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DVS Application Note 62

Water Activity(Aw)Measurements Using a Payne Cell with a Flux-Calibrated Membrane and DVS

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The measurement of water activity (Aw) is a very important metric in the food industry. It is used by food manufacturers and government agencies to evaluate the quality of food ingredients and to predict a product's potential shelf life. The most widely used method to determine Aw is the measurement of water vapour pressure emanating from a food material enclosed in a sealed chamber. This application note demonstrates a possible alternative to the traditional method employed by industry and describes advantages that may be gained by this new procedure.

Introduction

When a food product is first packaged for sale, be it at the end of a production line in a large manufacturing complex or at a small local bakery, it begins to lose the qualities that make it desirable. Those qualities are often associated with its internal water content and its water activity or Aw, defined as the vapour pressure due to free water in the sample [1]. Properties such as taste, texture, smell, stickiness, colour, solubility, shelf life, safety and others are highly dependent on the amount of water in the sample and the water activity. As a result, this is a common measurement in the food industry.

The most commonly used method to measure Aw involves sampling a representative portion of the food product and loading it into a cup or other sample holder. The sample is then inserted into a device that measures its temperature and attempts to measure the vapour pressure above the material in question. For this reason the sample space is kept as small as practical.

The vapour pressure over the sample is commonly measured using a dew point analyser. This device works by cooling the surface of a small mirror until the dew point of the surrounding vapour is reached and droplets form on the mirror surface. The dew temperature is used to calculate the water vapour pressure.

This application introduces a novel method that may be complimentary to the traditional Aw measuring technique described above. The method uses the capabilities of the SMS High Mass Dynamic Vapour Sorption instrument and Payne Cell. The method could also be performed on the SMS low mass instruments, but is better suited for the high mass models due to the larger sample size and ease of use.

Method

This new method should complement the more commonly used Aw measurement techniques by offering the following advantages:

a) Inherently simple in concept
b) Uses relatively small samples
c) Does not require periodic calibrations
d) Independent of chilled mirror calibrations
e) Independent of surface temperature calibrations
f) Relatively fast and robust





The technique uses a Payne Cell cup which has been described in SMS Application Notes 49, 52, and 56. In this study, a larger version was used (see Figure 1) with an active membrane opening size of 12.3 mm diameter which results in an active exposed area of 1.188 x 10 $^{-4}$ m^2. The sample volume in the cell is 356 mm^3.

In previous application notes, the Payne Cell has been used successfully to measure the flux of water or solvent through a sample membrane by loading the cell with desiccant and observing the mass gain of the assembly as the solvent diffuses through the membrane and into the desiccant. Additionally, in SMS Application Note 52, the flux through a membrane was measured at various RH levels external to the Payne cell assembly. In SMS Application Note 56, the wet cell method was used to quantify differences in treatments to a Vitro-Skin® membrane as a measure of Trans-Epidermal Water Loss (TEWL). It should then be possible to use a combination of these techniques to actually measure the vapour pressure of the material inside the Payne Cell as long as the membrane flux responds linearly to the internal vapour pressure.

Figure 1 - Payne Cell for high mass DVS.

Results

In order to test this methodology, a membrane film that allows a measurable amount of water vapour flux but that does not absorb significant amounts of water was required. This is to minimize the effect of swelling and the impact it may have on film flux. A film of polystyrene 20 microns thick was used for these experiments based on its hydrophobicity. To test whether the film responds linearly to humidity inside the Payne Cell, several experiments were performed using saturated salt solutions with the polystyrene film mounted in the Payne Cell. The water vapour pressures of these saturated salt solutions are well known in the literature [2]. The film was washed with high purity water (NERL®) after each experiment to avoid contamination. All experiments were performed at 25.0 ºC and 200 sccm dry gas flow (~0.5% RH). A representative data plot is shown below in Figure 2. The plot shows the mass loss of the Payne Cell assembly with polystyrene film covering the saturated salt solution of $Mg(NO_3)_2$.

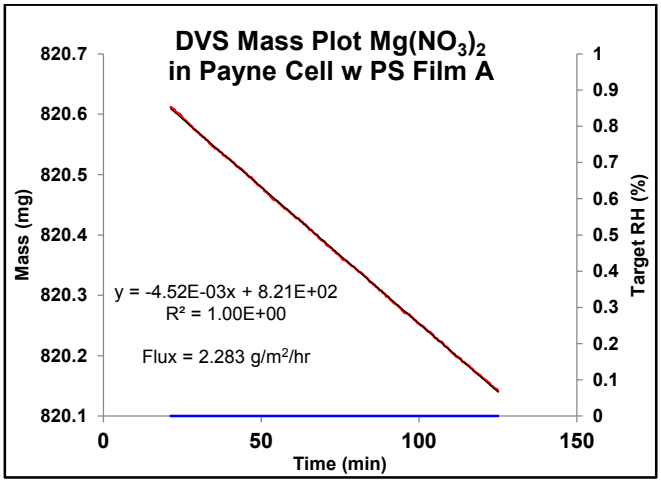

Figure 2 – Water flux experiment with PS film over $Mg(NO_3)_2$ saturated solution in Payne Cell

The fitted line has an R^2 = 1.00 and the slope results in a flux value of 2.283 g/m^2/hr. Similar experiments were performed with a range of saturated salt solutions. The results are shown in Table 1.

