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The energy of interaction between water and surfaces of biological reference materials

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Abstract

In the field of reference materials, long-term stability is of the highest importance. Particularly for biological matrices, any kind of deterioration must be avoided during shelf-life and several precautions are taken during production. It has been shown that several mechanisms of deterioration are associated with water activity and water content. Consideration of the availability of water for deteriorative processes will consequently lead to consideration of strong forces of interaction between water and the surface it is attached to. Data for the binding energy of water of four biological reference materials, cod fish muscle, whole grain wheat flour, whole milk powder and skim milk powder, will be presented as a function of the water content. Results obtained as isosteric heat of sorption, calculated from water sorption isotherms at several temperatures are compared with data resulting from a thermal analysis determination of the heat of evaporation of water from the surface. The latter approach combines the principles of differential scanning calorimetry and thermogravimetry. Findings are presented where the results for energy of interaction between water and surfaces, calculated as net isosteric heats of sorption, from water sorption isotherms, are confirmed by the heats of evaporation, determined from simultaneous thermal analysis. Furthermore, simultaneous thermal analysis has extended the range of validity towards dryness where data from water sorption isotherms become invalid.

Keywords: Water content; Moisture content; Water sorption isotherms; Reference materials; Isosteric heat; Calorimetry; Simultaneous thermal analysis

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1. Introduction

Water plays important roles in all biological systems as it also does in biological and environmental reference materials (BERMs) (Hill & Bender, 1994). It influences storing conditions and shelf life as well as textural and technological qualities (Lai & Schmidt, 1990). The influence of water on different requirements that BERMs must fulfil concerning their long-term stability, hygroscopicity and handling have been intensely discussed in former publications and findings for the influence of different determination methods for water and moisture on certified values of reference materials has been published (Rückold, Grobecker, & Isengard, 2000, 2001a, 2001b).

This paper focuses on the evaluation of the energy of interaction between water and the surface of BERMs.

The difference in results for the determination of water and moisture in biological matrices frequently leads to a consideration of the different binding forms of water (Hill & Bender, 1994). The weakness of defined properties, attributed to different physical states of water binding, is best expressed by a vocabulary to describe surface–water interactions. Terms in use are bound water, sorbed water, solid-like water, water of crystallization, imbibed water, water of hydration, immobilized water, unfreezable water, ice-like water, non-solvent water, monolayer water, and water available for certain processes such as microbial growth or chemical reactions (van den Berg, 1981).

A well-established and frequently applied method to quantify the magnitude of binding energy between water and surface is the calculation of net isosteric heat of sorption, ($Q_{st,net}$), from water sorption isotherms

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(WSIs) recorded at different temperatures (Gabas, Telis-Romero, & Menegalli, 1999; Gregg & Singh, 1997; Mulet, Garcia-Reverter, Sanjuán, & Bon, 1999; Rizvi, 1995). Nevertheless the determination of sorption isotherms reveals shortcomings in the area of very low relative humidity (RH) and water activity (a_w), where equilibrium states are difficult to achieve. This effect even led to conclusions that $Q_{st,net}$ reaches a maximum around the monolayer value and decreases towards dryness. This effect was for example attributed to a minimum of entropy around the monolayer region (Vivanco & Taboada, 1998).

Another technique employing differential scanning calorimetry (DSC) and thermogravimetry (TG) assesses the binding energy between water and surface directly; this is referred to as simultaneous thermal analysis (STA).

Combining these techniques with mass spectrometry (MS) allows control of produced vapours from substances other than water, particularly products of heat deterioration formed during the evaporation process and optimisation of heating conditions, so that water is well evaporated, but alterations, caused by heat during the evaporation of water, are avoided as much as possible.

Calorimetric techniques have been previously applied to determine isosteric heats of water on food, but data in literature are very rare (Mulet et al., 1999).

To our knowledge simultaneous measurement of DSC and TG, in combination with MS, has not yet been applied to determine the binding energies of water on biological matrices.

The object of this publication is to confirm the results for isosteric heats of sorption of four reference materials, cod fish muscle, whole grain wheat flour, whole milk powder and skim milk powder, obtained by water sorption isotherms at different temperatures with a second method. In addition, the results of the DSC/TG/MS technique are expected to contribute valuably, with practical data, to the theoretical discussion of the binding energy of water on surfaces in regions of very low relative humidity, where data obtained from water sorption isotherms lose their validity.

