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Comparison Between Static and Dynamic Methods for Sorption Isotherm Measurements

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COMPARISON BETWEEN STATIC AND DYNAMIC METHODS

FOR SORPTION ISOTHERM MEASUREMENTS

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ABSTRACT

Sorption isotherms of Microcrystalline Cellulose (MCC), pharmaceutical granules, PolyEtherBlocAmide (PEBA) membrane and sewage sludges were measured at various temperatures using three different experimental gravimetric methods: the saturated salt method, the Dynamic Vapor System (DVS) apparatus and a simultaneous gravimetric and calorimetric measurement techniques using a Setaram TGA-DSC111. A comparison between the salts method and DVS is proposed at ambient temperature for the MCC, the pharmaceutical granules and the PEBA membrane. The comparison between the static method and the DVS shows that the results are consistent as long as the apparent diffusion coefficient in the material is high. When the apparent diffusion coefficient becomes low, the difficulty to reach the thermodynamic equilibrium appears in the saturated salts method. Then, DVS and TGA-DSC apparatus were used to investigate the desorption isotherms for the MCC between the ambient temperature and

90°C. Finally, an application on biological products is proposed: the desorption isotherms for two sewage sludges coming from the same wastewater treatment plant were determined with the DVS and the TGA-DSC equipments at 45°C. The accuracy of the TGA-DSC is good as long as the apparent diffusion coefficient is above 10^{-9} m²/s. When this threshold value is overstepped, the desorption isotherms are overestimated.

Key Words: Saturated salts method, DVS, TGA-DSC, MCC, pharmaceutical granules, PEBA, sludge

INTRODUCTION

The thermodynamic concept of water activity is used in drying applications through the sorption isotherms, which represent the change in water activity versus the change in moisture content of a sample at equilibrium and at a specified temperature. Adsorption or desorption isotherms provide essential information on water solid interactions and solid porous structure (if any). Five general types of isotherms have been reported (Brunauer et al., 1938) and, for most food or organic materials, the sorption isotherms have a sigmoïd shape of type II. Applications for sorption isotherms in food processing and environmental sciences are process design and control, product stability determination to forecast the growth or the death rate of microorganisms, and thermodynamic properties prediction like the sorption enthalpy.

The measurement methods for water activity have been classified by Leung (1983) and Rouquerol et al. (1999). Two main classes were determined: the manometric methods in which the pressure above a known mass of sample is measured, and the gravimetric methods in which the pressure above the sample is fixed and the mass measured. Ritzi (1986) asserts that manometric methods were not suitable for materials containing large amounts of volatiles or those undergoing a respiration process. Among gravimetric methods, the saturated salts method is widely adopted as a standard. However, several days,

or even weeks, may be required to obtain the equilibrium and, at high relative humidity, this delay can lead to bacterial growth which consequently invalidates the results (Rahman, 1995).

Interest in using simultaneous gravimetric and calorimetric measurements such as a Setaram TGA-DSC111 during drying or using the Dynamic Vapor System arises from the necessity of obtaining basic knowledge of biological products like sewage sludges (Ferrasse, 2002). This paper presents a comparative study on three different measurement methods for water activity of materials with different properties: the microcrystalline cellulose (MCC), some pharmaceutical granules, a PolyEtherBlocAmide (PEBA) membrane, and two sewage sludges coming from the same wastewater treatment plant.

DEFINITION

Thermodynamics defines the activity a_i for a component i in a mixture, when liquid and vapor phases are in equilibrium conditions:

$$a_i = \gamma_i.x_i = \frac{\varphi_i.y_i.P}{f_{iL,pure}} \qquad (1)$$

Assuming that component i adsorbed on a solid is pure, the corresponding liquid molar fraction x_i is equal to 1 and thus the activity is equal to the activity coefficient γ_i. As the vapor phase is usually assumed to behave like an ideal gas, the fugacity coefficient φ_i is then taken equal to 1. Furthermore, at moderate pressure, an usual approximation is that the fugacity of the pure liquid in equilibrium with its vapor is equal to the saturation pressure of the component at the operating temperature, $P_{sat,i,}$. Thus, the activity of the component i may be written:

$$a_i = \frac{P_i}{P_{sat,i}} \qquad (2)$$

Thus, throughout this paper, the water activity will be defined as the ratio of partial pressure of water in the surrounding air to the saturation pressure of water at the given temperature. It should be noted that this is also the definition of the relative humidity.

THE EQUIPMENTS USED

Three experimental set-ups were used for the determination of the sorption isotherms: the standard equipment defined by a group of European research laboratories for the saturated salts method (Jowitt and Wagstaffe, 1989), a thermogravimetric analyzer (TGA) coupled with a differential scanning calorimeter DSC111 (Setaram, Caluire, France) and the Dynamic Vapor System (SMS, London, UK).

TGA – DSC apparatus

The furnace of the DSC, made of a silver cylindrical block with two refractory tubes inside, is heated with an electrical heater and a water-cooled coil heat exchanger. A Pt100 probe within the silver block allows to control the furnace temperature with an accuracy of 0.01K. Calorimetric measurements are made using a Tian-Calvet thermoelectric cells (Tian, 1924; Calvet and Prat, 1956) inserted between the refractory tubes and the furnace.

The thermobalance is made of a beam supporting two platinum crucibles set in the refractory tubes at the heat flux sensors level. One of the crucibles contains the sample, the other is called the reference. An electromagnetic device keeps the crucibles at a constant position during the measurement. This allows the determination of the mass loss with an accuracy of 1 μg. A conveying gas flows along the two crucibles. The recorded heat flux signal is the difference between the heat fluxes measured by the two thermoelectric cells. Its detection limit is 5 μW in isothermal mode and the measurement relative error is 1%.

