Wine/Enology Grape Chemistry Group at Va Tech

GRAPE MATURITY

Section 3.

pH and Acidity

pH and Potassium (K^+)

For a discussion and differentiation of pH and acidity, see the chapter entitled “Controlling Microbial Growth in Wines.”

Assessments of acidity and pH are used to help define the optimal time of harvest. Both fruit acidity and pH have a significant impact on wine. pH plays a major role in winemaking, affecting the following (Zoecklein et al., 1999):

- color
- oxidation rate
- ability to clarify
- biological stability
- protein stability
- tartrate stability
- metal complexation
- sensory attributes

The pH values for white wines may be 3.5 or less. Higher values usually are observed for red wines, largely because of contact of juice and skins before and during fermentation. Changes in fruit pH are complex, and a result of a number of environmental and viticultural management factors.

Grapes are very rich in potassium, an essential macronutrient for growth and development. Potassium (K^+) is the main cation (positively-charged ion) in must and wine (Blouin and Cruège, 2003). Potassium is absorbed by the roots and distributed to all parts of the vine. Early in the season, when the growth rate is high, much of the K^+ accumulates in the leaves. After véraison, a sharp increase in berry K^+ is observed as a result of K^+ redistribution from leaves to berries (Blouin and Cruège, 2003; Ollat and Gaudillère, 1996).

Excessive K^+ concentration in the fruit at harvest may result in increases in pH and thus negatively impact potential wine quality, particularly in red wines (Davies et al., 2006). A balance of tartaric acid protons with K^+ cations results in the formation of largely-insoluble potassium bitartrate, leading to a decrease in free acid and tartrate-malate ratio (Gawel et al., 2000). The overall result is an increase in pH.

High K^+ levels in the berry may decrease the rate of malate degradation by impairing malate transport from the storage pools in the vacuole to the cytoplasm. Grape skin contains from three to 15 times more K^+ than is present in the pulp. Therefore, berry K^+ levels are often more important to red than to white wines, due to skin contact in red wine production (Mpelasoka et al., 2003).

The levels of K^+ in grape berries may be affected by numerous factors, including K^+ level in the soil, antagonistic elements in the soil such as magnesium and calcium, grape variety, and viticultural practices (Davies et al., 2006; Mpelasoka et al., 2003).

A detailed knowledge of the mechanisms involved in K^+ transport from the soil, xylem and phloem translocation through the vine, and its accumulation in the berry, is crucial in order to develop strategies leading to reduction of excessive accumulation in grape berries and, subsequently, improve fruit and wine quality.

Potassium uptake occurs by multiple mechanisms, both a passive low-affinity K^+ transport across cell membranes, and a high-affinity uptake (Davies et al., 2006). External K^+ levels are thought to determine which mechanism is used. Several vineyard management considerations impact K^+ uptake and pH evolution. Severe stress late in the season can increase K^+ uptake. Crop and overall vine balance are also important in helping to manage pH evolution. Over-cropping may delay the rate of fruit maturity, which can result in increases in pH.

Titratable Acidity (TA)

The acid concentration of fruit and resultant wine is important to structural/textural balance. Titratable acidity (TA) in grapes normally ranges between 5.0 and 16.0 g/L as tartaric acid; these values are influenced by variety, climatic conditions, cultural practices, and maturity of the fruit.

The organic acid concentration of a wine is traceable to four sources. The grape contributes tartaric, malic and, to a much lesser extent, citric acid. By comparison to tartaric and malic acids, which are present at concentrations ranging from 2.0 to 10 g/L and 1.0 to 8.0 g/L, respectively, citric acid is found in unfermented grapes at 0.2 to 3.0 g/L (Amerine and Ough, 1980).

Alcoholic fermentation results in formation of lactic, acetic, and succinic acids, in addition to very small quantities of other acids from the tricarboxylic acid cycle (a metabolic process for cellular energy production). Bacterial involvement may produce substantial amounts of lactic and acetic and, on occasion, propionic and butyric acids. Lastly, mold growth on the grape may result in gluconic acid concentrations of 1.5 to 10 g/L in a finished wine (McCloskey, 1974).

