CHAPTER 4

Maple Syrup—Production, Composition, Chemistry, and Sensory Characteristics

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Contents

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Abstract Maple syrup is made from sap exuded from stems of the genus *Acer* during the springtime. Sap is a dilute solution of primarily water and sucrose, with varying amounts of amino and organic acids and phenolic substances. When concentrated, usually by heating, a series of complex reactions produce a wide variety of flavor compounds that vary due to processing and other management factors, seasonal changes in sap chemistry, and microbial contamination. Color also forms during thermal evaporation. Flavor and color together are the primary factors determining maple syrup grade, and syrup can range from very light-colored and delicate-flavored to very dark-colored and strong-flavored.

I. INTRODUCTION

Maple syrup is produced from the sap of several species of maple (*Acer*), chiefly through the concentration of sap via thermal evaporation. Although the chemistry of maple syrup is dominated by sucrose, a wide variety of sap collection and processing factors, microbiological interactions in sap, environmental influences, as well as the packing and storage of the finished product, combine to produce a range of chemistry and flavor profiles in maple syrup. Because of the large concentration factor (~40 gal of sap are required to produce 1 gal of syrup) and often delicate flavor profiles involved, several off-flavors are commonly found. Finally, the large price differential between maple syrup and other sweeteners provides incentive for adulteration.

II. HISTORY

Several different legends describe how Native Americans discovered that the sap of maple trees was sweet and could be boiled down to form maple sugar (Heiligmann *et al.*, 2006). The most likely explanation is that they observed birds and animals cutting holes or gashes into the twigs of trees, or drops of sap falling after branch breakage by snow or wind. These small wounds ooze sap in the spring, forming small drops of sap that are

concentrated by the sun and wind, or form sweet icicles of sap. The Native Americans undoubtedly recognized this and collected sap by cutting slashes in the trunks of maple trees and used skins, hollowed wooden vessels or clay pots to collect the sap, which was then concentrated by boiling to form a very dark and strong-tasting sugar. At certain times of the year, maple sugar could comprise a significant portion of their total caloric intake.

Early colonists throughout New England took up the practice of making maple sugar due to the high cost of imported sugars, and because the practice occurs at a time of year when other agricultural endeavors are not possible. Spouts made of hollowed out stem sections of elder or sumac twigs were inserted into holes cut in the trunks of maple trees with chisels. Later, metal spouts were produced and used in holes drilled with augers. Sap was first collected into hollowed-out tree trunks, then later wooden or metal buckets. In most cases, the final product was maple sugar (a solid), and only a relatively small amount of maple syrup (liquid) was produced.

Over the next few hundred years, the practice of tapping trees and collecting sap changed considerably. While some maple producers continue to use metal spouts and metal buckets to collect sap, plastic spouts and tubing are now relatively common. Some experimentation with metal tubing began in the late-1800s and early-1900s, however, the first successful commercial tubing systems arose in the 1950s and early-1960s with the introduction of plastic (PVC) tubing and associated plastic (Nylon) spouts and fittings to collect and transport sap to a central location, greatly reducing the labor required to collect sap. Initially tubing systems were run across the ground and vented, but continued experimentation and use resulted in tubing lines being suspended, unvented, and a drop line introduced to reduce reabsorption of sap by trees further down the line in the collection system. Shortly after tubing came into use, some researchers and producers began attempting to augment sap yield by applying vacuum to the tubing systems. The early results were encouraging, but maple sap yield was greatly bolstered with the advent of a new generation of tubing composed of Polyethylene, along with associated changes in spouts and fittings, and increased use of vacuum pumps designed for maple applications in the mid-1990s. The end result is that current high-yield production methods can achieve sometimes double or more the standard yield from buckets or gravity (nonvacuum) tubing installations.

The processing of sap into maple syrup has also changed greatly from colonial days. Early settlers used a batch method to boil sap in large kettles over open fires. This required a very long time and huge quantities of wood to produce a very dark and strong-tasting maple sugar with a moderate to substantial load of impurities. Modern maple evaporators

provide relatively continuous processing of sap, are very energy efficient, and generally produce a much lighter-colored and lighter-flavored maple syrup fairly quickly.

In addition to changes in collection and processing, the product itself has also changed. Presently, most maple is made into and marketed as syrup (liquid), with much smaller sales of maple sugar, cream, or candy than was historically the case.

III. MAPLE SAP FLOW

Under the appropriate conditions, a sweet sap can be collected from most maple (*Acer*) species. In general, however, only the sap of sugar, black, and red maple is commonly used to make maple syrup. Where maple trees are found in abundance and weather conditions are appropriate, commercial maple production can occur. This ranges from Nova Scotia to Minnesota from east to west, and from southern Ontario and Quebec in the north to areas of West Virginia in the south (Heiligmann *et al.*, 2006). Boxelder is sometimes tapped in areas of Manitoba and the Pacific northwest.

The physiological process responsible for sap flow in maple trees probably results from a combination of physical and osmotic forces (Cirelli *et al.*, 2008; Milburn and O'Mally, 1984; Tyree, 1983). In the physical model, fluctuations in wood temperature that span the freezing point during the leafless period (fall or spring) create alternating negative and positive pressures within the trunk and branches. When wood temperature falls below freezing, the water vapor within the billions of air-filled lumen of fiber cells freezes, forming a frost-like layer on the inside of the cell wall. Since the vapor pressure is much lower over ice than liquid water, this, and to a much lesser degree the contraction of the air bubble, create a vapor pressure gradient, causing water to move apoplastically (along cell walls) into the lumen, where it continues to freeze. Due to strong cohesion, and the vapor pressure gradient, water is pulled up through vessel elements towards the lumen. Eventually, the entire wood (fibers and vessel elements) and sap freezes. Freezing occurs first in the fine branches in the crown of the tree, then progressively downward. The amount of water uptake is dictated by soil water availability and the rate of freezing. A slow freeze ensures maximum uptake, whereas in a rapid freeze vessel elements in the stem of the tree may freeze before water uptake is complete.

During the warming phase, as the wood increases in temperature above the freezing point, the frost layer thaws, and the gas bubble expands. Sap pressure at the stem level increases very rapidly to a peak pressure, which is largely caused by gravitational potential, and

somewhat also by gas bubble expansion. This pressure may reach up to 40 psi (275 kPa). Over time, the pressure slowly recedes as sap is forced out of small wounds or into other areas of the tree, until the pressure within the tree equals the air pressure outside the tree, at which point flow ceases. The flow rate and total yield from tapholes is proportional to tree size and to the pressure gradient, thus sap flows faster earlier in a ''run'' than later. Root pressure is not a significant factor in maple sap exudation.

Recent evidence (Cirelli *et al.*, 2008) clearly demonstrates that there is also a considerable osmotic component to the development of sap pressure in maple due to anatomical barriers to sucrose between the vessel system and fibers. Further work is necessary to determine the precise contribution of physical and osmotic factors on sap exudation.

Maple producers exploit the sap flow phenomenon during the time of year when temperatures are expected to fluctuate around the freezing point by drilling small holes into the stem, inserting spouts, and collecting the sap in some fashion. Only trees that have reached a certain diameter (10–12 in. at breast height) are generally tapped. This ensures that the tree will be able to withstand the stress of tapping and regrow sufficient wood during the growing season to compensate for the loss due to tapping and the accompanying zone of discoloration (walling off, a normal wound response in trees to limit microbial infection). Sap will typically only flow for 1–2 months before microbial contamination of the taphole, or the lack of proper flow conditions (freeze–thaw) cause the flow to cease. In general, each taphole will produce about 10–20 gal of sap during the season, depending upon the collection technology employed, the environmental conditions during the season, and the size and sap sugar content of the tree.

Although sap will flow in both the fall and spring of the year, the vast majority of maple production occurs in the spring for several reasons. Sap in the spring is sweeter than in the fall, and decreasing temperatures as the season progresses from fall to winter can cause damage to equipment (split bags and buckets due to frozen sap) and frost-heaving of spouts out of tapholes. Trees should also not be tapped more than once per year.

Sap sugar content is not high at all times of the year. There is a strong seasonal pattern of production, accumulation, and utilization of nonstructural carbohydrate forms in maple. Starch, the dominant form of reserve carbohydrate in sugar maple, tends to be quite low during the photosynthetic period, and accumulates in the stem and twig wood towards the end of the growing season. Soluble sugars tend to increase during the winter and early spring as a function of temperature (Cortes and Sinclair, 1965). Sucrose is clearly the dominant soluble sugar in the xylem, with only minor amounts of glucose and fructose. Still lesser amounts of stachyose, raffinose, and xylose are also present (Wong *et al.*, 2003).

IV. SAP COLLECTION

Sap may be collected into galvanized or aluminum buckets or plastic bags, all of which require periodic (up to several time daily during high flow periods) emptying. When buckets or bags are used, maple producers must collect the sap into a larger, generally mobile container and bring it to the site where it is processed.

Sap may also be collected with a network of plastic tubing (Fig. 4.1). Collection with tubing generally does not require visiting each tree during the season after the intial tapping, as the sap flows through progressively larger tubing into a holding tank, often located at the site of sap processing into syrup. When using tubing, proper design, layout, and maintenance of the tubing system must be observed in order to maximize sap yield. The general rule for installing a tubing system is ''tight, straight, and downhill.'' Other factors that affect collection with tubing include the size of tubing, the number of taps on a lateral line, tubing layout, and several other considerations. Sap yields on gravity (buckets, bags, or tubing without vacuum) average about 8–10 gal of sap (~0.20–0.25 gal of syrup equivalent) per tap over a season.

Vacuum is used in many modern tubing installations, with a pump evacuating the tubing system to a level of 20–25 in. mercury (in Hg). By applying vacuum to the tubing network, the pressure gradient between the inside of the stem and the ambient air inside the tubing increases, resulting in a much higher sap flow rate and sap yield. This practice does

FIGURE 4.1 Maple tubing system. Spout is inserted into a hole drilled into the tree (on upper right), a dropline extends downward from the spout, and connects to the lateral 5/16 in. tubing line. The lateral line runs from tree to tree, and connects to the mainline (1 in. diameter pipeline in this case) which is suspended on tensioned steel wire.

not significantly impact sap sugar content, chemistry, or the amount of internal tree damage (Wilmot *et al.*, 2007a,b). The primary purpose is to augment sap yield, and to encourage sap flow during time periods when flows might otherwise be marginal. Sap yields on a well-designed and operated vacuum tubing system can reach 25 gal per tap (0.6 gal of syrup equivalent) each season.

