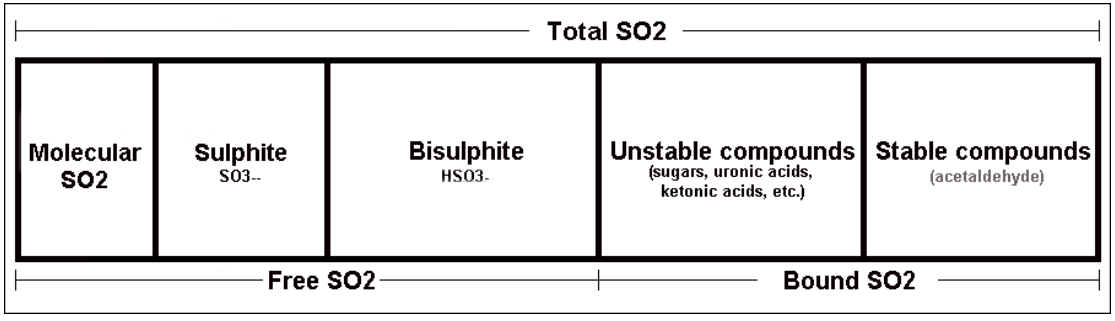
# Determination of Free Sulfur Dioxide Content by Rankine Aspiration followed by Titration

## Chemical Concepts and Techniques:

Sulfur dioxide is the most important preservative compound used in winemaking as well as for the preservation of other foods and beverages. It has been used in winemaking for millennia, and is effective due to its multi functional nature.
Free sulfur dioxide content monitoring is critical during wine storage and processing to ensure wines are adequately protected from chemical or microbiological storage.
In wine or fruit juice sulfur dioxide exists as either as 'bound' or 'free' sulfur dioxide dependent upon its relative availability take part in reactions:




Free Sulfur dioxide is further distributed across three different chemical species in equilibrium:

$$H_2O + SO_2 \leftrightarrows HSO_3^- + H^+ \leftrightarrows SO_3^{2-} + 2H^+$$

The equilibrium is pH dependant, with a shift to the left being observed under increasing acidity and a shift to the right on increasing alkalinity.

The presence of several different chemical forms of $SO_2$ in wine creates a conundrum for determining free $SO_2$ analytically. The simplest solution to this is to adjust the pH of the sample accordingly so that all the 'free' portion of SO2 exists as one species.

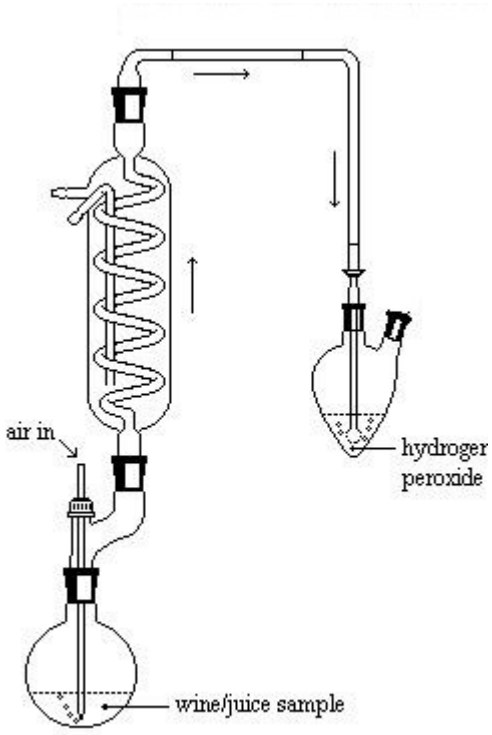
In the Rankine aspiration, this is achieved by acidifying the sample so that all SO2 is converted to the dissolved molecular form $SO_2(aq)$. Air or nitrogen is then bubbled through to displace the dissolved $SO_2$ and the gaseous molecules are swept into a hydrogen peroxide solution where they undergo stoichiometric oxidation as follows:

$$\mathbf{H_2O_2 + SO_2 \rightarrow SO_2 + H_2O \rightarrow H_2SO_4}$$

The sulfuric acid formed can then be titrated with weak sodium hydroxide to determine the free sulfur dioxide content of the wine.
Unlike the Ripper titration, this method has no significant interferences and is the method of choice in Australian wineries. (Note, however, under 'Points to Consider' that the method is more accurate for white wines than red wines due to sulphite-pigment interactions in red wines.)