The experimental protocol is as follows: a small sample of the material to be analyzed is introduced into the sample crucible, so that the thickness of the sample is small compared to the height of the crucible. Typically 5 to 10 mg of dry mass sample are used. The free surface of the sample is then covered with water. The crucible is hung to the beam and the calorimeter is closed. Dry air or nitrogen, flowing with a volumetric rate of 2 l/hr, is usually used as conveying gas. Then, the furnace temperature

is raised to the required level and the mass loss and calorimetric signal are continuously recorded. The amount of water laid on the sample surface should be higher than the amount of water which evaporates during the initial heating period.

From these experimental values, a theoretical model, based on the stagnant film theory (Bird et al.,1960), allows to calculate the desorption isotherm. This model is described in Ferrasse et al. ((a) 2000). With this experimental set up, the desorption isotherms can be determined at a temperature between 45°C and 95°C. This apparatus also enables a direct measurement of the total heat of sorption as a function of the moisture content (Ferrasse et al. (b), 2000).

Dynamic Vapor System (DVS)

This apparatus is made of a Cahn type microbalance inserted in a chamber at controlled temperature. The temperature level ranges between the ambient temperature and 45°C. As in the DSC apparatus, the beam supports two crucibles or two scales made of quartz. The sample to be analyzed is kept on one side, a reference weight is placed on the other side.

A mixture of dry nitrogen and saturated water vapor, whose proportions are fixed by mass flow controllers, is injected upwards on both sides of the balance. Two humidity and temperature probes (Rotronic, Switzerland) are set just below the crucibles. The head of the balance is kept under a constant rate of inert gas (nitrogen) to avoid instability and deflection. The accuracy of the temperature regulation, the moisture measurement and the mass loss are ±0.2°C, ±0.4% and ±0.1μg, respectively.

The experimental procedure begins with a verification of the baseline when recording sample mass as a function of time, hence verifying the dryness of the crucibles and the absence of static electricity. The desired sorption cycle (adsorption and/or desorption) and relative humidity values are defined. In addition, two equilibrium criteria are set. These criteria apply to each relative humidity conditions and decide on the transition from a humidity value to the next expected one. The first criterion is a limiting

value of the variation of sample mass with time, dm/dt, expressed in percentage of the initial sample mass. The second one is a minimum time during which the mass remains stable. For a 20 mg sample, typical values are twenty minutes for the minimum time and 10^{-3} %/min for the dm/dt criterion, which means that the equilibrium is considered when the mass variation will be less than 0.02 mg/min during at least 20 minutes. The experiment starts with the first relative humidity defined in the procedure and the mass loss is registered. Results are given in terms of sample mass in function of time for consecutive relative humidity values as defined by the sorption cycle.

Saturated salts method

The apparatus and the salts used in this method are the same as presented in the COST90 procedure (Jowitt and Wagstaffe, 1989). The equilibrium is assumed to be reached when the sample mass change between two consecutive days is less than 0.5 mg.

Differences between the dynamic methods and the static one

Using the TGA-DSC apparatus, it takes only a few hours to determine a desorption isotherm. However, this is linked to a major assumption of small moisture gradients in the sample. A local equilibrium is assumed between the surface of the sample and the flowing gas, and the superficial moisture content is supposed to be equal to the measured average moisture content. Thus, this method will be accurate if the difference between the measured mean moisture content and the surface moisture content is low. This could only be achieved for very thin samples and for relatively high moisture diffusion coefficients.

Unlike the TGA-DSC method, a thermodynamic equilibrium between the sample and the surrounding atmosphere is expected in the DVS and the saturated salts methods. But the equilibrium criterion on the variation of the sample mass with time applied for the DVS is not as severe as the one used for the saturated salts method. With the values given previously, the DVS criterion is 100 times higher than the

one fixed for the saturated salts method. As a result, a sorption isotherm could be obtained with DVS in a few days compared to the few weeks for the saturated salts method. Both apparatus could be used to determine adsorption and desorption isotherms.

TEST MATERIALS

The following materials with different physical properties were tested:

- Microcrystalline cellulose (MCC), referenced as Fluka, Cellulose Powder DS-0. This has been chosen as a reference material in food and pharmaceutical studies for its stability. The MCC has a density of 1630 kg/m^3 and a specific surface (measured with nitrogen gas) of 1.3 m^2/g. The average volume weighted diameter is 82µm;

- Pharmaceutical granules (Peré and Rodier, 2001), made up of lactose, starch and polyvinyl pyrolidone (PVP). The granules have a diameter between 1.25 and 4 mm, an internal porosity of 0.28 with a mean pore diameter of 2.5 µm;

- PolyEther Bloc Amide (PEBA) membrane, commercialized by TotalFinaElf. The thickness of this polymer membrane is about 30 µm as measured by scanning electronic microscope,

- and two biological materials, a primary and a biological sewage sludges coming from the same urban wastewater treatment plant. Their initial moisture contents are about 2.5 kg of water/kg of dry matter. The volatile mass fraction of the dried primary solid is 63,8% for the primary sewage sludge, this value decreases to 33,5% for the secondary sludge.

COMPARISON BETWEEN THE SATURATED SALTS METHOD AND THE DVS

The adsorption isotherms of the three non biological materials described above were determined at 25°C using the saturated salts method and the DVS.

Adsorption isotherms of the microcrystalline cellulose

Results coming from two different experiments performed with DVS are reported in Figure 1. To validate these experimental measurements, the mean adsorption isotherm curve determined during the COST90 program (Wolf et al., 1984) for ten water activities as well as the standard deviations for each point were used. This reference curve is also presented in Figure 1. The equilibrium moisture contents for water activity higher than 0.9 were not available from the COST90 program. With DVS, it was not possible to reach the target value of 1, but a water activity close to 0.98 was reached after an equilibration time of 6 hours. According to the classification by Brunauer et al.(1938), the desorption isotherms of MCC are of type II.

The DVS values are consistent with the data obtained from the COST program, especially for small values of water activity. Furthermore, the reproducibility of the experiments performed with DVS is quite good. Then, if we considered the time required to determine the complete isotherm, the equilibrium for a water activity of 0.9 (the highest value experimented) is reached after about 7 days with the saturated salts method while the complete isotherm was obtained with the DVS within 30 hours.