Tapholes are drilled into tree trunks at a height of 3–7 in. above the soil within an area that is free of visible damage or older tapholes (which become progressively harder to see as the tree grows). Tapholes are normally 7/16 in. in diameter, but 5/16 in. diameter spouts introduced in the mid-1990s produce similar yields under vacuum with less tree damage (Wilmot *et al.*, 2007a) are gaining widespread acceptance. Tapholes are drilled to ~1.5–2.5 in. deep into the wood at a slight uphill angle to allow sap to naturally flow out of the taphole. A metal spout (if using buckets or bags) or a plastic spout is placed in the hole and lightly hammered in place. Spouts are generally removed at the end of the maple sugaring season to allow the tree to heal.

Several attempts have been made to increase the length of time sap flows from the taphole. Paraformaldehyde (PFA) was used for a few decades as a microbicide to reduce taphole ''drying.'' PFA use was phased out when it was determined to be harmful to the tree, and the use of any microbicide is currently illegal in all maple production areas. More recently, a denatured ethanol has been promoted to ''sterilize'' tapholes in some areas, but the lack of any lasting impact on microbial populations has limited its effectiveness in producing higher sap yields; in fact, some research has shown the practice to significantly reduce sap flow from such ''sterilized'' tapholes. There is considerable ongoing research into how to maximize sap yield in maple production, particularly in vacuum tubing operations.

Because sap is a perishable product, it is generally processed relatively soon after collection to minimize microbial contamination and the accompanying reduction in syrup quality. Sap is often filtered and UV-sterilized after collection to reduce microbial loads in order to maintain sap quality. Ozone treatment, although useful in water treatment, does not appear to be effective in maple applications, presumably due to the strong protective effect of sugars on microbial populations (Labbe *et al.*, 2001).

V. SAP PROCESSING: EVAPORATION

After collection, maple sap must be transformed through some means of concentration into maple syrup. The two major processes utilized are evaporation by heating and reverse osmosis followed by heating. The modern maple evaporator (Fig. 4.2) is typically composed of several

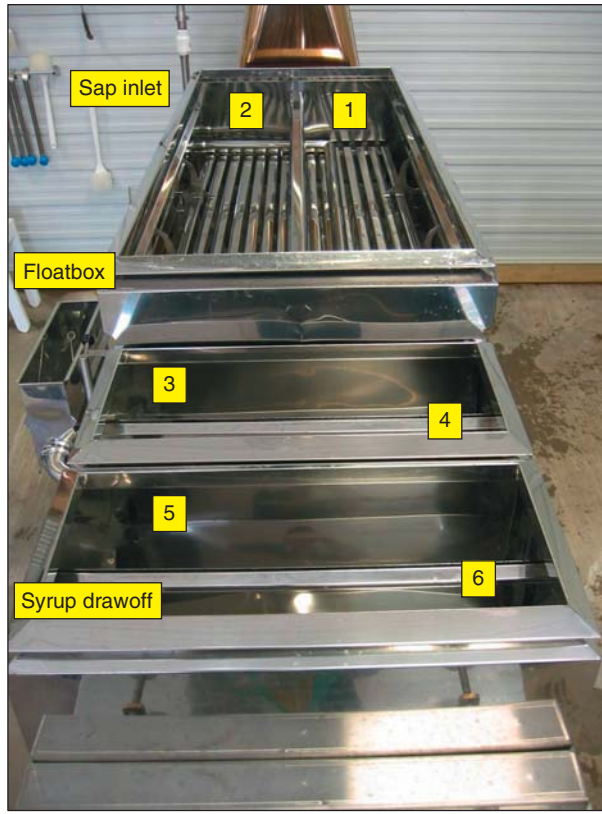

FIGURE 4.2 A contemporary maple syrup evaporator. Sap follows a winding path from the sap inlet, sequentially through the pan sections to the syrup drawoff.

parts: a heat source, an arch to contain and concentrate the heat, and pans, which contain the liquid and allow it to become concentrated.

Most evaporators utilize wood or oil as fuel, and commercial evaporators (as opposed to hobby-sized units) are insulated and efficient. Although wood was a common fuel source historically, it is being largely supplanted by oil due to the high cost of labor and convenience. Oil is easy to move around (as opposed to wood) and is easy to control (nearly instant on and off, with high and low settings). Most commercial evaporators are oil-fired, although some very large operations use high pressure steam to achieve a very rapid processing rate and to avoid scorching of evaporator pans.

The arch is made of cast iron or steel and sits under the pans to contain the heat. Oil-fired units have the burner located at the front, slanting upward, and with the fire pointing towards the rear (stack). The inside of an oil-fired arch is lined with ceramic blanket insulation. Wood-fired

units are usually lined with fire-brick and contain metal grates, sometimes with forced ventilation. A wood-fired evaporator has doors in the front through which wood is added. The hot gases flow back towards the rear of the unit and stack. Pans, normally composed of stainless steel, sit on top of the arch. Today, nearly all evaporator pans are Tungsten Inert Gas (TIG) or Metal Inert Gas (MIG) welded, and conform to widespread food industry construction practices. Formerly, most pans were soldered, and constructed of stainless steel, although sometimes older units were composed of English tin, or less frequently, copper. Prior to 1994, most solder contained lead; after 1994 lead-free silver solder (tin-silver) was used for pan fabrication. Considerable attention has been recently focused on developing and promulgating standards for maple equipment manufacturing (LMEA, 2001).

Most evaporators have two distinct types of pans, the back pan (also called the flue pan or sap pan) and the front pan (or syrup pan) (Figs. 4.2 and 4.3). The back pan, where the majority of the water is evaporated from the sap, has deep flues that are designed to maximize heat exchange and evaporation. Back pans come in two configurations, drop-flue and raised-flue, based upon whether the flues in the pan extend above or are even with the position of the pan on the arch rails. Neither type is clearly dominant in the industry. Sap enters into the back pan; generally via gravity feed through a pipe connected to the sap storage tank and is regulated by a mechanical float or an electronic valve. The back pan is internally divided into two or more sections which result in a semichanneled flow from the sap inlet to an outlet near the front pan.

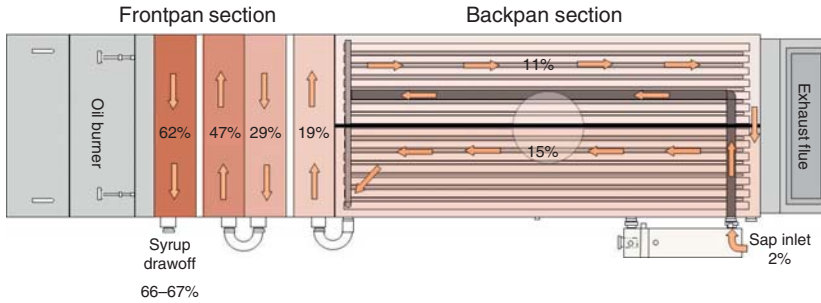

FIGURE 4.3 Schematic diagram of a maple evaporator. Numbers and shading density show the density (°Bx) of liquid within different partitions of the evaporator during evaporation. Sap enters the back pan section of the evaporator at the lower right and flows through a feed-pipe into the partition at the upper right. It then flows around the back, and then forward. Two front pans contain two partitions each. Sap flows into the front pan section through a pipe connecting the back pan to the front pan at the lower middle. Sap/syrup then flows through each front pan partition, increasing in density and developing color and flavor during the process. Syrup exits the evaporator at the lower left via an automatic drawoff, which opens when the density of syrup close to the drawoff area is correct, then closes again when the density drops below that of finished syrup.

Sap flows from the back pan into the front pan, sometimes using another float or valve to regulate the entry of sap. The bottom of the front pan is flat, and the front ''pan'' may actually be made up of one or more pans, with each separate pan itself divided into several partitions. Front pans are made in one of two configurations: those in which the sap runs parallel to the main axis of the evaporator, termed reverse-flow evaporators, and pans in which the sap flows from side-to-side, termed cross-flow evaporators. In both cases, syrup flows out the last partition of the front pan via a manual or automatic draw-off valve into a pail or directly into a pipeline feeding a filtration system.

Modern maple evaporators are designed to have a relatively continuous or semicontinuous flow. In theory, an evaporator can be envisioned as a long continuous stainless steel ''gutter,'' with heat applied under the entire surface. Sap flows in one end of the gutter (the back pan), and syrup flows out of the other (draw-off of the front pan). Because it is impractical to have an evaporator that is tens of feet long, the gutter is bent into sections to reduce the overall size, and to allow a single heat source to be located under the evaporator pans. Commercial evaporators are commonly sized to fit the number of taps in the sugaring operation, and range in size from 3 ft. $\times$ 10 ft. (width $\times$ length) up to 6 ft. $\times$ 18 ft., with the back pan section typically occupying about two-thirds of the overall evaporator surface area. The depth of sap in the pans is generally kept quite low, only 1.5–2.0 in., to maximize boiling rate.

Ancillary equipment is often used in conjunction with evaporators. Hoods are employed to channel steam out of the processing facility (termed a sugar house, sugar shack, maple house, etc.). Several types of devices are manufactured which sit over the evaporator pans to take advantage of the steam energy to preheat or preconcentrate the sap before it enters the back pan.

Often syrup is drawn off at a density slightly lower than of finished maple syrup, and is brought to final density in a separate finishing pan. Finished syrup is filtered to remove solids and generate a clear product. Filtration through a wool or synthetic cone filter is sometimes used in smaller operations; most modern commercial production scale operations employ a pressure filter utilizing diatomaceous earth as the filtering media. Bulk syrup is hot-packed in 30–50 gal drums (stainless or galvanized steel, epoxy lined steel, or plastic) for storage before being reheated and packaged into retail containers as needed.

VI. ANNUAL SYRUP PRODUCTION

The yearly worldwide production of maple syrup is roughly 8–9 million gal ($\sim$45,000 metric tons), of which $\sim$15% is produced in the United States, and 85% produced in Canada. The New England/New York region

cumulatively produce about 75% of the total domestic U.S. crop. Quebec is the largest Canadian producer, with about 90% of the total Canadian production originating there. The largest markets of maple are in the U.S., Canada, Europe, and, increasingly, Asia.

VII. SAP CHEMISTRY

Maple sap is a dilute solution of mainly water and sugar, along with trace amounts of other substances, including organic acids, free amino acids, protein, minerals, and phenolic compounds. Although the proportions are somewhat variable, sap is normally composed of 95–99% water and 1–5% sugar.

