Dynamic Dew Point Isotherm verses Other Moisture Sorption Isotherm Methods By Brady Carter and Anthony Fontana Ph.D.

The Dynamic Dewpoint Isotherm (DDI) method used by the AquaSorp Isotherm Generator is like other moisture sorption isotherm methods in that it provides the relationship between water activity and moisture content. However, the DDI method is unparalleled in the detail and speed with which it produces isotherm curves and the amount of additional information not previously possible with other methods.

Moisture Sorption Isotherm Methods

Traditional isotherm methods depend on establishing the equilibration of samples to known water activity values and then measuring the moisture contents of these samples. Common to all these isotherm methods is the dependence on equilibration to known water activity levels to determine each data point's water activity. Since true equilibration between the sample and the vapor source requires an infinitely long period of time, an apparent equilibrium when the weight stops changing by an acceptable level is used. Widening the tolerance in weight change will speed up the isotherm process but calls into question the validity of the water activity values.

The static desiccator method is performed by placing samples in sealed chambers over saturated salt slurries. Different water activity levels are achieved by using different saturated salts. Instrumentation, known as controlled atmosphere microbalances (CAM) exists to continuously monitor weight changes and control relative humidity by adjusting a mixture of wet and dry gas streams. Different relative humidity levels are achieved by changing the ratio of dry to wet gas. Some instruments are programmed to automatically change the water activity in a dynamic stepwise progression, usually referred to as Dynamic Vapor Sorption (DVS). The sample is held at each relative humidity level until weight stops changing before moving to the next relative humidity level.

The Dynamic Dewpoint Isotherm Method

The DDI method is very different from the other isotherm methods as neither water activity nor moisture content is controlled. Rather water activity is directly measured using a standard chilled mirror dewpoint sensor and moisture content is gravimetrically tracked using a balance. Wetting is imposed by saturating the air with water before it enters the chamber and drying is achieved by passing air through desiccant before it enters the sample chamber. The method is dynamic because the sample is not required to equilibrate to a known water activity level; rather its water activity is directly measured at each point. The DDI method without these long equilibration periods dramatically reduces the time required to develop a moisture sorption curve with an unmatched amount of data points. In addition, only water and desiccant are required to run an isotherm. Currently, the AquaSorp Isotherm Generator is the only instrument that utilizes the DDI method.

Comparing the Methods

For most samples, especially those with fast vapor diffusion, penetration by water vapor into the whole sample is rapid and isotherms from the DDI method are comparable to the other methods. Figure 1 compares the adsorption isotherm for microcrystalline cellulose (MCC) from a traditional static desiccator method from the COST-90 project (Wolf et al., 1985; Jowitt and Wagstaffe, 1989) to the DDI method. Figure 2 compares the isotherm curves for corn starch from traditional, DVS, and DDI isotherm methods. As shown in both Figures 1 and 2, the DDI method has very good agreement with the other moisture sorption isotherm methods.

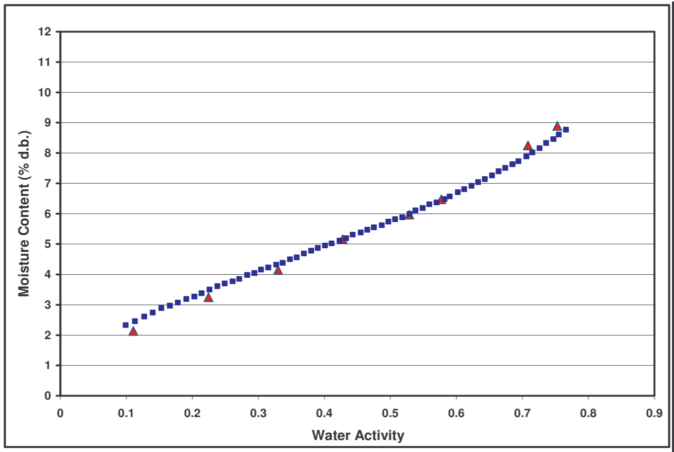

Figure 1. A comparison of adsorption isotherm curves for MCC as recorded by the COST 90 project (▲) and as generated by the DDI method (■).

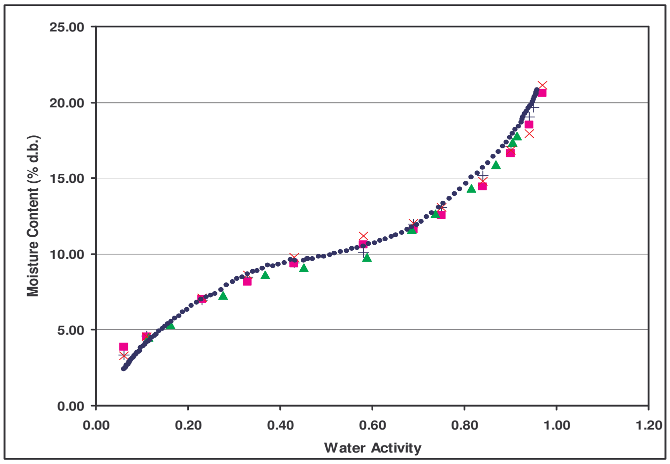

Figure 2. Corn starch working isotherms when using desiccators with saturated salts (■), Proximity Equilibration Cell (●), DVS instrument 1 (♦), DVS instrument 2 (▲), and DDI (×) (DDI data from Decagon Devices in-house testing, data for all other methods taken from (Xin Yu, 2007)).

