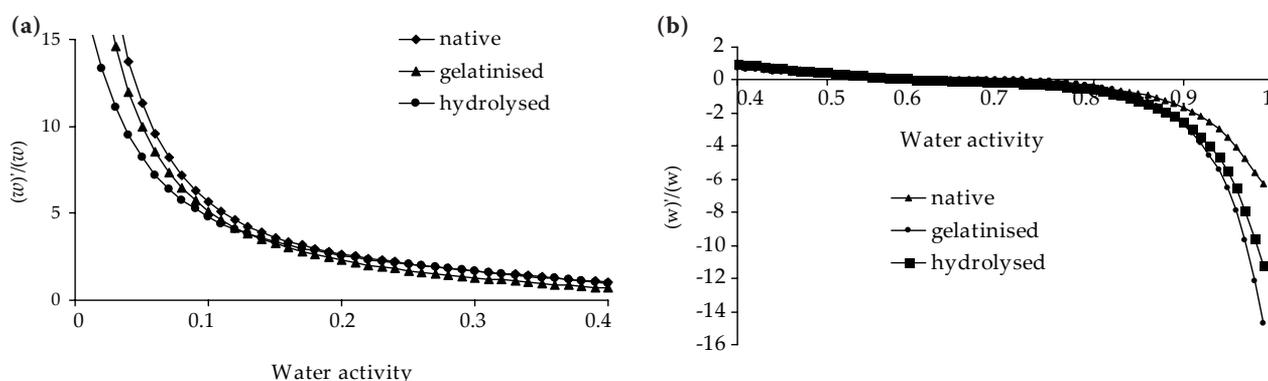


Figure 4. Spectral plot of the deviation $[w]'/[w]$ obtained similarly as in Fig. 3 for potato starch resorption. The results for native, gelatinized and hydrolysed starches are given: (a) data for a_w less than 0.4, (b) data for a_w higher than 0.4

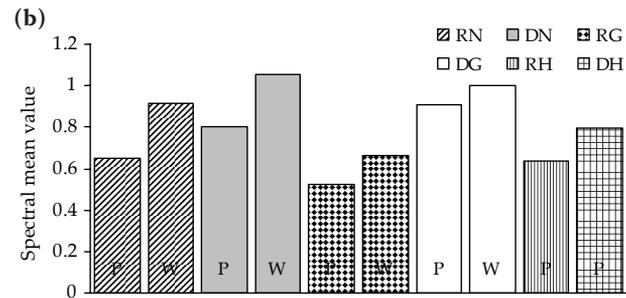
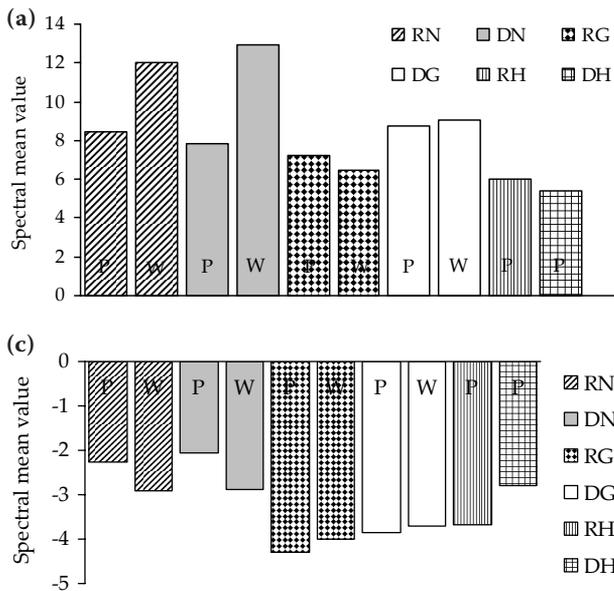


Figure 5. Mean values of $[w]'/[w]$ calculated in parts of the water activity scale for potato (P) and wheat (W) starches – (a) $a_w = 0.01 - 0.2$, (b) $a_w = 0.21 - 0.8$, (c) $a_w = 0.81 - 0.99$