The primary sugar found in uncontaminated sap is sucrose, which ranges from ~96–99% of the total sugar present (Table 4.1). As microorganisms contaminate sap, particularly later in the sap flow season, invert (reducing) sugar levels increase, reaching up to about 0.20–0.25% of the total sugar concentration in sap (Dumont, 1994; Heiligmann *et al.*, 2006). At times, several other sugar forms, including mono-, di-, tri-, and higher oligosaccharides, may also be found in maple sap (Dumont, 1994; Haq and Adams, 1961; Stinson *et al.*, 1967), although typically in very low concentrations.

Sap pH ranges from 3.9 to 7.9, but in most cases is only slightly acidic, with a typical range of 6.5–7.0. There is a slight trend for sap to become more acidic as the sap flow season progresses (probably due to microbial action). Conductivity normally ranges from 320 to 520 μS/cm.

The total concentration of sugars in sap varies due to several factors. Variation between individual trees may be quite large due to differences in genetics, growth rate, and crown density. However, the ranking of any one tree relative to its neighbors tends to remain relatively constant both within a season and from season to season (Taylor, 1956).

TABLE 4.1 Sugar composition (% dry weight) of the solid fraction of maple sap (from Perkins *et al.*, 2006, used with permission)

Sucrose	96–99
Polysaccharides	nd— 0.5
Oligosaccharides	nd—0.02
Glucose	nd—0.17
Fructose	nd—0.10
Quebrachitol	nd—0.15
Unidentified	nd—0.67

Sap sugar content within an individual tree may vary from one season to another to a relatively high degree, probably as a result of photosynthetic carbohydrate gain in the prior growing season. Sap sugar content also varies within a season, typically decreasing throughout the season.

Although at one time, it was believed that the use of tubing systems with vacuum might result in a dilution of sap sugar content and increased internal wounding in trees, recent research has shown that this is not the case. Wilmot *et al.* (2007b) demonstrated that sap collected at high vacuum levels (>18 in. Hg) did not result in diluted sugar content, did not contain significantly different levels of minerals, and did not cause larger zones of discoloration in maple stems.

The average sugar content of a forest stand utilized for maple production has a large impact on the economics of maple production, as a sugarbush containing a higher level of sugar in the sap will require considerably less energy to produce 1 gal of syrup compared to a sugarbush with a lower sugar content. Maple producers can increase sap sugar content by selecting individual trees with higher sap sugar content during thinning, and by encouraging good crown and stem growth through crop tree management techniques. Fertilization of trees, although not a common practice in maple operations for a number of reasons, can be used to correct nutritional deficiencies and stimulate growth (Perkins *et al.*, 2004a), and may increase sugar yield from a site (Perkins *et al.*, 2004b).

The inorganic composition of maple sap is highly variable (Table 4.2). Potassium and calcium make up the bulk of the inorganic fraction of sap, with substantial amounts of magnesium and manganese, and only trace amounts of sulfur, phosphorus, zinc, and copper, followed by aluminum, sodium, boron, and iron. In contrast to what is observed in sugar concentration, most of these elements show a slight or strong tendency to increase in concentration during the sap flow season (Marvin and Greene, 1959). Lead is generally below detection limits unless contaminated by lead-containing equipment.

The gases expressed from maple stems during sap exudation show higher carbon dioxide and correspondingly lower oxygen concentrations compared to ambient air, indicating substantial respiratory activity in maple wood during the leafless period of late-winter to early-spring (Marvin and Greene, 1959).

A wide range of free amino acids are found in sterile maple sap (Heiligmann *et al.*, 2006), including glycine, alanine, asparagines, threonine, leucine, isoleucine, valine, and methionine. Morselli and Whalen (1986) examined the change in the distribution of various amino acids over two maple sap seasons. Their results indicated that initially, only a small number (6–7) of amino acids were found in sap, all in relatively low concentration. As the season progressed, the diversity of amino acids increased to 12–15. In addition, the concentration of amino acids present

TABLE 4.2 Inorganic (minerals and metals) composition of maple sap

Element	Range[a] (ppm)	Range[b] (ppm)	Mean[b] (ppm)	Mean[c] (ppm)
Potassium	27–95	50–81	65	25
Calcium	21–77	35–75	50	40
Magnesium	2.6–9.0	3.9–8.1	5.6	3
Manganese	2.7–9.7	1.7–5.5	3.5	
Sulfur		0.18–1.80	0.77	
Phosphorus	2.5–8.0	0.2–1.1	0.65	
Zinc		0.24–1.47	0.55	
Copper		0.08–1.56	0.50	
Aluminum		0.04–0.20	0.10	
Sodium	nd—4.0	0.02–0.17	0.08	
Boron		0.02–0.16	0.08	
Iron	nd—3.7	0.01–0.07	0.04	
Lead		nd	nd	

[a] Marvin and Greene (1959).
[b] van den Berg and Perkins (unpublished).
[c] Dumont (1994).

in late season sap may rise to over 10 ppm (Dumont, 1994), probably reflecting the breaking of winter dormancy and an acceleration of metabolic activity in the trees. These changes could have a significant impact on the characteristics of syrup produced, as the nitrogen content of sap, primarily amino-N (Pollard and Sproston, 1954), has a large influence on the development of flavor and off-flavor compounds in maple syrup.

Uncontaminated maple sap has the same appearance as water in that it is nearly colorless, with very high light transmission through the visible range (Fig. 4.4). Some absorption is found in sections of the UV and near infrared (NIR) ranges.

Several organic acids are also found in maple sap (Table 4.3). In general, the total quantity of organic acids starts out low, and rises throughout the sap flow season. Malic acid (concentration 800–45,000 ppb) is by far the most common organic acid, ranging from just over 50–99% of the total acid present. Succinic acid and oxalic acid are also fairly dominant forms. Other acids occur sporadically in low concentration (Dumont, 1994; Mollica and Morselli, 1984).

A wide range of phenolic compounds, varying in type and concentration, can also be found in maple sap (Dumont, 1994). Most of these appear to be derived from lignin (Kermasha *et al.*, 1995). They range in concentration in sap up to 0.1 ppm. The most dominant phenols present tend to

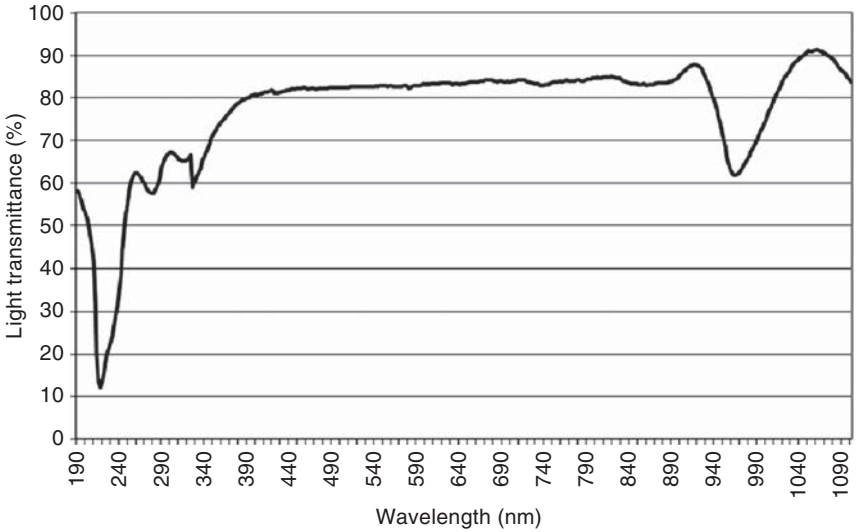

FIGURE 4.4 Transmission profile of maple sap at 2 °Bx from 190–1100 nm. Sap was collected on March 29, 2006, then stored frozen until analyzed.

TABLE 4.3 Organic acids in maple sap (Dumont, 1994).

Organic Acid	Mean (ppb)
Malic	14,940
Fumaric	1677
Succinic	910
Oxalic	380
Aconitic	193
Citric	109
Tartaric	59
Total	18,033

be: sinapic acid, coumaric acid, syringaldehyde, and coniferaldehyde, with lesser amounts of vanillic acid, syringic acid, homovanillic acid, and ferulic acid (Table 4.4). No clear temporal trends in total phenol levels are apparent (Dumont, 1994), although some work does suggest that variation in vanillin glycoside concentrations are correlated with seasonal changes during the sap flow period (Belford *et al.*, 2006). A variety of flavonoids, including catechin, flavanols, and dihydroflavonols, are also found in maple sap (Deslauriers, 2000). Some of these exhibit strong seasonal tendencies.

TABLE 4.4 Phenolic compounds in maple sap (after Dumont, 1994)

Compound	Mean (ng/ml)[a]
Sinapic acid	31.8
Coumaric acid	15.0
Syringaldehyde	14.9
Coniferaldehyde	13.4
Vanillin	9.7
Vanillic acid	9.5
Homovanillic acid	8.4
Syringic acid	3.9
Ferulic acid	2.4
Coniferol	1.6
Total	110.7

[a] Normalized to 1 °Bx.

Many of these compounds are likely to be flavor precursors, although the influence of each on the final flavor profile of the resulting maple syrup is greatly affected by storage, as well as the type and length of processing. Because there are a number of transformations during processing, and many of these compounds are volatile when heated, the concentration is not necessarily increased in maple syrup.

There is an increasing interest in the quantity and composition of phenols in maple sap and syrup, due to the antioxidant, antiradical, and antimutagenic activities of these compounds (Thériault *et al.*, 2006).

A. Transformation during storage

While in the xylem, sap generally is considered to be sterile. Immediately upon being exposed to taphole conditions, it is acted upon by a wide variety of microorganisms, including bacteria, fungi, and yeasts. The major impact of this contamination on the syrup making process is the conversion of a small quantity of sucrose by invertase.

Because it is colder and all the equipment is clean, sap collected early in the maple sap flow season tends to be very low in microbial load, and thus low in invert sugar concentration. As the season progresses, daily temperature tends to increase. This results in the sap collecting system becoming colonized with microorganisms, increasing the invert level of the sap. Some producers use intermediate season tubing washes or rinses to reduce microbial contamination, although the efficacy of mid-season cleaning is most likely relatively minor and short-lived.

Proper filtering of sap, cool storage before processing, and rapid processing are commonly used to reduce microbial growth in sap. Growth of microorganisms may slightly or significantly alter the form of several elements in sap, especially by causing the forms of nitrogen and phosphorus to be changed, by increasing the protein component in sap, and by altering the turbidity of sap. Sap that has been extensively colonized by yeasts may undergo fermentation. Extremely high levels of microorganisms, especially at the end of the season, may cause syrup to become ''ropey,'' a sticky, stringy, gelatinous texture that is almost impossible to remove, thus rendering it essentially unmarketable.

