

Water Activity

Definition:

Water activity is a measure of how efficiently the water present can take part in a chemical (physical) reaction. If half the water is so tightly bound to a protein molecule that it could not take part in a hydrolysis reaction the overall water activity would be reduced. Water activity (a_w) is defined as

$$a_w = p/p_o$$

where p and p_o are the partial pressures of water above the food and a pure solution under identical conditions respectively. The tightly bound water has no tendency to escape from a food as a vapor and therefore exerts no partial pressure and has an effective water activity of zero. Water activity is clearly a function of composition but is also a function of temperature. The approximate water activities of some common foods are given below:

1-0.95	Fresh fruit, meat, milk
0.95-0.9	Cheese
0.9-0.85	Margarine,
0.85-0.8	Salted meats
0.8-0.75	Jam
0.75-0.65	Nuts
0.65-0.60	Honey
0.5	Pasta
0.3	Cookies
0.2	Dried veg., crackers

Free water versus bound water

Water activity is sometimes defined as "free", "unbound", or "available water" in a system. Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in the sample. A portion of the total water content present in a product is strongly bound to specific sites on the chemicals that comprise the product. These sites may include the hydroxyl groups of polysaccharides, the carbonyl and amino groups of proteins, and other polar sites. Hydrogen bonds, ion-dipole bonds, and other strong chemical bonds tightly bound water. Some water is bound less tightly, but is still not available (as a solvent for water-soluble food components). Many preservation processes attempt to eliminate spoilage by lowering the availability of water to microorganisms. Reducing the amount of free--or unbound--water also minimizes other undesirable chemical changes that occur during storage. The processes used to reduce the amount of free water in consumer products include techniques like concentration, dehydration and freeze drying. Freezing is another common approach to controlling spoilage. Water in frozen foods is in the form of ice crystals and therefore unavailable to microorganisms and for reactions with food components.

Zones of moisture isotherm

Zone 3: Bulk water, effectively a dilute solution, easily removed with minimal impact on food stability

Zone 2: Loosely bound water, possibly additional layers bound to the Zone 1 water

Zone 1: tightly bound water, exceptionally hard to remove (i.e., needs very intense drying conditions).

Water Activity and Quality

Water activity is a critical factor that determines shelf life (Fig. 8-10). Most bacteria, for example, do not grow at water activities below 0.91, including pathogens such as *Clostridium botulinum*. Below 0.80 most molds cannot be grown and below 0.60 no microbiological growth is possible. However, there remain a number of food spoilage microbes that can grow within the range 0.8 - 0.6. The risk of food poisoning must be considered in low acid foods ($\text{pH} > 4.5$) with a water activity greater than a_w 0.86.

Staphylococcus aureus, a common food poisoning organism, can grow down to this relatively low water activity level. Foods that may support the growth of this bacterium include cheese and fermented sausages stored above correct refrigeration temperatures.

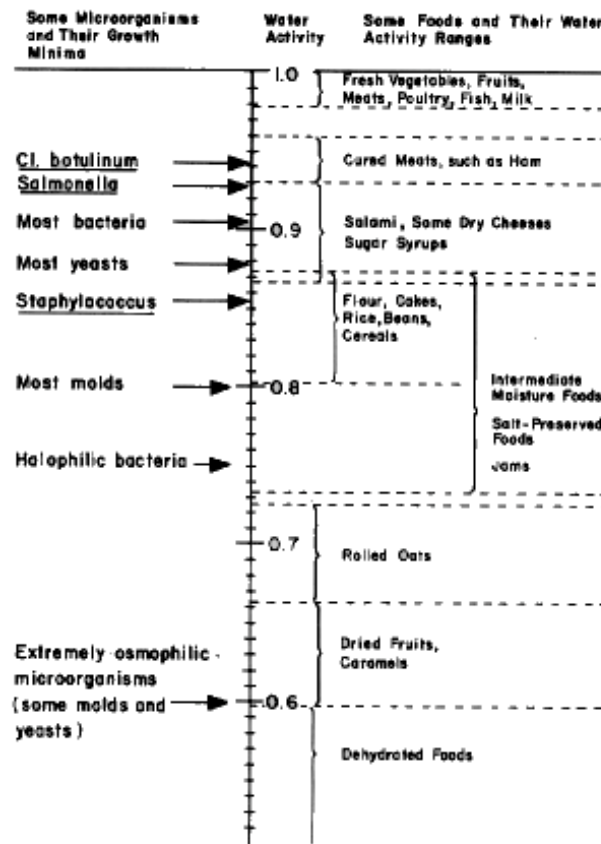


FIG. 8-10. Schematic representation of water activity minima for growth of microorganisms and of typical activity ranges for some foods.