Due to the matrix and/or composition of some samples the rate of vapor diffusion into or out of these samples may be slow. Thus, comparing isotherms by the DDI method to other methods, especially when equilibration required several weeks in a desiccator, may present problems. If the vapor diffusion is slow and moisture has not equilibrated within the sample, the water activity measurements will give the appearance of vapor equilibration. Isotherms for this type of sample using the DDI method have lower moisture contents during adsorption and higher moisture contents during desorption than isotherms conducted using other methods. This gives the appearance of higher levels of apparent hysteresis. Better agreement to other isotherms may be achieved, when using the DDI method by reducing the sample size, increasing the surface area of the sample by crushing or grinding, and reducing the flow rate to allow more moisture penetration.

Should the Methods be Compared?

It is important to understand that while DDI, DVS, and desiccator methods all produce sorption isotherms; the DDI method with its dynamic nature is fundamentally different. Since the different isotherm methods achieve different matrix states, none of which may be true equilibrium, it is impossible to say which method is best. There may be those that become concerned when a DDI isotherm does not reproduce results from other methods. They might argue that the moisture contents produced by the DDI method are not true equilibrium moisture contents. It is best to consider the DDI method as a different and unique isotherm. Furthermore, while for many samples the different isotherm methods give the same curves, as illustrated in Figures 1 and 2, it is when the curves are different that may be the most interesting.

For some material, the moisture content at a given water activity will be very different after weeks of equilibration time than after a short exposure to high or low humidity. Time dependent physical changes such as glass transition, crystallization, and dissolution may occur as a material equilibrates to different water activity levels over weeks and may not occur when using the DDI method. Figure 3 illustrates these different curves for spray dried milk powder. The isotherm methods produce different curves because they are measuring material in different physical states and it is inappropriate to compare the methods because they are providing different information.

This does not mean that the DDI method is wrong and the other methods are right. In fact, the dynamic nature of the DDI method may actually illustrate a more accurate sorption characteristic of this type of material in real conditions since samples are rarely exposed to changes in moisture in stepwise progression but instead in a dynamic progression.

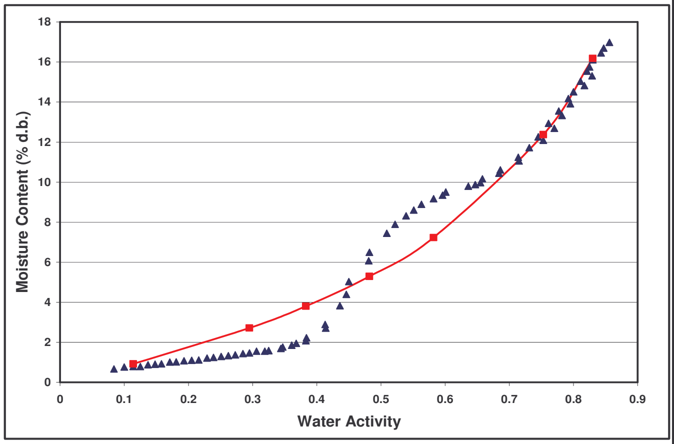

Figure 3. A comparison of adsorption isotherms for spray dried milk powder conducted using traditional desiccator method and fitted to the GAB equation(■) and the DDI method (no model fitting) (▲).

The Value of the DDI Method

The dynamic nature of the DDI method allows for the rapid (1-2 days) generation of a large data set not practically possible with other isotherm methods as it would take an inhibitory length of time. Typically, the DDI isotherm data set of 50 to 70 points has a 0.01a_w change between each collected data point. This detailed data resolution eliminates the need for extrapolation or interpolation, and gives a direct detailed view of the sorption curve. Figure 3 illustrates isotherms for spray dried milk powder produced using the desiccator method and the DDI method. Time and labor constraints limit the number of data points generated by the desiccator method and requires interpolation using the GAB equation to complete the curve. The detail data resolution of the DDI method produces a complete curve making interpolation by a model unnecessary. In fact, using a smooth curve model to characterize the isotherm would miss the most import results of the DDI analysis. The DDI data directly shows that important matrix changes are occurring as illustrated by changes in sorption rates, at 0.420, 0.559, and 0.724 a_w.

Phase transitions such as glass transitions, crystallization, and dissolution are identifiable by the DDI method. It would be impossible to identify any of the phase changes using just the desiccator method data as fitted to the GAB equation in Figure 3. This explains why many believe that moisture sorption isotherm data could not be used to identify phase transitions points such as glass transition. However, phase transitions are identifiable by the DDI method.

The Dynamic Dewpoint Isotherm Method is a unique analysis method that provides important information not previously possible with other isotherm methods. The DDI method with its unparalleled detail, speed, and amount of information generated from each isotherm curve will greatly aid in the understanding of water interactions within materials.

References

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Decagon Devices
2365 NE Hopkins Court
Pullman Washington 99163