

21 Packaging of Beverages

21.1 INTRODUCTION

Beverages are an important part of the diet of all humans and have been since the earliest times. Although the origins of many beverages are unknown, there is no doubt that the range and sophistication of beverages have increased dramatically over recent decades. Much of this growth can be attributed to developments in packaging, which have made it possible for a large national and international trade in beverages to flourish. Today, a wide variety of quite different beverages are consumed in the home, at work and at a myriad of sporting, leisure and entertainment activities, and the full range of packaging media is used (either alone or in varying combinations) to bring these beverages to consumers. This chapter discusses the major categories of beverages, including their manufacture, indices of failure and packaging.

21.2 WATER

21.2.1 INTRODUCTION

In Europe and China, spring and mineral waters have been consumed for centuries by local inhabitants, immigrants and invaders. For example, Evian natural mineral water began its present-day history in 1789 when a French marquis began bottling the “miraculous” waters on his estate bordering Lake Geneva (Lac Léman). Similarly, Perrier water was first bottled as Perrier sparkling mineral water in 1863 (Warburton and Austin, 2000). The very concept of “mineral water” was first defined in Germany in 1911 as water containing at least 1000 mg L⁻¹ of dissolved mineral constituents. Over the next 80 years or so, this definition was changed many times, resulting in waters with a lower mineral content also being labeled “mineral.” By 1990, the acceptable level had fallen to 200 mg L⁻¹ and the market became flooded with pseudo-mineral waters (Diduch et al., 2011). In the United States, if the total dissolved solids content of mineral water is less than 500 ppm or greater than 1500 ppm, the information “low mineral content” or “high mineral content,” respectively, must appear on the label (21 *CFR* § 165.110 (a)(3)).

Bottled water is now widely available for sale, and its consumption has risen dramatically over the past 20 years, particularly in countries where clean, potable tap water is available at very low or no cost. The growth in bottled water is influenced by three public concerns or fears: a declining quality from often overworked municipal water supplies, possible toxic contamination of groundwater sources and a general increased interest in personal health. It has also become a “must have” fashion accessory for many consumers. There is a public perception that bottled water is safe, natural and free from additives such as fluoride and chlorine. According to Wilk (2006), the contrast between tap water and bottled water can be seen as a reflection of a contest for authority and public trust between governments and corporations, in a context of heightened anxieties about risk and health. In his view, bottled water is a case where sound cultural logic leads to environmentally destructive behavior. In fact, the U.S. Federal Food, Drug and Cosmetic Act (FDCA) provides that FDA’s standards for bottled water must be at least as stringent and qualitative as EPA’s standards for public water systems; thus, the maximum contaminant levels for bottled water are very similar to those for tap water (Tarver, 2008).

Bottled water can be divided into nonsparkling or still, and sparkling. It can also be divided into either natural or processed categories, where natural water is bottled directly from underground sources while processed water is tap or well water that is highly filtered or distilled.

Natural bottled waters are sold with the understanding (and in Europe, the legal requirement) that they have not been subjected to any treatment that would remove natural indigenous bacteria, which are believed to have medicinal and therapeutic qualities. It has never been proven that the ingested levels of indigenous microorganisms in bottled water have an adverse effect on health. Despite this, much controversy surrounds the question of the potential pathogenicity of indigenous microorganisms in mineral waters (Warburton, 2002).

Bottled water is defined by the U.S. FDA as water that is intended for human consumption and that is sealed in bottles or other containers with no added ingredients, except that it may optionally contain safe and suitable antimicrobial agents; fluoride may optionally be added within FDA-specified limits (21 *CFR* § 165.110). However, antimicrobial agents are not permitted in many other countries, and in those countries, particularly within the EU, the term “natural mineral water” carries a requirement that the water source must meet certain stringent criteria (see Council Directive 80/777/EC). In particular, it must be free from pathogenic organisms such as fecal coliforms, fecal streptococci and staphylococcal organisms as well as parasites such as *Giardia* and *Cryptosporidium*.

The water may be subjected to a number of treatments including distillation, carbonation, ozonation, chlorination, filtration and so on, depending on the quality of the source water, the type of bottled water being manufactured, where it is being manufactured and local legislation (Senior and Dege, 2011).

21.2.2 INDICES OF FAILURE

The major index of failure in bottled water is microbial growth. The source of water is never sterile and contains sufficient trace nutrients for microbial growth. Various saprophytic bacteria, yeasts and molds are commonly found in water, which may also be contaminated with pathogenic bacteria and parasites (Hocking and Jensen, 2001). In addition, water may become contaminated during transport and processing, with bottles and closures also being possible sources of contamination.

Where legislation permits, water may be treated prior to bottling with chlorine or ozone, the latter being preferred since it is much faster acting than the former. In the EU, assuming that natural mineral water is free from pathogens, the presence of other microorganisms that arise from the environment from which the water is taken is accepted as a normal part of its composition (Ashurst, 2010). These environmental organisms are those characterized by growth in media at 20°C –22°C, although many bacterial species occurring naturally in groundwater will grow over a much wider temperature range. The presence of such flora has given rise to a wide range of questions and debates about effects on health, primarily because the flora is not particularly well characterized. However, since no disinfection that modifies or eliminates the biological constituents of water is permitted, the bacteria must be regarded as natural components in exactly the same way as their chemical counterparts.

The most obvious manifestation of spoilage in bottled water is the appearance of floating pieces of mold mycelium, with *Penicillium* species, together with *Cladosporium* and *Phaeoramularia*, being the most commonly isolated fungi (Hocking and Jensen, 2001). *Pseudomonas aeruginosa*, an organism associated with soil contaminated with human and animal feces, is not generally associated with spoilage of bottled water, but its presence can affect water color, clarity and taste. It is capable of growth to high numbers in minimal nutrient environments such as deionized and demineralized water and has been implicated in food- and waterborne diseases. Most *P. aeruginosa* strains are resistant to commonly used antibiotics and sanitizers/disinfectants but should be inactivated by pasteurization. It has been isolated from bottled waters from Brazil, Canada, France, Germany, Indonesia, Spain and the United States (Hocking and Jensen, 2001).

In non-carbonated water, the numbers of bacteria are known to increase rapidly after bottling. An example given by Ashurst (2010) for natural mineral water showed a level of colony counts of water emerging from the spring as about 1–4 cfu mL⁻¹, and immediately after bottling, the numbers were only slightly higher. During storage at 20°C, bacterial populations increased to reach a peak of more than 10⁵ cfu mL⁻¹ by the end of 1 week. During the next 4 weeks, bacterial populations then slowly declined or remained fairly constant. At the end of a 2-year storage period, colony counts were still likely to be of the order of 10³ cfu mL⁻¹.

Solar water disinfection (SODIS) is an effective, simple, household level, point-of-use technology suitable for application in developing countries (Muriner and Kraemer, 2008). Contaminated water is placed in a PET bottle, capped and then exposed to sunlight for at least 6 h. Laboratory and field trials have demonstrated SODIS to be effective against a wide range of waterborne pathogens, with health impact assessments demonstrating significant benefits from consumption of SODIS-treated water. The unavailability of PET bottles has been identified as a potential hindrance to the successful implementation of SODIS.

Biofilm proliferation has been reported on the walls of PVC containers and may be partly responsible for the long-term survival of bacteria in bottled water; several authors have found higher counts and faster growth in bottled water stored in plastic bottles than in glass bottles (Warburton, 2002).

The use of returnable containers for bottled water is common in many countries. Only a limited number of studies have been performed on the contamination risk by microorganisms when classical caustic cleaning is applied to rinse returnable containers. It has been found that under optimal conditions, the following classification could be made in decreasing order of microbial rinsability: glass > PET > PC > PP = PVC > HDPE. Even at optimal rinsing conditions, it was not possible to totally remove all bacteria from the sides of the containers, leading to the recommendation that bottled water should be disinfected by ozonation (Warburton and Austin, 2000).

The presence of dissolved O₂ in many non-carbonated waters is a major contributor to the desirable taste and mouth feel of the water. Loss of much of this dissolved O₂ leads to the water being judged unacceptable by consumers. A further deterioration in bottled water has been the development of a “plastic” taste, which is sometimes found in water which has been packaged in unsuitable plastic containers (Senior and Dege, 2011).

21.2.3 PACKAGING

Glass bottles were long considered the container of choice for sparkling waters and carbonated soft drinks (see Section 21.3.3.1), but, in recent years, PET bottles have gained an increasing share of this sector. The majority of still waters and many sparkling waters are now packaged in plastic containers, and PET is the principal resin with PC being used for large, refillable containers, typically of 11, 19 and 22 L capacity.

Recently, a model of the shelf life of sparkling water packed in PET bottles was proposed using computational fluid dynamics (CFD) and validated by Carrieri et al. (2012). The model considered the bottle weight and storage temperature as variables. The decrease in carbonation (initial values of 4.8–5.4 g L⁻¹) did not appear to depend on bottle weight, although diffusive non-uniformity was observed depending on PET bottle wall thickness variation. The importance of storage at low temperature was confirmed, as the diffusion of gas through PET is accelerated by temperature: the loss at 40°C was 83% higher than at 10°C. This model could be used as a design and verification tool for predicting shelf life in any carbonated beverage, and the results employed to rapidly establish the “best used by” date.

Water packed in PET is normally regarded as being free from taints. The major significant volatile compound in PET is acetaldehyde (AA) which is present as a thermal degradation product formed during the melt condensation reaction and melt processing of PET. AA possesses a distinct odor and taste, generally described as sweet, plastic-like and fruity, and has a low sensory detection threshold that ranges from 20 to 40 ppt. Present manufacturing techniques have dramatically

reduced residual AA levels in PET packaging to <1 ppm. AA scavengers are available to reduce AA formation in PET packaging by up to 80%; anthranilamide is particularly preferred because of its low cost, efficiency and ease of incorporation into PET (Bach et al., 2012).

Matsuga et al. (2006) analyzed commercial samples of water bottled in PET from Japan, Europe and North America and showed that AA and formaldehyde (FA) migrated into water from PET bottles. Concentrations of AA ranged from 5.0 to 25.7 ppb and for FA from <0.5 to 3.0 ppb. In commercial water without bacteria, the levels of FA and AA remained unchanged, whereas in natural mineral water containing heterotrophic bacteria, the FA and AA were decomposed. Of the carbonated water samples, one contained bacteria and showed a reduction in FA and AA, while the others had no bacteria and showed no decomposition activity. It was speculated that the existence of bacteria influenced the concentration of carbonate gas.

Antimony trioxide (Sb_2O_3) is used as an additive and initiator in the manufacture of 90% of the PET manufactured worldwide, at a maximum level of 0.035% as Sb. Welle and Franz (2011) reported a mean value of 224 ± 32 ppm Sb in 67 PET bottles from the European market. Although Sb is a potentially toxic trace element with no known physiological function, only a small fraction of the Sb contained in PET bottles migrates into water. Shotyk et al. (2006) reported that 12 brands of bottled natural waters from Canada contained 156 ± 86 ppt Sb, and 3 brands of deionized water contained 162 ± 30 ppt Sb. Comparison of three German brands of water available in both glass bottles and PET containers showed that waters bottled in PET contained up to 30 times more Sb, with a range of 253–546 ppt Sb. One German brand of water in PET bottles had 626 ± 15 ppt Sb 6 months after bottling. The median concentration of Sb in 35 brands of water bottled in PET from 11 other European countries was 343 ppt. All of the waters found to contain Sb were at concentrations well below the guidelines commonly recommended for drinking water, which are as follows: World Health Organization 20 ppb, U.S. EPA and Health Canada 6 ppb, German Federal Ministry of Environment 5 ppb and Japan 2 ppb. The EU SML for Sb is 40 ppb. Cheng et al. (2010) reported Sb leaching into water packed in PET bottles after various treatments that included cooling with frozen water, heating with boiling water, microwaving, incubating with low pH water, outdoor sunlight irradiation and in-car storage. Concentrations after heating and microwaving exceeded 6 ppb.