Data for native (RN – in resorption, DN – in desorption), gelatinised (RG – in resorption, DG – in desorption) and hydrolysed (RH – in resorption, DH – in desorption) starches were taken from van den Berg (1981)

with high spectral values for a_w below 0.2, the part with small spectral values for a_w between 0.2 and 0.8, and the part of the highest water activities where $[w]'/[w]$ decreases below zero. As shown in Figure 5, the mean values of the spectral parameter $[w]'/[w]$ in the three defined parts shows that $[w]'/[w]$ for starch decreases with the processing. Some exclusion is observed in desorption of the gelatinised starch at water activities below 0.8. In the native state, the $[w]'/[w]$ mean values are nearly comparable in desorption and resorption whereas in the case of processed starch, lower values of $[w]'/[w]$ are observed in resorption than in desorption. If we try to assess the role of surface and solution sorption in potato starch during resorption, we can arrange the different modifications in the decreasing order: for the surface adsorption (Figures 4a and 5a): native, gelatinised, hydrolysed; for the solution sorption (Figures 4b and 5c): gelatinised, hydrolysed, native. At desorption, the relations are similar. The difference between

hydrolysed starch and the other two starches may be due to the starch swelling and their saturation points (NARA 2006).

Figure 6 shows that the zero point of the spectral parameter $[w]'/[w]$ varies between 0.6 and approximately 0.85, being higher for desorption than for resorption. In the native state, the zero point is also higher for wheat starch in comparison with potato starch. This relation is not observed in the gelatinised state.

The spectral parameter varies also with temperature. This is demonstrated by the parameter $[w]'/[w]$ calculated in different water activity parts for three different temperatures (sorption data for potato starch from VAN DEN BERG 1981). As shown in Figure 7, $[w]'/[w]$ decreases with increasing temperature at least in the first two parts, that is for water activities below 0.8. The water activity (a_{w_0}) corresponding to the zero point of $[w]'/[w]$ was approximately the same (0.793) for all temperatures followed.

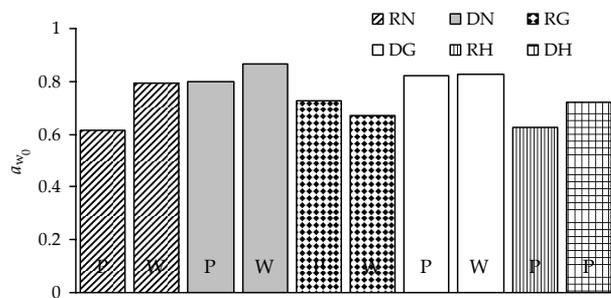


Figure 6. Water activity (a_{w_0}) at which spectral value $[w]'/[w]$ is equal zero. The symbols are the same as in Figure 5

The value $[w]'/[w]$ predetermines the w'/w plot as given in Figure 8 for the data obtained in resorption of native potato starch using polynomials of the second (GAB) and sixth orders. For comparison, the basic plot with $[w]'/[w] = 0$ is also given. The figure shows that the relative isotherm slope is not much model sensitive for water activity close to 0.5 whereas the opposite can be concluded for small and high water activities. The source of this higher model sensitivity can be found either in small w -values at low water activities (w is in the denominator of the ratio) or the real high model sensitivity at high water activities. This fact has a

Table 5. Parameters a and b_i of polynomial approximation for $[w]$ versus a_w plots for selected fruits and vegetables (YANNIOTIS & BLAHOVEC 2009)

Parameter	Pineapple		Lentils		Radish		Celery	
	$n = 4$	GAB	$n = 4$	GAB	$n = 4$	GAB	$n = 4$	GAB
a	5.19	7.69	0.77	0.93	0.82	2.15	1.39	2.34
b_1	36.62	-8.60	13.86	11.09	31.51	11.30	26.57	10.04
b_2	-200.72	1.66	-20.29	-9.44	-85.07	-14.98	-82.66	-12.24
b_3	327.53		15.13		81.06		108.28	
b_4	-175.18		-6.86		-26.98		-55.04	
R^2	0.981	0.926	1.000	0.998	0.998	0.842	0.992	0.920

