

# DVS Application Note 102

# Moisture Sorption Properties of Food Products and Packaging Materials Studied by DVS

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Dynamic Vapour Sorption (DVS) has long been used for investigating the interaction of water vapour with foods and food ingredients. This overview application note summarises several examples of using DVS for food-related applications including: water activity, moisture content, moisture-induced phase transitions, water-vapour transmission rates, and flavour loss.

# Introduction

The moisture sorption properties of food products are recognised as critical factors in determining their storage, stability, processing and application performance [1-2]. Moisture sorption properties for many food products and packaging materials have traditionally been evaluated by storing samples over saturated salt solutions of established relative humidities and then regularly weighing until equilibrium is reached [3]. However, there are a number of disadvantages with these methods, including: (i) the prolonged period of time taken for the samples to reach equilibrium using a static method, often many days and commonly many weeks; (ii) inherent inaccuracies as the samples have to be removed from the storage container to be weighed which can cause weight loss or gain; (iii) static methods necessitate the use of large samples sizes (typically 10-100g); and (iv) the highly labour intensive nature of static methods.

For the above reasons, a rapid, highly-sensitive and automated approach is desired. Hence, the invention of the Dynamic Vapour Sorption (DVS) instrument by Surface Measurement Systems in the early 1990's. Today, the DVS is widely used across numerous industries for investigating the vapour sorption properties of solids, fibres, gels, particulates, and composite materials. This application note summarises several DVS applications related to foods, food ingredients, and food packaging.

# Method

A schematic of the DVS-Advantage instrument is shown in Figure 1. The instrument measures the uptake and loss of vapour gravimetrically using the SMS UltraBalance with a mass resolution of  $\pm 0.1 \,\mu g$ . The vapour partial pressure around the sample is generated by mixing saturated and dry carrier gas streams using electronic mass flow controllers. In addition to controlling water vapour pressure (i.e. relative humidity), the DVS-Advantage instrument has the unique capability to actively measure and control the concentration of a wide range of organic vapours. This is accomplished by utilising a proprietary optical sensor which is specifically tuned for water and wide range of solvents. This technology allows the instrument to measure and control water and organic vapour concentrations in real time.



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Figure 1. Schematic overview of the SMS DVS-Advantage instrument.

## **Moisture Content/Sorption Isotherm**

The DVS family of instruments has been routinely used to determine moisture content isotherms. This is accomplished by exposing the sample to a certain relative humidity until equilibrium has been established. Then, this is repeated at numerous RH steps until a complete sorption and/or desorption isotherm has been established. Figure 2 displays typical moisture sorption/desorption kinetics (a.) and isotherms (b.) for a generic starch sample.



(a.)



Figure 2. Moisture sorption kinetic (a.) and isotherm (b.) plots for starch at 25  $^{\circ}$ C.

Unlike the desiccator jar method, the DVS allows continuous measurement of the sorption kinetics, which can be used to determine moisture diffusion coefficients. This will be discussed in detail later. Also, the DVS allows the determination of sorption and desorption isotherms on the same sample; thus moisture sorption hysteresis can be measured. Finally, due to the constant flux of (partially) humidified carrier gas, the DVS allows complete sorption/desorption isotherms to be determined in hours/days instead of days/weeks/months for the desiccator jar method.

## **Moisture-Induced Phase Changes**

Amorphous solids often absorb relatively large amounts of water vapour compared to their corresponding crystalline phases. Sorbed water often acts as a plasticising agent, thus significantly lowering the glass transition temperature causing spontaneous phase transitions and lyophile collapse. In fact, there is often a critical humidity at which the glass transition will occur at room temperature. In addition, this can lead to increased cohesiveness, powder caking and adhesion to other surfaces. To illustrate, it was determined that cohesion was related to the combined effects of temperature and moisture [4]. Only investigating one (i.e. temperature or moisture content alone) is not sufficient to understand the likelihood of a powder to cake. The mechanism for sticking and caking of



amorphous sugars is through the phase change of the amorphous sugar from a glass to a rubber at conditions above the glass transition point [4]. Therefore, determining the necessary threshold temperature and humidity conditions to prevent a glass transition is critical for storage and processing of amorphous food ingredients.

Detailed information and theory about moisture-induced glass transitions can be found in **SMS Application Note 32** and in Reference [5]. In short, a linear RH ramping experiment is performed, whereas several moisture-induced phase transitions can be identified by the nonlinear moisture sorption response by the sample. This phenomenon is illustrated in Figure 3 for a spray-dried lactose sample.



Figure 3. Relative humidity ramping experiment (6.0% RH/hour) for an amorphous lactose sample at 25.0 °C.

Similar experiments can be performed over a range of temperatures to establish a 2dimensional phase diagram (Figure 4). This can be used to determine the ideal storage and processing conditions to limit any moistureinduced phase transformations and subsequent powder caking.



Figure 4. Humidity-induced phase transitions for spraydried lactose measure via DVS.

