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Water – an important parameter for the preparation and proper use of certified reference materials

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Abstract

Property values of powdered certified reference materials (CRMs) are very often related to dry mass. The dry mass is indirectly determined by measuring the moisture content of the sample. The most commonly used methods are the drying oven method and the Karl Fischer titration (KFT). It is well known that these two methods may give different values for the moisture/water content. In this study thermogravimetry was used to simulate the drying oven method and to investigate the reasons of the differences between both moisture/water content determination methods. A mass spectrometer coupled to a thermobalance (TGMS) added further useful information regarding the release of volatile substances and the decomposition of the material during the drying process.

The relative humidity of the laboratory may influence the water content of powdered CRMs because of their more or less pronounced tendency to take up water (hygroscopicity). This fact can lead to biased property values. The water adsorption kinetics and the water uptake capacity vary, depending on the constitution of the sample. This was studied analysing several powdered food CRMs and individual constituents thereof. The speed of water uptake and the water uptake capacity were described using an exponential function.

The findings have consequences both for the producer and for the user of certified reference materials.

Keywords: Certified reference materials; Water content; Moisture content; Karl Fischer titration; Drying oven; Adsorption kinetics; Thermogravimetry; Mass spectrometry; TGMS

1. Introduction

Chemical, biological, clinical, industrial, environmental and nuclear reference materials are widely used for the calibration of instruments, method validation and quality control (van der Veen, 2003). Water plays an important role in producing and using powdered reference materials. If the assigned value is related to the dry mass, water content determination has to be performed. Several methods to determine the water content exist (Isengard, 2001). Depending on the method used for water/moisture content determination, the results may vary significantly (Rückold, Grobecker, & Isengard, 2000, 2001a). A difference is made between water and moisture content. Water content is obtained by determining water selectively. Moisture content is obtained by drying techniques under certain conditions and should correctly be called mass loss on drying (with indication of the drying conditions); it may, on the one hand, include other volatile material and, on the other hand, leave a part of the water not detected.

In a survey, Aregbe et al. (2003) asked the participants of an International Measurement Evaluation Programme (IMEP) what analytical methods have been applied for moisture correction for expressing the results of measurements for the determination of trace elements

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in rice (IMEP19). The majority of the laboratories (71%) used conventional drying oven methods for the determination of moisture Some participants used vacuum drying oven methods, others did not report the applied method and none of the participants used the Karl Fischer titration (KFT). The results varied between nearly 0% and more than 8%. In IMEP20 trace elements in tuna were analysed. Sixty-two percent of the participants used conventional drying oven methods and only 3% the KFT to analyse the moisture content in tuna fish. The moisture/water content varied between nearly 0% and more than 5% (Aregbe et al., 2004).

The reason for the different values obtained for moisture/water content using different methods is on the one hand the different bounding state of water in the matrix. Strongly bound water molecules are difficult to release by drying techniques (Rückold, Isengard, Hanss, & Grobecker, 2003). Even at high temperature, e.g. 102 °C according to the standard of the International Dairy Federation (IDF Standard 26A, 1993) for moisture determination in milk powder, not all the water might be released from the sample (Rückold et al., 2000). On the other hand, water can be produced during the drying process due to the decomposition of the material or due to chemical reactions like the Maillard reaction (Rückold, Grobecker, & Isengard, 2001b).

Another critical point in use of CRMs is the water uptake of powdered material due to their hygroscopicity. Depending on the relative humidity of the laboratory and on the matrix of the material, the content of water may change significantly (Bernreuther et al., 2003). In a preliminary experiment on gliadin it was shown that water uptake contributes to a mass change with a maximum of 7.9% weight gain at 75% of relative humidity (Klein, Yazgan, & Franchini, 2004).

Turhan, Sayar, and Gunasekaran (2002) studied the water adsorption in chickpea during soaking. For predicting water adsorption the Peleg model (Peleg, 1988) was applied. Sreekala, Kumaran, and Thomas (2002) analysed the mole percent water uptake by palm fibre at four different temperatures. To study the mechanism of water sorption kinetic parameters, diffusion coefficient, sorption coefficient and permeability of water sorption were analysed using a logarithmic equation. The water and oil uptake of mesquite and arabic gums were investigated by Beristain, Azuara, Garcia, and Vernon-Carter (1996). To obtain a good statistical fit of the experimental data an equation was applied, which was proposed by Azuara, Cortés, Garcia, and Beristain (1992). The highest water and oil adsorption showed mesquite gum at all temperatures. McCutcheon, Barton, and Wilson (2001) investigated the kinetics of water adsorption and desorption on nine bituminous coals. An empirical stretched-exponential model was used to quantify the sorption kinetics.

