The Wine Analyst's blog

pH: how to measure it, what it is, and how to use it.

Wine is an acidic substance, and there are ranges of acidity that are appropriate to each varietal. In general a wine that is too acidic will taste sharp or sour, while one that is not acidic enough will taste flat and insipid. It's no surprise to those of you on the quest for great achievements in winemaking that pH and acidity (TA) are important aspects that are key to know and control. I thought that it would be good to summarize some observations I've had as an equipment maker for you all.

We analyze wine's acidity by measuring its pH and TA. How these are related in a technical sense involves some explanation that we will get into later, but in terms of how they affect wine's taste and mouthfeel, I like to think of pH as the instant "activity" of the wine's acidity while the TA is its body or lasting power.

In this installment of the Wine Analyst's blog, we'll focus on the pH aspect of wine's acidity. Next month we'll delve more into TA.

Let's first go over the correct way to use Vinmetrica's equipment for measuring pH. Then we'll discuss some of the basics of what this parameter means. Finally there is some maintenance tips and theory.

Measuring pH.

Since we're mostly interested in wine, we're going to focus on measurement in the pH range of 3 to 4. Simply put, a pH electrode is calibrated with reference solutions at pH 7 and pH 4 (or 3), then the measurement is made by putting the calibrated electrode into the wine. With some provisos and tips that we'll discuss below, that's really about all there is to making a pH measurement. Later we'll talk more about what is pH, and the mechanics of the pH electrode as well as its use and maintenance.

Calibrating: This is important because the response of any pH electrode slowly drifts over time, so you must calibrate it at least once every day of use. Follow your instructions in the manual which go more or less like this:

1. Have your electrode and all reference and samples solutions at the same temperature, preferably about 70F, but at least close in temperature.
2. Carefully remove the storage solution bottle from the end of the electrode by unscrewing the bottle, then removing bottle followed by the cap.
3. Rinse the electrode with a little distilled water. Gently shake off excess water.
4. Place the electrode in the pH 7.00 reference solution and swirl briefly, then let stand upright .
5. Put the instrument in CAL mode.
6. When the CAL LED flashes, press the ENTER button. The message 'Good Cal' will scroll on the screen.
7. Rinse the electrode with distilled water, then place it in the pH 4.01 reference solution and swirl briefly, then let stand upright.
8. Repeat steps 5. and 6.
9. but note the "Provisos and tips" below

Measuring pH in wine: Once you have a properly calibrated pH electrode, you are ready to measure wine's pH.

1. Rinse the calibrated electrode with distilled water and shake off excess water.
2. Rinse your tri-stir beaker or suitable vessel well with distilled water. Shake out excess water thoroughly.
3. Put 20 mL of wine in the beaker.
4. Insert the electrode and swirl briefly, then let stand.
5. Put your SC-300 or -200 into pH mode.
6. Allow the reading to stabilize for 30-60 seconds before recording the pH value.

Provisos and tips to wine pH measurement.

1. <u>We used to recommend that you stir or swirl the solution at all times</u>. But newer-style electrodes perform better when allowed to stand after a brief swirling to reach equilibrium with the solution, and even older electrodes perform fine in this way. <u>Temperature</u>. There is an effect of temperature on pH of wine and reference solutions. While this effect is not large in most cases, it's a good idea to minimize temperature errors by having reference solutions and wine samples within a few degrees C of each other. Most reference solutions are defined at 25C (about 77F), but the error of using them down to 15C (59F) is pretty small, particularly if the wine is at the same temperature.
2. <u>Calibrate at least once daily</u> with reference solutions at pH 7 and 4 (or 3). All pH electrodes drift slightly over time, so it's essential to calibrate each day of use. By the way, most reference solutions have a shelf life of 2 years. Especially do not use them if they have any sign of deterioration, like presence of mold or cloudiness. Get fresh ones.
3. You can (and should) easily check your calibration with a <u>saturated solution of cream of tartar</u>, which has a pH of 3.56 (defined at 25°C but not changing much down to 15°C)
    a. Get pure cream of tartar (grocery store stuff is fine, provided it's pure), or reagent grade potassium hydrogen tartrate, also known as potassium acid tartrate or potassium bitartrate. Call it KHT for short.
    b. Place about 1/8 teaspoon of KHT in 20 mL of distilled water. Mix well for about 30 seconds. You want to be sure the solution is saturated, i.e., everything that can dissolve, has dissolved. There should be some undissolved solid left. [note: discard solution after 24 hours]
    c. I recommend you put your instrument in pH mode (i.e., take it OUT of calibrate mode so you don't accidentally calibrate it at this pH!)
    d. This solution has a standard pH of 3.56 at 25 degrees C (78 degrees F). It should be within 0.02 pH of this value at temperatures from 20 to 30 degrees Celsius.

   I am usually happy with a value between 3.50 and 3.60. If I don't hit this range I go back and try calibrating again. If I can't hit this range after a few tries, I begin to suspect something with the electrode or the instrument (could also be reference solutions, but not usually).