Table 1. - Polystyrene film water flux vs. internal humidity.

Saturated Salt Solution	Payne Cell Internal Salt Solution (%RH)	Polystyrene Film-Calculated Flux, 25°C (g/m²hr)
LiBr	6.40	0.2568
LiCl	11.30	0.4744
$MgCl_2$	32.80	1.4340
$Mg(NO_3)_2$	52.89	2.2830
NaCl	75.30	3.1920
KCl	84.30	3.6460
KNO_3	93.70	4.0000
H_2O Pure	100.00	4.2930

A plot of the data in Table 1 is shown Figure 2. Clearly, Figure 2 indicates that the polystyrene film exhibits a linear flux behaviour with respect to the water vapour pressure in the Payne Cell. Therefore, it should be possible to load the cell with any material that has a water vapour pressure and determine its Aw simply by measuring the slope of the mass loss (flux) across the same membrane and comparing it to the calibration curve.

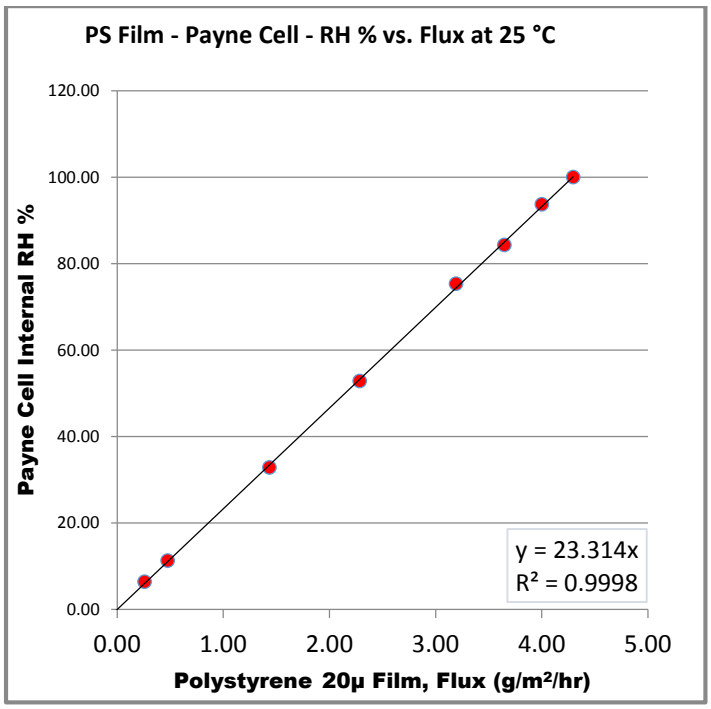

Figure 3 – Payne Cell internal RH vs. PS film flux, 25 °C

High Aw Food Samples

With the film calibration complete, it is now possible to test some actual food samples using the same procedure. All experiments were done at 25 °C and 200 sccm of dry gas flow. To check accuracy, four experiments on $Mg(NO_3)_2$ yielded an average Aw of 0.5229 with a standard deviation of 0.0057. This compares quite well with the literature value of 0.5289 [1].

Since water activity can vary significantly with the composition of prepared foods [3], it was desirable to have a list of common foods and their Aw as measured by accepted methods. A short list was found in several references [4, 5, 7]. From these lists a few items were chosen to cover the range of Aw from 0.30 to 0.99. These items were purchased at a local supermarket and tested as soon as possible. Shown below are the results of tests performed on some of these food items.

