

must wine pH = QUALITY

By Robert Beelman
Department of Food Science
Pennsylvania State University

The importance of must pH to wine quality is a subject of great current interest among both growers and winemakers. The purpose of this report is to review the principal factors affecting must and wine pH and the reasons whereby pH influences wine quality.

A grape must is an extremely complex 'biochemical soup' that contains significant quantities of several organic acids—mainly tartaric and malic. Thus, it could be described in simple terms as an acidic solution. Usually, the strength of the acidic solution is determined by measurement of the titratable acidity and/or pH.

Titratable acidity, sometimes erroneously called total acidity, is most often used by winemakers. It is measured by titrating a sample of the wine with a strong base (0.1N NaOH) to a given endpoint (usually pH 8.2) where the acids are essentially neutralized. However, a more correct determination of the strength of an acidic solution is achieved by the determination of the number of H⁺ ions present in solution by using a pH meter.

The chemical basis of pH was described (4) for beginning biology students as follows:

"The H⁺ ion concentration of solutions can be measured and symbolized by the term pH. This term was originated by the Danish biochemist Sorenson (1868-1939). The letter P stands for 'power'; the letter H stands for 'hydrogen-ion concentration'.

"pH of a solution is determined by measuring the number of H⁺ present. Table 1 shows the pH scale, numbered from 0 to 14. The lower the pH number on the scale, the more H⁺ ions present and, therefore, the more acid the solution. At pH 7, the solution is neutral; the number of H⁺ ions equals the number of OH⁻ ions. If the pH is above 7, the solution is basic, or alkaline, because the number of OH⁻ ions exceeds the number of H⁺ ions. Pure distilled water has a pH of 7.

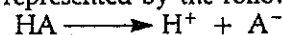
"Expressed in mathematical terms, the pH number stands for the negative logarithm of the H⁺ ion concentration. A pH of 7 means that there are 10⁻⁷ moles of H⁺ ions per liter of solution. A mole (gram molecular weight) is the molecular weight expressed in grams. 10⁻⁷ is equal to .0000001 or 1/10,000,000 of a mole per liter."

However, the question arises: where do these H⁺ ions come from? All acids that are dissolved in aqueous solutions, such as grape musts or wine, dissociate into hydrogen ions

TABLE 1. The pH Scale

pH	Conc. (H ⁺) (Moles/L)	Conc. (OH ⁻) (Moles/L)
0	1.0	0.00000000000001
1	0.1	0.0000000000001
2	0.01	0.000000000001
3	0.001	0.00000000001
4	0.0001	0.000000001
5	0.00001	0.00000001
6	0.000001	0.0000001
7 (Neutral)	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1
14	0.00000000000001	1.0

(H⁺) and the anion (A⁻) characteristic of each acid; the reaction can be represented by the following equation:



Strong inorganic acids, such as hydrochloric, dissociate almost completely. However, weak organic acids, like malic and tartaric which predominate in grapes, occur mostly (about 99%) in the undissociated (HA) form. Only about 1% of the weak acid molecules in must or wine are in the dissociated (H⁺ + A⁻) form (12).

Since pH measures only (H⁺) and in titration the undissociated acid (HA) as well as H⁺ ions are neutralized and measured, one can assume that titration is mostly a measure of the weak acid while pH measures the strong and dissociated weak acids. Generally in musts or wines, H⁺ ion concentration is 10⁻³ to 10⁻⁴M, producing pH reading of between 3 and 4.

Viticultural Considerations

The pH of musts prepared from mature grapes generally range from 3.0-4.0. However, Amerine *et al.* (2) recommended must pH values of less than 3.3 and less than 3.4 for making white and red table wine, respectively.

During maturation of grapes, the pH increases continuously from about 2.8 to values of 3.1 or higher depending upon the variety and growing season (2). This pH increase occurs at the same time that sugar increases and titratable acidity decreases (see Fig. 1). The decrease in titratable acidity is due partially to dilution by water during cell enlargement.