Genotoxic and estrogenic activities in water bottled in PET have been reported, and these are discussed in Section 22.3.4.1.

21.3 CARBONATED SOFT DRINKS

21.3.1 MANUFACTURE

Traditionally, soft drinks were prepared by dissolving granulated sugar in specially treated water or, alternatively, by diluting liquid sugar with this water. A variety of ingredients including flavoring and coloring agents, acidulants (invariably either citric or phosphoric acid) and preservatives were then added. Other constituents such as fruit juice or comminuted fruit, bodying agents, artificial sweeteners, clouding agents, antioxidants and foaming agents were added, depending on the particular product being made. Recently, “diet” soft drinks in which the sugar has been replaced with an artificial sweetener (typically aspartame) have become very popular.

Soft drinks are now prepared almost exclusively using the premix system whereby the blended syrup, after flash pasteurization if necessary, is mixed with carbonated, treated water prior to delivery to the filler. Although traditionally the product has been cooled to 1°C – 3°C before arrival at the filler in order to minimize loss of carbonation and facilitate filling, fillers and ancillary equipment capable of handling the product at ambient temperatures have been introduced.

The degree of carbonation of soft drinks is typically expressed in volumes or g L^{-1} of CO_2 . One volume equals approximately 2 g L^{-1} , and at room temperature, each volume produces about 1 atm (101 kPa) of internal pressure. Temperature has a significant effect on internal pressure, with

a 4 volume beverage such as a cola rising to 7 atm at 38°C and to 10 atm at maximum storage/pasteurization temperatures (Griff, 2009). The carbonation level of beverages ranges from 1.5 volumes for citrus and other fruit-based soft drinks to 4 volumes for common cola drinks and 5 volumes for club soda and ginger ale.

21.3.2 INDICES OF FAILURE

The three major indices of failure in carbonated beverages are loss of carbonation, oxidation and/or acid hydrolysis of the essential flavor oils and colorings and loss of color and undesirable changes in flavor caused by light. Loss of carbonation is largely a function of the effectiveness of the package in providing a barrier to gas permeation, while oxidation can be largely prevented by the use of high-quality flavorings and antioxidants, deaerating the mix prior to carbonation and minimizing exposure of the product to light. Colorings of both natural and artificial origin may be affected by O₂, and the usual result is a bleaching effect. Many manufacturers add ascorbic acid to act as an O₂ scavenger (Ashurst, 2010).

21.3.3 PACKAGING

21.3.3.1 Glass

From the beginning of the twentieth century, virtually all carbonated soft drinks were packaged in refillable glass bottles, which were sealed with crown cork closures (see Section 10.1.3.1.1). In recent years, nonreturnable glass bottles have replaced refillable glass bottles in many markets. These sometimes have a foam plastic protective label or a paper-polyolefin or all-plastic shrink sleeve, in part as a safety measure to prevent flying glass fragments should the bottle break (see Section 9.5.4 for more details). The crown cork closure has been largely replaced with a roll-on aluminum screw cap on threaded necks with a tamper-evident ring, or a plastic closure (typically PP with or without a liner), which fits and unscrews over the same threads as the roll-on and provides some visible indication of tampering.

21.3.3.2 Metal

Three-piece tinplate containers were used for many years for the packaging of carbonated beverages. The highly corrosive nature of carbonated soft drinks demanded complete protection of the metal container from the product by the use of one or more coatings of an impermeable enamel system. For three-piece cans, this involved spraying an additional coating of enamel (a process known as *sidestripping*) over the inside of the container down the sideseam area after welding. Control of iron migration is critical, because extremely small levels of iron (0.5 ppm) can compromise the flavor of the beverage. One study on the influence of two different compound systems applied during the end seaming operation (can closing) on the iron pickup from tinplate cans after storage with a cola soft drink for 180 days at 37°C found levels between 0.15 and 1.0 ppm depending on the compound/enamel combination (Bernardo et al., 2005).

Today, most carbonated beverages are packaged in two-piece containers usually made from aluminum. The two-piece container has made it much easier to retain the integrity of the enamel layer inside the can and thus minimize corrosion during storage. The cans must be able to withstand continual internal pressure of up to 5 atm.

Metal cans for beverages have an easy-open end consisting of a scored portion in the end panel and a levering tab (formed separately) that is riveted into a bubble-like structure fabricated during pressing. The aluminum alloy used to manufacture easy-open ends for beverage cans is specially developed to give the required mechanical properties but is subject to environmental stress cracking (ESC) corrosion due to reaction with moisture. The score area is particularly susceptible because of the tensile stress to which this part of the end is subjected (Page, 2006).

Container lightweighting and design have been the subject of much development work, and quadruple necking is now standard on many aluminum beverage cans. This has resulted in cost savings in the reduced aluminum required for the end, and smaller overall pack area as well as reduced weight. The introduction of a single-stage process of spin-necking has resulted in a smooth, conical-shaped top section.

21.3.3.3 Plastics

As early as the 1960s, the Coca-Cola™ and Pepsi-Cola™ companies were seriously considering the use of plastic bottles for soft drinks, and they began to develop their ideas with major polymer manufacturers in the United States. It soon became apparent that only the polyester and nitrile families of plastics had the necessary physical and chemical characteristics required. Because the nitrile plastics could be made into bottles using existing blow molding equipment, while PET could not because of its inclination to crystallize and go hazy at higher temperatures, early market development work in the 1970s was carried out with nitrile bottles. Coca-Cola successfully launched a 950 mL nitrile bottle in 1975, but the release in 1977 of toxicological data showing that AN monomer could be carcinogenic at high dosage led to the removal of the nitrile bottle from the market (Turtle, 1984).

Meanwhile, attempts to successfully manufacture PET bottles using a stretch blow molding process were continuing. In the spring of 1977, the plastic PET bottle for soft drinks was launched by Pepsi-Cola, followed later by Coca-Cola and other beverage producers. It has been described as probably the biggest single development in the soft drinks industry since the introduction of the ring-pull can a decade earlier (Turtle, 1984). Today, the greatest volume of soft drinks is packaged in PET bottles which have achieved their market share mainly at the expense of glass, albeit in an enlarged total market. The early designs had a round base which necessitated a flat base cup, usually injection molded from high density polyethylene (HDPE) and fixed to the bottle with hot-melt adhesives. The increase of PET recycling schemes accelerated the introduction of the petalloid base, thus obviating the need for a base cup. Although more material is required for a petalloid base, separation of the base cap is not required prior to recycling of the PET bottle.

Stress cracking of PET bottles filled with carbonated soft drinks is a complex process that is influenced by a large number of variables, including climate, chemistry, polymer quality and bottle engineering design. There is a growing awareness that “alkalinity,” including naturally occurring water alkalinity, is connected to stress crack failure of PET bottles (see Section 2.3.6.4.1).

The continuing trend for larger and larger containers of soft drink has helped penetration of the PET bottle. The 1 L glass bottle is considered to be near the limit of size and weight, above which it becomes difficult to handle easily, particularly by children. In contrast, PET bottles up to 5 L in size are now available, resulting in considerable savings in container cost per unit volume. In addition, the larger the bottle, the more CO₂ is retained per unit of time because of a smaller surface area:volume ratio (i.e., a reduced area for permeation).

The factors that influence the taste and odor of carbonated beverages packaged in plastic containers are depicted schematically in Figure 21.1. Most of these factors are applicable to many other foods or beverages packaged in plastic containers. Although O₂ pickup is a very critical item with beer, soft drinks are much less sensitive and a maximum ingress of 20 ppm for citrus-flavored soft drinks and 40 ppm for cola drinks has been suggested, together with a limit for water loss of 1%, the latter based primarily on maintaining labeled contents. The criteria for flavor absorption and permeation losses are necessarily general because of the great variety of flavorants and wide differences in sensory effects.

Compared to glass, there is a loss of CO₂ through the bottle walls which must be allowed for. While increasing the wall thickness will decrease the rate of CO₂ transmission, this will also increase the cost of the bottle, and so a compromise has been sought. In addition, PET (like most thermoplastics) exhibits the phenomenon of creep, and this occurs to the greatest extent in the first few days after the bottles have been filled. In addition, there will be an elastic deformation which,

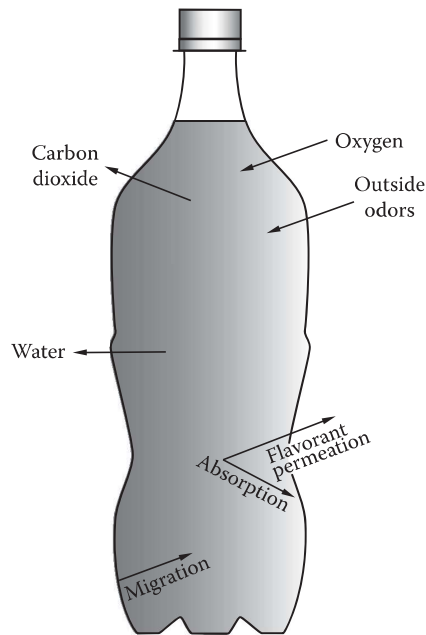


FIGURE 21.1 Factors influencing taste and odor of carbonated beverages packaged in plastic containers.

unlike the creep effect, will not be permanent but will disappear when the bottle is opened and the internal pressure is released. In combination, both these effects will produce an increase of about 2.5% in the volume of the bottle over the first 3–4 days after filling, given normal storage conditions.

A typical carbonation loss for 2L containers shows an initial loss of about 0.3 volumes in 3–4 days from the initial 4 volume figure, owing to the volume increase and absorption of CO₂ by the container wall. Thereafter, the rate of CO₂ loss becomes steady at about 0.04 volumes per week, giving a carbonation value around 3.4 after 12 weeks. The maximum shelf life for a 1.5–2L bottle is around 16–17 weeks by which time the carbonation will have dropped to a still acceptable level of 3.1–3.2 volumes (Turtle, 1984).

The PET bottle is usually fitted with either a standard aluminum roll-on closure or a pre-threaded plastic cap, both either in the standard or pilfer-proof form. The cap is ideal for use with PET bottles because its main sealing surface is on the inside bore of the neck finish, and this is very precisely controlled with regard to diameter and smooth surface finish during injection molding and has almost nil ovality (Turtle, 1984).

21.4 COFFEE

21.4.1 MANUFACTURE

The fruit (called a *cherry*) from trees of the genus *Coffea* (the two most important species are *C. arabica* and *C. robusta*) is a small pod that contains two coffee beans. The outer skin and pulp layers are removed using one of two processes: a “dry” method where the cherries are dried and then passed through a hulling machine, which removes the outer skin, dry fruit and parchment; and a “wet” method in which the beans are softened in water, depulped mechanically, fermented in large tanks to remove a mucilaginous parchment layer which encases the beans and then dried. Milling removes the parchment shell, leaving a gray-green colored bean.