In this study the moisture/water content of selected food CRMs was analysed by the drying oven method and the Karl Fischer titration. Both methods were compared with each other. Skimmed milk powder and cabbage powder were selected to investigate the reasons of the differences between both methods using thermogravimetry coupled to mass spectrometry (TGMS), which allows to simulate the drying process. Moreover, TGMS adds further useful information regarding the release of volatile substances and the decomposition of the material during the drying process.

Furthermore, the influence of the matrix of food models and certified reference materials on the hygroscopicity is investigated using a moisture sorption analyser. Usual sorption isotherms do not give sufficient information on the speed of water uptake and the water uptake capacity. Therefore, water uptake kinetics were studied and described using an exponential function.

2. Materials and methods

2.1. Materials

Certified reference materials:
- Whole milk powder (BCR-380R)
- Skimmed milk powder (BCR-685)
- Rice flour (IRMM-804)
- Cabbage powder (BCR-679)
- Dried carrot (BCR-515)
- Brussels sprouts (BCR-431)
- Mixed vegetables (BCR-485)
- Dried apple (BCR-516)

Food models:
- Pectin, esterification degree: 94%
- Pectin, esterification degree: 65%
- Pectin, esterification degree: 25%
- Starch, 73% amylopectin, 27% amylose
- Starch, 100% amylopectin
- Gelatine, 75 Bloom
- Gelatine, 225 Bloom
- Cellulose, microgranular
- Cellulose, fibrous medium
- Cellulose, fibrous long
- Casein

All food models were purchased from Sigma, Steinheim, Germany.

2.2. Methods for the determination of water content and mass loss

The drying oven method was used for mass loss determination. The samples were dried at 102 ± 2 °C, for 2 h (IDF Standard 26A, 1993) in a ventilated drying oven from Heraeus Instruments, Hanau, Germany. The presented results are mean values of six replicates.

The water content was measured by volumetric Karl Fischer titration by a 758 KFD Titrino from Metrohm, Herisau, Switzerland, using the two-component technique (Hydranal-Titrant 5 and Hydranal-Solvent from Riedel-de Haën, Seelze, Germany). The presented values are the means of 10 replicates.

2.3. Thermogravimetry–mass spectrometry

The thermogravimetry–mass spectrometry analysis was performed with a setsys 16/18 thermogravimeter (Setaram, Saluire, France). The samples were placed in a crucible suspended from the balance. The crucible is positioned in the homogeneous zone of the furnace. The lower part of the thermobalance is equipped with an outlet system for taking samples of the gases emitted by the original sample. This outlet system is coupled to a quadrupole mass spectrometer ThermoStar™(Pfeifer Vacuum, Asslar, Germany). The monitored masses (*m*/*z*) were 18 to detect losses of water as well as 44 (carbon dioxide) to detect possible degradation of the samples. To simulate the drying oven method the furnace was heated up to 102 °C, This temperature was held for three hours, 1 h more than the IDF Standard requires in order to check whether there is a further release of water or degradation of the sample.

2.4. Water adsorption kinetics

The adsorption of water was recorded at 25 °C with an IGAsorp Moisture Sorption Analyser from Hiden Isochema, Warrington, England. The sample is placed in a pan and attached to a balance in the sample chamber. The temperature of the chamber is regulated by a water bath. The relative humidity in the sample chamber is generated by combining different flows of wet and dry nitrogen with variable flow rates. The samples were first conditioned at a relative humidity of 15% to get the same starting condition for all samples. Then the relative humidity in the chamber was increased to 80%.

