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APPLICATION NOTE

SHELF STABLE MEAT: A LEGACY OF WATER ACTIVITY CONTROL

Meat preservation has been used by civilizations for thousands of years to provide a longterm protein source that won't spoil during storage or travel. The preservation of meat through curing dates to antiquity, often discovered through accidental mishandling of meat. The most common methods used to cure meat include salting, brining, smoking, and drying. All these preservation methods rely on the control of water activity. In fact, the legacy of Shelf Stable Meats (SSM) and water activity go hand in hand. Ancient civilizations did not have an exhaustive understanding of water activity or why these preservation steps worked, but instead discovered them through trial and error. In so doing, they discovered the fundamental truth that still alludes many processors today, that its water activity control, not moisture content control that makes cured meats shelf stable.

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THEORY OF WATER ACTIVITY

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.

Water activity is often referred to as the 'free water', but since 'free' is not scientifically defined and is interpreted differently depending on the context, this is incorrect. Free water gives the connotation of a quantitative measurement, while water activity is a qualitative measurement of the relative chemical potential energy. 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 then, the less the water in the system behaves like pure water.

For SSM, water activity is measured by equilibrating the liquid phase water in the sample with the vapor phase water in the headspace of a closed chamber and measuring the Equilibrium Relative Humidity (ERH) in the headspace using a sensor.

The relative humidity can be determined using a resistive electrolytic sensor, a chilled mirror sensor, or a capacitive hyroscopic polymer sensor.

Instruments from Novasina, like the Labmaster NEO, utilize an electrolytic sensor to determine the ERH inside a sealed chamber containing the sample. Changes in ERH are tracked by changes in the electrical resistance of the electrolyte sensor. The advantage of this approach is that it is very stable and resistant to inaccurate readings due to contamination, a particular weakness of the chilled mirror sensor. The resistive electrolytic sensor can achieve the highest level of accuracy and precision with no maintenance and infrequent calibration.

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, 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.

For shelf stable meat, moisture content provides a standard of identity and an expected mouthfeel but does not determine if the product is microbially safe. Water activity and moisture content are related through the moisture sorption isotherm. Table 1 shows that different SSM can have similar water activities, but very different moisture contents. Obviously, the moisture content associated with a safe water activity will be different for each product and as will be demonstrated in the next

Product	Moisture Content (% d.b.)	Water Activity
Beef Steak Strips	37.45	0.8664
Original Beef Jerky	40.66	0.8655
Pepperoni Sticks	25.89	0.8344
Spicy Beef Jerky	26.04	0.8309
Terakyi Beef Jerky	25.59	0.7899
Bacon Jerky	18.58	0.7542

Table 1. Water activity survey of common types of SSM

WATER ACTIVITY AND MICROBIAL GROWTH

Each microorganism has an ideal water activity inside their cell and their ability to reproduce and grow depends on maintaining that water activity.

When a microorganism encounters an environment where the water activity is lower than their internal water activity, they experience osmotic stress and begin to lose water to the environment since water moves from high water activity (energy) to low water activity (1). This loss of water reduces turgor pressure and retards normal metabolic activity. To continue reproducing, the organism must lower its internal water activity below that of the environment. It tries to achieve this by concentrating solutes internally.

The ability to reduce its internal water activity using these strategies is unique to each organism. Consequently, each microorganism has a unique limiting water activity below which they cannot grow (2, 3). Notice that an organism's ability to reproduce and grow does not depend on how much water is in its environment (moisture content or free water), only on the energy of the water (water activity) and whether it can access that water for growth.

A list of the water activity lower limits for growth for common spoilage organisms can be found in Table 2. These growth limits indicate that all pathogenic bacteria stop growing at water activities less than 0.87 while the growth of common spoilage yeasts and molds stops at 0.70 aw, which is known as the practical limit. Only xerophilic and osmophylic organisms can grow below 0.70 aw and all microbial growth stops at water activities less than 0.60.

Other intrinsic factors such as pH impact microbial growth as well. For an SSM product to be considered non-potentially hazardous, it's water activity must be less than 0.86 aw or its pH less than 4.2 to ensure that no pathogenic bacteria will be able to grow on the product as it sits on the shelf. Water activity and pH also work synergistically to provide microbial protection at values higher than those required when only one control factor is considered (4).

SSM with a water activity higher than 0.70 aw but less than 0.86 aw is considered shelf stable but will still support the growth of mold and yeast. Shelf stable meats in this range are not considered unsafe because the growth of molds and yeasts does not cause foodborne illness. However, the growth of non-pathogenic organisms does typically render the product undesirable to a consumer and is considered to have ended the shelf life of the product. Consequently, the water activity must be reduced to below 0.70 aw or other interventions such as a preservative system or vacuum packing must be used to prevent mold growth.