2. Materials and methods

2.1. Isosteric net heat of sorption or enthalpy of sorption

$Q_{st,net}$ is a thermodynamic parameter, obtained from equilibrium sorption data and represents the difference between the latent heat of adsorption and the latent heat of condensation of pure water. It can be determined according to an equation derived from the Clausius–Clapeyron equation (Rizvi, 1995):

$$\left[\partial \ln \left(p/p_0\right) / \partial(1/T)\right] = [\partial \ln (a_w) / \partial(1/T)] = Q_{st,net} / RT^2 \qquad (1)$$

where R is the universal gas constant, T the absolute temperature, p the equilibrium vapour pressure and p_0 the vapour pressure of pure water. WSIs were recorded at 20, 25, 30, 40 and 50 °C.

The water activity range was 0.05–0.75. Measurements were performed with an Igasorp moisture sorption analyser, Hiden Analytical, Warrington, England. The device flushes the sample with a mixture of dry and water-saturated nitrogen, whilst the sample temperature is maintained at constant temperatures with a water bath.

The water content of the samples at the moment of insertion into the device was determined with the Karl Fischer method.

Only desorption isotherms were employed for comparability reasons since, during STA measurements, dehydration processes are performed.

In particular, for the milk powders, the exposure to high relative humidities, before recording desorption processes, guaranteed complete crystallisation of amorphous lactose in milk powders (Jouppila & Roos, 1994; Lai & Schmidt, 1990).

2.2. Heat of evaporation (H_{evap}) by STA coupled with MS

STA was carried out using the STA 409 simultaneous thermal analysis device, NETZSCH-Gerätebau, Selb, Germany in combination with a skimmer-coupled MS.

The preliminary evaluation of produced vapours and of the DSC peaks indicated optimal parameters without detectable heat deterioration products in the mass range 0–300 u at heating rates of 10 K/min to a maximum temperature of 100 °C, which was subsequently kept constant for several minutes.

Samples were prepared by equilibration at defined relative humidities of 0, 11, 33, 53 and 75% above saturated salt solutions (Greenspan, 1977).

Hereby the equilibrium of a real sample with a RH of 0% is practically impossible to obtain. To be more precise, the water activity above the applied commercially available molecular sieve, generally used for drying air, was below the detection limit of the water activity determination device employed.

The water content of the samples at the moment of insertion into the containers was determined in the same way as proceeded for the WSIs. The actual water content was calculated from the change of sample mass in the container. The containers were kept at constant temperature of 25±1 °C. Sample masses in the container were recorded every second day to check for constancy of mass.

For STA determinations, the samples were placed in aluminium crucibles with lids. The enthalpy of vaporisation was calculated from the base-line corrected peak areas of the DSC signal, and mass loss was determined from the TG signal.