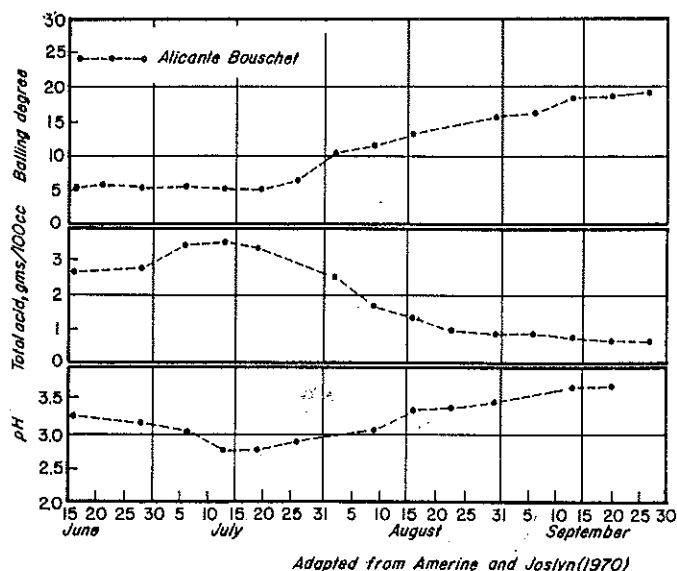


Figure 1—Changes in Balling (Brix) degrees, total acidity (titratable acidity) and pH in Alicante Bouschet grapes during maturation. This figure was adapted from original data of Amerine and Joslyn (1970) as presented by Amerine et al. (2).

However, some of the decrease, which can be detected on a per berry basis, is due to respiration of malic acid which occurs more readily during warm seasons (2). In cool seasons or growing areas, less malate is respired and this contributes to the high titratable acidity that often occurs in grapes produced under such conditions.

Amerine et al. 1980, suggested that the pH increase that occurs during grape maturation is probably due to translocation of potassium and other cations into the fruit. In that regard, both Somers (16) and Morris et al. (9) have demonstrated a significant positive correlation between K⁺ ion concentration and pH in grape musts.

However, Boulton (5) recently proposed that an apparent exchange between K⁺ and H⁺ ions occurs in grape berries during maturation, resulting in a pH increase because of the net loss of H⁺ ions. In a subsequent paper (6), he demonstrated that it was the extent of exchange between K⁺ and H⁺ ions and not just the number of K⁺ ions in the grape juice that determined the pH increase. He also showed that the lower the tartrate to malate ratio of the juice, the greater would be the pH increase at any given level of exchange.

Recently, Freeman (7) demonstrated that K⁺ accumulation in grape berries followed a sigmoidal pattern with increasing maturity (°Brix). The concentration of berry K⁺ ion increased rapidly up to 10° Brix, was relatively stable between 10 and 17° Brix and increased rapidly after 17° Brix. A rapid increase in juice pH also occurred after 17° Brix, but only a slight decrease in titratable acidity was observed. This indicated that K⁺ ion concentration was associated with the pH increase.

This observation suggests that competition may occur between K⁺ ions and sugar uptake into berries. This may help to explain why some grapes reach maturity with excessively high pH values.

A varietal influence on must pH is often observed. Certain grape varieties consistently produce high pH musts. Such varieties are generally ones that have a low tartrate to malate ratio.

On the other hand, varieties with high tartrate to malate ratios generally have lower pH values (2). This is due to the fact that tartaric acid is a stronger acid than malic (fig. 2) as indicated by its lower pKa values. This was also illustrated by Mattick et al. (8) in titration curves of pure acids of equal molar concentration (fig. 3). This figure demonstrates that at all stages of neutralization, solutions of tartaric acid have lower pH values compared to equimolar solutions of malic acid. For example, when the tartrate solution was titrated to pH 3.2, the malate solution was at pH 3.6.

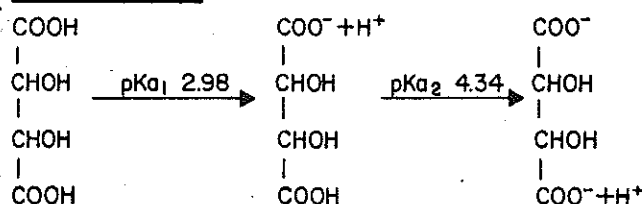
In some cases, grapes reach maturity with both high pH and high titratable acidity which presents a difficult problem for the winemaker. This condition may occur sporadically in many viticultural areas with certain varieties, but is a chronic problem with many varieties in some viticultural regions.

In some cases, high potassium soils have been implicated, but the problem is probably much more complex. Some of these regions tend to have cool growing seasons with high solar radiation; the grapes tend not only to develop high sugar contents but also high pH and high titratable acidity.