Microorganism	a_w limit	Microorganism	a_w limit
Clostridium botulinum E	0.97	Penicillum expansum	0.83
Pseudomonas fluorescens	0.97	Penicillum islandicum	0.83
Escherichia coli	0.95	Debarymoces hansenii	0.83
Clostridium perfringens	0.95	Aspergillus fumigatus	0.82
Salmonella spp.	0.95	Penicillum cyclopium	0.81
Clostridium botulinum A B	0.94	Saccharomyces bailii	0.8
Vibrio parahaemoliticus	0.94	Penicillum martensii	0.79
Bacillus cereus	0.93	Aspergillus niger	0.77
Rhizopus nigricans	0.93	Aspergillus ochraceous	0.77
Listeria monocytogenes	0.92	Aspergillus restrictus	0.75
Bacillus subtilis	0.91	Aspergillus candidus	0.75
Staphylococcus aureus (anaerobic)	0.9	Eurotium chevalieri	0.71
Saccharomyces cerevisiae	0.9	Eurotium amstelodami	0.7
Candida	0.88	Zygosaccharomyces rouxii	0.62
Staphylococcus aureus (aerobic)	0.86	Monascus bisporus	0.61

Table 2. Water activity lower limits for growth for common spoilage organisms

GOVERNMENTAL GUIDANCES AND REGULATIONS

Due to its risk of being microbially unsafe, SSM are regulated by governmental agencies. In the US, the product of SSM is under the jurisdiction of the USDA Food Safety and Inspection Service (FSIS). The Principles of Preservation of Shelf-Stable Dried Meat Products (USDA 2011) outlines the critical role of water activity control in the safety of SSM. It also warns that moisture-protein ratio, a traditional measurement for SSM, does not provide any indication of microbial safety and only provides a standard of identity. FSIS requires producers to establish a Hazard Analysis and Critical Control Points (HACCP) plan for their process that will identify how they will control their highest risk hazards. The use of water activity as a critical control point for SSM is outlined in Generic HACCP Model 10 and 15 available from the FSIS website (https://www.fsis.usda.gov/wps/portal/ fsis/home).

CHEMICAL STABILITY

The water activity of intermediate moisture and dry SSM will typically be less than 0.70 aw, indicating that microbial growth is not likely to occur. However, SSM in this range do not have unlimited shelf life. So what other modes of failure are likely to occur to end shelf life. For products in the 0.40-0.70 aw range, chemical degradation is a strong candidate because reactions rates are at a maximum. Due to their high lipid content, the chemical reaction most likely to cause problems for SSM is lipid oxidation, which leads to the off odors and flavors associated with rancidity. Water activity influences lipid oxidation reaction rates by reducing activation energy, increasing mobility, and increasing the rate constant. In general, as water activity increases so do reaction rates, but lipid oxidation is unique in that the reaction rate also increases at very low water activity (5). Since SSM need to be at high enough water activities to keep a moist mouth feel, it is not possible to slow the rate of oxidation by extensively lowering water activity. Instead, other interventions are typically warranted such as the inclusion of oxygen absorbers or modified atmosphere packaging, which has the additional advantage of slowing mold growth.

When changes in flavor or odor are the mode of failure for SSM, the time required for the oxidation of the product to have progressed to the point of unacceptability at a given water activity and temperature will be the product shelf life. The only fundamental shelf life model that includes both water activity and temperature is hygrothermal time (6). It is derived from a form of the Eyring (7) equation for rate change and Gibbs equation for free energy and is given by

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

Where T is the termperature (K), R is the gas constant (J mol-1 K-1), Ea is the activation energy (J mol-1), B is the molecular volume ratio, aw is the water activity, and r0 is the rate at the standard state. In practice, the values for B, Ea/R and r0 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 rate of oxidation at those conditions and hence the shelf life that the product will remain acceptable to the consumer. Your water activity application scientist can work with you to develop a tool that can predict shelf

CHEMICAL STABILITY

A particular mouthfeel and texture are associated with each variety of SSM and are undesirable to the consumer when they do not meet these desired physical characteristics. Products that are expected to have a stiffer texture need to be at a lower water activity while those that are expected to be soft need to be at a higher water activity. If either type is processed to the wrong water activity, they will not have the desired characteristics and will be rejected by the consumer. If SSM are processed and maintained at the correct water activity, texture is not likely to be the mode of failure that ends shelf life. Instead, for stiffer low water activity SSM, the likely mode of failure will be flavor related and for soft SSM, microbial spoilage is the likely mode of failure, as outlined above.

However, one scenario where texture changes could be the mode of failure for SSM is if the water activity changes due to exposure to ambient humdities that are lower or higher than their ideal water activity. As described in the theory section earlier, water activity is also the equilibrium relative humidity and consequently, is impacted by the storage humidity. If a soft SSM with a water activity of 0.80 aw is exposed to a storage relative humidity of 60%, the product will lose moisture to the environment until its water activity is equilibrated 0.60 aw. This process of course takes time, but if not protected, the water activity of the product will decrease outside the ideal range and become stiff and hard. Placing the product in moisture barrier packaging will slow down the change in water activity. The rate of water activity change inside a package of known moisture permeability can be modeled using Fickian diffusion, as can the required package permeability to achieve a desired shelf life (8). Your water activity application scientist can help you setup a tool to model water activity changes in package.

