FOOD SCIENCE AND TECHNOLOGY SERIES

Handbook of Food Science and Technology 1

Food Alteration and Food Quality

Edited by

Romain Jeantet, Thomas Croguennec
Pierre Schuck and Gérard Brulé

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Contents

Introduction

The first concern of primitive people was to find food in their immediate environment to meet their physiological needs to survive; with no knowledge of either their requirements or the properties of food products, whether they were of plant or animal origin, these food choices were based on very empirical observations. The development of agriculture and livestock farming gradually gave people greater control in procuring food compared to the randomness of gathering, hunting and fishing. However, the supply of agricultural and livestock products has long been highly irregular for reasons of climate, diseases or simply the seasonal nature of certain products. Due to this irregularity, and in order to meet the needs of people located far from production areas, man has always been in search of ways to preserve food, thereby creating the possibility of varying the time and place of consumption of agricultural products.

I.1. Traditional preservation methods at the beginning of the agri-food industry

Without any knowledge of the deterioration process of raw materials, man observed that certain natural changes led to more stable products with tasty characterisitics. This is how fermentation emerged as an effective method of preservation: products of lactic acid, acetic acid and alcoholic fermentation (cheese, bread, wine, beer, etc.) are consequently some of the oldest foods since the raw materials used to produce them all contain the elements necessary for fermentation to occur. The reduction in pH, the

Introduction written by Gérard BRULÉ.

presence of metabolites such as alcohol and lactic acid, the occupation of the medium by bacteria or yeast and the depletion of microbial growth factors all generate high resistance to the development of potentially pathogenic spoilage flora.

Other preservation methods have gradually been developed, based in particular on the use of salt, combined with dehydration in some cases, so as to reduce the availability of water. Water is a vector of all the elements involved in microbial growth and in chemical and biochemical reactions (solvent for metabolites and reaction products). The unavailability of water hinders microbial growth and most of the reactions. Water availability can be reduced by eliminating free water, by changing its state (ice) and by transfer or by immobilizing water through the addition of highly hydrophilic solutes such as salts and sugars. Salting has long been the most common preservation method for meat and fish in particular, and still forms the basis of the meat curing industry today. Salting is sometimes combined with dehydration or smoking: smoke constituents also contribute to good microbial and biochemical stability due to their bacteriostatic and antioxidant properties, and have a favorable impact on both color and flavor.

Stabilization through heat treatment appeared late compared to the methods just described, around the middle of the 19th Century. By destroying food spoilage agents (microorganisms and enzymes), heating food is an effective way of ensuring longer product life. The canning industry is based on this method.

By integrating the knowledge of the role of microorganisms into food spoilage and fermentation processes, work that was initiated by Pasteur, food production and stabilization gradually moved from an artisanal level to an industrial level. This transition was facilitated by the integration of technological progress, such as the development of pasteurization and sterilization tools, the introduction of refrigeration and freezing, drum-drying followed by spray-drying, freeze-drying, etc. This transition accelerated after World War II due to the large rural exodus that ensued. The concentration of the population in urban areas generated problems of supply of agricultural and food products, which had to be tackled by improving product stability and distribution in order to vary the time and place of consumption. This need to regulate supply and adapt it to demand was instrumental in the development of the agri-food industry.

I.2. From quantitative demand to qualitative demands

Agricultural production at the end of World War II was insufficient, both quantitatively and qualitatively, to satisfy the needs of people who had moved to urban areas: the most important aspects of food were availability and accessibility. Thus, one of the first objectives of the agricultural sector and the food industry was to meet the quantitative demand by increasing productivity and reducing production and processing costs. Progress in animal and plant genetics, developments in the agricultural sector, and changes in crop protection, forage and livestock management all resulted in a considerable increase in productivity within a few years, which in some cases was at the expense of quality.