Good agreement between the static COST 90 method and the dynamic DVS is due to poor adsorption properties of this MCC; water is mainly adsorbed at the surface of the grain, and the relatively large diffusion coefficient in the bed. It is probable that diffusion inside the grains is negligible. The diffusion coefficients in the bed were roughly evaluated using the DVS experimental variation of the product mass with time and the second Fick's law for two given relative humidities. For diffusion in a 500 μm thick slab of MCC powder at 25°C, the estimated diffusion coefficient was $1.7\ 10^{-9}\ m^2/s$ for a relative humidity of 0.8, which corresponds to an average moisture content of 0.0914 kg of water/kg of dry matter, and $4.4\ 10^{-9}\ m^2/s$ for a relative humidity of 0.2, which corresponds to an average value of 0.0288 kg of water/kg of dry matter.

Thus, if the apparent diffusion coefficient of the material is above $10^{-9}\ m^2/s$, internal diffusion is not limiting enough to induce a discrepancy between the compared static and dynamic methods.

Adsorption isotherms of the pharmaceutical granules

The adsorption isotherms of the pharmaceutical granules are reported in Figure 2. The agreement between the static and dynamic methods is good for the whole range of water activity. Besides, the equilibration times for these granules were similar to the MCC ones: the equilibration time for the highest water activity is about 7 days for the saturated salts method and 5 hours for the DVS method.

As the diameter of the granules was relatively large compared to the size of the crucible, it was not possible to set a powder layer on the crucible and thus internal transfer limitation could only occur inside the particles. Applying the second Fick's law to a sphere of radius 0.625 mm, a $9.1 \ 10^{-10} \ m^2/s$ diffusion coefficient is obtained for a relative humidity of 0.8, which corresponds to an average moisture content of 0.0498 kg of water/kg of dry matter. This value increases to $1.4 \ 10^{-9} \ m^2/s$ for a relative humidity of 0.2, which corresponds to an average value of 0.0183 kg of water/kg of dry matter. These apparent diffusion coefficients are probably underestimated as the internal porosity of the material is not considered in the diffusion model used. Nevertheless, even if the diffusion occurs in the whole granules, it does not affect the accuracy of the dynamic method.

Adsorption isotherms of the PEBA membrane

The adsorption isotherms of the PEBA membrane are presented in Figure 3. The reproducibility between the two experimental methods is good for water activity below 0.6 but, for larger activity values, a significant difference appears. For DVS, the equilibration time was about 19 hours. For the saturated salts method, this time was evaluated to 12 days for a relative humidity of 0.9 but, according to the results, the thermodynamic equilibrium was not reached even if the mass change between two consecutive days was less than the retained value.

It is well-known (Mulder, 1996) that diffusion occurs inside a polymer membrane and that the diffusion coefficient is tightly linked to the sorption step. The second Fick's law applied for a slab

geometry and three relative humidity confirms this statement. The calculated values are reported in Table 1. The internal diffusion increasingly controls the sorption process when the relative humidity increases. This could explain the growing discrepancies between the two methods as the water activity increases as shown in Figure 3. The low estimated values of the apparent diffusion coefficients strengthen the hypothesis of a non thermodynamic equilibrium in the case of the saturated salts experiment.

This brings to the fore the difficulty to define a reasonable equilibrium criterion: the variation of the sample mass should be significant to be measured with a good accuracy and the equilibrium time should not be too long. Furthermore, when the internal diffusion controls the moisture sorption, it seems easier to reach the thermodynamic equilibrium with the DVS than with the static method. This is probably due to a higher external mass transfer in the dynamic method.

COMPARISON BETWEEN THE DVS AND THE TGA-DSC METHOD

This section is devoted to the comparison of the two dynamic methods. Since there are constraints associated with the use of the TGA-DSC apparatus, only desorption isotherms are presented. MCC was chosen as the reference material and its desorption isotherms between 25°C and 90°C were determined with both the apparatus. In a second step, both equipments were used to measure the desorption isotherms at 45°C for two sewage sludge, coming from the same wastewater but subjected to different treatments.

Desorption isotherms of MCC

The DVS apparatus was used for measurements at 25°C and 35°C and at higher temperature levels (50°C and 90°C), the experiments were performed with the TGA-DSC. The complete isotherm was determined in 4 hours at 50°C and in 2 hours at 90°C. The results are reported in Figure 4.

The classical evolution with temperature is observed even if the temperature shift on the desorption isotherms is not very significant. The data obtained with the TGA-DSC are consistent with the values

measured with the DVS for water activity below 0.8. For higher values, the accuracy of the TGA-DSC seems to be poorer. An important assumption made in theoretical sorption models underlying TGA-DSC methods concerns the homogeneous moisture concentration in the analyzed sample, which can be expected using thin samples and for relatively high moisture diffusion coefficients. If the effective water diffusivity in the sample is low, the difference between the mean moisture content used in the theoretical model and the local superficial moisture content, which is in contact with the flowing air, is no longer negligible. In consequence, as the desorption isotherm represents the change of moisture content with the water activity and as the moisture content measured with the thermobalance is higher than the superficial one, the desorption isotherm determined with the TGA-DSC is overestimated, as can be seen in Figure 4. In the selected operating conditions and according to the diffusion coefficients determined in the first part of this paper, it seems that internal transfer limitations begins to play an important role in the TGA-DSC method for a threshold coefficient lower than $1.7 \ 10^{-9} \ m^2/s$.