Perhaps, the cool conditions favor the retention of high malate concentrations. Also, it is possible that greater than normal exchange of K⁺ for H⁺ occurs in the berries due to problems relating to competition with sugar uptake into the fruit.

Zoecklein (17) contends that any activity affecting carbohydrate production and translocation might affect fruit potassium levels and thereby fruit pH values. He indicated that increasing density of vineyard plantings, decreasing leaf area and reducing vine vigor could all reduce K⁺ translocation to the fruit, thereby stabilizing the fruit to excessive pH increases.

Tartaric Acid



Malic Acid

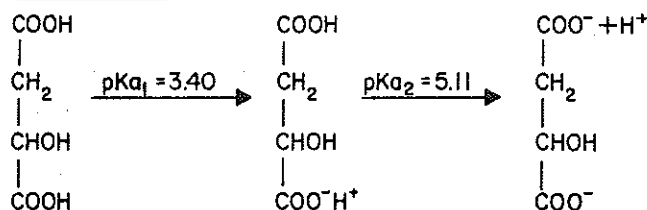


Figure 2—The dissociation of tartaric and malic acids in aqueous solutions as influenced by pH. The pKa values are the pH values when the dissociation (hydrogen ion release from the molecule) is 50% complete.

Zoecklein advocated research regarding the use of growth regulators and methods to reduce cane and leaf area (e.g. hedging) as potential means to control fruit potassium and pH.

Regardless of factors affecting the pH of grapes as they mature, it is important to the winemakers to work with fruit

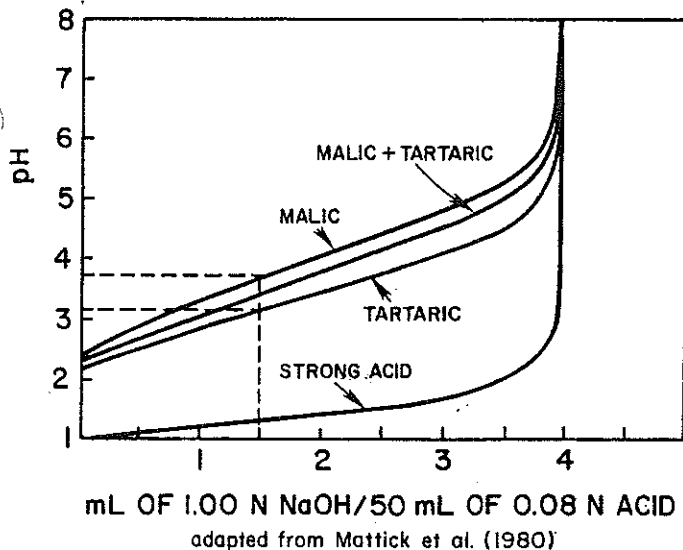


Figure 3-Titration curves of pure acids.

with reasonably low pH values. Amerine *et al.* (2) recommended maximum pH values of <3.3 for white musts and <3.4 for red musts. Thus, evaluation of berry samples for determination of harvest should include evaluation of pH as well as Brix and titratable acidity.

However, pH probably can't serve as the only criterion for harvesting decisions. In some cases, grapes could reach pH 3.5 when sugar content is extremely low (<15° Brix) or titratable acidity is excessively high (>15 g/L).

In many cases, growers in the eastern United States are making errors in the opposite direction. They try to ripen grapes to 20-22° Brix in order to produce 'premium' wines from 'ripe' fruit while they may be inadvertently harvesting fruit unsuitable for making sound wines because of excessively high pH values.

All things considered, it is easier and probably better for wine quality, to add sugar to grapes harvested earlier, than trying to reduce pH of musts from more mature grapes. The latter can be accomplished by the addition of tartaric acid to musts in sufficient quantity to reduce pH to proper levels prior to fermentation.

Acid addition is common practice in many areas of California, including many prestigious Napa Valley wineries, and may be appropriate in making more complex style wines in the eastern United States.

In production of light and/or soft wine styles, picking grapes at lower Brix levels, (about 16-18°) probably would be the favorable approach; since low alcohol and less complex wines are desired.

ENOLOGICAL CONSIDERATIONS

There are many reasons for advocating low must pH values for winemaking. Must pH has profound effects on wine flavor (taste and odor), color (both hue and intensity), pigment quality, protein stability, oxidation rate, and biological stability of the wine.