3. Results and discussion

3.1. Comparison of the Karl Fischer titration and the oven drying method

Fig. 1 shows the moisture/water contents of different CRMs, which were obtained by the oven drying method and the Karl Fischer titration. The drying oven results were all obtained by drying the sample at 102 °C for 2 h. The results show that whole and skimmed milk powder give similar values with both methods. Fig. 2 shows the TGMS curve of skimmed milk powder (BCR685). The TG curve shows a rapid mass loss (mass 18 = H_2O) at the beginning of the heating process and became almost constant.

Cabbage powder shows an enormous difference of almost 10% (absolute) between mass loss and water content, which is caused by its high sensitivity to heat. This could be confirmed by TGMS analysis (Fig. 3). The TG curve decreases constantly after a rapid mass loss at the beginning. The MS curve shows a decrease of the mass 18 (H_2O) and 44 (CO_2), which is an indication for the decomposition of the material.

The other samples show a similar, though less pronounced effect. It is therefore problematic to determine the mass loss of a sample and assume that this is the water content. The difference can be very substantial and lead to fateful and serious consequences.

3.2. Water adsorption kinetics

Fig. 4 shows the water uptake kinetics of the food models and some of the biological CRMs investigated in this study. Pectin with an esterification degree (ED) of 25% showed the highest water uptake capacity of

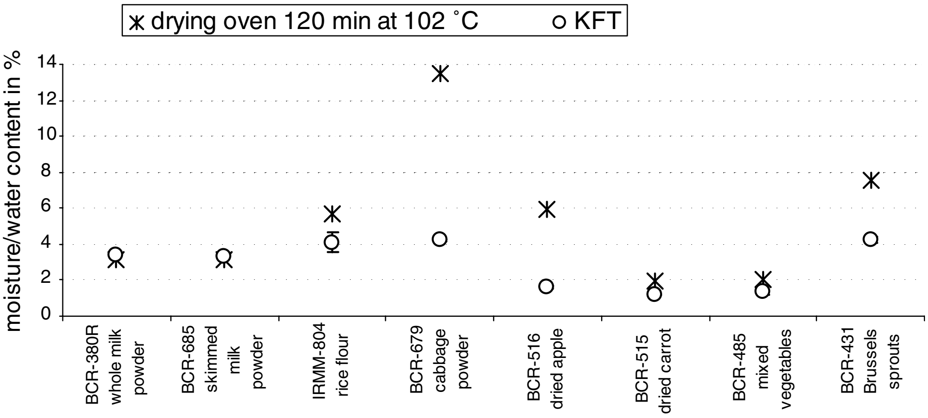

Fig. 1. Comparison of oven drying method and Karl Fischer titration for moisture/water determination.

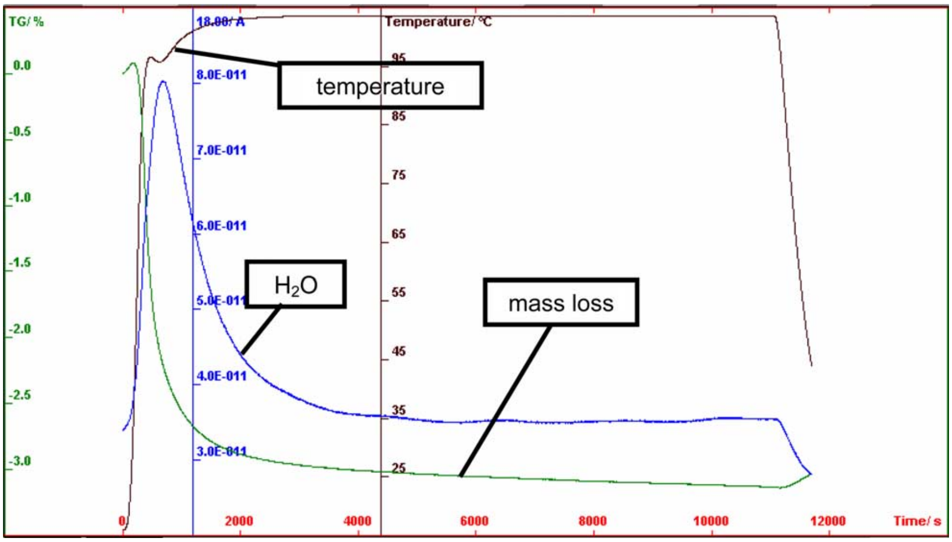

Fig. 2. TG–MS curve of BCR-685 skimmed milk powder.