Once the quantitative demand was satisfied, consumers became increasingly aware of the dangers and risks associated with poor-quality food. The number of reported food poisoning cases increased due to the obligation to conduct a more rigorous monitoring of food poisoning, the development of mass catering and the increase in immunocompromised people, some of whom live in institutions (geriatrics). A fear of shortages, which disappeared in industrialized countries, was replaced by food scares: this phenomenon was aggravated by a series of crises that adversely affected the food chain (bovine spongiform encephalopathy, genetically-modified organisms, *Listeria, Salmonella*, bird flu, dioxin, etc.). The consumer's desire to eliminate food risk meant that food hygiene and safety has become the most important quality requirement today.

A number of sociological changes (increase in female employment, organization of the working day, family breakdown and the development of leisure activities) have impacted eating habits and created new needs. In addition to the development of mass catering, there has also been a rise in single serving and food services. This in turn corresponds to a very high demand for food with a long shelf life, fast preparation, individual portion sizes and highly processed food (ready meals). Trying to combine quality service (proposing a high diversity of individual portions of tasty ready-to-eat food products with long shelf life) as well as a guaranteed hygiene with the control of physicochemical and thermodynamic stability and the preservation of the sensory qualities of food is a real challenge faced by the food industry today.

The health benefit of food is also a qualitative element that has started to dominate consumer expectations: progress in the area of nutrition and data from epidemiological studies now make it possible to better assess the effects of poor diet on health. The development of a number of physiological disorders and the so-called lifestyle diseases (e.g. obesity, heart disease, allergies, intestinal and colon cancer, and diabetes) is attributed to changes in eating habits and food. As a result, health-conscious consumers are very sensitive to any communication extolling the virtues and benefits of certain foods.

Over the years and throughout the many health crises that have hit the agricultural and food sectors, consumers have become aware that several foods were the result of a production system based on profit, with little concern for them and even less for the well-being of animals and the environment. They discovered that the various stages of the food chain from production to distribution were opaque and that local products were disappearing. The agricultural model established after World War II and the food chain that underpins our diet are currently facing growing opposition. For the consumer, food is not solely a product that generates pleasure and satisfies nutritional needs, but it is also a symbol of the choice of society that is being supported or opposed through the act of purchase. There has been a shift from a "goods-based economy" to a "services-based economy". These changes in expectations among consumers impact the entire food chain, and the agricultural sector should no longer be merely a place where raw materials and services are created, but also a place of living areas, beautiful countryside and natural resources.

The expectations and demands of consumers regarding their food are increasingly complex and sometimes difficult to understand because imagination also plays an important role, which in some cases can lead to contradictory behavior.

I.3. Better identification of quality criteria

Quality can be expressed in terms of five components: safety, health, sensory, service and society (Figure I.1); we can define a number of criteria for each of the five components.

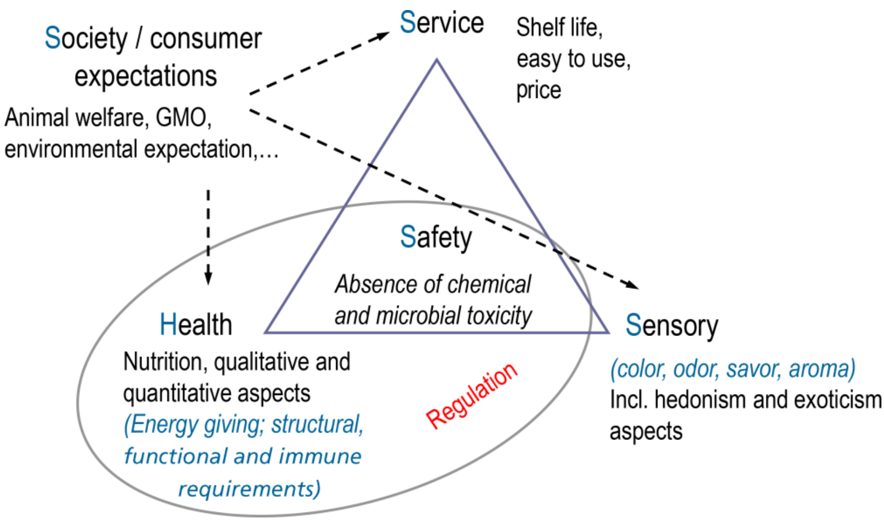

Figure I.1. *Quality of food*

I.4. Safety

Safety implies the absence of bacterial or viral pathogens, toxins or chemical residues. Pathogens can have several sources (e.g. raw materials and environment) and can be carried by different vectors (e.g. water, air and operators). The implementation of codes of good practice in production and processing, the application of health controls, the design of production and processing facilities, and ongoing progress are all elements that help reduce hygiene risks and limit cross contamination.

