Detecting and Modelling Porosity in Natural and Engineered Materials

Armando R. Garcia and Dan Burnett, Surface Measurement Systems Ltd.

Porosity is a common characteristic of many natural and man-made systems. The pores in these systems can have a significant impact on the way materials behave and react to conditions in the environment. Dynamic Vapour Sorption (DVS) can be a valuable technique in detecting and characterizing porosity in these systems.

Introduction

Many common materials and foods contain pores and pore networks. These can greatly impact material behaviour. Nature is full of examples where pores are an integral part of living organisms and inert materials. Fruits, vegetables and plants of all types have extensive pore networks that help deliver nutrients to cells, dispose of waste and store water. Other natural materials such as soils, rocks, and minerals can exist in natural forms where porosity can play an important role in the way they behave when interacting with the environment or when subjected to processes used to convert them into useful forms for society. Even human and animal tissue can have pore structures that help to perform specialized tasks.

While beneficial in many cases, sometimes porosity can be detrimental. Human bones become brittle and are prone to breakage when too many pores are present, as suffered by people with osteoporosis. Pores in metal welds can weaken important joints in support structures and transportation vehicles, leading to premature failure. Engineered materials such as ceramics and composites can also suffer fatigue or breakage if pores are present during manufacture.

In this study we will present evidence obtained using DVS (Dynamic Vapour Sorption) which shows porosity in natural and engineered materials. DVS is sensitive to pores less than 500 Å diameter (i.e. meso- or micro-pores). For pores larger than 500 Å (i.e. macro-pores), vapour or gas-phase techniques like DVS are not applicable and liquid-phase technique like mercury porosimetry are typically used. This note will illustrate how to recognize a system with porosity when analyzed with DVS and how to infer or measure certain characteristics of the pore structure.

Method

All experiments were run on a DVS Advantage-1 instrument. For the natural porous samples (i.e. *soft* porous networks); it was decided to begin the experiment at a high humidity as soon as the sample is transferred to the instrument. This is the opposite of a typical DVS experiment where humidity is stepped up from 0% RH. The humidity profile is then 95% RH → 0% RH → 95% RH in 5% RH steps. This profile should give us the maximum water content of the sample and

it should also detect the collapse of pore structure if it occurs. For engineered or *rigid* porous samples, the samples were first dried at 0% P/Po at the measurement temperature or elevated temperature using the *in-situ* preheater on the DVS-Advantage. Vapour sorption isotherms were collected using water and organic solvents for these materials. All experiments were run at 25 °C with sample sizes between 5 and 50mg.

Results

Porous Food Samples

Foods often are comprised of complex structures which may include extensive pore networks. These pores impact food taste, texture and freshness. Fruits may show the collapse of pore structures [1] upon dehydration. Figure 1 displays the isotherm for a small piece of apple which was subjected to the 95-0-95% RH sequence as explained in the method section for *soft* porous networks. In this case, once the sample is dried at 0% RH, the pore structure collapses and cannot be re-hydrated. The blue line is the initial desorption beginning at 95% RH. The red line is the sorption phase after reaching 0% RH. The second isotherm, green and pink lines, only regains a small portion of the initial water content.
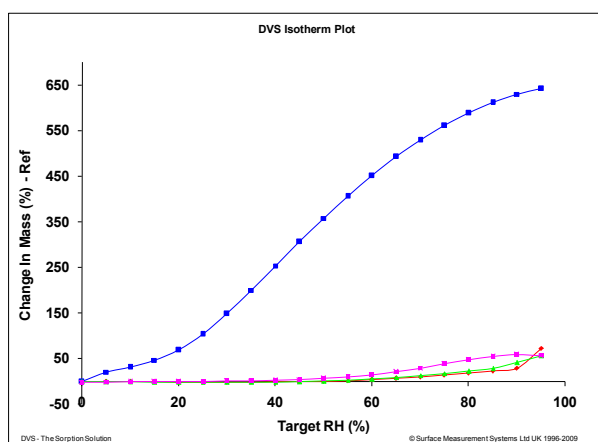

Figure 1. Apple piece, 95-0-95% RH, followed by 0-90-0% RH isotherms at 25 °C.

