Measurement of the water sorption properties of a Ritz Cracker sample

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Introduction

All the reported measurements were performed using the standard Hiden Isochema IGAsorp instrument (see technical data sheet 143) with a refrigerated water bath to thermostat the sample chamber. The IGAsorp is a fully automated system, which allows the accurate and efficient determination of moisture sorption equilibrium isotherms and kinetics in foodstuffs.

The purpose of this experiment was to demonstration the application of the IGAsorp in the area of food research.

The equilibrium isotherm with GAB analysis is presented together with the results of kinetic analysis showing the variation of equilibration time with humidity.

Experimental Method

A small quantity of ground cracker (particle size 200 – 300 μm) with a weight (as loaded) of 154.93mg was added to a standard gas permeable IGAsorp sample container. The in-situ loading method was used in which the above wet weight is directly determined by the IGAsorp balance. During the in-situ loading procedure the sample environment was controlled at 25°C and 30%RH.

The sample was dried in-situ at 25°C for 25 hours then the isotherm method with 5% steps of relative humidity was used (compared to the minimum control increment for high resolution scanning of 1%RH) up a relative humidity of 95% RH. The measurement temperature was 25°C +/- 0.05°C for the entire experiment including the drying stage.

The gas supply used is dry air from a laboratory compressor with a PSA dryer to reduce moisture content <1ppm. The total gas flow rate used during all these measurements is 250ml/min
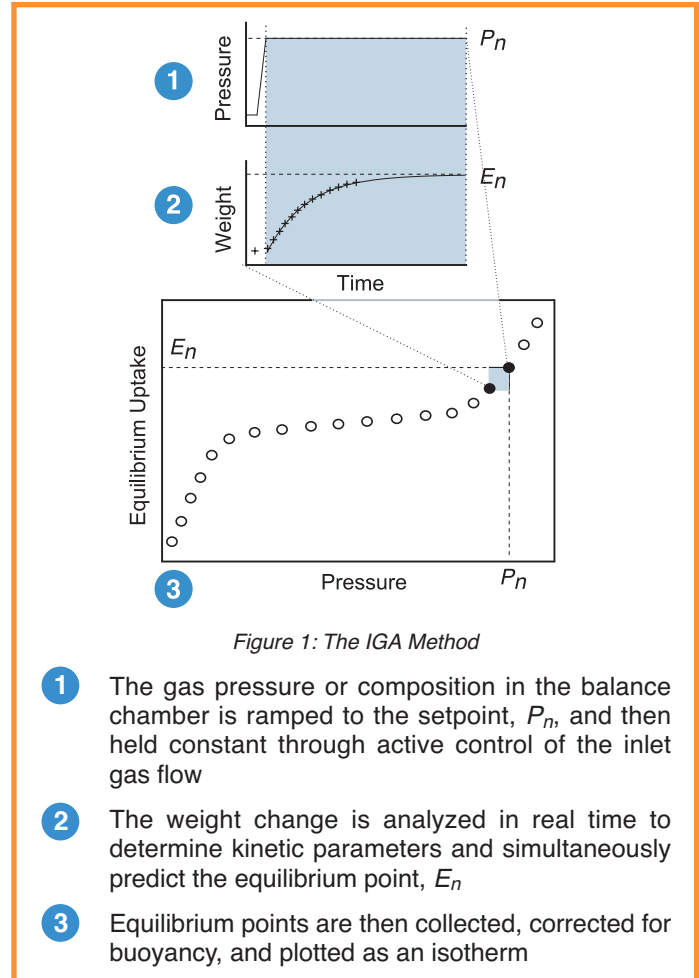
Figure 1: The IGA Method

1 The gas pressure or composition in the balance chamber is ramped to the setpoint, P_n, and then held constant through active control of the inlet gas flow

2 The weight change is analyzed in real time to determine kinetic parameters and simultaneously predict the equilibrium point, E_n

3 Equilibrium points are then collected, corrected for buoyancy, and plotted as an isotherm

compared to maximum possible setting of 500ml/min.

IGAsorp real-time analysis was used to determine equilibration time and to change the data collection time for each isotherm point with a target that the weight is 95% relaxed. The Avrami model was used to describe the weight change as a function of time (w(t) where,

$$w(t) = w_0 + \Delta w \, [\, 1 - \exp\,(-k(t\text{-}t0)^x]$$

and w_0 is the weight origin when t=t0, the asymptotic uptake is $w_0 + \Delta w$, k is the time constant, x is a power term and t0 is a time origin which the real-time analysis locates. This time origin is not the start of data collection following humidity change unless the process perfectly conforms to the Avrami model. The time origin will advance during analysis to search for the slowest exponential type tail in the sorption-time curve. See Figure 1, The IGA method.

