

Food Additives

Up until about 1906, food handled in the United States was often produced and processed under unsafe and unsanitary conditions and there was little control over chemical additives used as preservatives or colorings. In 1906, Upton Sinclair published his book entitled *The Jungle*, which was based upon the meat-packing industry in Chicago. In the book, Sinclair intended to focus on poor working conditions and exploitation of workers, but his description of how meat products were handled led to the passage of the Meat Inspection Act of 1907 and the Federal Food and Drug Act of 1906. At that time, it was quite common to have floor sweepings added to pepper, ash leaves to tea, brick dust to cocoa, copper salts to pickles and peas, and lead salts to candy. Approximately 80 different dyes were used in foods, and sometimes the same batch used for coloring textiles was used for coloring food.

In 1903, Dr. Harvey Washington Wiley, then the Chief of Bureau of Chemistry of the U.S. Department of Agriculture, established a “poison squad” that consisted of young men who consumed foods treated with known amounts of chemicals commonly used in foods. The goal of the project was to determine whether these compounds were deleterious to health. The result of the efforts of Dr. Wiley and the “squad” was the passage of the Food and Drug Act of 1906, which is also referred to as “The Pure Food Act.”

The Bureau of Chemistry was the enforcement agency of the 1906 Act until 1927, when research and enforcement functions were separated and the Food, Drug and Insecticide Administration was established. The name of this organization was changed to the Food and Drug Administration (FDA) in 1931, and in 1940 it became a unit of the Department of Health and Human Services. In 1938, the Food, Drug and Cosmetic Act (FD&C Act) was passed into law. This Act gave the government authority to conduct on-site inspections and provide for the establishment of standards of identity for individual food products. The Act also allowed the government to obtain federal court injunctions against violators.

Food additives have been defined as chemical substances deliberately added to foods, directly or indirectly, in known and regulated quantities, for purposes of assisting in the processing of foods; preservation of foods; or in improving the flavor, texture, or appearance of foods.

In September of 1958, the FD&C Act was amended to prohibit the use of food additives that had not been adequately tested to establish their safety. The term food additive was defined as follows:

... any substance the intended use of which results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of any food (including any substance intended for use in

producing, preparing, treating, packaging, transporting or holding food; and including any source of radiation intended for any such use), if such substance is not generally recognized among experts qualified by scientific training and experience to evaluate its safety, as having been adequately shown through scientific procedures (or in the case of a substance used in food prior to January 1, 1958, through either scientific procedures, or experience based on common use in food) to be safe under the conditions of its intended use . . .

An additive may be reactive or inactive; it may be nutritive or nonnutritive; it should be neither toxic nor hazardous. Some substances, such as pesticides, are added to foods unintentionally, and these are, of course, undesirable, and may be hazardous to health. Because of their toxicity, their presence is closely regulated by strict government tolerance guidelines. The Environmental Protection Agency (EPA), established in 1970, is responsible for establishing tolerances for pesticides and the FDA is responsible for monitoring and ensuring compliance to these tolerances for agricultural commodities.

As a result of the Food Additives Amendment of 1958, the term "Generally Recognized as Safe" (GRAS) evolved. Additives are classified as GRAS when they have been used without apparent harm for long periods of time, long before regulations had been put into effect. These include substances such as baking powder chemicals (e.g., sodium bicarbonate), fruit acids such as citric and malic, and gums such as agar-agar. The purpose of this list was to recognize the safety of basic substances without complicated safety testing.

To get new food additives approved, a petition must be submitted to FDA that contains scientific data that clearly show that the intended chemical is harmless in the intended food application at the intended use level. The burden of proving the safety of the additive lies with the company that wishes to use or sell the chemical. This testing can often require several years because the FDA often requires that the additive undergo at least a 2-year feeding study in two species of animals. These studies must reveal both long-term and short-term effects.

A very controversial clause was included in the Food, Drug and Cosmetic Act. A portion of it stated that:

“. . . no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal.”

This clause, known as the Delaney Clause or Amendment, is named after Representative James Delaney of New York, who introduced it into the legislation. It essentially states that if the additive, at any level, can produce cancer in humans or animals or can be shown to be carcinogenic by any other appropriate test, it will not be allowed. This has been a very controversial clause because, although it was added to ensure safety, some additives may cause cancer in some species of animal when fed at levels that would not be possible for humans to ingest under normal food consumption. The use of informed scientific judgment in regulatory decisions may result in a modification of the Delaney Clause in the future.

Ionization radiation is considered an additive because the treatment may induce changes in food. In this case, the FDA tests foods that have been irradiated and approves irradiation sources and maximum dosages.

Besides the requirements mentioned, food additives must also meet five general criteria:

1. Intentional additives must perform their intended function.
2. Additives must not deceive the consumer or conceal faulty ingredients or defects in manufacturing practices.
3. Additives cannot considerably reduce the food's nutritional value.
4. An additive cannot be used to achieve an effect that could be gained by good manufacturing practices.
5. A method of analysis must exist to monitor the use of the additive in foods or its incidental occurrence in foods (such as migration from a packaging material).

PHILOSOPHY OF FOOD ADDITIVES

Foods are made entirely of substances that, in the pure form, can be described as chemicals or chemical compounds. It is important to note that our knowledge of the composition of foods, because of its complexity, is by no means complete. For instance, it is reported that one of the most important of our natural foods, human milk, contains several hundred chemical compounds.

Unfortunately, the interpretation of the word *chemical* is too often inaccurate. Thus, some consumers are apprehensive about purchasing a food that is preserved by treating it with a chemical with which they are unfamiliar. However, a number of foods may be preserved with table salt, which is a chemical. Consumers are not apprehensive about using salt as a preservative, because they are familiar with it, at least for adding taste and sometimes for bringing out the flavor in foods, yet table salt is definitely a chemical, with the name sodium chloride, and the formula NaCl. Refined sugar, vinegar, spices, and other substances that are routinely added to foods are also chemicals or mixtures of chemicals, and the use of these is not questioned. The characteristics of chemicals that we use with confidence are familiarity and frequent use. The characteristics of chemicals that arouse skepticism in consumers are that they are uncommon and unfamiliar.

A large number of chemical additives are unfamiliar, and there is a need for regulatory agencies to question their use from the standpoint of safety. Obviously then, we should not fear the use of chemicals, but we do need to screen them for safety when their effects on human health are not known. Some lessons have been learned along these lines. For example, indiscreet use of certain additives for coloring candy and popcorn was reported to have caused diarrhea in children, resulting in the removal of these dyes from the FDA approved list of additives. There are a number of related concepts that must be remembered when dealing with food additives:

- All foods are composed of chemical compounds, many of which can be extracted and added to other foods, in which case they are classified as additives.
- Any additive or chemical compound can be injurious to health when particularly high levels of that compound are added to foods.
- Any additive or chemical compound can be safe to use when particularly low levels of that compound are added to foods.
- It is necessary to evaluate each additive for usefulness and toxicity in a sensible, scientific way, regardless of how safe its proponents say it is and how toxic its opponents say it is.

The use of radiation for preserving foods has been declared an additive, and whether or not it should be approved by the FDA makes it the prime example of extreme opposition and extreme favor. Quite often, the tendency to take a strong position for the use of an additive might make a proponent rationalize or overlook undesirable investigative scientific data concerning the additive. On the other hand, opponents tend to make irrational demands of investigators to prove the safety of an additive; for example, opponents of the use of radiation for preserving foods have suggested that radiation should not be approved for preserving foods until all possible chemical effects of the process have been identified. This, without going into detail, is an impossible task. It would be just as impossible to identify all the chemical effects of frying foods and of baking food.

Given present capabilities, our most reasonable evaluation of an additive for safety can be made through conventional animal feeding studies. The overall physiological effects that an additive may have on animals of two or three different species over a specified number of generations is the most comprehensive, as well as the most reliable, way to evaluate the safety of a food additive.

It should be remembered that chemical materials cannot be added to foods unless their use, in the quantities added, has been approved by the FDA. Moreover, additives are tested for toxicity in concentrations much greater than those allowed in foods. It should also be remembered that most food additives are components of natural foods and that without these additives the quality of many foods would be greatly inferior to that to which we have become accustomed. The shelf-life or availability of many foods would also be greatly limited were all additives to be eliminated from foods. Food additives are difficult to classify mainly because they overlap each other in numerous combinations of effects. It should be remembered, therefore, that the following classifications are not precise.

Food additives may be used for a number of reasons. At present, over 3000 intentional additives are allowed and they can be divided into several major groups. In this chapter, the major groups are covered and representative additives from each group are mentioned. No attempt is made to cover every food additive that exists.

ANTIOXIDANTS

Antioxidants are food additives used, since about 1947, to stabilize foods that by their composition would otherwise undergo significant loss in quality in the presence of oxygen. Oxidative quality changes in foods include: (1) the development of rancidity from the oxidation of unsaturated fats resulting in off-odors and off-flavors and (2) discoloration from oxidation of pigments or other components of the food.