Another good example of the similar dehydration-induced pore collapse is shown in Figure 2. A cross section of a carrot was subjected to the same experimental procedure as in Figure 1. The loss of water is dramatic during the first desorption isotherm. For apple and carrot slices, the major pore structure collapses when the sample is dehydrated. This is similar to moisture sorption results on low rank coals [2]. Other materials where the pores resist collapse do not show this behaviour. Some of these are engineered materials such as Zeolites and activated carbons.
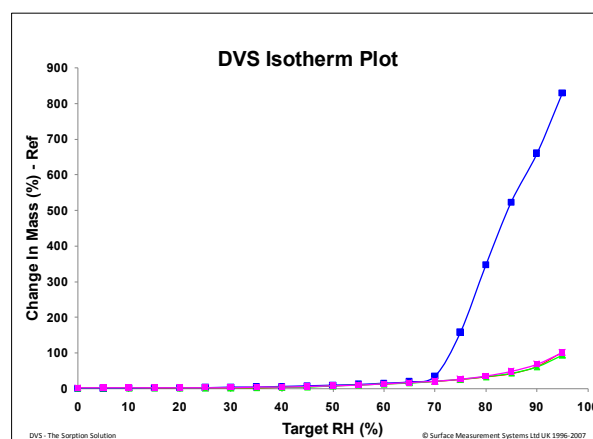

Figure 2. Carrot cross section, 95-0-95% RH, followed by 0-90-0% RH isotherms at 25 °C.

Zeolites

Zeolites can occur naturally but can also be engineered to have precise pore size distributions. In the case of 13X zeolite, the pores are in the range of 10 Å. Figure 3 shows two isotherms obtained on zeolite 13X with water. The isotherms are nearly identical, indicating that the pore structure does not change from one isotherm to the next under the conditions used for these experiments. This is opposite to the behaviour on the *soft* porous materials discussed previously. All sorbed water is free to move in and out of the pores for this material at the conditions measured. The isotherms show a dramatic increase in mass between 0 and 10% RH. This is typical for micro-porous materials (i.e. below 20 Å). There is some mild hysteresis at the high end of the RH scale, indicating that larger pores are present as well (i.e. meso-pores; 20 to 500 Å).
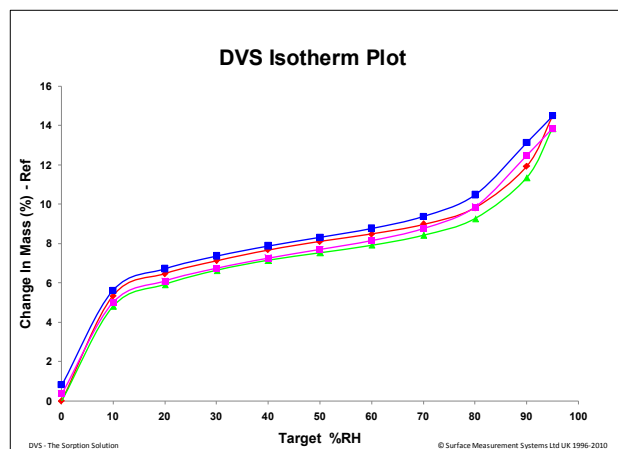
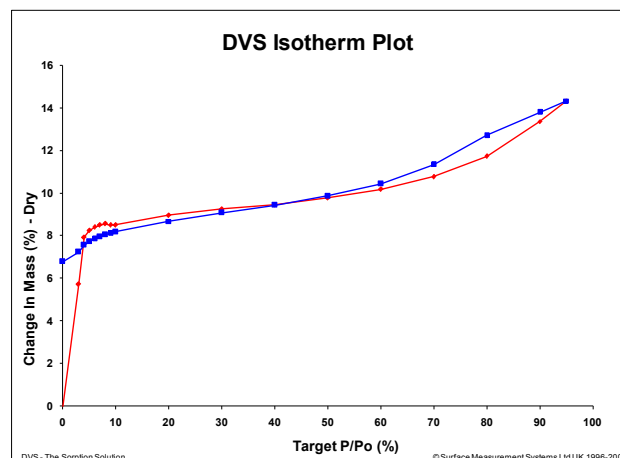*Figure 3. Two consecutive water isotherms of 13X zeolite at 25 °C.*

