

Grape Maturity Study – Fall 2007 – VWT 180 Napa Valley College

In the production of wine, the roles played by the grapegrowers and winemakers cannot be separated. It is true that winemaking starts in the vineyard. One of the most critical and difficult decisions that have a direct bearing on wine quality is determining when the grapes have reached optimum maturity to produce a specific wine style and quality. The French have no translation for winemaker. The closest thing is a vigneron...a winegrower. A grape grower and winemaker.

High quality wine results from the parallel maturing of several grape attributes. These attributes include aroma/flavor components, reduction of immature tannins, production of mature tannins, desirable sugar content and balanced acid levels. Figure A below shows the ideal world.

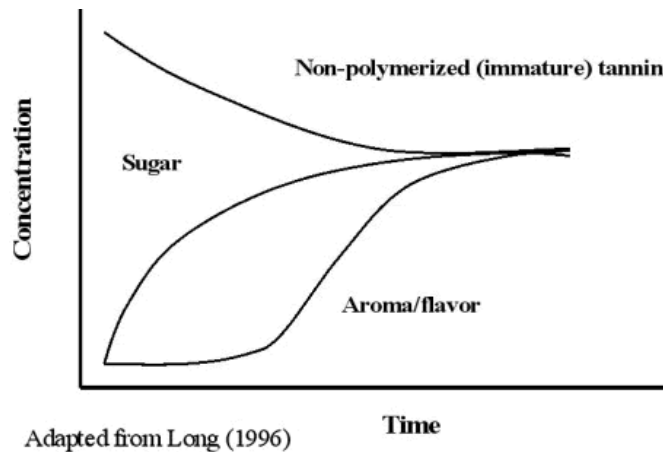


Figure A. grape Maturity

Hardly ever happens this way. It is important to remember that potential wine quality is largely dependent not on primary metabolites, such as sugar, but on secondary metabolites such as aroma/flavor and phenolic compounds. Grape-derived aroma/flavor and phenolic compounds are the principal source of wine aroma, flavor, color and taste. They must be considered in evaluating grape maturity.

The grape vine wants to survive and multiply. The berry functions to attract animals to eat the berry and then disperse the seed. If the vine is in an area where it multiplies readily, the grape flavorants do not have to develop to extremes. If the vine grows in an area with limiting conditions, the stressed vine must develop intense flavorants to attract animals to eat the berries and disperse the seeds. Berry ripening is tightly coordinated with seed development. The animals know how to find the most flavorful berry and the optimum ripeness.

Following flowering, there are three known stages of berry development:

1. green berry;
2. arrest of green berry development and pre-ripening development;
3. veraison or ripening.

See figure 1 below.

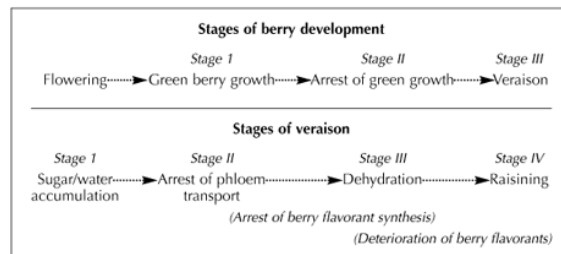


Figure 1: Stages of grape maturation

Based on berry metabolism and continued transport of substances (water, sugars and nitrogen compounds) from the vine via the phloem, véraison can be subdivided. In the berry, sucrose is hydrolyzed to glucose and fructose and flavor and aroma compounds are synthesized. The hindrance of phloem transport and onset of dehydration can both effect berry metabolism and composition. Someplace during veraison, creation of desirable characters in the grape ceases. Finding this optimum time to pick the grapes is the challenge. Just as the animal finds the berry with most intense flavors and optimum maturity, the winemaker must do the same.

So, how can we define the optimum time to pick the grapes? First, there is an important factor that trumps science in this case: Wine style. If a winery wants a wine with a large amount of aggressive aromas, described as “fruit forward” and does not care if the wine can be used to accompany food, then the Stages III and IV in Figure 1 are welcomed.

