PRINCIPLES OF WINE STABILIIZATION

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SULFUR DIOXIDE

History

Greeks and Romans knew about sulfur, but the main uses of this chemical were not a part of their grape growing and winemaking practices. In the 14th century, many differed in their opinion on the suitability and usefulness of sulfur.

Importance

1. Advantages: Sulfur dioxide in solution is unique, because it has both antimicrobial and antioxidative properties.

   a. As an antioxidant, sulfur dioxide protects musts and wines from browning by inhibiting enzymic and nonenzymic oxidation. Also, this chemical protects wines from oxidation by reducing the amount of available oxygen.

   b. The antiseptic activity of sulfur dioxide prevents microbial spoilage in wines. It is known that certain spoilage microorganisms such as acetic acid bacteria, lactic acid bacteria, molds, and wild yeasts are inhibited by sulfur dioxide.

   c. At certain levels, sulfur dioxide may promote a rapid and complete clarification of musts and wines.

2. Disadvantages: Although sulfur dioxide is necessary in preventing undesirable change in wines, excessive amounts may cause an incomplete fermentation, bleaching of color, and cause an objectionable, pungent odor.

Source

For a small winery operation, the most convenient method for adding sulfur dioxide is to treat musts and wines with potassium metabisulfite ($K_2S_2O_5$).

Chemistry

Since potassium metabisulfite ($K_2S_2O_5$) does not contain 100% sulfur dioxide (SO_2), it is essential to know the percentage of SO_2 in this salt.

1. Chemical reaction:

   $K_2S_2O_5 + H_2O \rightarrow 2\ KOH + 2\ SO_2$

2. Molecular weight:

   Atomic wt. of K = 40
   Atomic wt. of S = 32
   Atomic wt. of O = 16

   Molecular wt. of $K_2S_2O_5$ = 222
   Molecular wt. of SO_2 = 64 x 2 = 128

3. Percentage of SO_2 in $K_2S_2O_5$:

   $$\% \; SO_2 \text{ in } K_2S_2O_5 = \frac{128}{222} \times 100 = 58\%$$

   or

   1 gm of $K_2S_2O_5$ = 0.58 gm of SO_2

4. Conversion: grams of SO_2 to grams of $K_2S_2O_5$:

   $$\frac{1}{0.58} = \frac{\text{wt. of } K_2S_2O_5}{\text{wt. of } SO_2}$$

   $$\underline{1.72} = \frac{\text{wt. of } K_2S_2O_5}{\text{wt. of } SO_2}$$

   Wt. of $K_2S_2O_5$ = $\underline{1.72}$ x wt. of SO_2

pH

1. Importance: Acid levels, tartaric and malic acid, significantly influence must and wine pH. This factor is important to both color and keeping quality of wines. Problems with spoilage are likely to occur as pH values increase. Another reason for improved stability as the pH is lowered is the increased effectiveness of SO_2 as an antimicrobial agent.

2. Definition:

   a. pH refers to a numerical scale for expressing degrees of acidity or alkalinity.
   b. pH = - log [H^+ conc.]
   c. $H_2O \rightleftharpoons H^+ + OH^-$ (H^+ conc. = 10^{-7})

Reaction	gms. of H^+ per liter		Log	pH
acidic	.01	(10^{-2})	- 2	2
neutral	.0000001	(10^{-7})	- 7	7
alkaline	.0000000001	(10^{-10})	-10	10

Alcoholic Fermentation

1. Equation: For the alcoholic fermentation, the overall process can be represented by the following equation:

   1 glucose → 2 ethanol + 2 CO_2 + energy

2. By-Products: Although ethanol is the major product of this process, many minor constituents are also produced during alcoholic fermentation. In addition to their importance in wine quality (aroma and flavor), some have a high affinity to sulfur dioxide; thus, forming complexes.

Forms and pH Influence

1. Forms: When sulfur dioxide is added to musts and wines, the following reactions occur in equilibrium:

   $SO_2 + H_2O \rightleftharpoons H_2SO_3$ sulfurous (molecular)

   $H_2SO_3 \rightleftharpoons HSO_3^- + H^+$ bisulfite

   $HSO_3^- \rightleftharpoons SO_3^{=} + H^+$ sulfite

   All forms of SO_2 (molecular, bisulfite and sulfite) that are not chemically bound to other wine constituents are called “Free SO_2". The molecular form is almost entirely in the “Free” form. Furthermore, the “Free” unionized form (molecular) is the SO_2 form which prevents oxidation and spoilage.

   Those SO_2 forms that combine with other constituents are termed “Bound SO_2". “Total SO_2" refers to the amount of “Free” plus “Bound” SO_2.