Original sorption data were taken from WOLF *et al.* (1972); Two polynomials are used for the approximation: quadratic one (GAB – see Eq. (2)) and biquadratic polynomial ($n = 4$ – see Eq. (6)); R^2 is coefficient of determination

practical consequence; the usefulness of a sorption model has to be tested by experimental results at low and/or high water activities. The sorption data at water activities in the range 0.3–0.8 are not sufficient for the validation of a sorption equation. Many different equations can be used in this area for interpolation and/or smoothing purposes.

Fruit or vegetable data

Standard sorption data obtained experimentally with fruits and vegetables are not well approximated in many cases by the standard GAB theory (BLAHOVEC & YANNIOTIS 2008). These difficulties can be overcome by using the generalised GAB equation (Eq. (6)). The higher the polynomial degree, the better the approximation of the data; but some limi-

tations exist in this case: the polynomial degree is limited by the number of independent experimental points of the isotherm; the number of experimental points should be higher than $n + 4$, “ n ” is an even number (BLAHOVEC & YANNIOTIS 2008).

Since the number of available experimental points for fruits and vegetables is relatively low, $n = 4$ was used in our calculations.

The spectral values defined in Eq. (11) are plotted in Figure 9 for the parameters given in Table 5. It is clear that in most cases (Figure 9) the spectral plots of $[w]'/[w]$ versus a_w have very similar shapes as the spectral values for starch calculated with polynomials of the sixth order: the values are very low in the middle of the spectrum, i.e. for a_w values close to zero point of the plot; whereas in the other parts (well below and above the zero point), the spectral values are high in the absolute value but different for different sorption data. The results of spectral analysis are given in Table 6.

Table 6. Characteristic mean spectral values of $[w]'/[w]$ for sorption of selected fruits and vegetables; based on data from Table 5 (polynomial of 4-th order)

Water activity product	0–0.2	0.21–0.8	a_{w_0}
Pineapple	1.516	-2.189	0.13
Lentils	6.951	0.431	0.59
Radish	9.596	-1.318	0.29
Celery	6.001	-0.850	0.31

Two partial mean values of $[w]'/[w]$ are presented (the third part is missing due to missing sorption data for a_w higher than 0.8). The last column contains the water activity a_{w_0} corresponding to the zero value of $[w]'/[w]$ (at room temperature)

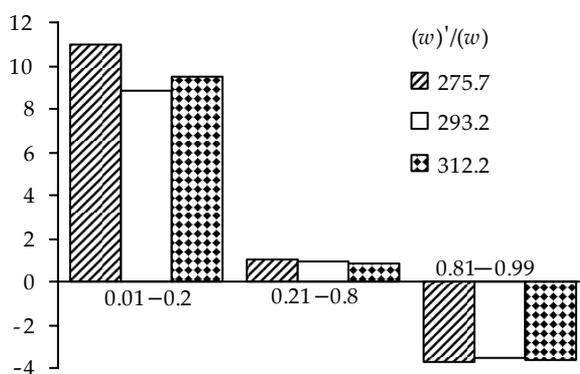


Figure 7. Mean values of $[w]'/[w]$ calculated in parts of the water activity scale for potato starch at different temperatures. The parts of water activity scale are the same as in Figure 5(a–c) and are denoted numerically close to the horizontal axis, the temperatures (in K) are given in the legend