Three operations are needed to convert green coffee beans into a consumable beverage—roasting, grinding and brewing. Roasting develops the characteristic flavor and headspace aroma of coffee, while grinding is necessary so that both the soluble solids and volatile flavor substances

can be sufficiently extracted by infusion or brewing with hot water to provide a beverage of required strength, either for immediate consumption or an extract for subsequent drying to make instant coffee.

Roasting of coffee beans involves rapid heating to raise the bean temperature to about 180°C. Roasting is normally carried out under atmospheric conditions with hot combustion gases and excess air and results in both chemical and physical changes in the green beans (Eggers and Pietsch, 2001). The chemical changes give rise to the characteristic flavor and aroma of roasted coffee, and, in addition, CO₂ is formed from decomposition of carbohydrates and other chemical reactions including the Maillard nonenzymic browning reaction. These latter processes have important implications for the packaging stage. The roasted whole beans may be packaged directly or else ground first prior to packaging. To maximize the retention of flavor volatiles within the roasted and ground coffee, cryogenic grinding (i.e., at sub-zero temperatures with the use of CO₂ or liquid N₂) is recommended.

The bulk density of ground coffee is assessed in two ways—free fall or packed measurement. Values will differ according to the blend, degree of roasting (decreasing with increasing severity), degree of grinding (increasing with increasing fineness) and moisture content. A fine grind coffee may have a bulk density of 0.39–0.47 g mL⁻¹ in free fall (Clarke, 1987). Bulk density is clearly of importance from a packaging point of view, because coffee is sold by weight, and if the bulk density varies, the headspace in the package will also vary.

Instant coffee is produced by extracting both soluble solids and volatile aroma/flavor compounds from roasted and ground coffee beans with water. Extracts of around 25% w/w soluble solids concentration are obtained, and these extracts are further concentrated using evaporation or freeze concentration and then dried using either spray drying or freeze drying. The latter is more common and is typically followed by agglomeration to produce granules of around 1400 μm on average. The agglomerates are then dried in a fluidized bed to the desired final moisture content. Freeze-dried coffee has a longer shelf life than spray-dried coffee, although the reason for this difference is not clear.

21.4.2 INDICES OF FAILURE

The major index of failure for coffee is staling, defined as “a sweet but unpleasant flavor and aroma of roasted coffee which reflects the oxidation of many of the pleasant volatiles and the loss of others” (Buffo et al., 2004). The aroma degeneration during staling has been described as changing from flat to old to sharply rancid, with a cocoa odor appearing in the advanced stage. Concurrently, the taste of the coffee changes from flat to bitter, old and rancid, at which stage it should no longer be sold. The extent of staling is increased by increased moisture content and storing at higher temperatures.

O₂ is believed to be absorbed by roast and ground coffee which provides a reservoir for O₂ to cause subsequent deterioration. It has been observed that in the vacuum packing of roasted coffee, the in-package O₂ value may in fact rise after several days as a result of desorption into the vacuum space, followed by its fall again during storage. There is little information on the precise relationship between the in-package percentage O₂ content and stability for roast whole beans (RWB) (Clarke, 1987). However, for roast and ground (R&G) coffee, there is some evidence of a linear correlation between the logarithm of the O₂ content and the time to end of shelf life for a constant quality level. For example, for a closed package at 0.5% initial O₂ content by volume, stored at 21°C, the corresponding shelf lives were 6, 12–17 and 20–25 months for high, medium and low flavor quality criteria, respectively; at 1% initial O₂ content, the shelf lives were 4, 9–17 and 14–20 months, respectively (Ratke-Granzer and Piringer, 1981). Extrapolation to 21% O₂ gave a shelf life of 10–15 days for medium flavor quality. Differences would be expected for coffees of different grind and roast degree and blend. Storage temperature would also have an important effect on shelf life.

Another study seeking to determine the shelf life of R&G coffee found that shelf life decreased with an increase in O₂ partial pressure, a_w and temperature (Cardelli and Labuza, 2001).

Oxygen had the greatest effect with an approximately 20-fold reduction in shelf life when the partial pressure was increased from 0.5 to 21.3 kPa (air). Increasing a_w by 0.1 led to a 60% decrease in shelf life, while a temperature increase of 10°C decreased shelf life by 15%–23%. Storing the coffee in air at 4°C gave a 44% increase in shelf life compared with that at 22°C.

Roast coffee will also gradually release its volatiles into the vapor phase, and once a certain proportion of the volatiles has been released, the coffee will be regarded as unacceptable. The physical and chemical changes occurring in roasted coffee during storage have been reviewed by Nicoli and Savonitto (2005).

Another reaction that is not strictly deterioration is the evolution of CO₂. During the roasting process, a large quantity of CO₂ is emitted both from the pyrolysis of the beans as well as the heating gases. The beans absorb a large amount of the CO₂ and part of this CO₂ is freed when the cells are crushed by grinding. During the first 24 h after grinding, CO₂ is given off quite rapidly. Fine grind coffee (500–600 μm) degasses more rapidly than coarse grind (800–1000 μm) coffee, and thus the latter presents more of a problem when vacuum packed.

The major index of failure in instant coffee is caking as a result of water vapor ingress; this occurs when the moisture content reaches 7%–8% or around 0.4 a_w (Figure 21.2). Instant coffee typically has a moisture content of 2%–4% at the time of packing, which corresponds to a very low a_w of <0.1, and therefore a package with a very low water vapor transmission rate (WVTR) is necessary. Some instant coffees have a surface application of coffee oils carrying aromatics which enhance the headspace aroma, and these are susceptible to flavor deterioration from O₂ and moisture pickup.

21.4.3 PACKAGING

21.4.3.1 Roasted Whole Beans

Depending on the shelf life required, the choice of packaging material has to be considered in regard to water vapor ingress, O₂ permeability, CO₂ and volatile component egress and grease resistance if oily, dark-roasted beans are being packaged. The major problem with the packaging of RWB is the evolution of CO₂.

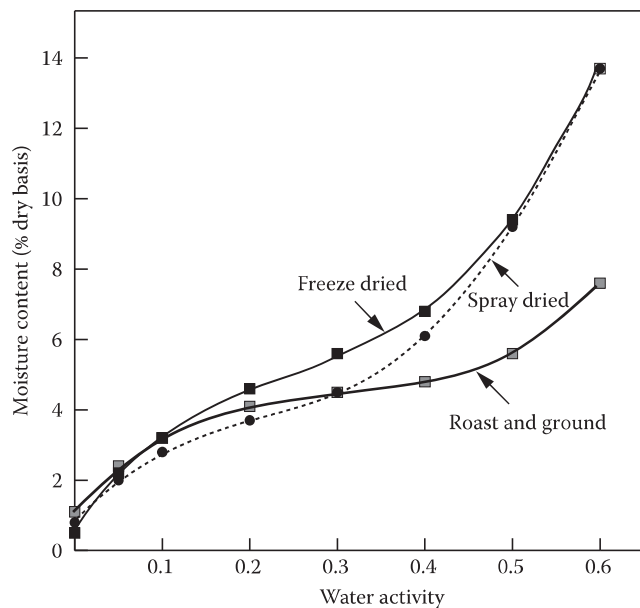


FIGURE 21.2 Moisture sorption isotherms for spray-dried and freeze-dried instant coffee and roast and ground coffee at 20°C. (Drawn from data presented in Hayakawa, K.-I., Matas, J., and Hwang, M.P., *J. Food Sci.*, 43, 1026, 1978.)

The quantity of CO₂ entrapped in RWB is of the order of 2–5 mL g⁻¹ (measured at standard temperature and pressure) and probably higher, depending on the method of measurement (Clarke, 1987). Thus, when RWB are placed within a closed package, the CO₂ released will have to be contained within the available headspace inside the package or, depending on the nature of the packaging material, permeate through the package.

Some useful calculations have been presented to illustrate the magnitude of the packaging problem and assist in evaluating alternative packages (Clarke, 1987). Assuming that 100 g of RWB are placed in a package, they will occupy about 330 mL, where about 150 mL is occupied by the beans themselves but only 75 mL by the solid material of the beans because their internal porosity is 50%. If it is further assumed that the internal volume of the package is 10% greater than that occupied by the beans, then the total package volume will be 366 mL, of which 366 – 150 = 216 mL will be available for take-up of released CO₂. Every 100 mL of CO₂ introduced inside the package will increase the total internal pressure by 100/216 = 0.46 atm. From 100 g of RWB, up to 500 mL of CO₂ could be released, generating a total internal pressure of 2.3 atm.

Five possible solutions to the problem created by CO₂ release from RWB have been suggested (Clarke, 1987):

1. Use a sufficiently rigid container to withstand the increase in internal pressure—this was considered to be impractical.
2. Use a packaging material either sufficiently permeable to CO₂ or fitted with a one-way valve.
3. Use a package under vacuum—this would not solve the problem since even if a full vacuum were obtained in the package, it might well be inadequate to cope with the quantity of CO₂ released.
4. Use a package with a very large headspace—this was judged to be commercially unacceptable.
5. Allow a substantial release of CO₂ by holding the beans before packing.

21.4.3.2 Roasted and Ground Coffee

Substantial quantities of CO₂ are released on grinding, especially with the finer grinds. For example, estimates have been given that 45% is released within 5 min of grinding for a fine ground coffee, while others have determined that 30% is lost within 5 min of grinding to an average particle size of 1000 μm, and 70% at 500 μm.

O₂ is a prime determinant of shelf life, and there are three main ways of lowering its concentration inside a package. The first method is to apply a high vacuum immediately after filling into the package and then sealing. The second is to flush the R&G coffee and package with an inert gas immediately prior to sealing. The third is to place an O₂-absorbing sachet inside the package.

When used by consumers, packages of R&G coffee will be opened and closed frequently. In such situations, the rate of coffee degradation increases rapidly owing to modification of the conditions inside the package as a result of interaction with air and moisture. In such situations, the shelf life becomes essentially that of an air pack. This is referred to as *secondary shelf life* and represents the length of time after opening of the package during which coffee maintains acceptable quality (Nicoli et al., 2010). The end of the secondary shelf life of R&G coffee at 30°C as a function of a_w was determined by Anese et al. (2006) based on consumer rejection methodology, choosing as the acceptability limit rejection by 50% of consumers. The end of secondary shelf life was almost constant, at around 20 days, at a_w values below 0.36. At higher a_w values, the secondary shelf life greatly decreased to about 13 days at an a_w of 0.44.

21.4.3.2.1 Metal Cans

The oldest type of commercial package for R&G coffee is the vacuum-packed tinfoil can. It provides impermeability to water vapor, gases and volatiles and can be made with a scored, removal

aluminum end over which a threaded screw cap is placed. After filling, a high vacuum is pulled on the can; this should be at least -95 kPa (71 cm Hg) to give an O_2 content of less than 1%. After sealing, evolution of CO_2 gas will reduce the vacuum until atmospheric pressure is restored. It is important that pressure does not build up inside the container during storage; to prevent this from occurring, the R&G coffee must be degassed in bulk to reduce its CO_2 content to an acceptable level. The type of calculation required to ensure that pressure will not develop during storage of the packaged coffee has been presented elsewhere (Clarke, 1987).