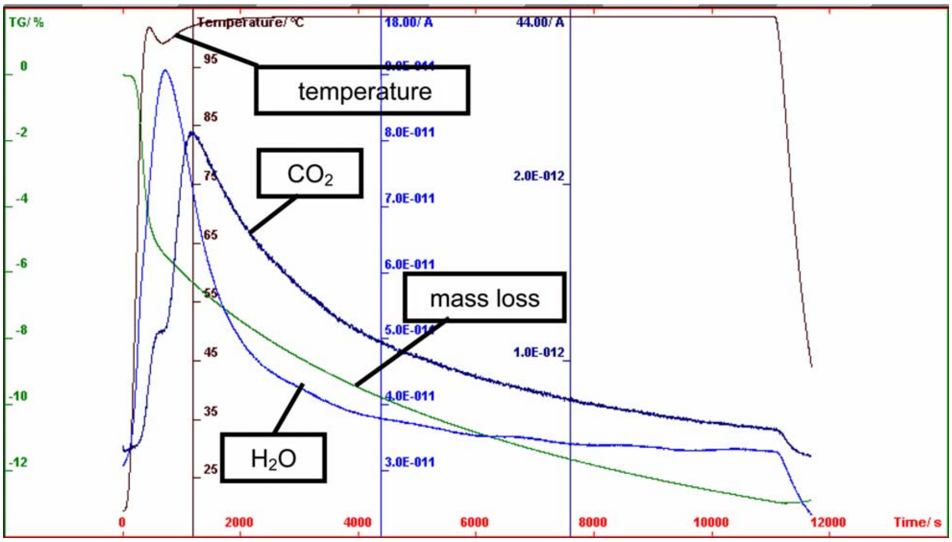

Fig. 3. TG–MS curve of BCR-679 cabbage powder.

the analysed samples. This high capacity compared to pectins with higher esterification degree can be explained by the higher affinity of the free carboxyl groups to water in comparison with the methyl esterified groups. The lowest water uptake capacity of the analysed samples can be observed for cellulose. A closer look at the curves reveals that the initial speed of water uptake and the amount of water adsorbed at the end are not necessarily related to each other. Thus, after 120 min cellulose had adsorbed less water than casein, but the initial speed of water uptake was higher than that of casein. Gelatine 225 Bloom had a much slower initial rate to adsorb water than starch, but at about 110 min the gelatine curve ''overtook'' the starch curve, indicating that gelatine 225 Bloom can take up more water if enough time is available.

It is therefore, interesting to characterise these adsorption curves by a mathematical model. To quantify the adsorption kinetics, the curves were fitted by an exponential model, which provided a good fit to water uptake:

$$m(t) = A \cdot (1 - \mathrm{e}^{-t \cdot B}),$$

where $m(t)$ is the water uptake in %; t the time in min; A and B are the factors which are shaping the curve. Factor A is the asymptote which gives the maximum water uptake of the sample. Factor B describes the steepness of the curve at the beginning of the adsorption, related to factor A.

Fig. 5 illustrates the A factor of the investigated samples. Dried apple (BCR616) showed the highest water uptake capacity compared to the other CRMs. This