B. Transformations during reverse osmosis/nanofiltration

Due to the high cost of fuel, and to reduce the time required to process sap into maple syrup, an increasing number of maple producers are using reverse osmosis/nanofiltration (hereafter collectively termed RO) to increase the sugar concentration of sap prior to boiling. Sap processed via RO is called ''concentrate,'' and tends to be slightly yellow in color. Although early units were adapted from water desalination units, commercial RO machines specialized for the maple industry are now available from a variety of manufacturers. There is also a strong trend towards increasing levels of concentration of sap with RO. In the past, most maple producers were content to concentrate sap to 8 °Bx. Currently, many producers are striving to concentrate to the highest degree possible (~25 °Bx). The major effect of preconcentration of sap via RO is the removal of water. Going from 2 to 8 °Bx achieves a 75% reduction in the amount of evaporation necessary (from about 43 gal of sap to about 11 gal to produce a gallon of maple syrup). A further concentration of sap to 16 °Bx would require only 5.5 gal of sap to produce 1 gal of maple syrup (Fig. 4.5).

Concentrate is extremely perishable. Most maple operations utilize RO machines that are capable of providing only slightly more concentrate per hour than can be utilized by the evaporator. In practice, most producers will concentrate a small amount of sap, start the evaporator, and continue to run the RO during boiling so that the concentrate is not allowed to build up and spoil.

The by-product of sap concentration by an RO, permeate, is also used in maple operations as a source of very clean water. Due to the low mineral concentration of permeate water, it is used for cleaning tubing and evaporator equipment, as well as the RO membrane itself, which should be run through a wash and rinse cycle after each use. The chemicals and dosage to be used are specified by the membrane and RO manufacturers, and should be carefully followed to avoid damaging the membrane or contaminating the sap concentrate.

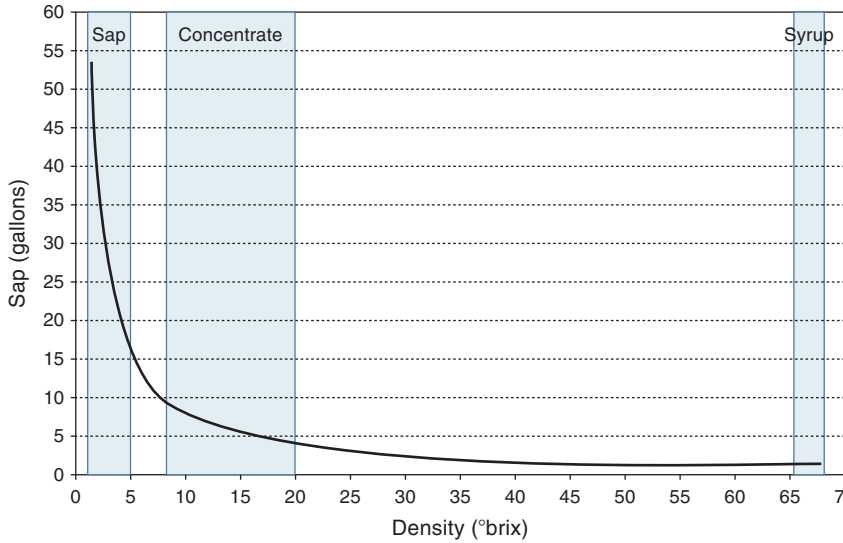

FIGURE 4.5 The relationship between the density and the number of gallons of sap required to produce 1 gal of maple syrup. The normal range of raw sap, sap concentrated by reverse osmosis (concentrate), and finished syrup are shown.

Obviously, the use of RO has tremendous consequences to the amount of evaporation, and thus heating time necessary to make syrup. Because much of the color and flavor development occur during the heating phase of processing, RO use should strongly affect the resultant color and flavor of maple syrup produced, although there has been little research clearly demonstrating the effects. Ongoing efforts (van den Berg and Perkins, unpublished data) do appear to indicate some significant changes in syrup compositional attributes.

Depending upon the membrane and RO used, the chemistry of the concentrated sap may be somewhat different than what might be expected by a simple concentration factor alone. Some membranes sacrifice a slight amount of sugar and mineral passage for high flow rates, while others provide very high sugar retention, with correspondingly low flow rates. Although it has not been extensively investigated, limited research has determined that phenols are concentrated, but aldehydes and alcohols in sap are reduced during RO use (Kermasha *et al.*, 1995). Prefilters and membranes may also serve as a source of microbial contamination of sap.

C. Transformations during evaporation by heating

Although the single greatest influence of the process of transforming sap into syrup is the removal of water, the effect on the chemistry and flavor is not simply due to concentration. Rather, a number of complex reactions

are involved which result in the chemistry and flavor profile of maple syrup. Given the huge number of permutations in storage, processing conditions and rates, and temporal variations in sap chemistry, only generalizations are possible.

The first and most obvious transformation that occurs during evaporation is the change in sugar content (Fig. 4.6). Sap enters the process at an average of around 2 °Bx, and the finished product, maple syrup is around 66–67 °Bx (Figs. 4.3 and 4.5). The process inside the evaporator is theoretically one in which a semicontinuous gradient of sugar is formed. Initially, as an evaporator is first started with sap only, the inflow of sap into the back pan will gradually cause a gradient to form. This gradient eventually perpetuates throughout the entire evaporator, with a density near that of syrup near the draw-off, and near that of sap at the inlet of the back pan. In reality, the evaporator is more or less a series of interconnected pans, each with their own sugar content, but certainly influenced by the sugar concentration in the pan immediately before and after it. The semicontinuous flow of sap in, and regular draw-off of syrup, maintains the sugar gradient within the entire evaporator system. Sometimes, after a short period of boiling, maple producers will ''sweeten'' the partition nearest the draw-off with syrup to hasten the development of a proper gradient, although this is not necessary for the gradient to form.

As the density gradient along the evaporator develops, a concomitant increase in boiling temperature also is found (Isselhardt *et al.*, 2007). Raw sap boils at 212 °F, and syrup at 66.5 °Bx boils at 219.3 °F (at standard atmospheric pressure). Most producers use a hydrometer, calibrated in Brix or Baume and corrected for temperature, to determine the finished syrup density.

The second most obvious transformation during heating is a change in color (Fig. 4.6). As sap progresses through the evaporator, it darkens due to nonenzymatic browning, a complex suite of chemical changes arising from nonenzymatic activity acting on sugar solutions. The longer the time and intensity of heating, the greater the effect on color and flavor development (Willits *et al.*, 1952). These same processes are also intimately involved in flavor formation. The rate of nonenzymatic browning reactions varies greatly depending upon sap chemistry (particularly the invert sugar and amino acid concentration) and on processing rate and conditions. In general, syrups that are low in invert sugar concentration (typical early season sap) produce light-colored and light-flavored maple syrup, whereas those that have high invert levels produce darker colored and stronger tasting syrups due to increased substrate availability for nonenzymatic browning reactions (Naghski and Willits, 1957).

Maple producers attempt to control the color and flavor profiles of the syrup they produce primarily though rapid processing of sap.

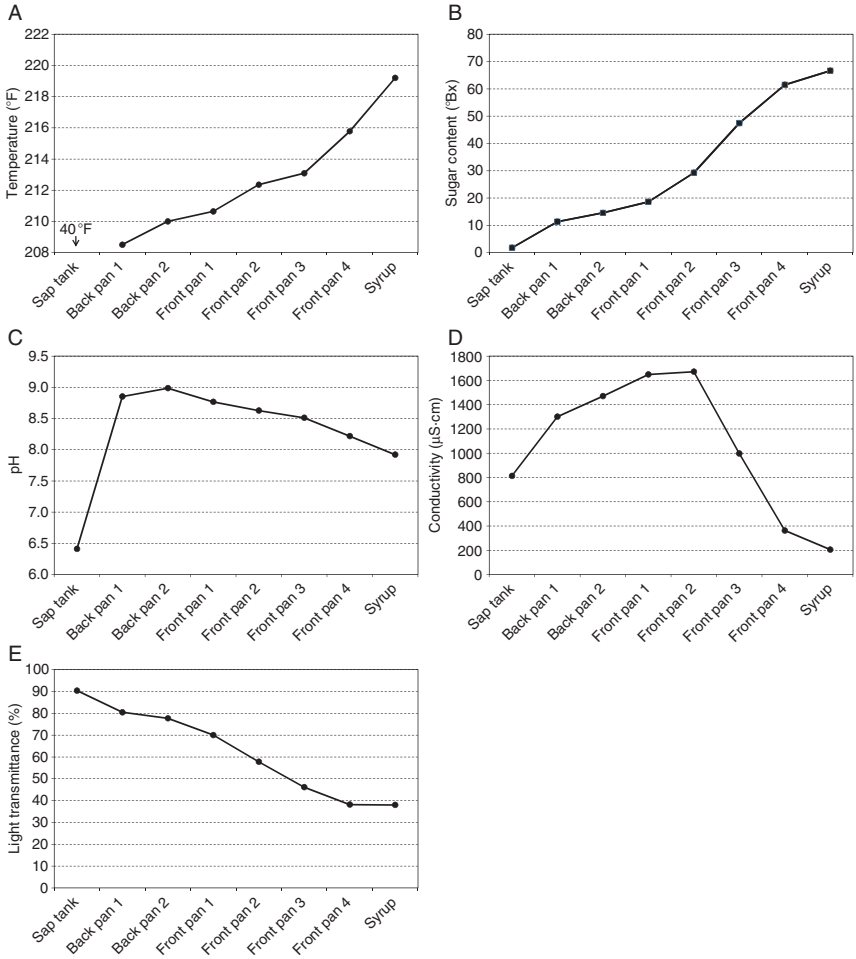

FIGURE 4.6 Changes in temperature (A), sugar content (B), pH (C), conductivity (D) and light transmittance (E) at different stages of thermal processing from maple sap to syrup.

Light-colored syrups are generally more difficult to produce, and are very useful in blending of maple syrup to achieve a good color and flavor balance. Lighter syrups therefore generally command a higher price than darker syrups.