Inert gas packing of R&G coffee in metal containers is also practiced. The usual procedure is to first apply a vacuum and then release it with an inert gas, typically N_2 . In order to prevent excessive pressures developing in the can, it is necessary to degas the coffee to a much lower level than for high vacuum packing. Alternatively, a relatively low vacuum can be applied to the gas-purged can before finally sealing (Clarke, 1987).

21.4.3.2.2 *Hard Packs*

As an alternative to the metal can, so-called hard or shape-retentive packages of flexible laminated materials shaped into bags have been developed and widely used. These packs are called “hard” because on application of a high vacuum after filling and sealing, the material collapses onto the coffee to form a “brick,” which is hard to the touch. However, if significant quantities of CO_2 are evolved and/or air enters from the atmosphere, the bag will become “soft.” This is an undesirable condition since consumers may erroneously perceive that the coffee has deteriorated, although this is not necessarily the case.

Many flexible laminates used for this type of package used to contain a central layer of aluminum foil, but this has been replaced in many situations by a metallized layer. A typical early construction was PET-alufoil-LDPE 12-12-70 μ m, while contemporary structures are mPET laminated to low density polyethylene (LDPE). Most U.S. coffee roasters employ a more durable four-ply structure, which utilizes BOPP or OPA in addition to OPET, alufoil and LDPE.

The internal pressure at which the packs will become noticeably soft is of the order of 0.5–0.75 atm (50–76 kPa) (Clarke, 1987). This means that coffee that has been satisfactorily packaged in metal containers will need to be degassed to a greater extent before packing in laminate packs if a similar shelf life is desired. Degassing times range from 1 to 30h depending on the degree of roasting and the fineness of the grinding.

Another approach to avoid the problem of softening of the package and/or permit the packaging of freshly ground coffee is to include inside the package a sachet containing an absorber for CO_2 . The use of such sachets is now quite widespread.

21.4.3.2.3 *Soft Packs*

These packs or pouches (sometimes referred to as *pillow packs*) are similar to those which were described earlier for the packaging of RWB, and similar considerations apply. No vacuum is used and the O_2 content is reduced by flushing with an inert gas immediately prior to sealing. To provide an adequate shelf life, the packaging material must provide a good barrier to gases and water vapor. Again, adequate degassing of the ground coffee must be carried out prior to packing to avoid pressure building up inside the package.

The use of sachets containing an absorber for CO_2 , as described earlier for hard packs, is also possible for soft packs. However, it has become more common to incorporate a one-way valve into the side of the package which opens and releases CO_2 when a certain internal pressure is exceeded. The increase in internal pressure caused by CO_2 initiates opening at a pressure of 0.00345 atm (350 Pa), allowing the CO_2 to escape. When the overpressure declines to about 0.0005 atm, the valve closes again. It should be noted that volatiles also escape through the valve, leading to beverages with diminished sensory quality.

A recent innovation in the R&G coffee sector is the coffee pod, which contains the optimal quantity of coffee for a single-cup preparation. The Easy Serving Espresso pod, or ESE pod, is

one example. It looks like a small disk and contains 7 g of coffee prepacked in its own paper filter. Coffee pods are generally individually sealed in a high barrier metallized secondary package flushed with an inert gas (typically N₂) prior to sealing. More recently, coffee capsules have been introduced into the market. Designed for specific espresso machines, capsules have different shapes and may contain varying amounts of coffee, ranging from 5.0 to 7.5 g. The capsules are generally made of aluminum foil coated on the inside with a protective film. Before sealing, they are saturated with N₂ to improve shelf life (Nicoli et al., 2010).

21.4.3.3 Instant Coffee

In a review of the limited shelf life data and accompanying information on instant coffee, it was concluded (Clarke, 1993) that provided the moisture content was maintained at less than 4%–5% w/w, coffee will retain its original quality for at least 2 years at ambient (temperate) conditions. With more sophisticated products (i.e., with higher retained levels of volatiles), a shelf life of at least 18 months is possible, provided that the initial O₂ in the headspace is less than 4.0%.

Alves and Bordin (1998) investigated the shelf life of portion packs (25 and 50 g) of instant coffee at 30°C and 80% RH in three different plastic structures. The surface areas of the packs were 8 × 11 cm for 25 g and 10 × 16 cm for 50 g. The structure of the packages, their WVTR and the shelf life of the coffee at 30°C and 80% RH are shown in Table 21.1. The end of shelf life was when the moisture content had reached 7.8%, at which time powder agglomeration or caking occurred. Data on the shelf life of agglomerated and powdered instant coffee packed in PP and PET pots were presented in a later paper (Alves et al., 2000), the shelf life in the former being up to 2.5 years, compared to 4 months in the latter.

Ocampo and Giraldo (2006) reported that instant coffee packed in glass was rejected by 50% of consumers after approximately 2 years of storage at 18°C. Flexible materials containing aluminum foil (i.e., PET-alufoil-LDPE) as an O₂ and moisture barrier may also be very effective, giving shelf lives of around 1 year. However, a much lower shelf life is obtained when instant coffee is stored in other plastic materials.

For many years, instant coffee for the retail market was packaged in either tinplate cans or glass jars of various shapes. A laminated paper or metal foil diaphragm sealed to the rim of the container provided an effective barrier to water vapor and O₂, over which was placed a tight-fitting metal lid in the case of tinplate containers, and a screw cap of plastic or metal in the case of glass jars. More recently, “refill” packs of instant coffee packaged in flexible laminates of PET-alufoil-LDPE or metallized PET-LDPE have reduced the quantity of coffee packaged in metal containers and glass jars. The contents of such packs after opening in the home are refilled into glass or metal containers, and adequate shelf lives are generally obtained.

TABLE 21.1
Shelf Life of Instant Coffee in Plastic Packages

Package Structure	WVTR (g m ⁻² day ⁻²)	Shelf Life (Days)	
		25 g	50 g
LDPE (30 μm)	6.1	15	16
BOPP-BOPPP ^a (20 μm–40 μm)	1.2	84	94
MetPET-LDPE (12 μm–70 μm)	0.9	108	112

Source: Alves, R.M.V. and Bordin, M.R., *Cienc. Tecnol. Aliment.*, 18, 19, 1998.

^a Biaxially oriented pearled polypropylene.

21.5 TEA

Tea is the most widely consumed drink in the world after water. The appealing characteristics of tea as a beverage are its taste, aroma and color. Polyphenols (such as catechins) and amino acids (such as theanine) are the main contributors to the unique taste and color of tea. The components of essential oil in fresh tea leaves and volatile compounds developed during the manufacturing process form the characteristic tea flavor.

Although many types of tea are available around the world, teas may be classified into three general categories according to the manufacturing process used: fermented (black tea), semifermented (oolong and pouchong) and nonfermented (green tea). The different manufacturing conditions result in differences in taste, aroma and color as well as in storage stability and shelf life.

21.5.1 MANUFACTURE

21.5.1.1 Black Tea

Black tea goes through four processes: withering, rolling, fermentation and firing. After picking, the leaves are placed on trays to wither or dry for about 18 h. Heat may be applied to reduce the time to 6–8 h. The leaves are then rolled, which distorts the shape and crushes the cell walls, releasing oxidizing enzymes. The leaves are then spread out and held at ambient temperature and saturated humidity for about 13 h. This is the fermentation stage and results in the leaves changing from green to copper-red, as well as developments in the flavor. The final stage is heating to 82°C–93°C to denature the enzymes and stop fermentation. The moisture content is reduced to about 3%.

Oolong and pouchong teas are semifermented teas, with the fermentation process typically lasting 5–6 h, after which the leaves are heated with agitation in a pan at 200°C until the desired final moisture content is reached.

21.5.1.2 Green Tea

After picking, the leaves are steamed (Japanese type) or panned (Chinese type) to inactivate polyphenoloxidase and other enzymes responsible for fermentation. The leaves are then rolled and dried by a process similar to that used for black tea.

21.5.2 INDICES OF FAILURE

21.5.2.1 Black Tea

During storage, black tea consumes O₂ and evolves CO₂. The major indices of failure for black tea are (1) loss of volatile components; (2) changes in catechins, amino acids, theaflavins and other pigments; and (3) increases in undesirable taints arising from oxidative reaction products from fatty acids, and oxidation and condensation products from soluble polyphenols such as catechins and theaflavins. All these reactions are accelerated by increases in tea moisture content, elevated temperature and exposure to light. Although lipid oxidation is insignificant except under hot, dry conditions, oxidation of free fatty acids released during storage occurs during brewing and has a profound influence on the quality of the liquor. Exclusion of light is clearly important because photooxidation of lipids and nonenzymic browning reactions, both of which contribute to quality loss in black tea, are accelerated by light.

21.5.2.2 Green Tea

The major indices of failure for green tea are (1) change in color from bright green to olive green and then brownish green, (2) change in characteristic leafy and refreshing odor to dull and heavy odor and (3) changes from a well-balanced, complex taste to a flat taste lacking in characteristic briskness. All these reactions are accelerated by moisture, O₂, elevated temperatures and exposure to light, much as in the case of black tea.

21.5.3 PACKAGING

A moisture sorption isotherm for oolong tea is depicted in Figure 21.3. Despite a number of MSIs for tea published over the past 40 years, there are no published data on the critical moisture contents and $a_{w,s}$, making it difficult to specify the required barrier properties of a suitable package. Given that the initial moisture content of tea is 3%–4%, a good water vapor barrier is required to prevent a relatively rapid increase in moisture content. However, a reduction in the levels of various chemical constituents is more likely to contribute to the end of shelf life of tea than an increase in moisture content. The volatile fraction of black tea shows an overall decline during storage that is accelerated by moisture uptake and, to some extent, storage at elevated temperatures.

Loose tea is packaged in a multitude of different shapes, sizes and types of materials, the most common being a paperboard carton with either an aluminum foil liner or an overwrap of PP or RCF. Metal containers with snap-on lids are also used for some premium products. Tea bags have now become the most popular form of retail packaging, and considerable development has gone into improving the tissue paper used for this type of package, with porous wet-strength paper being required. Once filled, the tea bags must be placed inside a package that provides an adequate barrier to water vapor. Paperboard cartons overwrapped with PP or RCF are the most common.

The storage stability of green tea is the lowest among the various teas including black tea, oolong tea and pouchong tea. To most effectively protect the quality of green tea during storage, N_2 flushing or vacuum packaging is recommended.

Changes in biologically active green tea catechins during long-term storage of commercial tea leaves in the dry state were evaluated by Friedman et al. (2009). Samples of eight commercial green tea leaves of unknown history sold as tea bags in the United States, Korea and Japan were stored at 20°C for up to 6 months. The results suggested that the consumer needs to be aware about possible adverse consequences of long-term storage of commercial tea brands because even in the absence of moisture, the quality of teas may degrade with time.

Lee and Chambers (2010) studied how flavor changes in green teas that are stored over a period of 2 years (a typical shelf life for green tea products in loose leaf form). Two Korean green teas were packaged in metallized multilayer plastic films and stored at an ambient temperature of ~20°C. Samples were evaluated by highly trained panelists at 3, 6, 12, 18 and 24 months. Green tea changed minimally during the first year of storage and changed slightly more during the second year. However, these changes appeared to be minimal when the samples were packaged in metallized multilayer plastic films. Unfortunately, specific details about the barrier properties and composition of the packaging material and changes in the moisture content over time were not given.