Note: There was a study done by UC Cooperative Extension and Ed Weber, Viticulture Farm Advisor in 2005 and 2006 related to hang time, titled “Napa County Hang Time Study”. Cabernet Sauvignon was picked from five different vineyards over seven-week periods. Sugars ranged from 22.5 to 28 °Brix. They found a 5% a reduction in cluster weight per degree Brix occurred. The Spring 2007 NVC VWT 173 Sensory Evaluation of Wine class tasted the wines and found no significant preference in wine quality. The paper is available as requested.

If we look past wine style, optimal maturity is still dependent on definition of quality, grape variety, rootstock, terroir, seasonal variations, viticulture practices and winemaking. So, if a wine target can be established, several characters can be used to find the optimum time. See Figure 2.

- Berry Macro-components:**
- Sugar*
 - pH
 - Acidity
 - Balance of Sugar/Acidity
 - Ratio of Malate to Tartrate
 - Berry Metabolites:*
 - Arginine
 - Glutathione
 - Phenolic Content:
 - Total
 - Profile
 - Anthocyanin Content:
 - Total
 - Specific components
 - Terpene Content:
 - Free
 - Bound
 - Glycoside-glucose (GG) Precursors
 - Berry Proteins:*
 - Total Protein
 - Protein Profile
 - Specific Proteins
 - Specific Enzymatic Activity
 - Taste:*
 - Fruit
 - Skins
 - Seeds
 - Stems

Figure 2: Components for assessment of grape maturity

Sugar content increases during ripening and is a function of berry age. Sugar is also easy to measure (Generally in California in degrees Brix.). Several studies have shown, however, there is no relation between sugar levels and the accumulation of grape flavorants. So, sugar can give a measure of maturity, but not necessarily the optimal maturity. Figure 3 shows a typical sugar profile during ripening.

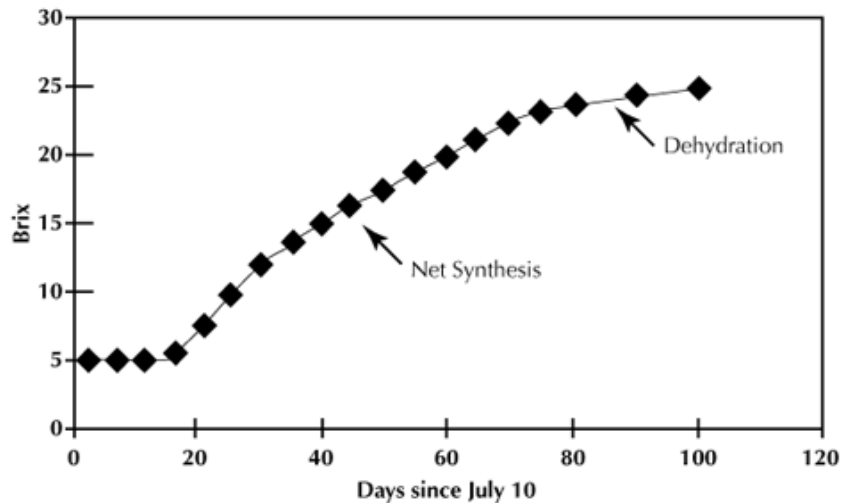


Figure 3: Changes in sugar concentration during ripening

Sugar transport in the vine, after a while, ceases. Once phloem transport stops, any resulting sugar increases will be due to water loss.

Assessment of acidity can also be used to find the optimal time. The two most common measures of acidity are pH and total acidity, or both. Changes in pH are very complex and not necessarily a function of berry age. However, historical indices of ripeness suggest optimal sugar/acidity balance is achieved if the product of the Brix value times the square of the pH is in the range of 220 to 260. (See Grape Ripeness Index file.) These are used to give rough ideas. They were developed based on historical indices. We'll discuss this later.

Changes in acidity level, as they reflect grape metabolism, may be of value. Malate is consumed as an energy source during veraison. Figure 4 shows how tartrate levels generally remain level during veraison, while Malate levels decrease.