During heating, sap pH initially increases rapidly as the solution becomes more concentrated, generally transitioning from neutral or slightly acidic to slightly to moderately alkaline (Fig. 4.6). Akochi *et al.* (1997) demonstrated that this change is most likely the result of chemical reactions occurring during the heating process rather than the loss of

organic acids. By the time sap reaches a concentration of 8–12 °Bx, sap pH begins to decline and continues to steadily drop until reaching the point when it is the density of syrup. During this time, hexoses undergo alkaline degradation to form triose sugars, which readily decompose during heating to produce color bodies. Alkaline degradation and color formation do not occur exactly simultaneously, as the conversion of hexoses to trioses appears to occur early in the boiling process, but most of the color formation occurs in the latter stages of heating, primarily in the last few partitions of the evaporator. Cyclotene, furaneol, isomaltol, and other thermal sugar degradation products are probably formed at this stage of processing (Potter and Fagerson, 1992).

A large number of lignin-derived flavors have been identified in maple syrup (Filipic *et al.*, 1969; Potter and Fagerson, 1992). During boiling, there are large increases in phenol-related flavor compounds such as furaldehydes, vanillin, and syringyl aldehyde (Kermasha *et al.*, 1995). Furfural and hydroxymethylfurfural color precursors form as a result of carmelization and Maillard reactions between amino acids and reducing sugars, as well as via oxidative polymerization of phenolic compounds. These are further reduced to caramels and melanoidins, and eventually to colored polymer bodies. Due to the variable concentration of precursors in sap, the range of color and of flavor compounds in maple syrup is very broad. Like the case for sap, there is a tendency for syrup to decrease in pH during the production season.

Because one of the dominant color formation pathways involves the reactions among amino acids and reducing sugars, controlling invert sugar levels has historically been the key to producing light maple syrup. RO usage and highly efficient evaporators that result in rapid processing and low sap residence time can also affect color and flavor development. The recent innovation of injecting air through small pipes into boiling sap has proven to also produce light-colored syrup. Recent work has shown that significant improvement in syrup light transmission can result from air injection (Fig. 4.7, van den Berg *et al.*, 2009a), with few other significant alterations to bulk syrup chemistry. The way in which air injection achieves this is still somewhat unclear. Air injection does result in an overall lowering of temperature of the boiling sap (Isselhardt *et al.*, 2007; UVM Proctor Maple Research Center, unpublished data), suggesting the lightening effect may be due simply to reduced thermal-induced browning. Research at Centre Acer in Quebec, Canada, has shown that air injection may increase the formation of oxidative species which affect color and flavor formation during evaporation. These projects are expected to elucidate in more detail the effects of air injection and other new maple processing technologies on the chemistry and flavor profiles of maple syrup.

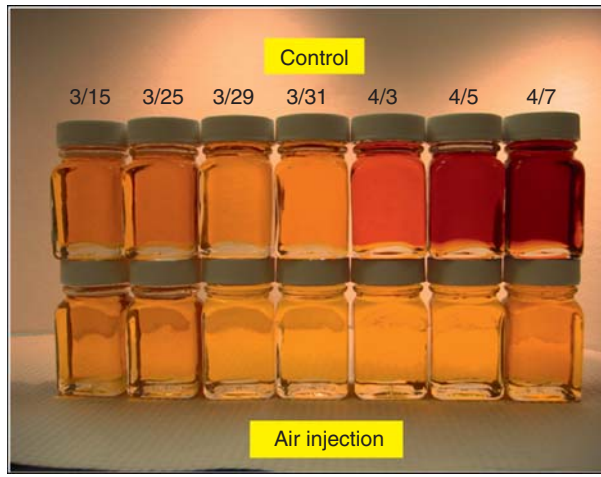

FIGURE 4.7 Maple syrup produced in paired evaporators boiling sap from the same source on the same dates. The evaporator that produced the syrup on the top was the standard, control evaporator. The syrup on the bottom was produced in an identical evaporator equipped with air injection.

VIII. SCALE/SUGAR SAND FORMATION DURING SAP PROCESSING

As the sap is boiled in an evaporator, the concentration of other substances also changes. Dissolved minerals and metals go through a saturation phase, and eventually precipitate as a scale-like substance on the surfaces of the evaporator. This scale, also termed ''niter'' or ''sugar sand,'' can take many forms, and is quite variable in composition (Table 4.5, Fig. 4.8). The type and amount of scale changes throughout the season, and is highly variable from one season to the next.

Nearest the sap inlet of the back pan it is composed of a protein-rich, sticky substrate that is rich in calcium malate and is probably largely caused by the denaturing of organic substances and microbes.

In general, sugar sand is a mixture of calcium malate and sugar. Generally, the higher the levels of calcium and malic acid present in the sap, the greater the amount of scale formation (Davis *et al.*, 1963). Further into the evaporator the scale deposited is denser and adheres strongly to pan surfaces. In the front pans, as the density of the solution becomes quite high, scale forms very rapidly on evaporator surfaces, and small particles of scale become suspended in the syrup. This suspended material, also often referred to as ''niter'' or ''sugar sand,'' must be filtered from syrup prior to packing in drums or into retail containers, as it will impart a gritty texture to syrup, and can cause an undesirable off-flavor in the syrup.

TABLE 4.5 Composition of maple sugar sand (from Perkins *et al.*, 2006, used with permission)

Sugar sand (in run)	0.05–1.42% dw
pH	6.30–7.20
Calcium	0.61–10.91%
Potassium	0.146–0.380%
Magnesium	0.011–0.190%
Manganese	0.06–0.29%
Phosphorus	0.03–1.18%
Iron	38–1,250 ppm
Copper	7–143 ppm
Boron	3.4–23 ppm
Molybdenum	0.17–2.46 ppm
Free Acid	0.07–0.37%
Total malic acid	0.76–38.87%
Acids other than malic	0.08–2.62%
Undetermined material	6.94–34.16%
Calcium malate	1.30–49.41%
Sugars in dried samples	33.90–85.74%
Sugar sand in dried samples	14.26–66.09%

FIGURE 4.8 Variation in maple scale (sugar sand/nitre) appearance and form.

Scale on evaporator surfaces, especially in the front pans, is a nuisance to the maple producer. If allowed to build up excessively, it reduces heat transfer to the liquid, can cause off-flavors, and may result in scorching of the pans. Maple sugar makers deal with scale accumulation in their evaporators in several ways. The most apparent is to shut down the process, drain the partially processed sap, and clean the pans. Often a food-approved acid solution is used to hasten the process (great care must be taken in handling and disposal of acids and in ensuring that all acid residues are adequately rinsed from the pans prior to using them again). An alternative process is used with reverse-flow pans in which the flow of sap in the front pans is changed by switching the location of the draw off. By alternating sides on which syrup is removed, the incoming partially processed sap will redissolve a portion of the scale from the pans, and thus delay the necessity to shut down and clean the pans. Producers using cross-flow pans will often remove the pan nearest the draw-off, move the second front pan forward, and insert a spare clean pan in that position, thereby reducing the amount of time in which the evaporator is shut down. When boiling sap concentrate (8–20 °Bx), producers obviously experience much more rapid build-up of scale in evaporators than when using sap (2 °Bx), and the scale can also begin to form further back in the evaporator system. Given the increasing quantity of syrup being produced using reverse osmosis, this problem (and the use of acid to clean pans) is increasing rapidly. Research is ongoing in several locations to better characterize the scale, and to find easier and more environmentally safe methods to deal with the problem. One recent interesting approach is the use of electrodialysis to demineralize sap prior to evaporation by heating (Bazinet *et al.*, 2007). Although the process did reduce calcium and malic acid levels in concentrated sap, thus presumably reducing scale formation, it may be considered illegal under most existing maple purity laws.

A similar issue in evaporator pans is foam. Foam develops in all portions of evaporator pans during boiling, and must be controlled to maximize heating and to prevent scorching of pans. Historically, milk, cream, or animal fats were used to cut the foam. Present practice is to use vegetable oils or other commercially available defoamers. The primary determinant of which defoamer to use is often based upon whether or not the maple producer is ''organic'' certified, as certification requires the use of certified organic vegetable oils. Although there has been relatively little scientific study of the composition of foam, an analysis of foam skimmings has shown foam to be a sink for lead (Stilwell and Musante, 1996), and occasionally foam has been suggested as a source of off-flavors in maple syrup.

IX. SYRUP STANDARDS

Pure maple syrup generally must meet strict standards for density, clarity, color, and flavor. In general, there is agreement between the various grades of maple syrup produced in the U.S. and Canada; however, the specific names may vary somewhat (Table 4.6). Some U.S. states have their own grade and color designations. A complete description of maple syrup grade and color descriptors is available in the North American Maple Syrup Producers Manual (Heiligmann *et al.*, 2006, p. 172). The Canadian standards are mandatory, whereas U.S.D.A. standards are voluntary.

The minimum solids content to meet U.S.D.A and Canadian regulations is 66% total solids (at 20 °C in Canada, unspecified in the U.S. Standards). Individual states in the U.S. are able to set their own standards. Vermont and New Hampshire set a minimum of 66.9 °Bx (at 60 °F). Some jurisdictions set an upper density limit (typically 68.9% solids), whereas others do not. Density is generally measured with a hydrometer, hydrotherm, or, increasingly with refractometers, although regulations often specify the ''legal'' method in each area.

In all cases, syrup must be clear of suspended crystals or particulates that might cause cloudiness and impart a gritty texture to the product.

Syrup color is determined by spectrophotometric light transmittance at 560 nm (Fig. 4.9). Syrup must meet (or exceed) a certain cut-off level in

TABLE 4.6 Grades of maple syrup in Canada and the U.S.

	Canada		U.S.	
	≥66.0% Solids		≥66.0% Solids	
Light transmittance[a]	Grade	Color	Grade	Color
≥75.0%	Canada No. 1	Extra light (AA)	U.S. Grade A	Light amber
60.5–74.9%	Canada No. 1	Light (A)	U.S. Grade A	Medium amber
44.0–60.4%	Canada No. 1	Medium (B)	U.S. Grade A	Dark amber
27.0–43.9%	Canada No. 2	Amber (B)	U.S. Grade B for reprocessing	
<27.0%	Canada No. 3	Dark (C)	Substandard	

[a] U.S. Standards are based upon the transmittance of permanent glass standards with photometric equivalents. Canadian Standards are based upon photometric light transmission at 560 nm. Some states may have different names for the grade classes or slightly different density requirements.

order to be placed within a grade. In practice, producers generally use a visual comparator based upon ''permanent'' glass or plastic filters, or more commonly, with a temporary standard composed of burnt sugar suspended in glycerol. Such temporary grading kits are useful as guides, but care should be taken in their use. At least one company has recently introduced a digital maple syrup transmittance meter, however, for several reasons such devices are not currently in widespread use within the industry.

