Characterizing Moisture Relations in Pet Food Formulations

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Introduction

Managing water is critical to ensuring the safety and stability of pet food. Traditionally, formulators have tried to control the moisture content (total amount of water) in the recipe, but while moisture content provides valuable information about pet food quality, it is only one part of a complete moisture analysis. Water activity is another important moisture measurement that provides essential information about the energy or availability of water in a pet food. Understanding the relationship between these two important moisture measurements is the key to formulating pet food with optimal safety and quality attributes.

Moisture Content

Moisture content is the total amount of water in a product and is determined using many different techniques such as Karl Fischer, loss on drying, microwave, and NIR. It is a common measurement in most labs and provides information about nutritional labeling, concentration of solids, product texture, and product weight.

Water Activity

Water activity measures the energy status of the water in a product. It is equal to the relative humidity of the air in equilibrium with a sample in a sealed chamber. It ranges from 0 for a perfectly dry sample to 1 for pure water. Water activity measurements provide valuable information about pet food safety and quality because they indicate susceptibility to microbial spoilage, chemical degradation, texture changes, and inhibited flow properties.

Moisture Sorption Isotherms

The relationship between moisture content and water activity is complex. An increase in moisture content is usually accompanied by an increase in water activity but the correspondence is not linear. This relationship between water activity and moisture content at a given temperature is called the moisture sorption isotherm (Figure 1). The nature of this relationship depends on the interaction between water and other ingredients and provides valuable insights into product characteristics. The amount of water vapor that can be absorbed by a product depends on its chemical composition, physical-chemical state, and physical structure. The isotherm shape is unique to each product type due to differences in capillary, surface, and colligative effects. For most foods, the isotherm is sigmoidal in shape, although foods that contain large amounts of sugar or small soluble molecules have a J-type isotherm curve.

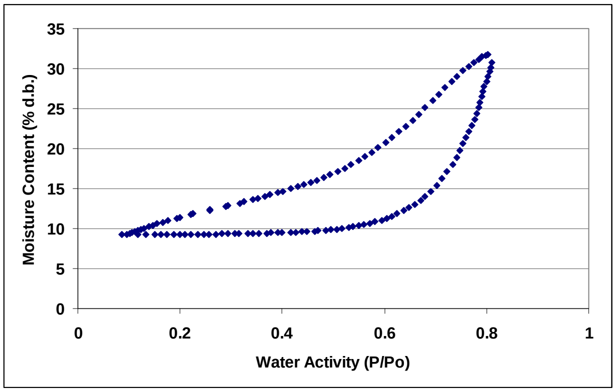

Figure 1. Typical moisture sorption isotherm for dry dog food at 25° C.

Measuring Sorption Isotherms

Constructing a moisture sorption isotherm involves collecting a range of water activities and corresponding moisture contents for a particular sample. One of three isotherm methods is typically used. For most sample types, the three methods provide similar results (Figure 2). However, for samples that experience a phase change during sorption measurement or have slow diffusion properties, the results may vary.

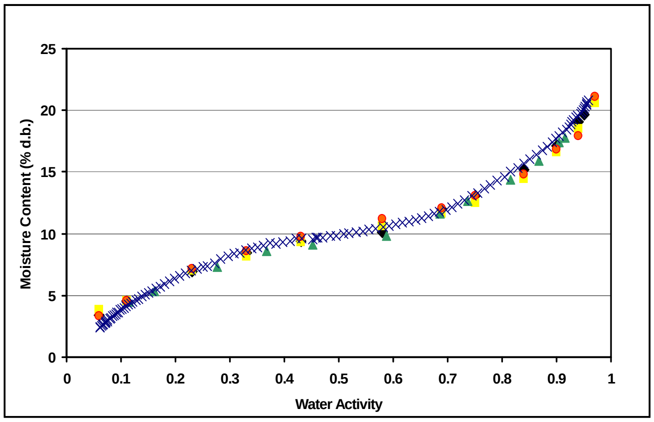

Figure 2. Corn starch working isotherms when using desiccators with saturated salts (■), Proximity Equilibration Cell (●), DVS instrument 1 (♦), DVS instrument 2 (▲), and DDI (×) (DDI data from Decagon Devices in-house testing, data for all other methods taken from (Xin Yu, 2007).