There is a large number of antioxidants, and although they may function in different ways, the purpose of each is to prevent, delay, or minimize the oxidation of the food to which they are added. One of the ways by which some antioxidants function involves their combination with oxygen. Others prevent oxygen from reacting with components of the food. When only a limited amount of oxygen is present, as in a hermetically sealed container, it is possible for some antioxidants to use up all of the available free oxygen, because they have a relatively great affinity for it. Some antioxidants lose their effectiveness when they combine with oxygen; therefore, there is no advantage to using this type of antioxidant unless the food is enclosed in a system from which oxygen or air can be excluded. With the use of antioxidants, it should be noted that

other precautions are necessary to minimize oxidation, because heat, light, and metals are prooxidants, that is, their presence favors oxidative reactions. Many of the antioxidants used commercially occur naturally in foods (e.g., vitamin C, vitamin E, citric acid, amines, and certain phenolic compounds). However, the amines and the phenolic compounds can be toxic to humans in low concentrations; therefore their use and that of synthetic antioxidants require strict regulation. It should be pointed out that the potency of the naturally occurring antioxidants is not as great as that of the commonly used synthetic antioxidants. The antioxidants that are considered to be the most effective and therefore are most widely used are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propylgallate. These are generally used in formulations that contain combinations of two or all three of them, and often in combination with a fourth component, frequently citric acid. The main purpose of adding citric acid is that it serves as a chelator or sequestrant (a chelator ties up metals, thereby preventing metal catalysis of oxidative reactions).

Fats and shortenings, especially those used in bakery goods and fried foods, are subject to oxidation and the development of rancidity after cooking. To prevent this, chemical antioxidants in concentrations up to 0.02% of the weight of the fat component may be added.

The use of antioxidants is regulated by the FDA and is subject to other regulations, such as the Meat Inspection Act and the Poultry Inspection Act. Their use is limited so that the maximum amount that can be added is generally 0.02% of the fat content of the food; however, there are some exceptions to, and variations of, that rule.

NUTRIENT ADDITIVES

The need for a balanced and ample nutrient intake by the human body is well known. Although nutrients are available in foods, losses of fractional amounts of some of them through processing and increasing frequency of improper dieting have led to the practice of adding minimum daily requirements or sizable fractions of minimum daily requirements of a number of nutrients to popular foods, such as breakfast cereals, baked goods, pasta products, and low-calorie breakfast drinks. Nutrient additives include mainly vitamins, proteins, and minerals.

Vitamin D is an exceptional example of the value of the food additive concept. The major source of vitamin D for humans is a precursor compound called 7-dehydrocholesterol which is produced in the liver. It circulates to an area just under the skin and is converted to previtamin D₃ by the ultraviolet rays of sunlight. Previtamin D₃ then goes through a number of steps and is converted to vitamin D₃ and finally to active vitamin D. However, in many cases, exposure to the sun is sporadic and insufficient, especially in areas where there is normally insufficient sunshine or in cases where sunlight exposure is of insufficient duration. Thus, vitamin D is added to nearly all commercial milk in a ration of 10 micrograms of vitamin D (as cholecalciferol). This is equivalent to the old 400 IU per quart (0.95 liter). Vitamins A and C and some of the B vitamins are also added to some foods.

The addition of protein concentrate (produced from fish or soybeans) to components of the diet of inhabitants of underdeveloped countries has been used successfully to remedy the high incidence of protein malnutrition. It should be noted that soybean protein is incomplete and requires the addition of some amino acids in which it is

deficient. Children, especially, succumb in large numbers to the disease, kwashiorkor, that results from insufficient protein intake.

Among minerals, iron has received major attention as a food additive, mainly because of its role in preventing certain anemias.

FLAVORINGS

Flavorings are compounds, natural or synthetic, that are added to foods to produce flavors or to modify existing flavors. In the early days of human existence, salt, sugar, vinegar, herbs, spices, smoke, honey, and berries were added to foods to improve their taste or to produce a special, desirable taste. The variety of natural and synthetic flavorings available to the modern food technologist is very large. Essential oils provide a major source of flavorings. Essential oils are odorous components of plants and plant materials that give the characteristic odors of the materials from which they are extracted.

Because of the large production of orange juice, quantities of essential oil of orange are produced as byproducts. For this reason, there is little need for the production of synthetic orange flavoring.

Fruit extracts have been used as flavorings, but these are relatively weak when compared to essential oils and oleoresins. An oleoresin is a solvent extract of spices from which the solvent, usually a hydrocarbon, has been removed by distillation. Because of their weak effects, fruit extracts may be intensified by combining them with other flavorings.

Synthetic flavorings are usually less expensive and more plentiful than natural flavorings. On the other hand, natural flavorings are often more acceptable, but they are quite complex and difficult to reproduce synthetically. In fact, one of the problems with natural flavorings is that they may vary according to season and other uncontrollable factors. Synthetic flavorings, however, can be reproduced quite accurately. Many artificial flavors, such as amyl acetate (artificial banana flavor), benzaldehyde (artificial cherry flavor), and ethyl caproate (artificial pineapple flavor), are added to confectioneries, baked products, soft drinks, and ice cream. These flavorings are added in very small amounts, often 0.03% or less.

FLAVOR ENHANCERS

Flavorings either impart a particular flavor to food or modify flavors already present. Flavor enhancers, on the other hand, intensify flavors already present, especially when the desirable flavors are relatively weak. Monosodium glutamate (MSG) is one of the best known and most widely used flavor enhancers. This compound occurs naturally in many foods and in a certain seaweed that was used for centuries as a flavor enhancer in soups and other foods. It is only within the last hundred years that the reason for the effectiveness of the seaweed was discovered to be MSG. While it is effective at relatively low levels (parts per thousand), there are other compounds called flavor potentiators that also enhance flavors but are extremely powerful, effective in parts per million and even per billion. These compounds have been identified as nucleotides, and their effect is attributed to their synergistic properties (properties that intensify

the effect of natural flavor components). Two in this group are disodium inosinate and disodium GMP.

Several theories attempt to explain how MSG and other flavor enhancers and potentiators work. One theory is that they increase the sensitivity of the taste buds, thus increasing flavor. A second suggests that an increase in salivation as a result of the flavor enhancers will increase flavor perception. A third theory of intensified flavor perception is based on the observation that flavor enhancers produce certain physical sensations in the mouth such as coolness and heat.

ACIDULANTS

From the root word, *acid*, in acidulants, one can conclude that this class of compounds tends to lower the pH of any food into which the compounds are incorporated. Acidulants also enhance desirable flavors, and in many cases, such as in pickled products, are the major taste component. Vinegar (acetic acid, CH_3COOH) is added to relishes, chili sauce, ketchup, and condiments as a flavor component and to aid in the preservation of these products. Because the microbial spoilage of food is inhibited as the pH is lowered, acidulants are used for that purpose in many cases. Many acidulants occur naturally in foods (e.g., citric acid in citrus fruits, malic acid in apples, acetic acid in vinegars; all three are contained in figs). Tartaric acid is widely used to lend tartness and enhance flavor. Citric acid is widely used in carbonated soft drinks. Phosphoric acid is one of the very few inorganic acids used as an acidulant in foods. It is widely used, comprising 25% of all the acidulants in foods. Citric acid accounts for 60% of all acidulants used in foods.

In addition to their preservative and flavor enhancing effects, acidulants are used to improve gelling properties and texture. Acidulants are also used as cleaners of dairy equipment.

Acidulants may be used in the manufacture of processed cheese and cheese spreads for the purpose of emulsification as well as to provide a desirable tartness.

Acid salts may be added to soft drinks to provide a buffering action (buffers tend to prevent changes in pH) which will prevent excess tartness. In some cases, acid salts are used to inhibit mold growth (e.g., calcium propionate added to bread).

As has been pointed out, all microorganisms have a pH at which they grow best (see Chapter 3), and a range of pH above or below which they will not grow. Generally, it is not possible to preserve all foods by adding acid to the point where microorganisms will not grow. Most foods would be too acid to be palatable. The amount of acid may be enough to inhibit the growth of microorganisms provided that such treatment is combined with some other method of preservation. Certain dairy products, such as sour cream, and fermented vegetables, such as sauerkraut, are preserved with lactic acid produced by the growth of bacteria. Addition of the acid, along with holding at refrigerator temperatures above freezing, in combination will prevent growth of pathogenic and spoilage organisms. When sauerkraut is canned, it is given a heat process sufficient to destroy all spoilage and disease microorganisms.

Pickles are preserved by the addition of some salt, some acid, and a heat process sufficient to raise the temperature of all parts of the food to or near 212°F (100°C).

Pickled herring are preserved by the addition of some salt, some acetic acid (vinegar), and holding at refrigerator temperatures above freezing. In this case, the nonacid part of the acetic acid molecule has an inhibiting effect on the growth of microorganisms.

