

Scope

This White Paper introduces a method to determine critical storage conditions and to calculate the shelf-life of dried food products. Predictions are based on the water vapor sorption characteristics of the dry food and on the water vapor permeability of the packaging.

The method presented is useful for estimating the shelf-life of packaged products depending on the storage conditions.

1. Introduction

1.1 Basics of shelf-life and packaging of food

Maintaining quality and sensory properties during production, delivery and storage is of great importance for food manufacturers, as consumer acceptance depends on a flawless product. Therefore, for each product, stability studies are conducted to determine the shelf-life. According to [1], the shelf-life is defined as “the time during which the food product will:

- remain safe
- be certain to retain desired sensory, chemical, physical and microbiological characteristics and
- comply with any label declaration of nutritional data.”

The shelf-life of a product is directly related to the storage conditions. In ensuring the product's shelf-life, the packaging of a product also plays an important role. In addition to protection against mechanical damage, such as shocks, vibrations, or compressive forces, protection against external climatic influences is an important task.

For dry products temperature and humidity, in particular, have a significant impact on quality and shelf-life. [1, 2]

Fig. 1 illustrates the effects associated with a change in the moisture content of a product. A critical value for

food stability and safety can be marked at a water activity of 0.7.

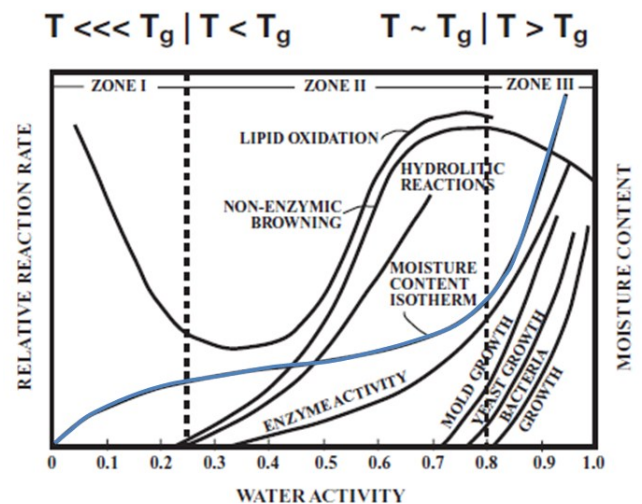


Fig. 1: Food stability map illustrating moisture related reactions in food products [3]

This is the point at which the growth of molds, yeasts, and bacteria begins, a process that not only results in sensory deterioration but can also lead to product spoilage that may be relevant to health.

A further point to consider in the quality of dry food is the inner structure, which is relevant for the crispiness of e.g. crackers or chips. Such products usually have a low water content and are in an amorphous state. With increasing moisture content, water acts as a plasticizer, inducing a reduction of the glass transition temperature. Higher molecular mobility enables crystallization processes, leading to a change of physical product characteristics.

Taking these points into account, it is evident that the protection of foodstuff against moisture uptake during storage is a crucial criterion regarding shelf-life.

Here the packaging becomes relevant. The decisive factor is the water vapor permeability which is a measurable material property that is referred to as WVTR.

Depending on the sensitivity of the product, the adequate packaging material should be used. On the one hand optimal protection should be guaranteed, on the other hand, regarding sustainability, over-packaging should be prevented to save material and costs.

Fig. 2 summarizes the WVTR and oxygen transition rate (OTR) of polymer materials commonly used in industrial packaging. Necessary barrier properties of selected products are given in Fig 3.

A variety of materials are utilized for packaging purposes, each with different protective properties. Metal and glass containers are regarded as impermeable to environmental influences such as gases, odors, and moisture. This same quality is observed in aluminum foils, provided a minimum thickness of 25 μm is reached. To achieve sufficient barrier and processing properties, packaging materials are usually composed of several layers. For instance, aluminum foils are laminated with plastic polymers, and paper-based materials are polymer-coated to reduce their permeability [2].

The required barrier properties of the packaging materials depend on several factors, including shelf-life requirements, storage conditions, and moisture adsorption properties of the packed product. In the latter case, the temperature-dependent sorption isotherm and the kinetics of moisture sorption are the key factors in defining critical limit values.

1.2 Dynamic Water Vapor Sorption measurements

The sorption test systems SPS and Vsortp, permit the analysis of the moisture sorption properties of the packed product as well as the determination of the permeability characteristics of the packaging material

(Fig. 4).



Fig. 4: Sorption analyzer SPS for up to 23 samples and Permeability Kit tablet as add-on.

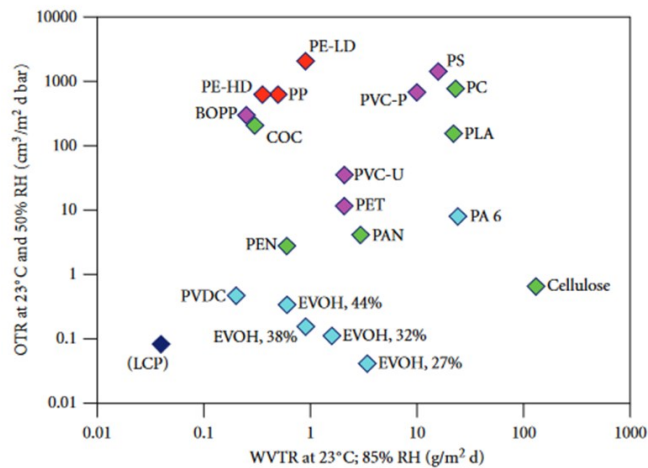


Fig. 2: Water vapor transition rates (WVTR) and Oxygen transition rates (OTR) of industrially used packaging materials (modified from [4]).