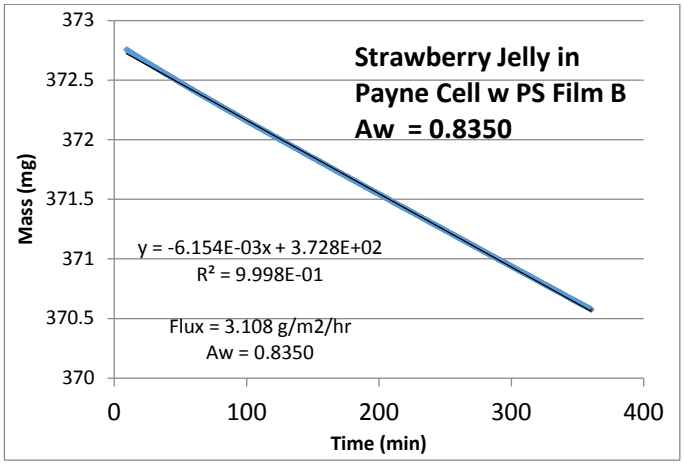

Figure 4 – Strawberry Jelly, measured Aw = 0.8350

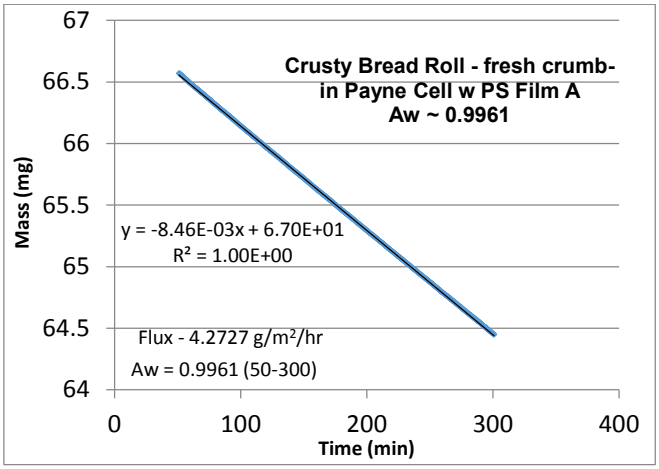

Fig. 5 – Fresh bread crumb from fresh bread roll, Aw = 0.9961.

The result shown in Figure 4 is for Strawberry Jelly. A supermarket brand jelly was chosen with the simplest formulation available. The test was allowed to proceed for more than 1200 minutes to see if there was any change in the flux being measured. The flux is very constant over the entire time period. A fit to the first 350 minutes of data results in an R^2 of 0.9998. The resultant Aw is 0.8350, in the upper range of the for jellies, jams and marmalades in reference 5 (0.75 to 0.80). The first 10 minutes were deleted to allow for temperature equilibration.

Several other experiments were performed in similar fashion to obtain statistical data on the method used. The best results were obtained when the sample was taken just below the surface of the jelly using a spatula or by using a pipette with a large opening for sampling deep into the jelly. Twelve such experiments were performed with an average Aw result of 0.8298 and a standard deviation of 0.0089. Sample sizes ranged from 250 to 450 mg. No correlation was observed with sample size.

In Figure 5, a sample of fresh bread crumb (or flesh) from a bread roll was measured using the same procedure. The Aw is high, 0.9961, as expected from Reference 6 (Aw>0.96).

A sample was also taken from the bread crust and tested using the same method. Shown below in Figure 6, the result of 0.8913 is in good agreement with Reference 6 (0.872 - 0.909).

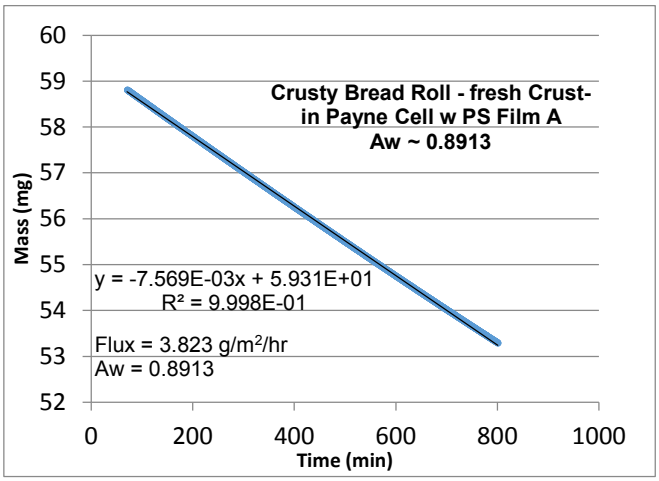

Figure 6 – Fresh crust from Crusty Bread Roll. Aw = 0.8913

Figure 7 – Payne Cell filled with sample.

Low Aw Food Samples

To sample food materials with lower Aw (<0.50) values, two materials were chosen after consulting references [4] and [5]. One of these is dry milk powder, which according to the above references, should have an Aw from 0.20 to 0.70. However reference [8, page 9] has a narrower range and clearly describes the manufacturing process. The desired Aw is 0.3 to 0.4 with 0.5 as maximum but can be as low as 0.20.

This food product proved more difficult to measure because it did not result in a straight line mass loss as in other materials, Figure 8 below.