Traditional Desiccator Method

Traditional isotherm methods equilibrate the sample to known water activities and then measure the equilibrium moisture content of the sample. Most methods control water activity levels using saturated salt slurries, acid solutions, glycerol solutions, or mechanical humidifiers. This is most easily done by placing the sample in a sealed chamber over a saturated salt slurry in excess. Different water activity levels are achieved by using different salts. Different concentrations of glycerol or acid solutions can also be used. Another method controls water activity by adjusting a mixture of wet and dry air while monitoring the water activity with a sensor. Equilibrium moisture contents are then determined at each water activity level. Equilibrium is reached when the weight of the sample stops changing. This equilibration process can take weeks. The temperature must be tightly controlled during equilibrium and steps must be taken to prevent microbial contamination at water activities higher than 0.60.

Dynamic Vapor Sorption

Some instruments are programmed to automatically change the water activity in a dynamic stepwise progression. These instruments, often referred to as controlled atmosphere balances, utilize the Dynamic Vapor Sorption (DVS) method. The instrument holds the sample at one water activity level until the sample weight stops changing and then dynamically moves to the next water activity. Instrument temperature is held constant. Humidity levels are usually controlled by mixing dry and wet air.

Automatic isotherm generators are much faster and less labor intensive than traditional desiccator methods. They also make it possible to conduct sorption kinetic studies. However, like traditional dessicator methods, DVS instruments equilibrate the sample to a known water activity level. Since true equilibration between the sample and the vapor source requires an infinitely long period of time, they measure apparent equilibrium at the point when the change in sample weight is negligibly small. Increasing the tolerable weight change can speed up the isotherm process but calls into question the validity of the water activity values.

Dynamic Dew Point Isotherm Method

The Dynamic Dewpoint Isotherm (DDI) method directly measures water activity while gravimetrically tracking weight, so there is no dependence on equilibration to known water activity levels to determine water activity. Adsorption occurs as saturated wet air is passed over the sample. Desorption is accomplished as desiccated air is passed over the sample. After roughly a 0.015 change in water activity, airflow is stopped and a snapshot of the sorption process is taken by directly measuring the water activity and the weight. Since the sample does not have to wait for equilibration to a known water activity, this method is faster without sacrificing accuracy. It is also able to produce an unmatched number of data points. Only water and desiccant are needed to run the isotherm.

Uses for Moisture Sorption Isotherms

Moisture sorption isotherms can help pet food formulators achieve specific qualities and attributes (Bell and Labuza, 2000).

Drying And Wetting Curve

For any producer who dries or wets a pet food product, the sorption isotherm serves as a drying and wetting curve and provides information about the moisture content of a product when dried or wetted to a specific water activity. It can be used to assist in process control by determining drying rates and optimal endpoints.

The isotherm will also show whether a product exhibits hysteresis and what impact that will have on water activity after drying to a given moisture content. Hysteresis describes a condition when the moisture content at a given water activity depends on the wetting or drying history of the sample. In almost all cases, if hysteresis occurs, the moisture content will be higher at a given water activity for desorption than for adsorption. The cause of hysteresis remains unclear, but the practical implications are important. In a product that exhibits hysteresis, a moisture content that is safe when drying a sample (because it corresponds to a safe water activity of 0.6 a_w or below) may not be safe when wetting the sample (because it corresponds to an unsafe water activity of above 0.70 a_w) (Figure 3).

A working isotherm represents the drying and wetting characteristics of a product from its native state and is a scanning curve that connects the adsorption and desorption curves. It most correctly describes the changes experienced by a product when it is wetted or dried from its native state.