ALKALINE COMPOUNDS

Alkaline compounds are compounds that raise the pH. Alkaline compounds, such as sodium hydroxide or potassium hydroxide, may be used to neutralize excess acid that can develop in natural or cultured fermented foods. Thus, the acid in cream may be partially neutralized prior to churning in the manufacture of butter. If this were not done, the excess acid would result in the development of undesirable flavors. Sodium carbonate and sodium bicarbonate are used to refine rendered fats. Alkaline compounds are also added to chlorinated drinking water to adjust the pH to high enough levels to control the corrosive effects of chlorine on pipes and equipment. Sodium carbonate is also used in conjunction with other compounds to reduce the amount of hardness in drinking water. Sodium hydroxide is used to modify starches and in the production of caramel. Sodium bicarbonate is used as an ingredient of baking powder, which is used in baked products. (It is also a common household item used in a variety of cooking recipes.) Its action is described in the "Leavening Agents" section of this chapter. Alkaline compounds are used in the production of chocolate and to adjust the acidity level in grape juice and other fruit juices that are to be fermented in the production of wine.

It is important to note that some alkaline compounds, such as sodium bicarbonate, are relatively mild and safe to use, while others, such as sodium hydroxide and potassium hydroxide, are relatively powerful reagents and should not be handled by inexperienced people.

SWEETENERS

Sweetening agents are added to a large number of foods and beverages. Table sugar (sucrose), the most commonly used sweetener in the country, and corn syrup, are covered in Chapter 22 and therefore are not described in any detail here. Sweeteners include other sugars, as well as an abundance of natural and synthetic agents of varying strengths and caloric values.

Many sweeteners are classified as nonnutritive sweeteners. Although this classification might imply a lack of nutritional value, the implication is correct only in a relative sense. That is, the caloric value of a nonnutritive sweetener, such as aspartame, is about 4 cal/g, the same as that for sugar. However, because it takes only 1 g of aspartame to provide the same sweetness level as about 180 g of sugar (sucrose), it can be seen that the caloric contribution of aspartame is only about 0.5% that of sucrose. It is on this basis that a nonnutritive sweetener is classified as such.

The sweeteners described in this chapter are fructose, molasses, honey, maple sugar, lactose, maltose, some polyhydric alcohols (xylitol, sorbitol, mannitol), aspartame, saccharin, glycyrrhizin, and acesulfame K.

Fructose

Of the natural sugars other than sucrose used by humans, fructose (also known as levulose), a monosaccharide ($C_6H_{12}O_6$), is the sweetest (nearly twice as sweet as table sugar, sucrose) and it is the most water-soluble. It is hygroscopic, making it an excellent humectant when used in baked goods. The value of a humectant in baked goods is

that it retards dehydration. Solutions of fructose have a low viscosity that results in lower “body” feel than sucrose but have greater flexibility of use over a wide range of temperatures. Because of its greater solubility and more effective sweetness than sucrose, fructose is a better choice than sucrose when very sweet solutions are required, as fructose will not crystallize out of solution, whereas sucrose will. Fructose has sometimes been called fruit sugar, since it occurs in many fruits and berries. It also occurs as a major component in honey, corn syrup, cane sugar, and beet sugar. In fact, sucrose, a disaccharide, is composed of glucose and fructose. Of these two components, the glucose moiety, or portion, cannot be metabolized by people with diabetes, and it is for this reason that the ingestion of sucrose cannot be tolerated by them. Fructose, on the other hand, does not require insulin for its metabolism and can, therefore, be used by diabetic individuals. Its use also appears to reduce the incidence of dental caries. When used with saccharin, it tends to mask the bitter aftertaste of saccharin. As it apparently accelerates the metabolism of alcohol, it has been used to treat those suffering from overdoses of alcohol. It has been recommended as a rapid source of energy for athletes and, in combination with gluconate and saccharin, as an economic, effective, safe, low-calorie sweetener for beverages.

Molasses

Molasses can be considered a byproduct of sugar production (see Chapter 22). The use of molasses as a sweetener in human foods is largely in baked goods that include bread, cookies, and cakes. In addition to sweetening, molasses adds flavor and acts as a humectant. It is also used in baked beans and in the production of rum and molasses alcohol. (The greatest use of molasses, however, is in the production of animal feed). Molasses comprises about 60% sucrose, but the sucrose content can be lower, depending on the grade of the molasses and on the raw material from which it was produced. Thus, the sucrose content of cane blackstrap (the final fraction of cane molasses) is only about one-half that of beet blackstrap (the final fraction of beet molasses). The fractions produced before the blackstrap are of higher grades and are those usually used for human consumption. Blackstrap generally is used for industrial purposes.

Honey

Honey, a natural viscous syrup, comprises mainly invert sugar. It is produced from the nectar of flowers, which is mainly sucrose, by the action of an invertase enzyme that is secreted by the honey bee. Honey is used as a direct sweetener, as an additive in a number of products, including baked goods, as well as in other ways. It is relatively expensive.

Invert sugar, corn sugar, and corn syrup are covered in Chapter 22 and are not covered here.

Maple Sugar

Maple sugar is produced from the sap of the sugar maple tree. It is comprised mainly of sucrose and small amounts of other sugars, including invert sugar. Maple sugar is used in the manufacture of candies, fudge, baked goods, and toppings. It is among the most expensive of sweeteners.

Lactose

Lactose ($C_{12}H_{22}O_{11}$), the sugar component of mammalian milk, is less sweet and less water-soluble than sucrose. Although most babies and young children generally are able to metabolize this sugar, some are unable to do so. The ability to metabolize the sugar appears to decrease with age. When a person is unable to metabolize lactose, the ingestion of milk may cause intestinal discomfort, cramps, and diarrhea. The major source of lactose is whey, a cheese byproduct. Because lactose is not as sweet as sucrose, larger amounts can be used in those foods in which the texture benefits from a high solids content.

Maltose

Maltose ($C_{12}H_{22}O_{11}$), or malt sugar, is produced during the malting process in brewing (enzyme conversion of starch). It is converted to alcohol by the action of yeasts through an intermediate conversion to dextrose. This sugar is much less sweet than sucrose, and it is used mainly in the manufacture of baked goods and infant foods.

Xylitol

Xylitol is a polyhydric alcohol having the formula ($C_5H_7(OH)_5$). At present it is used as a sweetener in chewing gum, mainly because of its noncariogenic property (it has not been found to cause tooth decay). It occurs naturally as a constituent of many fruits and vegetables, and is a normal intermediary product of carbohydrate metabolism in humans and in animals. Commercially, it is produced by the hydrolysis of xylan (which is present in many plants) to xylose, which is then hydrogenated to produce xylitol. The xylitol is then purified and crystallized. Xylitol imparts a sweet taste, which also appears to have a cooling effect. As it is not metabolized by many microorganisms, it is quite stable.

Sorbitol

Sorbitol is a polyhydric alcohol ($C_6H_8(OH)_6$) that is found in red seaweed and in fruits (apples, cherries, peaches, pears, and prunes). It was first isolated from the sorb berries of the mountain ash, hence its name. It is used as an additive because of its humectant property as well as its sweetening effect. It is used in cough syrup, mouthwashes, and toothpastes. Another of its desirable properties is that it is not easily fermented by microorganisms. Because sorbitol is largely transformed to fructose by liver enzymes in the body, it is tolerated by diabetic individuals, as fructose is not dependent on the availability of insulin for its metabolism. Sorbitol can be produced industrially by the electrochemical reduction or catalytic hydrogenation of glucose.

Mannitol

Mannitol is a polyhydric alcohol having the formula ($C_6H_8(OH)_6$). It is used in chewing gum, pharmaceuticals, and in some foods. It is a naturally occurring sweetener in many plants, algae, and mold. It occurs in the sap of the manna tree, an ash native to southern Italy, and can also be made by the reduction of either of the monosaccharides

mannose or galactose. Industrially, it is produced by electrochemical reduction or catalytic hydrogenation methods. Although it is similar to sorbitol in many respects, it is less soluble than sorbitol.

Aspartame

Aspartame is the common name for aspartyl-phenylalanine. It is a combination of the two amino acids from which its name is derived. First produced in 1969, it is reputed to be about 180 times sweeter than sucrose. Like cyclamate, it was approved and later banned by the FDA. Exhaustive evidence of its safety has been presented by animal testing and by definition of its metabolic fate in animals and humans. It was subsequently reinstated as safe for use by the FDA.

Unlike saccharin and cyclamate, aspartame leaves no bitter aftertaste. It is quite expensive, about 200 times more so than sucrose, but as it is about 180 times sweeter than sucrose, its cost for obtaining a given unit of sweetness is not much more.

Saccharin

Saccharin, the imide of *o*-benzosulfonic acid, is used as a sodium or calcium salt. It is about 300 times sweeter than sucrose (table sugar). It may leave a bitter aftertaste, and its safety has been questioned as a result of some animal feeding tests. As an intense sweetener it is useful for diabetic individuals, and it reduces the incidence of dental caries.

STARCHES

Although starches differ from each other somewhat, depending on the plant from which they are extracted, they are sufficiently similar chemically to be often classified together as starch. The two basic starch polymers are amylose and amylopectin. Starch is used as a source of carbohydrate, and because it is relatively inexpensive, is often used as an extender. Its properties also make it useful as a thickening agent. The major source of starch is corn, but some starch is also produced from sorghum, potatoes, and wheat. More on starches is discussed in Chapters 2 and 18.