Toxins can be present in some raw materials as natural defense mechanisms against predators or microbial attack, or produced *in situ* by bacterial or fungal microorganisms that colonize the raw materials: this is the case, for example, with aflatoxins or patulin.

Chemical residues can originate from raw materials contaminated by the treatment of plants or crops (herbicides and fungicides) or animals (antibiotics, anabolic steroids and hormones), or can be generated by processing methods such as smoking (benzopyrenes) and salting (nitrites and nitrosamines). Products from traditional processes and technology are often considered a guarantee of quality, which can be true from a sensory perspective, but is highly contestable from a health and safety perspective.

I.5. Health

The primary function of food is to satisfy the nutritional and physiological needs of the individual.

Energy requirements

Energy requirements vary not only depending on age and physiological condition, but also in relation to the amount of physical activity associated with muscular work during daily activities and sport. For adults, this can range from 8,000 to 15,000 kJ per day. Energy requirements are primarily fulfilled by the intake of fats and carbohydrates, which should constitute 30 and 55% of total energy, respectively, according to nutritional recommendations.

Structural and functional requirements

Our body needs certain amounts of organic and inorganic substances to build and repair bones and tissues as well as carry out certain biochemical reactions involved in metabolism.

In terms of minerals, macronutrient requirements (e.g. sodium, potassium, calcium, magnesium and phosphorous) are generally covered by diet. However, this is not always the case for some micronutrients (e.g. iron, iodine, selenium and fluoride).

Vitamin requirements can be met by a balanced diet that includes fruit, vegetables, and animal and vegetable fats.

Proteins supply amino acids, nine of which are essential since they are not synthesized by the body (methionine, lysine, tryptophan, threonine, phenylalanine, isoleucine, leucine, valine and histidine). Again, quantitative and qualitative needs change with age, physiological condition and activity. They are easily covered by an animal and vegetable protein-based diet.

Fats and carbohydrates, in addition to their energy function, play an important physiological role. Some fatty acids have reproductive, epidermal and platelet functions. Two families of polyunsaturated fatty acids, *n*-6 (linoleic acid, 18:2) and *n*-3 (alpha-linolenic acid, 18:3), play an essential role. The recommended daily allowance, expressed as a percentage of energy from fat, is 60% monounsaturated fatty acids, 25% saturated fatty acids and 15% polyunsaturated fatty acids (linoleic acid and alpha-linolenic acid at a ratio of 5:1). Carbohydrates other than glucose play an important role as components of serum and tissue glycoproteins (galactose, mannose, fucose, sialic acid, etc.). Indigestible oligosaccharides are crucial in maintaining a balanced gut flora and limiting the probability of developing certain diseases.

Protection and defense requirements

The body is exposed to a certain amount of stress and attack. The immune system can therefore be affected by various diseases and treatments or during the process of aging, which results in greater susceptibility to viral attack and microbial infection. The immune status is maintained and even improved by the intake of micronutrients (copper and zinc) and vitamins (B_6) as well as the consumption of prebiotics and probiotics.

I.6. Satisfaction

Eating has and always should remain a pleasure through the sensations that food provides. Sensory stimuli, whether visual, olfactory (nasally or retronasally), gustatory (taste), tactile or auditory, contribute in varying degrees to the organoleptic or sensory quality of food. The integration of all these stimuli results in sensory perception and its hedonic expression. It can differ from one individual to another, given that the discriminating power of smell and taste depends on eating habits, and can vary for organic and physiological reasons. The perception of food can also be heavily influenced by the sociocultural context; for example, the imaginative aspect associated with food can have a considerable impact.