As the influence of the temperature on the desorption isotherms of MCC is scarcely reported in the literature in the investigated temperature range, two commonly used models, the Brunauer-Emmet-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models, were applied to analyze the experimental results. The BET model, first postulated by Brunauer et al. (1938), derives from kinetics and statistical mechanics but also from thermodynamic considerations and is frequently used for water activities ranging between 0.05 and 0.45. The variation of the moisture content with the water activity is given by equation (3):

$$X = X_{BET} \ \frac{C \ a_w}{(1 - a_w)(1 + (C-1) \ aw)} \tag{3}$$

where X_{BET} and C respectively represent the monolayer moisture content and a constant related to the net heat of sorption.

The Guggenheim-Anderson-de Boer (GAB) model is a semi theoretical model, which has been considered the best-fit model for many food materials over a wide range of activity. It can be written as:

$$X = X_{GAB} \frac{C' K a_w}{(1 - K a_w)(1 - K a_w + C' K aw)} \tag{4}$$

where X_{GAB} is the GAB monolayer moisture content, C' and K are two constants related to the temperature effect.

Both models were used to fit the experimental data curves plotted in Figure 4. The optimized parameters are summarized in Table 2. When compared to the literature, the same order of magnitude is found for the optimized parameters of the GAB model. For instance, under desorption conditions at 20°C (Rahman, 1995), the GAB monolayer moisture content is 0.058 kg of water/kg of dry matter and the two constant parameters C' and K are estimated at 24.38 and 0.805. As it was observed by several authors (Van den Berg, 1981; Timmerman et al., 2001), at a given temperature, the monolayer moisture content by the BET model is always smaller than the GAB value and the constant C', arising in the GAB model, is always lower than the constant C used in the BET model. Considering the influence of temperature, it can be seen on Figure 5 that, for both models, the monolayer moisture content decreases with the temperature whereas the constants C, C' and K are almost independent from this parameter. These tendencies have already been reported in the literature for a large number of biological materials (Menkov et al., 1999).

Desorption isotherms of primary and secondary sewage sludge

Part of our research work concerns the design of sewage sludge dryers (Ferrasse et al., 2002), which requires the knowledge of the sorption isotherm. As the sludge properties change rapidly with time, it is necessary to use the dynamic method. Usually, the drying process temperature is 90°C, but for the comparison of the methods, the desorption isotherms of two sewage sludge were measured with the TGA-DSC and the DVS at 45°C.

The data obtained for the primary and secondary sewage sludge are plotted in Figure 6 and in Figure 7 respectively. As the results obtained at low temperature with the saturated salts method for secondary

activated sludge (Vaxelaire and Puiggali, 2002), the desorption isotherm are of type II. From Figures 6 and 7, it can be noticed that the nature of the treatment in the wastewater treatment plant has a great influence on the desorption isotherm, i.e, the amount of bound water is more important in the secondary activated sludge than in the primary one.

For both sludges, the experimental results achieved with the TGA-DSC apparatus at relative humidities below 0.8 are higher than the values determined with DVS. For high relative humidities, equilibrium is not reached in the DVS equipment, and high apparent moisture contents are observed. The reproducibility of the results is rather good and sampling problems cannot justify the discrepancy between the two dynamic methods. The only possible explanation lies in the existence of a moisture gradient in the product during the TGA-DSC experiment. If the second Fick's law is applied to a 1mm thick slab of primary sludge, a $5.7 \ 10^{-9} \ m^2/s$ diffusion coefficient is obtained for a relative humidity of 0.8. For a relative humidity of 0.2, the thickness of the primary sludge slab was estimated to 500µm and the diffusion coefficient is of $3.8 \ 10^{-9} \ m^2/s$. The same orders of magnitude were found for the secondary sludge. These values are close to the threshold coefficient determined from the experiments performed with the TGA-DSC on the MCC.

CONCLUSIONS

Sorption isotherms of Microcrystalline Cellulose, pharmaceutical granules, PolyEtherBlocAmide membrane and two sewage sludges were measured at various temperatures using three experimental gravimetric equipments: the standard equipment defined for the saturated salts method, the Dynamic Vapor System and a Setaram TGA-DSC111 apparatus. In the saturated salts method and in the DVS, a thermodynamic equilibrium is expected. For the TGA-DSC equipment, a local equilibrium at the surface of the material as well as a homogeneous moisture distribution in the sample are assumed.

The comparison between the static method and the DVS shows that the results are consistent as long as the apparent diffusion coefficient in the material is high. This was emphasized for the microcrystalline cellulose and the pharmaceutical granules in which the apparent diffusion coefficient was roughly evaluated at 10^{-9} m^2/s using the DVS experimental variation of the product mass with time and the second Fick's law. When the apparent diffusion coefficient becomes low, the difficulty to reach the thermodynamic equilibrium appears in the saturated salts method. This was stated for the PEBA membrane and set the problem of defining reasonable equilibrium criteria with a significant sample mass variation and a reasonably short equilibrium delay (specially for biological materials). In consequence, for materials with apparent diffusion coefficients close to 10^{-12} m^2/s, it would be better to use a dynamic method rather than the standard saturated salts method. The comparison between the two dynamic methods shows that the accuracy of the TGA-DSC is rather good as long as the apparent diffusion coefficient is above 10^{-9} m^2/s. When this threshold value is not achieved, the desorption isotherms are overestimated.

The difficulties to perform the experiment at high relative humidity should be emphasized for the three experimental equipments investigated. Accurate data could only be determined with method specially developed for high activity measurement (Baucour et Daudin, 2000).

The choice of one method rather than another one to determine a sorption isotherm is not very easy. The saturated salts method has a small investment cost and is rather easy to implement but the equilibrium criterion is difficult to define and the equilibration delay could be very long. In the DVS and the TGA-DSC, the experimental time to measure a complete isotherm is rather short. Nevertheless, the technology of these apparatus is sophisticated which involves a delicate use. Furthermore, these equipments are complementary as they give the possibility to investigate the sorption isotherms between the ambient temperature and 95°C. In some case, the drying temperature in the process will determine the choice of one experimental set up.

