MEASURING FREE SULFUR DIOXIDE

by

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Most small wineries use the Ripper method to measure sulfur dioxide in their wines. A wine sample can be measured in just a minute or two, so the Ripper method produces quick results. In addition, the Ripper measurement apparatus is simple to use and it is inexpensive.

Ripper Method

The Ripper method is a simple iodine titration. Iodine reacts with sulfur dioxide in the following way:

$$SO_2 + I_2 + 2H_2O \ ===> \ H_2SO_4 + 2HI$$

The equation shows sulfur dioxide + iodine + water produces sulfuric acid and hydrogen iodide.

Here is how a Ripper titration is accomplished. A measured amount of wine is placed in a small container together with 5 milliliter of 1% starch solution and 5 milliliters of 25% sulfuric acid. A dark purple color appears when iodine is added to a solution containing starch, so the starch solution is used to indicate the titration end point The sulfuric acid is used to lower the pH of the wine sample.

When a very small amount of calibrated iodine (I) solution is added to the wine sample, SO_2 and water in the wine react with the iodine and sulfuric acid (H_2SO_4) and hydrogen iodide (HI) are formed until all the iodine is consumed. The equation tells us that the wine sample now contains a tiny amount of additional sulfuric acid, a tiny amount of hydrogen iodide, slightly less sulfur dioxide, slightly less water (H_2O) and no iodine.

A second small amount of iodine is added to the wine sample produces the same results. But, after several small iodine additions, all the SO_2 in the sample is gone and the situation changes. Now, when the next iodine addition is made, a small amount of residual iodine will remain in the wine sample because there is no longer any SO_2.to react with the iodine. The iodine will react with the starch in the wine sample and produce a dark color. The "end point" of the titration has been reached, and the amount of SO_2 in the solution can be calculated from the total amount of iodine used

The formula for calculating free sulfur dioxide is

$$SO_2 \text{ (mg/l)} = Mw * V * N * 1000) / 2 * v$$

Mw = 64 (the molecular weight of SO_2); V = milliliters of iodine used; N = the normality of the iodine solution; v = milliliters of wine used. If the normality of the iodine is 0.02 N and 20 milliliters of wine are used, the formula becomes:

$$\text{Free } SO_2 \text{ (mg/l)} = 32 \text{ X ml of iodine used}$$

Most large wineries use the Ripper method to measure SO_2 in their white and blush wines, but they use the **aeration-oxidation** (AO) method to measure SO_2 in red wines. The Ripper method can yield significant errors when used with red wines because some of the iodine is consumed by

phenolic materials (pigments) in red wines. The errors can range from 5 to 20 ppm and the results are always too high (the measurement indicates more SO_2 than is really present). Even though the Ripper method produces large errors in red wines, most small producers avoid AO method because the measurement times are long and the equipment is fragile and expensive.

Modified Ripper

Here is a method that eliminates some of the problems when measuring free sulfur dioxide in red wines. It attempts to account for the iodine consumed by the phenolic materials in red wine.

When sulfur dioxide is added to wine, the gas reacts with water in the wine and forms sulfurous acid. Sulfurous acid ionizes producing a hydrogen ion and a bisulfite ion. Bisulfite can then ionize and produce an additional hydrogen ion and a sulfite ion.

$$SO_2 + H_2O \;<==========>\; H^{1+} + HSO_3^{1-}$$
$$HSO_3^{1-} \;<==========>\; H^{1+} + SO_3^{2-}$$

Please note that these are equilibrium equations and the reactions can go in both directions.

Sulfite ions can react with hydrogen peroxide and form sulfuric acid and water.

$$SO_3^{2-} + H_2O_2 \;==========>\; SO_4^{2-} + H_2O$$

This equation shows that sulfite plus hydrogen peroxide (H_2O_2) form sulfate plus water. Please note that this equation only progresses from left to right. (ie sulfate plus water does **not** produce hydrogen peroxide and sulfur dioxide).

The modified Ripper method is based on the above equation, and it assumes that hydrogen peroxide removes all of the free sulfur dioxide from the wine sample. It also assumes that the hydrogen sulfide does not interfere with any other measurement parameter. The modified method is used in the following way.

(1) Free sulfur dioxide is measured using the standard Ripper method.
(2) A second wine sample is treated with hydrogen peroxide and then measured using the standard Ripper method.
(3) The results from the second measurement is subtracted from the first measurement.

In other words, step (1) measures both the free sulfur dioxide plus the phenolic-iodine interaction. In step (2), the sulfur dioxide has been removed by the peroxide, so only the phenolic-iodine interaction is measured. Then step (3) removes the error caused by the phenolic-iodine interaction. Of course, the modified Ripper method is not perfect. But, it does provide reasonable accuracy and it is an easy, rapid way of measuring free sulfur dioxide in red wines.