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Analyzing Juice and Wine

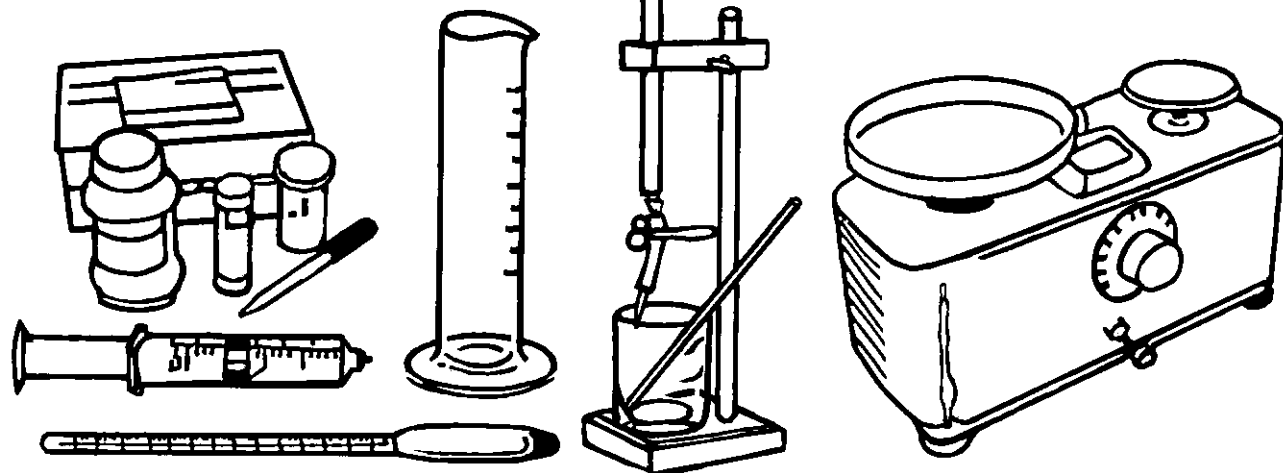
Several constituents in grape juice and wine must be measured to help the winemaker make decisions throughout wine making. For example, knowledge of the soluble solids ($^{\circ}$ Brix) content of a given juice will indicate whether adding sugar may be necessary. Knowing the amount of sulfur dioxide in a wine, as well as its pH, can serve as the basis for determining the amount that may be needed for adjusting SO_2 . A paper chromatograph without a developed malic acid spot, but showing a lactic acid spot, can be evidence that a particular wine had undergone malolactic fermentation (see malic acid analysis below). Although it is possible to make wines without analysis, consistent production of sound, superior quality wines is enhanced considerably with accurate analytical data.

Many suppliers sell the chemicals and equipment or kits/assemblies, along with instructions, required to perform all of the common juice and wine analyses. However, the reliability of these materials can vary.

Therefore, exercise caution in selecting the supplier(s) of reagents, equipment, and instructions. Certainly, the ambitious and serious winemaker would find *Methods for Analyses of Musts and Wines* valuable (see Selected References).

Wine acidity and pH

Because of their importance, the acidity and pH of grapes and wine are discussed first. Earlier, the acid composition of grapes was said to directly affect wine quality and pH also played an important role in wine quality and stability. As previously mentioned, grapes and wine owe their acid composition and taste primarily to the presence of tartaric and malic acids (lactic acid replaces malic in wines that have undergone malolactic fermentation). These fruit acids are defined as weak acids, compared with such strong mineral acids as sulfuric and hydrochloric. In solution, strong acids