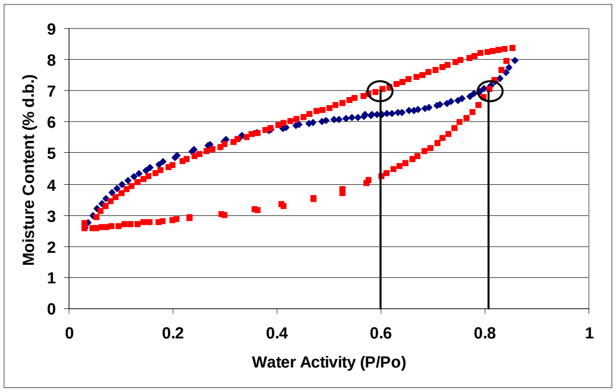

Figure 3. A working isotherm (♦) superimposed over a full isotherm curve (■) indicating that the working isotherm scans between the adsorption and desorption curves of the full isotherm. Also shown are the different water activities associated with 7% moisture depending on if the product is wetted or dried.

Moisture Content Prediction

An additional function of the isotherm is moisture content prediction. Since both water activity and moisture content are needed in certain situations, it would be advantageous to measure both simultaneously. In addition, moisture content measurements can be inaccurate, time-consuming and require expensive instrumentation. As an alternative to moisture content measurement methods, the sorption isotherm can be used to determine moisture content based on water activity, usually with better repeatability than actually running a moisture content analysis and in much less time. This requires determination of a product's isotherm, characterization of the isotherm by a model or equation, and then loading that model into a specialized water activity instrument.

Temperature Abuse Modeling

Isotherms can be used to determine the effect of temperature on a product's water activity and moisture content. A product with a safe water activity at room temperature may become unsafe under temperature abuse conditions. Isotherms conducted at several different temperatures will show the temperature at which a product in a sealed package (at constant moisture content) will be at unstable water activity levels. For example, soft dog bits at 25% moisture content will have a water activity (0.60) at 15°C that will not support mold growth; however, at 40°C, the water activity will be high enough (0.70) for mold to grow (Figure 4).

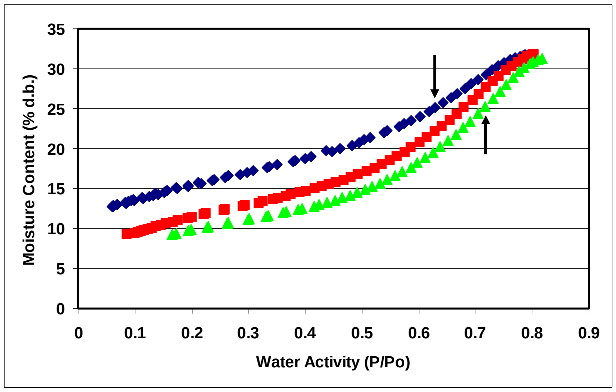

Figure 4. Moisture sorption isotherms of soft dog bits conducted at 15°C (♦), 25°C (■), and 40°C (▲).

Formulating For Water Activity Control

Isotherms can be very valuable for formulation and product development. By comparing the isotherms of different formulations, it is possible to determine if a product can be adjusted to allow higher moisture content at a given water activity or a lower water activity at a given moisture content. The result can be a moister product that is still shelf stable.

Likewise, two ingredients at the same moisture content may not be compatible when mixed together. If two materials of differing water activities but the same water content are mixed together, the water will adjust between the materials until an equilibrium water activity is obtained. Thus, to prevent moisture migration in a multi-component product, one should match the water activity of the two components. A great example of this type of product is dog food with hard kibbles and soft bits. The kibbles and bits have very different moisture contents, and hence very different textures, but the same water activity (Figure 5). This provides a product with variety that is still shelf stable.

