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Fundamentals of Water Activity

"It is now generally accepted that a_w is more closely related to the physical, chemical, and biological properties of foods and other natural products than is total moisture content. Specific changes in color, aroma, flavor, texture, stability, and acceptability of raw and processed food products have been associated with relatively narrow a_w ranges."

—Rockland LB & Nishi SK, Food Tech 34:42-59 (1980).

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What is Water Activity?

Water is recognized as being very important, if not critical, to the stability of most products. Controlling the water within a product, by some method of drying or by chemically/structurally binding (salting or sugaring) has long been used by man for preservation. This not only controls microbial spoilage, but also chemical and physical stability.

Water Content Alone is Not a Reliable Predictor

Traditionally, discussions about water in products or ingredients focus on moisture or water content, which is a quantitative or volumetric analysis that determines the total amount of water present. Water content of a product is a familiar concept to most people. One measures the water content by loss on drying, infrared, NMR or Karl Fisher titration. Moisture content determination is essential in meeting product nutritional labeling regulations, specifying recipes and monitoring processes. However, water content alone is not a reliable predictor of microbial responses and chemical reactions in materials.

Chemically Bound Water is Unavailable to Microbes

The limitations of water content measurement as an indicator of safety and quality are attributed to differences in the intensity which water associates with other components in the product. The water content of a safe product varies from product to product and from formulation to formulation. One safe, stable product might contain 15% water while another containing just 8% water is susceptible to microbial growth. Although the wetter product contains proportionally more water, its water is chemically bound by other components, making it unavailable to microbes. Using only water content values, it's impossible to know how "available" the water in the product is to support microbial growth or influence product quality.

Water Activity is Most Relevant for Quality and Safety Issues

Another more important type of water analysis is water activity (a_w). Water activity describes the energy status or escaping tendency of the water in a sample. It indicates how tightly water is "bound," structurally or chemically, in products. Both the water content and the water activity of a sample must be specified to fully describe its water status. However, water activity is the property most relevant for quality and safety issues. Water activity is closely related to the partial specific Gibbs free energy of the system. Thus, water activity is a thermodynamic concept and has requirements for measurements. These requirements are that the system be in equilibrium, the temperature defined, and a standard state specified. Pure water is taken as the reference or standard state from which the energy status of water in food systems is measured. The Gibbs free energy of free water is zero; thus, the water activity is 1.0.

Water Activity is a Ratio of Vapor Pressures

Water activity is the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water (p_o) at the same temperature. Relative humidity of air is the ratio of the vapor pressure of air to its saturation vapor pressure. When vapor and temperature equilibrium are obtained, the water activity of the sample is equal to the relative humidity of air surrounding the sample in a sealed measurement chamber. Multiplication of water activity by 100 gives the equilibrium relative humidity (ERH) in percent.

$$a_w = p/p_o = \text{ERH}\ (\%)\ /\ 100$$

As described by the above equation, water activity is a ratio of vapor pressures and thus has no units. It ranges from $0.0a_w$ (bone dry) to $1.0a_w$ (pure water).

"Bound" Water is Not Totally Immobilized

Water activity is sometimes described in terms of the amounts of "bound" and "free" water in a product. Although these terms are easier to conceptualize, they fail to define all aspects of the concept of water activity. "Free" water is not subjected to any force that reduces its energy; therefore, all water in food is "bound" water. The issue is not whether water is "bound," but how tightly it is "bound". Water activity is a measure of how tightly water is "bound" and related to the work required to remove water from the system. Water that is "bound" should not be thought of as totally immobilized. Microbial and chemical processes are related to this "bound" energy status in a fundamental way. Because water is present in varying energy states, analytical methods that attempt to measure total moisture in samples don't always agree or relate to safety and quality. Water activity tells the real story.

■ "There is now wide agreement that a_w is the most useful expression of the water requirements for microbial growth and enzyme activity. The alternatives of solute concentration and water content have been shown very clearly by Scott (1962) to be inadequate for describing the availability of water for the multiplication of certain bacteria."
Troller JA, & Christian JHB, Water Activity—Basic Concepts. *in* Water Activity and Food, *(Academic Press, New York, 1978), Chap. 1, pp. 1–12.*

"Bound" or "Free" Water are Not Very Useful Descriptions

There are several factors (osmotic, matrix, and capillary) that control water activity in a system. It is a combination of these factors in a product that reduces the energy of the water and thus reduces the vapor pressure above the sample as compared to pure water. Due to varying degrees of osmotic and matrix interactions, water activity describes the continuum of energy states of the water in a system rather than a static "boundness". "Bound" or "free" are not a very useful description since it is an attempt to classify a continuum in terms of discrete states.

