

Acidity in Wine: The importance of management through measurement

The typical acidity measurements in grape juice and wine are pH and titratable acidity (TA). The pH measurement is used in the vineyard to assess the ripening pre-harvest, e.g., (Brix * pH²), to calculate sulfur dioxide requirements after fermentation, and to assess oxidation risk because high pH wines are generally more prone to oxidation. TA is applied to sensory perception of a wine's acidity, i.e. its tartness, sourness, crispness. While pH and TA are related, pH is a measurement of the likelihood and speed of occurrence of pH dependent reactions, while TA is the best estimate of a wine's perceived acidity.

Titrateable acidity should not be confused with total acidity: total acidity only quantifies the molar weights of acids contained in a grape, must or wine; TA is an approximation of total acidity by titration with a strong base (NaOH) to a pH of 8.2, i.e. TA is the sum of both acid content and cation content, such as potassium (K⁺), sodium (Na⁺), and calcium (Ca⁺⁺) (1). While the quantified TA is inflated with cations, measuring total acidity is difficult as it requires the ability to directly quantify organic acids.

In the winery TA is the best practical expression of the organic acid concentration within must or wine. The principal organic acids found in grapes are tartaric, malic; to a small extent, citric and others. Tartaric and malic acid account for over 90% of the total acids present, existing at roughly a 1:1 to 1:3 ratio of tartaric to malic acid. The actual acid composition and concentration within the must or wine is influenced by many factors such as variety, climatic region, and cultural practices; their presence contributes to both a wine's flavor and to its stability, color, and pH. By knowing the exact organic acid makeup of a wine or must a producer can make educated vinification decisions to optimize flavor and stability.

During the berry's progression to veraison, acids accumulate within the fruit. At veraison, the total acidity in the fruit decreases, primarily due to the reduction of malic acid; at harvest, the fruit usually contains more tartaric acid than malic acid, the exact concentrations and ratios to one another being cultivar specific and harvest date dependent (3). Grapes are one of the rare fruits that contain tartaric acid. It is present as free acid and in its salt form, e.g. potassium bitartrate (KC₄H₅O₆), sodium bitartrate (C₄H₅NaO₆), and calcium bitartrate (CaC₄H₄O₆). The presence of the salt form is an important constituent, affecting pH and the cold stability of the wine (5).

Basic difference between pH and TA

While one may think that TA and pH are directly correlated as acidity indicators, they are not: The measurement of pH is the number of H⁺ ions in a solution using a *logarithmic* scale, with a lower number denoting a higher concentration of H⁺ ions. Translation: the difference between a wine with a pH of 4.0 and with a pH of 3.0 is that the wine with the pH of 3.0 has 10x the

number of hydrogen ions as the pH 4.0 wine (or 1×10^{-3} versus 1×10^{-4} H⁺ ions). The measurement of acidic content is the acid's potential to liberate H⁺ ions as it dissociates. While acid content affects pH, it is not directly predictive of pH (or vice versa). This non-direct correlation is partially due to pH "buffering" caused by a number of compounds in wines, such as sugars, acids, and phenolic compounds. Buffering occurs because these compounds exist in equilibrium between their acid and conjugate base forms; the ratio of the two forms to one another must be significantly shifted before a noticeable pH change can occur. Just as pH calibration buffer solutions effectively calibrate pH equipment due to their reliable stability, the addition of a given amount of acid to a wine may not reduce the pH as expected due to the wine's buffering capacity to maintain a stable pH.

In taking pH and TA measurement one is also measuring two different chemical attributes of the wine or must. With a pH meter one is measuring an electrical gradient created by the solution inside the cell of the pH probe and the wine. With TA one is measuring the amount of strong base that it takes to raise the solution to pH 8.2 accounting for both acid content and buffering capacity. Within the US wine industry, TA is typically quantified in terms of g/L of tartaric acid, as if it were a quantification of *only* tartaric acid; in fact, the number represents the concentration of all titratable acids, e.g. including malic, citric, lactic, succinic acids. (*Note*-some industries use Sulfuric acid as the acid of reference, so one may see values given in g/l as Sulfuric in some European publications).

Due to the presence of various kinds of acids and their salts, the relationship between titratable acidity and pH is necessarily a complex one. For instance, pH also depends on the ratio between tartaric and malic acids; so any loss of malic acid, i.e. in the vineyard from respiration during ripening in warm climates, or in the winery from unintentional MLF, will reduce TA and increase pH.

Briefly, understanding the role of pH and TA in winemaking is crucial to making good wines.

Overview of the Acids in Wine

Tartaric Acid- A diprotic (two H⁺ ions) acid - (C₄H₆O₆), tartaric acid is relatively microbial stable and accounts for a large proportion of a wine's acidity (along with malic acid) and normally exists at a concentration between 2.5-5g/l at harvest.

Malic Acid- A diprotic (two H⁺ ions) acid - (C₄H₆O₅), the levels of malic acid in grape berries are at their peak just before veraison when they can be found in concentrations as high as 20 g/L. As the vine progresses through the ripening stage, malic acid is metabolized in the process of respiration, and by harvest, its concentration falls to around 1-4 g/l.

Lactic Acid- A monoprotic acid (one H⁺ ion) - (C₃H₆O₃), lactic acid bacteria (LAB) convert sugar and malic acid into lactic acid, the latter through MLF. This process can be beneficial for some wines, adding complexity and softening the harshness of malic acidity, but it can generate off flavors and turbidity in others. Note that lactic acid does not naturally exist within the grape, but can be produced during vinification.

Citric Acid- A triprotic acid (three H⁺ ions) - (C₆H₈O₇), citric acid often has a concentration of less than 1 g/L at harvest; note that citric acid may be converted by LAB to acetic acid and diacetyl.