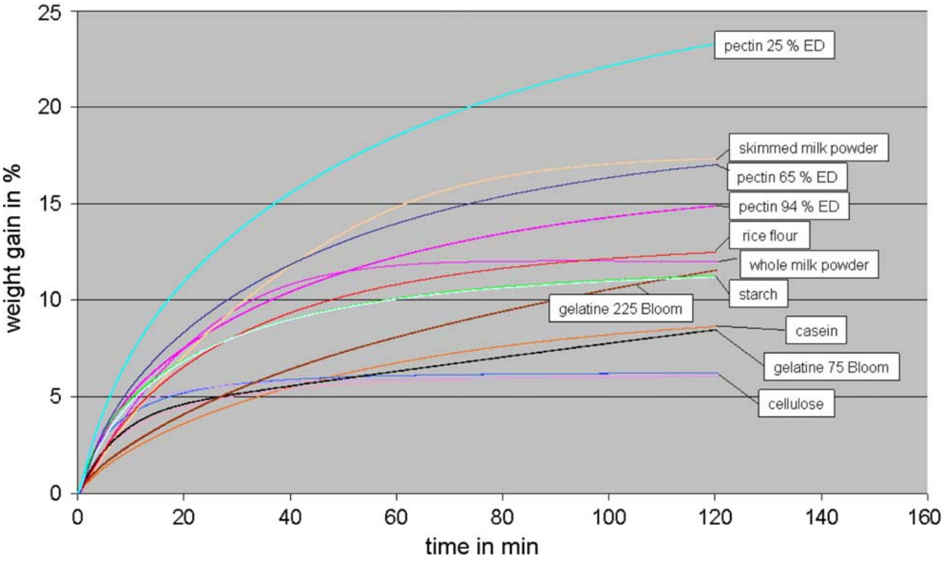

Fig. 4. Water uptake kinetics of food models and powdered CRMs.

was most probably due to its high content of pectin. The maximum water uptake capacity of skimmed milk powder (BCR685) was higher than that of whole milk powder (BCR380R). Skimmed milk powder has a higher lactose content (~50 g/100 g) than whole milk powder (~35 g/100 g) whereas whole milk powder has a higher fat content (Der kleine "Souci, Fachmann, Kraut" Lebensmitteltabelle für die Praxis 1991). Because of the higher hygroscopicity of lactose compared to that of fat, skimmed milk powder is expected to have a higher water uptake capacity than whole milk powder.

Looking to factor *B* (Fig. 6) it can be observed that cellulose had a fast water uptake but a relatively low maximum water uptake capacity. The form of cellulose (microgranular, long- and short-fibrous) affected the water uptake kinetics significantly. The compactness of cellulose increases from microgranular towards long-fibrous. In the case of microgranular cellulose it takes more time until the water molecules reach the binding zones of cellulose.

Water uptake capacity was not related proportionally to water uptake kinetics. For this reason knowledge about the sorption isotherm of a material is not enough to have information about the speed of water uptake. Sorption isotherms show only the maximum water uptake capacity of a material at different relative humidity. For the practical use of reference materials it is, however, important to know how fast water is adsorbed

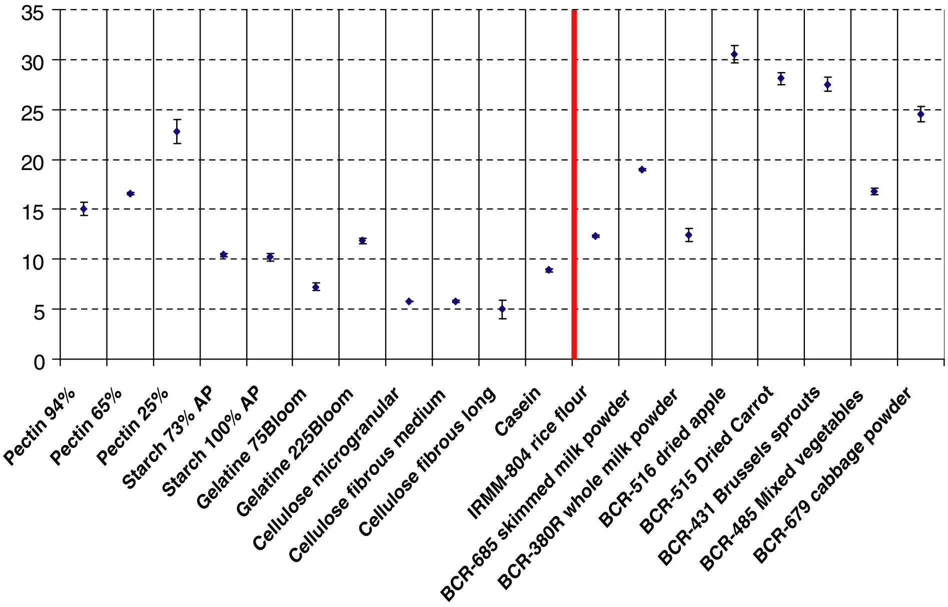

Fig. 5. Factor *A* of food models and powdered CRMs (for details see text).