Two Methods of Water Activity Instruments are Available

There is no device that can be put into a product that directly measures the water activity. Rather, a_w is measured with an indirect method. 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 relative humidity of the headspace. Methods for water activity determinations are detailed in the Official Methods of Analysis of AOAC International (1995). New instrument technologies have vastly improved speed, accuracy and reliability of measurements. Reliable laboratory instrumentation is required to guarantee the safety of products and enforce government regulations. Two different types of water activity instruments are commercially available. One uses chilled mirror dewpoint technology while the other utilizes relative humidity sensors that change electrical resistance or capacitance. Each has advantages and disadvantages. The methods vary in accuracy, repeatability, speed of measurement, stability in calibration, linearity, and convenience of use.

Chilled Mirror Dewpoint

In a chilled mirror dewpoint system, a sample is placed in a sample cup which is sealed against a sensor block. Inside the sensor block is a dewpoint sensor, an infrared thermometer, and a fan. The dewpoint sensor measures the dewpoint temperature of the air, and the infrared thermometer measures the sample temperature. From these measurements the relative humidity of the headspace is computed as the ratio of dewpoint temperature saturation vapor pressure to saturation vapor pressure at the sample temperature. When the water activity of the sample and the relative humidity of the air are in equilibrium, the measurement of the headspace humidity gives the water activity of the sample. The fan is to speed equilibrium and to control the boundary layer conductance of the dewpoint sensor.

Water Activity Measurement in Less than 5 Minutes

The major advantages of the chilled mirror dewpoint method are speed and accuracy. Chilled mirror dewpoint is a primary approach to measurement of relative humidity based on fundamental thermodynamic principles. Chilled mirror instruments make accurate ($\pm 0.003 a_w$) measurements in less than 5 minutes. Since the measurement is based on temperature determination, calibration is unnecessary, but running a standard salt solution checks proper functioning of the instrument. If there is a problem, the mirror is easily accessible and can be cleaned in a few minutes. For some applications, fast readings allow manufacturers to perform at-line monitoring of a product's water activity.

Electric Hygrometers

Other water activity instruments use resistance or capacitance sensors to measure relative humidity. These sensors are made from a hygroscopic polymer and associated circuitry that gives a signal relative to the equilibrium relative humidity (ERH). Commercially available instruments measure over the entire a_w range with an accuracy of $\pm 0.015 a_w$. Since these instruments relate an electrical signal to relative humidity, the sensor must be calibrated with known salt standards. In addition, the ERH is equal to the sample water activity only as long as the sample and sensor temperatures are the same. Accurate measurements require good temperature control or measurement. Advantages of capacitance sensors include simple design and inexpensive implementation. ●

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Water activity for product safety and quality.

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Water activity's usefulness as a quality and safety measurement was suggested when it became evident moisture content could not adequately account for microbial growth fluctuations. Water activity is a measure of the energy status of the water in a system. The water activity (a_w) concept has served the microbiologist and food technologist for decades and is the most commonly used criterion for safety and quality. Its usefulness cannot be denied.

Predicting Safety and Stability

National Institute of Standards and Technology NIST

Your AquaLab is calibrated to a NIST traceable temperature standard.

Water activity predicts safety and stability with respect to microbial growth, chemical and biochemical reaction rates, and physical properties. Figure 1 shows stability in terms of microbial growth limits and rates of degradative reactions as a function of water activity. Therfore, by measuring and controlling the water activity, it is possible to: a) predict which microorganisms will be potential sources of spoilage and infection, b) maintain the chemical stability of products, c) minimize nonenzymatic browning reactions and spontaneous autocatalytic lipid oxidization reactions, d) prolong the activity of enzymes and vitamins, and e) optimize the physical properties of products such as moisture migration, texture, and shelf life.

Microbial Growth

AOAC INTERNATIONAL

AOAC Method 978.18

Microorganisms have a limiting water activity level below which they will not grow. Water activity, not moisture content, determines the lower limit of "available" water for microbial growth. Since bacteria, yeast, and molds require a certain amount of "available" water to support growth, designing a product below a critical a_w level provides an effective means to control growth. Water may be present, even at high content levels, in a product, but if its energy level is sufficiently low the microorganisms cannot remove the water to support their growth. This 'desert-like' condition creates an osmotic imbalance between the microorganisms and the local environment. Consequently, the microbes cannot grow and its numbers will decline until it eventually dies.

