



Use of DVS-NEAR IR Technique for Material Characterization

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This Application note describes the combination of Near IR Spectroscopy with Gravimetric vapour Sorption analysis for Material Characterization.

Introduction

The combination of dynamic vapour sorption and near infrared spectroscopy (DVS- NIR) has been considered a novel technique for studying various materials and making in-depth analysis into their sorption/desorption properties. The investigation under this technique would provide a better understanding of solid-state reactions and establish the relationship between the stability of materials and their structural changes

Dynamic gravimetric vapour sorption instruments have now become the standard method for investigating the vapour sorption properties for various materials. However, routine bulk characterisation may not ensure a comprehensive picture of transitions and gravimetric changes in the different part of the body of the solid/organic structure such as Avicel [1,2,3].

Theory

Near-infrared spectroscopy (NIRS) is a fast and non-destructive method that provides multi-constituent analysis of virtually any matrix. It uses the near-infrared region of the electromagnetic spectrum (from about 800 nm to 2500 nm) and covers the wavelength range adjacent to the mid infrared and extends up to the visible region. Typical applications of NIR spectroscopy include the analysis of foodstuffs, pharmaceuticals, combustion products, agrochemical, material science, and is a major branch of astronomical spectroscopy.

Near IR operates in two primary modes: reflectance and transmittance. Best for solid objects (grain, soil, stover), reflectance measures how much light is reflected off the sample, while transmittance is better for liquid samples since it measures how much light passes through the sample.

In recent years, NIR spectroscopy has gained wide acceptance within the pharmaceutical industry for raw material testing, product quality control, and process monitoring. The growing pharmaceutical interest in NIR spectroscopy is probably a direct result of its major advantages over other techniques. In particular, these advantages include being able to prepare





samples without any pre-treatments, the ability to separate the sample measurement position and spectrometer by use of fiber optic probes, and the capability to predict chemical and physical sample parameters from a single spectrum.

In this study, various solid-vapour interactions are studied by using DVS, gravimetrically, an automated temperature and humidity controlled ultra-balance system coupled with a near infrared spectrophotometer (NIR).

Method

Materials

DVS- NIR studies were performed on Avicel, Spray Dried Lactose, Spray Dried Salbutamol Sulphate, and Nafion Membranes.

NIR spectra were recorded using a fiber- optic probe situated approximately 4mm below the flat quartz glass sample pan. NIR intensity spectra for all samples were recorded.

The details of the NIR system (detector and spectrometer) are listed in Table 1.

Table 1. NIR detector and spectrometer specifications from B&W Tek

System		
Measurements	Transmittance, Reflectance, Absorbance Fiber Optic Probes and Sampling Accessories Required (sold separately)	
Connections	Illumination and Collection SMA905 ports for fiber optic coupling	
Triggering	Triggering Front panel connection for use with sampling probes with triggering feature	
Computer Interface	USB 2.0/1.1	
Software	iSpec™	
Software Options	Software Developer's Kit (SDK) Sample Code: C#, C++, Visual C++, Visual Basic, VBA, Labview, VB.NET	
Instrument Dimensions	9.5 (H) x 6.7 (W) x 13.7 (D) in 242 (H) x 170 (W) x 347 (D) mm	
Weight (model dependant)	7.9 - 10.8lbs 3.6 - 4.9kg	
Power	12V DC @ 10.8 Amps, Battery Option Available	
Operating Temperature	0°C to 45°C	
Spectrometer		
Optical Design	Crossed Czerny-Turner Spectrographs	
Digitization Resolution	16-bit or 65,535 to 1	
Integration Time	250ms - 5ms (Min. Spectrometer Dependant), 63,535ms x multiplier (Max.)	
Light Source	Tungsten Halogen 5W	Tungsten Halogen 20W
Spectral Output Range	350 to > 2600nm	350 to > 2600nm
Color Temperature	2800 K	2900 K
Warm Up Time	~40 Minutes	~40 Minutes
Rated Life	10,000 Hours	2,000 Hours

Results

Avicel

Typical net percent change in mass (based on dry mass) versus time plots for the Avicel sample for the half cycle are shown in Figure 1a.