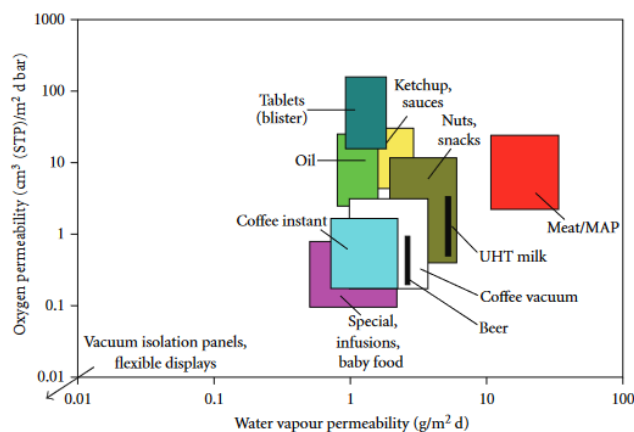


Fig. 3: Barrier requirements of exemplary food and pharmaceutical products [4].

The principle of the SPS and Vsortp multi-sample DVS instruments is the gravimetric measurement of the increase or decrease in sample weight through moisture adsorption or desorption. The devices are controlled by a intuitive software that enables convenient programming of the measuring conditions, including relative humidity cycles and temperature, as well as clear data evaluation via an Excel macro.

In conjunction with additional sensors attached to the Sorption Analyzer, such as a camera system or a Raman probe, moisture-related changes of the product can be observed directly during the sorption analysis.

1.3 Principle of Permeability measurements

Similar to the DVS measurement described above, the permeability analysis is also based on a gravimetric principle.

For measurement set-up the permeability cups are covered with a film to be analyzed. By filling the cups with either with a desiccant, a saturated salt solution or water, a difference to the partial water vapor pressure of the ambience is created. This results in a migration of water molecules through the film. The principle is shown schematically in Fig. 5.

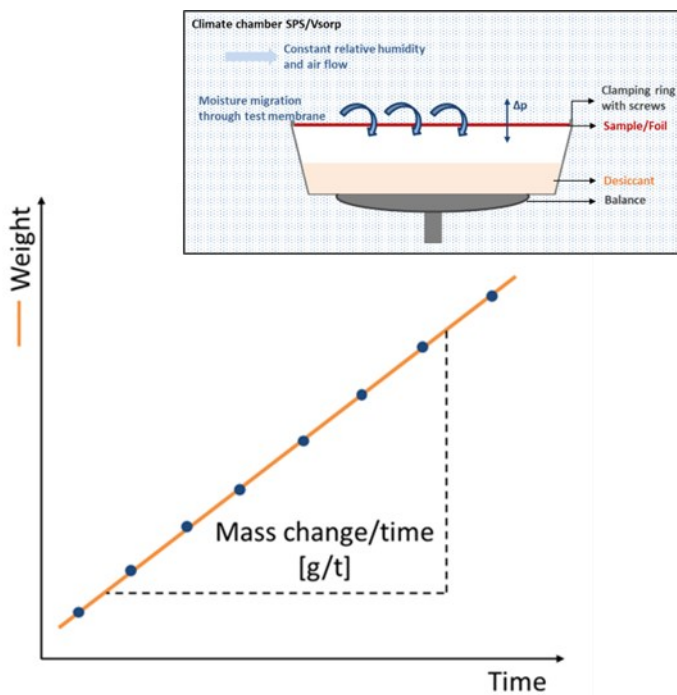


Fig. 5: Schematic draw of permeability test set-up and exemplary curve of a permeability measurement

Calculation of the Water Vapor Transmission Rate

According to Fick's 1. law (Eq. 1), the permeability of a packaging material is influenced by the relative humidity and partial water vapor pressure differences and the temperature. Higher gradients and temperatures lead to increased permeability and thus less effective moisture protection. The relationship is explained by Eq. 1-4.

$$Q = \frac{DS \cdot (p_1 - p_2) \cdot A \cdot t}{X} \quad \text{Eq. 1}$$

Here, variable Q is the quantity of vapor that permeates through the packaging with thickness X. D and S are the diffusion and the solubility coefficient of the permeate. "p1-p2" represents the pressure gradient across both sides of the film; A is the surface area and t the time.

With "D·S" representing the Permeability coefficient P, and P/X the Permeance, the water vapor permeation through the film can be calculated by rearranging the equation as follows:

$$P = \frac{QX}{A \cdot t \cdot (p_1 - p_2)} \quad \text{Eq. 2}$$

$$\frac{Q}{t} = \frac{P}{X} \cdot A \cdot (\Delta p) \quad \text{Eq. 3}$$

Based on the Permeability coefficient the WVTR can be expressed as:

$$WVTR = D \cdot S \cdot \Delta p \quad \text{Eq. 4}$$

With the help of permeability measurements, as explained previously, the WVTR is calculated directly from the experimental results by determining the slope of the linear section of the mass change over time as explained in Fig. 5. The WVTR is then related to the area of the foil sample and usually to a time unit of one day (Eq. 5).

$$WVTR = \frac{\Delta m}{\Delta t \cdot A \cdot 24} \quad \text{Eq. 5}$$

Δm: Weight change in [g]; Δt: Time interval in [h]
A: Sample surface in [m²]

4. Experimental

4.1 Water vapor sorption of dry foods

To assess the shelf-life of dry food products based on their moisture sorption properties, a DVS analysis was performed in combination with a camera connected to the instruments. Two instant coffee preparations and an instant chocolate drink powder were chosen as exemplary products. The samples, their main ingredients as well as the packaging characteristics are summarized in Table 1.

Basic DVS settings are summarized in Table 2. Measurement conditions were 22 °C and relative humidity (RH) was varied from 0 % RH to 90 % RH in 10 % steps. A second analysis at 38 °C was done to consider the influence of higher storage temperatures. The stability of the products was evaluated based on the water vapor sorption curve and the moisture-induced product changes which were observed by the inline image recording.