GUMS

Gums, a class of complex polysaccharides, are defined as materials that are dispersible in water and capable of making the water viscous. Many gums occur naturally in certain land and sea plants. Examples are gum arabic and agar. Many gums, such as the cellulose derivatives, are modified or semisynthetic, and some gums, such as the vinyl polymers, are synthetic. Gums are used to stabilize ice cream and desserts, thicken certain beverages and preserves, stabilize foam in beer, emulsify salad dressings, and form protective coatings for meat, fish, and other products. Gums add "body" and prevent settling of suspended particles in chocolate milk, ice cream, and desserts.

They may also prevent the formation of large ice crystals in frozen desserts. A significant potential for the use of gums lies in the production of certain low-calorie foods. For example, the oil in salad dressing can be replaced with gums to result in a product with the normal appearance, texture, and taste but without the calories normally associated with the product.

ENZYMES

Enzymes occur naturally in foods, and their presence may be either beneficial or detrimental, depending on the particular enzyme (see Chapter 8). When the presence of enzymes is undesirable, steps are taken to inactivate them. When their presence is desirable, either the enzymes or sources of the enzymes are intentionally added to foods. For example, the enzyme papain (from the papaya fruit) is added to steak to tenderize it. Many of the useful enzymes used in food processing are produced by microbes; consequently those microbes producing the desired enzyme may be added intentionally to food. For example, specific yeasts are intentionally added in the production of bread, beer, or cheese.

The use of enzymes as food additives presents no problem from the standpoint of safety, because enzymes occur naturally, are nontoxic, and are easily inactivated when desired reactions are completed. Enzymes called amylases are used together with acids to hydrolyze starch in the production of syrups, sugars, and other products.

Invertase

Certain enzymes, such as invertase, split disaccharides, such as sucrose (table sugar), to lower sugars (glucose and levulose). Invertase has many applications, and is used, for example, to prevent crystallization of the sucrose that is used in large amounts in the production of liqueurs. Without invertase, the liqueurs would appear cloudy.

Pectinase

Pectinases are enzymes that split pectin, a polysaccharide that occurs naturally in plant tissues, especially those of fruit. Pectin holds dispersed particles in suspension, as in tomato juice. Because it is desirable to keep the thick suspension in tomato juice, pectinases that occur naturally in it are inactivated by heat. On the other hand, products such as apple juice are customarily clear, and this is accomplished by adding commercial pectinase to the product, which degrades the pectin in the apple juice, resulting in the settling out of the suspended particles, which are then separated from the clear juice. In the manufacture of clear jellies from fruits, it is first necessary to add pectinase to destroy the naturally occurring pectin in order to clarify the juice. This pectinase must now be inactivated by heat. Then more pectin must be added to the clarified juice to produce the thick consistency of jelly. If the pectinase is not inactivated after clarification, the enzyme would also break down the newly added pectin required to produce the thick consistency.

Cellulases

Cellulases are enzymes that can break down cellulose, said to be the most abundant form of carbohydrate in nature. Cellulose, the principal structural material in plants,

is insoluble in water and is indigestible by humans and many animals. Ruminants are able to digest cellulose because of a cellulase (produced by microorganisms in the large stomach) contained in their gastric juice. Commercial applications of cellulases are not widespread at present. Cellulases are used for tenderizing fibrous vegetables and other indigestible plant material for the production of foods or animal feed.

Proteases

Proteases are enzymes that break down proteins, polypeptides, and peptides. Peptides are the structural units of which polypeptides consist, and polypeptides are larger structural units that make up the protein. There is a large number of specific proteases, and each attacks protein molecules at different sites, producing a variety of end products. Proteases are used to produce soy sauce from roasted soybeans, cheese from milk, and bread dough from flour. They are also used to tenderize meat and chill-proof beer which, if untreated, develops an undesirable haze when chilled.

Lipases

Lipases, the lipid (fat or oil) splitting enzymes, have limited commercial application, with oral lipases having the widest. Lipases prepared from oral glands of lambs and calves are used in a controlled way in the production of certain cheeses and other dairy products, as well as lipase-treated butter fat used in the manufacture of candles, confections, and baked products. Lipases are also used to remove fat residuals from egg whites and in drain cleaner preparations.

Glucose Oxidase

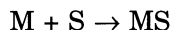
Glucose oxidase is an enzyme that specifically catalyzes the oxidation of glucose to gluconic acid. This reaction is important in preventing nonenzymatic browning, because glucose is a reactant in the undesirable browning reaction. The most important application of this enzyme is in the treatment of egg products, especially egg whites, prior to drying. Eggs treated with this enzyme before they are dried do not undergo nonenzymatic browning during storage, because the sugar has been removed. In some cases, the enzyme is added to remove traces of oxygen to prevent oxidative degradation of quality. Examples of this type of application are mayonnaise and bottled and canned beverages (especially beer and citrus drinks).

Catalase

Catalases are used to break down hydrogen peroxide (H_2O_2) to water and oxygen. Therefore, catalases are used when the presence of hydrogen peroxide is undesirable or when hydrogen peroxide is used for specific purposes, such as in bleaching, but then must be removed from the system. Examples of the latter case are the uses of hydrogen peroxide for preserving milk in areas where heat pasteurization and refrigeration are unavailable and in the manufacture of cheese from unpasteurized milk. Hydrogen peroxide is produced during the spray-drying process. Catalase is used to convert the unwanted H_2O_2 to water and oxygen.

SEQUESTRANTS

The role of sequestrants is to combine with metals, forming complexes with them and making them unavailable for other reactions.



where

M = metal

S = sequestrant

MS = complex.

Sequestrants, like many other additives used for enhancing specific properties of foods, occur naturally in foods. Many sequestrants have other properties; for example, citric, malic, and tartaric acids are acidulants but they also have sequestering properties.

Because metals catalyze oxidative reactions, sequestrants can be considered to have antioxidant properties. Thus, they stabilize foods against oxidative rancidity and oxidative discoloration. One of the important uses of sequestrants as additives is to protect vitamins, as these important nutrients are especially unstable when exposed to metal-catalyzed oxidation. Sequestrants are used to stabilize the color of many canned products and they help stabilize antioxidants. Sequestrants are especially helpful in stabilizing color and lipids in canned fish and shellfish. Because fish and shellfish naturally contain relatively high concentrations of metal, these products normally have poor color stability, and the lipids tend to rancidify during storage.

Sequestrants are also used to stabilize the flavors and odors in dairy products and the color in meat products.

POLYHYDRIC ALCOHOLS

In addition to their use as sweeteners, many polyhydric alcohols (also called polyols) are used to improve texture and moisture retention because of their affinity for water. Many polyols are present in foods naturally, glycerine (glycerol) being the predominant one. However, only four of the many polyols are allowed as food additives. They are glycerine, sorbitol, mannitol, and propylene glycol. All but the last have a moderately sweet taste (see section on sweeteners), although none are as sweet as sugar. Propylene glycol has a somewhat undesirable bitter taste, but is acceptable in small amounts. Sorbitol imparts a cool sensation. Glycerine, on the other hand, imparts a hot sensation.

Polyols are used in the production of dietetic products including beverages, candy, gum, and ice cream to contribute to texture as well as to sweetness. These compounds have a less adverse effect on teeth than sugar, because they are not fermented as quickly as sugar and are usually washed away before they can be utilized by microorganisms.

SURFACE-ACTIVE AGENTS

Surface-active agents affect the physical force at the interface of surfaces. Commonly called surfactants, they are present in all natural foods, because by their nature they

play a role in the growth process of plants and animals. They are defined as organic compounds that affect surface activities of certain materials. They act as wetting agents, lubricants, dispersing agents, detergents, emulsifiers, solubilizers, and so forth. One use for wetting agents is to reduce the surface tension of materials to permit absorption of water by the material. An example of their use is in powdered chocolate mixes used to prepare chocolate milk by addition of water.

Dispersions of materials depend on the reduction of interfacial energy, and this can be accomplished by certain surfactants.

Surfactants are used in the production of foods to prevent sticking, such as in untreated peanut butter. Surfactants are also used in cleaning detergents used on food equipment, and they can stabilize or break down foams.

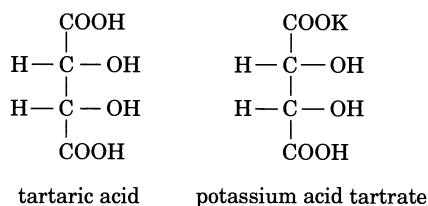
Emulsifiers, such as lecithin, mono- and diglycerides, and wetting agents, such as a class of chemicals known as "tweens," may be added to bakery products (to improve volume and texture of the finished products and the working properties of the dough and to prevent staling of the crumb), cake mixes, ice cream, and frozen desserts (to improve whipping properties). Except for the tweens, the chemicals cited above are natural components of certain foods.