#### Moisture-Induced Flavour Release

There are two main factors that trigger flavour release from encapsulated matrices: (1) physicochemical properties of the matrix and (2) volatile compounds' thermodyanamic and kinetic properties [6]. Regarding the encapsulated matrix, important properties include physical state, surface area, moisture content, water activity and glass transition temperature. The previous section describes how water vapour can affect the glass transition and physical state (i.e. amorphous to crystalline transformation). In addition, the DVS instrument can directly measure moisture content and water activity determination will be discussed later. Therefore, the DVS instruments can add valuable information for the formulation and stability of encapsulated flavours.

Previous researchers have investigated moisture-induced flavour release using a variety of matrices [7,8,9]. In one study, researchers found a clear transition point around 60% RH for limonene flavour loss in a yeast matrix. The attributed mechanism was dependent on how the yeast cell wall structure/properties are related to water sorption/desorption. The flavour on/off release mechanism was strongly dependent on moisture content [9]. In another study, benzaldehyde release from an amorphous glass was studied as a function of relative humidity. The researchers found that benzaldehyde release



was significantly higher above 60% RH. This was due to water plasticizing the matrix and lowering the Tg down to room temperature [7].

## **Powder Caking and Amorphous Content**

The caking behaviour of powders can depend on the amount of material present in the amorphous state [10]. In addition, powders with greater amounts of amorphous lactose are more sensitive to absorbing moisture, thus increasing the tendency to lumping and caking problems [11]. There are several methods in the literature using gravimetric vapour sorption techniques to quantify amorphous contents [12,13,14,15,16]. Most of these methods are based on the amorphous phase sorbing more vapour than the crystalline phase. Amorphous materials typically have a higher surface area and vapour affinity than their crystalline counterparts. For vapour sorption methods a calibration of known amorphous contents is typically necessary. Then, the equilibrium vapour uptake at a particular vapour concentration is plotted versus the known amorphous content. The result is a calibration curve to which unknown amorphous contents can be compared. Due to the above mentioned changes in crystalline state induced by water (solvation, polymorph conversion, etc.), use of a non-polar organic vapour is recommended for hydrophobic materials. To illustrate, Figure 5 shows the octane vapour sorption isotherms (a.) and calibration curve (b.) for lactose samples with varying amorphous contents. The error margins in Figure 5b were based on the 1<sup>st</sup> standard deviation for repeat measurements (n=3).

Amorphous standards were created by making physical mixtures of 100% amorphous and 100% crystalline lactose. The resulting calibration curve and correlation coefficient ( $R^2$ =0.9994) suggests that amorphous contents below 0.5% were achievable with an accuracy of ± 0.3%.



(b)

Figure 5. Octane vapor sorption isotherms (a.) and resulting calibration curve (b.) for lactose samples with various amorphous fractions.

## Video Microscopy

The physical changes inferred from the gravimetric data can be further supported by *insitu* microscopic images collected during the experiment. This is done using the DVS-Video accessory. The long-working distance digital microscope allows the automatic collection of images during a DVS experiment with magnification up to 200X.

Figure 6 shows 100x images of amorphous lactose taken at 0% (A), 50% (B), 60% (C), and 90% RH (D). This is the same material used in Figure 3. By 50% RH the sample is clearly changed to the rubbery form due to the humidity-induced glass transition. By 60% RH, the sample begins to crystallize, where at 90% RH crystallization of amorphous lactose is evident by an increase in the opacity of the image. When combined with the change in mass results in



Figure 3, the images shown in Figure 6 clearly identify different humidity-induced phase changes.



Figure 6. In-situ images collected on amorphous lactose at 0% (A), 50% (B), 60% (C), and 90% RH (D).

#### Raman/Near-IR

Vibrational spectroscopic techniques, such as Near-IR [17,18] and Raman spectroscopy [19] have also been combined with gravimetric sorption methods. As moisture is absorbed by a sample, the intermolecular structure and forces within it adapt to accommodate water molecules. This leads to changes in the sample's molecular vibrational characteristics, which can be monitored by changes in the Raman spectrum [20] or Near-IR spectrum [21].

To illustrate, Raman spectroscopy can be sensitive to changes in hydrogen bonding and other subtle reorientation of the solid material. For instance, Raman spectroscopy has been previously used to determine the changes in strength of hydrogen bonding between water and different pharmaceutical polymers [22]. In the same study, changes in Raman spectra due to water plasticizing the polymers have been observed. Figure 7 displays the water sorption/desorption (a.) and Raman spectra (b.) for microcrystalline cellulose (MCC) at 25 °C. MCC is not expected to form a stoichiometric hydrated species or undergo any first-order phase change when exposed to increasing humidity. However, there are clear differences in the Raman spectra as the humidity is increased. MCC does experience a significant amount of bulk water absorption as humidity is increased. Therefore, the changes observed in Figure 7b could be due to increased hydrogen bonding, decrease in void spaces, or other structural rearrangements.



(a.)



Figure 7. DVS water sorption/desorption results (a.) and in-situ Raman spectra (b.) for MCC at 25 °C.