4.2 Water vapor permeability of the packaging material

To determine the influence of the packaging on the shelf-life, the packaging materials of the tested products were analyzed with the proUmid Permeability Kit, and the water vapor permeability was determined as a characteristic parameter of the material.

The dry cup procedure, using a molecular sieve as desiccant, was used and climate conditions were set to 23 °C/85 % RH and 38 °C/93 % RH. The packing materials were attached to the lower part of the sample dish by the clamping ring and fixed by screws to ensure tightness. Sample area was 23 cm². Water vapor transmission rates were determined from the slope of the linear section as described in Chapter 1.3.

Table 1: Sample description and main ingredients

Sample	Description	Main Ingredients	Packaging
Instant coffee A	Beverage powder with soluble coffee powder and creamer	Glucose syrup, skim milk powder, coconut oil, instant coffee powder, milk protein.	Filling: 14 g/sachet Surface area: 105 cm ²
Instant coffee B	Beverage powder with soluble coffee powder, creamer and sugar	Sugar, creamer, lactose, instant coffee powder	Filling: 16 g/sachet Surface area: 105 cm ²
Instant chocolate drink	Beverage powder containing cocoa	Sugar, low-fat cocoa powder, dextrose, salt, natural flavoring.	Filling: 400 g/ bag Surface area: 690 cm ²

Table 2: DVS analysis: Measurement settings

Time between weighing cycles	10.0 min
Min. time per climate cycle	60.0 min
Max. time per climate cycle	48.0 h
Default weight limit	150.0 %
Equilibrium condition	0.0015 % per 60 min

5. Results

5.1 Dynamic water vapor sorption

Results of DVS analysis are shown in Fig. 6. Temperature was set to 22 °C and the relative humidity was varied from 0 - 90 % RH in 10 % steps.

Samples were automatically measured every 10 min. The initial sample mass was between 1.4 - 2.4 g and equilibrium conditions were assumed with a weight change of less than 0.0015 %/60 min.

As the course of the curves in Fig. 6 shows, the instant coffee samples A and B only show a strong increase in weight at a relative humidity of 90 % RH. For the instant chocolate drink, strong moisture adsorption was already observed at a relative humidity of 80 %. In addition, the instant coffee B and the chocolate drink no longer reached an equilibrium state at the highest relative humidities, which indicates a liquefaction of the samples

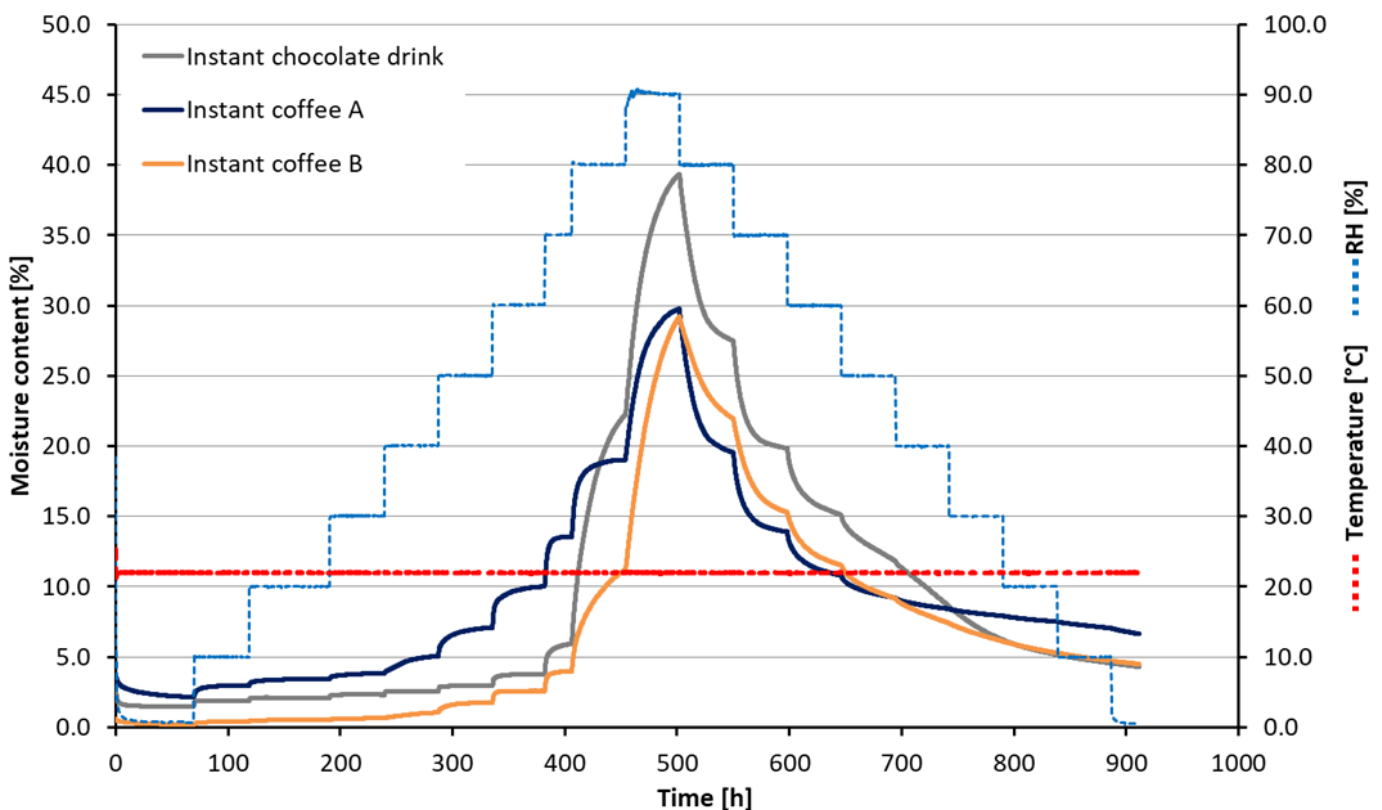


Fig. 6: Dynamic water vapor sorption of the food samples at 22 °C and a relative humidity in the range of 0 - 90 % (sorption/desorption)

Fig. 7 shows the moisture sorption isotherms of the samples. In addition, the images that were taken automatically during the measurement are shown as a function of the respective humidity condition in Fig. 8 A-C. The images were taken each time a sample reached equilibrium, or the next moisture level was set.