Syrup is also graded based upon its flavor. Although this is somewhat subjective, experienced producers are able to distinguish the general category and intensity of maple flavors, as well as detect gross off-flavors that cause syrup to be down-graded to a commercial or substandard level.

Because of maple purity laws in both the U.S. and Canada, there are relatively few processing techniques which can be employed by maple producers. In general, processes may neither add, nor remove substances from the product, other than what is accomplished through evaporation. Certain exceptions are allowed, such as the use of diatomaceous earth for filtering, the use of reverse osmosis machines, and various defoaming agents. Addition of other sugars, decolorizing agents (activated carbon, anion exchange decolorizing resins, bone char, flavor modifying agents, pH modifiers), preservatives, flavorings, colorants, and other food additives are not allowed.

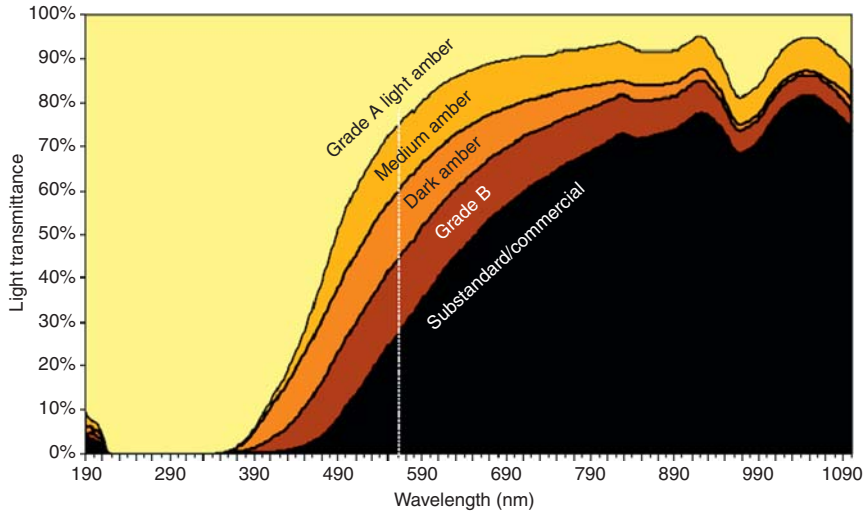

FIGURE 4.9 Transmission profiles of maple syrup. Profile for each grade was derived from 10–40 scans of individual syrups. Grades delineations are based upon U.S.D.A. standards. Color grade is determined by the transmittance of light at 560 nm.

X. SYRUP CHEMISTRY

A. Density

Maple syrup is, by definition, ~66–68% total dissolved solids (at 20 °C). Since the major solid constituent (98% or more) of syrup is sugar, % total solids and °Bx are generally used interchangeably. Syrup that is less dense than 66 °Bx is subject to fermentation if contaminated by microbes. Syrup denser than 67 °Bx may develop crystals inside the container. Therefore, a fairly narrow range of acceptable density is required to ensure that quality issues are not found. Water makes up the bulk of the remaining solution (~32–34%), but due to the high concentration of dissolved solids, the water activity of maple syrup is fairly low, averaging around 0.87–0.88, thereby restricting the development of pathogenic microorganisms.

B. Carbohydrates

Most of the total carbohydrate fraction of syrup (88–99 + %) is in the form of sucrose, with varying amounts of invert sugars present, primarily as a function of microbial contamination of sap during storage prior to processing (Edson, 1910; Edson and Jones, 1912). In some cases, conversion of sucrose to invert sugars may continue after packing into retail containers, especially if syrup is low in density and fermentation occurs. A slight amount of sucrose hydrolysis may also occur during thermal processing. Total sucrose composition in syrup may range from ~47–74%, typically with a mean of 65–68%. Glucose and fructose may range from nondetectible up to over 9% (Stuckel and Low, 1996), but typically are both found in the 0.4–0.5% range in finished syrup. A recent study by van den Berg *et al.* (2006) revealed no consistent relationships among maple syrup grades and carbohydrate profiles (sucrose, glucose, fructose). However, lighter-colored syrups are generally thought to contain lower amounts of invert sugars than darker syrups, and are thus selected for use in making maple candy and cream, where crystallization properties are important.

C. pH

The published range of pH of maple syrup varies from somewhat acidic (4.7) to slightly basic (8.7), but typically is near neutral, with reported mean values around pH 6.3–6.8 (Chénard and Gagnon, 1997; Perkins *et al.*, 2006). The pH of the syrup is related to several factors, including collection and storage of sap, the methods employed to process the sap into syrup, time of season, and microbial contamination.

D. Conductivity

Due to dissolved minerals in maple syrup, the conductivity can range from about 90 to slightly above 230 μS/cm, with a trend towards increasing conductivity as light transmittance of syrup decreases. Conductivity of syrup is sometimes used as a rapid screening test for adulteration of syrup, especially in Canada.

E. Color

Maple syrup ranges greatly in color and opacity. The light transmittance from the UV through the near IR regions is shown in Fig. 4.9. UV light is not well transmitted through maple syrup. Transmittance increases rapidly in the visible spectrum, reaching a gradually upward sloping plateau at around 650 nm before reaching a peak in the near IR range at around 920 nm. The color of maple syrup ranges from a very light yellow-amber to near black. Generally, most syrups have a light yellow to a dark red-brown color, due mostly to color bodies originating from nonenzymatic browning during evaporation. Because invert sugar browns at a lower temperature than sucrose, the level of glucose and fructose in sap, as well as rate of processing are the primary determinants of syrup color and light transmission. Maple syrup produced by vacuum or microwave processing is nearly colorless as a result of there being no or low thermal degradation of the sugars (Favreau *et al.*, 2001; Willits *et al.*, 1952). Chen *et al.* (2001) analyzed the colorimetric properties of maple syrup and found that total color value and ''redness'' increased strongly with increasing color grade, but that color was not an adequate tool to discern compositional differences between authentic maple syrup and table syrups composed of other sugars. Most likely, this is because table syrups utilize burnt caramel as a color agent in the formulation of these products.

F. Rheology

The rheological properties of Canadian maple syrup have been described by Ngadi and Yu (2004). Although maple syrup is primarily Newtonian in its flow characteristics, grade, temperature, and density can independently and interactively influence the apparent viscosity, with a range of 0.138–0.160 Pa s at 25 °C. Colder, more dense, and darker grade syrups have higher viscosity than warmer, thinner, and lighter grades. Chen *et al.* (2001) found a slightly higher range of 0.128–0.247 Pa s at 25 °C, with a mean of 0.164 Pa s at 25 °C, probably as a result of a higher variation in syrup density and geographic origin. They did not find a relationship between syrup grade and viscosity. Corn syrup

containing cellulose gum as a thickening agent had a vastly different rheological signature, making structural analysis a possible method to detect some forms of maple syrup adulteration.

G. Inorganic composition

A number of studies have described the range of minerals and metals found in maple syrup (Dumont, 1996; Morselli, 1975; Stuckel and Low, 1996). These studies and other unpublished works are summarized in Chénard and Gagnon (1997), and by Perkins *et al.* (2006) (Table 4.7). While many of these constituents originate in the composition of the sap as it comes directly from the tree (which can vary widely), other elements may be introduced during the collection and evaporation process.

Potassium is by far the mineral found in highest concentration in maple syrup, with a range from various studies of 541–4031 ppm. Typically, the average values are around 2000–3300 ppm. Calcium is also found in substantial quantities, with a mean of 630–1470 ppm. The mean magnesium concentration is 130–375 ppm. Lesser amounts of manganese, sodium, and phosphorus are usually found.

The content of various metals in maple syrup fluctuates widely, often as a result of contact with sap collection and processing equipment. Iron, zinc, copper, and tin are generally present to varying degrees. Tin often originates from uncoated metal containers sometimes used to market maple syrup. Upon opening a metal container, oxidation can cause tin levels to rise to the point where syrup begins to appear slightly greenish, and acquire a distinct ''metallic'' off-flavor over several months time.

Little research has focused on the differences in syrup composition by grade. While light transmittance is different (by grade definition), the trends in other aspects of syrup chemistry are not as simple. Two unpublished studies at the University of Vermont Proctor Maple Research Center show that there are no consistently predictable trends in bulk syrup chemistry related to grade (color class).

Maple sap collection and processing equipment produced prior to 1994 was frequently made with lead solder, terneplate, or galvanizing material containing lead. Lead is not detectable in sap collected directly from the tree, but fairly rapidly dissolves in sap. The composition of the sap collection and processing materials, surface area, and length of contact time are important factors in determining the degree of lead contamination of sap. Upon boiling, lead is concentrated; however, a great deal of lead is sequestered in scale and sugar sand, and is thus filtered out. The dissolved lead fraction cannot be filtered, and thus may contaminate the syrup. The U.S., Canada, and some states have set maximum permissible lead levels ranging from 250 to 500 ppb, and the vast majority of syrup produced falls well under those limits. As equipment

TABLE 4.7 Reported values and ranges for composition of maple syrup (adapted from Perkins *et al.*, 2006, used with permission)

	Morselli[a]	Stuckel and Low[b]	Dumont[c]	Perkins[d]	van den Berg, Perkins and Isselhardt[e]	Typical mean
General						
Total Solids (%)	66.5	63.2–69.5	–	–	62.0–68.0	65
Moisture (%)	33.5	26.5–39.4	–	–	–	–
pH	–	5.6–7.9	5.7–8.5	–	5.5–7.3	6.4
Conductivity $\mu S/cm^2$	–	–	–	–	96–318	189
Carbohydrates						
Sucrose (%)	58.5–65.8	51.7–75.6	42.3–74.0	–	59.4–73.8	66
Glucose (%)	0–7.3	0.0–9.6	0.0–7.2	–	0.0–1.6	0.4
Fructose (%)	Trace	0.0–4.0	0.0–6.8	–	0.0–1.1	0.5
Minerals and Metals						
Nitrogen (%)	–	–	–	–	0.001–0.077	0.03
Potassium (ppm)	1300–3900	1055–2990	541–4031	1600–2590	963–3319	2283
Calcium (ppm)	400–2800	266–1707	183–1943	600–1250	278–2494	911
Magnesium (ppm)	12–360	10–380	11–575	0–198	25–543	177
Manganese (ppm)	2–220	–	<1–252	0–117	0.01–223	39.8
Sodium (ppm)	0–6	–	<1–261	0–27	0.01–492	36

(*continued*)

TABLE 4.7 (*continued*)

	Morselli[a]	Stuckel and Low[b]	Dumont[c]	Perkins[d]	van den Berg, Perkins and Isselhardt[e]	Typical mean
Phosphorus (ppm)	79–183	–	<2–2335	20–113	0.01–91	37
Iron (ppm)	0–36	–	0–18	0–18	0.01–61	10
Zinc (ppm)	0–90	–	2–43	0–96	0.01–527	22
Aluminum (ppm)	–	–	–	–	0.01–18	2
Boron (ppm)	–	–	–	–	0.01–3	0.2
Sulfur (ppm)	–	–	–	–	0.01–100	18.2
Copper (ppm)	0–2	–	0–8	0–6	–	1.2
Tin (ppm)	0–33	–	–	0–24	–	8
Lead (ppm)	0–0.25	–	0–0.49	0–0.35	–	0.20
Cadmium (ppm)	–	–	0–0.09	0–0.07	–	0.02
Chloride (ppm)	31–191				20–400	93
Organic Acids						
Malic Acid (%)	0.141	0.06–0.66	0.32–0.90	–	–	
Fumaric Acid (%)	0.006	0.001–0.012	0.0–0.13	–	–	
Citric Acid (%)	0.015	–	–	–	–	
Succinic Acid (%)	0.012	–	0.0–0.26	–	–	

[a] Morselli (1975)
[b] Stuckel and Low (1996)
[c] Dumont (1996)
[d] Perkins (1998, unpublished data)
[e] van den Berg, Perkins and Isselhardt (unpublished data).

containing lead reaches the end of its service lifetime, the overall level of lead in maple syrup should decrease.