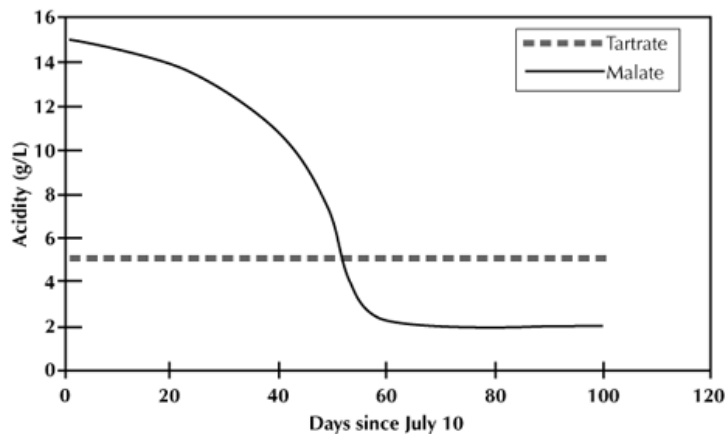


Figure 4: Changes in acidity during ripening

During grape dehydration, tartrate levels may increase a bit. Depending on the variety, if the Malate levels get too low, the grape may catabolize sugar for energy sources.

Any attempts to use Malate/tartrate combinations as an index to ripeness have not correlated with grape flavorants development.

Several studies try to find the link between various compounds and optimal ripening. One theory suggests that reduction in the amino acid arginine levels signals a deterioration of the fruit. The problem is arginine is subject to variety and season. Other studies have examined glutathione, phenolic content, anthocyanin levels, norisoprenoid glycoside conjugates,

nitrogen and water availability, terpene level, pruning practices, total protein content, and many others. No correlations can be found.

All of the factors noted above (sugar, acid, pH, specific flavorants, metabolic levels and protein) changing during ripening are fairly easy to measure. It is not clear, however, whether they are truly related to each other or to any other type of fruit quality assessment.

Tasting the fruit seems obvious. A typical progression of character qualities described for red grapes is shown in Figure 5.

Vegetation (Plant matter)	→	Herbaceousness (Straw, herb, vegetal, Tobacco)	→	Unripe fruit (Green apple, citrus rind)	→	Red fruit (Cherry, strawberry raspberry, cranberry)	→	Black fruit (Plum, blackberry black cherry)	→	Jam (Prune, date raisin)
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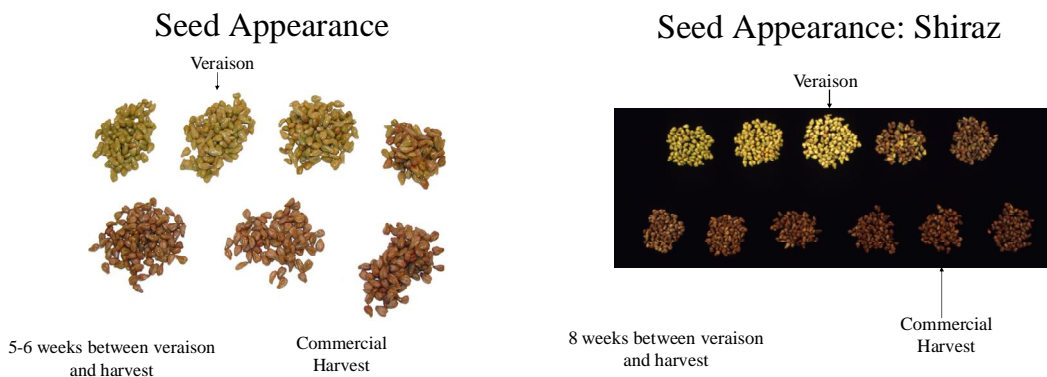
Figure 5: Evolution of flavorants in Cabernet Sauvignon

Varietal aroma and general fruitiness can be very important, but difficult to measure and tend to be lost rather than improved with over maturation. It can be important to taste for the absence of negative characters, as it is to focus on the positive. The loss of vegetative characters can be observed.