LEAVENING AGENTS

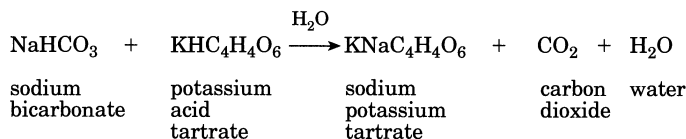
Leavening agents are used to enhance the rising of dough in the manufacture of baked products. Inorganic salts, especially ammonium and phosphate salts, favor the growth of yeasts, which produce the carbon dioxide gas that causes dough to rise. Chemical reagents that react to form carbon dioxide are also used in baked goods. When sodium bicarbonate, ammonium carbonate, or ammonium bicarbonate is reacted with potassium acid tartrate, sodium aluminum tartrate, sodium aluminum phosphate, or tartaric acid, carbon dioxide is produced. Baking powder is a common household leavening agent that contains a mixture of chemical compounds that react to form carbon dioxide, producing the leavening effect. Baking powder can be either single acting or double acting, giving the desired leavening effect in different products. The chemistry is shown below.

Single-Acting Baking Powder (Quick-Acting Baking Powder):

The CO_2 is liberated when sodium bicarbonate (the base) reacts with potassium acid tartrate (the potassium salt of tartaric acid).



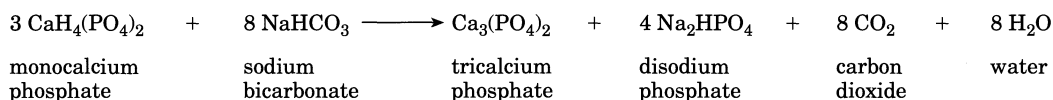
The reaction is as follows:



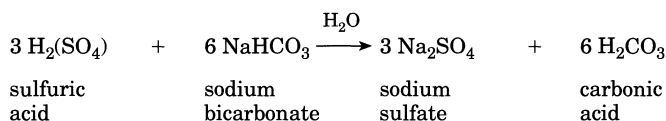
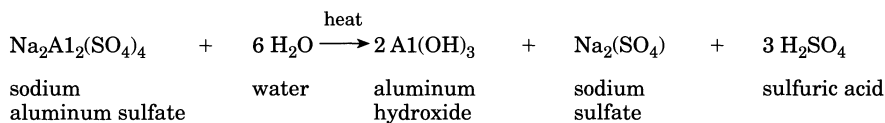
Double-Acting Baking Powder:

The double-acting type has two acid-reacting ingredients (monocalcium phosphate monohydrate and sodium aluminum sulfate). The hydrated form of monocalcium phosphate reacts with sodium bicarbonate to release a portion of CO₂ during mixing a batter or dough. The remaining sodium bicarbonate will react with sulfuric acid which is produced from the sodium aluminum sulfate in hot water.

First action:



Second action:



In this reaction, the major portion of the CO₂ is released after the product is heated in the oven.

IONIZING RADIATION

Earlier in this chapter, the Food Additives Amendment of 1958 was discussed and it was shown that in the definition of a food additive, the statement: “. . . any source of radiation intended for such use . . .” is included. Thus, ionizing radiation is considered a food additive.

Irradiation does not leave a residue in food and it does not make it radioactive. The levels of irradiation allowed in food processing do not induce measurable radioactivity. Any radioactivity found in irradiated foods has been shown to be “background radiation” or that which is already present naturally. Irradiation does, however, cause small chemical changes in the food as do other methods of food processing.

Foods that have been irradiated must be labeled with the green international logo (see Fig. 13.1) to inform the consumer that the food has been processed by ionizing radiation. The words “Treated with Radiation” or “Treated by Irradiation” must also appear and must be in the same print style as the product name and be no smaller than one-third the size of the largest letter in the product name.

The effectiveness of this process is understood and agreed upon, but is it safe? The HACCP program discussed in Chapter 4 was developed to ensure the safety of the astronauts against food poisoning. They ate irradiated food. It has been established that ionization radiation of foods can destroy pathogenic bacteria but what about the



Figure 13.1. International Radiation Logo (green in color)

long-term effects of consumption of these products? The safety of irradiated foods has been tested in feeding studies for over 40 years. The studies include both animal and human subjects. Chemistry studies, feeding studies, and mutagenicity and teratogenicity studies have not revealed any confirmable negative evidence as to the wholesomeness of foods preserved by ionization radiation. Nutrient retention of irradiated foods is comparable to that of heat-processed foods. Irradiated foods may be more susceptible to oxidation but this can be controlled by use of low temperatures and elimination of oxygen.

The future of irradiation of foods is uncertain but it seems that scientific evidence and logic will have more effect on legislation in this area. There will always be risks, so food scientists must decide which will be the least likely cause of danger and proceed accordingly.

CHEMICAL PRESERVATIVES

The practice of preserving food by the addition of chemical is quite old, ordinary table salt (sodium chloride) having been used as a preservative for centuries. It might be surprising to think of a naturally occurring substance as a chemical preservative, but many chemical substances used in the preservation of foods occur naturally. When they are used with the proper intent, they can be used to preserve foods that cannot be easily preserved by other means. They should not be used as a substitute for sanitation and proper handling procedures. Sometimes chemicals are used together with other processes, such as holding at refrigerator temperatures above freezing.

To preserve food, it is necessary either to destroy all of the spoilage microorganisms that contaminate it or to create and maintain conditions that prevent the microbes from carrying out their ordinary life processes. Although preservation is aimed mainly at microbial spoilage, it must be remembered that there are other types of spoilage factors, such as oxidation.

Although foods can be sterilized (such as by heat processing) and contained in such a way as to prevent contamination by microbes during storage, it still is often necessary in some cases to forego sterilization, thus making it necessary to take other steps to prevent microbial degradation of the food. Foods can be protected against microbial attack for long periods (months to years) by holding them at temperatures below freezing (see chapter 12). They can be preserved for shorter periods (several days) by

holding them in ice or in a refrigerator at temperatures in the range 32 to 40°F (0 to 7.8°C) (see Chapter 12). Foods can also be preserved by altering them to make them incapable of supporting microbial growth. Drying is an example of this type of preservation. Foods must also be preserved against color and texture changes.

Quite often it is either impossible or undesirable to employ conventional preservation methods, and a large variety of food additives is available for use, alone or in combination with other additives or with mild forms of conventional processes, to preserve foods. Usually, chemical preservatives are used in concentrations of 0.1% or less. Sodium diacetate and sodium or calcium propionate are used in breads to prevent mold growth and the development of bacteria that may produce a slimy material known as rope. Sorbic acid and its salts may be used in bakery products, cheeses, syrups, and pie fillings to prevent mold growth. Sulfur dioxide is used to prevent browning in certain dried fruits and to prevent wild yeast growth in wines used to make vinegar. Benzoic acid and sodium benzoate may be used to inhibit mold and bacterial growth in some fruit juices, oleomargarines, pickles, and condiments. It should also be noted that benzoic acid is a natural component of cranberries.

Salt is an excellent microbe inhibitor, mainly as a result of its suppression of the water activity of the material to which it is added. Its effectiveness is enhanced when the food is also dried or smoked or both. Smoking also imparts a partial preservative effect.

Weak acids, such as sorbic acid, or salts of weak acids, benzoates, propionates, nitrites, certain chelating agents (chemicals that tie up metals and prevent the catalytic action of metals), and other chemical additives are effective preservatives. Natural spices also have antimicrobial properties. Antibiotics have been used as food additives and are still used to preserve animal feeds and human foods in some countries. Their use in human foods is banned in the United States and in some other countries.

Because many antimicrobial agents are generally toxic to humans, their use must be regulated not to exceed established levels beyond which they are hazardous to human health.

Nitrites, proven inhibitors of *Cl. botulinum*, and nitrates are added to cured meats, not only to prevent botulism, but also to conserve the desirable color as well as add to the flavor of the products. Some of these preservatives are discussed further in this chapter.

Sodium Chloride

When sufficient salt is added to food, it makes water unavailable to microorganisms. Because microorganisms require water to survive, they cannot exist when their water requirement is diminished by the addition of salt. We can reduce the amount of water available to microorganisms by lowering the water activity (a_w). (For more on a_w see Chapter 3.) Microorganisms require high levels of a_w . Most bacteria require a minimum a_w level of 0.96, although halophilic bacteria can grow at a_w of 0.75. Most yeasts grow at a_w levels of 0.90 and above, although a few can grow at an a_w level of 0.81. Molds can grow at lower a_w levels, with some able to grow at an a_w level of 0.62. While salt preserves foods mainly by lowering the a_w , the chloride ion is believed to inhibit bacterial growth, independently.

