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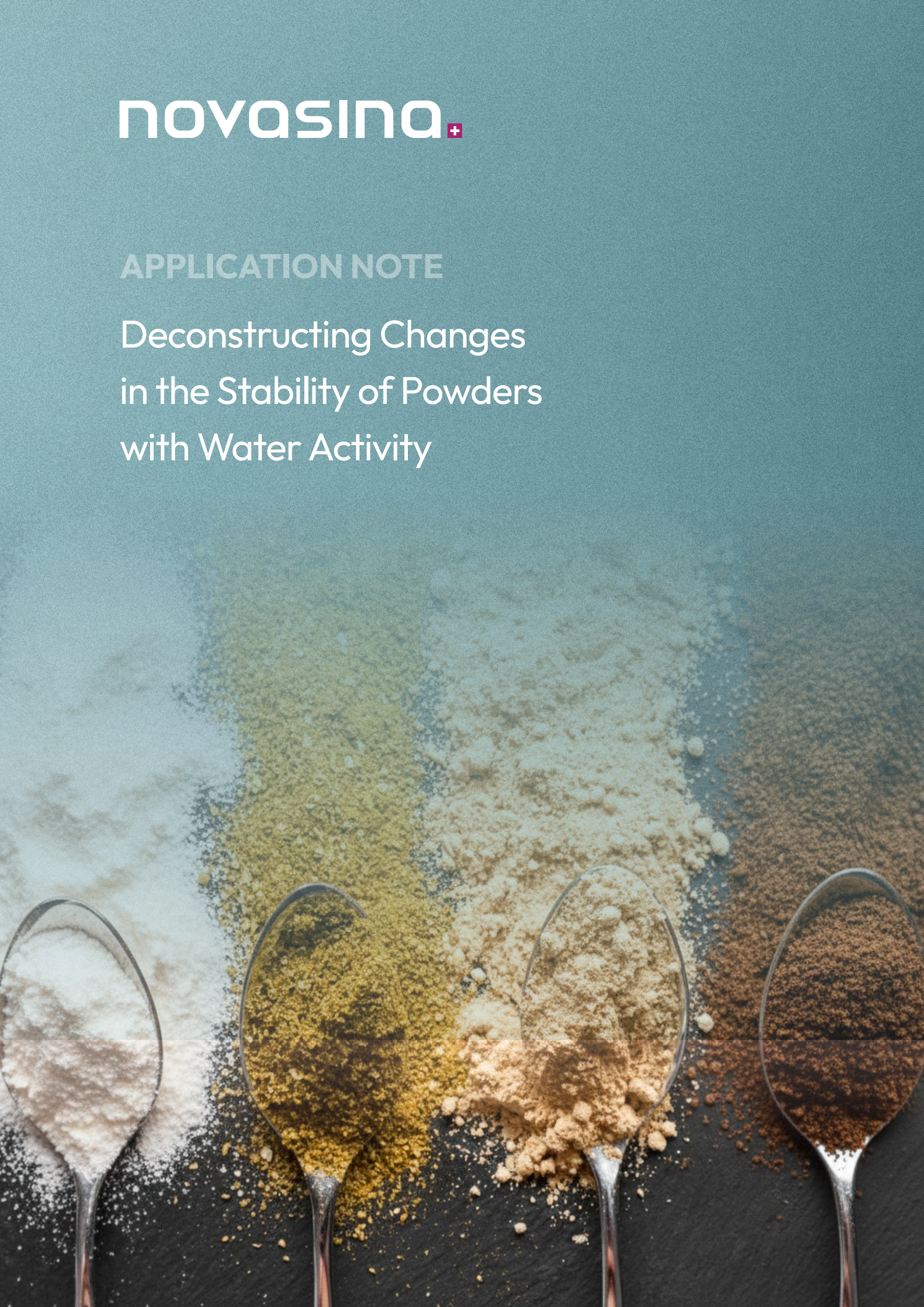
APPLICATION NOTE

Deconstructing Changes in the Stability of Powders with Water Activity



Introduction

Low-moisture food powders are widely used as ingredients by food manufacturers due to their ease of handling and extended shelf life. Beyond the food industry, these powders serve as essential raw materials in sectors such as pharmaceuticals, where they function as excipients, and plastics manufacturing, where resin powders are utilized. Common examples of low-moisture ingredients include baking powder, flour, sugar, and starches.