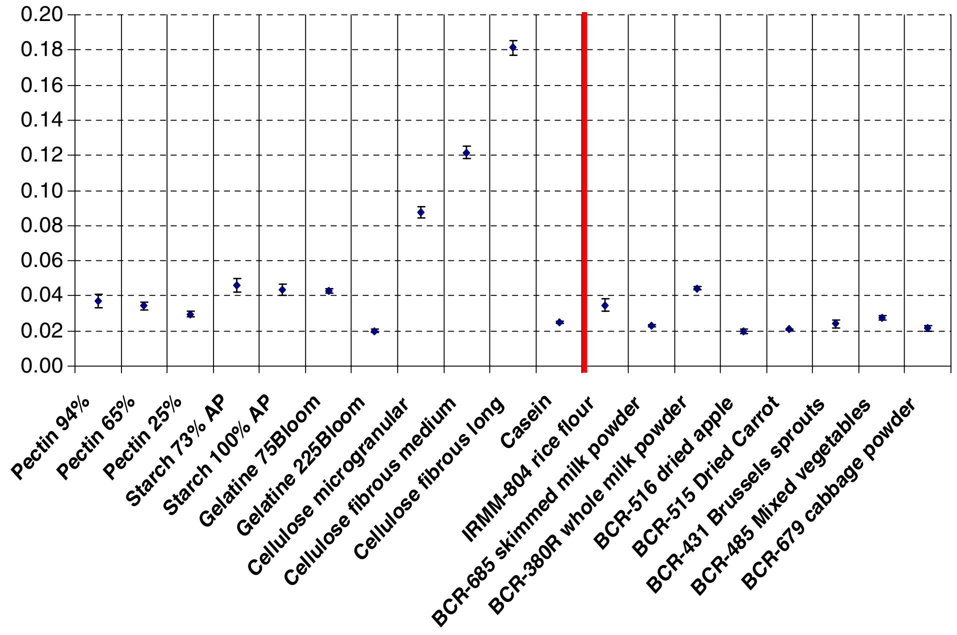

Fig. 6. Factor *B* of food models and powdered CRMs (for details see text).

from the laboratory surroundings, particularly after opening the flask. One material might have a high capacity to adsorb water, but this process takes a relatively long time, which means that the material is relatively stable when the flask is reclosed immediately after taking a sample from it. Another material might, on the contrary, have a low capacity to take up water, but does it very quickly. In this case the material is more "in danger" to change its contents in terms of certified values (which depend on the water content).

4. Conclusions and consequences

High temperatures used for oven drying may cause a decomposition of the material, which leads to artificially higher moisture contents. On the other hand not all of the water in the sample may be detected if the temperature is not high enough. As these two effects are in conflict with each other, it may be impossible to find an appropriate temperature and, consequently, to determine the water content of the sample by drying. The drying time has also an influence. Long times favour the completeness of water detection but also decomposition reactions.

Water uptake kinetics and water uptake capacity depend on the composition of the sample. Depending on the composition of the sample the hygroscopicity may vary significantly. The speed of water uptake does not necessarily correlate with the maximum water uptake capacity. Sorption isotherms (if they are recorded correctly in the respective equilibrated states of the sample) deliver information only on the water uptake capacity, but not on how fast this situation (of equilibrium) is reached.

The CRM user should be aware of the hygroscopicity of CRMs, not only in terms of maximum water uptake of the material ("equilibrial hygroscopicity"), but also in terms of the speed of water uptake ("kinetic hygroscopicity"). If the user is informed about this "kinetic hygroscopicity", he can judge how long he can expose the material to surrounding humidity. As an additional service to the end user CRM producers may, therefore, wish to provide information about the water uptake kinetics (e.g. instruction for use in a CRM certificate). He should also indicate that the water content and its correct determination is a source of uncertainty for the certified values; in some cases even the major source. The uncertainty of moisture/water content determination can be higher than the change in water content of the sample during storage and use. It should, therefore, be considered if the certified values should be referred to dry mass and to inform on the initial water content (which may change in the course of time); additionally the customer should, particularly in "critical" cases, be advised to check the water content by a method recommended by the producer of the CRM. This means, consequently, that the CRM producer should carry out investigations about the CRMs and their water adsorption behaviour including the adsorption kinetics and the method to determine water content correctly.