Some precautions must be observed in the salting preservation of flesh-type foods, such as fish or meats. When these products are salted, several days will be required before enough salt has diffused into all parts of the product to inhibit the growth of microorganisms. If, therefore, precautions are not observed, the growth of spoilage or

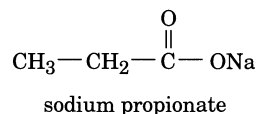
even disease-causing bacteria may occur in some parts of the food before enough salt has diffused into the product to inhibit growth. The usual procedure is to hold products under refrigeration during salting until there has been an adequate "take-up" of salt throughout the food. Fish and meats should never be held at temperatures above 60°F (15.6°C) during salting. Preferably, holding temperatures during such procedures should be at 40°F (4.4°C) or slightly below.

Salted, undried meats, such as corned beef, should be held at 40°F (4.4°C) or below at all times after curing because there are some microorganisms that may still grow at salt concentrations present in such products. Chipped beef, which is dried as well as salted, has a low enough moisture content to prevent the growth of all microorganisms and may be held at room temperature.

Salt cod, which has a moisture content of 40% or higher, should be held at temperatures of 40°F (4.4°C) or slightly below because it is subject to spoilage through bacterial growth. On the other hand, well-dried salt cod and certain types of salted and smoked herring that have dried during smoking may be held at room temperature without spoilage.

Fatty Acids

The salts of certain fatty acids have an inhibitory effect on the growth of microorganisms. Thus, sodium diacetate (a mixture of sodium acetate and acetic acid) and sodium or calcium propionate



are added to bread and other bakery products to prevent mold growth, as well as the development of a slimy condition known as "ropiness," which results from the growth of certain aerobic, spore-forming bacteria (see Chapter 3 for the definition of spore-forming bacteria). Caprylic acid, $\text{CH}_3\text{CH}_2\text{—CH}_2\text{—CH}_2\text{—COOH}$, or its salts or the salts of other fatty acids may be used in cheese to prevent the growth of mold.

As pointed out previously, it is the nonacid part of the molecule of fatty acids or their salts that inhibits the growth of microorganisms. It is believed that the effect of these compounds is the destruction of the cell membrane of microorganisms.

Sulfur Dioxide

Sulfur dioxide (SO_2) is used in some foods to inhibit the growth of microorganisms. Sulfur dioxide may be used as such, or a source of this compound such as sodium bisulfite (NaHSO_3) may be added to the foods. Sulfur dioxide inhibits a rather narrow range of microorganisms and is usually applied together with another chemical inhibitor to prevent the growth of undesirable yeasts or bacteria in fruit juices, which are stored prior to fermentation, in the production of wine or vinegar. Sulfur dioxide may inhibit microbial growth by preventing the utilization of certain carbohydrates as a source of energy or by tying up certain compounds concerned with the metabolism of some microorganisms.

For many years, sulfiting agents have been classified as GRAS (generally regarded as safe) substances by the FDA for use as food preservatives when used in accordance

with GMP (good manufacturing practice). But in 1986, following several deaths from the consumption of fresh fruits or vegetables that had been treated with sulfites, the FDA withdrew the GRAS status of sulfites for this use. It was found that asthmatic individuals react, sometimes severely, when exposed to sulfites. Also, because sulfites have been found to destroy thiamin, these agents may not be used in meats and other foods containing thiamin. Although sulfites may still be used in foods that have not been excluded by the FDA, their presence must be declared on the label when their concentrations exceed 10 ppm (parts per million). Research has shown that in concentrations of 10 ppm or less, these agents should not cause adverse reactions in humans.

Sorbic Acid

Sorbic acid, $\text{CH}_3\text{—CH=CH—CH=CH—COOH}$, inhibits the growth of both yeasts and molds. This compound is most effective at pH 5.0 or below. This compound can be metabolized by humans, as can fatty acids, and hence is generally recognized as safe. Sorbic acid is used in certain bakery products (not yeast-leavened products, because it inhibits yeast growth), in cheeses, and in some fruit drinks, especially for the purpose of preventing molding. It is believed to inhibit the metabolic enzymes required by certain microorganisms for growth and multiplication.

Sodium Nitrite

Sodium nitrite (NaNO_2) is added to some food products to inhibit bacterial growth (especially *Cl. botulinum*) and to enhance color. It is added to most cured meats, including hams, bacon, cooked sausage (such as frankfurters, bologna, salami), and to some kinds of corned beef. Nitrite provides for the red or pink color of the cured and cooked sausages and of the other cured products after cooking. The nitrite combines with the reddish pigment of meat, the myoglobin, and prevents its oxidation. If the meat were not treated with nitrite, it would discolor to a brown color during cooking or during storage. When red meat is heated, as in cooking, the color turns from red to gray or brown as a result of the conversion of myoglobin to the oxidized form, metmyoglobin. On extremely long or extremely high heating or on exposure to light and oxygen, even the nitrated myoglobin may be oxidized to metmyoglobin, with the result that the red or pink color is lost.

In addition to stabilizing the color of cured or cured and cooked meats, the industry claims that nitrite acts as a preservative in that it tends to prevent the growth of spores of *Cl. botulinum* that may be present. *Cl. botulinum*, of course, is the most dangerous disease-causing organism.

Nitrite is also used in some fish products, such as smoked whitefish and chubs, for the specific purpose of preventing the growth of *Cl. botulinum*.

Sodium or potassium nitrite may not be used in meats or on fish that are to be sold as fresh. In cured products, it is allowed in concentrations not to exceed 0.0156% (156 parts of nitrite per million parts of the food). The amounts to $\frac{1}{4}$ oz or 7.09 g per 100 lbs of meat. In practice, however, it is closer to 120 ppm or less. The residual nitrite or that which actually appears in the final product is much less. A study done by Robert Cassens of the University of Wisconsin in 1995 showed residual levels of nitrite as low as 7 ppm for bacon, 6 ppm for sliced ham, and 4 ppm for hot dogs (expressed

as nitrite ion). Numerous factors affect residual nitrite levels but it is accurate to say that the amounts are much lower than that added at the time of processing. There is some question as to whether or not nitrites should be allowed in food in any concentration. It has been found that nitrite-cured products, especially those cooked at high temperatures, such as bacon, may develop nitrosamines, compounds formed by the reaction of nitrites with amines, and nitrosamines are known to be extremely carcinogenic or cancer-promoting. It is clear that the amount of nitrites used must be minimized but the level must remain high enough to protect against botulism and other microbiologically based foodborne diseases.

Cured meats are not the only sources of nitrites in the diet. Vegetables, baked goods, cereals, and water are also sources. Nitrites can also be made in the body from intakes of nitrates (NO_3) by a simple reduction. This can happen in the oral cavity as a result of action of bacteria in the saliva. Vegetables account for about 85% of our dietary intake of nitrates.

Processing methods and formulations have changed dramatically. The result is lowered residual nitrites and decreased levels of volatile nitrosamines. Some estimates are that the levels are one-third of those of a decade ago. This must be placed in proper perspective, however, because it is minor in relation to nitrite synthesized by the body. Steps can be taken to reduce amounts of nitrites ingested but, to ensure microbiological safety, their continued use in cured meats seems inevitable.

Oxidizing Agents

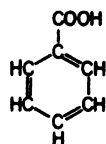
Oxidizing agents, such as chlorine, iodine, and hydrogen peroxide, are not ordinarily used in food, but they are used to sanitize food-processing equipment and apparatus and even the walls and floors of areas where food is processed. Thus, there is no doubt that small residuals, especially of chlorine or iodine, can get into food.

Hydrogen peroxide may be used to destroy the natural bacterial flora of milk, prior to inoculation with cultures of known bacterial species, for producing specific dairy products. In such cases, all of the residual hydrogen peroxide must be removed by treatment with the enzyme catalase (see Chapter 8). This treatment with catalase must be carried out prior to the inoculation of milk with cultures of desirable bacteria; otherwise the hydrogen peroxide will destroy the added bacterial culture, the growth of which is the objective of culturing milk.

Oxidizing agents are believed to inhibit and destroy the growth of microorganisms by destroying certain parts of the enzymes essential to the metabolic processes of these organisms.

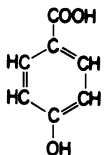
Benzoates

The benzoates and parabenzoates have been used as preservatives mainly in fruit juices, syrups (especially chocolate syrup), candied fruit peel, pie fillings, pickled vegetables, relishes, horseradish, and some cheeses. The probable reason that the benzoates and the related parabenzoates have been allowed as additives to food is that benzoic acid is present in cranberries as a natural component in concentrations that are higher than 0.1%. Benzoic acid or its sodium salt is allowed in food in concentrations up to



benzoic acid

0.1%. Parahydroxybenzoic acid or its esters, for instance, propyl para-hydroxybenzoic acid, may also be used.



para-hydroxybenzoic acid

The benzoates are most effective in acid foods in which the pH is as low as 4.0 or below. The parabenzoates are said to be more effective than the benzoates over a wider range of pH and against wider groups of microorganisms.

Investigations have indicated that benzoates prevent the utilization of energy-rich compounds by microorganisms. It has also been found that when bacteria form spores in the presence of benzoate, the spore may take up water and germinate to the point of bursting and shedding the spore wall, but enlargement and outgrowth into the vegetable cell with subsequent cell division and multiplication does not occur.

