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An improved method to validate the relative humidity generation in sorption balances

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Keywords

Sorption balance; relative humidity validation; saturated salt solutions

Abstract

Sorption balances are instruments in which samples are weighed as they are exposed to a programmed relative humidity (RH). Such instruments are used to measure sorption isotherms and to study solid-vapour interaction. There are different methods to validate the performance of the RH generation in such instruments by charging them with saturated salt solutions and ramping/stepping the RH past the deliquescence RH of the salts. In this paper an improved approach to perform validation is presented where the RH is kept stepwise constant at a quasi-randomly chosen set of RH-values above and below the deliquescence RH. From the rates of

change of mass as a function of RH it is possible to calculate the RH at which deliquescence takes place. This alternative method gives similar results as the slow ramp method, but is less sensitive to disturbances and less time consuming.

Introduction

Sorption balances are instruments in which samples are weighed as they are exposed to a programmed relative humidity (RH). Such instruments are now widely used at pharmaceutical industries and elsewhere to measure sorption isotherms and to study solid-vapour interaction [1-5]. They can also be used for other related types of studies, for example to measure transport properties of films and materials [6; 7] and to study film formation in latex dispersions [8; 9]. In sorption balances it is important that the mass determination and the RH-generation are correct. The mass determination is calibrated with a reference mass, and the RH-generation is calibrated or validated with saturated salt solutions that have constant RH (water activity).

In a sorption balance a gas stream flows past a sample that is usually kept in a glass or steel pan. The loss rate of the sample mass is proportional to the vapour pressure difference between the sample surface and the gas stream:

$$\frac{dm}{dt} = k_p A(p_{gas} - p_{sample}) \qquad (1)$$

Here, m (g) is the measured mass, t (s) is the time, k_p (g s^{-1} Pa^{-1} m^{-2}) is the mass transfer coefficient, A (m^2) is the area through which the mass transfer takes place, and p (Pa) is the

vapour pressure. The indices ‘gas’ and ‘sample’ refer to the gas stream and the surface of the sample. In a sorption balance k_p and A are not well defined as the gas flow pattern is complex. However, the product k_pA in Eq. 1 can be seen as an overall mass transfer coefficient. It is assumed that the whole sample surface has one vapour pressure and that the gas flow rate and pattern are constant. Then constant k_pA will be a function of gas flow rate, sample geometry etc., but for a single run where these parameters are constant k_pA will not change. The relative humidity (φ) is proportional to vapour pressure (at constant temperature):

$$\varphi = \frac{p}{p_{sat}}, \qquad (2)$$

Here, p_{sat} (Pa) is the saturation vapour pressure. Therefore the mass change rate will be proportional to the difference in RH between the gas stream and the sample.

The RH generation can either be under closed or open loop control. In the closed loop control the RH is constantly measured with an RH-sensor and the mass flow controllers are adjusted so that the correct RH (according to the RH sensor) is generated. In the open loop mode it is assumed that the mass flow controllers that generate the RH are correctly set and the RH is generated “blindly” using these settings. An advantage with open loop control is that one does not use an RH sensor; a type of device that commonly shows various problems like contamination of mirrors (dew point sensors) and drift (capacitive sensors). Generally, even precision RH sensors cannot measure RH better than precision mass flow controllers can generate RH. In practice, these two ways of controlling RH generation are probably as good and some manufacturers have incorporated both possibilities in their instruments.

Both for closed and open loop instruments there is a need for methods to validate the performance of the RH generation. For the closed loop instruments the validation is mainly a check of the RH sensor, while for the open loop instruments it is a validation that the mass flow controllers (or other devices that generate the RH) are still working as intended. Information from four manufacturers of sorption balances [10-13] showed that all recommend validation procedures in which the RH is changed past the deliquescence RH of a salt. Common salts used are $MgCl_2$ (33.1% RH), NaCl (75.5% RH) and KNO_3 (94.6% RH) (20°C data from [14]), although some manufacturers also recommend the use of commercial standards or – in one case - measurements of sorption isotherms of a well defined material (polyvinyl pyrrolidone, PVP). Below we describe some validation methods using NaCl as an example. We use the following terms: *set RH* is the RH that the instrument is programmed to generate, *actual RH* is the RH that is generated, and *deliquescence RH* is the RH at which the saturated salt solution is in equilibrium with water vapour.

