

Estimating Grape Maturity with the Potential Power of Hydrogen (pH)

What is pH

pH or "pouvoir Hydrogène" in French, means hydrogen power and is related to the real acidity of must or wine. pH measures the strength and the concentration of acids able to dissociate into protons (H⁺) and negative ions (A⁻). From a theoretical concept, pH is defined as the base 10 logarithm of the concentration of hydrogen ions in solution and has no unit, as shown by the following equation:

 $pH = -\log 10 [H^+]$

pH is expressed on a scale of 0-14, where 0 is acidic, 7 is neutral and 14 is alkaline. The more acidic the wine, the lower the pH will be. For most wines, pH ranges from 2.8-4.0 with a pH > 3.8 increasing the risk of spoilage.

The pH is based on the dissociation equilibrium of the various acids, AH, in wine at fixed temperature and pressure. The emission of hydronium ions H_3O^+ (or hydrogen ions H⁺) defines the acidity of the AH (acid) molecule, as shown below:

 $AH + H_2O = A^2 + H_3O^2$ where A^2 is the conjugate base from the dissociation of the acid AH.

Musts and wines are mixtures of acids and salts acting as acidobasic buffer solutions and a modification in their chemical composition produces only a limited variation in pH. pKa is the negative log of the acid dissociation constant or Ka value. A lower pKa value indicates a stronger acid.

pH = pKa + log [salt formed]/[remaining acid] = pKa + log [A⁻]/[AH]

As an example, tartaric acid is the strongest organic acid from grapes that can easily dissociate the two acidic functions (COOH) at wine pH leading to the formation of bitartrate form (HT⁻) in wine. (See Iowa State University Extension and Outreach publication FS40k <u>Tartrate Crystal Precipitation</u>, store.extension. iastate.edu/Product/15980.

What happens during grape ripening

In grapes, the main organic acids are tartaric and malic acids constituting more than 90% of the acidity of the grape. Organic acids rapidly accumulate during the berry development before fruit set. Tartaric acid is specific to grapes and is found in unripe grapes at about 15 g/L. Malic acid is the most prevalent acid in unripe grapes at about 25 g/L. During berry ripening, the tartaric acid level does not decrease markedly while malic acid content decreases rapidly depending on the temperature conditions. The decrease of organic acids is directly related to the decrease in titratable acidity. See Iowa State University Extension and Outreach publication FS49e: Estimating Grape Maturity by Titratable Acidity,



https://store.extension.iastate.edu/product/16077. The level of specific organic acids can be measured in the grapes using enzymatic measurements or by high performance liquid chromatography (HPLC) with a diode array detector and a refractive index detector (DAD and RID) to estimate the harvest grape maturity.

Grape pH increases after véraison but is not directly related to the decrease of the level of organic acids as it depends also on salts and ions present in the system. pH is an important quality parameter used to estimate grape harvest maturity, in addition to titratable acidity and total soluble solids or °Brix.

An optimal grape juice pH varies from 2.9-3.3 in red and white cold-hardy grape varieties. It varies from 3.2-3.5 in red and white *Vitis vinifera* grape varieties.

It is worth noting that a small variation of pH, such as a difference of 0.2, can lead to important changes in wine as pH affects the forms of sulfites, alcoholic and malolactic fermentations; the color, protein and tartrate stability; and the taste of sourness in wine.

How to measure pH

• pH paper

Strips of pH paper can be used to give a rough estimation of grape must or wine pH. However, most of them have a large range and have an interval of 1.0 pH unit. A strip of pH paper is immersed in the grape must or wine and the color of the pH paper will change. On the kit, match the color with the corresponding pH value.

This method is not recommended to precisely measure pH. A pH meter is preferred.

• pH meter

Materials

- pH meter including a temperature probe and a pH electrode
- Stir plate and small stir bars
- Standardized buffers at pH 4.0 and pH 7.0 (a buffer pH 2.0 could be used in addition to the two other buffers)
- Deionized water
- Grape must or wine
- 100 mL and 250 mL beakers
- Soft paper towels or "Kimwipes"



Measurement of pH on red wine sample.

Method to measure the pH:

1. Remove electrode from storage solution and rinse with deionized water. Gently dry the electrode with a soft paper towel. Calibrate the pH meter according to manufacturer's directions using either two or three standard buffers at pH 2.0, pH 4.0 and pH 7.0. Be sure to calibrate with pH 7.0 first and then calibrate with pH 4.0 and pH 2.0. Ensure buffers are at room temperature and the temperature probe, if any, is cleaned with deionized water before placing it and the pH electrode into the buffer solutions.

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- 2. Check the accuracy of the calibration by retesting the pH of the buffers after cleaning the electrode and probe with deionized water and drying with soft paper towel.
- 3. Pour approximately 50-75 mL of room temperature grape must or wine into a 100 mL beaker and add a stir bar. Place the beaker on the stir plate and start stirring the sample at low speed.
- 4. Immerse the pH electrode into the sample and make sure the stir bar does not come in contact with the pH electrode to avoid any damage and no vortex is formed under the pH electrode while stirring.
- 5.Allow the pH reading to stabilize for 10-15 seconds or until the value is stable. Record the pH value.
- 6. Repeat steps 3-5 of this procedure for each sample and make sure to clean and dry the temperature probe and the pH electrode between each measurement.
- 7. Rinse the electrode with deionized water and return to the storage solution, commonly potassium chloride solution.

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