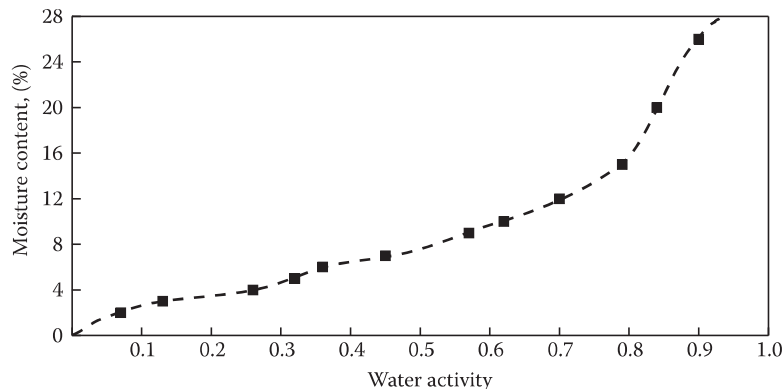


FIGURE 21.3 Moisture sorption isotherm for oolong tea at 25°C. (From Chen, C. and Weng, Y.-K., *Food Bioprocess Technol.*, 3, 226, 2010.)

Ready-to-drink (RTD) teas are a growing segment in the beverage category, brought about by improvements in the flavor of these products, their perceived health benefits and convenience. Kim et al. (2011) evaluated the impact of packaging materials on green tea polyphenolics and antioxidant capacity. RTD infusions were packed in glass, PET and a PET-PP retortable pouch (RP) and stored in the dark at 3°C for 12 weeks. Concentrations of the three major polyphenolics were better retained in glass bottles as compared to other packages over 12 weeks, while the antioxidant capacity was better retained in glass and PET versus RP. Because commercial RTD teas generally have a relatively long retail shelf life, significant losses in polyphenolic compounds or antioxidant capacity are to be expected, even under refrigerated conditions. Packaging materials with different OTRs are likely to be a significant shelf life predictor due to the relationship between O₂ permeability and antioxidant polyphenolic degradation observed in these trials.

21.6 JUICES

21.6.1 MANUFACTURE

Although fruit juices were originally developed to use up surplus fresh fruit production, fruit (in particular citrus and apple) is now specially grown for juicing. A variety of different types of juice is available. These include clear clarified juices such as grape, apple and blackcurrant; light cloud juices like pineapple; heavy cloud juices containing cellular material in suspension such as orange and grapefruit juices; pulpy juices such as tomato-based products; and nectars made by pulping whole fruits like peaches, apricots and comminuted citrus products.

The quality of a juice depends essentially on the species and maturity of the fresh fruit. The main factors that influence the quality are the sugar:acid ratio, the aroma volatiles, the phenolic components and the ascorbic acid content. Satisfactory fruit juice production depends on sound judgment of the raw materials and the blending procedures adopted. Details of the juice extraction and subsequent processing operations used are outside the scope of this book since they tend to be specific for the different types of juices; the reader is referred to standard texts on the subject for more specific information (Ashurst, 2005; Barrett et al., 2005).

A key step in the processing of fruit juices from the packaging point of view is the *deaeration* step. This is important both to minimize oxidative reactions in the juice and reduce corrosion if the juice is subsequently packaged in a metal container. O₂ in air, present in the spaces between the juice vesicles and from the surroundings, saturates the juice during extraction, producing oxidation reactions that often result in browning, changes in aroma and loss of nutritional value. These reactions are exacerbated by the increase in temperature during pasteurization and reduce the overall quality of the juice during storage (Garcia-Torres et al., 2009).

Pasteurization involves heating the juice in tubular or plate heat exchangers to temperatures in the region of 85°C–100°C for 2–45 s. Pasteurization was originally used as a means of controlling microflora, but it is also important for stabilizing the cloud of orange juices, as consumers regard orange juices without a stable cloud as inferior and unacceptable. Although pasteurization ensures the safety and extends the shelf life of orange juice, it often leads to detrimental changes in the sensory qualities of the product.

21.6.2 INDICES OF FAILURE

The five key indices of failure in juices are microbiological spoilage, nonenzymic browning, oxidation resulting in loss or degradation of flavor components and nutrients (essentially ascorbic acid), absorption of flavor compounds by the package (scalping) and, in some cases, cloud loss. Although preservatives were commonly added to fruit juices to overcome microbiological problems, the recent consumer preference for preservative-free foods has seen their use diminish. Instead, attention to good manufacturing practice in the plant, coupled in many cases with aseptic processing and packaging, has obviated the need for them.

The rate of browning and nutrient degradation in fruit juices is largely a function of storage temperature, although the rate is partly dependent on the packaging material. For example, Mannheim et al. (1988) compared the quality of citrus juices aseptically packaged in plastic-alufoil-paperboard laminated cartons and glass containers and found that the extent of browning and loss of ascorbic acid was greater in cartons than in glass, presumably because of O₂ permeation into the carton. Ahrné et al. (1997) reported OTRs for a 1 L laminated carton (surface area not given) of 0.009 mL pack⁻¹ day⁻¹ at 10°C, 0.014 at 20°C, 0.023 at 30°C and 0.038 at 40°C and noted that O₂ permeation occurred mainly through the seals. Assuming an inner surface area of 495 cm² (0.0495 m²) for the cartons analyzed by Ahrné et al. (1997), 0.009 mL pack⁻¹ day⁻¹ corresponds to an OTR of <0.18 mL m⁻² day⁻¹ at 10°C, 0.28 at 20°C, 0.47 at 30°C and 0.77 at 40°C (Lopez-Gomez et al., 2010).

Pasteurization was originally used as a means of controlling microflora. The acid conditions that prevail in most fruit juices will not support pathogens and tend to inhibit organisms in general, although acid-tolerant types may germinate and cause spoilage. The low pH conditions assist pasteurization so that 80°C for 30 s is adequate for virtually all juices except for the less-acid fruits such as apricot and tomato.

The sorption of key aroma and flavor compounds by plastic packaging in contact with juice is referred to as “scalping” (Sajilata et al., 2007). Because of its lipophilic nature, the oil fraction of orange juices will be absorbed by many nonpolar packaging polymers. Factors that affect absorption include molecular size of the aroma compounds and polarity and solubility properties of both the polymer and the aroma compounds.

Pasteurization is also important for stabilizing the cloud of certain juices (typically orange, grapefruit and tomato) because cloud particles impart characteristic flavor, color and mouthfeel, and consumers regard clarified versions of these juices as inferior and unacceptable. Such a reaction is based largely on tradition because lemon, lime and apple juices are invariably preferred in the clarified state but can be (and sometimes are) made to have a stable cloud. The major enzyme responsible for destabilizing the cloud is pectinmethylesterase, and it must be inactivated as soon as possible after extraction of the juice. This is generally done by pasteurizing the juice at 90°C–95°C for 15–30 s, the precise time depending on the pulp content. Recently, nonthermal methods such as high pressure processing have been commercialized for inactivating microorganisms and enzymes in fruit juices.

The oil fraction of citrus juices contains many volatiles which have a major impact on citrus aroma and flavor. These oil-based flavor compounds are relatively easily oxidized, resulting in the development of undesirable, terpene-like off-flavors. This form of flavor deterioration can be minimized by removing O₂ from the juice prior to packaging, avoiding high pressures during juice extraction so as to limit oil transfer to the juice and using a package that is a good barrier to O₂.

21.6.3 PACKAGING

From a packaging point of view, there are three categories of juices: single strength (10°–13° Brix), concentrated juices (42° or 65° Brix) and nectars (20°–35° Brix).

The traditional packaging procedure for single strength juices involved heating the deaerated juice to around 90°C–95°C in a tubular or plate heat exchanger, filling the hot juice directly into metal cans, sealing and inverting the cans, holding them for 10–20 min and then cooling. This hot-fill/hold/cool process ensured that the juice was commercially sterile and provided that the seams were of good quality, the cans had an acid-resistant enamel coating and the juice had been properly deaerated, a shelf life of at least 1–2 years was attainable. However, because of the acidic nature of fruit juices, any imperfections or scratches in the enamel coating or tin layer resulted in rapid corrosion, dissolution of metal into the juice, production of H₂ and container failure due to swelling. The use of glass containers obviated these problems provided that the container closure (typically metal) was resistant to attack by the juice.

The use of glass bottles for the packaging of fruit juices was widespread and is still used for high quality, single serve juices. The hot-fill/hold/cool process has to be applied with care to avoid

breakage of the glass containers. Gable top cartons consist of paperboard coated on both sides with polyolefins; aluminum foil or EVOH may be incorporated into the structure to improve its O_2 barrier and extend the shelf life to 4–6 weeks. Although the cartons are handled under nonsterile conditions, steps are taken to avoid recontamination. The filling temperature of the juice is typically 4–5°C to minimize microbial growth, although foaming can be a problem at this low temperature. The cartons are filled to leave a positively controlled headspace, and an inert gas such as N_2 can be injected immediately prior to sealing to remove O_2 from the headspace.

Fruit juices and concentrates can be packaged aseptically into plastic-alufoil-paperboard-laminated cartons. These products are then held at room temperature and the shelf life and nutrient composition are greatly influenced by the barrier properties of the carton, the interactions of the juice with the carton and the storage environment. The end of shelf life is typically 6–8 months and is related to the extent of nonenzymic browning and the sorption of key aroma and flavor compounds by the plastic in contact with the juice.

The stability of aseptically packaged fruit juices in cartons and LLDPE pouches with either EVOH or PVdC copolymer barrier layers was investigated by Alves et al. (2001). The OTRs in $mL m^{-2} day^{-1}$ were <0.1 for the cartons, 0.3 and 0.6 for the pouches containing EVOH at two thicknesses and 2.9 for those with PVdC. The performance of the packages with EVOH was virtually equivalent to that of the cartons throughout the storage period studied (90 days at 25°C).

Two flexible packaging formats are used for juices and especially for sports drinks. One consists of a stand-up pouch (SUP) constructed (from inside to out) of LDPE-alufoil-PET with a drinking straw attached to the side of the pouch; the sharpened end of the straw is used to pierce a specially prepared area on the pouch. Another is made up of four panels or sections combined to form a SUP with two side gussets, and a variety of laminate constructions are available. For beverages, the most common structure (from inside to out) is LDPE-PET-alufoil-PET. For specific applications, EVOH, OPA or PP can be included in the structure. A HDPE neck and straw is sealed into the top portion of the pack, which is filled through the neck and then sealed by a tamper evident closure. The packs can be cold or hot filled (up to 95°C) and pasteurized after filling if required.

Extrusion blow molded HDPE bottles have been used for many years to package fruit juices and drinks. As HDPE is a poor barrier to O_2 , such bottles can be used only for chilled juices with a shelf life of up to 3 weeks. The barrier properties can be improved by incorporating a layer of EVOH copolymer or PA, permitting shelf lives of up to 6 months, depending on the choice and thickness of the barrier layer.

