Calibration of a Moisture Sorption Analyzer

– Application Note 18-01

Introduction

For dynamic water vapor sorption measurements, the integrated humidity sensor is a key element. To obtain reliable results in dynamic water vapor sorption measurements, a frequent calibration of the humidity sensor is essential. A recommended time interval is at least every six months.

It is important to note that a calibration only validates the past time period - not the future.

Fig. 1: Humidity sensor “Hygroclip” of a SPS or Vsorp device

In general, calibration means to measure accepted standards with the instrument to be calibrated, compare the obtained results with these reference values and re-adjust possible deviations.

For humidity calibration, saturated salt solutions are typically used. The addition of salt to an aqueous solution reduces the partial water vapor pressure above the solution compared to pure water.

In equilibrium with their environment, saturated salt solutions thus generate a defined salt- and temperature- dependent relative humidity which makes them suitable as a reference for humidity calibrations.

By selecting suitable salts, the entire calibration range can be covered in this way.

For reliable calibration, reference salts as well as the water should be certified for standardization purposes. At least analytical grade is recommended to exclude any impurities which could influence the calibration results.

In literature several reference tables are given. For comprehensible and reliable results only officially approved tables should be used. The source of the reference values should always be indicated in order to be able to trace the calibration. Commonly accepted reference values are given by Greenspan [1] which are summarized in Table 1.

Table 1: Reference values for the relative humidity of saturated salt solutions dependent on temperature, modified from Greenspan [1]

Salt \ Temperature [°C]	5.0	10.0	15.0	20.0	25.0
Lithium chloride	11.3	11.3	11.3	11.3	11.3
Magnesium chloride	33.6	33.5	33.3	33.1	32.8
Magnesium nitrate	58.9	57.4	55.9	54.4	52.9
Sodium chloride	75.7	75.7	75.6	75.7	75.3
Potassium chloride	87.7	86.8	85.9	85.1	84.3
Potassium nitrate	96.3	96.0	95.4	94.6	93.6

Sample preparation

For the calibration of the SPS/Vsorp humidity sensor, a saturated solution – or rather a slurry – of the reference salt with double distilled water has to be prepared.

If saturated solutions were used instead, the excess of undissolved salt crystals, which are mainly at the bottom of the solutions, could cause concentration differences and thus influence the results.

Figures 2 and 3 show the sample preparation in a SPS/Vsorp sample dish. The reference salt should ideally be filled into the dish as a conical shaped bulk (Fig. 2).

Fig. 2: Preparing a salt cone in the SPS/Vsorp sample dish

Fig. 3: Moistening of the reference salt with double dist. water

Moistening is preferably done dropwise, starting from the edge of the cone by using a pipette (Fig. 3).

Attention should be paid to the correct solid-to-liquid ratio. Both, too high portion of dry crystals (Fig. 4) and over-moistening with excess liquid (Fig. 5) should be avoided to prevent delayed or extended drying or adsorption periods.

Optimally, a few single dry crystals remain visible which are able to adsorb additional moisture during the calibration routine.

Fig. 4: Slurry with dry salt crystals

Fig. 5: Over-moistened salt slurry with excess free water

Calibration routine

To calibrate the humidity sensor in a SPS or Vsorp device, the relative humidity is cycled from ∽2 % below to ∽2 % above the reference value of the salt (Table 1). Fig. 6 schematically shows the profile of a relative humidity cycle, phases of water desorption and adsorption as well as the detection of equilibrium points.

The reference values correspond to the equilibrium points of the individual salt. As shown in Fig. 6 A and B, RH values below this equilibrium point – here 11.3 % – lead to drying and weight loss of the salt.

With increasing RH in the device and approaching the equilibrium point, the drying process slows down until the salt is in equilibrium with the environment (Fig. 6). At this equilibrium point the rate of change of mass per time (dm/dt) equals zero.

A further increase in relative humidity leads to water adsorption and weight increase of the salt crystals as shown in Fig. 6 C. After having passed the maximum RH of the cycle – here 13 % – in the following phase of decreasing relative humidity (Fig. 6 D), the water adsorption slows down until the equilibrium state is reached a second time.

Afterwards, a further RH decrease below the equilibrium point leads to desorption and weight loss of the salt (Fig. 6 E).