While water activity is widely recognized as critical for intermediate-moisture foods, it is often overlooked for powders under the assumption that their low moisture makes testing unnecessary. However, all common failure modes in powders are closely linked to water activity and can often be controlled by monitoring it. The most frequent issue is caking or clumping, which complicates handling and reduces production efficiency [1]. More recently, microbial safety has emerged as an additional concern, highlighted by several product recalls involving low-moisture ingredients [2,3]. Although it may seem counterintuitive to discuss microbial risks in products with water activity levels well below the threshold for microbial growth, low-moisture ingredients can still act as carriers of microorganisms.

Identifying and maintaining an optimal water activity range is one of the most effective strategies for ensuring powder stability, maximizing utility, and extending shelf life. This white paper aims to explain the theory behind water activity and outline methods for determining the critical water activity level that minimizes common failure modes in powders, including glass transition, caking and clumping, chemical degradation, and microbial safety.

Water Activity Basics

Water activity is defined as the energy status of water in a system and is rooted in the fundamental laws of thermodynamics through Gibb's free energy equation. It represents the relative chemical potential energy of water as dictated by the surface, colligative, and capillary interactions in a matrix. Practically, it is measured as the partial vapor pressure of water in a headspace that is at equilibrium with the sample, divided by the saturated vapor pressure of water at the same temperature. The water activity covers a range of 0 for bone dry conditions, up to a water activity 1.00 for pure water, resulting from the partial pressure and the saturated pressure being equal. Water activity is often referred to as the 'free water' and while useful when referring to higher energy, it is incorrect since 'free' is not scientifically defined and is interpreted differently depending on the context. As a result, the concept of free water can cause confusion between the physical binding of water, a quantitative measurement, and the chemical binding of water to lower energy, a qualitative measurement. Rather than a water activity of 0.50 indicating 50% free water, it more correctly indicates that the water in the product has 50% of the energy that pure water would have in the same situation. The lower the water activity, the less the water in the system behaves like pure water.

While water activity is an intensive property that provides the energy of the water in a system, moisture content is an extensive property that determines the amount of moisture in a product. Water activity and moisture content, while related through the moisture sorption isotherm, are not the same measurement. Moisture content is typically determined through loss-on-drying as the difference in weight between a wet and dried sample. While useful as a measurement of purity and a standard of identity, as this paper will describe, moisture content does not correlate as well as water activity with microbial growth, chemical stability, or physical stability.

Water Activity Measurement of Powders

Water activity is measured by equilibrating the liquid-phase water in a sample with the vapor-phase water in the headspace of a sealed chamber, then determining the Equilibrium Relative Humidity (ERH) using a sensor. ERH can be measured with several sensor technologies, including resistive electrolytic sensors, chilled mirror sensors, and capacitive hygroscopic polymer sensors. Instruments from Novasina, such as the Labmaster NEO, employ a resistive electrolytic sensor to monitor ERH inside the sealed chamber. This sensor detects changes in ERH through variations in electrical resistance within the electrolyte. The key advantage of this method is its exceptional stability and resistance to contamination, an issue that commonly affects chilled mirror sensors. Additionally, resistive electrolytic sensors deliver the highest accuracy and precision with minimal maintenance and infrequent calibration requirements.

Because powders typically have low moisture content, their water activity is also generally low, ranging from approximately 0.10 aw to 0.60 aw, as shown in Table 1. When measuring the water activity of powder samples, the primary concern is preventing powder puffing during placement in the instrument, as this can contaminate both the chamber and the sensor. To minimize this risk, fill the sample cup only about one-quarter full and insert it slowly into the instrument to avoid sudden displacement of the powder. Additionally, regularly wipe the chamber with a Kimwipe moistened with distilled water to remove residual powder and prevent buildup. Always ensure the protective filter is in place while cleaning to avoid damaging the electrolytic sensor.