One common validation method is to charge the instrument with a saturated salt solution and ramp the set RH slowly past the expected deliquescence RH of the salt. When the sample mass change rate is plotted as a function of set RH one will see a linear dependence between these variables as is expected from Eq. 1. When the mass change rate is zero the water vapour and the water in the salt solution are in equilibrium and the actual RH then equals the deliquescence RH. Typically the RH-program used will start with 10 min at 70% RH for stabilization and then continue with a ramp from 70 to 80% RH followed by a ramp from 80 to 70% RH. The ramping is in some recommendations made at a low rate (typically 2 RH%/h) to avoid transient effects, while other manufacturers’ instructions call for much higher scanning rates (0.2%/min). As one absorption ramp and one desorption ramp are made,

transient effects due to high scanning rates are possibly removed by taking the mean result from the two ramps.

A similar validation procedure is to step the RH in small increments and determine when the mass does not change, i.e., when the actual RH equals the deliquescence RH. Typically one would use 10 min 0.2 RH% steps from 74.6 to 75.6% RH and then step back to 74.6%.

A third possibility is to charge the instrument with dry salt or a saturated salt solution and then increase the set RH to a level above the deliquescence point, and then stepwise decrease the set RH, passing the expected deliquescence RH. For NaCl one could use 84, 80, 78, 77, 76, 75, 74 and 73% RH. The actual RH equals the deliquescence RH at the set RH with the highest mass, as the mass starts to decrease when the RH is stepped below the deliquescence RH.

A fourth method is to use a dry salt and slowly increase the RH from below and look for the set RH at which the mass starts to increase. At this set RH the actual RH equals the deliquescence RH.

When evaluating the results of calibrations/validations with the above methods one can use either the mass or the mass change rate dm/dt, both as a function of set RH. The mass will show a maximum when the actual RH equals the deliquescence RH when scanning from above, and a minimum when scanning from below with a saturated solution. The mass change rate as a function of RH will be zero at the same point.

In this paper we describe an alternative method to validate the RH-generation in sorption balances based on the measurement of mass change rates at quasi-randomly chosen constant RH levels. We also calculate mass transfer Biot numbers for the sorption balance validation set-up with saturated salt solutions to check whether internal gradients in the salt solutions can be neglected. For this we measured the diffusion coefficients of water in saturated salt solutions with an NMR method and the sorption isotherms of the salts with a microcalorimetric technique.

Materials and method

Sorption balance RH validation

In the proposed method the RH is kept constant during 10-20 min at different RH levels above and below the expected RH of deliquescence. The levels are quasi-randomly chosen so that if one RH is above the deliquescence RH, the next will be below, and vice-versa. Thus the salt solution will alternately absorb and desorb moisture, so that the mass of the salt solution is approximately constant. This is an advantage when working at high temperatures where the saturated salt solutions quickly tend to either dry out or become unsaturated. At each level one will – after an initial period of transitional change – obtain a constant mass change rate (according to Eq. 1). When these mass change rates are plotted as a function of the target RH they should fall on one line, and by making a linear curve fit one can evaluate the set RH at which the salt deliquesces.

We have compared the new “random step method” with the “ramp method” using lithium chloride (LiCl), magnesium chloride ($MgCl_2$), magnesium nitrate ($Mg(NO_3)_2$) and sodium

chloride (NaCl). All salts were of pro analysi quality from Merck. In all cases a combined sorption balance program with both methods was run on a DVS Advantage (Surface Measurement System Ltd., London, UK) using glass pans at 20 or 25°C. In all cases two drops of mixed saturated solution and crystals (approx. 100 mg) were used. The RH programs are given in Table 1 and the data collection rate was 1 min^{-1}. The ramp programs started with 10-15 min constant RH and then an absorption ramp followed by a symmetrical desorption ramp. All ramps were made with 2%RH/h. The “random steps” were arranged so that consecutive steps alternated being above and below the deliquescence RH. Most integer RH values within a certain distance from the deliquescence point RH were used, and each value was in most cases only used once, cf. Table 1.

Place Table 1 approx. here

Water diffusion coefficients

To be able to calculate mass transfer Biot numbers (see Discusssion), self-diffusion measurements of water in saturated salt solutions were done at 25°C using an ordinary pulsed-field-gradient spin echo sequence [15]. The gradient pulse length was 0.5 ms and the two pulses were 20.2 ms apart for all measurements. The gradient pulses were increased linearly in 25 steps. To obtain appropriate range for fitting, the maximum gradient strength for the lithium and magnesium salts were 8 T/m while it was 3 T/m for the sodium and potassium salts.

The spectrometer used was a Bruker DMX-200 with a proton resonance frequency of 200.13 MHz. The probe was a Bruker Diff-25 with a maximum gradient strength of 9.6 T/m.