By measuring water activity, it is possible to predict which microorganisms will and will not be potential sources of spoilage. In addition to influencing microbial spoilage, water activity can play a significant role in determining the activity of enzymes and vitamins in foods and can have a major impact their color, taste, and aroma. It can also significantly impact the potency and consistency of pharmaceuticals.

With the exception of lipid oxidation, all of the rates decrease at least 100 fold as the zone 2 water is removed and effectively stop at the monolayer value. This is because whatever the reagents responsible for a reaction, they always need a solvent to move around in order to encounter each other and react. As the solvent is removed the rate decreases and, as monolayer water is not adequately liquid-like to act as a solvent, the reaction stops. Several rates may slightly decrease at high water activities due to dilution of the reagents.

Sorption Isotherms

The relationship between water content and water activity is complex. An increase in a_w is almost always accompanied by an increase in the water content, but in a nonlinear trend. This relationship between water activity and moisture content at a given temperature is called the moisture sorption isotherm. These curves are determined experimentally. Moisture sorption isotherms are sigmoidal in shape for most foods, and a moisture sorption isotherm prepared by adsorption (starting from the dry state) will not necessarily be the same as an isotherm prepared by desorption (starting from the wet state). This phenomenon of different a_w vs moisture values by the two methods is called moisture sorption hysteresis and is exhibited by many foods. Hysteresis represents the difference in a_w between the absorption and desorption isotherms (Figure 8-6).

A hydrated food can be dehydrated to remove moisture until the desired a_w is reached (desorption) or completely dehydrated and then re-hydrated to the desired a_w (absorption). A food is more stable against microbial spoilage when its a_w is adjusted by absorption rather than by desorption.

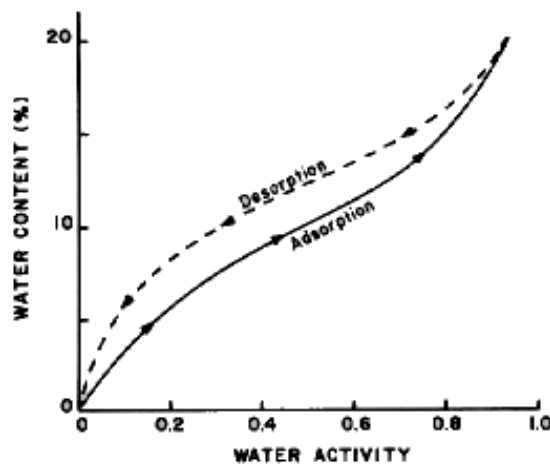


FIG. 8-6. Water sorption hysteresis.

Absorption and desorption isotherms for a food system at a given temperature are plotted using a_w along the horizontal axis and the % water along the vertical. When plotted, the phenomenon of hysteresis can be observed (Fig. 8-6).

Overview of the Laboratory Exercise

The objective of this lab exercise is to collect the raw data necessary to construct moisture sorption and desorption isotherms for a food product and to estimate the initial water activity of a food product if a water activity meter or hydrometer is not available. To collect the necessary data you will also have to perform oven drying techniques on the food sample to assess the initial moisture content of the product. In addition, we will use a water activity meter to directly measure the water activity of the product. You will compare and contrast the data for each product and each method used to determine a_w .

Saturated salt solutions will be used to create a specific relative humidity within a closed environment. Food samples will be placed in these environments and allowed to equilibrate.

A totally dehydrated food (crackers equilibrated over drierite) and an intermediate moisture food (crackers with increased moisture equilibrated over K_2SO_4) will be studied in five different relative humidity environments using five different saturated salt solutions. Since equilibrium relative humidity (ERH) and a_w are related, saturated salt solutions will be used to determine the ERH of the five “environments” we will study. The foods with two different water activities will be placed in these environments and changes in their moisture content will be followed.

Outline of Sorption Isotherm Exercise

The initial moisture content of crackers will be measured using an oven drying technique. Also, the water activity of the food product will be measured using a water activity meter. Prepare tables in your lab notebooks to record ALL data you will need to complete the lab report both from your own lab group and other lab groups.