Limiting Microorganism Growth

While temperature, pH, and several other factors can influence whether an organism will grow in a product and the rate at which it will grow, water activity is often the most important factor. Water activity may be combined with other preservative factors (hurdles), such as temperature, pH, redox potential, etc., to establish conditions that inhibit microorganisms. The water activity level that limits the growth of the vast majority of pathogenic bacteria is 0.90a_w, 0.70a_w for spoilage molds, and the lower limit for all microorganisms is 0.60a_w. Table 1 (back page), lists the water activity limits for growth of microorganisms significant to public health and examples of products in those ranges.

Chemical/Biochemical Reactivity

Water activity influences not only microbial spoilage but also chemical and enzymatic reactivity. Water may influence chemical reactivity in different ways; it may act as a solvent, reactant, or change the mobility of the reactants by affecting the viscosity of the system. Water activity influences nonenzymatic browning, lipid oxidization, degradation of vitamins and other nutrients, enzymatic reactions, protein denaturation, starch gelatinization, and starch retrogradation (see Figure 1). Typically, as the water activity level is lowered, the rate of chemical degradative reactions decreases.

Physical Properties

Besides predicting the rates of various chemical and enzymatic reactions, water activity affects the textural properties of foods. Foods with high a_w have a texture that is described as moist, juicy, tender, and chewy. When the water activity of these products is lowered, undesirable textural attributes, such as hardness, dryness, staleness, and toughness, are observed. Low a_w products normally have texture attributes described as crisp and crunchy, while these products at higher a_w levels change to soggy texture. Critical water activities determine where products become unacceptable from a sensory standpoint.

Caking, Clumping, Collapse and Stickiness

Water activity is an important factor affecting the stability of powders and dehydrated products during storage. Controlling water activity in a powder product maintains proper product structure, texture, stability, density, and rehydration properties. Knowledge of the water activity of powders as a function of moisture content and temperature is essential during processing, handling, packaging and storage to prevent the deleterious phenomenon of caking, clumping, collapse and stickiness. Caking is water activity, time, and temperature dependent and is related to the collapse phenomena of the powder under gravitational force.

Moisture Migration

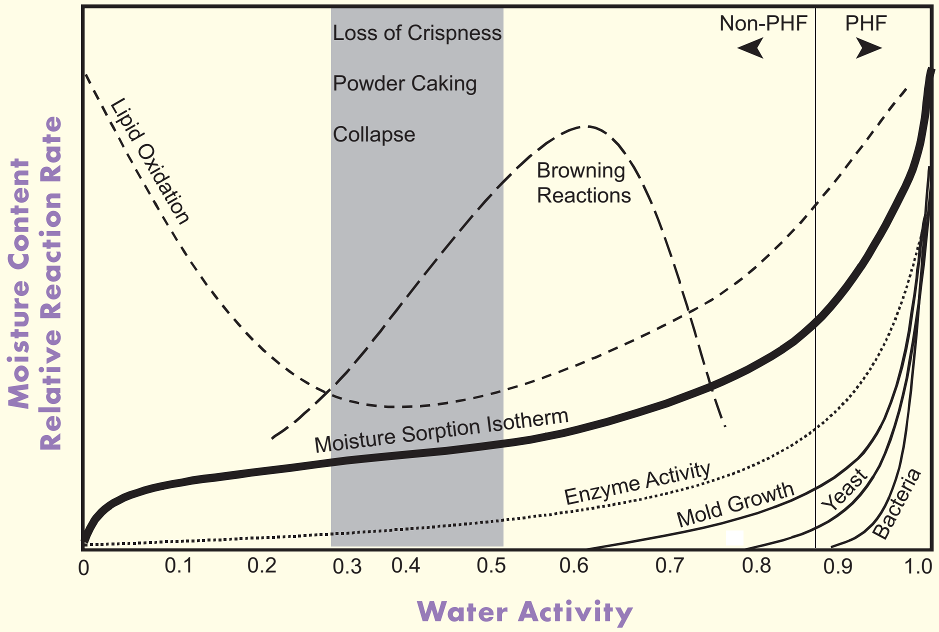
Because water activity is a measure of the energy status of the water, differences in water activity between components is the driving force for