The reduction in TA during fruit ripening is partly related to the respiration of malic acid in the berry and is, therefore, related to temperature. Grapes grown in warmer regions (higher heat summation units) mature earlier and have a lower TA at the same soluble solids concentration, when compared to fruit grown in a cooler climate (Gladstones, 1992). A characteristic of cooler growing regions is lower daily temperature fluctuations during the late stages of fruit ripening, an important contributor to acid retention (Gladstones, 1992).

A historic index of ripeness involves the product of °Brix times the square of the pH (Amerine and Joslyn, 1970). Another historical scale relates TA and sugar; in this case the °Brix value is divided by the TA (Gallander, 1983). This is designed to indicate the optimal sugar/acidity balance. Others have suggested that this value can be higher for late-harvest fruit (Amerine et al., 1980).

There are several problems associated with using only sugar and acid as primary maturity gauges. For example, the sugar-to-acid ratio is variable across different varieties and growing conditions and, therefore, may be difficult to use as a general predictive value. However, changes in TA may be useful in assessing maturity and the changes in the rate of maturity.

Organic Acids

Malate is consumed as an energy source in the berry during véraison, and the concentrations decrease relative to tartrate (Jackson and Lombard, 1993). Tartrate concentrations generally remain constant during véraison, but may rise slightly during grape dehydration. Malate concentrations decrease with maturity, and may plateau at a low level, roughly 2 to 3 g/L (Jackson and Lombard, 1993). Grapes may catabolize sugar if malate concentrations decline too much, depending upon the variety (Conde et al., 2007).

Generally, the malate-to-tartrate ratio does not appear to correlate well with aroma/flavor production in the fruit (Amerine et al., 1980). Its use as a maturity gauge is confounded by varietal and seasonal differences. However, there is a strong correlation between the malic acid concentration and the concentration of an important group of grape-derived aroma compounds, the methoxypyrazines. Methoxypyrazines such as IBMP (2-methoxy-3-isobutylpyrazine), a nitrogen-containing plant metabolite, can impart a vegetal aroma to some varieties, including Cabernet Sauvignon, Cabernet franc, and Sauvignon blanc.

Described as bell- or green pepper-like, excessive concentrations of IBMP can negatively impact the aromatic quality of wines. Decreases in pyrazines are the result of fruit maturation and temperature (M. S. Allen, personal communication, 2006). The decrease in IBMP is correlated to malic acid decline (Roujou de Boubee, 2000).

Phenolic Compounds

The quantitative and qualitative measurement of phenolic compounds is used as a maturity gauge in stylistic winemaking (González-san José et al., 1991). Increases in the total phenolic concentration are associated with maturity, as is grape anthocyanin pigment concentration and general fruit color.

Tannins are located mainly in the skin, stems, and seeds of grapes, which contain different types of tannins. The two important tannin phases in the grape berry include accumulation and maturation. In skins, tannin accumulation starts around flowering and is completed before véraison. In seeds, tannin accumulation starts around flowering and is completed one to two weeks after véraison.

Tannin maturation occurs during ripening and results in progressively decreased extractability, coinciding with perceived softening and “ripening” of tannins. Tannin perception is complex and depends not only on tannin composition, but on the matrix in which the tannin is present. In Virginia, on occasion we have excessive tannin maturation as a result of prolonged hang time, excessive sun exposure, or both. This can result in direct sensory impacts and the loss of reductive strength (see chapters on Redox and Sulfur-Like Off Odors).

The methods of measuring fruit color, and the correlation between color and other grape quality parameters, continue to be evaluated. Environmental and vineyard management practices have a large impact on fruit pigment accumulation. However, the concentration of one pigment, malvidin-3-glucoside, has been shown to be relatively unresponsive to growing conditions, with concentrations increasing as a function of maturity only (Keller and Hrazdina, 1998).

Anthocyanins, as a group, have an optimum temperature range of about 17 to 26°C, suggesting that berry color would be more difficult to achieve in extremely warm and extremely cool regions. Excessive berry exposure and excessive canopy shade can also impact the rate of berry maturity and, thus, color development. Excessive irrigation, too much nitrogen, calcium deficiency and *Botrytis* growth can negatively impact grape color.

Berry color is used as a harvest gauge, predictor of potential red wine quality, and as a means of grower compensation. Using fruit color as a predictor of ultimate wine color or quality may not be easy, due to several factors (Boulton, 2005). Grape and wine color relate to aroma/flavor, but are not strongly correlated.