Many feel berry flavor is the most accurate measure of grape and resulting wine flavors. In practice, it is not so clear. First, some flavors are masked by other flavors. Second, most aroma compounds are present as glycosyl-glucose (GC) precursors and only released during fermentation and aging. That is, a significant amount of potential aroma compounds are bound by two sugar molecules. Studies have shown about 90% of the aromas in grapes is in the form of precursors. So, walking through a vineyard and popping berries in your mouth to decide if the proper maturity has been attained is not a valid exercise. It must also be remembered that we are human and all humans have different taste thresholds. We may not all taste the same thing.

Grape maturity can also be judged by assessing the physical conditions of the berries. Are the berries the correct firmness? Berry softening is due to changes in the composition of the berry cell wall. When the xylem flow to the berry is halted, both pectin and xyloglucan depolymerize. Current evidence indicates that xylem is functional in grapes early in development (up to véraison), but afterwards its function is reduced or eliminated.

Some winemakers taste seeds to determine grape maturity. The problems are that seeds can be very bitter. Super tasters (those with more papillae) may find the bitterness overpowering. Also, levels of seed bitterness are not widely known and tastes can be misinterpreted. Physical characters of seeds may be more straightforward. Color, texture and brittleness can be important. It is common to look at seeds waiting for them to turn green to tan brown. And become dry or woodier looking. The compounds that provide red wines with bitterness and astringency are the polyphenolic flavan-3-ol monomers and polymeric procyanidins. Grape seeds contain high amounts of these compounds. Both flavan-3-ol monomers and polymeric procyanidins can be divided into a period of accumulation and a period of decline. These periods are separated by véraison. The first period is of polyphenol biosynthesis followed by a period of polyphenol modification leading to a decline in their extractability. Visual changes in seed color occurring after véraison are consistent with polyphenol oxidation in the seed, which leads to decline in extractability. A key point is that for most red grape varieties, much of the decline occurs when the berries reach approximately 20° Brix. (It appears that early ripening red grapes have more “unripe” seeds and later ripening varieties have more “ripe” seeds, e.g., Pinot noir seeds change right through harvest.)



There is a reason for this observation. Once the grapes are crushed into a tank and the juice, pulp, skins and seeds stay together (maceration), the browner seeds produce less bitterness and hard tannin characters than the greener seeds, if they

happen to be broken, as the musts are pumped over and pressed. This is one reason why gentle handling of must and pressing of pomace is important, no matter what color the seeds are.

For some varieties, stems change while grapes ripen. They change from green (unripe) to brown (ripe) to brittle (overripe). In some varieties they never change from green. Figure 6 outlines some stem flavorants.

Stem flavorant composition		
Status	Color	Characteristics
<i>Unripe</i>	Green	Vegetal, leafy
<i>Ripe</i>	Brown	Resinous wood, spice: cloves, cinnamon, pepper
<i>Over-ripe</i>	Brittle brown	Dried leaf, tea, herbal

Figure 6: Characteristics of stems

Stems can be tasted to judge ripeness. Again, it may be difficult to interpret results. Plus, good stemmer-crushers should keep stems out of the fermenters.

The tasting of anything (berries, seeds or stems) is done by people. We get tired. Have different thresholds and biases. Clearly, the ideal method for judging grape maturity would be numerical and reproducible by any winemaker. How they choose to use those results will be the winemakers' prerogative. All the proposed measures do not show a direct correlation to overall grape quality.

Generally, berry flavors are synthesized independently of each other in the berry. Synthesis of most flavor molecules varies significantly with vineyards, clones, vintage and vineyard practices.

It must be remembered that the grape composition is very important in the quality of the resulting wine. Special concerns must be shown to high pH grapes. High pH values at higher levels of sugar/maturity, can lead to undesirable bacteria and yeast.