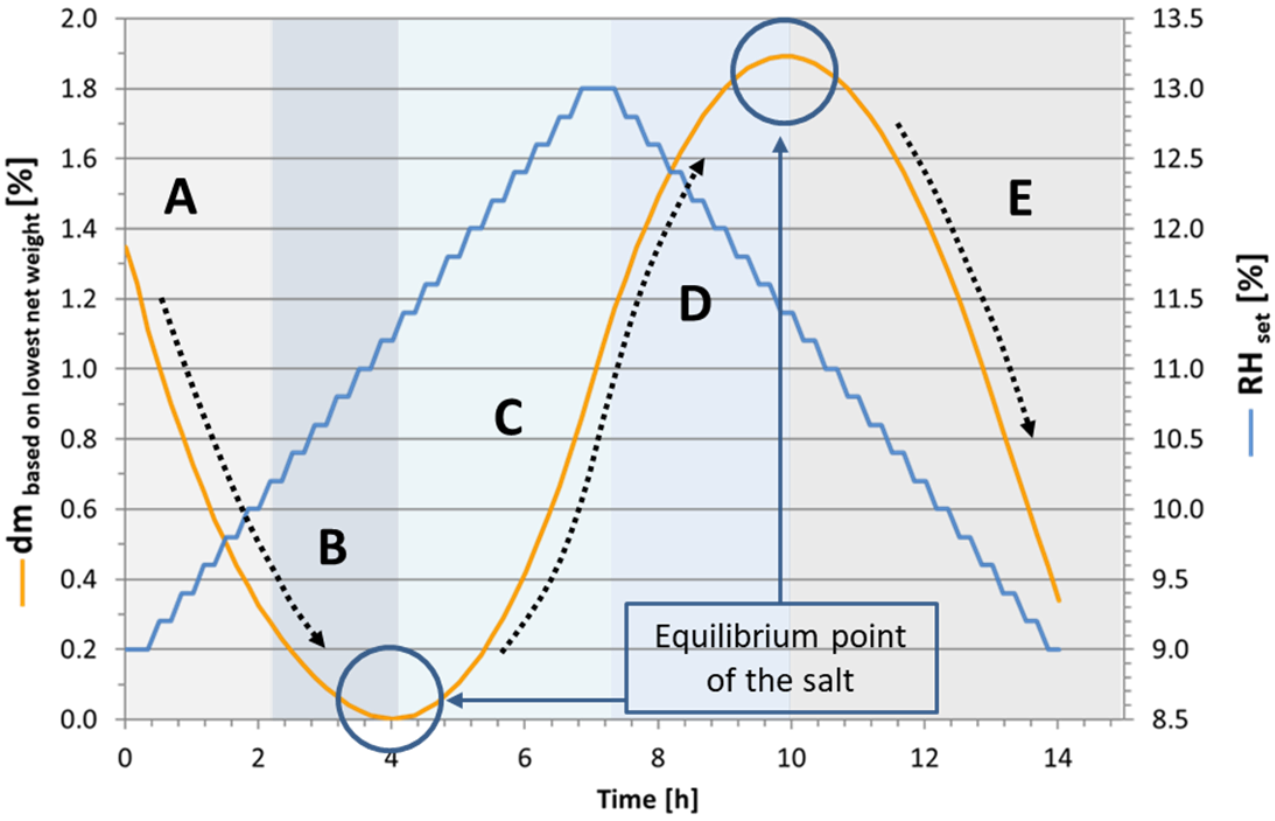

Fig. 6: Schematic draw of the RH cycle profile, phases of water adsorption and desorption and detection of equilibrium points in “Dynamic view” of the Sorption control software

Result evaluation and re-adjusting the sensor

As explained previously by Fig. 6, within the calibration routine the relative humidity cycle is specifically adjusted so that the equilibrium point of the reference salt is passed twice – during adsorption and desorption cycle.

For the evaluation and re-adjustment of the humidity sensor, advantage is taken from the fact that the relative humidity at the turning points always corresponds to the state of equilibrium and thus to the reference RH of the salt, independent of the value measured by the humidity sensor of the instrument.

In this way, the deviation of the sensor can be corrected by comparing the target humidity (= reference RH of the salt) and the actual measured humidity.

Using the calibration results of LiCl shown in Fig. 7, equilibrium is detected after a measuring time of ∽4 h and ∽10 h. From the recorded measurement data (Table 2), equilibrium state is obtained at the points of minimum and maximum weight change dm [%] (Table. 2, red markings). The humidity at these points corresponds to the RH values measured by the sensor. In the example, measured relative humidity values were 11.2 % and 11.4 %. The averaged value corresponds to the reference value of LiCl of 11.3 %. That means, a re-adjustment of the sensor is not necessary.