The self-diffusion coefficient D^* is the diffusion coefficient when the chemical potential gradient is zero. It is related to the Fickan diffusion coefficient D by [16]:

$$D^* = D\frac{\partial \ln c}{\partial \ln a} \qquad (3)$$

Here, c is concentration and a is activity. The activity can can closely be approximated by the relative humidity (Eq. 2) at the present conditions close to normal temperature and pressure [17]. We have used the results from the sorption measurements to calculate diffusion coefficients from the measured self-diffusion coefficients.

Sorption isotherms

The sorption isotherms of the salts were needed for the calculation of the mass transfer Biot number (see Discussion), and these were measured at 25°C with a sorption microcalorimetric technique described in detail in [18; 19]. In this technique an initially dry sample is exposed to water vapour from a water source, so that the moisture content of the sample is continuously increased. In contrast to the sorption balance ramp method, there is no fixed rate of increase of the RH; instead the sample receives moisture at a rate so that it is still close to equilibrium conditions. For example, if deliquescence (vapour uptake at constant sample RH) takes place, the RH of the sample and its surroundings will stay at the deliquescence RH until the deliquescence is complete [20]. It is therefore an ideal technique to measure the sorption isotherm of a salt and – more specifically – the slope of the sorption isotherm just above the deliquescence RH.

Results

Sorption balance RH validation

Figure 1 shows the RH program and the resulting mass of a NaCl sample. The first part of the measurement is the slow RH-ramp and the second part is the random steps procedure. An example of one step with the latter approach is shown in Fig. 2 where it is seen that a constant mass change rate was established quickly.

Place Fig. 1 approx. here

Place Fig. 2 approx. here

The results for NaCl are shown in Figs. 3 (ramps) and 4 (steps) and the results for all measurements are summarized in Table 1. The ramp method resulted in linear dm/dt as a function of t and the actual RH equaled the deliquescence RH when dm/dt was zero (obtained from separate linear regressions on the absorption and desorption parts). For the random step method the slopes were found when the mass change rates of the second half of each step was plotted against the set RH. The actual RH equaled the deliquescence RH when dm/dt was zero in a similar way as for the ramp method. In Fig. 2 it is seen that the curve rapidly becomes linear and that the present method of using the slope of the second half of the step is reasonable.

Place Fig. 3 approx. here

Place Fig. 4 approx. here

The results (Table 1) were similar for the ramp and the step methods (and have been so in a large number of similar tests made). The largest difference between the mean of the absorption and desorption ramp validations and the random step validations was 0.35% for $Mg(NO_3)_2$ at 25°C. For all validations made the measured deliquescence point RH was within

the ±1.5 RH% given by the manufacturer; the highest deviation in these validations was 1.1% RH for NaCl.

Water diffusion coefficients and salt isotherm slopes

The results of the NMR measurements of water diffusion coefficients and the slopes of the salt sorption isotherms just above the deliquescence RH are given in Table 2. The use of these values is discussed below. The echo attenuation of the self-diffusion measurement was fitted using a mono-exponential decay using one of Matlabs least-square-fit algorithms. The error estimations were done using a Monte Carlo uncertainty estimation procedure[21].

Place Table 2 approx. here

Discussion

The new method presented here has several advantages compared to the approaches commonly used:

1. It is faster than ramp methods that ramp the RH slowly to be close to equilibrium. The reason is that in ramp methods the RH is continuously changed (and one thus has to ramp slowly to be close to equilibrium), but in the step method one waits for 15-20 min at each step and will then be close to equilibrium.

2. In the step method there is a clear distinction between the transitional change and steady-state (Eq. 1). It is thus easy to assess whether one is at (or close enough to) equilibrium. This

is more difficult to do with the ramp methods unless one runs measurements at different RH change rates.

3. Disturbances – for example from ambient temperature variations – to ramp validations will sometimes make it difficult to evaluate the result, but for the random step method a short term disturbance will only affect one or two points and these can be disregarded after a closer inspection of the result.

4. It is easier to quantify random errors, e.g., by calculating the r^2-value of the regression, in the proposed method as the result are from a linear regression of about ten data points from different measurements. A similar procedure for the ramp method will mainly show how noisy the primary data are.

5. The proposed method can be tailored to suit different needs, e.g., by using only five RH-levels one obtains a quite rough validation, while the use of 15 RH-levels, possibly waiting for longer time at each level, produces a more precise result.