Further investigations are ongoing to optimise drying oven conditions using TGMS to achieve comparable results with both methods (KFT and drying oven). It is recommended to add these conditions to the instruction for use in the CRM certificate, which is important if dry mass correction is required.

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References

Aregbe, Y., Harper, C., Nørgaard, J., De Smet, M., Van Nevel, L., & Smeyers, P., *et al.* (2003). IMEP19 trace elements in rice, report to participants, EUR 20551 EN. Available from http://www.irmm.jrc.be/imep/imep19/imep19_participants_report.pdf.

Aregbe, Y., Harper, C., Verbist, I., Van Nevel, L., Smeyers, P., & Quétel, C. *et al.* (2004). IMEP20 trace elements in tuna fish, report to participants, EUR 21018 EN. Available from http://www.irmm.jrc.be/imep/imep20/IMEP-20_Participants%20Report%20in%20full.pdf.

Azuara, E., Cortés, R., Garcia, H. S., & Beristain, C. I. (1992). Kinetic model for osmotic dehydration and its relationship with Fick's second law. *International Journal of Food Science and Technology, 27*, 409–418.

Beristain, C. I., Azuara, E., Garcia, H. S., & Vernon-Carter, E. J. (1996). Kinetic model for water/oil adsorption of mesquite gum (*Prosopis juliflora*) and gum arabic (*Acacia senegal*). *International Journal of Food Science and Technology, 31*, 379–386.

Bernreuther, A., Yazgan, S., Klein, C. L., Robouch, P., Rückold, S., & Isengard, H.-D. (2003). Sorption isotherms, an additional valuable information for CRMs. In: *Poster presentation at the Ninth International Symposium on Biological and Environmental Reference Materials*, 15–19th June 2003, Berlin, Germany.

Isengard, H.-D. (2001). Water content, one of the most important properties of food. *Food Control, 12*, 395–400.

IDF Standard 26A (1993). International Dairy Federation, Brussels, Belgium.

Klein, C. L., Yazgan, S., & Franchini, F. (2004). A certified reference material for gliadin: status and methodological approaches. In M. Stern (Ed.), *Proceedings of the 18th meeting working group on prolamin analysis and toxicity* (pp. 125–127). Zwickau, Germany: Verlag wissenschaftliche Skripten.

Der kleine "Souci, Fachmann, Kraut" Lebensmitteltabelle für die Praxis (1991). Deutsche Forschungsanstalt für Lebensmittelchemie (2nd ed.) Stuttgart, Germany: Wissenschaftliche Verlagsgesellschaft mbH.

McCutcheon, A. L., Barton, W. A., & Wilson, M. A. (2001). Kinetics of water adsorption/desorption on bituminous coals. *Energy & Fuels, 15*, 1387–1395.

Peleg, M. (1988). An empirical model for the description of moisture sorption curves. *Journal of Food Science, 53*, 1216–1217.

Rückold, S., Grobecker, K. H., & Isengard, H.-D. (2000). Determination of the contents of water and moisture in milk powder. *Fresenius' Journal of Analytical Chemistry, 368*, 522–527.

Rückold, S., Grobecker, K. H., & Isengard, H.-D. (2001a). Water as a source of errors in reference materials. *Fresenius' Journal of Analytical Chemistry, 370*, 189–193.

Rückold, S., Grobecker, K. H., & Isengard, H.-D. (2001b). The effects of drying on biological matrices and the consequences for reference materials. *Food Control, 12*, 401–407.

Rückold, S., Isengard, H.-D., Hanss, J., & Grobecker, K. H. (2003). The energy of interaction between water and surfaces of biological reference materials. *Food Chemistry, 82*, 51–59.

Sreekala, M. S., Kumaran, M. G., & Thomas, S. (2002). Water sorption in oil palm fiber reinforced phenol formaldehyde composites. *Composites: Part A, 33*, 763–777.

Turhan, M., Sayar, S., & Gunasekaran, S. (2002). Application of Peleg model to study water adsorption in chickpea during soaking. *Journal of Food Engineering, 53*, 153–159.

van der Veen, A. M. H. (2003). Measurement uncertainty and the use of reference materials. *Accreditation and Quality Assurance, 8*, 555–558.