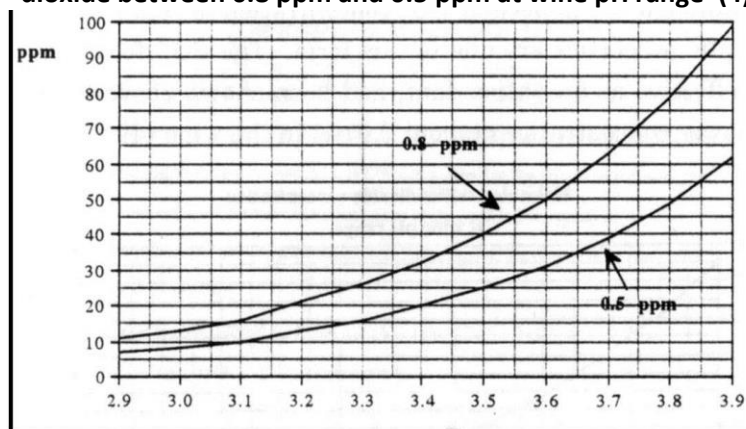
Acetic acid- A monoprotic acid (one H⁺ ion) - (C₂H₄O₂), acetic acid is produced in wine during or after the fermentation period. It is the most volatile of the primary acids associated with wine and is responsible for the sour taste of vinegar. During fermentation, activity by yeast cells naturally produces a small amount of acetic acid if the wine is exposed to oxygen. The U.S. legal limits of Volatile Acidity are 1.2 g/L in red table wine and 1.1 g/L in white table wine.

Succinic acid- A diprotic (two H⁺ ions) acid – (C₄H₆O₄), succinic acid is more commonly found in wine, but can also be present in trace amounts in ripened grapes. While concentration varies among grape varieties, it is usually found in higher levels with red wine grapes. The acid is created as a byproduct of the metabolization of nitrogen by yeast cells during fermentation.

The importance of precise measurement

It is recommended that pH for table wines be in the range of 3.1 to 3.3 for musts to ensure microbial and chemical stability (2); in reality Missouri white wines run close to 3.5 and MO red wines can exceed 3.6. At these pH values only a tiny proportion of SO₂ is in the active, molecular form; to shift the equilibrium to a point that will allow good stability, one must lower the pH.

Free sulfur dioxide (SO₂) ppm concentration required to maintain concentration of *molecular* sulfur dioxide between 0.8 ppm and 0.5 ppm at wine pH range (4)



If the wine's pH is **3.35**, and the intent is to maintain 0.8 ppm of molecular sulfur dioxide to stabilize the wine, then the winemaker must add the equivalent of **30 ppm** free sulfur dioxide concentration; if the wine's pH is **3.60**, and the intent is to maintain 0.8 ppm of molecular sulfur dioxide to stabilize the wine, then the winemaker must add the equivalent of **50 ppm** free sulfur dioxide concentration; if pH is **3.75**, then add equivalent of **70 ppm**...

To achieve the recommended pH, one method to lower the pH of the must is to add an organic acid. The tricky part is calculating the amount to add to lower the pH without increasing the TA to an unpleasant level of excessive tartness or sourness in the wine. Given the continual chemical and microbiological reactions in wine, e.g. pH buffering, MLF, and tartrate precipitation, it is not always possible to add X amount of an organic acid and achieve Y reduction in pH.

Before adding organic acids to ultimately lower the pH, it is necessary to have baseline readings of both TA and pH.

Tartaric acid, in practice, is the preferred acid addition to wine because it is not as easily degraded microbiologically, as are malic and citric acids, which may lead to unexpected changes. Because tartaric acid is poorly soluble in ethanol in water solutions, e.g. wine, there is a limit to the amount of tartaric acid that a winemaker might add without causing cold instability.

While malic or citric could potentially be used, such practice is a riskier prospect: malic acid can degrade to lactic acid, and citric acid to diacetyl, the "buttery" aroma found in some wines. Citric acid may also degrade into acetic acid, which is federally regulated regarding maximum concentration in wine. There are also commercial acid "blends" that seek to mimic the proportions naturally found in the grape.

As many winemaking decisions will be affected not only by the total or titratable acidity, it is necessary to know concentration of the individual acids comprising the wine's overall acidity. There are a variety of measurement methods available to the winemaker:

One of the classic methods used by winemakers is paper chromatography, which separates acids dependent on the speed at which the samples travel up paper moistened by a solvent at one end. The problem with this method is that it is not quantitative and relies on hazardous chemicals.

Another method that has gained popularity within wineries is the enzymatic based method. This method employs an enzyme that selectively uses a given acid to cause a reaction that leads to a change in absorbance as measured by a spectrophotometer. These tend to be as accurate as an individual's ability to pipette. The equipment needed is a spectrophotometer; the

consumable supplies include an enzymatic kit and appropriate micro-pipettes. It should be noted though that these kits have expiration dates and need to be used soon after opening.

Another method is high performance liquid chromatography (HPLC). This works off the same basic principle as paper chromatography, but the solvent in this case is forced through a column at high pressure. Unlike paper chromatography this method is both quantitative and very sensitive; the required equipment is not cost beneficial for the average winery. At the GWI we have such units in place for research; we plan to soon offer acid quantification and characterization to the Missouri industry on a trial basis.

GWI will offer a pilot program to gauge interest in this acid measurement service. We would like interested industry members to contact Michael Leonardelli for information on how to prepare the sample and where to send it. Our plan is to initially offer this service for free during our testing period, and then charge a modest fee to cover costs when fully implemented. For any questions, concerns or suggestions for additional services, please feel free to contact either Michael Leonardelli (leonardellim@missouri.edu) or Misha Kwasniewski (kwasniewskim@missouri.edu) at the GWI.

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