From Figures 2a and 2b, the Avicel water vapour sorption characteristics over 0-95% RH shows that there is a significant spectral change due to uptake of moisture by Avicel at 25 °C. This change appears to be reversible when the Avicel dries out. The NIR spectra is comparable with the kinetics results.

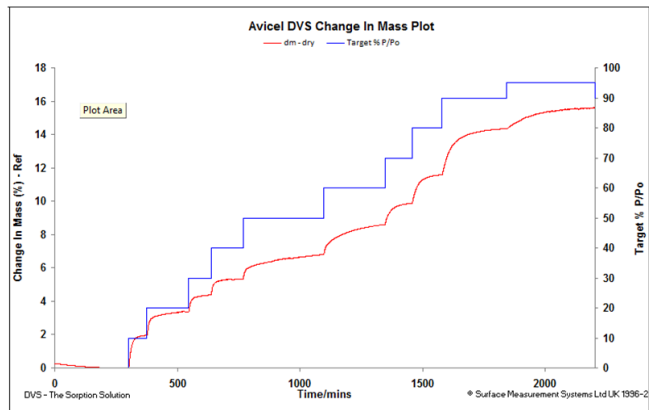


Figure 1a: Water vapour sorption kinetics at 25°C of Avicel.

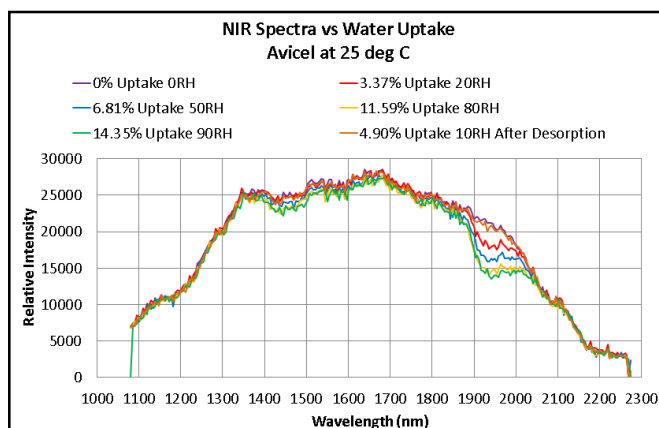


Figure 2a: Avicel NIR Spectra.

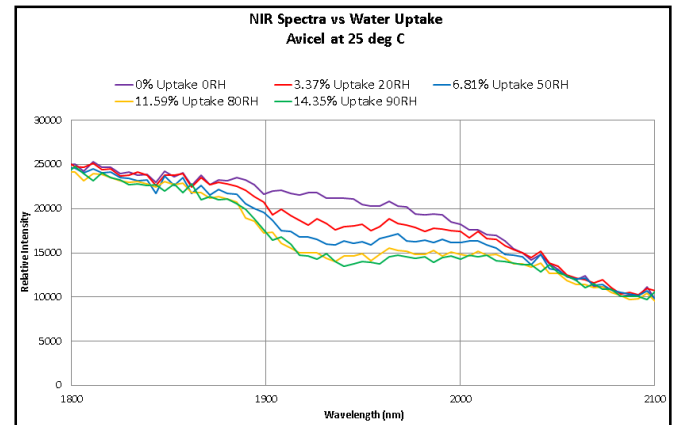


Figure 2b: Avicel NIR Spectra- expanded.

Spray Dried Lactose

In this study DVS-NIRS has been used to study the structural changes in amorphous lactose when exposed to different humidity levels for different lengths of time. It is known that amorphous lactose will collapse, trapping water in its mass, and then crystallise on exposure to 50% RH or more at 25°C [4].

The water vapour sorption data of spray-dried amorphous lactose is shown in Figure 3.