Must pH can have both a direct and indirect influence on wine flavor. Amerine and Joslyn (1) indicated that musts of low pH value resulted in better-flavored wines. They also stated that table wines with pH values <3.4 tasted fresher and fruitier than wines of higher pH. This could be due to indirect effects such as reducing the rate of fermentation, since slower fermentations generally result in better flavored wines.

Must pH values <3.0 are known to reduce fermentation

rate. This can become a problem as well; some white musts with pH values around 3.0 may resist initiation of alcoholic fermentation for more than a week. This certainly may cause numerous problems including the possibility of mold growth in the juice.

The pH of wine obviously has a direct influence on wine flavor. Tartness is related to both titratable acidity and pH (3) because the acid taste on the tongue is produced both by H⁺ concentration and the fraction of the acids which are partially neutralized at low pH.

Plane *et al.* (12) recently demonstrated that sensory response of the tongue to acids in the wine is about ten times greater to hydrogen ions (H⁺) than to the undissociated acids (HA). But in wine, HA exceeds H⁺ by about 100 times. Thus, tartness is mainly (by a factor of about 10:1) due to the undissociated acids. This fact probably explains why most winemakers commonly balance wine acidity based on titratable acidity.

Knowledge concerning the optimum relationship between pH and total acidity in regard to sensory quality is limited. Nagel and McElwain (10) attempted to determine this relationship for table wines based on sensory scores of wines where pH and total acidity data were known.

They found in white table wines with pH values in the range 3.05-3.2, 3.2-3.3 and 3.2-3.5 that optimum range of titratable acidities were 0.6-0.65%, 0.6-0.85% and 0.85%, respectively. They also demonstrated that in wines of very low pH (<3.1), only minor differences in sensory scores were observed with the entire range of titratable acidity. They speculated that this might have been due to the generally better quality of the wines fermented at low pH.

In a later study with dry Riesling wine, Nagel *et al.* (11) demonstrated that lower titratable acidities were preferred at lower pH values; wine below pH 3.3 scored well from 0.5-0.8% titratable acidity. In general, wines over 0.9% titratable or pH 3.4 were ranked poorly.

In the same study, Sauvignon Blanc wines were considered fruitier at low pH (3.0) and more fullbodied at high pH (3.6). Based on this observation, high pH may be at least partially responsible for so-called 'flabby' wines.

Plane *et al.* (12) proposed a quantitative measure of the relationship between acid taste, titratable acidity and pH that they termed acidity index (Ia). They described it with the following equation:

$$Ia = \text{Titratable acidity (g/L)} - \text{pH}$$

As pH increases in a must or wine, the organic acids dissociate as indicated by their pK_a values (fig. 2). The dissociation of tartaric acid is of particular importance to winemaking. The dissociation curve for tartaric acid in an aqueous solution, illustrated in figure 4, demonstrates the relative concentrations of the ionic species as the pH increases.

This curve can be used to explain pH changes that occur in winemaking, especially during tartrate stabilization (8). The key point in the curve is at pH 3.5, because at this point each ionic species has an average of one proton (H⁺ ion).

Below this point, precipitation of the bitartrate anion (HT⁻) as KHT (potassium bitartrate) causes a release of H⁺ ions into the wine from H₂T, (tartaric acid), resulting in a pH decrease. Above this point, when KHT precipitates H⁺ ions are removed from the wine by the tartrate anion (T⁼) thus causing a pH increase.

Because wine is a lower dielectric medium than water, the critical value in wine is approximately pH 3.65. This phenomenon can be used advantageously by winemakers to control excessive pH of wines.

Tartaric acid can be added to high pH musts or wine in sufficient quantities to reduce the pH below 3.6 prior to cold stabilization. As KHT is precipitated, the pH will be decreased without an excessive increase in titratable acidity. The amount of tartaric acid required for a specific wine needs to be determined experimentally.

Must and wine pH also have a profound influence on the microbial stability and incidence of malolactic fermentation in wine. In general, low pH inhibits growth of both malolactic and potential spoilage bacteria in wine.

This is primarily due to the effect of pH on the ionic nature of various antimicrobial agents in wine in the same way it affects the ratio of the ionic species of tartrate. This can best be illustrated with sulfur dioxide, the primary antimicrobial agent used in wine.