6. As the RH is alternatively above and below the deliquescence RH there is a significantly lowered risk that the solution will dry out or become unsaturated; something that commonly happens during ramp validations at elevated temperatures where vapour pressures and diffusion rates are much higher than at room temperature.

Figure 5 shows how the evaluated RH is influenced by the number of RH levels used. For each of the five measurements presented evaluations were made using different numbers of RH levels. These calculations were made using the first two, the first three etc. up to all levels

measured. It is seen that the result is rather accurate already after 4-5 levels. If only 5 levels are used a validation with the step method will take about one hour, whereas ramp validations often take about 10 hours. Even ten levels with the step method – for an increased precision – will take only about 2 h.

Place Fig. 5 approx. here

The overall mass transfer coefficient k_pA in Eq. 1 was 1.7±0.3 ng s^{-1} Pa^{-1} for the five measurements reported. Such coefficients are of interest if one wants to assess the sorption kinetics of a sample, as one then has to take the influence of the external mass transfer coefficient into consideration in the evaluation. However, note that k_pA is a function of flow rate and flow pattern. It is different for different instruments, different sample pans etc. Note also that evaporation/condensation will influence the temperature of this type of samples with a free liquid surface [8], an effect that we have not taken into account here as this influence decreases towards zero when coming close to the deliquescence point.

A point of interest is whether the sorption/desorption takes place without significant internal gradients in the salt solutions. If there are significant internal gradients in the salt solutions, the surface RH will not equal the literature values of saturated salt solutions. A check on whether internal gradients are of importance can be made by calculating the mass transfer Biot number:

$$Bi_m = \frac{k \cdot L_c}{D} \qquad (4)$$

Here, k (ms^{-1}) is the internal mass transfer coefficient, L_c (m) is a characteristic length, and D (m^2s^{-1}) is the diffusion coefficient of water in the saturated solutions. The length L_c was approximately 2 mm in the present set-up (the distance between the salt crystals on the bottom of the pan and the surface of the saturated solution). The mass transfer Biot number is the ratio between the internal and the external mass transfer resistances.

Table 2 gives measured values of water self-diffusion coefficients and Fickan diffusion coefficients for the used saturated salt solutions. It should be noted the self-diffusion coefficients are significantly lower than the self-diffusion coefficients of bulk water ($2.30 \cdot 10^{-9}$ m^2s^{-1} [22]). As is discussed above, the overall mass transfer coefficient k_pA in Eq. 1 was 1.7±0.3 ng s^{-1} Pa^{-1}. By dividing this product with an area we will get k_p. In the calculations A was taken as the surface area of the salt solutions in the sorption balance pans, which was approx. $5 \cdot 10^{-5}$ m^2.

The mass transfer coefficient k_p is not directly applicable to k in Eq. 4 as k_p is expressed with vapour pressure as potential, and for Eq. 3 to be valid the external mass transfer coefficient has to be expressed with the same gradient as the diffusion coefficient, i.e., the mass concentration. A transformation of a transport coefficient from driving potential A to potential B can be made by multiplying the coefficient with the derivative of A with respect to B. In the present case, k_p and k have vapour pressure p and water concentration c (g_{water} m^{-3}) as potentials so the transformation will be:

$$k = k_p \frac{dp}{dc} = k_p \frac{p_s \, d\varphi}{c_s \, dm} \qquad (5)$$

We have here indicated that the vapour pressure equals the saturation vapour pressure p_s times the relative humidity φ (Pa Pa^{-1}) and that the water concentration is the salt concentration c_s (g_{salt} m^{-3}) times the moisture content m (g_{water} g_{salt}^{-1}). A sorption isotherm is usually expressed as moisture content as a function of relative humidity and therefore $d\varphi/dm$ is the inverse of the slope of the isotherm. The sorption isotherms measured for the used salt solutions are presented in Fig. 6.

In the present case we are interested in a saturated solution in contact with salt crystals. Essentially the same argument can be used both for absorption and desorption of water vapour from the salt solution. In the case of water absorption the solution at the top surface tends to become dilute and follow the isotherm with a positive and finite slope to the right (indicated with dotted lines in Fig. 6; the saturated solution is found at the top of the almost vertical deliquescence step in the sorption isotherm). The mass transfer Biot number is then a good indicator whether the dilution of the top of the solution is significant. It is generally assumed that if $Bi_m<0.1$, internal gradients may be neglected (although such an assumption may not hold for a calibration/validation method). As seen in Table 2 Bi_m is in the order of 0.1 for all salts except NaCl, where it is lower. The internal mass transfer resistance in the saturated salt solutions will therefore prevent the surface of the used saturated solutions reach saturated conditions during vapour absorption.

