Automated Multi-sample Moisture Sorption Analysis:
Instrumental Facts and Characterization of Food Products

Erwin E. Marti[a], Ulrich J. Griesser[b], M. Noisternig[b] & Jürgen Dillenz[d]

[a]APCh Marti Consulting, 4054 Basel, Switzerland
[b]Institute of Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria
[c]Projekt Messtechnik, 89077 Ulm, Germany

Introduction

Moisture sorption analysis is an important analytical tool in the characterization of food- or food ingredient properties with respects to manufacturing, processing, storage and stability. Automated devices are recording the weight changes of the sample under controlled atmosphere conditions in short time intervals with a high precision. However, moisture sorption/desorption processes particularly of food ingredients and products can be rather slow and therefore the measurement of a full equilibrium moisture isotherm which requires the adjustment of many subsequent equilibria may take one even several weeks. In order to meet the needs of a research laboratory it is therefore essential to run more than one sample at a time. In contrast to the different commercially available single sample instruments, the **SPS11 systems** [1] provide this feature in one instrument and is ideally designed for the characterization of food ingredients and food products.

This contribution introduces the functionality and features of this moisture analyzer and shows a few specific applications.

Multiple moisture sorption analyzer SPS11, complete system.

Description of the Instruments

The two models are equipped with a top loading analytical balance and differ mainly in the balance sensitivity and the size of their sample pans.

SPS11-10μ: Balance resolution: 10 μg, designed for the study of samples of rather large volume and size up to 200 g sample weight & samples down to small sample amounts of about 100 mg. Particularly useful for food products.

SPS11-100n: Balance resolution: 100 ng, designed for small samples of 1 to 100 mg (food ingredients) rather than bulky materials (food products).) Upper sample weight limit: 2 g.

A high weighing precision and reproducibility is guaranteed by an automatic balance calibration routine and a continuous drift compensation via the reference sample.

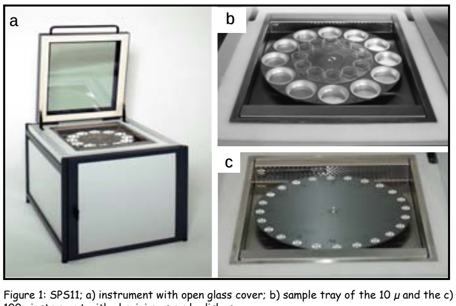


Figure 1: SPS11; a) instrument with open glass cover; b) sample tray of the 10 μ and the c) 100n instrument with aluminium sample dishes.

The analyzer requires only **compressed air** and due to the comparatively **small dimensions** (560 x 700 x 440 cm) the system can be installed in laboratories with limited space. The instruments are equipped with a specially designed **climatic chamber** that provides a range of climate settings from 0 to 98% r.h. and temperatures between +10 and +60°C (SPS11-10μ) resp. +10 and +40°C (SPS11-100n).

All samples are placed in **aluminum** dishes of 50 (SPS11-10μ) or 18 mm (SPS11-10n) in diameter (Fig. 1, insert b and c). The large dimension of the **sample dishes** of SPS11-10μ allows the investigation of representative sample amounts, voluminous, fluffy and light samples (e.g. potatoe chips) as well as dense and heavy samples. The dishes (**11 samples** + reference) sit in 12 drillings of a tray that can be easily removed and reloaded via a glass cover (Fig. 1). This glass cover allows the direct **observation** of the samples **during** the whole **measuring** cycle and to recognize visible changes of the samples such as deliquescence and discoloring.

The multi-sample devices use a sensor cell to continuously measure and adjust the actual relative humidity inside the chamber. The **atmosphere** is **dynamic** and continuously revolved, which guarantees constant conditions in the entire chamber and a good heat and moisture convection in the sample. The 11 sample positions allow an in-process calibration with several salts and salt solutions.

The measurement is fully controlled by the system and runs unattended due to the **automated measurement and data acquisition**. The results are transferred into an ExceL™ spreadsheet which can be designed individually and the data are also saved in an extra text file. The software allows the fully automatic application of standard operation and calibration procedures. From **12 extra sample positions** which are not weighed but exposed to the atmosphere samples can be withdrawn at any time during the running measurement and analyzed additionally by suitable external analytical methods.

Applications

The SPS11 systems allow now a very high sample throughput which enables the access to more information and a better insight in moisture interaction principles. The potential applications of moisture sorption/desorption studies are manifold and definitely not fully exploited. The most important applications are:

- Determination of equilibrium moisture sorption isotherms
- Moisture uptake/loss kinetics
- Moisture induced phase transformations

Conclusion

Automated multi-sample moisture sorption analysis provides many benefits compared to classical methods. Due to the contin-uous in-process determination of the mass, the devices enables not only a precise recording of the total water exchange bet-ween samples and the adjusted atmosphere but also moisture scanning experiments and exact kinetic studies. The unbeatable features of the SPS11 systems are the simultaneous measure-ment of up to eleven samples and the possibility to measure bulky samples and sample amounts from few mg up to many grams. Due to these and other features this instruments is highly eligible for basic and applied research tasks in food science.

