Measuring pH

When we measure pH, we are measuring the strength of the acid in a solution. In the case of a grape juice or wine solution, the predominant acids are tartaric and malic. There is also a small amount of citric acid in grape and wine, as well as fermentation-derived lactic, succinic, and acetic acids. The pH electrode is measuring these acids by quantifying the protons (i.e. hydrogen ions) that have dissociated from the acid molecules, i.e. the H^+ shown here:

$$\boldsymbol{H} - Acid \leftrightharpoons \boldsymbol{H}^+ + Acid^-$$

Neutral acid with undissociated H — Anion species of acid with dissociated H

Somewhat counterintuitively, a greater number of free protons mean a lower pH. Since the acids in grapes and wine are all weak organic acids, they will predominantly remain in their neutral (undissociated) state, resulting in a typical wine pH range of 3 – 4.

To ensure an accurate pH measurement, a properly calibrated, well maintained pH meter is essential. Though each pH meter is different (reading the instruction manual for your specific instrument is also essential), here is a general protocol and some tips for calibrating and measuring the pH of grape juice and wine.

General protocol

1) Gather and prepare necessary supplies
    a. pH meter with electrode (sometimes called the probe) attached
    b. Beakers or similar containers for calibration (buffer) solutions. Label appropriately, e.g. pH 3, 4, 7.
    c. Bottles of calibration (buffer) solutions between 20 – 25 °C
    d. Lint-free tissue, e.g. KimWipes (regular tissues, paper towels, etc. will contaminate electrode)
    e. Distilled water, preferably in a squirt bottle
    f. Waste beaker or similar container
    g. Sample(s), also between 20 – 25 °C. Major soluble solids should be removed from juice. Options for clarification include settling/decanting, or straining through coffee filters or cheesecloth.

2) Pour calibration solutions from bottles into labeled beakers. Never place electrode directly in buffer bottles, as this risks contaminating the entire container.

3) Remove electrode from storage solution. *Note:* electrode should be kept in the storage solution recommended for your pH meter. Do not store in water (even distilled water) or any other substances. The electrode should always be in storage solution when not in use.

4) Check the electrolyte fill level and replenish as necessary. Usually, electrodes should be filled to within ½" of the fill hole. If there is a fill hole cap, it must be loosened (or sometimes removed) during operation of the electrode.

5) Rinse electrode with distilled water over the waste beaker.

6) Blot or gently pat electrode with lint-free tissue to remove excess moisture. Do not rub or wipe; this will create an electrostatic charge that can interfere with pH readings. An alternate method is to give the electrode a quick shake to dispel water droplets. If using this technique, be careful to avoid hitting it against an objects, e.g. table, lab bench. *Note:* the shake method is not recommended when working with caustic solutions.

7) Place electrode in the 1st calibration (buffer) solution.* It should be immersed so that the reference junction is fully submerged (often denoted by a thin line. If not, a 1-2" submersion should suffice). The electrode should not be touching the sides or bottom of the container. Allow pH to stabilize… this may take a few minutes! Remove electrode, rinse with distilled water, blot with tissue.

8) Place electrode in the 2nd calibration solution and allow pH to stabilize. Remove, rinse with distilled water, blot with tissue.

9) Place electrode in the 3rd calibration solution and allow pH to stabilize. Remove, rinse with distilled water, blot with tissue.

10) Place electrode in the sample. Stir or gently shake the sample, avoiding contact with the container's sides or bottom. The agitation ensures a homogeneous mixture, and therefore a more accurate reading. Allow pH to stabilize; in a complex matrix like grape juice or wine, this often takes a few minutes.

11) Record pH value (you will not remember it). Remove electrode, rinse <u>thoroughly</u> with distilled water (juice and wine are very sticky!), blot with tissue.

12) Repeat step 8 for remaining samples.

13) When finished, place clean, dry electrode in storage solution. Tighten or replace fill hole cap, as needed.

14) Discard used calibration solutions and waste water.

***Notes on calibrating with buffer solutions:**

- Calibrate every day that the electrode is used; more frequently if "drift" is noticed
- At minimum, a two-point calibration is necessary; a three-point calibration is preferred
- Always use a pH 7 buffer solution as one of the calibration points, this establishes the "offset" that is needed for the most accurate pH calculations
- Best practices:
    - Buffer solutions (calibration points) should be within a few units of the expected sample pH
    - Calibration points should be both above and below the expected sample pH (i.e. bracketing)
    - The last calibration point should be the one closest to the expected sample pH
    - *For example, for a wine with an estimated pH of 3.65, calibrating using buffer solutions at pH 7, 3, and 4 (in that order) would be recommended*

For a good video on proper usage of a pH electrode, click here.

For an excellent video on the electrochemistry of how a pH electrode works, click here.

References

(1) Waterhouse, A. L.; Sacks, G. L.; Jeffery, D. W. *Understanding Wine Chemistry*; John Wiley & Sons, Ltd: Chichester, UK, 2016.
(2) Iland, P.; Bruer, N.; Edwards, G.; Weeks, S.; Wilkes, E. *Chemical Analysis of Grapes and Wine*; Patrick Iland Wine Promotions PTY LTD: Campbelltown, Australia, 2004.
(3) Boulton, R. B.; Singleton, V. L.; Bisson, L. F.; Kunkee, R. E. *Principles and Practices of Winemaking*; Springer US: Boston, MA, 1999.