Figure 4. Octane isotherm with 13X zeolite at 25 °C.

In contrast, Figure 4 shows an Octane isotherm for Zeolite 13X, where a significant hysteresis is present at the low range of partial pressures. This indicates that octane behaves differently in the pore structure and requires heating in order to vacate the pores when the partial pressure is lowered to 0% P/Po. This is a good example of solvent selectivity. Water has a cross section area of 10.5 Å2, while an octane molecule has a cross sectional area of 63.0 Å2. Figures 3 and 4 clearly indicate that the smaller water molecules are free to move in and out of the pores, while the larger octane molecules become trapped in the 13X pore structure at 25 °C.

Applying the Dubinin-Radushkevich [3] model (SMS Isotherm Analysis Package) to the octane isotherm in Figure 4, results in a total pore volume of 0.14 cm3/g, R2 = 0.919. A similar experiment using cyclohexane (data not shown) resulted in a pore volume of 0.20 cm3/g, R2 = 0.986. Cyclohexane has a cross section area of 39 Å2, so the larger pore volume measured using cyclohexane may be due to the smaller cyclohexane molecules reaching smaller pores. The ability to tailor the probe molecule with different cross-sectional areas and different functional groups may help yield important information for steric and chemical selectivity of porous networks.

Activated Carbon

Another type of engineered material with a large pore structure is activated carbon. Some activated carbons are derived from coals. Figure 5 shows two isotherms taken for Norit Granulated Activated Carbon. Again, as in the case for zeolite, repeated isotherms on the same sample do not alter the pore structure. Both isotherms are nearly identical. The large hysteresis at the higher humidity indicates the presence of meso-pores that are being filled with water and require more time to empty during desorption phase of the experiment, due to capillary condensation. The hysteresis is not present in the earlier part of the isotherm. This indicates that the sample does not have a significant quantity of micro-pores accessible to water. Using the Young and Nelson [4] isotherm model (SMS Isotherm Analysis Package) on this data, shows water to be mostly sorbed into the internal structure of the material. The fit parameters yield 3.3×10^{-4} moles/g for monolayer water and 2.6×10^{-2} moles/g for internal water. The Young and Nelson model is a mathematical fit which deconvolutes vapour sorption into three components: monolayer sorption, multilayer sorption, and bulk (or internal) sorption.
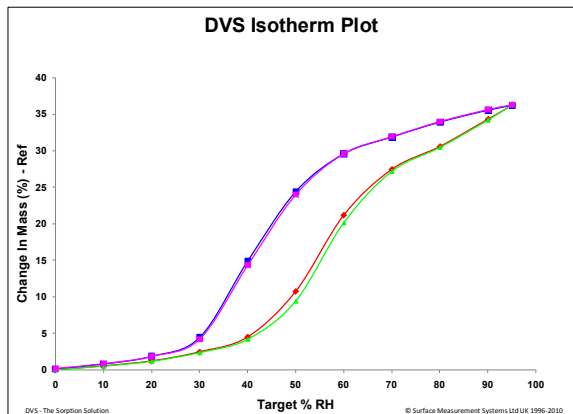
Figure 5. Two water vapour isotherms on Norit GAC at 25 °C.