Place Fig. 6 approx. here

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In the case of water desorption the water leaves the saturated solution, which will therefore become super-saturated and crystals will tend to form to restore the equilibrium. In most cases

– especially when Bi_m is low – the crystals will form on the old crystals as these act as nucleation sites. Then the same calculation as for absorption is applicable as the slope of the sorption isotherm for a slightly super-saturated solution will be the same as the slope for the slightly dilute solution. The dashed lines in Fig. 6 therefore also represent the sorption isotherms for super-saturated solution.

A potential problem with desorption is that crystals are sometimes formed on the surface of saturated solutions, and could then possibly exert a significant resistance to water diffusion. In the present case the Bi_m numbers indicate that we may have to take internal mass transfer into account. However, we have no indications that crystals have formed on the surfaces. If the surfaces would have been covered by salt crusts during desorption, the mass loss rates during desorption would have been lower than those during absorption; something that was not seen.

As seen in Table 2, the calculated Bi_m-values are approx. 0.1 for three of the salts. The sorption balance system used can then have non-negligible internal resistances during validation with saturated salt solutions. This is true for both the commonly used validation methods and the one presented in this paper. However, note that the calculations made of the mass transfer Biot number are only approximate. The main uncertainties are what length L_c and area A to use. As the geometry of the system is complex these two values should only be seen as characteristic values.

If the mass transfer Biot number is high, the vapour pressure of the sample surface (Eq. 1) will not equal the vapour pressure at equilibrium with the saturated salt solutions. This is possibly not a serious problem in the present case, as this error in the RH will vanish when there is equilibrium between the gas and the solution (no mass transfer). Possibly it could

make the present method somewhat uncertain, as there could be kinetic effects because of the short RH steps that are used in the present method. However, as the mass change rate was a linear function of the set RH for all tested salts in this study (cf. Fig. 4), the error that is made is probably proportional to the difference between the actual RH and the equilibrium RH of the saturated solutions. As long as one is searching for the deliquescence point this is not a problem. In all cases, the most commonly used calibration salt – NaCl – is less concentrated than the other salts and has low internal gradients and should be preferred.

Conclusions

An improved RH step method to validate the RH generation in sorption balances has been presented and shown to give results comparable to a standard RH ramp method. The alternative method has several advantages over the traditional method, for example that it is takes shorter time and that it is less sensitive to disturbances. Some salts solutions have internal gradients, but this does not seem to cause problems in using them to validate the RH generation.

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FIGURE CAPTIONS

Figure 1. The RH programs and the measured mass for NaCl. The vertical dashed line shows when the ramp method ends and the step method starts.

Figure 2. Detail showing the mass during a typical 15 min RH step for the NaCl validation shown in Fig. 1. The mass change rate was evaluated with linear regression of all data points on the second half of the step.

Figure 3. Evaluation of the ramp method for NaCl. Data points and linear regression are shown for absorption and desorption. The dotted lines indicate how the RH was evaluated.

Figure 4. Evaluation of the step method for NaCl. Each point is the d*m*/d*t* calculated for one RH step. The dashed lines indicate how the RH was evaluated.

Figure 5. The RH evaluated from the RH-steps using different number of data points. From top to bottom the curves refer to the following runs: LiCl (20^{o}C), NaCl (25^{o}C), $MgCl_2$ (25^{o}C), $Mg(NO_3)_2$ (25^{o}C), and $Mg(NO_3)_2$ (20^{o}C).

Figure 6. Sorption isotherms measured with a sorption microcalorimeter at 25°C for the four used salts. The slopes of interest are indicated by dotted lines. Literature values of deliquescence RH and moisture contents of saturated solutions are indicated with filled circles and a vertical line. Note that because of kinetic effects, the deliquescence steps are not perfectly vertical as they should be. Note also that $MgCl_2$ and $Mg(NO_3)_2$ show the formation of hexa-hydrates at lower RH than deliquescence (for $MgCl_2$ this step does not correspond to

the full anhydrous to hexa-hydrate transformation as this salt was not completely dried before the measurements).