Only a few studies have examined the minor inorganic constituents of maple syrup. Both sodium and chloride are sometimes found in maple syrup, occasionally at fairly high levels. Morselli and Whalen (1987) found a mean chloride concentration of 93 ppm in syrup, with a range of 31–191 ppm. Trees growing in areas of heavy road-salt use had higher concentrations of salt in sap, and eventually in syrup. Sodium ranges from 0.1 to 492 ppm, with a typical mean of 2–36 ppm. Sodium can be elevated due to roadside salt, or more commonly, to the use of sanitizers (sodium hypochlorite) in maple tubing. More recently, the ratio of sodium to chloride has been investigated as an indicator of artificial decolorization of syrup (an illegal activity) with anion exchange resins (Perkins and van den Berg, unpublished data).

H. Organic acids

Several organic acids are typically present in maple syrup (Table 4.7). Malic acid is the predominant form, comprising on average about 0.5% of the total weight of syrup. Various studies have yielded a range of 0.06–0.90%, but typically average about 0.5 ppm. Citric acid, succinic acid, and fumaric acid are also present in trace amounts in syrup (Stuckel and Low, 1996), but typically are found in far lower concentrations than malic acid. Malic acid is a dominant constituent of sugar sand, and malic and citric acids are sometimes used to detect different forms of adulteration, as the signatures of these compounds are quite different in some other types of sugars.

I. Flavor compounds

Over 130 volatile flavor compounds have been identified in maple syrup, although in widely varying levels and combinations depending upon the grade of syrup as influenced by the type and intensity of processing, the time of season (probably as a result of microbial influence on sap chemistry), and possibly by geographic location. Many of the flavor compounds are phenol derivatives. Several published studies describe some of these (Akochi *et al.*, 1994, 1997; Alli *et al.*, 1992; Belford *et al.*, 1991; Deslauriers, 2000; Filipic *et al.*, 1969; Kermasha *et al.*, 1995; Potter *et al.*, 1995; Underwood, 1971). The dominant types of flavor compounds include: phenolics, pyrazines, carbonyl-based molecules, and others. Analysis of the primary flavor contributors to maple syrup is complicated by the large number, combinations, and levels of flavor compounds present, as well as the detection threshold and saturation nature of the taste reaction of these compounds.

In general, lighter-color (higher grade) syrups tend to contain lower levels of flavor compounds than darker (lower grade) syrups. Some extremely light syrups have very little flavor (other than sweet). In the maple industry, these are sometimes termed ''techno-syrup,'' as they are considered to be more prevalent in operations using a higher level of processing technology (reverse osmosis, steam- or vapor compression evaporators). The veracity of this connection has not been established, however, it is enough of a concern that researchers are beginning to investigate the effects of processing equipment and intensity on maple syrup chemistry and flavor.

Phenolic flavor compounds present in syrup are largely the degradation products of lignin components of sap. These compounds include: vanillin, syringaldehyde, dehydroconiferyl alcohol, syringoyl methyl ketone, and 2,6-dimethoxyphenol. Vanillin is generally a strong contributor to the flavor of light-colored, early-season maple syrup (Potter *et al.*, 1995), whereas a variety of furanones, cyclotene, and other caramelization-derived compounds appear to dominate in darker syrups (Belford *et al.*, 1991; Potter *et al.*, 1995).

Pyrazines are generally products of Maillard reactions, and tend to increase fairly steadily during boiling (Akochi *et al.*, 1997). The presence and concentration of several forms of pyrazine in maple syrup are quite variable, and they contribute both to the flavor and off-flavor attributes of maple syrup depending upon the form and concentration of both the pyrazine and other flavor compounds present which may mask any off-flavor. In particular, moderately high levels of 2,5-dimethylpyrazine are thought to result in the objectionable ''metabolism'' off-flavor found occasionally in maple syrup (van den Berg *et al.*, 2009b). In some years, ''metabolism'' (also called ''woody'') can affect up to 25% of the total annual maple syrup crop. At lower concentrations, especially when combined with strong carmelization flavors, 2,5-dimethylpyrazine likely contributes acceptable flavors to maple syrup. Research is ongoing to investigate processes to reduce or mitigate ''metabolism'' off-flavor in maple syrup.

Reverse osmosis of sap increases the relative proportion of phenolic compounds, while decreasing aldehydes and alcohols (Kermasha *et al.*, 1995). Most maple producers concentrate sap to around 8–10%, reducing the amount of water to be evaporated by 75%. Maple syrup produced from concentrated sap tends to be lighter in flavor and color, due to the far reduced boiling time required to achieve the proper density. Given the increasing cost of fuel, the tendency among some producers in recent years has been to increase the level of concentration. Sap concentration by RO up to 15–25% is not unheard of at the present time. Many producers and packers in the maple industry feel that high concentration ($> 10\%$) of sap by RO produces a ''flat'' syrup, lacking in flavor. This topic is also the focus of ongoing research.

Overall, dozens of compounds are involved in the development of the characteristic flavors found in maple syrup. The number of compounds, the different sap to syrup processing involved, the wide range of maple syrup flavor and intensity, and somewhat frequent off-flavors all complicate the understanding of the flavor of maple syrup.

J. Sensory evaluation of flavor

Although the dominant taste is usually sweet, maple syrup can range from a very light, sweet, but otherwise nearly tasteless substance, to a very dark, bitter, burnt taste. Most syrups used for table use on pancakes or in cooking are intermediate in color and have a moderate to strong maple-caramel flavor, without objectionable off-flavors. Light colored, low-flavor syrups are generally used for blending with darker syrups to achieve the correct color and flavor profile. Moderate syrups can be used without blending. Dark syrups usually have strong flavors (and sometimes slight-moderate off-flavors that are masked by strong ''good'' flavors) and are used for blending, or as ingredients in recipes requiring a maple flavor. Very dark, commercial syrups (which are not sold for table use) range from very strong tasting syrups with good flavor, to very strongly bitter syrups with mild to moderate off-flavors. These syrups are used in commercial food manufacturing processes where a strong maple flavor is required. The degree of off-flavor deemed acceptable is determined by the user and the application.

For most producers and consumers, the description of syrup flavor is generally fairly straightforward, focusing on a simple scale of light flavor to strong (dark) flavor. The lightest syrups (Canada No. 1 Extra Light and U.S.D.A. Grade A Light Amber) are generally sweet, with only a slight hint of maple flavor. As one tastes progressively darker syrups, the taste becomes dominated less by sweet alone, and more by a maple-caramel flavor. The strongest table grades (Canada No. 2 Amber and Vermont Grade B) are dominated by an intense caramel flavor (although not enough to cause a bite or bitter taste), generally with a mix of several other flavors in lesser amounts. Often the darker color and strong flavors cause people to believe that these syrups are thicker, although all syrups must legally meet the same density requirements.

A relatively recent addition to the maple industry is the ''Flavor Wheel for Maple Products'' (Agriculture and AgriFood Canada, 2004), patterned after similar classification systems in wines and other food products. The Flavor Wheel for Maple Products (hereafter FWMP) contains 13 flavor families, including: maple, confectionary, vanilla, milky, empyreumatic, floral, fruity, spicy, foreign (deterioration/fermentation), foreign (environment), plant—herbaceous, plant—humus/forest/cereals, and plant—ligneous. Within each family are one or more subfamilies of flavors,

which on the outer ring are further divided into individual flavors. The FWMP is a useful tool in the maple industry, and although it is fairly new, and requires substantial training to be used correctly, is likely to become more widespread in maple research and large-scale marketing as it provides a common lexicon for those in the industry to describe the sensory characteristics of maple in a very detailed way.

Typically, there is a progression from lighter-colored and flavored syrups (Canadian No. 1 AA or U.S.D.A. Grade A Light Amber) early in the maple production season, dominated by delicate maple and vanilla flavors, to moderately colored and tasting syrups (Canadian No. 1 A and U.S.D.A. Grade A Medium Amber) in the middle of the season, with light-moderate confectionary (light brown sugar) and empyreumatic (light caramel) flavors, to dark-colored and strong flavored syrups (Canadian No. 2 B or U.S.D.A. Grade B), characterized by heavy confectionary (molasses) and empyreumatic (burnt-sugar) notes.

There has been some recent research investigating the ''Terroir'' of maple. Preliminary work has shown that the underlying bedrock composition may influence the chemistry of the sap and resulting syrup (Corbett and Munroe, 2006), but the effects on maple syrup flavor are not as clear (Costanza-Robinson *et al.*, 2007).