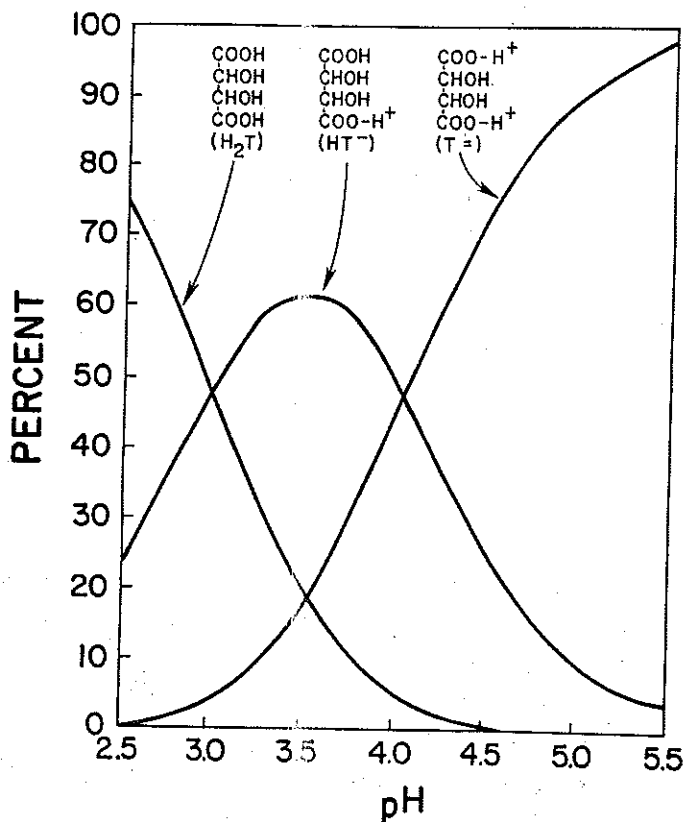


Figure 4-Relative concentrations of tartrate ionic species in water at various pH values.

When sulfur dioxide is added to aqueous systems, like must or wine, molecular SO_2 [SO_2] is present only at low pH (fig 5a). As pH is increased, bisulfite ions (HSO_3^-) and sulfite ions (SO_3^{2-}) are formed which have no antimicrobial properties. Thus, at pH 3.0, 61% of the free SO_2 in wine is in the molecular form but as the pH increases to 3.3, the molecular SO_2 is reduced to 3.1% of the amount of the free SO_2 present.

At pH 4.0, only 0.6% of the amount added is in the molecular form. It is currently recommended that wines contain 0.8 ppm molecular SO_2 (15). This is equivalent to 26 ppm free SO_2 at pH 3.3, but 79 ppm free SO_2 would be required to obtain the same concentration at pH 3.8 (fig. 5B).

In wines where malolactic fermentation activity is desired, the use of SO_2 must be maintained at low levels, since even bound SO_2 can inhibit the causative bacteria. Thus, the use of SO_2 must be kept low (< 50 ppm total) especially at low pH (< 3.3).

Another approach is to increase the pH of wines to about 3.3-3.4 with potassium bicarbonate (KHCO_3) to encourage the bacterial growth. Then, if the pH of the wine is higher than desirable after the malolactic conversion (> 3.6), the pH can be lowered by the addition of tartaric acid prior to cold stabilization. This will result in a further drop in pH without excessive increase in titratable acidity as discussed above.

However, the addition of tartaric acid would be illegal if the wine was previously ameliorated by addition of either sugar or water.

Another approach to handling wines with excessively high pH values after malolactic fermentation is to blend them with wines of low pH and high titratable acidity. One can use wines which have not undergone malolactic fermentation or wine made from the same must where bacterial growth was controlled.

The latter approach was used successfully by Romberger (13) with Catawba wines. However, she cautioned that great care in stabilizing such wines against microbial (malolactic) activity following bottling would be required.

Low pH generally renders wine more microbiologically stable, since most microorganisms associated with wines have definite pH limits for growth and activity. Also, most microbial inhibitors used in winemaking, like sulfur dioxide, have their most pronounced effects at low pH where the molecules are fully protonated (undissociated).