Powders can be moisture-sensitive or hygroscopic, so they should never be left exposed to ambient humidity for extended periods, even during sampling. Exposure can cause powders to either absorb or release moisture, depending on whether the surrounding humidity is higher or lower than their inherent water activity. Leaving samples uncovered for more than a minute may result in inaccurate readings that reflect room conditions rather than the true water activity of the product. To avoid this, perform sampling quickly and cover the sample cup with a lid until it is placed in the instrument. Keep the lid of the instrument ready to close immediately once the sample is placed in the testing chamber. Additionally, store products in a moisture-barrier container prior to sampling to maintain their integrity.

Table 1. Water activity values, repeatability, and test time of different powder samples measured at 25°C using the ISO18787 stability mode.

Sample Type	Water Activity	Repeatability	Test Time
Dextrose Powder	0.5673	0.019	16.7
Corn Starch	0.3587	0.001	7.3
Baking Powder	0.3557	0.002	6.7
Powdered Sugar	0.3552	0.018	9.0
Table Sugar	0.3549	0.010	13.7
Protein Powder	0.3511	0.002	7.0
Flour	0.3464	0.001	9.7
Baking Soda	0.3421	0.013	10.7
Pancake Mix	0.3258	0.001	6.0
Hot Chocolate Powder	0.2860	0.014	13.3
PEG 3500 - Laxative	0.1396	0.004	9.0

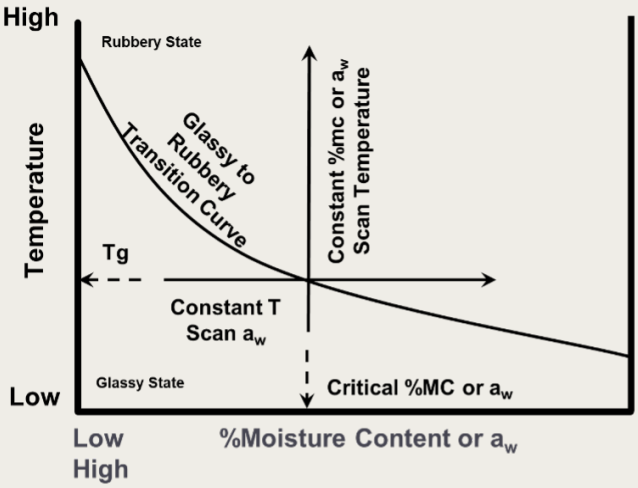
Water Activity and Glass Transition of Powders

Glass transition refers to the change in amorphous materials from a high-viscosity, "frozen" glassy state to a lower-viscosity, rubbery state [4]. In the glassy state, a material behaves like a brittle solid without a crystalline structure, exhibiting only short-range molecular order. The application of glass transition concepts, long established in polymer science, to food polymers was pioneered by Slade and Levine [5]. Low-moisture ingredients such as powders often enter an amorphous glassy state during processes like spray-drying, freeze-drying, or grinding. Maintaining this state is critical for optimal shelf life and handling. Powders in the glassy state are metastable and can remain stable for months or even years. However, once they transition to the rubbery state, product performance and stability deteriorate rapidly, reducing shelf life to weeks, days, or even hours [6, 7, 8, 9].

The glass transition can roughly be categorized as a second order phase change that is accompanied by thermodynamic changes in enthalpy, changes in dielectric properties, and mechanical changes [5]. The important parameter in glassy to rubbery phase transitions is the temperature that initiates the change, termed the glass transition temperature (Tg). Common methods for investigating glass transitions have focused on identifying thermodynamic, mechanical, or dielectric changes while scanning temperature to identify the Tg. However, increasing the amount of plasticizer in a glass matrix can also induce a glass transition even while temperature is held steady. Because moisture is the most common plasticizer in food materials, scanning water activity while holding temperature constant will also induce a glass transition. The water activity where changes in the sorption properties can be observed due to a glass transition is defined as the critical water activity (RHc). In theory, scanning temperature and scanning plasticizer level should lead to the same glass transition event (Fig. 1).