The NIR spectra for spray-dried lactose are shown in Figures 4 and 5 and illustrate different time lengths of exposure to 58% relative humidity. The NIR spectra show that these structural changes occur at 50% RH where as the DVS mass plot shows a higher %RH value of 60 for the crystallisation step.

The comparison NIR plot, shown in Figure 5, shows the reproducibility of the experiments.

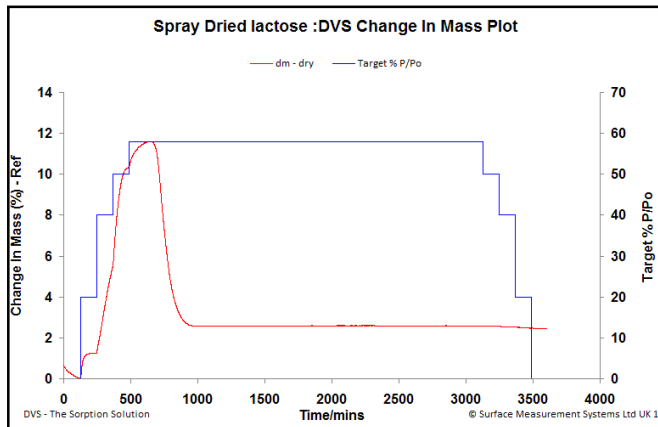


Figure 3: Water vapour sorption kinetics at 25 °C of spray-dried lactose (44 hours at 58RH).

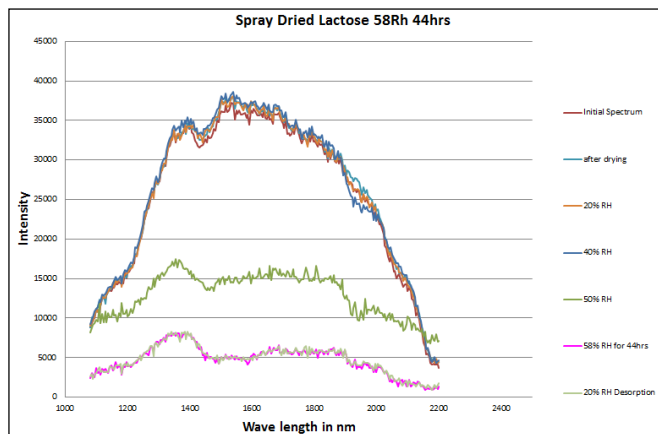


Figure 4: NIR Spectra for Spray dried Lactose exposed to 58% RH for 44hrs.

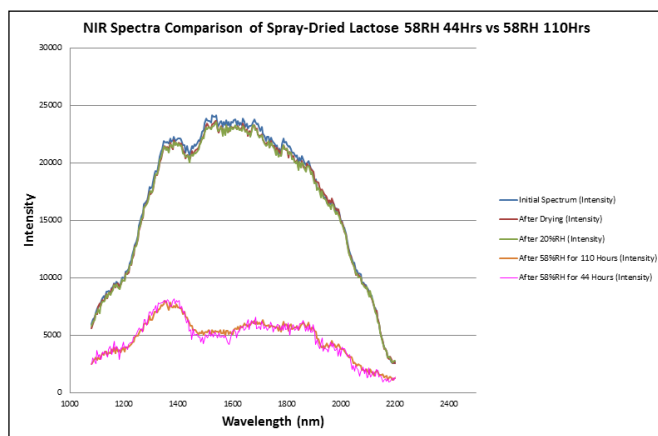


Figure 5: NIR Spectra comparison for spray-dried Lactose exposed to 58% RH for 44hrs vs 58% RH for 110hrs.

From the DVS-NIRS it is therefore possible to conclude that spray-dried lactose undergoes

irreversible crystallisation after exposure to 58% RH as seen in the NIR spectra.