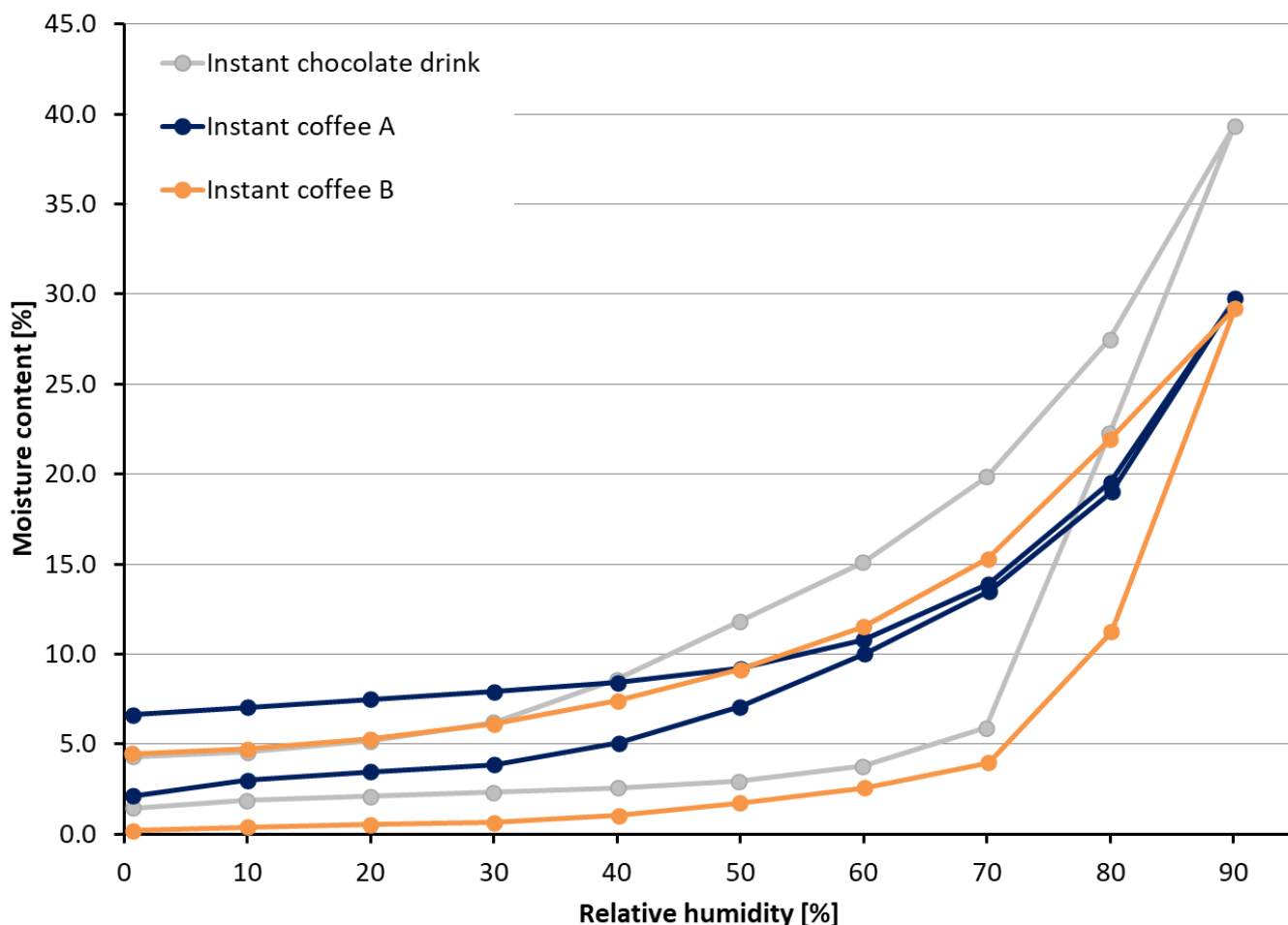


Fig. 7: Sorption isotherm of the instant chocolate drink and instant coffee samples A and B. Isotherms were recorded at a temperature of 22 °C and relative humidities were varied from 0-90 % RH (adsorption/desorption)

In accordance with the dynamic representation in Fig. 6, the strongest moisture adsorption was observed for the chocolate drink after the relative humidity level exceeded 70 % RH. The course of the coffee B isotherm also demonstrates a more pronounced increase at 80 % RH, which becomes even steeper at 90 % RH.

In the case of the instant coffee A sample, a relatively uniform increase in moisture was observed over the entire range of relative humidities without a clear liquefaction point. This suggests that this sample preparation is the least sensitive to the effects of moisture.

The sorption kinetics and isotherm data presented above provide the basis for identifying critical points regarding the interaction between the sample and relative humidity of the ambient.

Furthermore, the integration of image analysis facilitates a more comprehensive characterization, enabling the visualization of even subtle changes in the sample induced by moisture influences.

For example, although the sorption data indicate that the coffee sample A is stable, the image analysis reveals a color change at 60 % RH and the formation of liquefied spots at 80 % RH.

A similar observation could be made for coffee sample B, where color changes were also observed at 60 % RH and advanced liquefaction at 80 % RH, as expected from the sorption data.