<u>Interpreting pH and wine</u>:

1. Lower pH is generally desirable for stability, and better activates SO2 (sulfite) to improve preservation
2. Normal ranges are 3.0-3.4 for most whites, 3.3 to 3.8 for reds.
3. A pH that is high (3.9 or more) can often have a flat taste, flatter as pH goes higher.
4. pH can be lowered with tartaric acid. Rough rule of thumb is that 1 g/gallon lowers pH by 0.1 unit, but this depends on many things. [More on this next time…]

What is pH?

The term 'pH' is said to stand for “power of hydrogen” (there is some debate about the history of this acronym, but we'll go with it). pH is a way to represent the amount of *hydrogen ion,* H^+*,* in a solution. When an acid is added to water, it causes an increase in the hydrogen ion concentration (often represented as c_H , signifying moles per liter or mol/L of hydrogen ion). For example, if you add hydrochloric acid (HCl) to water, it dissolves completely and produces hydrogen (H^+) and chloride (Cl^-) ions:

$$HCl \rightarrow H^+ + Cl^-$$

This solution will be acidic due to the hydrogen ions, directly in proportion to the amount of HCl added, i.e., c_H will be the same as the amount of HCl added. If you add 3.6 g of HCl, which is 0.1 mole of HCl, to 1 liter of water, you will have 0.1mole/liter (mol/L) of H^+, i.e. $c_H = 0.1$ or 1×10^{-1}. If you add 3.6 *mg* HCl – i.e., 1/1000th as much, or 0.0001 mole – to 1 liter of water, you will have 0.0001 mol/L and $c_H = 0.0001$ or 1×10^{-4}.

Over 100 years ago, scientists recognized that c_H could range widely, over 14 orders of magnitude, so it was convenient to represent its concentration on a log scale. The pH term was coined and defined as the negative logarithm of the hydrogen ion concentration

$$pH = -log(c_H)$$

So in the above two examples of HCl, the pH values would be 1.0 and 4.0 for the 0.1 mol/L and 0.0001 mol/L solutions, respectively. As we know, wines typically are in the pH range of 3 to 4, meaning that their hydrogen ion concentrations lie between 0.001 and 0.0001 mol/L.

In modern usage, pH is defined as the negative logarithm of the hydrogen ion *activity,* a_H

$$pH = -log(a_H).$$

This activity is related to, but not quite identical with, the hydrogen ion concentration in solution. A factor γ*,* called the “activity coefficient” relates these:

$$a_H = \gamma \times c_H$$

I bring this up because the pH electrode we use responds to hydrogen ion *activity* rather than its concentration *per se*. For a very dilute solution in pure water, γ approaches 1.00 and so the activity and concentration are the same, but in real world solutions, particularly wine with its alcohol, salts and fruit acids present, this value is nearly always less than 1.00.

Fortunately we don't need to worry about this difference of activity and concentration most of the time, because we calibrate our electrodes against standard solutions whose pH was extensively characterized and standardized over 40 years ago by the National Bureau of Standards (since renamed the National Institute of Standards and Technology or NIST). We are using an *operational* definition of pH based on a response of a defined measurement system to agreed-to reference solutions. It's nevertheless good to keep in mind what a pH electrode responds to in understanding what a measured value of pH tells us.

The pH electrode measurement system: mechanics and maintenance

A *combination* pH electrode, like the one we provide, really consists of two electrodes: a glass electrode and a reference electrode. The glass electrode is the small glass bulb that you see on the end of the probe. The reference electrode is internal so it's harder to see it, but it is connected to the test solution by a pair of ceramic frits that can be seen on either side of the glass bulb.

The glass electrode is the pH sensing part of the pH electrode. It has an internal reference solution that has a constant pH, and the thin glass bulb provides a surface that creates a voltage difference that depends on the pH of the external solution (the test solution). This "half cell" voltage cannot be measured directly, so a reference half cell is needed to keep a constant reference against which the pH half cell voltage can be measured.