WATER ACTIVITY AND DEGRADATION OF ACTIVE INGREDIENTS

The water activity of solid dosage pharmaceuticals will typically be less than 0.70 aw, indicating that microbial growth is not likely to occur. However, products in this range do not have an unlimited shelf life. For these products in the 0.40–0.70 aw range, chemical degradation of the API is a strong candidate for the mode of failure because reaction rates are at a maximum. In general, as water activity increases so do reaction rates (8). The most common reaction that can result in the degradation of APIs is hydrolysis although lipid oxidation (rancidity) and enzymatic reactions may also play a role in the loss of active ingredients. The most effective way to prevent these reactions from resulting in significant loss of the API is to process them to a low water activity where reactions will be at a minimum and then choose the appropriate excipient that will do the best job of maintaining that water activity.

TRACKING MOISTURE CHANGE WITH WATER ACTIVITY

As shown by the moisture sorption isotherm, an increase in water activity is accompanied by a subsequent increase in moisture; however, the relationship is non-linear and unique to each product. An increase in the slope of the isotherm indicates an increase in hygroscopicity, which will limit the change in the water activity as moisture is absorbed. This is often a desirable characteristic in excipients because it allows the product to absorb moisture while still maintaining the water activity of the API at levels that limit the rate of degradative reactions as shown in the previous section.

Another way that the water activity of an API can increase to unsafe levels is through moisture migration in multiple component pharmaceuticals such as capsules. If the components are at different water activities, then water will move between the components regardless of their moisture content. Water moves from high water activity (energy) to low water activity (9). Moisture will continue to move between the components until an equilibrium water activity is achieved, which is dictated by the moisture sorption isotherms of each component and is not the midpoint between the initial water activities (Figure 4). If the water activity of the API increases, it could possibly be at high enough levels to speed up degradation. To avoid this problem, the components must be designed to have the same water activity.

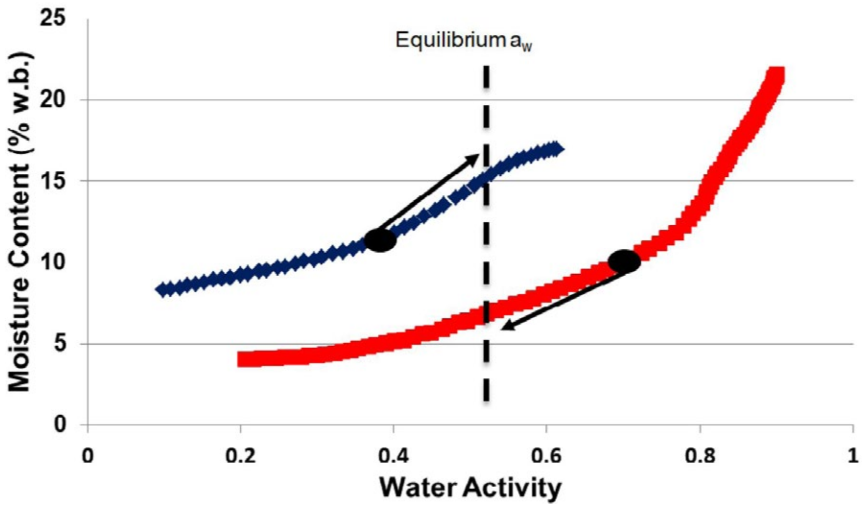

Figure 4. Moisture sorption isotherms for a product with two components at different initial water activities. The black dots indicate the initial water activity while the arrows indicate the direction of water movement for each component and the accompanying change in moisture content. The dotted vertical line indicates the water activity where the components will come into equilibrium and moisture movement will stop. The points where the isotherm curves cross the dotted vertical line indicate the moisture content of each component at the final water activity (9).

THE MOST IMPORTANT SPECIFICATIONTIVITY

For SSM, setting an ideal water activity specification is a critical step in formulating for safety and quality. The specification can be set to avoid microbial proliferation, minimize chemical reactions, and provide the desired textural properties. The ideal value can be determined based on the most likely mode of failure, such as texture change for low water activity SSM, chemical degradation for semimoist SSM, and microbial growth for moist SSM. Once the ideal water activity is determined, a combination of processing and formulation can be used to achieve that ideal water activity.

The most common processing steps used to produce SSM that meet their required water activity specification is to remove moisture through drying. However, SSM are typically sold on a weight basis, so removing water also reduces the weight of the product and results in lost revenue. Formulation adjustment can maximize the amount of moisture in SSM at the water activity specification through the addition of humectants such as sugar, salt, and glycerin, which lower water activity without the removal of moisture. The amount of humectant needed to reduce water activity to a desired level can be predicted using the Norrish and Ross equations and water activity application scientists can help setup a simple predictive tool to assist in formulation.

In addition, the careful monitoring of the water activity of SSM during production can reduce energy inputs and prevent undesirable weight loss due to processing to lower than ideal water activities. This will reduce energy waste while maximizing revenue. In summary, establishing an ideal water activity specification, formulating to meet that specification, and monitoring production with frequent water activity testing will ensure a safe, quality product with an optimal shelf life and maximum revenue. In short, the success of SSM throughout history is directly tied to a legacy of water activity control.

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