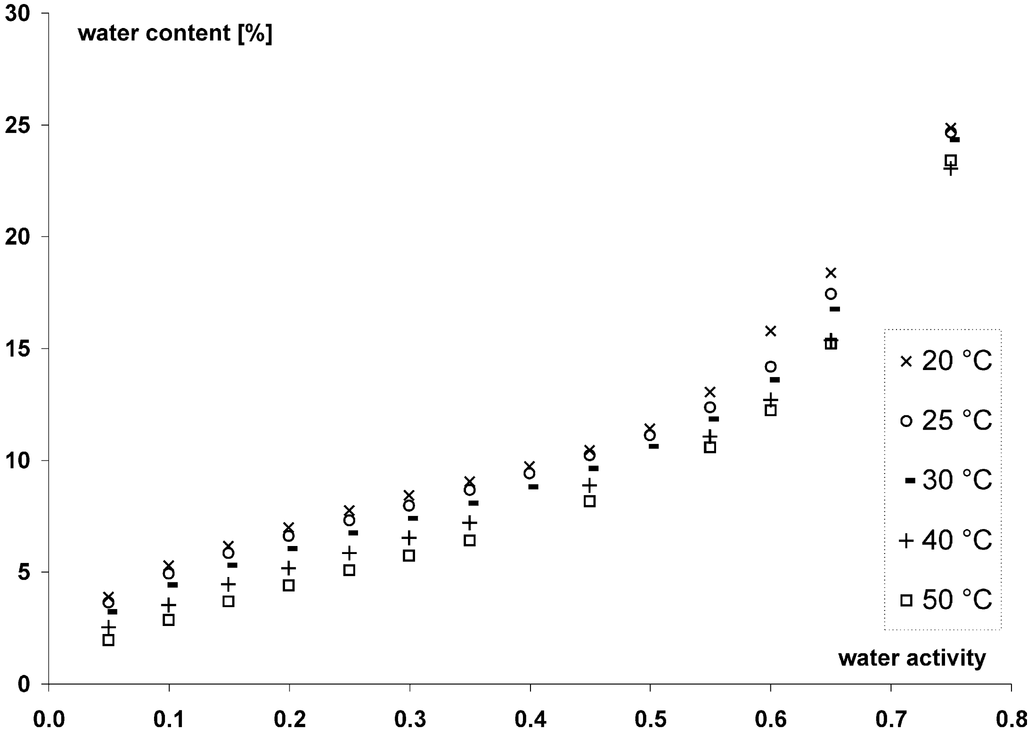

Fig. 1. Desorption isotherms for sample 1 at different temperatures.

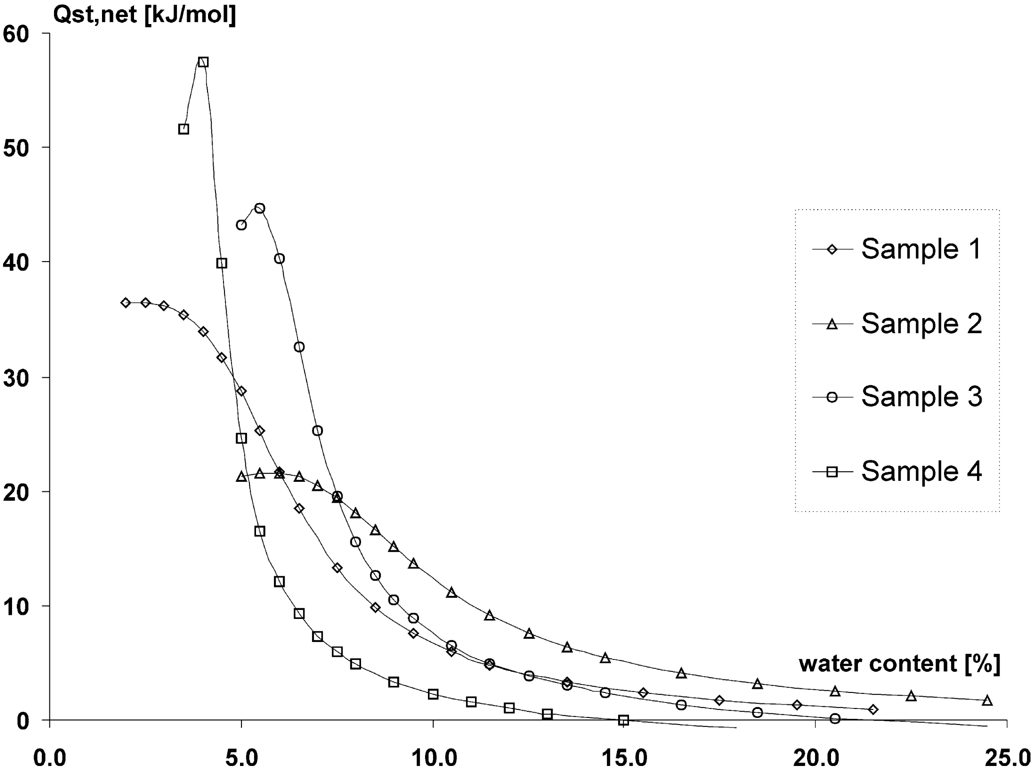

Fig. 2. Isosteric net heat of sorption, $Q_{st,net}$, for all samples.