An evaluation of fruit maturity should be based upon an understanding of the importance of secondary metabolites to wine quality and should involve the following:

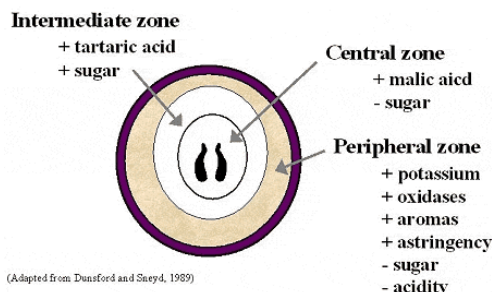
- Assessment of varietal aroma/flavor and intensity of aroma/flavor (green herbaceous to fruit jam, for example)
- Taste assessment of the grape tannins (texture of skin tannins - degree of polymerization or suppleness)
- Seed ripeness (ripeness of seeds and °Brix development are not the same. Unripe seeds increase the 'load' of hard or harsh tannins)
- Sugar per berry
- °Brix, acidity and pH
- General fruit condition including skin extractability- berry softness
- Berry size/ weight
- Ability to ripen further

It is important to note that the physiological mechanism the plant uses to make berry sugar is not the same as used to produce secondary metabolites such as aroma/flavor and phenolic compounds. Therefore, there is no reason to assume that Brix equals desirable aroma/flavor of phenols and that we would get a maturity picture like Figure A.

It is common to view grape berries as homogeneous entities, but they are not. As Figure 5 demonstrates, there are three distinctive juice zones which have different components.

Because of concentration gradients within the fruit, it is essential that growers and vintners standardize fruit sample processing.

Figure 5. The Grape Berry

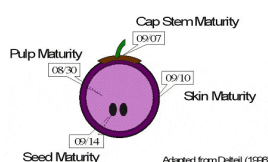


As fruit maturity increases there is an increase in varietal character. For example, Cabernet Sauvignon grapes may go through a progression of aromas which could be described as: green, under ripe to lightly herbaceous, to herbaceous, to minty-black current, to blackberry. It is important to note that if the winemaker is looking for a certain varietal expression in the wine such as black current, it must be in the fruit. Should growers evaluate juice aroma? Because of the relationship between juice aroma and wine varietal aroma, the answer is yes. Such an evaluation involves one of the most sophisticated instruments known to man, your nose. While requiring some practice, this evaluation is within the capability of all growers. The sample preparation procedure is provided in Appendix 1. Growers can easily monitor changes in the varietal expression by processing fruit, conducting a simple sensory evaluation and freezing the juice. At the next sampling date a new set of berries is processed, evaluated and compared with the thawed sample from the previous date.

Grape phenols include many compounds with different chemical and sensory properties. Grape phenols have a significant influence on wine structure including volume or body, tannin intensity, astringency, bitterness and dryness. As fruit and wines mature, their phenolic compounds bind together or polymerize. This polymerization, along with binding to other molecules such as sugar and proteins, causes a sensory change from 'hard' and bitter to astringent and finally to soft and supple.

We generally view grape berries as homogeneous entities. However, if we examine the phenols of a grape berry we note that there are different types located in different parts of the fruit. Not surprising is the fact that the different parts of the grape ripen at different rates and are thus mature at different times. For example, Figure 6 shows a red berry and the maturity dates of the important components-skin pulp, seeds and cap stem.

Figure 6. Fruit Maturities



Given that all parts enter the fermenter in red wine production, the wine quality may be negatively influenced if they are not all physiologically mature.

Figure 7 shows the relationship between skin and seed tannins of Virginia-grown Cabernet Sauvignon at three sampling intervals.