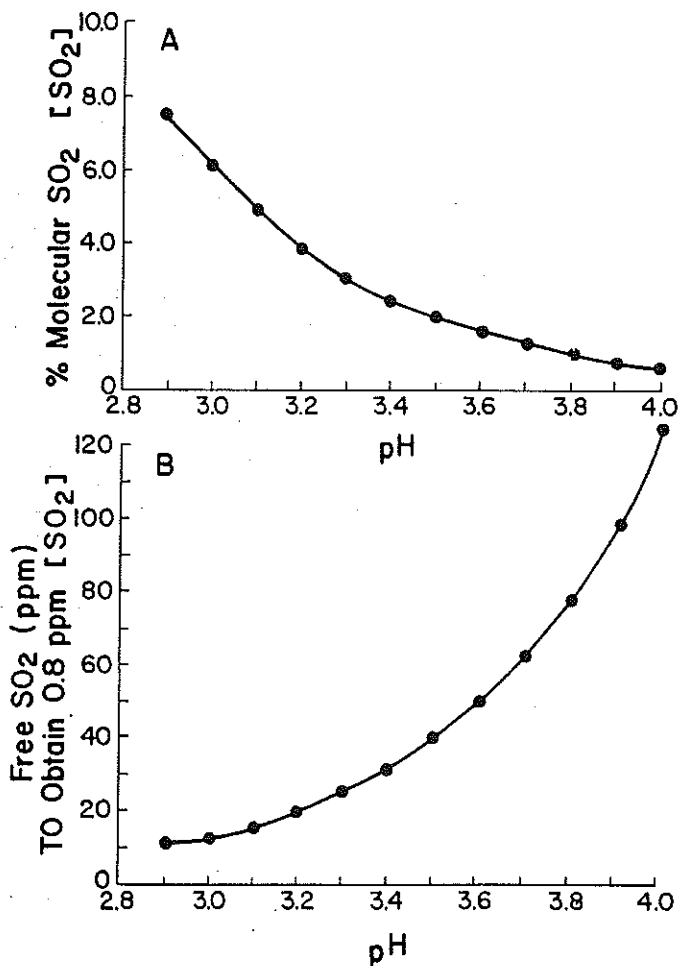


Figure 5-Effect of pH on the concentration of molecular sulfur dioxide [SO_2] present in aqueous solution (A) and the amount of free sulfur dioxide needed to obtain 0.8 ppm molecular sulfur dioxide (B).

Inhibition of yeasts by sorbic acid (or potassium sorbate) and control of malolactic bacterial growth by fumaric acid are greatest in wines with low pH, because the undissociated molecules are the actual inhibitors.

These molecules have dissociation curves similar to sulfur dioxide; thus, as the pH of wine increases, larger amounts of the inhibitors must be added to maintain the concentration of the undissociated molecules necessary for the antimicrobial effect.

In many cases, as the pH increases above 3.5-3.6 the amount of chemical that must be added exceeds sensory threshold (e.g. sorbate and SO₂) or solubility limits (e.g. fumarate). Thus, low wine pH is desirable from the standpoint of rendering wine microbiologically stable with minimal use of preservatives.

Low wine pH is known to be desirable for wine color. Both the intensity and hue of red wine color is affected adversely by high pH. Figure 6 illustrates the effect of pH on the equilibria and polymerization of malvadin-3-glucoside, a common anthocyanin pigment that influences red color of many wines (14).

When pH increases, the chemical form of the pigment shifts to colorless or violet-colored forms. At high pH, red wines have less red intensity and/or a more purple or violet hue. Anyone who has titrated a red wine sample has observed this change; as pH increases, the wine turns from red to blue to green at complete neutralization.

High pH increases the tendency of wine to oxidize. As pH increases, the phenolic compounds dissociate (hydrogen ions dissociate) to produce phenolic anions. These phenolic anions are much more prone to oxidation.

Singleton (14) estimates that as the pH increases from 3.2 to 3.8, the oxidation rate of wine doubles. Thus, wines with high pH oxidize more readily, leading to potential problems with off odors and color deterioration.

The pH of wine can have an important effect on protein stability. At lower pH, proteins precipitate at a faster rate, thus wines fermented at low pH generally contain lower amounts of protein. Amerine *et al.* (2) indicated that bentonite requirements of a wine at pH 3.0 is about 25% that of a wine at pH 3.6.

The pH value is known to affect other factors affecting the chemical stability of wine such as metal ion complexes and both calcium and potassium tartrate stability. Generally, low pH values are considered desirable to render wines chemically stable.