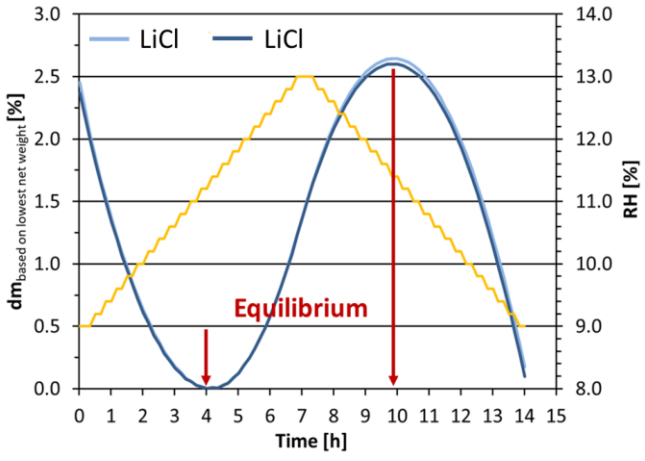

Fig. 7: Results of LiCl calibration in “Dynamic view”

Table 2: Measurement data

no.	time [h]	total weight [mg]	net weight$_{corr.}$ [mg]	Rh$_{set}$ [%]	dm$_{based\ on\ initial\ net\ weight}$ [%]
20	3.2	1,253.544	294.712	10.8	-2.2708
21	3.3	1,253.399	294.571	10.8	-2.3176
22	3.5	1,253.323	294.494	11.0	-2.3431
23	3.7	1,253.235	294.404	11.0	-2.3730
24	3.8	1,253.196	294.370	11.2	-2.3843
25	4.0	1,253.148	294.318	11.2	-2.4015
26	4.2	1,253.164	294.339	11.4	-2.3945
27	4.3	1,253.165	294.338	11.4	-2.3949
28	4.5	1,253.248	294.405	11.6	-2.3727
29	4.7	1,253.282	294.456	11.6	-2.3558
30	4.8	1,253.405	294.579	11.8	-2.3150
54	8.8	1,260.464	301.636	12.0	0.0252
55	9.0	1,260.611	301.776	12.0	0.0716
56	9.2	1,260.712	301.886	11.8	0.1081
57	9.3	1,260.819	301.977	11.8	0.1383
58	9.5	1,260.865	302.037	11.6	0.1582
59	9.7	1,260.918	302.090	11.6	0.1758
60	9.8	1,260.925	302.097	11.4	0.1781
61	10.0	1,260.920	302.093	11.4	0.1767
62	10.2	1,260.894	302.066	11.2	0.1678
63	10.3	1,260.844	302.014	11.2	0.1505
64	10.5	1,260.757	301.929	11.0	0.1224
65	10.7	1,260.662	301.832	11.0	0.0902

Alternatively, in the “Equilibrium view” the weight change dm [%] is plotted over the relative humidity. Here, for evaluation, the sensor RH at the turning points can be read directly from the diagram. In case of NaCl (Fig. 8), the averaged RH value is 77.1 %. Compared with the reference RH of 75.3 % a sensor deviation of 1.8 % has to be corrected here.

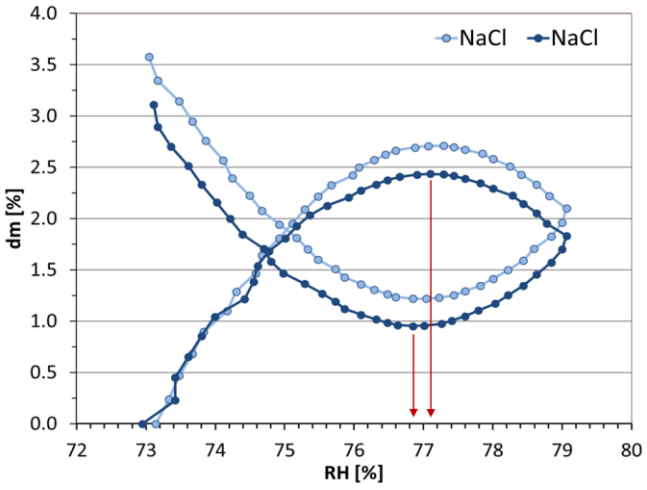

Fig. 8: Results of sodium chloride (NaCl) in “Equilibrium view”

Summary

By default, calibration of the SPS and Vsorp devices is performed with the reference salts listed in Table 1 at a temperature of 25 °C.

The methods and settings used for the calibration routines are stored in the Sorption Control software as standard procedures.

The presented method allows an easy and standardized calibration of the SPS and Vsorp humidity sensor. Together with a subsequent validation procedure using the microcrystalline cellulose MCC012 [2,3], certified as a reference standard by proUmid, this guarantees a reliable investigation of the water vapor sorption behavior of various materials.

References

[1] Lewis Greenspan, 'Humidity fixed points of binary saturated aqueous solutions', J. of Research, National Bureau of Standards, 81A (1977) pp 89-96

[2] proUmid Application Note 18-02 Certification of Microcrystalline Cellulose as a humidity reference for gravimetric DVS instruments

[3] proUmid Application Note 18-03 Microcrystalline Cellulose as a humidity reference for gravimetric DVS instruments