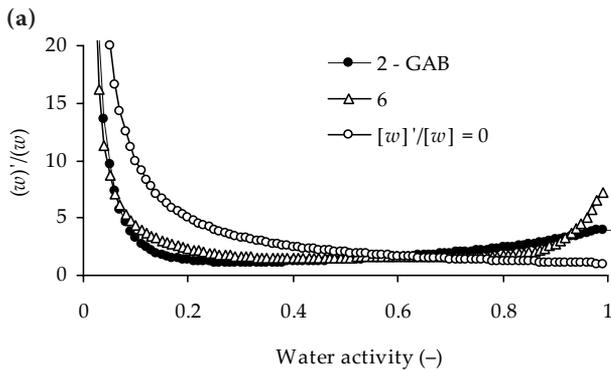


Figure 8. Spectral plot of the deviation w'/w computed from Eq. (11) for resorption of native potato starch. $[w]'/[w]$ was obtained similarly as in Figure 4 for $n = 2$ (GAB) or 6. The plot with $[w]'/[w] = 0$ is given for comparison

The $[w]'/[w] - a_w$ plot for lentils has the standard shape; at low a_w values, the $[w]'/[w]$ values are relatively high and slowly decrease, indicating a slow decrease of surface sorption. As shown in Table 6, the mean values of $[w]'/[w]$ equal 6.951 for $a_w = 0-0.2$ and 0.43 for $a_w = 0.2-0.8$. The negative values of $[w]'/[w]$, indicating the domination of solution sorption, appear at $a_w \sim 0.6$. The sorption properties of lentils are close to those of starch (Table 4). Radish and celery have intermediate properties with $[w]'/[w]$ zero point at a_w about 0.3. In this case, solution sorption dominates in the majority of water activities; The mean value of $[w]'/[w]$ for $a_w = 0.2-0.8$ is negative in both cases. The least effect of surface sorption is observed with pineapple. The $[w]'/[w]$ value at $a_w = 0$ is lower than half of the value for radish and celery, and at a_w little higher than 0.1, $[w]'/[w]$ changes the sign from positive to negative. The role of solution sorption is not simple in pineapple and in fruits and vegetables generally. Figure 9 shows some form of $[w]'/[w]$ recovery in falling down at higher a_w values. This behaviour could be caused by the activation of additional substances coming into solution at higher moisture contents.

CONCLUSIONS

Brunauer's classification of sorption isotherms can be reduced only to two basic isotherms: Lagmuir's type (Brunauer's type I) with a positive slope of the $[w]-a_w$ plot and Raoult's type (Brunauer's type III) with a negative slope of the $[w]-a_w$ plot. The other isotherms should be understood as the products of the 'GAB' generalisation using polynomials of

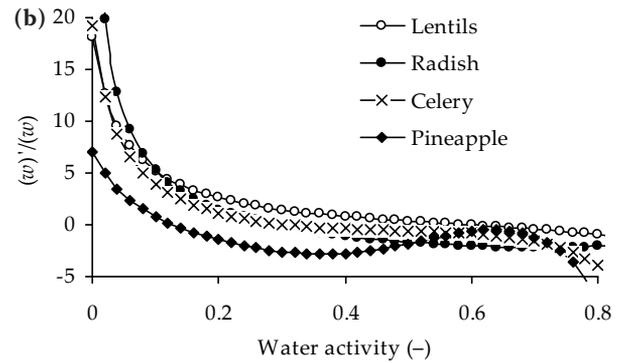


Figure 9. Spectral values of $[w]'/[w]$ corresponding to polynomial of the fourth order applied to the fruit and vegetable data of Table 5

the order higher than the second one in Eq. (6). They are well described via spectral plots of the relative first derivative of the transformed moisture content $[w]'/[w]$ versus water activity, where $[w] = a_w/w$ and w are the moisture contents d.b. $[w]'/[w]$ is termed spectral value and its local deviations from zero expresses isotherm deviations from the proportional relation between the moisture content and water activity. The positive $[w]'/[w]$ values denote deviations to the Lagmuir's sorption whereas negative values indicate deviations to the Raoult's sorption. The practical use of the polynomial approximation to a better description of the sorption phenomena in fruits and vegetables is also demonstrated.

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Received for publication July 8, 2009
Accepted after corrections March 16, 2010

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