I.7. Service

Sociological changes (e.g. increase in female labor force participation, organization of working time and growing importance of leisure time) tend to limit the time spent by consumers in preparing meals. They have thus contributed to the development of non-domestic catering and food services, i.e. shelf-stable prepared and/or cooked products that are easy to use. The development of freezing and thawing (using household microwaves, for example) has promoted the penetration of these ready-to-use foods into the market.

I.8. Society

The relationship between the consumer and food has evolved considerably. Consumers are increasingly aware of buying local, demanding more “naturalness” and “authenticity” and refusing any technical developments that might damage the quality of rural areas, animal well-being or the environment. Food, the link between consumers and their locality, conveys the values and choices of a society, of which consumers are increasingly aware.

PART 1

Water and Other Food Constituents

1

Water

Water is the most abundant constituent of the majority of foods. It therefore plays a crucial role in the physicochemical characteristics and properties of the plant and animal foods we eat. These characteristics can be desired due to their contribution to food quality (the texture of fruit, vegetables and meat, which depends, among other things, on cell turgidity as well as on specific and complex interactions between water and other constituents). However, they can also contribute to food spoilage through biochemical and microbiological processes. As a result, several food preservation methods are based, at least partially, on lowering the water activity (a_w) or the water availability.

1.1. Structure and state of water

The water molecule, composed of two hydrogen atoms and one oxygen atom (H_2O), can exist, like many substances, in three different states: solid, liquid or gas.

In the liquid and vapor state, the water molecule is a polar monomer (see Figure 1.1).

In the solid state (i.e. ice), water molecules are linked by hydrogen bonds and form a crystalline polymer in which each monomer molecule is connected to four other molecules by hydrogen bonds. The distance between two oxygen atoms is 0.276 nm. At temperatures below −173°C, all hydrogen

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Chapter written by Pierre SCHUCK.

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atoms are involved in hydrogen bonds, whereas at 0°C only around 50% are involved, and at 100°C only a small percentage are involved.

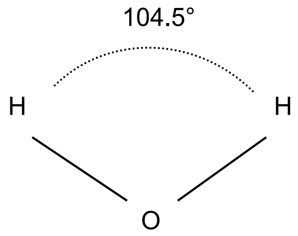

Figure 1.1. *Water molecule*

Certain water properties can be attributed to these intermolecular bonds, in particular the boiling point, melting point, latent heat of fusion, latent heat of vaporization, specific heat, surface tension and the dielectric constant. However, water in a liquid state behaves like a monomer in terms of viscosity and the diffusion coefficient (Tables 1.1 and 1.2).

Properties	Unit	Value
Molar mass	$g\ mol^{-1}$	18.01528
Melting point (at 101,325 Pa)	°C	0.00
Boiling point (at 101,325 Pa)	°C	100.00
Maximum density	$kg\ m^{-3}$	999.95
Temperature of maximum density	°C	4.00
Triple-point temperature	°C	0.01
Triple-point density (liquid)	$kg\ m^{-3}$	999.78
Triple-point density (gas)	$10^{-3}\ kg\ m^{-3}$	4.88
Latent heat of sublimation at the triple point	$10^{3}\ J\ kg^{-1}$	2800
Critical temperature	°C	373.99
Critical pressure	MPa	22.064
Critical density	$kg\ m^{-3}$	322
Specific volume at the critical point	$10^{-3}\ m^{3}\ kg^{-1}$	3.11
Latent heat of freezing at 0°C	$10^{3}\ J\ kg^{-1}$	335

Table 1.1 *Properties of water*

Different theoretical models have been proposed to explain the liquid and solid state behavior of water. Monomers as well as higher-energy molecules exist in a static equilibrium: each molecule is involved in one to four hydrogen bonds; the latter can form short-lived labile clusters.