The pronounced rise in sample weight measured for the chocolate drink sample beyond 70 % RH, as shown by the sorption data, indicated that this sample exhibits the highest sensitivity to humidity-related effects. This was confirmed by the image analysis. Here, a critical moisture influence could already be observed at 60 % RH, which was initially reflected in moist spots and finally in complete liquefaction at a relative humidity of 80 %.

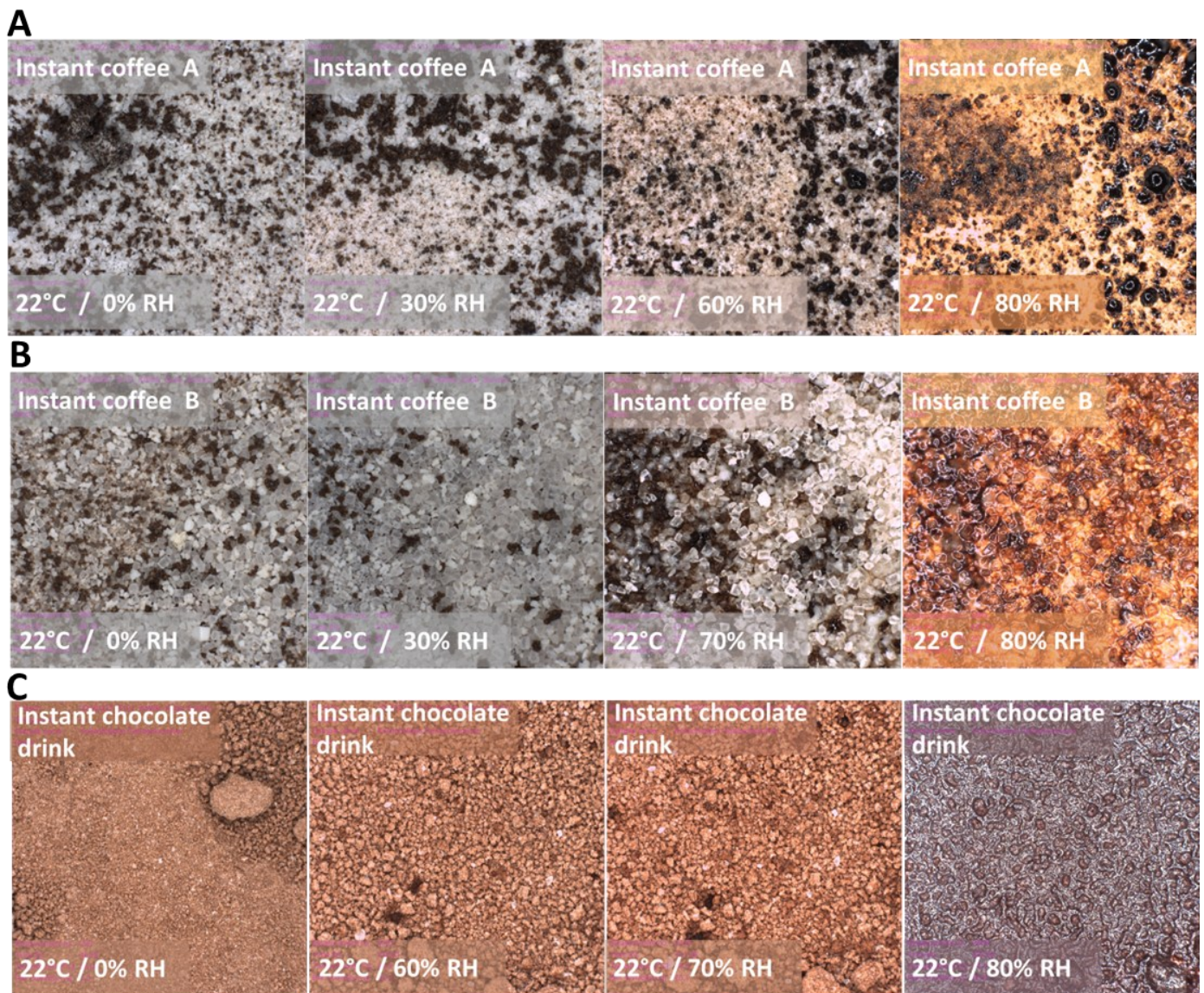


Fig. 8: Images of instant coffee A and B and instant chocolate powder recorded throughout the DVS measurement showing critical relative humidity levels for liquefaction

5.2 Water vapor transmission rates of packaging materials

Analysis and evaluation of permeability results was done as described in Chapter 1.3.

To test the influence of these parameters and thus account for different storage conditions, measurements were run using two different settings, namely 23 °C / 85 % RH and 38 °C / 93 % RH.

As illustrated in Fig. 9, the packaging materials of coffee samples A and B are almost vapor-tight, which can be explained by the aluminum coating of the foil material.

In comparison, the packaging of the instant chocolate drink displays a markedly higher water vapor permeability.

For 38 °C/93 % RH water vapor permeability of the chocolate drink packaging increased by over 5-fold, whereas the coffee foils remained vapor tight.

Results of the permeability measurements are summarized in Table 3.