FIGURES SOURCES

Figure 1: randvalfig1.eps

(Fig 11 in randval2.m in c:\measure3\DVS\randval\sectry\randval2.m)

Figure 2: randvalfig2.eps

(Fig 15 in randval2.m in c:\measure3\DVS\randval\sectry\randval2.m)

Figure 3: randvalfig3.eps

(Fig 14 in randval2.m in c:\measure3\DVS\randval\sectry\randval2.m)

Figure 4: randvalfig4.eps

(Fig 13 in randval2.m in c:\measure3\DVS\randval\sectry\randval2.m)

Figure 5: randvalfig5.eps

(Fig 1 in npoints.m in c:\measure3\DVS\randval\sectry\randval2.m)

Figure 6: randvalfig6.eps

(Fig. 1 in c:\measure\measure4\sorp\salter\evalsalts.m)

Figure 1

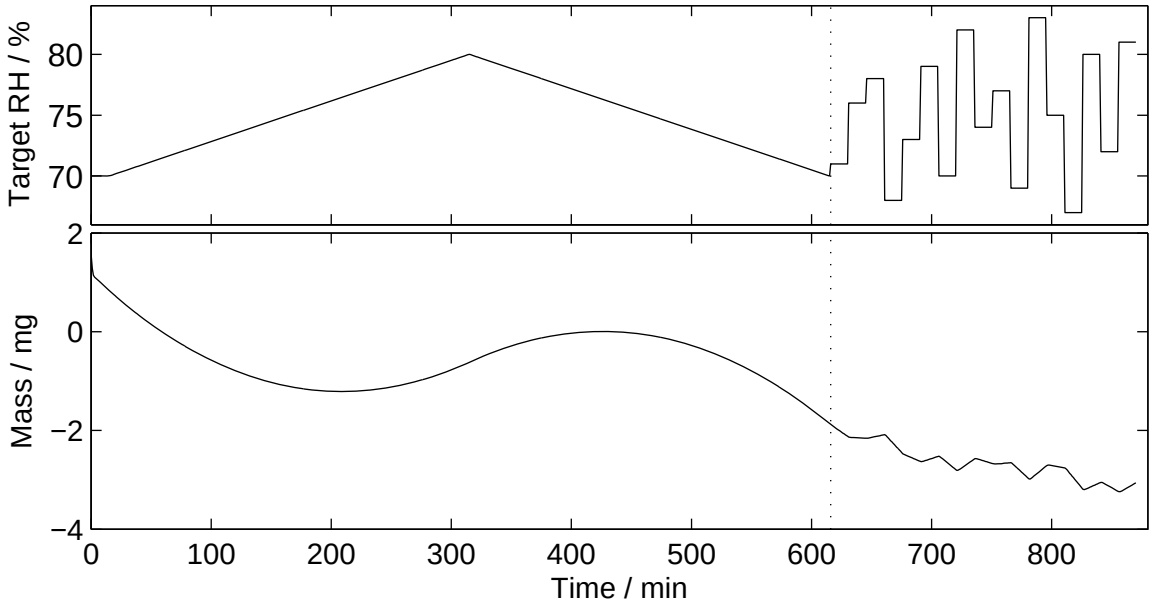
Target RH / %
80
75
70
Mass / mg
2
0
−2
−4
0
100
200
300
400
500
600
700
800
Time / min

Figure 2

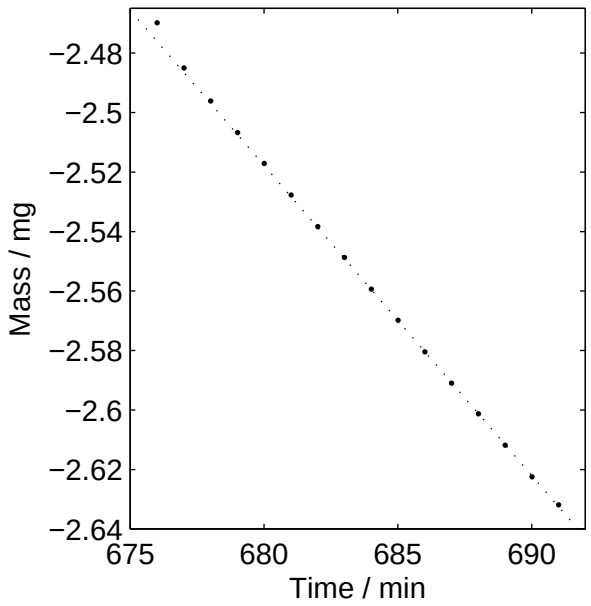
−2.48
−2.5
−2.52
−2.54
−2.56
−2.58
−2.6
−2.62
−2.64
Mass / mg
675
680
685
690
Time / min