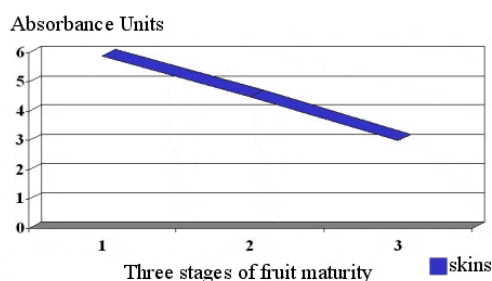
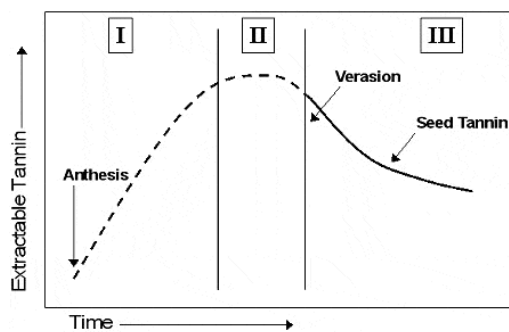


Figure 7. Changes in Phenol Polymerization (gelatin index) With Grape Maturity

With increased fruit maturity there is a change in the skin phenols which corresponds to an increase in the phenol maturity or polymerization. This is an example of an important qualitative change occurring with fruit maturation. The skin tannin polymerization parallels a sensory transformation, an evolution from hard and astringent to dusty to soft and supple. It should be noted that the change in phenol polymerization depicted in Figure 7 represents a limited change in °Brix (21-22 °Brix from the first to the last sampling). Polymerized skin tannins have a large molecular weight and are smoother on the palate than smaller low molecular weight tannins which are considered to be hard and astringent.

In cooler growing regions, it is not uncommon for winemakers to process red grapes with immature seed tannins. The resulting wines are harsh and hard. As indicated in Figure 7, seed tannin astringency changes little with time. What does change is the extractability of these compounds into the wine. During fruit maturation, seeds mature at a different rate than that of degrees Brix. As seeds mature they change color from green to brown to dark brown. This color change represents oxidative reactions and corresponds to the degree of extractable tannins. As indicated in Figure 8, tannin extractability decreases during phase 2 and 3 of berry development.



Source: J. Kennedy, 2000

Figure 8. Changes in Seed Tannin Extractability

In conventional red wine production, seed tannins make up over 60% of the total tannin concentration. It should be noted that changes in tannin maturity can occur late season when it would appear that no additional ripening can transpire. It does vary with variety.

Evaluations of red fruit maturity should include the assessment of seed and cell wall maturity or berry softness. Berry softness may be an important feature influencing extraction of phenols during red wine fermentation. Tannin maturity of red grapes should be evaluated seriously as described by Zoecklein et al. (10).

Appendix 1. Sensory Evaluation as a Maturity Index Adapted from Zoecklein et al. (1995)

Method 1. Maturity and vineyard management practices can influence the pool of free aroma components. Most of the aroma components are located in the skins. The following is a procedure used to evaluate red grape aroma:

1. Approximately 200 berries are lightly crushed and pressed in a hand press.
2. The skins are separated from the pulp and seeds and placed in approximately 200 ml of 10-15% ethanol adjusted to pH 3.0 with tartaric acid.
3. The skins and alcohol are placed in an airtight jar for several days. The alcohol solution is decanted and evaluated. Smelling the solution will provide an indication of the odor and odor intensity. Red grapes should have an odor of fruit, cherries, etc. along with "notes" of pomace or tea from the tannins. If there is little varietal aroma or aroma intensity in the grape, these two features will be deficient in the resultant wine.

Method 2. In a non-alcoholic medium juice aroma evaluation must be done with care. Rapid enzymatic oxidation can occur if berries are warm or exposed to air. For example, oxidation produces aldehydes as the result of enzymatic oxidative cleavage of linoleic and linolenic acids to hexenal. These aldehydes can produce grassy aromas that mask fruit characteristics and make aroma assessment very difficult. The procedure suggested by Jordan and Croser (1983) is as follows:

1. Use a cone-in-cone juicer, a potato ricer, a hand press etc. to press the chilled grape sample (<2C).
2. Estimate the quantity of juice that the sample will yield beforehand and add pectinolytic enzyme at the supplier's recommended level. Then add 50 mg/L ascorbic acid and 30mg/L sulfur dioxide. Ascorbic acid or vitamin C is an antioxidizing agent which along with sulfur dioxide will help minimize degradation of aroma components.