COLORANTS

We are accustomed to specific colors in certain food, and colors often provide a clue to the quality of the foods. Color additives can be categorized into three major types: natural, nature-identical, or synthetic.

Many colorants (compounds that add colors to foods) are natural, and these include the yellow from the annatto seed; green from chlorophyll; orange from carotene; brown from burnt sugar; and red from beets, tomatoes, and the cochineal insect. Natural colors are simply pigments obtained from animal, vegetable, or mineral sources.

If synthetic counterparts of colors and pigments are derived from natural sources, the term "nature-identical" applies. These include the pure carotenoids such as canthaxanthin (red), apocarotenal (orange-red), and beta-carotene (yellow-orange). These have all gone through toxicological studies and are approved by the FDA. Canthaxanthin and apocarotenal have maximum addition limits but beta-carotene can be added at the necessary level to accomplish its intended purpose.

Some colorants, however, are derived from synthetic dyes. The synthetic dyes in use have been approved and certified by the FDA. These certified color additives are divided into two groups: FD&C dyes and FD&C lakes. Dyes are water-soluble and are available in powders, granules, liquids, blends, and pastes. GMPs suggest that they not be used in amounts exceeding 300 ppm. The lakes are water-soluble FD&C certified dyes on a substratum of aluminum hydrate or aluminum hydroxide. The lakes must also be certified by the FDA. They are useful in foods that have very little water such as coloring oils. They are used in icings, fondant coatings, cake and doughnut mixes, hard candy, and gum products. They do not solubilize as do dyes but color by dispersion rather than solution.

In 1960 the Color Additive Amendments separated “color additives” from “food additives.” Colors (which include black, white, and intermediate grays) no longer were to be classified as food additives. In determining whether a color additive is safe, the FDA must take into account the probable consumption of the additive and of any substance formed as a result of its use. There is also a cancer clause similar to the Delaney Clause in the amendments.

Some compounds are not color additives but are used to produce a white color. Thus, oxidizing agents including benzoyl peroxide, chlorine dioxide, nitrosyl chloride, and chlorine are used at the end of the production cycle to whiten wheat flour, which is pale yellow in color if untreated. Titanium dioxide, on the other hand, is considered a color additive and may be added to some foods, such as artificial cream or coffee whiteners to add a white color.

———— Part III ————

Handling and Processing
of Foods

13.1 INTRODUCTION

There are two interrelated concepts in food analysis that deal with acidity: **pH** and **titratable acidity**. Each of these quantities is analytically determined in separate ways and each has its own particular impact on food quality. **Titratable acidity** deals with measurement of the **total acid concentration** contained within a food (also called **total acidity**). This quantity is determined by exhaustive titration of intrinsic acids with a standard base. Titratable acidity is a better predictor of acid's impact on flavor than pH.

Total acidity does not tell the full story, however. Foods establish elaborate buffering systems that dictate how **hydrogen ions** (H^+), the fundamental unit of acidity, are expressed. Even in the absence of buffering, less than 3% of any food acid is ionized into H^+ and its anionic parent species (its **conjugate base**). This percentage is further suppressed by buffering. In aqueous solution, hydrogen ions combine with water to form **hydronium ions**, H_3O^+ . The ability of a microorganism to grow in a specific food is an important example of a process that is more dependent on hydronium ion concentration than titratable acidity. The need to quantify only the free H_3O^+ concentration leads to the second major concept of acidity, that of **pH** (also called **active acidity**). In nature, the H_3O^+ concentration can span a range of 14 orders of magnitudes. The term pH is a mathematical shorthand for expressing this broad continuum of H_3O^+ concentration in a concise and convenient notation. In contemporary food analysis, pH is usually determined instrumentally with a pH meter; however, chemical pH indicators also exist. [For the pH and titratable acidity of select foods, see resource (8).]

13.2 CALCULATION AND CONVERSION FOR NEUTRALIZATION REACTIONS

13.2.1 Concentration Units

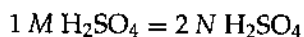
This chapter deals with the theory and practical application of titratable acidity calculation and pH determination. To quantitatively measure components of foods, solutions must be prepared to accurate concentrations and diluted into the desired working range.

The terms used for concentration in food analysis should be reviewed. The most common concentration terms are given in Table 13-1. Molarity and normality are the most common SI (International Scientific) terms used in food analysis, but solutions also can be expressed as percentages. It is important that the analyst be able to convert between both systems.

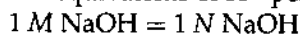
Molarity (M) is a concentration unit representing the number of moles of the solute per liter of solution.

Normality (N) is a concentration unit representing the number of equivalents (Eq) of a solute per liter of solution. In acid and base solutions, the normality represents the concentration or moles of H^+ or OH^- per liter that will be exchanged in a neutralization reaction when taken to completion. For oxidation-reduction reagents, the normality represents the concentration or moles of electrons per liter to be exchanged when the reaction is taken to completion. The following are some examples of molarity versus normality (equivalents):

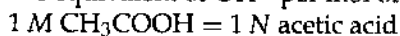
Acid-Base Reactions



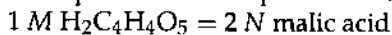
2 equivalents of H^+ per mol of acid



1 equivalent of OH^- per mol of base



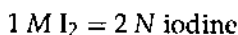
1 equivalent of H^+ per mol of acid



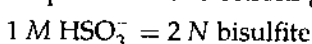
2 equivalents of H^+ per mol of acid

Oxidation-Reduction Reactions

for example, $HSO_3^- + I_2 + H_2O \rightleftharpoons SO_4^{2-} + 2I^- + 3H^+$



2 equivalents of electrons gained per mol of I_2



2 equivalents of electrons lost per mol of bisulfite

Many analytical determinations in food analysis use the concept of equivalents to measure the amount of an unknown. Perhaps the most familiar of these are **acid-base reactions** in which hydrogen ions are exchanged and can be quantified through stoichiometric neutralization with a standard base. Acid-base reactions are used to determine nitrogen in the Kjeldahl protein determination (see Chapter 9), benzoic acid in sodas, and in determining percent titratable acidity. The concept of equivalents also is used in oxidation-reduction problems to quantify unknown analytes that are capable of direct electron transfer.

Equivalent weight can be defined as the molecular weight divided by the number of equivalents in the reactions. For example, the molecular weight of H_2SO_4 is 98.08 g. Since there are 2 equivalents per mole of H_2SO_4 , the equivalent weight of H_2SO_4 is 49.04 g. Table 13-2 provides a list of molecular and equivalent weights for acids important in food analysis. In working with normality and milliliters, the term **milliequivalents** (mEq) is usually preferred. Milliequivalent weight is the equivalent weight divided by 1000.

Percentage concentrations are the mass amount of solute or analyte per 100 ml or 100 g of material. Percentage can be expressed for solutions or for solids and can

13-1

table

Concentration Expressions Terms

<i>Unit</i>	<i>Symbol</i>	<i>Definition</i>	<i>Relationship</i>
Molarity	<i>M</i>	Number of moles of solute per liter of solution	$M = \frac{\text{moles}}{\text{liter}}$
Normality	<i>N</i>	Number of equivalents of solute per liter of solution	$N = \frac{\text{equivalents}}{\text{liter}}$
Percent by weight (parts per hundred)	wt %	Ratio of weight of solute to weight of solute plus weight of solvent $\times 100$	$\text{wt} = \frac{\text{wt solute} \times 100}{\text{total wt}}$
	wt/vol %	Ratio of weight of solute to total vol. $\times 100$	$\text{wt \%} = \frac{\text{wt solute} \times 100}{\text{total volume}}$
Percent by volume	vol %	Ratio of volume of solute to total volume	$\text{vol \%} = \frac{\text{vol solute} \times 100}{\text{total volume}}$
Parts per million	ppm	Ratio of solute (wt or vol) to total wt or vol. $\times 1,000,000$	$\text{ppm} = \frac{\text{mg solute}}{\text{kg solution}}$
			$= \frac{\text{ng solute}}{\text{g solution}}$
			$= \frac{\text{mg solute}}{\text{liters solution}}$
			$= \frac{\text{ng solute}}{\text{ml solution}}$
			$= \frac{\text{ng solute}}{\text{liters solution}}$
Parts per billion	ppb	Ratio of solute (wt or vol) to total wt or vol. $\times 1,000,000,000$	$\text{ppm} = \frac{\text{ng solute}}{\text{kg}}$
			$= \frac{\text{fg solute}}{\text{ml}}$
			$= \frac{\text{fg solute}}{\text{g}}$

13-2

table

Molecular and Equivalent Weights of Common Food Acids

<i>Acid</i>	<i>Chemical Formula</i>	<i>Molecular Weight</i>	<i>Equivalents per Mole</i>	<i>Equivalent Weight</i>
Citric (anhydrous)	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	192.12	3	64.04
Citric (hydrous)	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	210.14	3	70.05
Acetic	$\text{HC}_2\text{H}_3\text{O}_2$	60.06	1	60.05
Lactic	$\text{HC}_3\text{H}_5\text{O}_3$	90.08	1	90.08
Malic	$\text{H}_2\text{C}_4\text{H}_4\text{O}_5$	134.09	2	67.05
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	90.04	2	45.02
Tartaric	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	150.09	2	75.05
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	176.12	2	88.06
Hydrochloric	HCl	36.47	1	36.47
Sulfuric	H_2SO_4	98.08	2	49.04
Phosphoric	H_3PO_4	98.00	3	32.67
Potassium acid phthalate	$\text{KHC}_8\text{H}_4\text{O}_4$	204.22	1	204.22

be on a volume basis or mass basis. When the percentage becomes a number less than 1% **parts per million** (ppm), **parts per billion** (ppb), and even **parts per trillion** (ppt) usually are preferred. If percentage is defined as the mass of the solute or analyte per mass (or volume) of sample $\times 100$, then ppm is simply the same ratio of mass of solute per mass of sample $\times 1,000,000$.