Results

<table>
<tr><td colspan="4">Table 1. Weight loss and Dry mass values.</td></tr>
<tr><td></td><td>Loaded Mass</td><td>Mass loss due to drying</td><td>Dry Mass</td></tr>
<tr><td>Ritz Cracker</td><td>154.93mg</td><td>7.0465mg</td><td>147.8835mg</td></tr>
</table>

<table>
<tr><td colspan="7">Table 2. Parameters determined from the GAB isotherm fit.</td></tr>
<tr><td></td><td>a_w range</td><td>No. data points</td><td>m_m momolayer capacity</td><td>K</td><td>C</td><td>R^2 Quadratic regression $(a_w/m = \alpha a_w^2 + \beta a_w + \gamma$</td></tr>
<tr><td>Ritz Cracker</td><td>0.05 - 0.6</td><td>12</td><td>6.36g/100g</td><td>0.7285</td><td>9.1123</td><td>0.99841</td></tr>
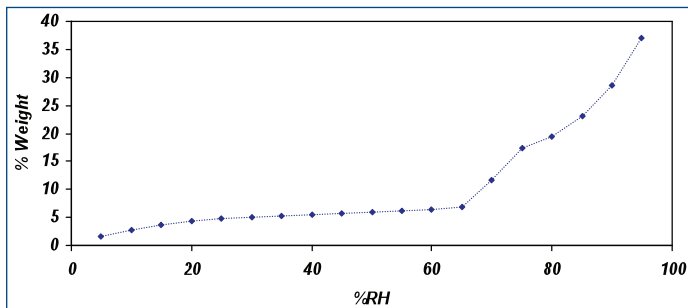</table>

Figures

Figure 2: A plot of the moisture adsorption isotherm measured on the Ritz Cracker at 25°C. Displayed as uptake (calculated as a percentage of the dry weight of sample at 25°C) against %RH.
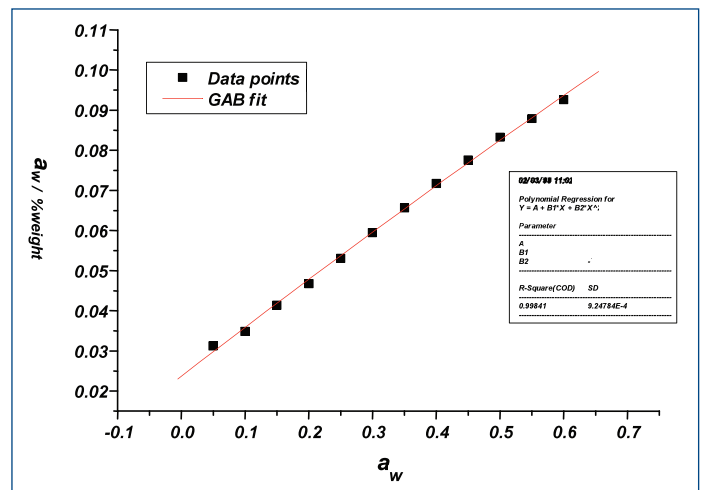

Figure 4: A plot of the GAB fit through the raw data of the moisture adsorption isotherm measured on the Ritz Cracker at 25°C between 5 and 60%RH.
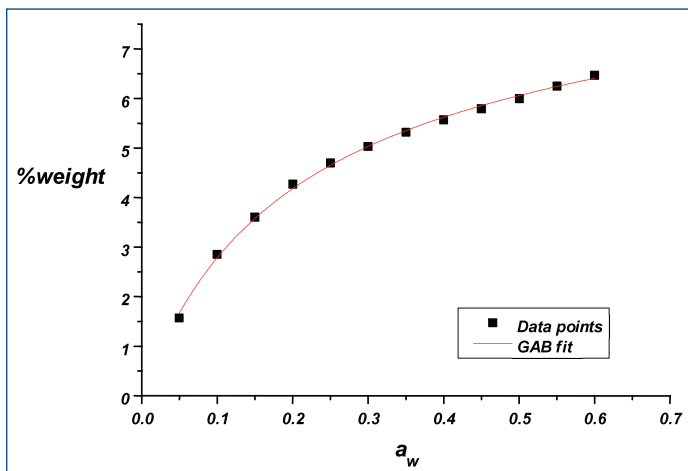