ACKNOWLEDGMENTS

NOMENCLATURE

a	Activity	(-)
C, C', K	Model constants	(-)
$f_{i\,L,pure}$	Fugacity of i as a pure liquid, in equilibrium with its vapor	(Pa)
P_i	Partial pressure of i in vapor phase	(Pa)
$P_{sat,i}$	Saturation pressure of i at the operating temperature	(Pa)
P	Total vapor pressure	(Pa)
T	Temperature	(°C)
X	Moisture content	(kg water / kg dry solid)
x_i	Molar fraction of i in the liquid phase	(mol/mol)
y_i	Molar fraction of i in the vapor phase	(mol/mol)
γ_i	Activity coefficient	(-)
φ_i	Fugacity coefficient	(-)

Subscripts

BET	Brunauer-Emmet-Teller model
GAB	Guggenheim-Anderson-de Boer model
i	Component
w	Water

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TABLE TITLES

Table 1 – Variation of the diffusion coefficients of the PEBA membrane with the relative humidity

Table 2 - Optimized parameters for the estimation of the MCC desorption isotherms plotted in Figure 4

Table 1, "Comparison between static and dynamic methods for sorption isotherm measurements" by Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Relative humidity	Average moisture content (kg water/kg of dry matter)	Diffusion coefficient (m^2/s)
1	$3.7 \ 10^{-1}$	$4.5.10^{-14}$
0.6	$3.2 \ 10^{-2}$	$2.3 \ 10^{-13}$
0.2	$8.8 \ 10^{-3}$	$1.2 \ 10^{-12}$

Table 2, "Comparison between static and dynamic methods for sorption isotherm measurements" by Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Model	Apparatus	T(°C)	Parameters		
BET	DVS	25	$X_{BET} = 0.039$	C=10.070	
	DVS	35	$X_{BET} = 0.038$	C=10.339	
	TGA-DSC	50	$X_{BET} = 0.034$	C=8.167	
	TGA-DSC	90	$X_{BET} = 0.025$	C=10.718	
GAB	DVS	25	$X_{GAB} = 0.053$	C'=7.623	K=0.722
	DVS	35	$X_{GAB} = 0.049$	C'=8.612	K=0.740
	TGA-DSC	50	$X_{GAB} = 0.046$	C'=6.327	K=0.778
	TGA-DSC	90	$X_{GAB} = 0.037$	C'=5.805	K=0.806

FIGURE CAPTIONS

Figure 1 - Comparison of the MCC isotherms (—△— and —◆—) measured with DVS to the standard mean adsorption isotherm (—•—) measured using the saturated salt method (Wolf, 1985)

Figure 2 - Adsorption isotherms of pharmaceutical granules measured at 25°C using DVS (—△—) and the saturated salt method (—•—).

Figure 3 - Adsorption isotherms of PEBA membrane measured at 25°C using DVS (—△—) and the saturated salt method (—•—).

Figure 4 - Influence of the sample temperature on the desorption isotherm of MCC: (—•—) T=25°C, (—◆—)T=35°C, (✳✳✳) T=50°C and (+++) T=90°C.

Figure 5 - Influence of the temperature on the monolayer moisture content determined with the BET model (—•—) or the GAB model (—■—).

Figure 6 - Desorption isotherm of the primary sewage sludge measured at 45°C (± 5°C) with DVS (—•—) and the TGA-DSC (——).

Figure 7 - Desorption isotherm of the secondary sewage sludge measured at 45°C (± 5°C) with DVS (—•—) and the TGA-DSC (——).

Figure 1, "Comparison between static and dynamic methods for sorption isotherm measurements" by

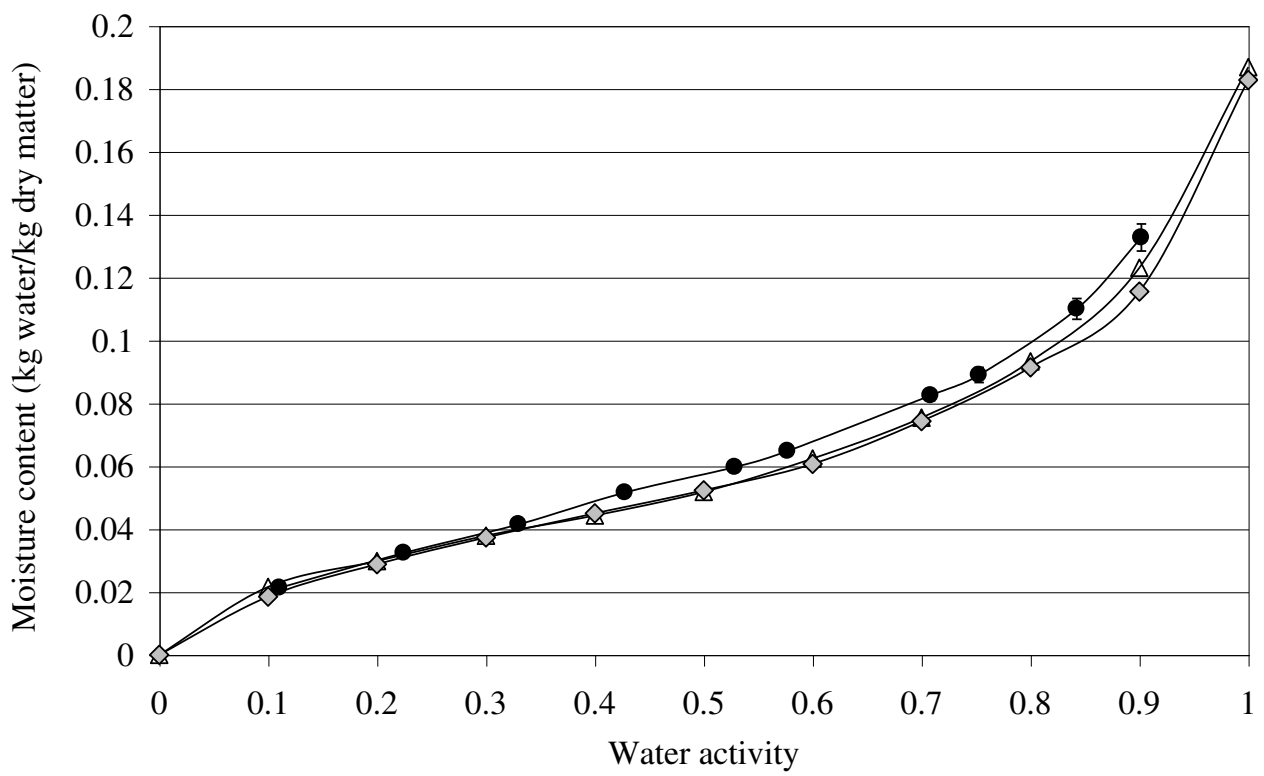Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Figure 2, "Comparison between static and dynamic methods for sorption isotherm measurements" by