Properties	Units	Frozen water		Liquid water						Water vapor	
Temperature	(°C)	–20	0	0	20	40	60	80	100	100	200
Density	kg m^{-3}	919.3	916.8	999.8	998.2	992.2	983.2	971.8	958.4	0.589	0.452
Viscosity	10^{-6} Pa s	–	–	1,793	1,002	653	466	354	281	12.5	16.4
Surface tension	10^{-3} N m^{-1}	–	–	75.64	72.75	69.60	66.24	62.67	58.91	–	–
Vapor pressure	(Pa)	103.4	611.3	611.3	2,338.8	7,381.4	19,932	47,373	101,325	–	–
Specific heat C_p	J.kg^{-1} k^{-1}	1,954	2,101	4,217	4,182	4,178	4,184	4,196	4,216	2,041	1,960
Energy of vaporization	10^3 J kg^{-1}	–	–	2,494	2,448	2,402	2,357	2,309	2,258	–	–
Thermal conductivity	W m^{-1} °K^{-1}	2.43	2.22	0.561	0.598	0.630	0.654	0.670	0.679	0.0248	0.0391
Diffusivity in the air	10^{-6} m^2 s^{-1}	–	–	21.8	24.6	27.5	30.5	33.7	–	–	–
Thermal diffusivity at 10^5 Pa	10^{-6} m^2 s^{-1}	–	–	0.135	0.143	0.151	0.161	0.164	0.170	19.6	32.6

Table 1.2. *Properties of water*

The structure of water is largely influenced by its organic and inorganic environment:

– electrolytes such as Na^+, K^+ and Cl^- are highly hydrated in solution, and lower the number of hydrogen bonds between water molecules, whereas hydrocarbon chains and non-polar groups of protein side-chains tend to increase it;

– substances in solution (carbohydrates and amino acids), which can themselves form hydrogen bonds, can modify the bonds between water molecules depending on their geometric compatibility with the existing network, e.g. urea has a strong effect whereas ammonia has none;

– substances with several different functional groups (e.g. amino acids, proteins, fatty acids and carbohydrates) affect the structure of water.

The effect of the environment is very pronounced in highly concentrated solutions and weakly hydrated systems. Water can form crystalline hydrates (clathrates) above 0°C with some gases (e.g. freon and propane). The formation of these hydrates can be used in the concentration or demineralization of aqueous solutions. Table 1.3 shows the different binding energies of water.

Type of bond	Binding energy (kJ mol^{-1})
Covalent bond	460
Hydrogen bond (liquid water)	< 20
Hydrogen bond (frozen water)	23
Hydration of polar group (monolayer)	4–6
Hydration of polar group (multilayer)	1–3
Van der Waals bond	0.5
Water retained by capillary forces	0.3

Table 1.3. *Binding energy of water [FAI 03]*

Water also affects properties such as the structure, diffusion and reactivity of substances in solution. For example, the role of water in the structure and functional properties of macromolecular compounds such as proteins is known [LEM 02]. The main functions of water in food are shown in Table 1.4.

Role of water	Example
Solvent	Molecule dissolution
Reaction medium	Enzymatic reactions
Mobility of reagents	Maillard reactions
Reagent	Lipid hydrolysis
Anti-oxidant	Hydrogen bond with peroxides blocking the oxidation of lipids, for low a_w
Pro-oxidant	– Swelling of proteins and accessibility of oxidizable sites – Sources of free radicals in irradiated foods
Structural role	– Formation of hydrogen bonds between texturing molecules – Acts on lipid/protein bonds in bakery products – Acts on the conformation and interactions between gelling agents and proteins

Table 1.4. *Functions of water in food [DUC 76, FAI 03]*

1.2. Properties of water

Among the physical and physicochemical properties of water, some greatly influence phase transitions as well as mass and heat transfers. Examples include specific heat, latent heat of fusion, latent heat of vaporization, thermal conductivity and viscosity. They determine the design and control of heat treatment (sterilization, cooking, etc.), concentration, drying or freezing processes. Others relate to the solvent properties of water: dielectric constant, surface tension or dipole moment. Water is, in fact, the dilution medium for many chemical species that can diffuse and react with each other. In addition to this, water can diffuse and participate in various reactions, such as hydrolysis. The introduction of different chemical species in solution or colloidal suspension in water also creates the so-called colligative properties, which depend on the number of molecules present. This is the case, for example, with lowering the freezing point and surface tension, increasing the boiling point and viscosity, and establishing osmotic pressure gradients through semi-permeable membranes.