Table 3: WVTR of packaging materials

Packaging of:	WVTR [g/m ² /d]	
	23 °C/85 % RH	38 °C/93 % RH
Instant coffee A	~ 0	
Instant coffee B	~ 0	
Instant chocolate drink	0.7	3.8

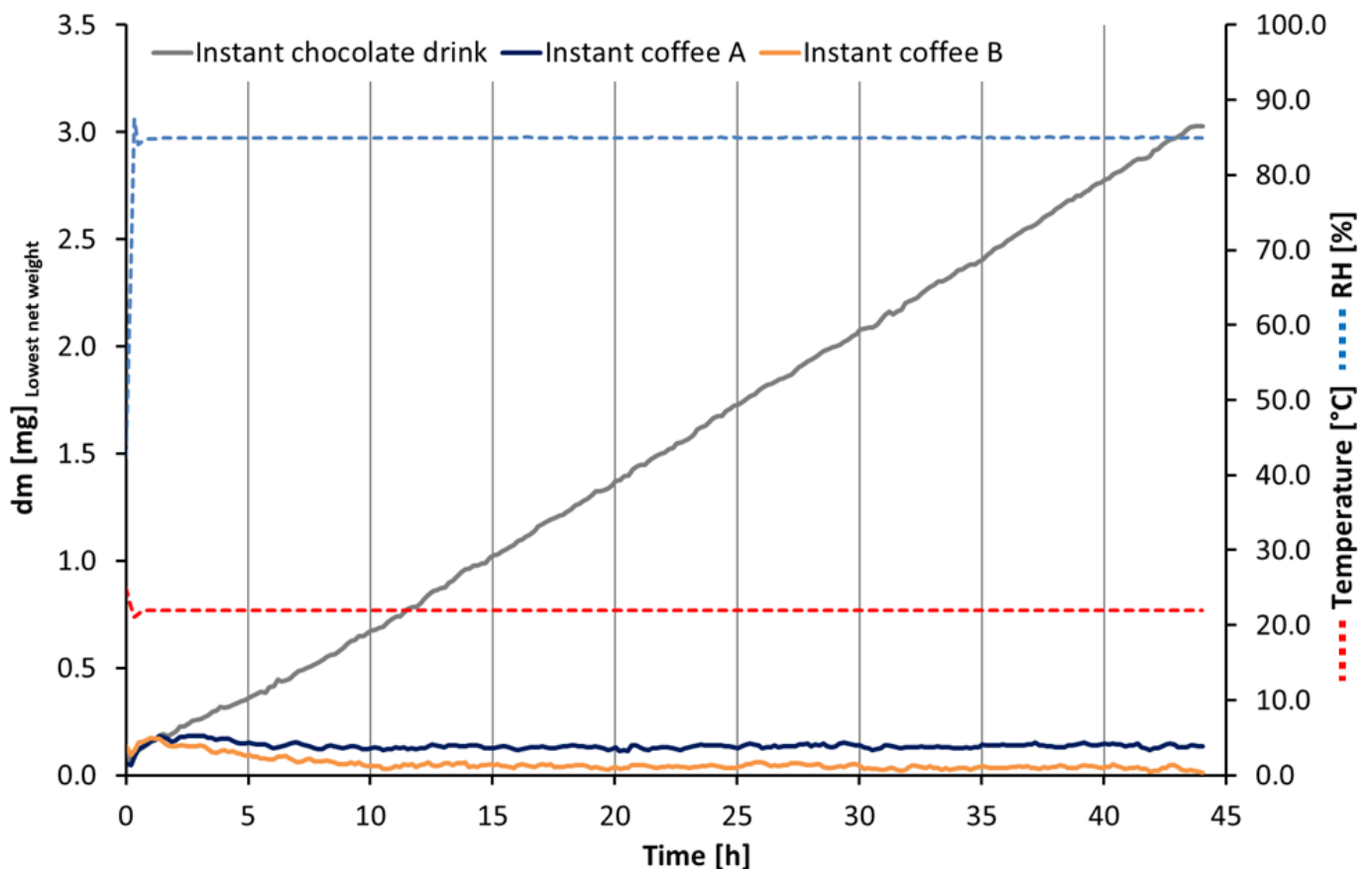


Fig. 9: Water vapor permeability of the packaging materials at 23 °C and 85 % RH. Data were determined based on the moisture adsorption of the desiccant in the dish.

5.3 Shelf-life calculation

The shelf-life of packaged products can be estimated by using the permeability characteristics of the packaging together with the moisture uptake and critical humidity value determined from DVS measurements.

Calculation of the shelf-life of the packaged product was done using Equation 6 as proposed by [6]. The sorption isotherm is fitted by the BET model to determine the moisture content and respectively the water activity of the product at the characteristic sorption points (m_i , m_c , m_e) as schematically shown in Fig. 10. Based on these values, which are highlighted in Fig. 10, the shelf-life of the product can be calculated.

The pseudo-equilibrium moisture content is used for shelf-life calculation. As already indicated by [6], in reality, the driving force for water vapor transmission is higher whereby the calculated shelf lives might be overestimated and should be verified in practice [6]

$$\ln \frac{m_e - m_i}{m_e - m_c} = \left[\frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \right] \cdot \theta \quad \text{Eq. 6}$$

m_e : Pseudo-Eq. moisture content of the food if exposed to external relative humidity

m_i : Initial moisture content of the food

θ : shelf-life of the product

p_0 : Vapor pressure of pure water at storage temperature

A : Area of packaging

P/X : Water vapor permeance

W_s : Weight of dry product in the package

b : Slope of the linear fit of moisture uptake ($m_i - m_c$)