■ *Modern water activity instruments ensure safe quality food products.*

■ "The practical applications of a_w throughout the food industry have generated creative new food products worth many billions of dollars since the 1960s. Perhaps of even greater potential value is the pool of basic information about a_w and its connection to moisture relations and food qualities that has been generated since the 1960s."
Bone DP, Practical Applications of Water Activity and Moisture Relations in Foods. in Water Activity: Theory and Applications to Food, *L. B. Rockland, L. R. Beuchat, Eds. (Marcel Dekker Inc., New York, 1987), Chap. 15, pp. 369-395.*

Figure 1

Water Activity – Stability Diagram



moisture migration as the system comes to an equilibrium. Thus, water activity is an important parameter in controlling water migration of multicomponent products. Some foods contain components at different water activity levels, such as filled snacks or cereals with dried fruits. By definition, water activity dictates that moisture will migrate from a region of high a_w to a region of lower a_w, but the rate of migration depends on many factors. Undesirable textural changes can result from moisture migration in multicomponent foods. For example, moisture migrating from the higher a_w dried fruit into the lower a_w cereal causes the fruit to become hard and dry while the cereal becomes soggy.

ISO 21807

Water Adjusts Between Materials Until Water Activity Equilibrium

Differences in water activity levels between components or a component and environmental humidity are a driving force for moisture migration. Knowledge of whether water will absorb or desorb from a particular component is essential to prevent degradation, especially if the substance is moisture sensitive. For example, if equal amounts of component 1 at 2% and component 2 at 10% moisture content must be blended together, will there be moisture exchange between the components? The final moisture content of the blended material would be 6%, but did any moisture exchange between component 1 and 2? The answer depends on the water activities of the two components. If the water activities of the two components are the same, then no moisture will exchange between the two components. Also, two ingredients at the same moisture content may not be compatible when mixed. If two materials of differing water activities but the same water content are mixed, the water will adjust between the materials until an equilibrium water activity is obtained.

Shelf-life/Packaging

Water activity is a critical factor in determining the shelf life of products. Critical upper and lower water activity levels can be established with respect to microbial, texture, flavor, appearance, aroma, nutritional, and cooking qualities for food products. Rates of exchange of moisture through the package and the rate of change in a_w of the food towards a critical limit will determine the shelf life of a product. Knowledge of the temperature, ambient relative humidity and critical a_w values will aid in selection of a package with the correct barrier properties to optimize quality and shelf life. ●

Government Compliance

The U.S. food, drug, and cosmetic laws are intended to assure the consumer that foods are pure, wholesome, safe to eat, and produced under sanitary conditions; that drugs and medical devices are safe and effective for their intended uses; that cosmetics are safe and made from appropriate ingredients; and that all labeling and packaging is truthful, informative, and not deceptive. Modern scientific methods are required to enforce the Federal Food, Drug, and Cosmetic Act. Laws to ensure the wholesomeness of foods and the safety and efficacy of drugs would be impractical without reliable methods of laboratory analysis to determine whether products are up to a standard.

Good Manufacturing Practice

The United States has one of the safest food supplies of any country in the world. The FDA's Good Manufacturing Practice Regulations incorporates water activity guidelines in defining food safety regulations. GMP regulations detail the specific requirements and practices to be followed by industry to assure that foods are produced under sanitary conditions and are pure, wholesome, and safe to eat. Specific parts and paragraphs of applicable GMP regulations from Title 21 of the Code of Federal Regulations use a_w in relation to control measures and food safety. However, neither GMP's alone nor activities of regulatory agencies alone can guarantee a completely safe food supply. Consequently, a science based system, Hazard Analysis and Critical Control Points (HACCP), has been created to improve food safety and reduce the incidence of foodborne illness.

In-process Detection

HACCP is a way for industry to control and prevent problems, and ensure safe food by controlling the production process from beginning to end, rather than detecting problems at the end of the line. It identifies where hazards might occur in the food production process and puts into place actions to prevent the hazards from occurring. For example, a target water activity must be established to prevent hazardous organisms from growing. By controlling major food risks, such as microbiological, chemical and physical contaminants, the industry can better assure consumers that its products are safe.