13.2.2 Equation for Neutralization and Dilution

There are some general rules in evaluating equilibrium reactions that are helpful in most situations. At full neutralization the milliequivalents (mEq) of one reactant in the neutralization equals the milliequivalents of the other reactant. This can be expressed mathematically as:

$$(\text{ml of } X)(N \text{ of } X) = (\text{ml of } Y)(N \text{ of } Y) \quad [1]$$

Equation [1] also can be used to solve dilution problems where X represents the stock solution and Y represents the working solution. When Equation [1] is used for dilution problems, any value of concentration (grams, moles, ppm, etc.) can be substituted for N . Units should be recorded with each number. Cancellation of units provides a quick check on proper setup of the problem. (See Practice Problems 1–8 at the end of Chapter 13.)

13.3 pH

13.3.1 Acid–Base Equilibria

The Brønsted–Lowry theory of neutralization is based upon the following definitions for acid and base:

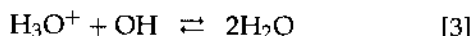
Acid: A substance capable of donating protons.
In food systems the only significant proton donor is the hydrogen ion.

Base: A substance capable of accepting protons.

Neutralization is the reaction of an acid with a base to form a salt as shown below:



Acids form hydrated protons called **hydronium ions** (H_3O^+) and bases form **hydroxide ions** (OH^-) in aqueous solutions:



At any temperature, the product of the molar concentrations (moles/liter) of H_3O^+ and OH^- is a constant referred to as the **ion product constant for water** (K_w):

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad [4]$$

K_w varies with the temperature. For example, at 25°C , $K_w = 1.04 \times 10^{-14}$ but at 100°C , $K_w = 58.2 \times 10^{-14}$.

The above concept of K_w leads to the question of what the concentrations of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are in pure water. Experimentation has revealed that the concentration of $[\text{H}_3\text{O}^+]$ is approximately $1.0 \times 10^{-7} \text{ M}$, as is that of the $[\text{OH}^-]$ at 25°C . Because the concentrations of these ions are equal, pure water is referred to as being **neutral**.

Suppose that a drop of acid is added to pure water. The $[\text{H}_3\text{O}^+]$ concentration would increase. However, K_w would remain constant (1.0×10^{-14}), revealing a decrease in the $[\text{OH}^-]$ concentration. Conversely, if a drop of base is added to pure water, the $[\text{H}_3\text{O}^+]$ would decrease while the $[\text{OH}^-]$ would increase, maintaining the K_w at 1.0×10^{-14} at 25°C .

How did the term pH derive from the above considerations? In approaching the answer to this question, one must observe the concentrations of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in various foods, as shown in Table 13-3. The numerical values found in Table 13-3 for $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are bulky and led a Swedish

13-3
table
Concentrations of H_3O^+ and OH^- in Various Foods at 25°C

Food	$[\text{H}_3\text{O}^+]$ ¹	$[\text{OH}^-]$ ¹	K_w
Cola	2.24×10^{-3}	4.66×10^{-12}	1×10^{-14}
Grape juice	5.62×10^{-4}	1.78×10^{-11}	1×10^{-14}
SevenUp	3.55×10^{-4}	2.82×10^{-11}	1×10^{-14}
Schlitz beer	7.95×10^{-5}	1.26×10^{-10}	1×10^{-14}
Pure water	1.00×10^{-7}	1.00×10^{-7}	1×10^{-14}
Tap water	4.78×10^{-9}	2.09×10^{-6}	1×10^{-14}
Milk of magnesia	7.94×10^{-11}	1.26×10^{-4}	1×10^{-14}

From [12], used with permission. Copyright 1971 American Chemical Society.

¹Moles per liter.

Calculating the pH of the cola:

Step 1. Substitute the $[\text{H}^+]$ into the pH equation:

$$\text{pH} = -\log(\text{H}^+)$$

$$\text{pH} = -\log(2.24 \times 10^{-3})$$

Step 2. Separate 2.24×10^{-3} into two parts; determine the logarithm of each part:

$$\log 2.24 = 0.350$$

$$\log 10^{-3} = -3$$

Step 3. Add the two logs together since adding logs is equivalent to multiplying the two numbers:

$$0.350 + (-3) = 2.65$$

Step 4. Place the value into the pH equation:

$$\text{pH} = -(-2.65)$$

$$\text{pH} = 2.65$$

chemist, S.L.P. Sørensen, to develop the pH system in 1909.

pH is defined as the logarithm of the reciprocal of the hydrogen ion concentration. It also may be defined as the negative logarithm of the molar concentration of hydrogen ions. Thus, a $[H_3O^+]$ concentration of 1×10^{-6} is expressed simply as pH 6. The $[OH^-]$ concentration is expressed as pOH and would be pOH 8 in this case, as shown in Table 13-4.

While the use of pH notation is simpler from the numerical standpoint, it is a confusing concept in the

minds of many students. One must remember that it is a logarithmic value and that a change in one pH unit is actually a 10-fold change in the concentration of $[H_3O^+]$. (See Practice Problems 9–12 at the end of Chapter 13.)

It is important to understand that pH and titratable acidity are not the same. Strong acids such as hydrochloric, sulfuric, and nitric acids are almost fully dissociated at pH 1. Only a small percentage of food acid molecules (citric, malic, acetic, tartaric, etc) dissociate in solution. This point may be illustrated by comparing the pH of 0.1 N solutions of hydrochloric and acetic acids.

13-4 table

Relationship of $[H^+]$ versus pH and $[OH^-]$ versus pOH at 25°C.

$[H^+]$ ¹	pH	$[OH^-]$ ¹	pOH
1×10^0	0	1×10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^0	0

From (12), used with permission. Copyright 1971 American Chemical Society.

¹Moles per liter. Note that the product of $[H^+][OH^-]$ is always 1×10^{-14} .

Calculation of $[H^+]$ of a beer with pH 4.30:

Step 1. Substitute numbers into the pH equation:

$$\begin{aligned} \text{pH} &= -\log[H^+] \\ 4.30 &= -\log[H^+] \\ -4.30 &= \log[H^+] \end{aligned}$$

Step 2. Divide the -4.30 into two parts so that the first part contains the decimal places and second part the whole number:

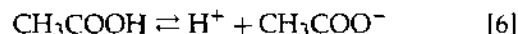
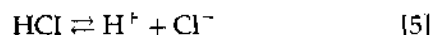
$$-4.30 = 0.70 - 5 = \log[H^+]$$

Step 3. Find the antilogs:

$$\begin{aligned} \text{antilog of } 0.70 &= 5.0 \\ \text{antilog of } -5 &= 10^{-5} \end{aligned}$$

Step 4. Multiply the two antilogs to get $[H^+]$:

$$\begin{aligned} 5 \times 10^{-5} &= [H^+] \\ [H^+] &= 5 \times 10^{-5} M \end{aligned}$$



The HCl fully dissociates in solution to produce a pH of 1.02 at 25°C. By contrast, only about 1% of CH_3COOH is ionized at 25°C, producing a significantly higher pH of 2.89. The calculation and significance of partial dissociation on pH is presented in more detail in section 13.4.2.1.

13.3.2 pH Meter

13.3.2.1 Activity versus Concentration

In using pH electrodes, the concept of activity versus concentration must be considered. **Activity** is a measure of expressed chemical reactivity, while **concentration** is a measure of all forms (free and bound) of ions in solution. Due to interactions of ions between themselves and with the solvent, the effective concentration or activity is, in general, lower than the actual concentration, although activity and concentration tend to approach each other at infinite dilution. Activity and concentration are related by the following equation:

$$A = \gamma C \quad [7]$$

where:

A = activity
 γ = activity coefficient
 C = concentration

The **activity coefficient** is a function of ionic strength. Ionic strength is a function of the concentration of, and the charge on, all ions in solution. Activity issues can become significant for hydronium ions below pH 1 and for hydroxyl ions at pH 13 and above.

13.3.2.2 General Principles

The pH meter is a good example of a **potentiometer** (a device that measures voltage at infinitesimal current flow). The basic principle of **potentiometry** (an electrochemical method of voltammetry at zero current)