## **Diffusion/Flux Experiments**

Real-time mass change data can be collected as frequently as once every second, which allows the determination of diffusion coefficients for various geometries. DVS has been successfully used to measure diffusion coefficients for films. powders, and fibres. Diffusion into films can be particularly useful for packaging applications. SMS Application Note 16 outlines the theory and method for thin film diffusion coefficient determination. In short, diffusion constants for the thin films utilises diffusion equations first employed by Crank and Park [23]. For a single step in humidity, and a thin film of known thickness, the initial kinetics of sorption into the bulk may be used to determine the diffusion coefficient. This can be performed over a range of temperatures to investigate a range of storage conditions. Figure 8 displays the water diffusion coefficients into a fluoropolymer-copolymer film over a range of temperatures.



Figure 8. Diffusion coefficients at 30 ° C (red), 50 °C (blue), and 70 °C (green) for a fluoropolymercopolymer film (183 microns).

# Water Vapour Transmission Rates (WVTR)

A novel Payne style diffusion cell was designed and developed to measure the permeability/rate of diffusion of a thin film. The design of this cell is shown in Figure 9. Full description of the cell, including dry-cup and wet-cup methods, can be found in **SMS Application Note 52**. This cell can be readily used to determine WVTR values. Combined with the diffusion coefficients mentioned previously, WVTR determination can be used for packaging/barrier applications.



*Figure 9. Experimental set-up for moisture vapour transmission rate measurement.* 

To illustrate the utility of this Payne cell, Table 1 displays the steady-state water vapour flux values on an electro spun PCL membrane over a range of humidity boundary conditions. As expected, as the surrounding relative humidity increases, the flux across the membrane increases, as well.

Table 1: Water vapour flux through electrospun PCL
membrane at varying relative humidity values

% Relative Humidity	Diffusion rate [mg/min]	Water vapour flux [g/(hr.m²)]
100	0.1152	444.82
80	0.1109	428.28
50	0.0751	289.94
30	0.0432	166.90

## Membrane Flavour Flux

The Payne cell can also be used to measure flavour flux through packaging membranes. To illustrate this application, a commercially available food storage bag was used as a model membrane. The thickness was 40 microns. Limonene, ethyl acetate, and amyl acetate were used as model flavour compounds. Limonene was chosen as a hydrophobic



molecule, while ethyl acetate and amyl acetate were chosen as more hydrophilic flavours. The following conditions were used: 25.0 °C; 200 sccm of dry flow outside of the Payne cell; and neat liquid with headspace inside the Payne cell. A summary of the results are shown in Table 2. Repeat experiments were performed with the limonene vapour, indicating a reproducibility of +/- $0.2 \text{ g/m}^2\text{hr}$  (n=2).

Comparing molecules of similar chemistry, but different size, it is clear that the larger amyl acetate vapour has a slower flux than the smaller ethyl acetate vapour. Also, the more hydrophobic, limonene vapour has a higher flux than the hydrophilic amyl acetate. These two molecules have similar molecular weights (130.19 amu for amyl acetate and 136.24 amu for limonene) and vapour pressures at room temperature (4 mmHg for amyl acetate and 2 mmHg for limonene). Although other factors cannot be completely ignored, this data does indicate that molecule chemistry does have a profound effect on flavour loss through this packaging material.

**Table 2:** Flavor vapour flux through a food storage bag(40 micron thickness) at 25 °C.

Flavour Molecule	Flux [g/m²hr]
Limonene	18.4
Ethyl Acetate	37.7
Amyl Acetate	7.0

## Water Activity (Aw)

The Payne cell can also be used in a novel method to determine the water activity of a food material. The methodology and validation of this technique is detailed in **SMS Application Note 62**. The combination of DVS and the Payne cell has the following advantages for Aw determination: inherently simple in concept; uses relatively small samples; does not require periodic calibrations; independent of chilled mirror calibrations; independent of surface temperature calibrations; and relatively fast and robust. Table 2 displays the Aw values for some common foods and their literature values. Note the excellent agreement with the DVS determined water activity values and those obtained using more traditional techniques.

# **Table 2:** Water activity values determined using combination of DVS and Payne cell.

Sample	DVS Value	Literature Value
Honey	0.5749	0.55 – 0.65
Corn Starch	0.3952	0.28 - 0.46
Ketchup	0.9306	0.93 – 0.95
Dried Cranberries	0.5121	0.42 – 0.56
Dried Milk Powder	0.2453	0.2-0.4
Bread Crumb	0.9961	>0.96
Bread Crust	0.8913	0.872-0.909



# Conclusion

Utilizing the functionality of DVS instrumentation for the study of foods allows the vapour sorption characteristics to be studied on raw materials, food ingredients, final food formulations, flavours, fragrances, and packaging materials. Water sorption on these materials can be vital in understanding material stability and improving customer satisfaction. The use of a novel Payne cell allows barrier property characterisation and water activity measurements. This overview application note only summarises a handful of these applications, but hopefully illustrates how DVS technology could be applied to a wide range of food-related materials and challenges.

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