Figure 3

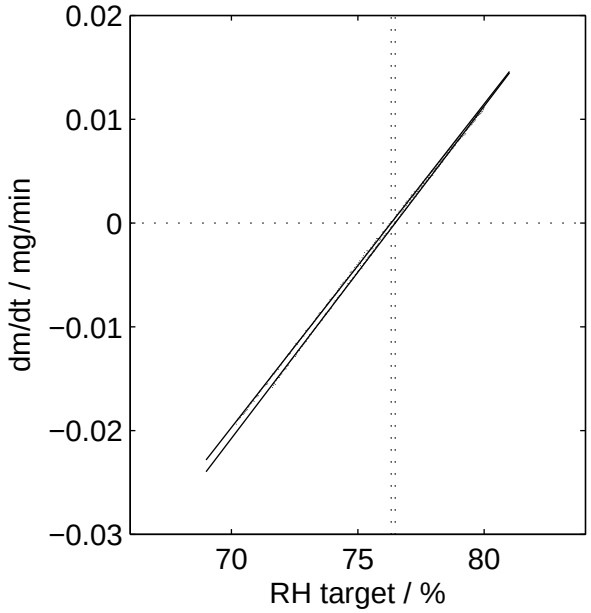

Figure 4

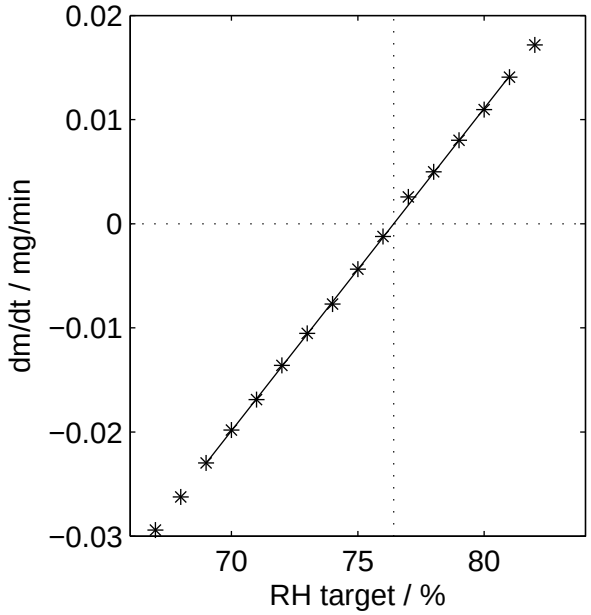

Figure 5

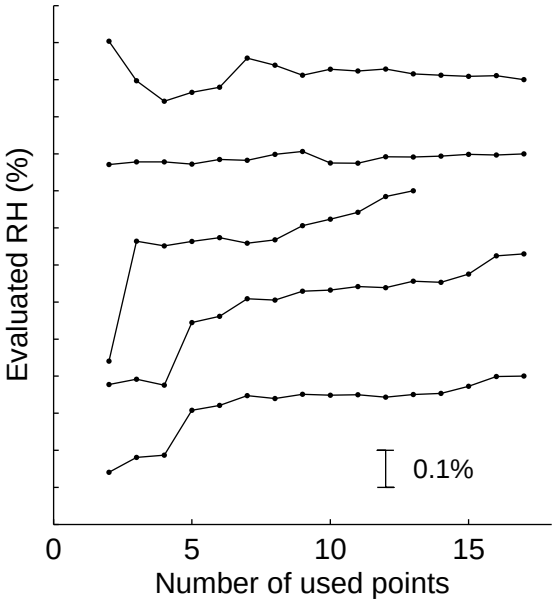

Figure 6

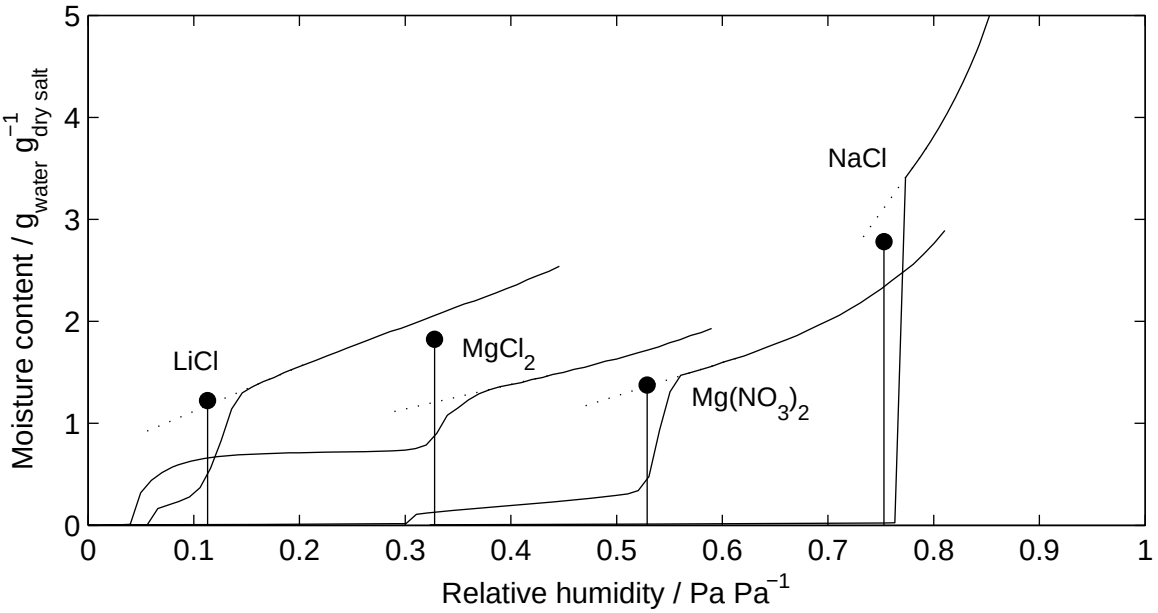
Moisture content / g_{water} $g^{-1}_{dry\ salt}$
Relative humidity / Pa Pa^{-1}
LiCl
$MgCl_2$
$Mg(NO_3)_2$
NaCl
0
1
2
3
4
5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Table 1. The RH programs and the results. All ramps were made with 2% RH/h. “Abs” and “Des” refers to the ramp method and “Step” is the method described in this paper. “Lit” is a literature value taken from [14] .

	Ramp part	Step part	RH results / %			
			Abs	Des	Step	Lit
LiCl 20°C	15 min at 6% ramp 6%→16% ramp 16%→6%	15 min at 6, 2, 6, 8, 18, 13, 9, 0, 12, 4, 17, 9, 14, 5, 11, 10, 14, 3%	10.3	10.2	10.3	11.31
$MgCl_2$ 25°C	10 min at 30% ramp 30%→36% ramp 36%→30%	20 min at 30, 33, 35.5, 31, 30.5, 34.5, 30, 32.5, 36, 31.5 , 33.5, 35, 31, 34%	31.8	32.6	32.4	32.78
$Mg(NO_3)_2$ 20°C	15 min at 50% ramp 50%→60% ramp 60%→50%	15 min at 51, 56, 58, 68, 53, 59, 50, 62, 54, 57, 49, 63, 55, 67, 60, 52, 61%	55.0	54.8	55.0	54.38
$Mg(NO_3)_2$ 25°C	same as above	same as above	53.1	53.0	53.4	52.89