Developments in barrier coatings for PET have led to increasing use of PET bottles for fruit juices and drinks. Berlinet et al. (2006) evaluated three different commercial 330 mL PET bottles: standard monolayer PET (PET1), multilayer PET containing an O_2 scavenger and complexed with nylon-MXD6 (PET2) and plasma-treated (internal amorphous carbon coating) PET (PET3). The O_2 permeabilities of the PET bottles were 0.0632, 0.0058 and 0.0056 *barrer* for PET1, PET2 and PET3, respectively. Glass bottles (500 mL) were used as the reference packaging. The bottles were stored at 20°C under artificial light (750 lx), and after 9 months, ascorbic acid had decreased from 383 to 310 $mg L^{-1}$ in glass, 132 $mg L^{-1}$ in PET1, 255 $mg L^{-1}$ in PET2 and 230 $mg L^{-1}$ in PET3, as shown in Figure 21.4. In the EU, orange juice must have $\geq 200 mg L^{-1}$ ascorbic acid at the end of shelf life. Thus, juice in PET1 would be unacceptable after 9 months, a result confirmed by Ros-Chumillas et al. (2007). In a later study, Berlinet et al. (2008) investigated the loss of aroma compounds from orange juice by permeation through the bottle (PET1 and PET2) and the cap. The results showed that permeation took place mainly through the cap. The use of an HDPE multilayer cap with an internal barrier layer of LDPE-EVOH-LDPE considerably limited the permeation of the aroma compounds, regardless of which PET bottle was used.

In the United States, the production of frozen concentrated orange juice has become a huge industry. The 42° Brix juice is usually held at $-12^\circ C$ at which temperature it is still liquid. Typical packaging materials for this product consist of spiral wound paperboard tubes with aluminum ends or aluminum cans.

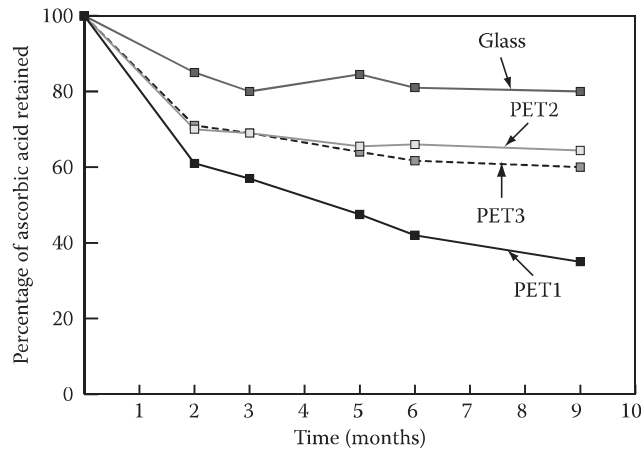


FIGURE 21.4 Percentage of ascorbic acid retained in orange juice stored for 9 months at 20°C under artificial light in glass and three types of PET (see text for details). Initial concentration was 383 mg 100L⁻¹. (From Berlinet, C., Brat, P., Brillouet, J.-M., and Ducruet, V., *J. Sci. Food Agric.*, 86, 2206, 2006.)

21.7 BEER

21.7.1 MANUFACTURE

Beer is an alcoholic beverage made by brewing and fermentation from cereals (usually malted barley) with added hops to give a bitter flavor. Two major technological steps are required to complete the transformation of the raw material into the finished product: controlled germination (i.e., malting) which allows the ultimate production of a fermentable extract through the activities of enzymes formed during seedling growth and fermentation.

Malted barley is crushed and “mashed” by mixing with water at temperatures of up to 67°C, resulting in rapid degradation of solubilized starch and less extensive hydrolysis of other high MW substances. This is followed by a leaching process, which completes the separation of the solutes from the spent grains. The resulting “sweet wort” is boiled in a copper or kettle together with hops (*Humulus lupulus* L.), after which the spent hops and precipitated high MW material are removed. The specific gravity of the wort rises as increasing amounts of sugars are extracted. After adjustment to the desired specific gravity, a selected strain of yeast is added. As the yeast grows and ferments the sugars of the wort, alcohol is formed and the specific gravity falls.

At the end of fermentation, the yeast is separated from the immature or “green” beer which is allowed to mature for an appropriate period. Before it is ready for consumption, freshly fermented beer must undergo a number of changes, including the elimination of certain fermentation products, supersaturation with CO₂, separation of yeast cells and removal of some of the polyphenolic and other material that will eventually give rise to turbidity in the beer. After centrifugation and filtration to remove residual yeast and assorted detritus from conditioned beer, followed by pasteurization and possibly other treatments, the beer is ready for packaging (Briggs et al., 2004).

The most common procedure for bulk beer is flash pasteurization where the beer is held at 70°C for ~20s before cooling and packaging. Tunnel pasteurizers are used with bottled and canned beer where the containers travel through an enclosed area in which they are sprayed with hot water, left for an appropriate time and then treated with a cold water spray.

21.7.2 INDICES OF FAILURE

The vast majority of beers are never better than when they are first filled into their containers (Bamforth and Krochta, 2010). The major indices of failure involve the production of off-flavors and off-colors due to oxidation, which is accelerated by light, transition metal ions (e.g., iron, copper and

aluminum) and heat. Oxidation of alcohols, iso- α -acids and fatty acids in beer produces carbonyl compounds that are detectable in sensory tests at low levels (Kuchel et al., 2006). In addition to residual O₂ from the brewing process, O₂ can find its way into packaged beer from three sources: (1) O₂ in the package headspace that is not removed during the filling operation, (2) penetration of O₂ through the package closure and (3) permeation of O₂ through the packaging material (Bamforth and Krochta, 2010). Even very low levels of O₂ (≤ 1 ppm) can lead to detectable flavor and color problems in beer. Typically, commercial brewers use a measurement of total package oxygen (TPO) which includes both the dissolved O₂ in the liquid and the amount of O₂ in the headspace of the package, typically a bottle or can. Continual improvements in packaging capabilities have brought the TPO down to <50 ppb (Kuchel et al., 2006).

Beer is sensitive to light, especially in the 350–500 nm range, and clear and green glass bottles allow penetration of light at these wavelengths, resulting in nauseous off-flavors. Such beer is said to be “sunstruck” and the taste and aroma are referred to as “skunky.” The compound responsible is 3-methyl-2-butene-1-thiol, which has a flavor threshold of 4–35 ppt. One strategy to overcome this problem is to use specialized reduced hop extracts that do not yield this breakdown product (Stewart and Priest, 2011). The more obvious solution in the present context is to avoid packaging beer in clear and green glass bottles if it is likely to be exposed to light.

One of the major oxidative reactions is the oxidation of linoleic acid (introduced into the wort from the malt) to yield the unsaturated aldehyde *trans*-2-nonenal which gives beer a “cardboard-like” flavor; it has a flavor threshold of 0.1 ppb and has been associated with human body odor. Flavor loss is accelerated in the presence of light and certain metal ions. Early on, it was assumed that it was mainly *trans*-2-nonenal that was responsible for sensory changes, but it is now evident that a myriad of flavor compounds is responsible (Vanderhaegen et al., 2006).

Because the fermentation process itself consumes O₂, brewing reduces the level of O₂ in beer down to 40–50 ppb prior to packaging. However, during the filling process, air enters the package and the level of O₂ can reach 250–500 ppb, which corresponds to 0.1–0.2 mL of O₂ per 355 mL bottle or can. This results in a shelf life for the beer of 80–120 days and even then significant flavor deterioration is likely to occur. Brewers would like to be able to reduce the O₂ level in beer to less than 50 ppb immediately after packing and hold it at that level for as long as possible. Use of a double evacuation technique with glass bottles which involves flushing with CO₂ can essentially eliminate any addition of O₂ to beer during the filling operation (Bamforth and Krochta, 2010).

One method by which flavor compounds can be depleted in beer is from sorption by the packaging material. Some of the more nonpolar flavor compounds in beer are more soluble in soft plastics such as the PVC liners in crown corks than in water. The degree of partitioning into such materials is a function of the polarity of the molecule in question, the volume and chemical composition of the plastic or other lining material, the volume and alcohol content of the beer and the temperature. For many bottled beers, loss of hop flavor to the packaging material occurs and may be a major source of hop flavor loss.

Owing to its low pH (<4.4), microbial degradation is not usually a problem with beer, and the use of pasteurization and aseptic cold filtration excludes wild (i.e., noncultured) yeasts that could thrive.

21.7.3 PACKAGING

21.7.3.1 Glass

The traditional packaging media for beer is the glass bottle sealed with a crown cork (see Section 10.1.3.1.1). Pasteurization of the beer in the bottle after sealing is the most common means of securing microbial stability. The aim is to heat the beer to a high enough temperature and hold it there long enough to destroy any beer spoilage organisms. The brewing industry has developed its own standard measure of the effectiveness of the pasteurization process and uses the term *pasteurization units* (PUs) where one PU is equivalent to holding beer at 60°C for 1 min. About 10 PUs is regarded as a suitable heat treatment for most bottled beers produced under good manufacturing practices.

The crown cork closure is made of tinplate or electrolytic chrome-coated steel and contains a compressible lining material, the composition of which has changed over the years from solid cork to composition cork, plastic and aluminum foil in various combinations. Today, the use of cork-based linings is relatively rare, and most crown closures are lined with PVC (often foamed) or sometimes HDPE. Where cork is still used, it is common to laminate it to aluminum foil to improve its barrier properties.

The material properties as well as the shape of the lining have a great effect on the rate of O₂ permeation through crown cork linings. Linings with aluminum foil provide a perfect barrier. Although PVC linings are normally foamed to different degrees, they appear almost solid after closing and permeation rates are almost identical. Ingress of O₂ does not appear to be measurably influenced by the condition of the glass sealing surface or the amount of pressure used in applying the crown to the bottle. The total ingress of O₂ through closure linings ranges from 0.6 to 1.2 μL day⁻¹ or 2.0 to 8.4 ppb day⁻¹ for a 355 mL bottle. If no O₂ is added to a bottle of beer during filling, the resulting shelf life for the beer would be 4–13 months for a maximum O₂ ingress of 1 ppm.

In an attempt to extend the shelf life of bottled beer, O₂-absorbing materials have been incorporated into the lining material of crown seals to remove O₂ present in the headspace at the time of filling as well as absorbing O₂ permeating into the bottle through the crown closure. The linings containing the O₂ absorber can be used in metal crowns as well as roll-on metal and screw-on plastic caps. They also find limited application in the fruit juice and carbonated beverage industries. It is recognized that pry-off crown closures provide a tighter seal than do twist-off crowns.

21.7.3.2 Metal

The first successful canning of beer occurred in 1933 in Newark, New Jersey, when 2000 cans were produced for a test market. In January 1935, the first beer cans went on sale—Kruegers Finest Beer and Kruegers Cream Ale. By the end of 1935, no less than 36 American breweries were canning beer.

The greatest problem with using cans for beer packaging was preventing the pickup of metal ions from the tinplated steel and lead solder of the early three-piece cans. The metal ions resulted in undesirable metallic flavors and the rapid onset of haze or “metal turbidity” as it was called. Although several reasonably successful enamel coatings were developed and used, it was not until the development of epoxy-phenolic resin linings around 1960 that a truly effective lining capable of eliminating metal pickup over a long term was found. These linings resulted in less than 0.3 ppm iron pickup over a 6 month period.

Until the late 1950s, tinplate was used almost exclusively. However, three-piece aluminum cans were launched in 1958 by Primo of Hawaii and in 1959 by Coors. This was followed in 1963 by some test markets of two-piece D&I aluminum cans. This latter type of can began to be mass produced in 1966.

Aluminum was used for beer can ends by Schlitz in 1960 when it introduced the “soft top” can to facilitate opening with a special tool known as a “church key.” A detachable pull-tab aluminum end was developed in 1962 by Ermal Frazee of Dayton, Ohio (see Section 7.7.5.1). It was test marketed and emerged in 1965 as the ring-pull tab. However, because it was detachable, it resulted in litter, and so, in 1975, a patent was granted for a can end with an inseparable tear strip that is the familiar stay-on tab in use today.