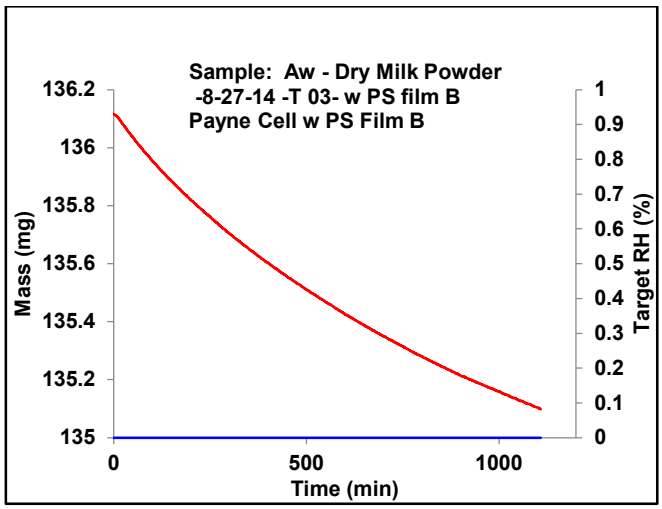

Figure 8 – Dry Milk Powder – Aw measurement

The milk powder is very dry, approximately 4 wt% water as measured by total mass loss. This curving line may indicate that the water content is so low that the sample cannot provide enough water for a constant decay curve as in the other materials which have high water content. In this case the slope at the start of the curve should give us a more accurate measure of Aw. In Figure 9 is plotted the first 100 minutes of data from Figure 8. The data is quite linear and the Aw result is 0.2254. Four measurements were made using this procedure and the average Aw for the first 100 minutes of data was 0.2453 (Std. Dev. = 0.0257). This is in good agreement with the reference [8] range (0.2 – 0.5) considering that this is a highly engineered food.

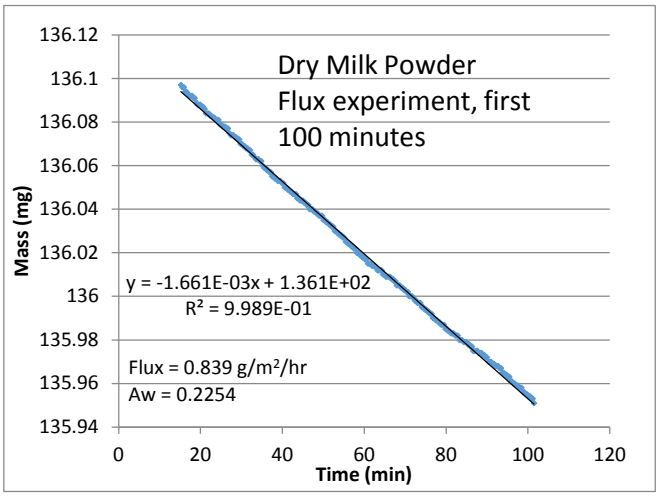

Figure 9 – Dry Milk Powder, first 100 minutes from flux experiment in Figure 8.

Another class of food items with low Aw values are spices. Onion powder was chosen for our test. The data for this item is similar to Dry Milk, it has a slight curve rather than a straight line. For the same reason described previously, the reservoir of water in the sample is not sufficient to provide a constant moisture vapour pressure (Aw) above the sample during the experiment. Therefore the Aw is measured during the first 100 minutes of data. Four experiments were performed with an average Aw of 0.3232, (Std. Dev. 0.0210)

However, just as high Aw materials should be sampled quickly to prevent the sample drying out, these low Aw items should also be sampled carefully because the ambient humidity is often higher than the sample Aw, causing the sample to absorb moisture which is then released during the experiment. This results in erroneous high values of Aw regardless of what measurement method is used. Therefore, samples with Aw lower than ambient humidity should be sampled in controlled RH environments such as a glove box with dry air. For additional information on environmental RH control of enclosures, please see the Gen-RH product line at http://surfacemeasurementsystems.com/products/genrh-family/

Other Foods Tested

Other food items were also tested successfully. Table 2 shows the Aw results for these additional items. All items were purchased just prior to the experiments. These results agree well with the listed references.

Table 2 – Additional foods tested

Food Item	DVS Measured Aw	Literature Reference
Honey	0.5749	0.55 – 0.65 [10]
Corn Starch	0.3952	0.28 – 0.46 [11]
Ketchup	0.9306	0.93 – 0.95 [12]
Dried Cranberries	0.5121	0.42 – 0.56 [13]

Conclusion

This new method for the measurement of water activity (Aw) in foods and other materials, provides reliable, accurate and independent values when compared with more traditional measurement techniques. The method may be used to identify issues related to equipment calibration and/or sampling errors in other methods.

This new method also provides us with the ability to measure Aw in small samples which reach temperature stability very quickly. The data shows that the full range of Aw values may be measured using this technique. Attention should be paid to sampling low Aw materials as these can acquire water from the environment and produce inaccurate results with this or any other method being used. It should also be possible to use variable width films to tailor the measurement to the type of foods being tested.

Because the mass decay is linear for high Aw foods and also for low Aw foods at short times, the experiment time may be reduced to less than 120 minutes. The DVS instrument can also be used at variable temperatures offering another important variable to explore.

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