NaCl 25°C	10 min at 70% ramp 70%→80% ramp 80%→70%	15 min at 71, 76, 78, 68, 73, 79, 70, 82, 74, 77, 69, 83, 75, 67, 80, 72, 81%	76.5	76.3	76.4	75.29

Table 2. Data for the calculation of mass transfer Biot numbers for the used saturated salt solutions. D^* is the self-diffusion coefficient, σ the estimated error in the self-diffusion measurements, D is the diffusion coefficient, $dm/d\varphi$ is the slope of the sorption isotherm just above the deliquescence RH, and Bi_m is the mass transfer Biot number (Eq. 4). Concentrations and densities of the saturated salt solutions used in the calculations were taken from the Gmelin handbook.

Salt	D^* / m^2s^{-1}	σ / m^2s^{-1}	D / m^2s^{-1}	$dm/d\varphi$	Bi_m
LiCl	$0.179 \cdot 10^{-9}$	$0.117 \cdot 10^{-12}$	$0.832 \cdot 10^{-9}$	4.40	0.10
$MgCl_2$	$0.200 \cdot 10^{-9}$	$0.148 \cdot 10^{-12}$	$0.924 \cdot 10^{-9}$ [(a)]	3.64 [(a)]	0.14
$Mg(NO_3)_2$	$0.436 \cdot 10^{-9}$	$0.310 \cdot 10^{-12}$	$0.904 \cdot 10^{-9}$	3.26	0.13
NaCl	$1.44 \cdot 10^{-9}$	$12.9 \cdot 10^{-12}$	$1.99 \cdot 10^{-9}$	14.5	0.024

a. A correction for that the salt was not anhydrous at the start of the sorption measurement was used in calculating these values.