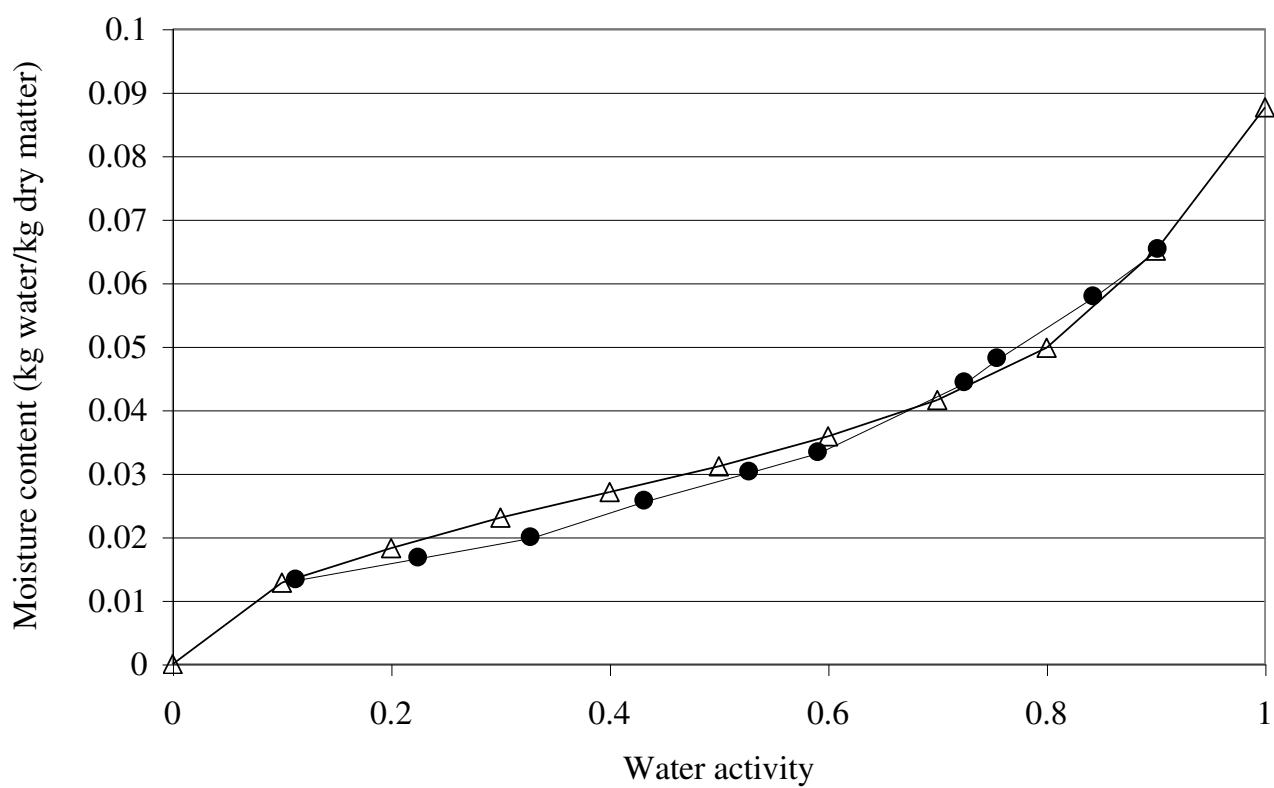Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Figure 3, "Comparison between static and dynamic methods for sorption isotherm measurements" by