Previous studies have shown a two-step crystallisation mechanism for amorphous Lactose. The gravimetric results in Figure 6 indicate a one-step crystallisation process at 53%, 55%, 57%, and 60% RH. For these experiments, the amorphous fraction decreases precipitously in one step. However, at 51% and 50% RH, there is an initial decrease, followed by a 'levelling off' in the amorphous fraction. This is followed by a second decrease, indicating a two step crystallisation mechanism. The NIRS data in this current study support this two-step mechanism.

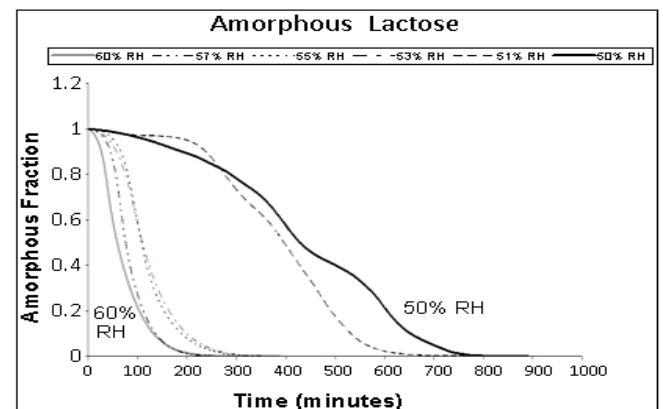


Figure 6: Amorphous fraction as a function of time between 50% and 60% RH at 25 °C.

Spray Dried Salbutamol sulphate

The crystallization of spray dried salbutamol sulphate at 75% RH was studied with the DVS-NIR technique. From Figure 7, the DVS mass plot shows that the material crystallises shortly after the exposure to 75% RH, and the crystallization process during the following 2 hours can be monitored by the NIR spectra shown in Figure 8. The spectra show that the first significant change in intensity occurs after 43 minutes at 75% RH and the crystallisation is complete after 58 minutes.

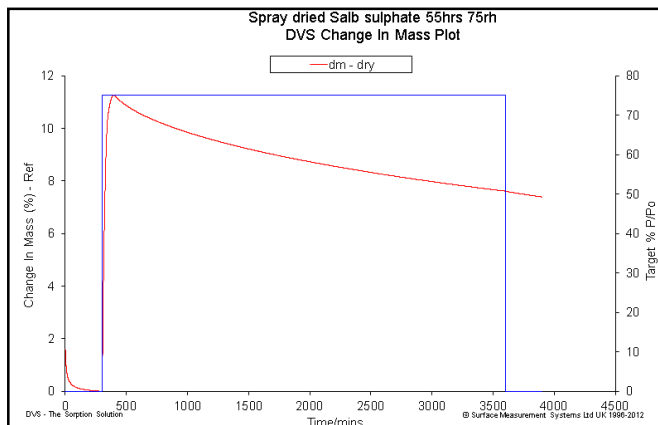


Figure 7: Water vapour sorption kinetics at 25°C spray-dried Salbutamol Sulphate (55 hours at 75% RH).

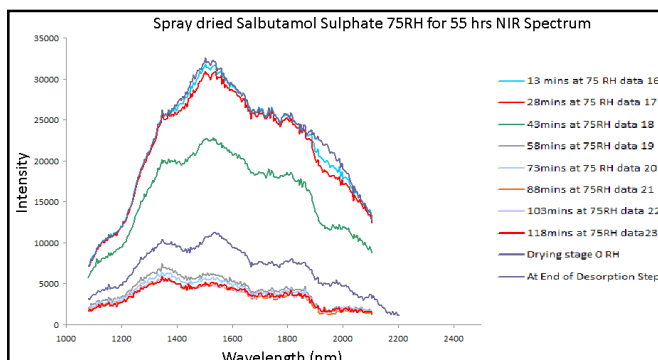


Figure 8: NIR spectra of Spray dried Salbutamol Sulphate.