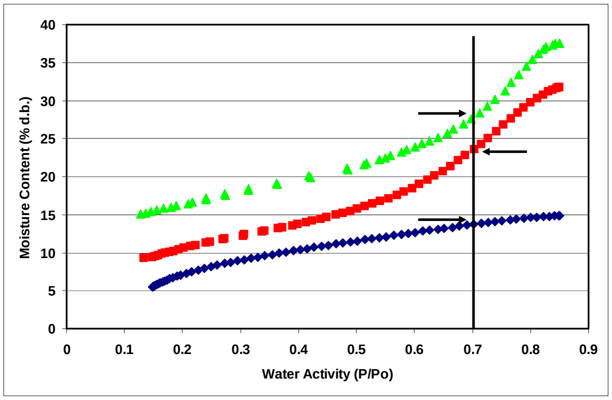

Figure 5. Moisture sorption isotherms for hard kibbles (♦), one type of soft bits (■), and another type of soft bits (▲). The line at 0.70 a_W represents the natural water activity of the product.

Dry Ingredient Mixing

For those producing multi-component products, it is possible using the isotherms of the two components to determine what the final water activity of the mixture will be without actually making the product. The equation for this process is:

$$a_{eq} = \frac{\sum(a_i b_i W_{si})}{\sum(b_i W_{si})}$$

where a_{eq} is the initial a_W of each ingredient (i), b_i is the absolute value of the moisture isotherm slope of each ingredient, and $W_{s,i}$ is the weight of dry solids of each ingredient (Bell and Labuza, 2000).

Shelf Life Determination

Sorption isotherms are valuable for shelf life prediction. An isotherm can be used to determine a pet food's monolayer moisture content and the corresponding water activity, which represents its most stable state. The monolayer value is determined by modeling isotherm data using the GAB or BET equations. It is usually around 0.2-0.3 a_W. Increasing water activity 0.1 above the monolayer value will decrease shelf life by two to three times.

A product's isotherm can also be used to determine package requirements depending on the product's sensitivity to moisture and the conditions it may be exposed to.

Phase Changes And Critical Water Activities

The shape of the isotherm can provide information about the level of amorphous to crystalline material in a product. Sharp inflection points in the isotherm indicate phase transitions (equivalent to a glass transition) and indicate critical water activities for maintaining texture properties and preventing caking and clumping (Figure 6). If the water activity of a product moves above the critical water activity for phase transition, the stability of the product will decrease as time dependent processes such as caking and crystallization speed up significantly.

Increasing temperature will lower that critical water activity point and can also result in loss of stability with no change in water activity. Determining phase transitions using isotherms is like determining glass transitions with differential scanning calorimetry, except instead of holding water activity constant and scanning temperature, the isotherm analysis holds temperature constant and scans water activity.

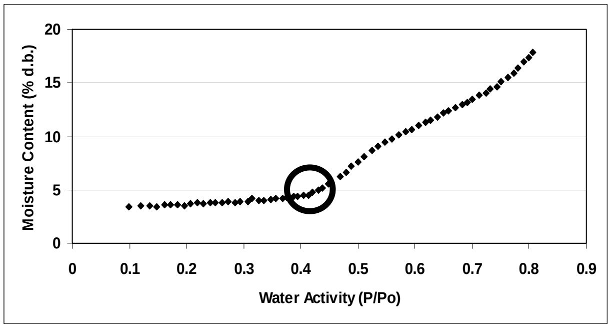

Figure 6. Moisture sorption isotherm for spray dried milk powder showing a phase change occurring at a critical water activity of 0.43.

Conclusion

Moisture sorption isotherms are a blueprint for moisture relations in a pet food product. They provide valuable information concerning product safety and quality and can be an effective tool for the pet food formulator.

Reference:

Bell,L.N., and T.P.Labuza. 2000. Moisture sorption: practical aspects of isotherm measurement and use. American Association of Cereal Chemists, St. Paul, MN.

Xin Yu. 2007. Investigation of moisture sorption properties of food materials using saturated salt solution and humidity generating techniques. Ph.D. thesis, University of Illinois at Urbana-Champaign.

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