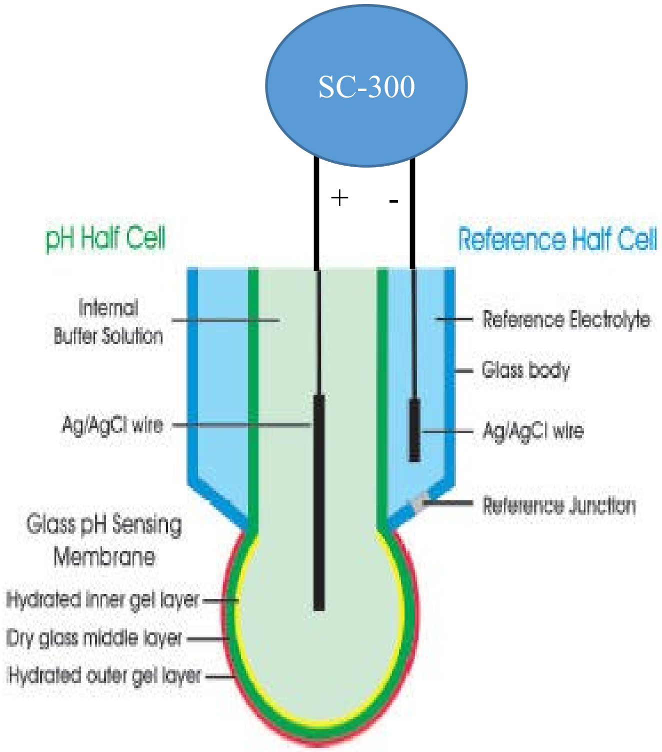
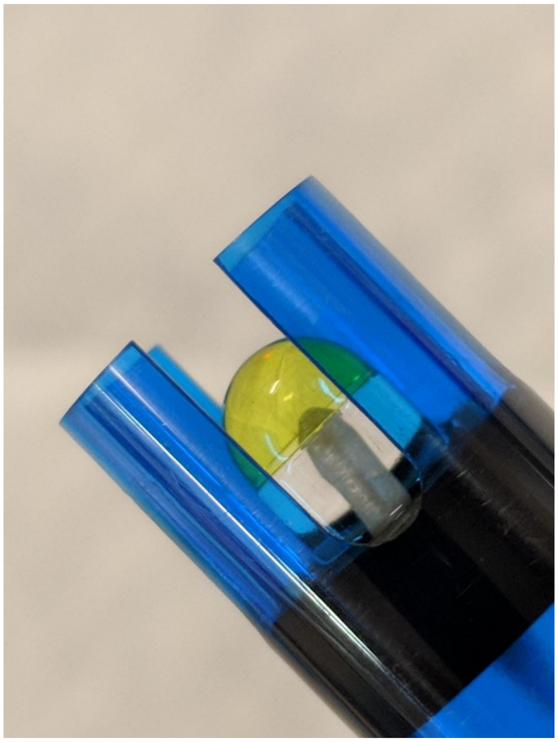


Diagram of the pH electrode with the SC-300's pH system. The glass pH sensing membrane (pH half cell) is a thin bulb of special glass, inside of which is a silver/silver chloride electrode and a potassium chloride reference buffer solution. The reference half cell is a reference electrolyte and a similar silver/silver chloride electrode, but it does not change with pH; a reference junction (essentially a fine porous frit) simply provides electrochemical contact with the solution being measured.



Side view of a pH electrode. The glass bulb is the pH sensing element. Inside is a silver/silver chloride electrode and a potassium chloride reference buffer solution

Bottom view of a pH electrode. The glass bulb is the pH sensing element. On either side are the ceramic frits (reddish from use in red wines) of the reference junction that provide contact of the test solution to the reference electrode inside.

Maintaining the pH electrode:

Basically, the key to long life of a pH electrode is to always store it properly when not in use. The glass bulb needs to stay wet, and the reference junction needs to be in contact with the storage solution (Vinmetrica's is 2M KCl with 25 mM potassium hydrogen phthalate) to keep the reference electrode's response accurate.

1. Rinse the pH electrode in distilled water and shake off excess water.
2. Place the cap of the electrode storage bottle onto the electrode. A slight twisting motion helps to slide it up the shaft. Then screw the bottle onto the cap, adjusting the cap's height as needed so that the electrode is in the middle of the solution.
3. Store the electrode in an upright position so that the end of the electrode is in constant contact with the solution.
4. If your pH electrode is ever accidentally left out and dries up, put it back into storage solution as soon as possible. Usually it will recover after several hours.
5. The pH electrode storage solution should be replaced at least once a year, more if heavily used.

Avoid damaging your electrode:

1. The glass membrane-bulb is very fragile! Don't touch it with anything! Don't drop it! Don't bang it against the bench!
2. When removing or replacing the electrode storage bottle, always unscrew the bottle first before trying to pull it away from the electrode. If you try to pull the bottle off without unscrewing it, it can pull the whole electrode assembly out of the body of the electrode, ruining it.
3. Keep the electrode properly stored as above. If you can't put it in the storage solution for some reason, put it temporarily in the pH 4.01 reference solution, or a little distilled vinegar in a pinch. As soon as possible, get the right storage solution. (see above), either Vinmetrica's, or the pH electrode storage solution at your local winemaking supply shop. Do not store the electrode in distilled water.
4. Prolonged storage in the wrong solution will cause the reference junction to become depleted of its proper potassium chloride concentration. This can take several days of proper storage to remedy, and sometimes the response never recovers.
5. Shock treatment: an electrode that is difficult to calibrate, or that is very slow in response time (or "drifting") can sometimes be reinvigorated by cleaning in acid and alkali. Place the electrode in 2 M HCl (this is the "Acid Solution" of the SO2 reagents set) and let it sit for 15 minutes with occasional stirring. Then remove it and rinse with water, followed by 15 minutes in 0.1 to 1 M NaOH (the TA Titrant or 1N NaOH). Remove and rinse, then place in electrode storage solution for at least 1 hour before trying to use it again.

For an excellent discussion of various aspects of measuring pH, see this page from our pH electrode manufacturer, Alpha Measure: *Alpha Measure pH article*