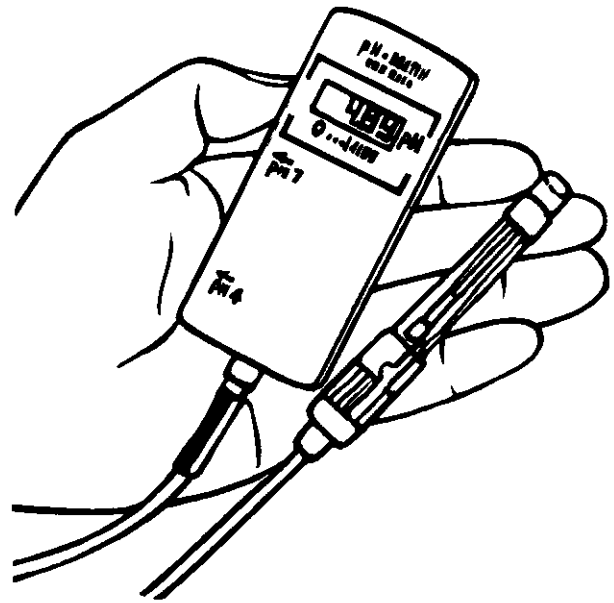


tend to dissociate or yield their hydrogen ion (H^+) component nearly completely; weak acids dissociate only about 1 percent or less of their hydrogen ions. Aqueous solutions owe their acidity or alkalinity to the ratio of hydrogen ion content to hydroxyl ions (OH^-). Thus, such acid solutions as wine have more H^+ ions than OH^- ions.

A solution's pH is a measure of the concentration of H^+ ions of an acidic solution, such as grape juice or wine, or conversely the concentration of OH^- ions of an alkaline solution, such as lye. Because the numerical values for the H^+ ion concentration are often extremely small fractions, say $1/10,000,000$ (equals 1×10^{-7}), the pH unit is used to express this concentration. A pH unit has been defined as the *negative of the logarithm* (or log of the reciprocal) of the H^+ ion concentration. The arbitrary term pH is thus a logarithmic index, employing small numbers, to express this ion concentration. As an example, in the case of distilled water, it means that 1×10^{-7} grams of H^+ ions in 1 liter has a pH of 7, where 7 is the logarithm of 10,000,000. The pH scale extends from 0 to 14, with 7 being the point of neutrality, wherein there exists the same concentration of H^+ and OH^- ions.

The important thing to note about the pH scale is that the lower the numerical value, the higher the concentration of H^+ ions and hence the higher the degree of acidity. Thus, there is an *inverse* relationship between decreasing pH units and increasing H^+ ion concentration. Note also, that because pH units are on a logarithmic scale, wine at pH 3.0 is 10 times more acidic than wine at pH 4.0—that is, there is a tenfold change in acidity for each unit change in pH. Since the pH of most table wine ranges from 3.1 to 3.6, it should be evident from the foregoing that very small numerical changes within this pH range actually reflect significant changes in wine acidity. Finally, it should be stressed that pH can profoundly affect microorganisms (low pH inhibits acetic acid bacteria and malolactics), the ratio of free to bound SO_2 , both protein and KHT stability, and wine color and flavor.

With pH defined and its importance established, how is it measured? The preferred method employs an ion-selective electrode that measures hydrogen ion concentration potentiometrically. More simply stated: A pH meter is used. Until recently, pH meters have been expensive, with bench models ranging from \$400 to more than \$900. There are now available \$150 to \$200 “hand-held” pH meters, with an accuracy resolution of from 0.01 to 0.02 pH units and temperature compensation. For most home wine making needs, a determination of ± 0.05 pH unit would be satisfactory. Instructions for standardizing the instrument, supplied by the manufacturer, must be followed exactly.



Hand-held pH meter

Even though pH can also be determined with “pH paper” (paper strips impregnated with organic dyes that produce color changes in response to various pH levels), they are not sufficiently sensitive to provide the accuracy and precision required to determine pH in grape juice or wine. Hence, we do not recommend their use for this application.