Figure 3: A plot of the GAB fit through the raw data of the moisture adsorption isotherm measured on the Ritz Cracker at 25°C between 5 and 60%RH. Displayed as uptake (calculated as a percentage of the dry weight of sample at 25°C) against aw (water activity).
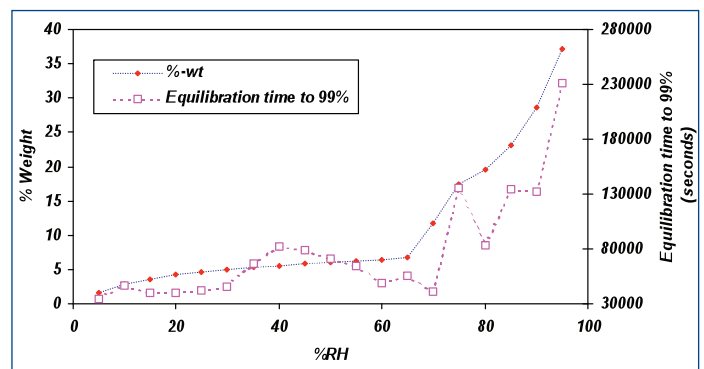

Figure 5: A plot of the time taken to reach 99% of the predicted equilibrium against %RH, measured during the moisture adsorption isotherm on the Ritz Cracker at 25°C. A plot of the uptake versus %RH is also plotted to aid comparison.

Comments

The isotherm plotted as % dry weight versus %RH is displayed in figure 2 and shows a complex behaviour. The initial portion of the curve (0-65%RH) shows a type II behaviour followed by a discontinuous dramatic gain in weight. A discontinuity in the weight gain also occurs at 75%RH above which the isotherm is smooth. This behaviour indicates that the sample contains several components each having significantly different isotherms, different isotherms being dominant in different regions. The isotherm appears to be a summation of several type II and type III isotherms. The type III isotherms have negligible contribution at low RH but significant contribution at high RH.

The equilibrium isotherm is shown in figure 3 and 4 together with a trend line from the Guggenheim-Anderson-de Boer (G.A.B) model, see Appendix 1;

$$\frac{m}{m_m} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)}$$

where mm, C and K are parameters of the fit, m is the equilibrium moisture content (dry basis, d.b.) and aw is the water activity. The fit was restricted to the initial portion of the curve between 5% and 60% RH.

The parameter 'mm' corresponds with the 'monolayer' moisture content and is for example, considered the optimal moisture content to prevent alteration of the quality of food products. In the present case this content is equivalent to equilibration at a humidity of ~57%RH.

The parameters resulting from the fit are presented in Table 2. An attempt to fit the data using a BET model was made over the same region as for the GAB fit but linearisation was not achieved and therefore it was found impossible to determine parameters by fitting.

A plot of the equilibration time (Δt99%) versus %RH is presented in figure 5 along with a plot of the %weight versus %RH to aid comparison. An increase and then decrease in the equilibration time is observed between 30 and 60%RH which may indicate a phase transition such as a glass transition but no associated changes are observed in the isotherm. The most significant changes in the equilibration time are observed

above 70%RH where the uptake curve displayed discontinuity. The variation in equilibration time in this region is noisy. This is because the rate is very slow at these points and thus the data acquisition was terminated before the data had reached 95% of the equilibrium asymptote. Therefore a significant error results in their determination. The measured times are still useful to demonstrate the slower rates compared with those measured previous to this point.

Conclusions

The equilibrium isotherm of the Ritz cracker is complex but can be well described by the GAB model between 5% and 60%RH. In this regard the water sorption properties are similar to many foodstuffs in the literature. The equivalent monolayer water content was found to be 6.36 wt% (d.b) by GAB analysis.

The IGAsorp was shown to be an accurate and time saving tool in the study of moisture properties of food stuffs.

Application Note 119: Appendix

GAB Model

The GAB model may be used to fit moisture isotherms of food materials and pharmaceuticals. The model contains three parameters one of which is the monolayer capacity of the sample.

m is the %weight of sorbed water, m_m is the monolayer capacity, aw is the water activity, C is the Guggenheim constant and K is a correction factor for the difference in behaviour between multilayer water and ideal water.

$$\frac{m}{m_m} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)}$$

$$\frac{a_w}{m} = \alpha a_w^2 + \beta a_w + \gamma$$

Where:

$$\alpha = \frac{K}{m_m}\left[\left(\frac{1}{C}\right) - 1\right] \qquad \beta = \frac{1}{m_m}\left[1 - \left(\frac{2}{C}\right)\right] \qquad \gamma = \frac{1}{CKm_m}$$

α, β and γ may be determined by fitting a 2nd order polymomial to an aw versus %weight data set.

m$_m$, K and C may be calculated from the equations below using the parameters determined by the fit.

$$m_m^2 = -\frac{1}{4\alpha\gamma - \beta^2}$$

$$K = \frac{\beta - \left(\frac{1}{m_m}\right)}{-2\gamma}$$

$$C = \frac{1}{m_m\gamma K}$$

Reference
[1]   Y.H. Roos, J Food Processing and Preservation. 16 (1993) 433-447