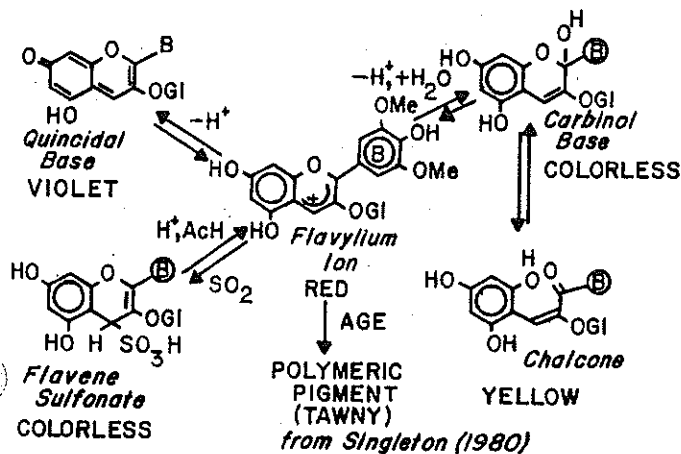


Figure 6-The effect of pH on equilibria and polymerization of malvadin-3-diglucoside; figure was redrawn from Singleton (14).

In summary, it is evident that must and wine pH is of critical importance to wine quality. Relatively low pH value, in the range of 3.0-3.4, appear to be a prime requisite to producing stable, high quality wines.

In some cases, pH can increase excessively during maturation and with such grapes, harvest decisions must include pH rather than just sugar and/or titratable acidity. Also pH value can increase excessively during vinification. Winemakers must be aware of this possibility and monitor and control pH to levels that result in optimum wine quality.

Literature Cited

1. Amerine, M.A. and Joslyn, M.A. 1970. Table Wine. The Technology of Their Production, Second Edition. University of California Press, Berkeley and Los Angeles, CA.
 2. Amerine, M.A., Berg, H.W., Kunkee, R.E., Ough, C.S., Singleton, V.L. and Webb, A.D. 1980. The Technology of Winemaking, Fourth Edition, AVI Publishing Co., Westport, Conn.
 3. Beelman, R.B. and Gallander, J.F. 1979. Wine Deacidification. Adv. Food Research: 25-1-53.
 4. Breed, A., Rodella, T. and Basmajian, R. 1975. Through the Molecular Maze, Experimental Edition. William Kaufman, Inc., Los Altos, CA.
 5. Boulton, R.B. 1980. The relationships between total acidity, titratable acidity and pH in a wine. Am. J. Enol. Vitic. 31:76- 80.
 6. Boulton, R.B. 1980. The general relationship between potassium, sodium and pH in grape juice and wine. Am. J. Enol. Vitic. 31:182-186.
 7. Freeman, B.M., 1982. Regulation of potassium in grapevines (*Vitis vinifera* L.). Ph.D. Thesis, University of California, Davis.
 8. Mattick, L.R., Plane, R.A. and L.D. Weirs. 1980. Lowering wine with carbonates. Am. J. Enol. Vitic. 31:350-355.
 9. Morris, J.R., Sims, Ca. A. and Cawthon, D.L. 1983. Effects of excessive potassium levels on pH, acidity and color of fresh and stored grape juice. Am. J. Enol. Vitic. 34(1):35-39.
 10. Nagel, C.W. and McElwain, K.R. 1977. An analysis of the influence of titratable acidity in the scoring of wine. Am. J. Enol. Vitic. 28:69-73.
 11. Nagel, C.W., Amistoso, J.L. and Bendel, R.B. 1982. The effect of pH and titratable acidity on the quality of dry white wines. Am. J. Enol. Vitic. 33:75-79.
 12. Plane, R.A., Mattick, L.R. and Weirs, L.D. 1980. An acidity index for the taste of wines. Am. J. Enol. Vitic. 31:265-268.
 13. Romberger, R.M. 1982. The use of potassium bicarbonate and complementary methods of wine deacidification. M.S. Thesis. Pennsylvania State University.
 14. Singleton, V.L. 1980. Grape and wine phenolics; background and prospects. Proc. of Grape and Wine Cent. Symp., University of California, Davis.
 15. Smith, C. 1982. Review of basics on sulfur dioxide. Enology Briefs. 1:2-3.
 16. Somers, T.C. 1977. A connection between potassium levels in the harvest and relative quality in Australian red wines. OIV Int. Symp. Quality Vitage. p. 143-148.
 17. Zoecklein, B. 1982. Research on controlling pH in the vineyard. Eastern Grape Grower and Winery News, p. 26, 69.
- Editor's Note: This paper was presented at the 15th Pennsylvania Wine Conference at Pennsylvania State University, University Park, PA on March 2-5, 1983 and published in the Proceedings thereof.