Nafion Membrane

Proton Exchange Membrane Fuel Cells (PEMFC) consist of several layers that allow transport of water. In this study the water content and diffusion kinetics were studied on Nafion® based membrane, which is commercially available and often used as an exchange membrane in PEMFC's. Combined DVS water sorption and Near IR studies on the hydration of Nafion® membranes shows change in NIR spectra (Figure 10 and 11) and is comparable with DVS change in mass data, Figure 9, where the spectral changes are observed in NIR with water uptakes of the Nafion Membranes.

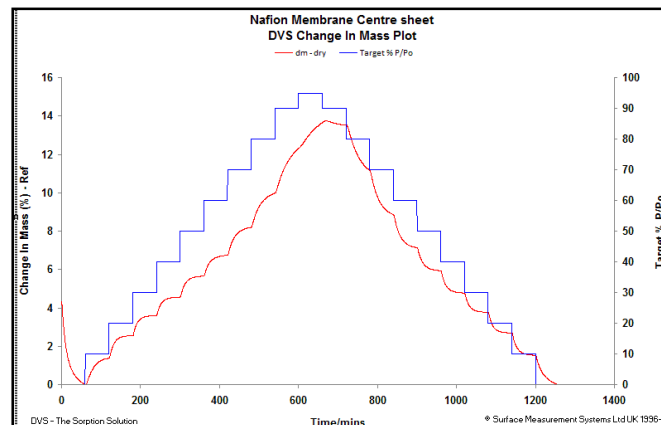


Figure 9: NIR Spectra for Nafion Membrane centre sheet.

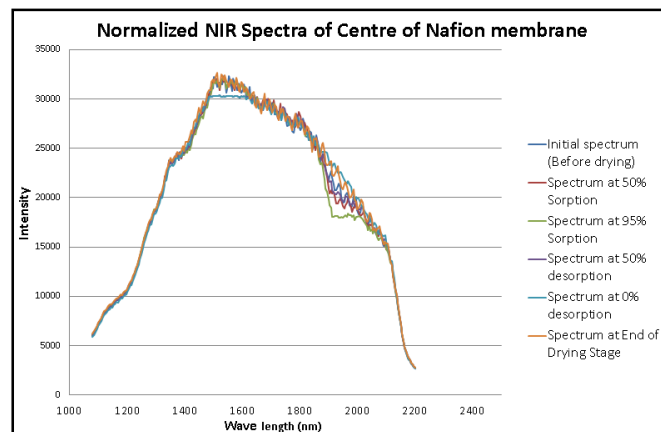


Figure 10: NIR Spectra of Nafion sample.

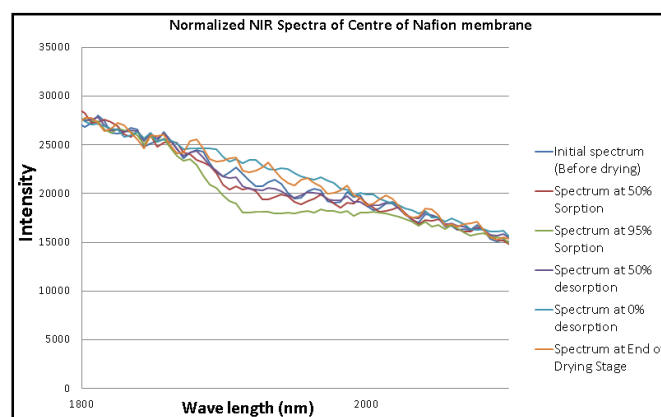


Figure 11: NIR Spectra of Nafion sample-expanded.



Conclusion

The results show that the use of gravimetric analysis together with NIR spectroscopy provides information about the dynamics of water interaction with various materials [5]. Recording an NIR spectrum takes only a few seconds and complete recovery of the sample is also possible. DVS, on the other hand, provides more tangible information in the form of mass change. There are obvious advantages to having both techniques operating in combination because an immediate check of the NIR data can be obtained from the DVS sorption response. Furthermore, measuring the NIR data in the DVS system ensures the complete control of the environment and thus control of the water sorption peaks that would otherwise make a major contribution to the NIR response [6].

References

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