Titratable Acidity
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Grapes contain significant amounts of organic acids. The major organic acids in the must are tartaric, malic, and citric. Of these three acids, tartaric and malic acids account for over 90% of the total acid constituents of the juice (Amerine and Joslyn 1950). During ripening, the tartrate and malate content of the fruit decrease. This is accompanied by a steady increase in pH. Due to variation in buffer capacity, there is no direct relationship between titratable acidity and pH. In general, however, higher acid levels in fruit are often associated with lower pH values and vice versa. Thus the acids of the fruit have a significant bearing on pH. They also play a significant role in taste, color, and microbial stability of the juice.

The organic acids in wine are primarily derived from grapes. However, many other acids are formed during the fermentation. The major acids produced during and after the alcoholic fermentation are acetic, lactic, and succinic.

A good understanding of the organic acid composition of the must is very important to the vintner for the following reasons:

1. To determine the harvest time.
2. To decide the wine style.
3. To determine must treatment prior to fermentation.
4. To monitor the stability of a wine (e.g. Is a malolactic fermentation occurring when you don't want it?).
5. To comply with TTB regulations. The regulations dictate the minimum acid levels of 0.5 percent in table wines if the must or wine is ameliorated. Most of the commercially produced wines contain acid levels in the range of 0.6 to .9 percent.

The acid content of the must is determined by titrating a sample (a given volume) with a base such as sodium hydroxide solution to a phenolphthalein end point or alternatively, to a pH of 8.2. The titratable acidity is expressed as grams of tartaric acid per 100 ml.

Materials:

- 500 ml wide mouth Erlenmeyer flask and a 250 ml beaker
- 25 ml burette and burette stand
- 5 ml pipet and a 1 ml pipet
- Stir plate and magnetic stirrer
- pH meter with buffer solutions
- Distilled water
- 0.1 Normal NaOH (sodium hydroxide)
- Phenolphthalein indicator
- Thermometer
- Pipet bulb or pump

Procedure A - Titration without using pH meter

1. Place 200 ml of boiled and cooled distilled water into a 500 ml Erlenmeyer flask and add 1 ml of phenolphthalein indicator.
2. Titrate the water with 0.1 N, NaOH to a definite pink end point.
3. Add 5 ml of must/wine sample to the flask.
4. Titrate the sample with 0.1 NaOH to the same distinct end point.
5. Note the volume of N aOH used in the titration.

$$\text{TA as tartaric acid (g/100 ml)} = \frac{(V)\,(N)\,(75)\,(100)}{(1000)\,(v)}$$

V = ml of sodium hydroxide solution used for titration
N = Normality of sodium hydroxide solution
v = sample volume (ml)

If the above procedure is followed, the total titratable acidity can be calculated by multiplying the volume of 0.1 N NaOH used by a factor of .15.

Example: 6 ml of 0.1 N, NaOH was used to titrate a 5 ml wine sample, what is the TA of the wine?

Answer: 6 x .15 = .9% TA

Procedure B - Titration using a pH meter

1. Standardize the pH meter using buffer solutions of pH 4 and 7.
2. Place about 100 ml of boiled and cooled distilled water into a 250 ml beaker. Adjust the pH of the water to pH 8.2 or as close to 8.2 as practically possible by adding 0.1 N NaOH.*
3. Add 5 ml of de-gassed must sample (e.g. red wine). If the sample contains carbon dioxide, it should be degassed by heating a small (25 ml) must sample to incipient boil for 30 seconds and then cooling it.
4. Place a small stir bar in the beaker.
5. Immerse the electrode(s) in the sample and gently stir, making sure to keep the stir bar away from the electrode(s).
6. Slowly add 0.1 N NaOH to the sample and titrate to a pH of 8.2.
7. Record the volume of 0.1 N NaOH used in the titration.
8. Using the formula given above, calculate the total titratable acidity.

Notes:

1. The normality of NaOH should be periodically checked by titrating with standard HCl.
2. Since distilled water is not buffered, addition of even a small amount of NaOH may raise the pH well above 8.2. This will contribute to a slight error in the titratable acid determination.
3. Always use distilled water.
4. When using a pH meter, be sure to follow the operating procedure recommended by the manufacturer.

Determining Normality of Sodium Hydroxide (NaOH)

The normality of 0.1 N sodium hydroxide changes during storage. it should be periodically checked so that correct normality value is used in calculating the titratable acidity. The procedure for determining normality, which is also referred to as standardizing NaOH, is as follows:

1. Pipet 10 ml of 0.1 N hydrochloric acid into a 250 ml Erlenmeyer flask.
2. Add about 50 ml of water and 3 drops of methyl red indicator.
3. Place sodium hydroxide solution in a 25 ml buret.
4. Titrate the hydrochloric acid with sodium hydroxide until the end point in reached.
5. The end point is indicated by the development of a lemon yellow color.
6. Record the volume of NaOH used in the titration.

Normality of NaOH is calculated using the following formula:

$$\text{Normality of NaOH} = \frac{V \times N}{v}$$

V = Volume of hydrochloric acid, 10 ml.
N = Normality of hydrochloric acid, 0.1 N.
v = Volume of sodium hydroxide used.

Comments: The newly calculated normality of NaOH should be used in titratable acidity calculations.

References:

1. Amerine, M. A. and M. A. Joslyn. (1950). Table wines: the technology of their production. University of California Press.

2. Amerine, M. A. and C. S. Ough. (1980). Methods for analysis of musts and wines. John Wiley and Sons, New York.

3. Gallander, et. al. (1987). Manual for wine analysis and laboratory techniques. Ohio State University, OARDC, Wooster, Ohio.