Keeping records

Maintaining accurate and complete records of all steps in wine making is vital. No winemaker can rely on memory alone for rational explanations or remedies. The serious winemaker must develop and maintain a complete chronological log for every processing activity for each wine lot produced. The wine making record book should contain:

- Date
- Time
- Wine lot identification
- Operation performed
- Juice/wine analysis data
- Amounts and kinds of sugar, acid, or other adjustments in composition
- °Brix readings of fermentation progress
- Fermentation temperature

Table 6. Corrections for Brix hydrometers calibrated at 68°F (20°C)*

Temperature in °F	Temperature in °C	Observed % sugar						
		0	5	10	15	20	25	30
		Subtract						
59.0	15	0.20	0.22	0.24	0.26	0.28	0.30	0.32
60.8	16	0.17	0.18	0.20	0.22	0.23	0.25	0.26
62.6	17	0.13	0.14	0.15	0.16	0.18	0.19	0.20
64.4	18	0.09	0.10	0.10	0.11	0.12	0.13	0.13
66.2	19	0.05	0.05	0.05	0.06	0.06	0.06	0.07
		Add						
69.8	21	0.04	0.05	0.06	0.06	0.06	0.07	0.07
71.6	22	0.10	0.10	0.11	0.12	0.12	0.13	0.14
73.4	23	0.16	0.16	0.17	0.17	0.19	0.20	0.21
75.2	24	0.21	0.22	0.23	0.24	0.26	0.27	0.28
77.0	25	0.27	0.28	0.30	0.31	0.32	0.34	0.35
78.8	26	0.33	0.34	0.36	0.37	0.40	0.40	0.42
80.6	27	0.40	0.41	0.42	0.44	0.46	0.48	0.50
82.4	28	0.46	0.47	0.49	0.51	0.54	0.56	0.58
84.2	29	0.54	0.55	0.56	0.59	0.61	0.63	0.66
86.0	30	0.61	0.62	0.63	0.66	0.68	0.71	0.73
95.0	35	0.99	1.01	1.02	1.06	1.10	1.13	1.16

*From page 80, *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 1955. Note: These corrections are satisfactory for musts and nearly correct for dry wines of low alcohol.

- SO₂ adjustments made
- Fining treatments
- Stabilization procedures performed
- Filtrations
- Aging times and in which barrels by wine lot
- Barrel cleaning treatments
- Other pertinent details.

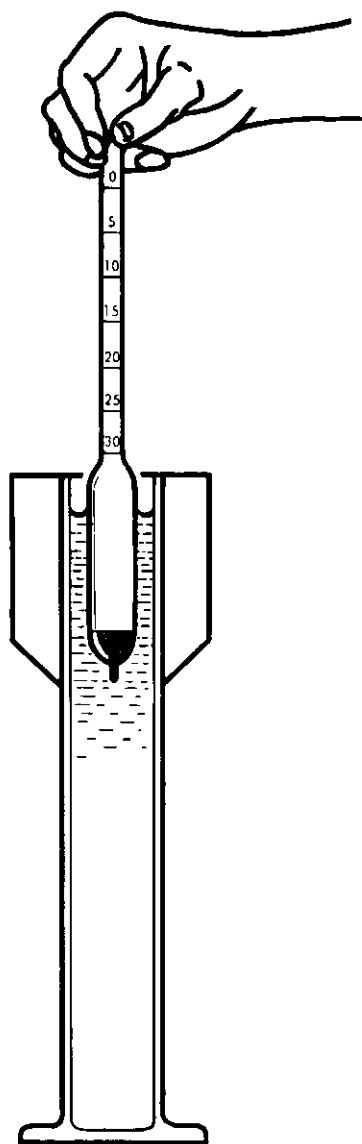
Excessive information is better than insufficient records. Finally, when performing analyses, always record the date and how analysis is performed, any deviations from the standard procedure, and the data obtained.

Soluble solids (°Brix)

Grape juice soluble solids are composed mainly of glucose and fructose and hence are approximately equivalent to the percent sugar by weight, or grams sugar per

100 grams of solution expressed as °Brix. The °Brix of juice, must, or wine can be determined with a hydrometer or a refractometer; the refractometer cannot be used to measure the soluble solids content of wine because the presence of alcohol interferes with the reading. Because hydrometers can be used in juice or wine, a series of hydrometers covering the following or similar °Brix ranges are recommended: 19° to 31°B; 9° to 21°B; 0° to 12°B; and -5° to +5°B. Negative °Brix values (those less than zero) are due to the presence of alcohol, which depresses the specific gravity. Hydrometers are usually calibrated at 68°F (20°C) and require using a correction factor when used in juice or wine of a different temperature. Use a good quality mercury bulb chemical thermometer, one of the newer probe types, or a remote sensor thermometer with a temperature scale range of 20° to 220°F or -10° to 110°C with one-degree scale divisions and a precision of ±1°, to measure the temperature of the sample. Add or subtract the appropriate correction factor to the hydrometer reading as given in table 6.