Reagents	Equipment
dried crackers (decreased moisture content _ equilibrium with drierite)*	10 mL graduate cylinder
“moist” crackers (increased moisture content _ equilibrium with K_2SO_4)**	desicators
crackers (original moisture content)	microwave oven
potassium acetate	Vacuum oven
$Mg(NO_3)_2 \cdot 6H_2O$	small plastic cups
NaCl	aluminum weigh cups
KCl	weighing pads for use in microwave
KNO_3	water activity meter
	water activity sample containers

* %RH <1; ** %RH = 97.5

PROCEDURE

ERH Chambers

Calculate the amount of each salt needed to prepare a saturated solution of 5.0 ml volume given the solubility constants below. Using these values prepare 5 ml of a saturated salt solution in water to make relative humidity chambers with the following %RH:

<u>solute</u>	<u>solubility</u> g/100ml H ₂ O	<u>g/5 mL H₂O</u>	<u>%RH</u>
K-acetate	320		22.5
Mg(NO ₃) ₂ •6H ₂ O	426		52.0
NaCl	37		75.5
KCl	40		84.5
KNO ₃	25		93.0

1. Prepare 5 ERH chambers as follows

- label chambers with the solute, sample name, and your group number
- put calculated amount of salt and 5 mL of water into the corresponding chamber
- cut 3 triangles/incisions in the bottom of a plastic cup
- invert the plastic cup in the chamber to use as a sample stand
- cover the chamber and seal with the lid

Over time, the corresponding ERH will be reached within the enclosed environment

2. Dehydrated food sample (dried crackers)

- weigh an aluminum pan and record the weight of the empty pan
- calculate the weight of the pan + 2.5 g
- weigh 2.5 g of dried crackers into the pan and record the actual weight of the pan + sample
- place the sample in the appropriate ERH
- repeat for 4 other samples, recording in your labbook the weight of each pan + sample going into each ERH chamber
- in next week lab period you will reweigh your samples to get the final weight of pan + sample

3. Intermediate Moisture Food (crackers with increased moisture content)

- weigh an aluminum pan and record the weight of the empty pan
- calculate the weight of the pan + 4.0 g
- weigh 4 g of "increased moisture" crackers into pan and record the actual weight of the pan + sample
- mash the sample with a glass rod to increase surface area after weighing
- place the sample in the appropriate ERH

- repeat for 4 other samples, recording in your labbook the weight of each pan + sample going into each ERH chamber
- in next week lab period you will reweigh your samples to get the final weight of pan + sample

Important: Be sure to note in your labbook the balance that you used and use the same balance for all portions of the experiment.

Initial Moisture Content

Initial moisture content of the sample will be determined using either the vacuum oven or the microwave oven drying techniques.

- weigh 1.0 g of “normal” cracker sample and record the value
- press the crackers to increase surface area
- place the sample in the oven and dry it
- record dried weight of crackers + weighing pads

Water Activity, a_w

- weigh 2.0 g of sample
- place sample in small plastic container
- open the drawer of the water activity meter,
- insert your sample, close and turn the knob to the “read” position
- allow sample to equilibrate
- read a_w and record in your labbook

Definition of Terms

$$a_w = p/p_0 = \%RH/100$$

p = vapor pressure of water in food

p_0 = partial pressure of water at same temperature

w_{ti} = initial sample weight

w_{tf} = sample weight after adjustment to the selected water activity

w_{td} = dry sample weight = $(1 - X_{water}) w_{ti}$

x_{water} = decimal fraction of H₂O in sample

$$\% \text{ moisture final, dry weight} = \frac{w_{tf} - w_{td}}{w_{td}} \times 100$$

$$\% \text{ moisture change, dry weight basis} = \frac{w_{tf} - w_{ti}}{w_{td}} \times 100$$

Data to be recorded in lab-book:

Raw Data

- pan weight
- initial pan + sample weight
- final pan + sample weight
- % water initial in “normal” crackers

a_w of dried crackers
 a_w of "increased moisture" crackers

Calculated Data

Crackers: initial weight and % moisture (dry basis)

Dried crackers: initial, and final sample weights (w_{ti} , w_{tf} , w_{td})
% moisture final on a dry weight basis

"Increased moisture" crackers: initial, dry and final sample weights (w_{ti} , w_{tf} , w_{td})
% moisture final on a dry weight basis
% moisture change on a dry weight basis

Graphs

% moisture change (dry weight) vs. a_w (sorption and desorption curves)

QUESTIONS

1. Determine the initial a_w of the crackers from the graph of % moisture change vs a_w .
Discuss the stability of this product against microbial growth.
2. Define saturated salt solution.
3. Why do absorption and desorption curves of a moisture isotherm differ?