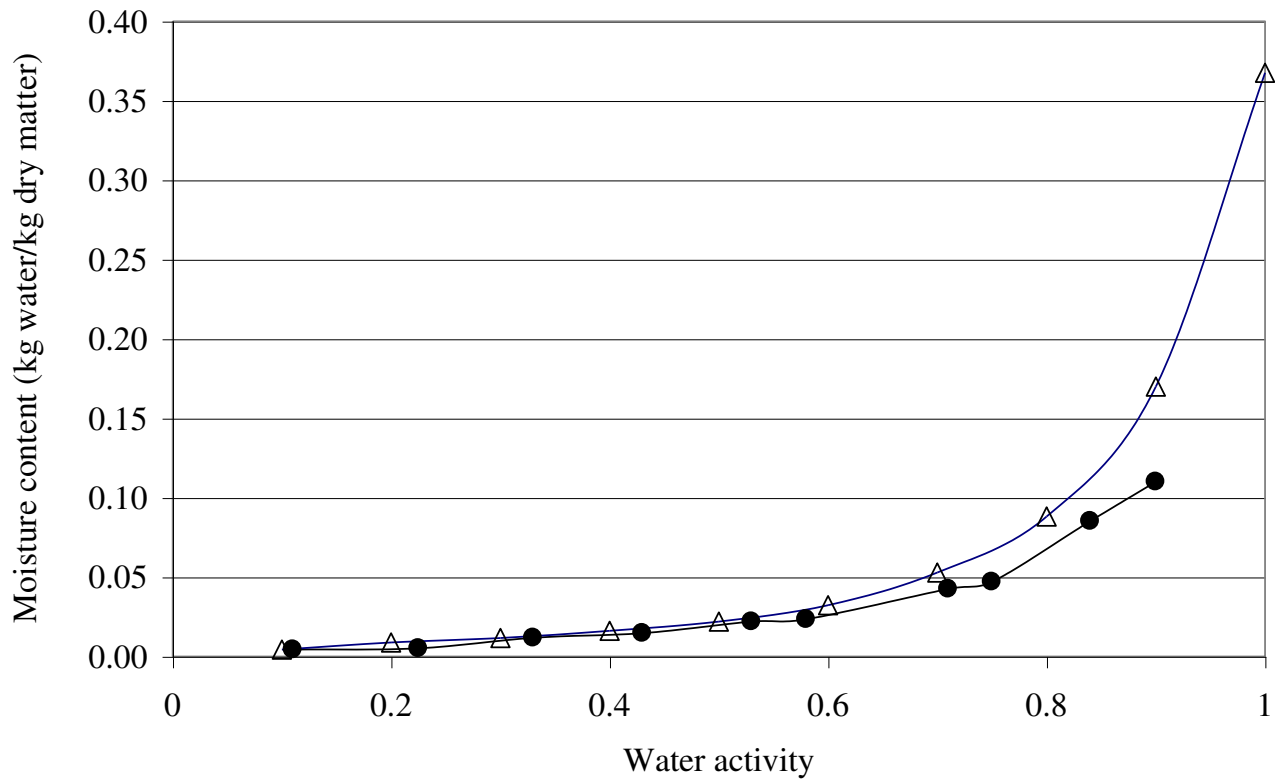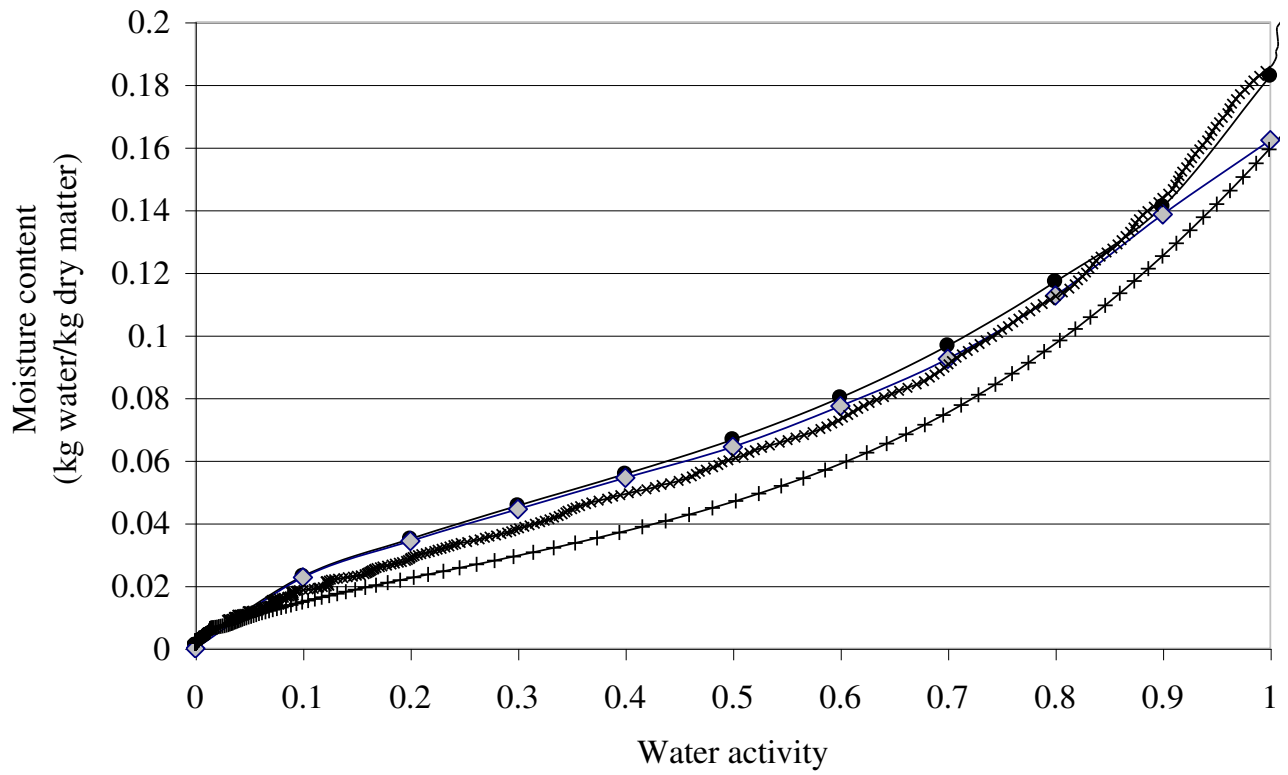Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Figure 4, "Comparison between static and dynamic methods for sorption isotherm measurements" by