Potentially Hazardous Food

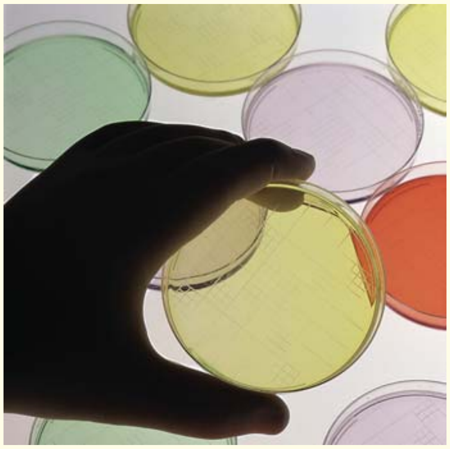
The term potentially hazardous food (PHF) was developed by the U.S. Public Health Service during the last half of the twentieth century to regulate perishable food. Potentially hazardous food means a food that requires time/temperature control for safety (TCS) to limit pathogenic microorganism growth or toxin formation. Foods were considered non-PHF when their a_w A 0.85, which is below the water activity for Staphylococcus aureus growth and toxin production or the pH A 4.6, which is below the pH for proteolytic Clostridium botulinum growth and toxin production.

New Scientific Based Criteria

The 2005 version of the Food Code updates the definitions of PHF by using a scientific based criteria that considers the interaction of a_w and pH in determining if a food is designated as a non-PHF/non-TCS food. Interaction Tables A & B consider the interaction of a_w and pH under certain conditions of heat-treatment and packaging. The hurdle effect will control or eliminate pathogens that would otherwise be ineffective when used alone. The effect of a heat treatment which destroys vegetative cells and the effect of packaging which prevent recontamination is considered.

0.85 or Less a_w Will Not Support Pathogenic Bacterial Growth

The USDA and FSIS also use water activity in Generic HACCP Model 10 for Heat-treated, Shelf-stable Meat and Poultry Products. The science states and verifies that all pathogenic bacteria stop growing at a water activity of 0.86. The model states that "Manufacturers should not use the moisture protein ratio (MPR) as a measure of proper drying for shelf-stability or safety. It is product water activity that is best correlated to inhibition of each pathogen's growth." Thus, if you produce jerky to a water activity of 0.85 or less, then the product will not support the



■ "Water activity plays an important role in the safety, quality, processing, shelf life, texture and sensory properties of foods." Fontana AJ & Campbell CS, Water Activity. in Handbook of Food Analysis, Physical Characterization and Nutrient Analysis, *L. M. L. Nollet, Ed. (Marcel Dekker, New York, 2004), Chap. 3, pp. 39-54.*

growth of any pathogenic bacteria. Drying your product to a water activity of 0.80 or less does not make the product any safer. The product will have less consumer appeal (because it will be tougher and chewier) and because jerky is sold on a weight basis, you will be losing profit.

Pharmaceutical and Cosmetics

Currently there are no water activity regulations for pharmaceutical or cosmetic products. Although, there is a proposed USP (United States Pharmacopeial) Method <1112> using water activity. USP Method <1112> Microbiological Attributes of Nonsterile Pharmaceutical Products – Application of Water Activity Determination provides guidance on the influence of water activity as it pertains to product formulation susceptibility to microbial contamination. The chapter discusses the potential for improving product preservation by maintaining low water activity. The determination of the water activity of nonsterile pharmaceutical dosage forms aids in the decisions about the following:

- Optimizing product formulations to improve antimicrobial effectiveness of preservative systems.

- Reducing the degradation of active pharmaceutical ingredients within product formulations susceptible to chemical hydrolysis.

- Reducing the susceptibility of formulations (especially liquids, ointments, lotions, and creams) to microbial contamination.

- Providing a tool for the rationale for reducing the frequency of microbial limit testing and screening for objectionable microorganisms for product release and stability testing using methods contained in the general test chapter Microbial Limit Tests <61>. ●

Interaction Table A

Table A. Interaction of pH and a_w for control of spores in food heat-treated to destroy vegetative cells and subsequently packaged.

a_w Values	pH Values		
	4.6 or less	> 4.6 – 5.6	> 5.6
0.92 or less	Non-PHF*/non-TCS**	Non-PHF/non-TCS	Non-PHF/non-TCS
> 0.92 – 0.95	Non-PHF/non-TCS	Non-PHF/non-TCS	PA***
> 0.95	Non-PHF/non-TCS	PA	PA

* PHF means "Potentially Hazardous Food"
** TCS means "Time/Temperature Control for Safety Food"
*** PA means "Product Assessment Required"

■ Table A can be used to determine if a food which is heat-treated and packaged is PHF, Non-PHF or Requires Product Assessment. Food must meet cooking requirements of Food Code section 3-401.11 (no partial cooks) to eliminate vegetative pathogens. Spore forming pathogens are the only remaining biological hazards of concern. Food is packaged to prevent re-contamination. Therefore, higher pH & a_w can be safely tolerated.