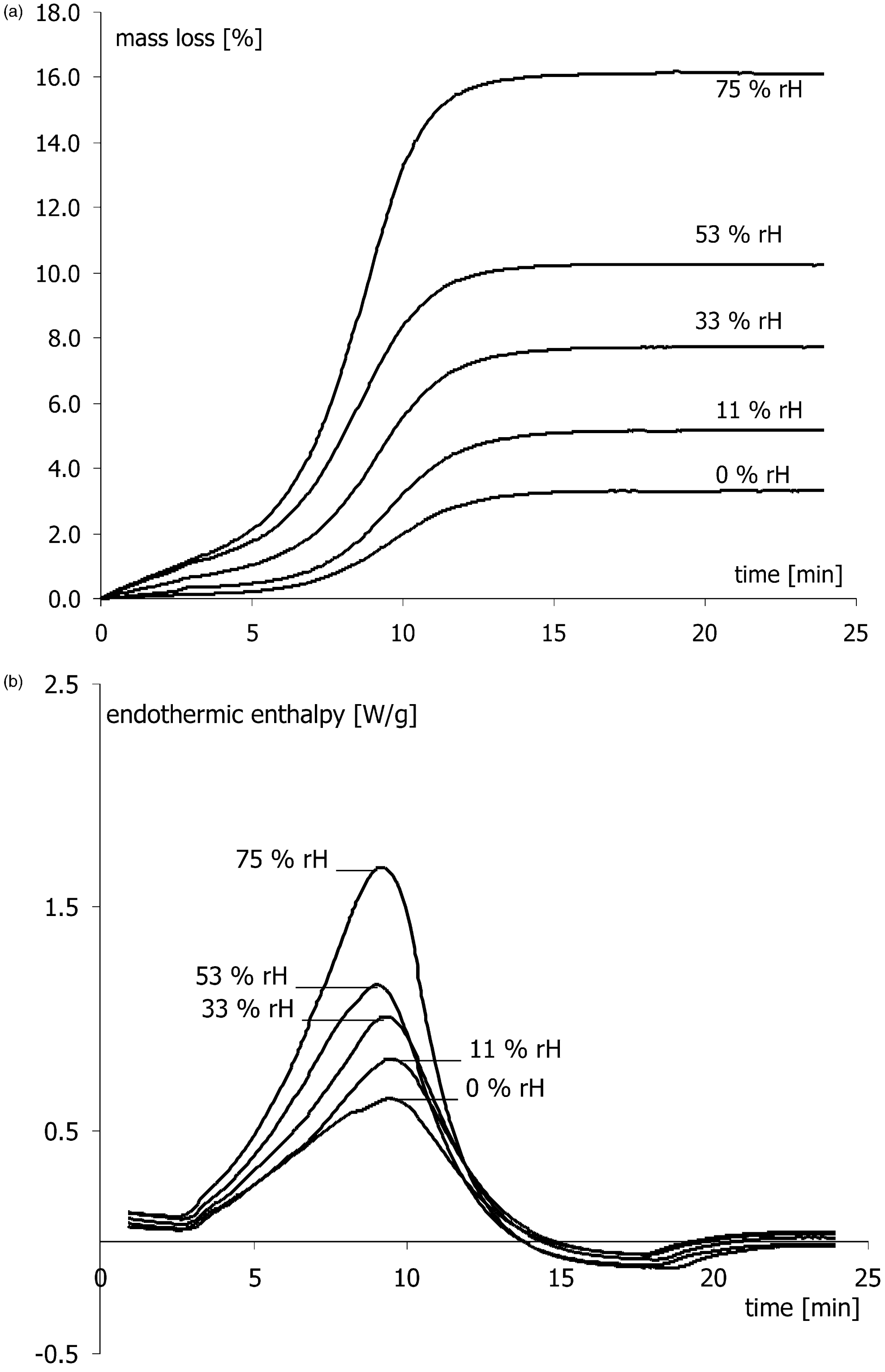

Fig. 3. (a) Graphs for mass loss from TG measurements: sample 1, equilibrated at 0, 11, 33, 53 and 75% RH. (b) Graphs for endothermic peaks from DSC measurements: sample 1, equilibrated at 0, 11, 33, 53 and 75% RH.

2.3. Samples

Sample 1—certified reference material (CRM) 422 Cod muscle, freeze-dried and certified for major and trace elements. Details are described elsewhere (Catalogue, 2002).

Sample 2—whole grain wheat flour candidate reference material. A freeze-dried powder, spiked with trace elements and pesticides during production.

Sample 3—CRM 063R, skim milk powder, spray-dried and certified for major and trace elements. Details are described elsewhere (Catalogue, 2002).

Sample 4—whole milk powder, spray-dried.

3. Results and discussion

Fig. 1 exemplarily depicts the water sorption data for sample 1, CRM 422, cod muscle powder. The isotherms are type 2-shaped, indicating strong interacting forces between surface and water monolayer (Brunauer, Deming, & Teller, 1940).

The resulting WSIs for all samples are type 2-shaped. Consequently, an increase in the net isosteric heats of sorption may be observed below a certain water content. Beyond this water content, the water of the samples may be regarded as really free water, where $Q_{\mathrm{st,net}}$ equals the heat of evaporation of pure water. The amount of increase of net isosteric heat of sorption for all samples is significant, even though the magnitudes differ. Furthermore, all graphs for net isosteric heat of sorption show a maximum value around a water content of approximately 5% with a decreasing tendency towards dryness (see Fig. 2). This maximum is observed frequently and has been tentatively explained by several theories (Aguilera, Cuadros, & del Valle, 1998; Vivanco & Taboada, 1998), none of which has interpreted the effect completely.