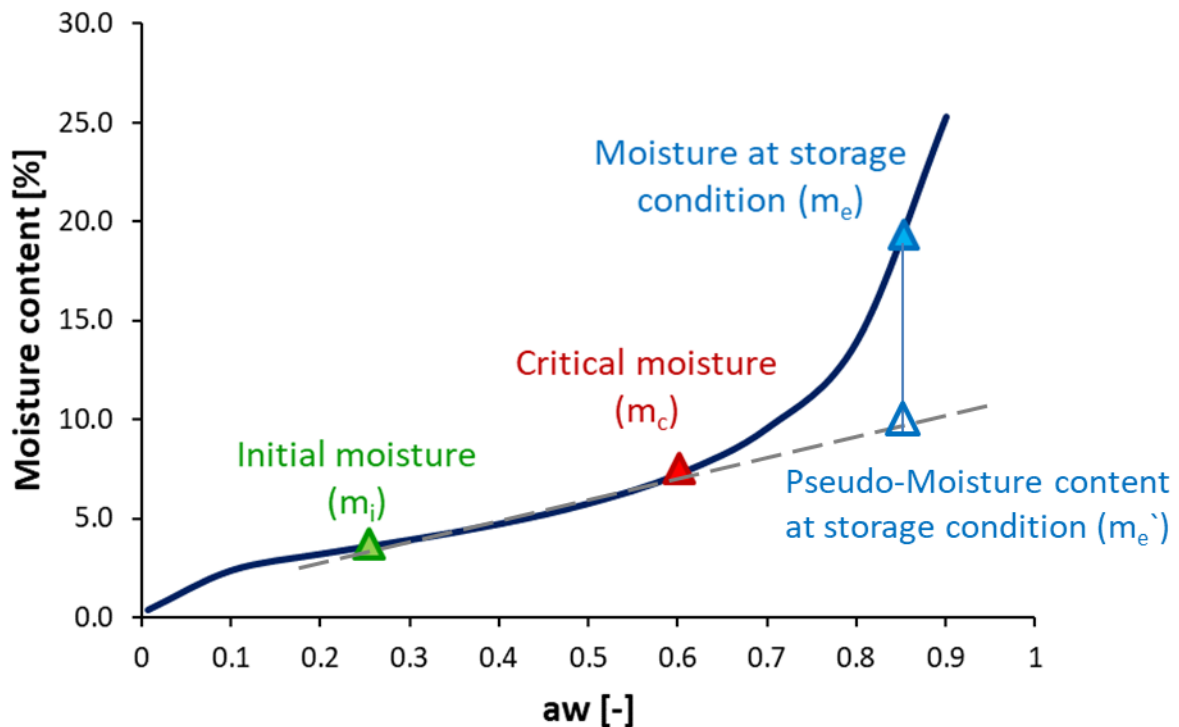


Fig. 10: Illustration of data evaluation for shelf-life calculation of packaged products, modified from [6]

Example: Shelf-life calculation

In follow, shelf-life calculation is demonstrated using the example of instant chocolate drink.

Fig. 11 shows the sorption isotherm and BET fit as well as the characteristic sorption points of initial-, critical-, equilibrium- and pseudo-equilibrium moisture content of the sample. Further data that are necessary for calculation are summarized in Table 3.

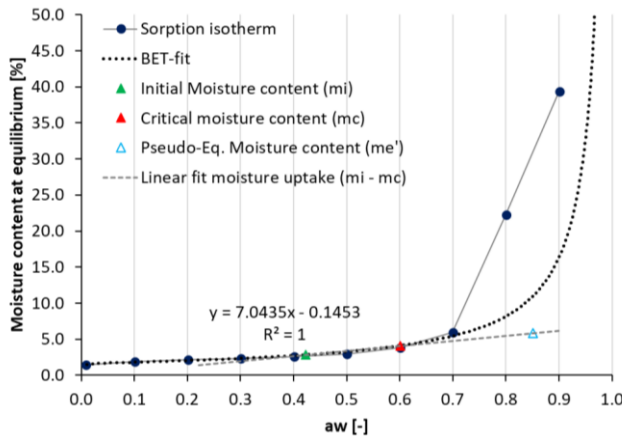


Fig. 11: Data evaluation for shelf-life calculation of the instant chocolate drink sample (22°C/85% RH)

According to Eq. 2 and data summarized in Table 3 shelf-life of the instant chocolate drink is:

Storage condition 22°C and 85% RH:

$$\ln \frac{m_e' - m_i}{m_e' - m_c} = \left[\frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \right] \cdot \theta$$

$$\ln \frac{5.8 - 2.8}{5.8 - 4.1} = \left[\frac{0.725}{1.6864} \cdot \frac{0.07}{400} \cdot \frac{1.9841}{0.0744} \right] \cdot \theta$$

$$\theta = \frac{[\ln 1.7647]}{2.006 \cdot 10^{-3}} = 709 \text{ days}$$

Storage condition 38°C and 93 % RH:

$$\ln \frac{m_e' - m_i}{m_e' - m_c} = \left[\frac{P}{X} \frac{A}{W_s} \frac{p_0}{b} \right] \cdot \theta$$

$$\ln \frac{12.5 - 2.8}{12.5 - 4.7} = \left[\frac{3.890}{4.6268} \cdot \frac{0.07}{400} \cdot \frac{4.975}{0.235} \right] \cdot \theta$$

$$\theta = \frac{[\ln 1.2435]}{3.19 \cdot 10^{-3}} = 68 \text{ days}$$

Table 4: Data for shelf-life calculation

Packaging characteristics		22°C/85% RH	38°C/93% RH	
Surface area	A		0.07	m ²
WVTR	WVTR	0.725	3.809	g/m ² /d
Water vapor permeance	WVTR/ΔP	0.4299	0.8233	(g/m ² /d)/cmHg
Weight of dry solids	W _s		400	g
Ambient conditions				
Temperatur	T	22	38	°C
Humidity	RH	85	93	%
Water vapor pressure of pure water	p ₀	1.9841	4.975	cmHg
Vapor pressure difference (in/outside Permea dish)	ΔP	1.6864	4.6268	cmHg
Sorption data				
Initial Moisture content	m _i		2.82	%
Critical moisture content (at aw 0.6)	m _c	4.1	4.7	%
Pseudo-Eq. Moisture content	m _{e'}	5.8	12.5	%
Slop of linear section mi/mc	b	0.0744	0.235	g H ₂ O/g Solid

6. Parameter variation study

The permeability of a packaging material is influenced by the relative humidity, the partial water vapor differences and the temperature.