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Figure 5, "Comparison between static and dynamic methods for sorption isotherm measurements" by
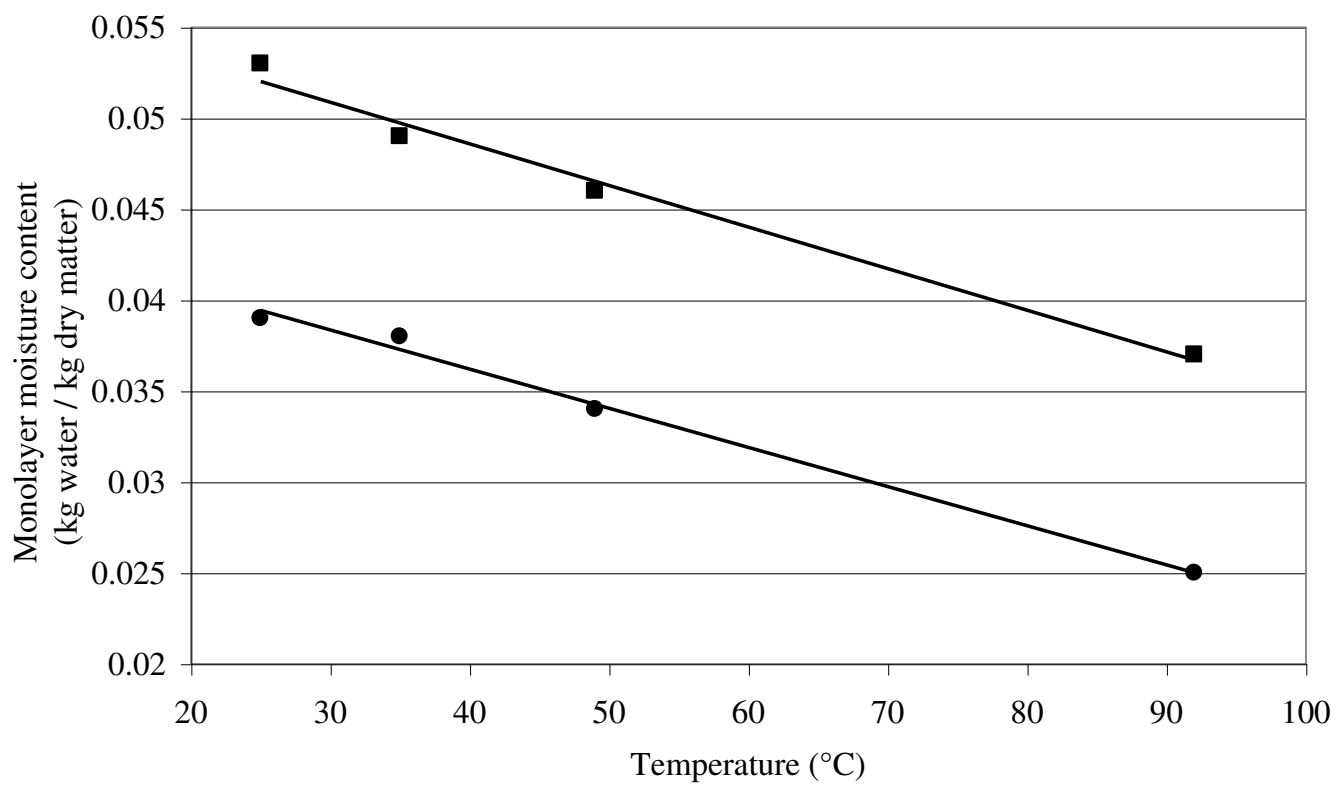
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Figure 6, "Comparison between static and dynamic methods for sorption isotherm measurements" by

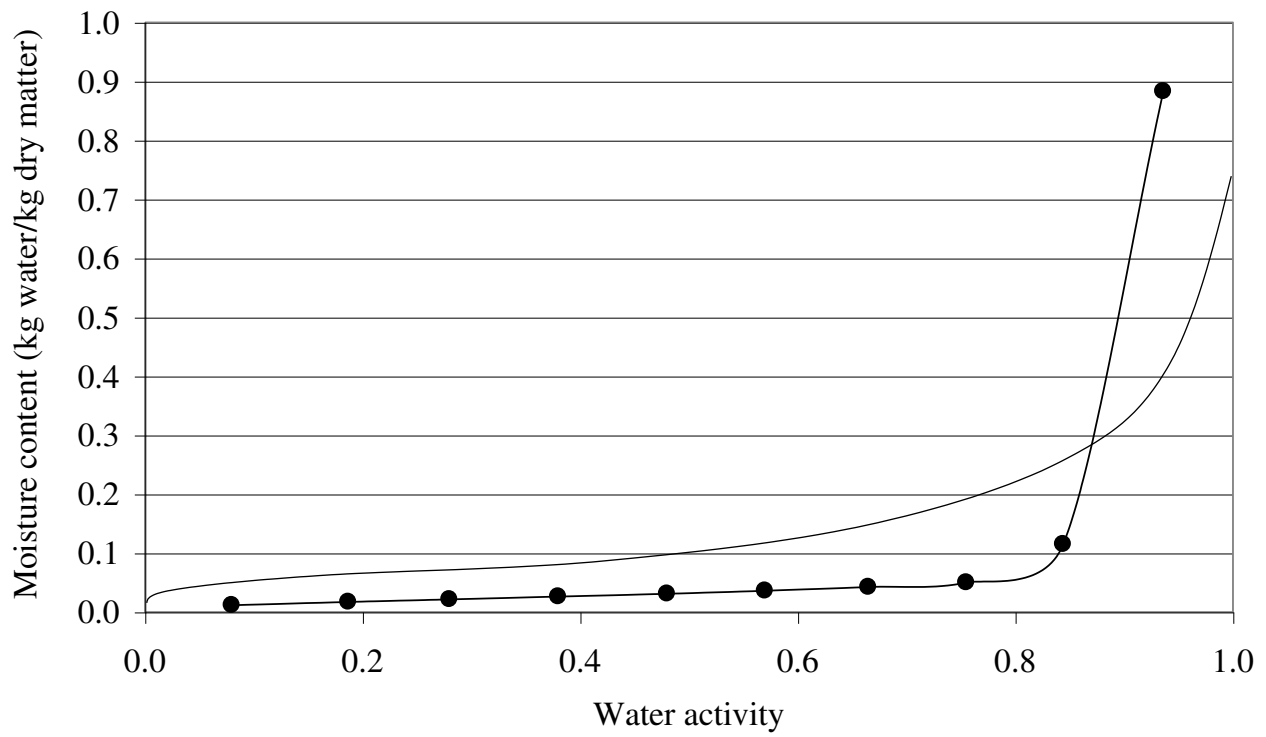Arlabosse, Rodier, Ferrasse, Chavez et Lecomte

Figure 7, "Comparison between static and dynamic methods for sorption isotherm measurements" by

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