Further doubt of data obtained from WSIs in the very dry region is justified, as equilibrium conditions between sample and surrounding relative humidity are difficult to achieve. The term equilibrium itself in the context of

Table 1
Results for isosteric heat of sorption calculated from desorption isotherms, and heat of evaporation determined by STA for sample 1, equilibrated at 0, 11, 33, 53 and 75 RH

water content [%]	$Q_{\mathrm{st.net}}$ [kJ/mol]	H_{evap} [kJ/mol]				
		sample 1; 75 % rH evaporated water: 20.6 % - 5.5 %	sample 1; 53 % rH evaporated water: 10.8 % - 1.8 %	sample 1; 33 % rH evaporated water: 7.4 % - 0.7 %	sample 1; 11 % rH evaporated water: 5.2 % - 0.4 %	sample 1; 0 % rH evaporated water: 3.1 % - 0.1 %
0	-				**57**	**86**
1	-			**35**		
2	88		**25**			
3	93					
4	90					
5	77					
6	58	**11**				
7	41					
8	29					
9	21					
10	16					
11	12					
12	9					
13	7					
14	6					
15	5					
16	4					
17	3					
18	2					
19	1					
20	1					

WSIs and sorption hysteresis, raises arguments about the validity of thermodynamic calculations applied to data obtained from measurements which exhibit differences between adsorption and desorption (Rizvi, 1995; Rizvi & Benado, 1984).

STA offers insight into the process of desorption, as it directly detemines the calorimetric properties of the evaporation of water, even at humidities where WSI data become vague.

Fig. 3 outlines, exemplarily, the graphs for mass loss and endothermic peaks of sample 1, equilibrated at different relative humidities. The graphs show the mass loss of the sample which is experienced during a dehydration process, caused by the temperature ramp. This mass loss, preliminarily checked for other vapours than water by means of the attached MS, is attributed to a certain amount of energy calculated from the corresponding base-line corrected peak areas of the endothermic enthalpy of the DSC measurement. The obtained results therefore present an integral amount of energy required to evaporate an amount of water from the initial water content to the water content at the end point of dehydration.

Thereabove it becomes clear that the energy of interaction between water and surface, at very low water contents and corresponding relative humidities, is strong enough to overcome the drying potential of the employed desiccant. Due to this, not all the water is removed during equilibration and further heating energy, provided by the STA procedure, is required to evaporate the remaining water.

Table 1 compares the results for $Q_{\mathrm{st,net}}$ and heat of evaporation, resulting from STA determinations at different water content regions. The STA results clearly contradict the aforementioned theories of declining binding energies between water and surface towards very low water activities, resulting from sorption isotherms.

Table 2

Results for isosteric heat of sorption calculated from desorption isotherms, and heat of evaporation determined by STA for sample 2, equilibrated at 0, 11, 33, 53 and 75% RH

<table>
<tr><th rowspan="2">water content [%]</th><th rowspan="2">Q_{st.net} [kJ/mol]</th><th colspan="5">H_{evap} [kJ/mol]</th></tr>
<tr><th>sample 2; 75 % rH evaporated water: 15.8 % - 3.4 %</th><th>sample 2; 53 % rH evaporated water: 12.4 % - 2.0 %</th><th>sample 2; 33 % rH evaporated water: 9.4 % - 1.4 %</th><th>sample 2; 11 % rH evaporated water: 6.1 % - 0.5 %</th><th>sample 2; 0 % rH evaporated water: 4.0. % - 0.1 %</th></tr>
<tr><td>0</td><td>-</td><td rowspan="3"></td><td rowspan="2"></td><td></td><td rowspan="6">43</td><td rowspan="4">46</td></tr>
<tr><td>1</td><td>-</td><td rowspan="9">32</td></tr>
<tr><td>2</td><td>-</td><td rowspan="11">23</td></tr>
<tr><td>3</td><td>19</td><td rowspan="14">18</td></tr>
<tr><td>4</td><td>20</td><td rowspan="17"></td></tr>
<tr><td>5</td><td>21</td></tr>
<tr><td>6</td><td>22</td><td rowspan="15"></td></tr>
<tr><td>7</td><td>21</td></tr>
<tr><td>8</td><td>18</td></tr>
<tr><td>9</td><td>15</td></tr>
<tr><td>10</td><td>12</td><td rowspan="11"></td></tr>
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<tr><td>13</td><td>7</td><td rowspan="8"></td></tr>
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<tr><td>15</td><td>5</td></tr>
<tr><td>16</td><td>4</td></tr>
<tr><td>17</td><td>4</td><td rowspan="4"></td></tr>
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<tr><td>19</td><td>3</td></tr>
<tr><td>20</td><td>3</td></tr>
</table>