A simple and effective method to identify the RHc is using dynamic moisture sorption profiles [10]. Moisture sorption profiles characterize the relationship between moisture content and water activity for a material as moisture is adsorbed or desorbed. Traditional methods for producing moisture sorption profiles are static in nature as water activity is controlled and held constant and the weight change experienced at each water activity level is used to determine changes in moisture content [11]. These methods are disadvantaged by analysis time and data resolution limitations due to the time required to reach equilibrium at each water activity.

Figure 1. Comparison between thermal methods that scan temperature while holding moisture content (% moisture content) constant to determine the glass transition temperature (Tg) and sorption isotherm methods that scan water activity to identify a critical water activity (RHc) while holding temperature constant. In theory, both methods should provide the same information [9].

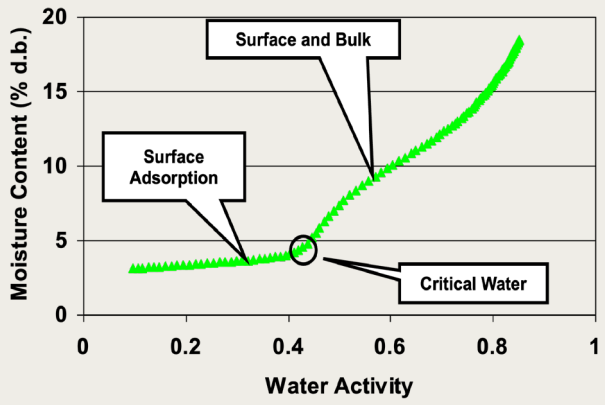


Alternatively, dynamic isotherms can produce high resolution sorption profiles by tracking the real-time changes in sample water activity and weight as the sample is exposed to either saturated wet air (adsorption) or desiccated air (desorption) [10]. Since no equilibration step is required, this approach enables data points to be collected at every 0.01 change in water activity, resulting in high resolution sorption profiles that can detect sudden changes in sorption properties. A glass transition to the rubbery state results in a sudden increase in the slope of the sorption profile, observed as a sharp inflection point in the dynamic curve. The water activity associated with this sharp inflection in the sorption curve is identified as the RHc for glass transition (Figure 2). Maximizing product shelf life for glassy powders then depends on preventing their water activity from exceeding their RHc due to moisture uptake.

Water Activity, Caking, and the Glass Transition

Caking or clumping of powders during handling, packaging, and storage is a common and persistent issue. It can occur during both processing and storage, leading to significant operational challenges. Caking is the formation of permanent clumps caused by particle stickiness, which ultimately reduces functionality and product quality [11, 12]. This phenomenon can hinder product recovery during drying, slow processing by clogging hoppers and pipes, and shorten shelf life. Caking is influenced by water activity, time, and temperature. Factors affecting caking kinetics can be grouped into intrinsic properties of the powder – such as water activity, particle size distribution, presence of impurities, and glass transition temperature – and external conditions like temperature, relative humidity, and mechanical stress [13]. If the powder is in an amorphous glassy state, a transition to the rubbery state significantly increases susceptibility to caking due to enhanced molecular mobility [14].

Figure 2. DD isotherm of spray dried milk powder showing an inflection point at a critical water activity of 0.43 a_w. The high resolution of the DDI method makes it possible to visualize inflection points in the curve. In the amorphous glassy state, sorption is limited adsorption, but the glass transition causes sorption to switch from surface to bulk absorption and results in a drastic sharpening of the isotherm curve. (10)



Since most ingredient powders are produced through spray-drying, they are typically amorphous and in a glassy state. Consequently, the most common cause of caking or clumping is a glass transition. The key to preventing this lies in determining the critical relative humidity (RHc) for glass transition, as described in the previous section, and ensuring that the powder's water activity never exceeds this threshold.