3. If possible, lightly sparge the juice sample with nitrogen and sieve into sample bottles which have been CO₂ filled, seal and cold settle at 2C or less.
4. Decant the clear juice into CO₂ filled bottles and carry out both chemical analysis and aroma/flavor evaluations. Note that the sample preparation method, pressing, degree of pressing vs. crushing and cold settling affects the titratable acidity and pH (see Zoecklein et al., 1995). Under optimum conditions, juices prepared using this methodology and stored at 0C will remain viable for aroma/ flavor assessment for several months.

It is unlikely that any single index of maturity will be discovered that can be used on all varieties, by any winemaker in any vintage. Historical experience with specific regions, vineyards and varieties may be the most valuable measure.

Grape Sampling

Regardless of what maturity gauge is used, the vineyard must be accurately sampled. How can you be sure the sampling of a specific vineyard block is representative of that vineyard? Generally, there are two ways to sample a vineyard; cluster sampling and berry sampling. Cluster sampling can be either gathering clusters throughout the vineyard or sampling one or more targeted vines. The problem is, some vines develop more quickly than others. Therefore single vine sampling is not wise. Studies have shown, the closest correlation between sample values and true vineyard value (once the grapes are crushed in the tank and the values taken) result from taking the smallest number of berries from the largest number of vines. If you had a vineyard with 10,000 vines, one berry from each vine, mixed together, would give a good assessment of the values of the entire vineyard.

The following Table 1 gives information on the number of clusters and berries needed to obtain specific levels of accuracy. Guideline regarding sampling procedures is shown in Table 2. It must be remembered that berry sampling must involve locating the berries in a statistical random fashion. You don't pick only berries or cluster on the south side of the vine, totally exposed to the sun. Get a feel for the vines and try to take a random sample.

Table 1. Grape Sampling

- Berry Sampling
 - ❖ +/- 1.0 °Brix 2x100 berries
 - ❖ +/- 0.5 °Brix 5x100 berries
- Cluster Sampling
 - ❖ +/- 1.0 °Brix 10 clusters

Sources: Jordan and Croser, 1983;
Kasimatis and Vilas, 1985

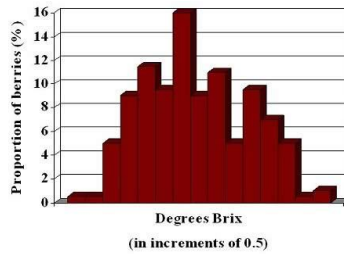
The three factors, which have a major role in maturation dynamics, are heat, light and soil moisture. Therefore, variation of these within a vineyard block can result in significant sample variation. About 90% of the variation in berry sampling is believed to come from variation in the position of the cluster on the vine and the degree of sun exposure. The vineyard must be sampled based on the degree of fruit exposure.

Table 2. Berry Sampling

Avoid edge rows and the first two vines in a row
 Collect samples from both sides of the vine
 For each row, estimate the proportion of shaded bunches and sample accordingly
 Collect berries from the top, middle and bottom of the cluster
 Randomize the side of the cluster sampled
 Maximum sample area should be less than 5 acres

Even if the sampling follows above suggestions, all the berries on a cluster, or clusters on a vine, do not develop at the same rate. This is asynchronous berry, cluster or vine development. Figure B shows one study of berry variation.

If a winery reports a Brix of 22, the juice might be composed of a narrow distribution of a few berries at 20 and a few at 24 Brix with the majority nearer to 22. However, there may be a much wider distribution with berries below 18 and greater than 24. Because Brix is a distribution average, juices with similar Brix values can produce wines that are quite different due to variations in aroma/flavor and phenol content. The importance of asynchronous development is often overlooked and is a major factor limiting the quality potential of some wines.



Source: Long, 1986

Figure B. Sugar concentration of individual berries in a 400-berry sample of Cabernet Sauvignon

References:

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