2. pH Influence: The amount of each SO_2 form in musts and wines depends upon the pH

value. The following data indicate that as the pH decreases, the amount of molecular SO_2 increases (more antiseptic activity).

pH	%SO_2 (molecular)	% HSO_3^-	% $SO_3^=$
3.0	6.1	93.9	0.012
3.2	3.9	96.1	0.019
3.4	2.5	97.5	0.030
3.6	1.6	98.4	0.048
3.8	1.0	98.9	0.077

Weight and Volume

1. Weight:
   1 lb = 16 ozs = 454 gms

2. Volume:
   1 gal = 3.8 liters = 3790 ml

3. Measure:
   1 gal of wine = 8.2 lbs = 132 ozs = 3723 gms
   1 gal of wine = 3.8 liters = 3790 ml
   1 gal of juice (crushed grapes) = 9.0 lbs = 144 oz

Conversions

ppm	%	mg/L	Multiplication factor
100,000	10	100,000	.1
10,000	1	10,000	.01
100	.01	100	.0001
10	.001	10	.00001

Example: 100 ppm of 1000 gallons of wine

By Volume:
100 ppm = .01%
1000 gal x .0001 (factor) = .1 gallon = 380 ml

By Weight:
1000 gal x 8.2 lbs/gal = 8,200 lbs
8200 lbs x .0001 (factor) = .82 lbs x 454 g/gal = 372.3 gms

Dosage

1. Crushed Grapes: Condition of grapes, temperature, and pH are important factors in determining the amount of SO_2 to be added to the crushed grapes or musts. In general, sound grapes without spoilage, cool, and low pH require about 50 ppm SO_2.

   a. Estimate weight of crushed grapes (9.0 lbs per gallon).
   b. Determine the ppm of SO_2 to be added to the crushed grapes.
   c. Equation:

      Wt. of $K_2S_2O_5$ = Y x Z x 1.72
      Where: Y = weight of crushed grapes
      Z = multiplication factor of desired ppm SO_2
      1.72 = Conversion factor to change SO_2 to $K_2S_2O_5$

   d. Example: for a 50 ppm SO_2 treatment, calculate the weight of $K_2S_2O_5$ to be added to 2000 lbs (ton) of crushed grapes

      Wt. of $K_2S_2O_5$ = 2000 lbs (Y) x .00005 (Z) x 1.72
      = <u>.172 lbs</u> = <u>2.8 ozs</u>

2. Wine Storage: Immediately after alcoholic fermentation, the amount of free SO_2 is relatively low in the wines. Also during wine storage, SO_2 is constantly being lost due to such factors as oxidation and volatilization. Therefore, it is essential to treat wines with additional amounts of SO_2 at regular storage intervals. Under most conditions, maintaining 20 to 40 ppm of free SO_2 will protect wines against oxidation and spoilage.

   a. Estimate volume of wine in storage (3.8 liters per gallon).
   b. Determine the ppm (mg/liter) of SO_2 to be added to the wine.
   c. Equation:

      $$\text{Wt. of } K_2S_2O_5 = \frac{Y \times 3.8 \times 1.72 \times Z}{1000}$$

      Where: Y = Volume of wine in gallons
      3.8 = Conversion factor to change gallons to liters (L/gal)
      1.72 = Conversion factor to change SO_2 to $K_2S_2O_5$
      1000 = Conversion mg/L to gms/L

   d. Example: for a 20 ppm SO_2 treatment, calculate the weight of $K_2S_2O_5$ to be added to 500 gallons of wine.

      $$\text{Wt. of } K_2S_2O_5 = \frac{500 \times 3.8 \text{ L/gal} \times 1.72 \times 20 \text{ mg/L}}{1000}$$

      = 65.4 gms or .14 lbs or 2.3 ozs

3. Bottling: It is important to inhibit spoilage yeast and bacteria in the bottle. Therefore, winemakers always adjust the free SO_2 level of their wines at the time of bottling. In

general, a molecular SO_2 level of 0.8 ppm has been reported to be an acceptable concentration for most wines. The table below offers those free SO_2 levels to obtain 0.8 ppm molecular SO_2 at various pH values.

pH	Free SO_2 to obtain 0.8 ppm molecular SO_2	pH	Free SO_2 to to obtain 0.8 ppm molecular SO_2
2.9	11	3.5	40
3.0	13	3.6	50
3.1	16	3.7	63
3.2	21	3.8	79
3.3	26	3.9	99
3.4	32	4.0	125

Source: C. Smith, Enology Briefs, Feb/March, 1982, Univ. of Calif., Davis.

BATF Consideration

The finished wine shall contain not more than 350 ppm of total sulfur dioxide.