Testing for soluble solids in juice. Fill the hydrometer cylinder with a juice sample previously clarified by allowing suspended matter to settle. Grasp the hydrometer stem and gently lower the hydrometer into the juice with a slight spinning motion. Make certain the hydrometer does not rest on the bottom or cling to the sides of the cylinder and make a reading to the nearest 0.1 °Brix after the hydrometer is freely floating and at rest. Add or subtract the appropriate temperature correction to obtain the final value.



Testing °Brix in fermenting must/wine. Withdraw a sample from the fermentor and dispel most of the CO₂ bubbles with shaking. Suspend the hydrometer in the sample, as with juice, and allow to stand briefly. Use more spinning to free bubbles of gas from the hydrometer sides and make the reading.

Reducing sugar

Hydrometers are not only used to determine the sugar in juice before fermentation, but they are necessary for monitoring fermentation progress. Near the end of fermentation, when readings are less than -2° Brix (remember, minus readings occur due to the alcohol) and remain so for several days, the wine should be analyzed for reducing sugar (fermentable sugar) content to determine if the wine is, in fact, dry. A very simple and rapid tablet test (Dextrochek) can measure the sugar in the range of 0.1 to 0.2 percent. The test should be replicated at least twice. Because the tablets decompose rapidly when exposed to air or moisture, they should be kept tightly sealed. It is difficult to read the color endpoint in cloudy wine; therefore, the sample should be filtered or a sample allowed to clarify by settling for a few days in a refrigerator. Red wines are also impossible to test without first removing the pigment. Decolorize the wine by adding about 1 gram (0.03 ounce, 1 to 2 teaspoons) activated carbon to 50 ml of wine, mix, filter or settle, and proceed with the test.

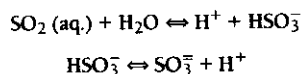
Titrateable acidity

As indicated in the **Introduction**, the titrateable acidity (TA) content of grapes and the wine is important to quality. Analysis for TA involves titrating a standard dilute sodium hydroxide (alkali) solution against a small juice or wine sample to a color change end-point of an indicator dye solution. Titration kits for determining TA, complete with detailed instructions, are available from home wine making shops. With care and practice, reasonably accurate and useful results can be obtained. The calculated values are expressed as tartaric acid in grams per liter. Note that the accuracy of the titration depends upon the strength of the standardized sodium hydroxide solution which, when exposed to air, loses its strength by reacting with carbon dioxide. Utilize this solution quickly or replace it with a fresh supply, daily if needed, to ensure accurate results. Accuracy can be checked by titrating against a known standardized solution of dilute hydrochloric acid, which should be part of the kit.

Total and free sulfur dioxide

As previously discussed, SO₂ is required to prevent oxidation and growth of undesirable yeast and bacteria. The usual amount added to sound crushed grapes is 50 to 100 ppm. Addition of 75 ppm SO₂ to most musts is sufficient to prevent oxygen uptake by polyphenoloxidase enzymes, which promote browning. During fermentation some SO₂ is oxidized to sulfate (SO₄⁻) and some is bound with such compounds as acetaldehyde.

Only SO₂ that is not bound or combined is, therefore, free to provide the desired properties. When SO₂ is dissolved in water, it exists as several ionic species: molecular SO₂, bisulfite (HSO₃⁻) and sulfite (SO₃²⁻). These forms are in equilibrium, depending upon the amount present, the pH, and temperature, in accordance with the following reactions:



These equilibrium reactions illustrate the effect of pH, wherein it can be seen that increasing the acidity (H⁺) or lowering the pH shifts the reaction to the left. It has been shown that the antimicrobial activity is the greatest for the SO₂ in the nonionized form (first formula at left in upper equation above). This further underscores the importance of low pH.