Interaction Table B

Table B. Interaction of pH and a_w for control of vegetative cells and spores in food not heat-treated or heat-treated but not packaged.

a_w Values	pH Values			
	< 4.2	4.2 – 4.6	> 4.6 – 5.0	> 5.0
< 0.88	Non-PHF*/non-TCS**	Non-PHF/non-TCS	Non-PHD/non-TCS	Non-PHF/non-TCS
0.88 – 0.90	Non-PHF/non-TCS	Non-PHF/non-TCS	Non-PHF/non-TCS	PA***
> 0.90 – 0.92	Non-PHF/non-TCS	Non-PHF/non-TCS	PA	PA
> 0.92	Non-PHF/non-TCS	PA	PA	PA

* PHF means "Potentially Hazardous Food"
** TCS means "Time/Temperature Control for Safety Food"
*** PA means "Product Assessment Required"

■ Table B can be used to determine if a food which is not heat-treated or heat-treated but not packaged is PHF, Non-PHF or Requires Product Assessment. Food not heat-treated may contain vegetative cells and pathogenic spores. Food that was heat-treated but not packaged may become re-contaminated. pH values considered in Table B must include 4.2 because Staphylococcus aureus can grow at that level.

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■ *"The importance of the water activity—moisture content concept of foods cannot be overemphasized. More importantly, the value of water activity has been shown to control the stability of dehydrated and semi-moist foods."*
Labuza TP, Sorption Phenomena in Foods: Theoretical and Practical Aspects. in Theory, Determination and Control of Physical Properties of Food Materials, *C. Rha, Ed. (D. Reidel Publishing Co., Dordrecht-Holland, 1975), Chap. 10, pp. 197-219.*

a_w	Microorganism: Bacteria	Microorganism: Molds	Microorganism: Yeast	Typical Products
0.97	*Clostridium botulinum E* *Pseudomonas fluorescens*	—	—	Fresh meat, fruit, vegetables, canned fruit, canned vegetable, low-salt bacon, cooked sausages, nasal spray, eye drops
0.95	*Escherichia coli* *Clostridium perfringens* *Salmonella spp.* *Vibrio cholerae*	—	—	
0.94	*Clostridium botulinum A, B* *Vibrio parahaemolyticus*	*Stachybotrys atra*	—	Some cheeses, cured meat (ham), bakery goods, evaporated milk, Oral liquid suspensions, topical lotions
0.93	*Bacillus cereus*	*Rhizopus nigricans*	—	
0.92	*Listeria monocytogenes*	—	—	
0.91	*Bacillus subtilis*	—	—	
0.90	*Staphylococcus aureus* (anaerobic)	*Trichothecium roseum*	*Saccharomyces cerevisiae*	
0.88	—	—	*Candida*	Sweetened condensed milk, aged cheeses (cheddar), fermented sausage (salami), dried meats (jerky), bacon, most fruit juice concentrates, chocolate syrup, fruit cake, fondants, Cough syrup, oral analgesic suspensions
0.87	*Staphylococcus aureus* (aerobic)	—	—	
0.85	—	*Aspergillus clavatus*	—	
0.84	—	*Byssochlamys nivea*	—	
0.83	—	*Penicillium expansum* *Penicillium islandicum* *Penicillium viridicatum*	*Debarymoces hansenii*	
0.82	—	*Aspergillus fumigatus* *Aspergillus parasiticus*	—	
0.81	—	*Penicillium cyclopium* *Penicillium patulum*	—	
0.80	—	—	*Saccharomyces bailii*	
0.79	—	*Penicillum martensii*	—	Jam, marmalade, marzipan, glace fruits, molasses, dried figs, heavily salted fish
0.78	—	*Aspergillus flavus*	—	
0.77	—	*Aspergillus niger* *Aspergillus ochraceous*	—	
0.75	—	*Aspergillus restrictus* *Aspergillus candidus*	—	
0.71	—	*Eurotium chevalieri*	—	
0.70	—	*Eurotium amstelodami*	—	Dried fruit, corn syrup, licorice, marshmallow, chewing gums, dried pet foods
0.62	—	—	*Saccharomyces rouxii*	
0.61	—	*Monascus bisporus*	—	
0.60	No microbial proliferation			
0.50	No microbial proliferation			Caramels, toffees, honey, noodles, topical ointment
0.40	No microbial proliferation			Whole egg powder, cocoa, liquid center cough drop
0.30	No microbial proliferation			Crackers, starch based snack foods, cake mixes, vitamin tablets, suppositories
<0.20	No microbial proliferation			Boiled sweets, milk powder, infant formula

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