Moreover, the dimensions of the packaging and the mass of the packaged product exert an influence on the shelf-life. In Figure 12 A-C, these influences are modeled by a parameter variation study. A power correlation was identified between the water vapor permeability and the packaging size, while the shelf-life increased linearly with the product mass within the package.

From these results, it can be concluded that for the same amount of product, a larger package will result in a shorter shelf-life. The same is true if the product mass and the dimensions of the package are reduced due to the resulting unfavorable volume/area ratios. This also means that the shape of the package - e.g. spherical, cylindrical or rectangular - leads to a change in product shelf-life despite the same volume.

This is consistent with the conclusion of [2] that a shelf-life test and, if necessary, an adjustment of the packaging characteristics should always be conducted when such changes are implemented.

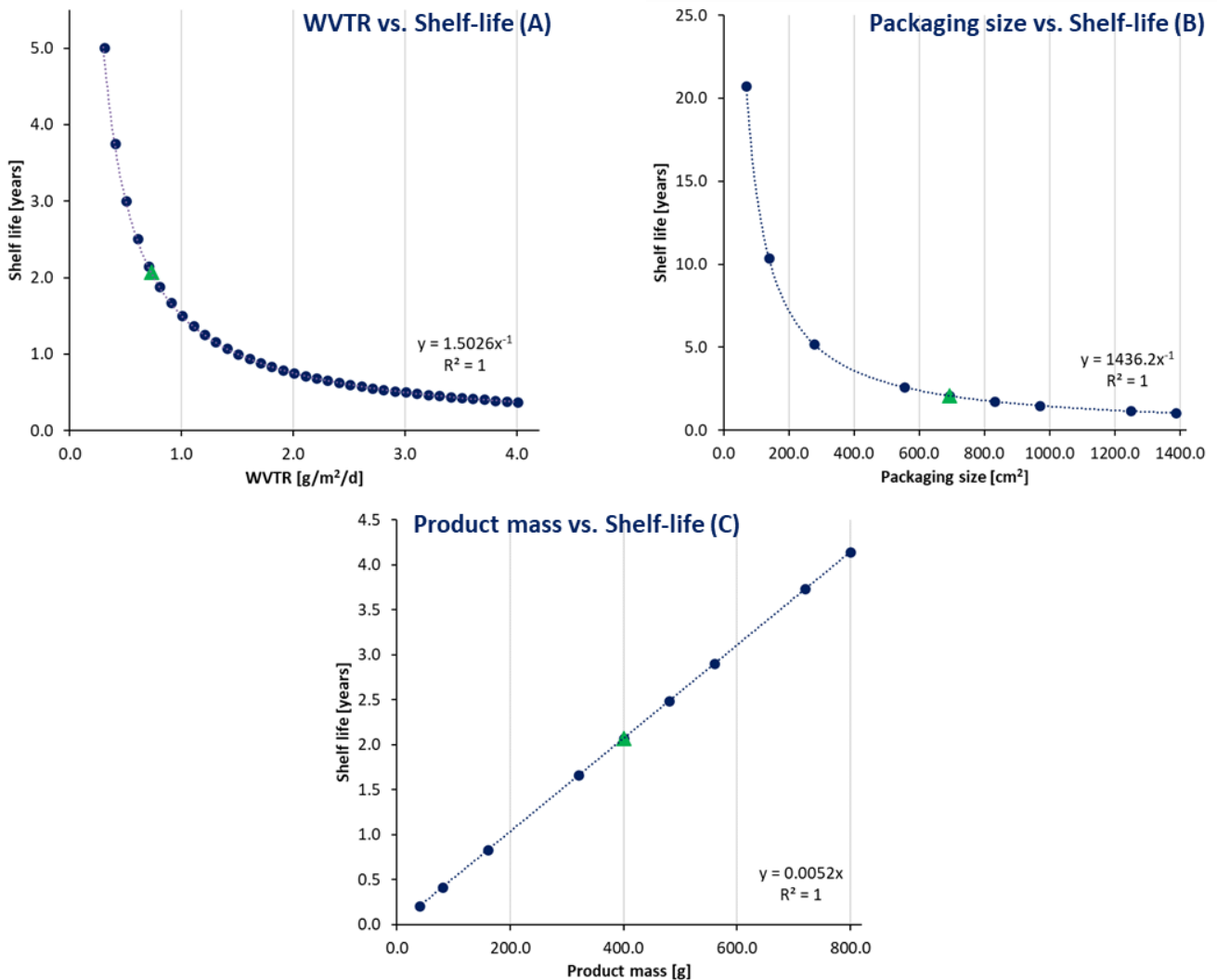


Fig. 12: Shelf-life modeling. Influence of WVTR (A), packaging size (B) and product mass (C).

▲: Measured values of the instant chocolate drink sample

7. Conclusion

The previous results showed that the shelf-life of a product depends on its sensitivity against ambient moisture. In this context, the knowledge of moisture-related product behavior is essential and DVS analysis, as explained in the previous chapters, is essential for shelf-life estimation

To increase the shelf-life, packaging materials are used to provide a barrier against moisture influences and thus protecting the product. The tightness against water vapor is characterized by the Water Vapor Transmission Rate. This material-specific constant was analyzed using the proUmid Permeability Kit.

By knowing the product and packaging characteristics suitable packaging can be developed to ensure product stability.

The materials tested in this study showed significant differences with values close to zero up to 0.7 and 3.8 g/m²/d.

As described above, the permeability measurements were performed on film samples of the packaging material. For further studies, it might be interesting to analyze the entire packaged product to take into account possible packaging defects, e.g. at the sealing point. Especially for the instant coffee samples, this could have an impact on the shelf-life of the product. proUmid's *Large Object Kit* is a recommended add-on module for this type of analysis.

Finally, by the help of a parameter variation study, the influence of the WVTR, the packed product mass and packaging size on the shelf-life was demonstrated.

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