The fact that the water present in food is more or less in interaction with the other constituents gives rise to concepts of “free water” and “bound water”. Various observations show that the so-called bound water can itself be bound to varying degrees and the state of water is just as important for the stability of a foodstuff as the total water content. This concept of “bound water” is also underpinned by the knowledge of the dipolar nature of water and its possible interactions with different chemical groups of other constituents.

In order to determine to what extent the concept of “bound water” is a physical reality, two categories of properties can be used to characterize this potential binding state: molecular mobility and thermodynamic properties. Of these, water activity (a_w) has attracted the most attention in food science and technology. The ability of water to freeze has also long been considered an indication of the binding state of water. These concepts are now combined with dynamic data (glass transition – T_g) to establish the state diagram [SIM 02]. These three concepts (a_w, T_g and the phase diagram) are explained hereafter.

1.2.1. *Water activity (a_w)*

1.2.1.1. *Definition*

The a_w of a food product is characterized by the ratio of the partial vapor pressure in a food product (P_p) and the saturated vapor pressure (P_w) at the same temperature θ:

$$a_w = \frac{P_p}{P_w} \quad [1.1]$$

The a_w is, therefore, a non-dimensional ratio and is thus a relative measure compared to a standard (pure water). Consequently, the a_w of pure water is equal to 1, with every other product having an a_w value below 1. The decrease in water activity can be explained by the fact that the solubilized chemical components partially mobilize the water and, therefore, decrease its capacity to vaporize; they also alter the chemical reactivity of water, which is exactly proportional to a_w.

The a_w of a food product should not be confused with its relative humidity (H_R). The H_R is the ratio of the partial vapor pressure in air (P_a) and the saturated vapor pressure (P_{sv}) at the same temperature θ:

$$H_R = \frac{P_a}{P_{sv}} \times 100 \quad [1.2]$$

At equilibrium, $P_p = P_a$ and $P_w = P_{sv}$ for a given food product and at a given temperature θ. The a_w or the H_R at equilibrium (H_{RE}) of a food product is the H_R of an atmosphere in equilibrium with the product. In other words, the a_w of a solution or a food is equal to the relative partial pressure of water vapor of the solution or food in a confined atmosphere at equilibrium. Therefore, H_R at equilibrium and a_w are proportional physical quantities linked by the following equation:

$$H_{RE} = a_w \times 100 \quad [1.3]$$

Some authors believe that such a thermodynamic equilibrium is never reached in the case of food. The a_w values obtained from measurements on food should therefore not be considered as absolute.

The a_w of a food product accounts for the availability of water as a solvent or a reagent. As a result, a_w is crucial in estimating the stability of food during processing and storage. The relative rates of change in food as a function of a_w are clearly illustrated in Figure 1.2. For low a_w values (< 0.1), the risk of lipid oxidation is very high. This negative correlation with a_w in this range can be explained by the fact that a monolayer of water molecules around the lipid fraction constitutes a resistance to oxygen transfer and, thus, a protective shell against lipid oxidation. For a_w values between 0.3 and 0.8, the reaction rates linked to non-enzymatic browning (maximum of 0.6–0.7 a_w), non-enzymatic hydrolysis and enzymatic activity gradually increase with a_w. There is very little microorganism growth when a_w is less than 0.6. Efstathiou *et al*. [EFS 02] estimated an optimum stability range for a_w values of between 0.2 and 0.3.

During freezing, the a_w of ice is calculated by using the vapor pressure value of subcooled water at the corresponding temperature as a reference [BLO 02]. It is equal to 1 at 0°C and decreases with temperature (see Table 1.5).