Sandstone

A naturally occurring porous material that is often studied is sandstone. This and other types of stone are of great importance to the oil and gas industries since in the proper environments and conditions their pore space can contain hydrocarbons. Berea sandstone has become a model stone in the petrochemical industry. Figure 6 displays cyclohexane vapour sorption and desorption isotherms on a Berea sandstone measured at 25 °C. Prior to vapour sorption measurement, the sample was pre-treated at 200 °C for several hours. The resulting isotherms show a hysteresis gap between 30 and 85% P/Po, which is typical for meso-porous materials due to capillary condensation.

Figure 6. Cyclohexane vapour isotherms on Berea sandstone measured at 25 °C.

The meso-pores were characterized using at t-plot and the BJH [5] model (SMS Isotherm Analysis Package). Using this approach the plot in Figure 7 was obtained. This plot gives us the cumulative meso-pore volume of the sandstone and complements data obtained using mercury porosimetry experiments [6].
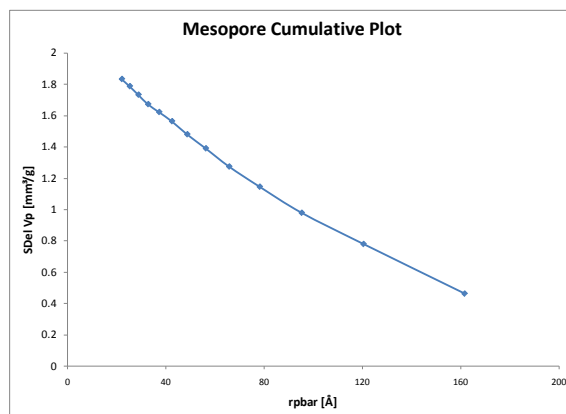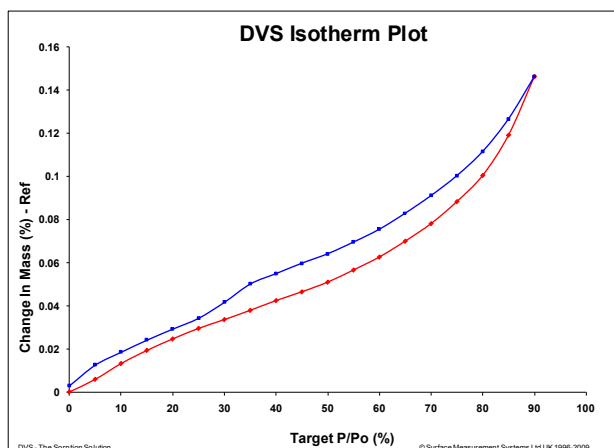

Figure 7. Meso-pore cumulative plot for Berea sandstone using Cyclohexane vapour at 25 °C.

Conclusion

A variety of materials have been analyzed using DVS to detect porosity. It was possible to detect porosity in very complex organic materials such as fruit tissue. By using modified experimental techniques, the presence of *soft* collapsible pores was detected. The initial water content of these materials is easily determined using DVS. Inorganic materials such as Zeolite and sandstone can also be analyzed using DVS to detect the presence of macro- and micro-pores. The *rigid* pores in these materials are robust and behave in a predictable manner. Isotherm modelling was applied to all the isotherms and was shown to provide useful information about the nature of the pore structure.

References

1 "Three-Dimensional Gas Exchange Pathways in Pome Fruit …", Pieter Veerboven, et. al., Plant Physiology, 147, 518-527 (2008).

2 "Moisture Sorption and Pore Collapse of Coals", SMS Application Note 53.

3 "Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures", M.M. Dubinin, Carbon, Vol. 27, 457-467, (1988).

4 "Theory of Hysteresis Between Sorption and Desorption Isotherms in Biological Materials", J.H. Young and G.L. Nelson, Trans. ASAE, 260-263, (1967).

5 "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms", E. P. Barrett, L.G. Joyner, and P.P. Halenda, JACS, 73, 373-380, (1951).

6 "Fractal Characterization of The Geysers Rock", Kewen Li and Roland N. Horne, Geothermal Resources Council Transactions, 27, (2003).