K. Off-flavors in maple syrup

Within the maple industry, more attention is sometimes given to recognizing off-flavors, as these can result in syrups being down-graded, or placed into the commercial or substandard class. The origin of off-flavors may be either intrinsic to the sap, or arise from external factors. Off-flavors regularly found in maple syrup include: metabolism (a poorly understood woody-cardboard flavor arising from environmental conditions), buddy (made from late season sap, characterized by a strong, bitter chocolate flavor), salty (inadequate rinsing of equipment), chemical (inadequate cleaning/rinsing procedures), scorch/burnt (overheating damage), moldy or fermentation (microbial contamination), and several others (Heiligmann *et al.*, 2006). Producers, packers, and agricultural inspectors generally learn to recognize these and are able to diagnose production and/or storage issues causing the off-flavor. Although typically color and flavor development progress hand-in-hand during evaporation, those in the maple industry must also assess whether the flavor of the syrup is typical of the color. A syrup found to have a flavor not characteristic of the grade is usually down-graded (placed into the next lowest syrup grade). Although primarily designed as a tool to describe positive sensory attributes of maple flavor, the FWMP does include some off-flavors as well. Some off-flavors are dealt with by blending, an attempt to reduce the off-flavor to undetectable or unobjectionable levels.

Other off-flavors (metabolism, buddy, chemical) are often too severe to allow the syrup to be used in this manner, and are thus relegated to commercial status and used for industrial flavoring, or to make sugar (during which the process reduces or eliminates most of the volatile off-flavor compounds).

Due to improper packing or storage conditions, more frequently found in syrups packed at too low a density, microbial contamination can sometimes cause off-flavors. Because of the low water activity of maple syrup, few organisms are generally able to successfully colonize maple syrup. When contamination does occur, it will result in a moldy off-flavor. Bulk storage of syrup low in density will result in a fermentation off-flavor (fruity). Generally these barrels are easy to spot, as the top and bottom of the drum will bulge outward due to the buildup of carbon dioxide. Both moldy and fermented syrup, unless severely damaged, can be reheated, filtered, and blended with a good-flavored syrup to achieve an acceptable result. Bulk storage of syrup in barrels in good condition, especially stainless steel barrels, will maintain syrup color and flavor for a long period of time (1–2 years).

Syrup is packed into retail containers at a temperature of ~180–185 °F. Exceeding this temperature may promote the development of nitre, whereas packing too cool does not result in complete kill of any microorganisms that may be in the container. After packing, containers are usually turned on their sides to sterilize the container top as well. If containers are not cooled rapidly (especially when large orders are packed tightly together before cooling), they are subject to ''stack burn,'' wherein the syrup darkens rapidly. Maple syrup is commonly packaged in tin, glass, and plastic containers. Glass retains syrup color and flavor well for 6+ months, especially if kept cold. Syrup packed into plastic may begin to darken rapidly, although flavor is generally unaffected. For this reason, maple producers and packers will often pack a syrup that is somewhat lighter than the grade to account for darkening on the retail shelf. Alternatively, packing is done frequently with only a small amount of syrup in plastic kept in storage or on retail shelves. Tin, although less common presently, is particularly good for short-term maple syrup storage. Tin retains syrup color very well. Prolonged storage of syrup in tin, especially after the container has been opened, may result in a ''tin'' or ''metallic'' off-flavor. With long-term storage in tin containers a slightly green off-color may develop.

L. Nutritional aspects of maple syrup

Although predominantly sugar, maple syrup does contain some amount of several minerals and vitamins (Tables 4.7–4.8). A one-fourth cup serving contains 217 calories, but supplies 100% of the Canadian

TABLE 4.8 Vitamins in maple syrup (adapted from Perkins *et al.*, 2006, used with permission)

	Morselli[a]	CANDI[b]
Thiamin (ppm)	–	1.3
Niacin (ppm)	0.16	1
Riboflavin (ppm)	0.046	0.6
Folic Acid	Trace	–
Biotin	Trace	–
Pyridoxine (B6)	Trace	–
A	Trace	–

[a] Morselli (1975).
[b] CANDI (1997).

and U.S. F.D.A. daily recommended value of manganese, 34% riboflavin (vitamin B2), 11% zinc, and lesser amounts of magnesium, calcium, and potassium. Frequently it is said that darker syrups contain higher levels of minerals and vitamins, and while some limited studies have demonstrated this to some degree, the rather high variability in syrup chemistry often overwhelms this trend. Of more interest, recent work has shown that the phenolic compounds in maple sap and syrup confer some degree of antioxidant, antiradical, and antimutagenic properties to maple products (Thériault *et al.*, 2006).

Consumer preference of maple syrup appears to be trending towards darker (stronger tasting) grades.

XI. OTHER MAPLE PRODUCTS

A variety of other ''value-added'' maple products are made from maple syrup. These include maple cream (also known as maple butter), which despite the name, does not contain any dairy product. It is made by heating syrup to 12–13 °C above the temperature of boiling water, then cooling it rapidly (usually in a water bath), and then stirring it slowly, either mechanically or by hand, to encourage the formation of fine crystals. To prevent separation, the enzyme invertase is used in some areas (it is not legal in every U.S. state) to encourage the conversion of a portion of the sucrose to glucose and fructose. Similarly, a small amount of potassium sorbate is used in some areas to inhibit mold formation to lengthen shelf-life of the product.

Maple candy, maple block or cake sugar, loose maple sugar (Indian sugar), and other types of maple products are made by boiling syrup to different densities followed by pouring into molds, pans, or grinding to a

fine texture. Specific procedures to follow can be found in Heiligmann *et al.* (2006).

A new product consisting of maple syrup in which a portion of the sucrose has been converted to invert sugar (using invertase) was introduced recently. The advantages are that higher density syrup can be sold with a greatly reduced tendency to crystallize. In some areas this product is not allowed to be sold as ''maple syrup,'' due to the addition of invertase and because some areas have upper limits on the density of maple syrup (which this product exceeds). Due to the high level of invert sugar in this syrup, this product has a somewhat different flavor profile as well, with a more pronounced caramel-like flavor.

Maple syrup and maple sugar are often used as flavoring agents in commercial and retail cooking. When added as an ingredient, typically a dark and strong tasting syrup will be used. Maple can add a distinctive flavor to foods, and is also often used as a humectant in some recipes.

XII. CONTAMINATION

Due to the large concentration factor involved in converting sap to syrup (typically 40:1), any slight contamination of sap can result in off-flavors in syrup. All sap collection and processing materials must be kept very clean and free from cleaning or other residues, as these may impact the flavor of the resultant syrup. Soap is used very sparingly, if at all, in maple sugaring operations, as most detergents leave a residue that is almost impossible to entirely remove. Most cleaning is done with copious amounts of hot water. Chlorine or other special-purpose agents are used for sanitizing tubing and processing equipment, with repeated rinsing necessary to remove all residues. Given the increasing use of RO machines and the use of strong acids to clean evaporators, strict attention to chemical safety, particularly in using proper procedures to eliminate the risk of inadvertent contamination, is very important.

XIII. ADULTERATION

Due to the wide differences in the price of maple and sugars from other origins, there is a considerable incentive for adulteration. The simplest is the addition of cane, corn, or beet sugar to maple syrup. A great deal of research has been conducted on this problem.

As a general screening method for addition of nonmaple sugars, the conductivity of maple syrup can be checked. Syrups with conductivity readings above 1200 μS/cm are suspect, and thus subjected to additional testing.

Determination of the carbohydrate profile in suspect syrups may also be used. One historical method was to examine the specific rotation induced in linearly polarized light by the syrup using a polarimeter. Sucrose has an optical rotation of +66.5°, glucose +52.7°, and fructose −92 °. Addition of sugars with a proportion of sucrose to invert sugars different from maple is readily detectible. Currently, HPLC can be used to readily determine the sucrose/invert ratios. These methods are only able to detect gross adulteration of maple syrup, due to the large natural variation in invert sugars found in maple syrup (0–12%).

More recently, the carbon stable isotope ratio test (SIRA) has become an easy method to detect adulteration with cane and corn syrup (Carro *et al.*, 1980). Because maple trees are C_3 plants with a somewhat different photosynthetic pathway for carbon fixation, the ratio of $^{13}C/^{12}C$ in the sugar produced is different than cane or corn. Maple has a $\delta^{13}C$ of approximately −24.5, whereas corn and cane are closer to a $\delta^{13}C$ of −8 to −12. Thus, even a small addition of cane or corn syrup is readily detectable. Because beets are also C_3 plants, the SIRA test is not able to detect adulteration with beet sugar. Improvement of the SIRA method is possible using malic acid as an internal standard (Tremblay and Paquin, 2007).

Due to the inability to reliably detect beet sugar additions, the site-specific natural isotope fractionation nuclear magnetic resonance (SNIF–NMR) method used widely in the wine industry was adapted for the maple industry (Martin *et al.*, 1996). This method determines the site specific isotope concentrations of organic compounds by nuclear magnetic resonance of ethanol fermented from the suspect sample.

Other methods to detect adulteration include anion-exchange liquid chromatography in combination with pulsed amperometric detection (Stuckel and Low, 1995) and FTIR, FT-Ramen, and NIR Spectroscopy (Paradkar *et al.*, 2002, 2003).

At times, a large price differential between light and dark grades of maple syrup has given rise to another type of adulteration in the form of bleaching of syrup. Such a practice is illegal throughout the U.S. and Canada. A variety of methods can be employed (Fig. 4.10). Hydrogen peroxide serves as a direct bleaching agent which acts by oxidation of color bodies in syrup. Use of hydrogen peroxide also causes serious flavor defects, the effect wears off somewhat over time, and residual hydrogen peroxide is readily detectible using simple test strips. Acid, which is added to the backpan during evaporation, can also result in syrup lightening, probably by lowering the pH enough to reduce the rate of alkaline degradation, and thus color body precursor formation. Carbon filtration is another method of syrup lightening. Formerly somewhat difficult to do, as it required charcoal or bone char, lightening via carbon filtration is somewhat easier now given the prevalence of a wide selection of resins that are designed specifically for sugar decolorization. Although adulteration via decolorization with

FIGURE 4.10 Effect of treatment of syrup with decolorizing resin (Top: from left to right, control syrup, decolorized, further decolorized) and hydrogen peroxide (Bottom: control syrup, treated syrup).

resins can be difficult to detect, there have been some methods developed to screen suspect syrup. One promising method is to examine syrup for increased level of anions substituted for the highly positively charged syrup color bodies (Perkins and van den Berg, unpublished data).

XIV. SUMMARY

Although pure maple sap is predominately a dilute solution of sucrose and water, and maple syrup is mostly concentrated sap, the mixture of minor amounts of minerals, amino acids, phenolic compounds, and organic acids found in sap in varying amounts during the short sap exudation season, along with substances added, formed, or sequestered during the collection and processing phases of maple syrup manufacturing, and the interactions of sap and syrup with microorganisms at many stages of the process, make the chemistry of maple syrup rather complicated. In all cases, regardless of how sap is collected or processed, the end result is usually a pure product—maple syrup—with a unique and distinctive flavor.

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