Anthocyanins and aroma/flavor are produced by different biochemical mechanisms, and therefore their concentrations are not strongly correlated. Levengood (1996) reported that total phenols correlated more strongly to red wine color than did total anthocyanin concentration. Forty percent of the variation in red wine color was explained by vineyard variables. Red wine color is dependent upon a number of factors, including the following:

- amount of color produced by the fruit prior to harvest
- uniformity of ripening: clusters, berries, and fruit components
- fungal degradation of fruit
- berry size and skin-to-pulp ratio
- extraction during processing
- extent of loss during processing and fermentation due to laccase, yeast adsorption, etc.
- amount of color lost via extended maturation
- pH
- degree of interaction between anthocyanins, cofactors, and polymeric phenols

Grape Aroma/Flavor and Maturity Evaluation

Major aroma/flavor components in fruit are present in low concentrations, in the order of 10 to 6000 µg (micrograms) per kg fresh weight (Winter, 2004). For example, the concentration of a methoxypyrazine is generally in the range of 8 to 20 ng/L (Allen et al., 1995). Such small concentrations have profound implications with respect to both analytical measurement, and sensory evaluation as a maturity gauge.

Most varieties have a spectrum of 5-20 aroma/flavor volatiles that may be sufficient to characterize them (Winter, 2004). The pool of free aroma components and their precursors increases rapidly in the advanced stages of fruit maturity, a process referred to as *engustment* (Coombe and McCarthy, 1997). Engustment likely occurs with all varieties but is not notable in Viognier. With this cultivar in Virginia, the fruit can go from being very neutral to having the characteristic varietal notes with a few days.

Many, but not all, varietal aroma/flavor compounds are chemically bound, odorless precursors. Hydrolysis, as a result of heat, acidity, UV, or fungal enzyme activity, can convert a percentage of aroma/flavor precursors to their odor-active forms (Francis et al., 1992; Günata et al., 1988; Sefton et al., 1993). Analysis of the total and/or non-phenolic precursor concentration, by assessment of the glycoconjugates (glycosyl-glucose or GG analysis), is used by some to evaluate fruit aroma/flavor potential (Williams and Francis, 2000; Zoecklein at al., 2000).

Many juice aroma evaluation methods recommend addition of pectolytic enzymes to aid in the conversion of a portion of the bound glycosidic precursors to their odor-active forms. Additionally, salivary enzymes, which contain lyase, may be an important reason for tasting fruit such as Sauvignon blanc, versus simple evaluation of processed juice aroma. It has been reported that cysteine-bound conjugates may be hydrolyzed by yeast lyases, thus releasing volatile thiols that contribute to varietal aroma/flavor (Dubourdieu et al., 2000).

As with many primary metabolites, aroma/flavor components may be dramatically affected by growing conditions and viticulture practices (Zoecklein et al., 1992, 1996). As such, any aroma/flavor index of ripeness must be customized to site-specific factors and cultural practices.

For example, cluster microclimate may exert more of an influence than does the vine environment (Bureau et al., 2000). Cluster and vine shading decrease the concentration of norisoprenoid glycoside conjugates, while light exposure increases the levels of compounds such as 2-methoxy-3-isopropyl and 2-methoxy-3-isobutyl pyrazines in unripe grapes.

Light also catalyzes photodecomposition of these compounds in mature grapes (Hashizume and Samuta, 1999). Nitrogen and water availability also exert a strong impact on grape flavorant composition, as does the length of the ripening period (Keller et al., 1998; Sipiora and Granda, 1998).

Additional Chemical Maturity Gauges

Arginine has been reported as a maturity gauge (Jackson and Lombard, 1993). A decline in arginine may signal maturation. However, arginine concentrations are variable and influenced by varietal and seasonal differences. More recently, there has been some interest in measuring another amino acid, proline, as a maturity gauge and a monitor of vine water stress.

The role of glutathione as an antioxidant is well established. Increased attention has focused on the positive correlation between glutathione concentration and preserving some thiol-based wine aroma/flavor compounds (Dubourdieu et al., 2000). The glutathione concentration of grapes increases at the onset of véraison and during ripening, but it is unclear if this compound is correlated with aroma/flavor development in the fruit (Okuda and Yokotsuka, 1999).