The most common reason for a powder's water activity to exceed its critical relative humidity (RHc) is exposure to ambient humidity above the RHc or to temperatures higher than the glass transition temperature (Tg). RHc and temperature work together to reduce stability because, as temperature increases, RHc shifts to a lower water activity. Eventually, the temperature may rise enough that the RHc falls below the powder's current water activity, triggering a glass transition [10]. While controlling storage conditions is the most effective way to prevent caking, it is not always feasible. As an alternative, packaging with a strong moisture barrier can slow water activity changes caused by high ambient humidity. For optimal performance, powders should be processed to a water activity sufficiently below the RHc for the most extreme expected storage temperature. Then, packaging should be selected to delay water activity changes under high humidity conditions. Tools are available to help identify suitable packaging by calculating the water vapor transmission rate required to maintain stability.

Critical Water Activity and chemical Stability

Unwanted chemical reactions in powders can lead to the development of off colors, odors and flavors. For powders in the glassy state, chemical reaction rates will be at a minimum and caking remains the most likely mode of failure, but reactions can still occur and potentially reduce the shelf life. That said, if the water activity increases above the RHc and a glass transition occurs, as with caking, the susceptibility to chemical degradation increases significantly.

The primary chemical reactions responsible for the quality loss in powders are Maillard browning, lipid oxidation, enzymatic, and hydrolysis reactions. The products of these reactions, when the reaction progresses sufficiently, affect the taste, appearance, and nutritional quality. Water activity influences reaction rates by reducing activation energy, increasing mobility, and increasing the rate constant. Consequently, reaction rates are better correlated to water activity than moisture content. In general, as water activity increases so do reaction rates, but specific correlations depend on the type of product and the reaction (Figure 3). Most reactions will reach a maximum in the range of 0.70-0.80 a_w due to dilution at high water activities, but lipid oxidation also increases at low water activity.

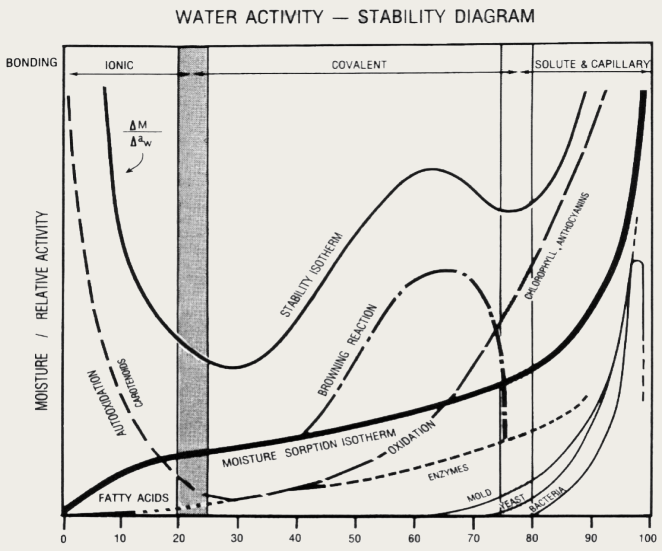
These reactions are often complex with multiple possible pathways and requires the presence of specific reactants or enzymes to occur. While lower water activity often reduces the reaction rate to provide sufficient stability, it may also be necessary to restrict the reactants, such as oxygen for rancidity or reducing sugars for Maillard Browning. High sugar powders are susceptible to browning over time or if exposed to high water activity and milk powders, due to the presence of milkfat, are susceptible to lipid oxidation.