Aluminum cans provide a total barrier to light and prevent ingress of O₂ or egress of CO₂. Any oxidation leading to off-flavors, off-colors and haze is due to O₂ remaining in the beer after the brewing process and any O₂ added during the filling operation. Thus, the extension of shelf life of beer in cans appears to be dependent on reducing levels of O₂ exposure from these two sources (Bamforth and Krochta, 2010).

The use of foam-producing widgets, originally developed for stout beer packaged in metal cans, has been described in Section 15.3.5.

21.7.3.3 Plastics

The end of shelf life for beer is when O_2 ingress exceeds 500 ppb and CO_2 egress 10%. The shelf life of beer at 21°C in a standard monolayer PET bottle was shown to be only 3 weeks before ingress of 500 ppb O_2 and 4 weeks before 10% loss of CO_2 (Boutroy et al., 2006). To overcome these problems, a variety of barriers are offered commercially including amorphous carbon on the inside, SiO_x on either the inside or outside and O_2 -absorbing compounds as the middle layer in the bottle wall (see Section 5.5.2). The improved barrier to O_2 resulting from an amorphous carbon coating on PET bottles is shown in Figure 21.5. Today, a small but increasing quantity of beer is packaged in PET bottles with a barrier to provide acceptable shelf life, and this market sector is expected to expand rapidly over the next decade, mainly at the expense of glass bottles.

Interior DLC or amorphous carbon coatings were shown by Shirakura et al. (2006) to reduce O_2 and CO_2 transmission rates of PET bottles by 95% and 90%, respectively, with a resulting reduction in stale flavor (Table 21.2). Boutroy et al. (2006) reported that PET bottles with an amorphous carbon coating of 100 nm showed a shelf life at 21°C of 25 weeks based on ingress of 500 ppb O_2 or 38 weeks based on 10% CO_2 loss.

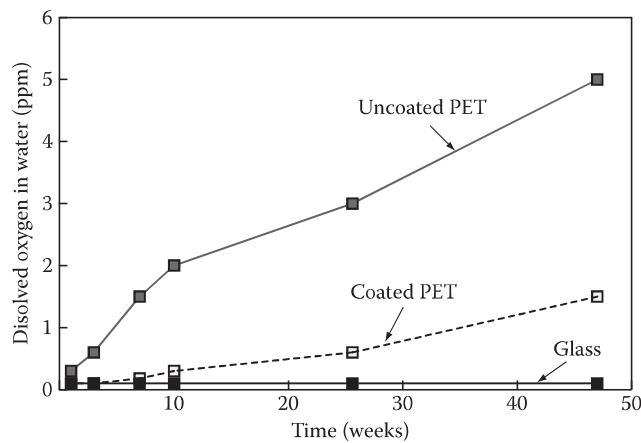


FIGURE 21.5 Dissolved O_2 in water versus time of uncoated and amorphous-carbon-coated PET bottles compared to a glass bottle. (From Boutroy, N. et al., *Diamond Relat. Mater.*, 15, 921, 2006.)

TABLE 21.2

Bottle O_2 Transmission Rate (OTR), CO_2 Transmission Rate (CDTR) and Bottled Beer Sensory Evaluation After Storage for 2 Weeks

	OTR (mL Bottle ⁻¹ Day ⁻¹)		CDTR (g Bottle ⁻¹ Day ⁻¹ atm ⁻¹)		Stale Flavor ^a	
	30°C	40°C	30°C	40°C	30°C	40°C
	PET bottle	0.1132	0.2167	0.0048	0.0071	6.5
DLC-coated PET bottle	0.0043	0.0061	0.00044	0.00059	4.7	5.0
Glass bottle	0	0	0	0	3.9	5.7

Source: Adapted from Shirakura, A., Nakaya, M., Koga, Y., Kodama, H., Hasebe, T., and Suzuki, T., *Thin Solid Films*, 494, 84, 2006.

^a 0, Not perceptible; 9, very strongly perceptible.

21.8 WINE

21.8.1 INTRODUCTION

Unlike most other foods and beverages, consumers generally expect wines to improve with age. However, this change is neither universal nor everlasting and varies from wine to wine, and expectations differ from consumer to consumer. Most wines improve only for a few months to a few years before showing irreversible loss in quality, and the changes are difficult to predict precisely. Thus, the required shelf life can be a few weeks to many years. Wine quality is a mix of extrinsic and intrinsic factors, and with prices ranging from as little as \$2 to more than \$1000 per bottle, it is not surprising that there is a significant variation in consumer quality expectations (Reeves, 2010).

21.8.2 CLASSIFICATION

Wine is a beverage resulting from the fermentation by yeasts of the juice of the grape with appropriate processing and additions. Wines can be assigned to one or the other of two major groups—table wines and fortified or appetizer wines. In the first group, the fermentable sugar has been largely consumed so that further fermentation by yeasts is prevented; spoilage organisms should not develop if the wine is kept anaerobic. Owing to the natural limit of sugar present in wine grapes, the alcohol content of such wines is normally about 12%–14%. The major subclass of these wines is the still wines, which have no evident CO₂. Further subdivision depends on color and residual sugar. It is possible to produce microbiologically stable wines having a moderate or high amount of residual sugar. The other major subclass of table wines is the sparkling wines. These have undergone two complete fermentations, where the CO₂ of the second fermentation is retained. Sometimes, cheap sparkling wines are produced by carbonation of still wines.

The second major group includes the dessert and appetizer wines which contain 15%–21% alcohol. The nature and keeping quality of these wines depend heavily on the addition of spirits (alcohol) distilled from wine, the amount of extra alcohol added being sufficient to prevent spoilage by further growth of yeasts or other microorganisms. There are three major subclasses in this group: sweet wines in which the addition of wine spirits serves to arrest the yeast fermentation with part of the sugar unfermented; sherries, which may be sweet or dry and are characterized by flavors induced by various types and degrees of oxidation; and flavored wines such as vermouths and trade-named proprietary specialty wines.

21.8.3 WINEMAKING

After harvesting at the correct stage of maturity, the grapes are destemmed, crushed and sulfur dioxide added to inhibit the growth of undesirable microorganisms, inhibit browning enzymes and serve as an antioxidant. If white wine is being made, the next step is the separation of the fluid must from the pomace (skins, seeds and part of the pulp). This is usually achieved by holding the crushed grapes in a large tank fitted with a screen through which free-run juice can pass. Juice is removed from the remaining material using a press. If red wine is being made, the separation occurs during fermentation; after the fermented juice has been run off, the remaining material is pressed to increase the yield and concentration of extractives.

Fermentation commonly occurs in large tanks in which the must is inoculated with selected yeasts. After fermentation has been completed, the wine is allowed to settle so that yeast cells and other fine suspended materials (known as *sediment* or *lees*) can collect at the bottom of the container. The relatively clear wine is then racked off its lees and stored in tanks or casks. Several additional rackings, along with finings, filtrations and stabilization treatments, may be required to produce wine that is and will stay clear until consumed. It is usual to age red (and some white) wines in wooden barrels for varying periods of time (up to 2 years in some instances) prior to blending and filling into the final package (Jackson, 2008).

Sparkling wines are made by fermenting for a second time wine that has been stabilized and fined beforehand. Yeast is added, together with fermentable sugar (typically sucrose), a rule of thumb being that 4 g of sugar per liter of wine will produce 1 atm of CO₂ pressure on fermentation; a final pressure of 6 atm is usually desired. For bottle-fermented sparkling wine, the wine is filled into champagne-type bottles, which are sealed with large wired- or clamped-on corks especially made for sparkling wines, or with plastic-lined crown seal caps. The sealed bottles are then stacked horizontally in a cool place to ferment (a process which typically takes several weeks) and then left undisturbed for 1–4 years to allow the wine to age.

The bottles are then placed on racks and a process (known as *riddling*) begins to remove the yeast sediment. By a process of turning and tilting each bottle, the sediment is moved into the mouth of the bottle. Following this, the neck of the bottle is placed in a bath at –15°C, which results in the formation of an ice plug containing the sediment. The bottle is then turned about 45° from the vertical and opened, whereupon the ice plug is pushed out by gas pressure. The *dosage* (syrup to adjust the sweetness of the wine) is then added, the level of wine is replenished if necessary and the bottle recorked with its final natural cork or plastic stopper which is wired into place. Today, automatic equipment is used in many wineries to perform these tasks.

21.8.4 INDICES OF FAILURE

The major index of failure in wines is oxidation resulting in dull, flat, “oxidized” flavors. With their lower levels of phenolics, white wines are more prone to oxidation and exhibit a loss of freshness, fruitiness and the development of browning and undesirable flavors. With red wines, the situation is more complicated, and some red wines are even given small, controlled doses of O₂ during maturation in a process termed *micro-oxygenation* with the objective of improving wine color, aroma and texture (Reeves, 2010). Oxidation in red wines involves condensation polymerization reactions between tannins and anthocyanins, resulting in loss of pigmentation and changes in color.

As discussed in Chapter 10, the style and development of wine is strongly influenced by the choice of closure because of the different O₂ barrier properties of the closures. Experts disagree as to whether some amount of O₂ benefits wine maturation after bottling, and some consider that a certain degree of oxidation is desirable in some wines (e.g., tannic reds, sherries and tawny ports) and undesirable in others (e.g., most whites and rosés). Oxidation reactions are assumed to play a dominant role in wine aging and seem to be related to measured values of O₂ transfer through various types of closures.

21.8.5 PACKAGING

Immediately prior to packaging, a small amount of sulfur dioxide may be added to the wine which is then given a final filtration. The potentially harmful effects of oxidation by air in the headspace of the package and dissolved in the wine are minimized or prevented by various procedures. The wine may be stripped of dissolved O₂ by passing bubbles of N₂ through it, and the package may be purged with N₂ or Ar and filled so as to displace the gas without introducing air. Other antioxidants (such as ascorbic acid) or other microbial inhibitors may be used, and the wine may be pasteurized or filtered through a membrane so as to be effectively sterile as it is packaged.

21.8.5.1 Glass

The most common form of packaging used for wines is the glass bottle sealed with natural cork. Cork is the outer bark of the cork oak tree (*Quercus suber* L.) and is tough, light and elastic. They are typically sterilized by exposure of damp corks in sealed plastic bags to SO₂, which seems to inactivate any microorganisms of concern. However, this treatment has no influence over the development of cork taint.

Copete et al. (2009) reported the incidence of halophenols and haloanisoles in aged Spanish red wines, with the most abundant being 2,3,4,6-tetrachloroanisole (TeCA) and TCA (6.8% and 5.3%, respectively). Of total wines sampled, 16.1% were contaminated with one or more compounds, with the most contaminated wines being those aged for at least 12 months. The cork stopper was not the only source of the tainting compounds; other possible sources were the wooden materials used during winemaking.

A variety of alternatives to the traditional cork closure have been developed, and these were discussed in Section 10.1.3.2. There is no doubt that closures have an important influence on wine quality during aging in bottles, and the increasing diversity of wine closures and their effect on wine development after bottling has been the subject of intense research. A review by Silva et al. (2011) focused on the impact of closures on wine quality during bottle storage and discussed the effectiveness of closures in protecting wine and the impact of closures on wine organoleptic properties. The role of closures in the removal and/or addition of undesirable compounds from/to wine was also discussed.