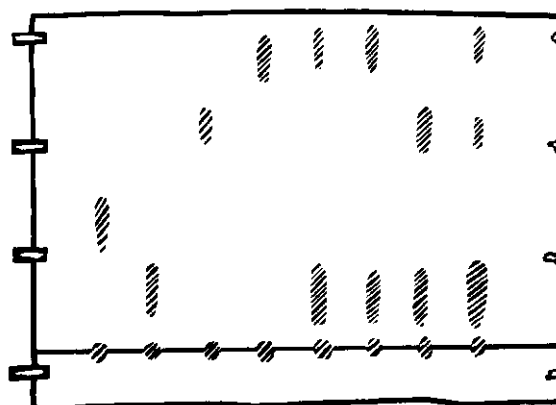
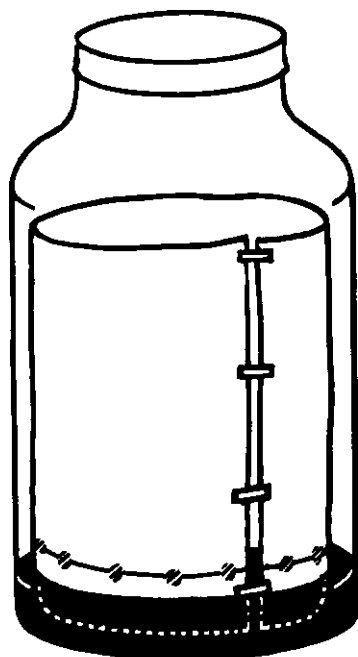
As noted, when SO₂ is added to juice or wine, it will react immediately with dissolved oxygen, the HSO₃⁻ with acetaldehyde (compound naturally present) and with other compounds. Also, moldy fruit has more binding sites for SO₂. All of the bisulfite reaction products are in equilibrium with the free SO₂ and together are called total SO₂. This fact alone renders an analysis for free SO₂ difficult, as it changes rapidly. Nevertheless, an analysis can be performed sufficiently accurately to obtain an estimate of the free SO₂. The total SO₂ analysis seems more straightforward, since it is performed after hydrolysis of the reaction products for direct titration. It should be cautioned that red wines, because of pigment and higher tannin content, can give erroneously high results in free SO₂ determinations. Therefore, values of free SO₂ that are less than 10 to 15 ppm in white wine or less

than about 20 ppm in red wine are not considered reliable.

The preceding discussion, it is hoped, has provided some helpful background for analyzing free and total SO₂. Titration kits that include the chemicals, equipment, and instructions for these analyses are available from home wine making shops. Although these titrations require considerably more skill than the analysis for TA, with some practice useful results should be possible. Additional instruction is contained in *Methods for Analyses of Musts and Wines* (see Selected References).

Malic acid

It can be very important to determine whether the malolactic fermentation has occurred, and the wine is therefore biologically stable. If fermentation has occurred or has been definitely inhibited, the wine can be safely bottled. Paper chromatography, a technique for qualitatively determining organic acids, is universally employed in detecting malolactic fermentation, specifically the presence or absence of malic acid. The method is simple, relatively inexpensive, and reliable. Actually, many wine-makers find this analysis fun to do. Again, home wine shops provide kits that contain equipment, chemicals, and instructions. A few words of caution: For best results, work in a clean, dry place and handle the chromatographic paper with clean dry hands to avoid contaminating the paper. Also, since the solvent is flammable and the fumes noxious and irritating, the air-drying process should be performed outdoors or in a well ventilated area, such as near an exhaust fan. (A stove hood exhaust might help, but don't leave the burners on!)



Paper chromatographic setup for malic acid

Courtesy of Desmond Lundy and Reynold Knowlton, Fermenthous Press Ltd., 1986