To aid in determining the ideal water activity for slowing down chemical degradation, the reaction rate can be predicted using shelf-life models. To be effective, these models need to account for the effect of water activity and temperature. The only fundamental shelf-life model that includes both water activity and temperature is hygrothermal time (15). It is derived from a form of the Eyring (16) equation for rate change and Gibbs equation for free energy and is given by

$$r = r_0 \exp\left(Ba_w - \frac{E_a}{RT} \right) \quad [1]$$

where T is the termperature (K), R is the gas constant (J mol^{-1} K^{-1}), E_a is the activation energy (J mol^{-1}), B is the molecular volume ratio, a_w is the water activity, and r_0 is the rate at the standard state. In practice, the values for B, E_a/R and r_0 will be unique to each situation and are derived empirically through least squares iteration. Once the constants are known, any temperature and water activity can be used with the hygrothermal time model to determine the rate of change at those conditions and hence the shelf life for a particular product, as it relates to that change. This model can then be used to establish the critical water activity where chemical degradation is at a minimum, thereby maximizing shelf life.

Figure 3. Water activity stability map showing the typically response of modes f failure to increasing water activity (by permission Ted Labuza).



Critical Water Activity and low Moisture Ingredient Pasteurization

Recent high-profile recalls involving ingredients with low water activity (<0.70 aw) have highlighted the microbial contamination risks associated with low-moisture ingredients, including powders. While low water activity prevents the growth of pathogenic bacteria and other microorganisms [17], it is not a lethality step and does not eliminate existing microbial loads. Microorganisms present in powders remain dormant and will not proliferate, but if present in sufficient numbers, they can still cause infection when incorporated into a recipe. Furthermore, many pathogenic bacteria can survive for years at low water activity. Although dormant organisms may not pose an immediate risk when consumed directly, they can resume growth when introduced into high-moisture formulations where water activity supports microbial proliferation, potentially leading to foodborne illness.

In response to the recognized risk of microbial contamination in low-moisture ingredients, the Food Safety Modernization Act (FSMA) guidelines for Hazard Analysis and Risk-Based Preventive Control (HARPC) programs recommend incorporating pasteurization steps for these ingredients, along with monitoring activities to verify lethality. This means that powder processing will increasingly require some form of lethality treatment. While heat treatment is the most common approach, it poses challenges for powders due to their low water activity. The time required to achieve lethality at a given temperature – known as the D-value – increases

as water activity decreases [18]. Consequently, the time and temperature needed for effective lethality depend on the powder's water activity, making it essential to identify a critical water activity where lethality efficiency is maximized. Because heat treatments are difficult to apply to powders, FSMA's *Hazard Analysis and Risk-Based Preventive Controls for Human Food: Guidance for Industry* document (Section 4.3 Process Controls) provides alternative suggestions for achieving microbial lethality.

Summary

Deconstructing the quality and stability of powders can be complex and frustrating without a way to anticipate variability. A practical approach is to identify the critical water activity that minimizes the risk of the most likely failure modes and then monitor changes in water activity over time. In summary, establishing an optimal water activity specification, processing to meet that specification, and verifying compliance through frequent water activity testing will ensure maximum powder stability. Ultimately, water activity is the key to understanding and controlling changes in powder stability. To learn more about applying the tools and models discussed in this white paper to your specific application, please contact Dr. Brady Carter for additional information.

The Author

Dr. Brady Carter is a Senior Research Scientist with Carter Scientific Solutions. He specializes in Water Activity and Moisture Sorption applications. Dr. Carter earned his Ph.D. and M.S Degree in Food Engineering and Crop Science from Washington State University and a B.A. Degree in Botany from Weber State University. He has 20 years of experience in research and development and prior to starting his own company, he held positions at Decagon Devices and Washington State University. Dr. Carter currently provides contract scientific support to Novasina AG and Netuec Group. He has been the instructor for water activity seminars in over 23 different countries and has provided on-site water activity training for companies around the world. He has authored over 20 white papers on water activity, moisture sorption isotherms, and complete moisture analysis. He has participated in hundreds of extension presentations andhas given talks at numerous scientific conferences. He developed the shelflife simplified paradigm and hygrothermal time shelf life model.

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