Examples

Microcrystalline Cellulose (MCC) is recommended as a reference material for sorption measurements and rather ideal as test substance because of the considerable and reproducible water uptake and water loss. An EC Standard Reference Material RM 302 has been used for the validation moisture sorption isotherms of food materials according to the COST 90 procedure. The water uptake of the standard from 0 to 90.2 % r.h. was specified with 13.27 ± 0.43 (95% confidence interval) at 25 °C [2]. Test measurements were performed with MCC DFS-0, Fluka (Nr. 09906). The measured mass difference of this material (0 - 90 % r.h, 25 °C) is 12.6 %.

The equilibration step from 20 to 40 % r.h. was further analyzed in order to display the equilibration kinetics of the water uptake process. The data of this step are given in Tab. 1. The approach of the equilibrium is given by the conversion factor alpha calculated according to Equation 1.

m_0 is the lowest mass of the sample equilibrated at 20 % r.h. (start value, t = 0), m_{eq} the mass at the equilibrium at the given r.h. value of 40% r.h. and m_t the mass at the time t. The Δm is calculated by the sample mass at equilibrium and the mass at time t: $\Delta m = m_{eq} - m_t$.

The mean of the 6 mass values between 60 and 110 min reveal no drift only noise on a level of micrograms. The mean m_{eq} at equilibrium (40% r.h., 25°C) is 12.2445 mg. The standard deviations of the mean and of a single measurement are ± 0.0002 mg and ± 0.0006 mg respectively.

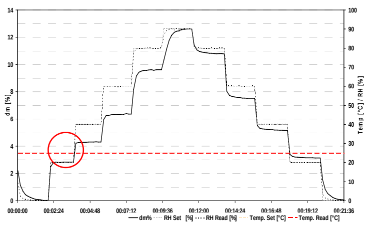
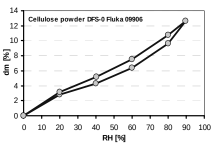


Figure 2: Time versus mass change curve of MCC (Fluka, Nr. 09906, sorption and desorption cycles, 20 % resp. 10 % r.h. steps, 25°C, SPS11-100n); the circle highlights the region which was examined in further detail (Tab. 1).



Equilibrium isotherm. The hysteresis between sorption and desorption cycle is characteristic for the microcrystalline, partially amorphous structure of cellulose.

Table 1: Equilibration kinetics of a single equilibration step (20 to 40 % r.h), of microcrystalline cellulose at 25°C.

Time t (min)	m_t (mg)	α (%) Eq. 1	Δm (μg)
0	12.0704	00.0	174.1
10	12.2343	94.1	10.2
20	12.2404	97.6	4.1
30	12.2417	98.4	2.8
40	12.2424	98.8	2.1
50	12.2421	98.6	2.4
60	12.2447	100.1	- 0.2
70	12.2442	99.8	0.3
80	12.2439	99.7	0.6
90	12.2455	100.6	- 1.0
100	12.2446	100.1	- 0.1
110	12.2441	99.8	0.4

$$\alpha = \frac{m_t - m_0}{m_{eq} - m_0} \cdot 100 \qquad \text{Eq. 1}$$

The results show that the equilibrium values at the different r.h. levels can be perfectly achieved in a short time. Different samples of this material, measured simultaneously under practically identical conditions in the SPS11-100n, match perfectly in their extent of water uptake or loss. The relative resolution of the microbalance (SPS11-100n) is sufficient to get very robust values with sample amounts of a few mg.

Food Products: Fig. 3 shows examples of moisture sorption/desorption isotherms of different food products, measured simultaneously (SPS11-10μ). White rice takes much longer to reach an equilibrium than for the other samples. At 30% the equilibrium was not even achieved within two days. Chamomille flowers contain mucilage and absorb considerable amounts of water. The equilibrium is not achieved at 90% r.h. (< 2d). In contrast to the other samples the isotherm of the chamo-mille flowers shows practically no hysteresis between sorp-tion and desorption cycle. Linseeds, also containing mucilage, show a weak hysteresis and a much smaller water uptake. The uptake of about two thirds of the total water between 80 and 90% r.h. by the salted potatoe chips is attributed to NaCl which liquefies above 75% r.h.

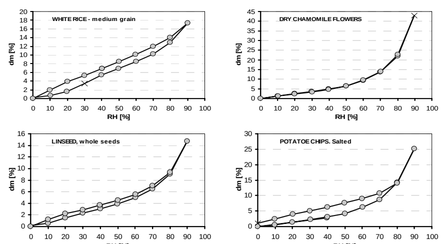


Figure 3: Equilibrium moisture sorption isotherm of white rice (medium grain), chamomile flowers, whole linseed and salted potatoe chips at 25°C (10 % r.h. steps). Circles mark equilibrium data and the "x" marks data points which are not at equilibrium within the set time limit of 2 days).

References:
[1] Griesser, U.J., Dillenz J. (2002): Novel fully auto¬matic moisture-sorption analyzer with a high sample throughput..Proceeding, 11. Weimarer Feuchtetagung.
[2] Jowitt R., Wagstaffe P. J.: Community Bureau of Reference, EUR 12429EN.

ISFRS 2006, 4th International Symposium on Food Rheology and Structure, Feb. 19-23, 2006, ETH Zürich, Switzerland.