Variables such as closure type, gas flushing of empty bottles with inert gas, filler style, equipment maintenance, filler speed and preclosure headspace flushing affect the DO level in bottled wine (Reeves, 2010). An empty bottle contains 750 mL of air or over 200 mg O₂, and flushing bottles with 1–2 volumes of inert gas (CO₂, N₂ or Ar) may reduce the potential O₂ contribution from the bottle to 1–3 mg L⁻¹. Once the bottle is closed, it contains O₂ from the original bulk wine, headspace O₂ remaining after any gas flushing or vacuum application at the time of closure application and any O₂ within a cellular structured closure if such was used.

Headspace height depends on the wine filling level (55–63 mm) and on the length of the cork stopper (38, 44, 49 or 53 mm). Generally, a 15 mm headspace is maintained to avoid partial cork ejection in the case of headspace gas compression caused by thermal expansion of the liquid. This corresponds to 1–2 mg of O₂ available for dissolution in wine (or 1.3–2.7 mg L⁻¹) if a vacuum has been drawn in the neck of the bottle (Karbowiak et al., 2010). During the corking operation, the closure compresses the headspace atmosphere and, if no vacuum is drawn, this displacement creates a potential increase of O₂ dissolution into wine that could lead to a fourfold increase of O₂ uptake. Because cork contains between 80% and 85% of air in its cellular structure, a classical closure, with pre-compression dimensions of 44 mm length × 24 mm diameter, already contains about 4.8 mg of O₂ which represents a potential source of O₂ that could slowly diffuse into the headspace, even if the headspace has been sparged with inert gas (Karbowiak et al., 2010). With O₂ playing a pivotal role in the development and longevity of bottled wine, the O₂ level in the newly packaged wine and the quantity that subsequently ingresses are key determinants of shelf life (Reeves, 2010).

Because many types of wine are damaged by sunlight, the bottles are usually of colored glass, commonly dark green or brown. Bottled wine with cork closures is normally stored in the horizontal position so that the corks are kept moist, as it is assumed that this provides a better barrier to the ingress of O₂. However, a recent review (Karbowiak et al., 2010) concluded that there is no consensus on the effect of bottle position on O₂ mass transfer and wine aging over time and cited contradictory research findings to support their conclusion.

In champagne and sparkling wine, the concentration of dissolved CO₂ is an important parameter because it directly affects the sensory properties. Consequently, keeping the dissolved CO₂ molecules as long as possible inside the bottle during aging is an important challenge for champagne and sparkling winemakers. Natural cork stoppers are commonly used for champagne corking, but they are not completely hermetic with regard to gas transfers. Liger-Belair and Villaume (2011) reported losses of dissolved CO₂ close to 30% (11.5–3.5 g L⁻¹) in champagne aged for 75 months at 12°C. Both champagne temperature and bottle volume were found to be key parameters with regard to the kinetics of CO₂ losses through the cork, with smaller bottles showing a greater loss (Figure 21.6).

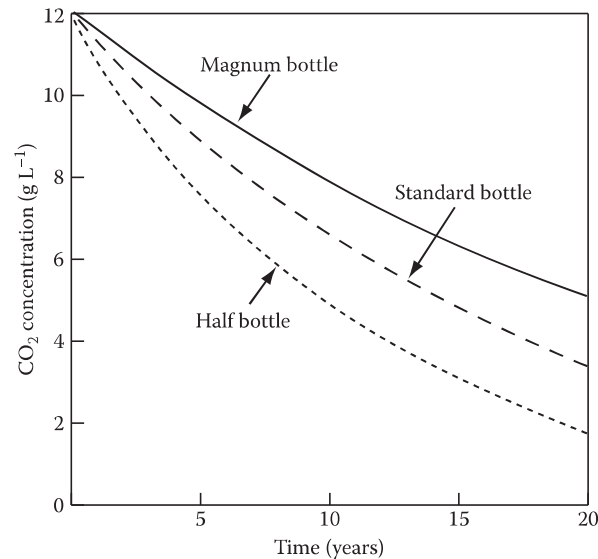


FIGURE 21.6 Theoretical concentrations of dissolved CO₂ in champagne during the aging process (cellar temperature of 12°C) for three distinct bottle types, namely, a magnum bottle (1.5L), a standard bottle (750mL) and a half bottle (375 mL). (From Liger-Belair, G. and Villaume, S., *J. Agric. Food Chem.*, 59, 4051, 2011.)

21.8.5.2 Plastics

21.8.5.2.1 Bag-in-Box

The most significant change in the packaging of wine (especially white wine) resulted from the development of the bag-in-box (BIB) package, a flexible, collapsible, fully sealed bag made from one or more plies of synthetic films, a closure and tubular spout through which the contents are filled and dispensed and a rigid outer fiberboard box or container. The bag-in-box concept appeared in the United States in the late 1950s, being introduced into the dairy industry in the form of a disposable, single-ply bag for bulk milk in 1957. By 1962, it had gained acceptance as a replacement for the returnable 19L can used in institutional bulk milk dispensers (Arch et al., 2009). It also found use in nonfood applications such as the packaging of sulfuric acid to activate dry-charge batteries.

Interest grew during the mid-1960s in Australia, and a PVdC copolymer-coated PA-LDPE laminate inside a fiberboard box entered the market in Melbourne in the 1970s as the first BIB package for wine. Today, five-layer coextruded bags are used that rely on the barrier properties of EVOH copolymer, the strength of PA and the sealability of LLDPE.

Metalized PET can also be used to improve O₂ barrier properties, but it has lower flex resistance. The OTR of multilayer metalized laminates can be as low as 0.0043 mL m⁻² day⁻¹. The physical strength of the bag is of prime importance, and it must remain intact during distribution and subsequent storage. During transportation, the bag is subjected to vibration which is transmitted to the wine through the materials that flex. Because all flexible materials have a fatigue life, eventually a hole appears and the bag fails. Methods of overcoming this problem include the use of polymers which have high flexure resistance and ensuring that the bag and box volumes are close.

Taps used in BIBs are now typically multicomponent types made from a variety of compounds including PP, LDPE and thermoplastic elastomer resin. Doyon et al. (2005) reported that up to 60% of total O₂ ingress in BIB is through the tap, and it is highly temperature sensitive ($Q_{10} = 1.9$ between 23°C and 30°C). Published values for OTRs of tap systems are in the range 0.04–0.2 mL tap⁻¹ day⁻¹.

Fu et al. (2009) investigated the effects of temperature (22°C, 35°C and 45°C) and storage time (48, 30 and 15 days) on the quality of white wine in BIB. Color, free and total SO₂, total aldehyde and total phenol were monitored and correlated with OTR. The quality changes were significantly affected by OTR of the BIB, and the valve contributed to more than 60% of the OTR of the whole package.

21.8.5.2.2 Bottles

Wine packaged in PET bottles is becoming increasingly accepted as it offers considerable reductions in weight and not insignificant reductions in total volume for the same content volume (Reeves, 2010). For example, an airline can save between 35% and 45% of the total weight currently involved in carrying wine and gain about 15%–20% additional space in a bar cart by replacing glass bottles with PET bottles.

The decrease in quality of red and white wines packaged in 1 L PET bottles with and without an O₂ scavenger was compared to wine packed in glass bottles by Mentana et al. (2009). All bottles were closed with screw caps and stored at 15°C–18°C in the dark for 7 months. Classical enological parameters including the anthocyanin fraction and the volatile fraction were monitored. Wines in the PET bottle with O₂ scavenger were similar to those in glass, particularly for red wines, although some oxidation as well as scalping occurred in the PET bottles. Red wine bottled in PET showed significant losses in most of the volatile compounds, including alcohols, acids and esters, although the concentration of some compounds increased which the authors could not explain. Fewer compounds were scalped by the PET bottles with an O₂ scavenger, and from white wines in both types of PET bottles.

Changes in the chemical and sensory quality of white and red wines packed in glass bottles, monolayer and multilayer (with nylon-MXD6) PET bottles and BIB with EVOH copolymer were assessed by Ghidossi et al. (2012). Commonly used and commercially available package volumes were used (185 and 750 mL for bottles and 3 L for BIB) and the wines were stored for up to 18 months at 20°C in the dark. White wine was noticeably affected after 6 months in PET monolayer bottles. In multilayer PET bottles, as well as in BIB containers, the results were similar to those in glass bottles. No significant differences were detected for red wine. Sensory analysis confirmed the chemical analyses and no differences were observed.

The 10–20 ng g⁻¹ of acetaldehyde that may be present in PET bottles prior to filling is not a problem for wine because not only will any free acetaldehyde rapidly react with free SO₂ rendering it non-odorous but the resulting reduction in free SO₂ (about 0.003 mg L⁻¹) will be insignificant. Moreover, acetaldehyde bound to SO₂ is found in wine as a result of normal fermentation (Reeves, 2010).

21.8.5.3 Metal

Wine has been canned in small quantities since the 1960s, using beverage cans made from aluminum or very occasionally tinplate. Although widely accepted for many beverages, cans have not been especially well received as packaging for wine. When packaging still wines in cans, it is necessary to increase the internal pressure in the cans by injection of N₂ or carbonating the wine to an internal pressure of about 170 kPa in order to prevent collapse of the can body. This is because the beverage cans are constructed in such a way that they rely on a significant internal pressure to augment the inherently low strength of the can body itself. The two main requirements for the successful packaging of wine in cans are the nature and integrity of the enamel lining on the inside walls of the can and the O₂ content of the wine at the time of filling. Modern epoxy enamel coatings are claimed to withstand 35 mg L⁻¹ free SO₂ and up to 250 mg L⁻¹ total SO₂. The O₂ content should be as close to zero as possible to minimize undesirable degradative reactions; this can be achieved by using N₂ gas flow closure. Wine in metal cans may from time to time show problems with sulfur-like odors (Reeves, 2010).

21.8.5.4 Laminated Paperboard Cartons

Since the early 1980s, increasing quantities of popular still wines have been packaged aseptically in plastic-alufoil-paperboard laminated cartons. It is not expected that the wine in cartons would be held by consumers for aging over long periods of time, and thus a shelf life of 6–12 months is all that

is required. This can be achieved, as the foil in laminates provides a good O₂ barrier (OTR about 0.02 mL m⁻² day⁻¹) providing about 12 months' shelf life even with packs as small as 200 mL. As with all other forms of wine packaging, the DO and headspace O₂ would be a significant contributor to loss of initial free SO₂ and hence influence shelf life. Brick-type packs can be formed with zero headspace, and so with good wine handling and filling technology, there is no reason why the initial DO levels in the packed wine would be significantly different to bottled wine (Reeves, 2010).

Buiatti et al. (1997) found that wine in cartons could be stored for up to 24 months, as measured by several quality-related properties, and that this was longer than for PET and BIB packaging. However, recent improvements to the barrier and scavenging properties of PET, as discussed earlier, have improved the performance of this type of package.

Scalping of flavors by plastic in contact with wine could present problems in certain situations. Licciardello et al. (2009) determined the sorption kinetics in LLDPE and CPP of two wine volatiles (ethyl octanoate and linalool) chosen on the basis of their low threshold and high odor activity value from a model solution simulating wine composition. Ethyl octanoate was sorbed more into CPP than LLDPE, and to a much greater extent than linalool, as a consequence of the different polarity of the molecules. The amount of ethyl octanoate lost at steady state led to a significant imbalance in the original aroma composition.

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