Table 3
Results for isosteric heat of sorption calculated from desorption isotherms, and heat of evaporation determined by STA for sample 3, equilibrated at 0, 11, 33, 53 and 75% RH

water content [%]	$Q_{st.net}$ [kJ/mol]	H_{evap} [kJ/mol]				
		sample 3; 75 % rH evaporated water: 13.4 % - 4.6 %	sample 3; 53 % rH evaporated water: 7.8 % - 1.2 %	sample 3; 33 % rH evaporated water: 6.4 % - 0.9 %	sample 3; 11 % rH evaporated water: 5.3 % - 0.8 %	sample 3; 0 % rH evaporated water: 2.7 % - 0.2 %
0	-					**94**
1	-		**28**	**44**	**51**	
2	-					
3	-					
4	29					
5	43	**21**				
6	40					
7	25					
8	16					
9	11					
10	8					
11	6					
12	4					
13	3					
14	3					
15	2					
16	2					
17	1					
18	1					
19	1					
20	0					

The interactive forces between water and surface do not cease to rise towards dryness.

It may further be concluded that, in the overlapping regions of the two methods, the results for binding energies confirm each other well in the frame of achievable accuracy of these techniques.

The results for sample 2, presented in Table 2, confirm the findings for sample 1 and the same may be seen from the results of samples 3 and 4 in Tables 3 and 4.

Large differences do exist between the absolute values of binding energies between the samples. This becomes particularly obvious when data of those samples being stored at low relative humidities are compared.

This effect may have several explanations, the first of which is the difference in sample composition. Sample 1, CRM 422, cod muscle powder, is a matrix dominated by muscular proteins which did undergo a strong drying procedure during production. Sample 2, whole grain wheat flour, consists mainly of starchy material and was intensely freeze-dried. Sample 3, CRM 063R, skim milk powder, mainly consisting of lactose and proteins, did experience an intense spray-drying procedure during production. Sample 4, spray-dried whole milk powder, having a similar composition to sample 3 but a higher amount of fat, is the only sample which did not experience an intense drying procedure and has not been stored for longer periods of time.

This may lead to the assumption that, in addition to the sample composition, the pre-treatment of the material may contribute to the energy of interaction between material and surface, especially as sample 4 shows higher binding energies than sample 3, even though sample 4 has the higher fat content.

4. Conclusion

Determinations of binding energies of water on four biological matrices with two different approaches of determination, water sorption isotherms at different

Table 4
Results for isosteric heat of sorption calculated from desorption isotherms, and heat of evaporation determined by STA for sample 4, equilibrated at 0, 11, 33, 53, and 75% rH

water content [%]	$Q_{st.net}$ [kJ/mol]	H_{evap} [kJ/mol]				
		sample 4; 75 % rH evaporated water: 9.4 % - 2.3 %	sample 4; 53 % rH evaporated water: 5.2 % - 2.3 %	sample 4; 33 % rH evaporated water: 4.5 % - 0.4 %	sample 4; 11 % rH evaporated water: 3.8 % - 0.3 %	sample 4; 0 % rH evaporated water: 1.7 % - 0.2 %
0	-			60	74	192
1	-		43			
2	-	26				
3	4					
4	57					
5	25					
6	12					
7	7					
8	5					
9	3					
10	2					
11	2					
12	1					
13	1					
14	0					
15	0					
16	0					
17	0					
18	0					
19	0					
20	0					

temperatures with subsequent application of the Clausius–Clapeyron equation and simultaneous thermal analysis, were performed.

In the range of validity, the results obtained from the two methods confirmed each other.

It could be shown that isosteric net heats of sorption obtained from water sorption data reveal shortcomings in the low water activity area, and that theories explaining decreasing $Q_{st,net}$ values below certain water contents fail.

With the help of the STA technique, a method to measure binding forces between water and biological surfaces, even at very low water contents and correspondingly in low water activities, could be successfully applied.

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