## Equipment Required:

**Aspiration apparatus set up as in the picture below:**




**50mL or 100mL short neck Quickfit™ round bottom flask**
**Glass tubing or long Pasteur pipette**
**Quickfit™ swan neck adaptor** with screw-on thermometer holder
**Condenser** (type not critical)
**Adaptor joint** for top of condenser
**Plastic tubing** to connect condenser adaptor with ball joint adaptor
**Ball joint adaptor**
**Glass bubbler with socket joint**
**Ball and socket joint clamp** to hold ball joint adaptor and bubbler together

**50mL Quickfit™ two-neck Pear shaped flask**
**Aquarium air pump (or vacuum source)** to provide air-flow, with tubing to connect
**Retort stands and clamps** to support apparatus set up.

**10mL micro burette** (25mL burette can be substituted if necessary)
**20mL bulb pipette**
**20mL measuring cylinder**

## Reagent Preparation:

***0.3% w/v Hydrogen Peroxide ($H_2O_2$):*** *Pipette 10mL of 100 Volume (30% w/v, available commercially) Hydrogen Peroxide solution into a 1.0L volumetric flask. Dilute to volume with distilled water and mix well. Store in the refrigerator to prevent degradation.*
***Mixed Indicator:*** *Weigh 0.1g of methyl red sodium salt and 0.05g methylene blue into a beaker. Dissolve in a 50% ethanol:water mixture, and dilute to 100mL with the 50% ethanol: water mixture. Store in an amber glass eyedropper bottle. Note that this reagent is available commercially from wine chemical suppliers.*
***25% v/v (approx 18%w/v) Orthophosphoric acid:*** *Measure 294mL of concentrated (85% w/w) Orthophosphoric acid. Add slowly and carefully with stirring, to around 700mL cold distilled water. (Caution: some heat evolved). Store in a sealed bottle at room temperature.*
***0.01M Sodium Hydroxide:*** *Dilute 0.1M Sodium hydroxide tenfold. Store in plastic, keep bottles full if possible, preferably with a CO2 trap in line. Note that solution is only stable for around a week and should be standardised against standard 0.01M HCl prior to use.*

## Method:

***Procedure for the aspiration:***

1. Set up the aspiration apparatus as shown.
2. If possible, check the air flow rate, for best results it should be 1 litre/minute (it is not generally possible to check the air flow when using a pump, however the flow rate should be such that there is a constant stream if bubbles entering the solution in the round bottomed flask, but the aeration should not be excessively vigorous).
3. Remove the pear shaped flask with bubbler attached and add about 10mL of the 0.3% w/v hydrogen peroxide solution through the side neck.
4. Add 4 drops of the mixed indicator to the peroxide solution. The solution should turn purple. (if not, refer to ‘Points to Consider’ below)
5. Add 0.01M sodium hydroxide solution drop-wise until the peroxide solution turns green. Do not add any further NaOH once the colour has changed.
6. Reconnect the flask to the assembly.
7. Disconnect the round-bottomed flask and add accurately 20.0mL of the wine sample, using a pipette.
8. Add about 10mL of the 25% v/v Orthophosphoric acid solution to the wine and immediately reconnect the flask to the assembly.
9. Check all joints on the assembly for tightness.

10. Turn on the air pump or vacuum to commence the aspiration. Set the time for 15 minutes and start the timer.
11. The peroxide solution should turn from green to purple as the aspiration proceeds.
12. After 15 minutes, turn off the pump and remove the pear shaped flask with the bubbler in place.

***Procedure for the titration:***

1. Fill the burette with 0.01M sodium hydroxide solution.
2. Record the initial burette reading to at least 0.05mL accuracy.
3. Titrate the solution on the pear-shaped flask to the point where one drop of NaOH titrant causes the peroxide solution to turn green.
4. Record the final burette reading to at least 0.05mL accuracy.

***Calculation of Free $SO_2$ content:***

1. Calculate the difference between the final and the initial burette readings (Net Titre).
2. Calculate the free Sulfur dioxide content of the wine using the formula below

**Free SO2 (mg/L) = Net Titre (mL) x 16**

## Points to consider:

- Some commercial grades of 30% hydrogen peroxide are not naturally acidic. It is important that the 0.3% $H_2O_2$ solution is slightly acidic, and it may be necessary to add a small amount of acid to the bulk 0.3% $H_2O_2$ reagent after preparation, to ensure that it turns purple, not green, on addition of the indicator.
- When adjusting the pH of the peroxide solution with 0.01N NaOH in the pear-shaped flask, it is critical not to overshoot the point at which the colour of the solution changes, as this will affect the final result. The solution should be within one drop of 0.01M NaOH of the colour change from purple to green.
- Incorrect air flow rates can affect the accuracy of the result, particularly if too vigorous, as the $SO_2$ gas may not have time to react with the peroxide prior to escaping to the atmosphere. If the flow rate cannot be measured it may be necessary to run some trials with standard $SO_2$ solutions.
- Aspiration rate, length or aspiration and sample temperature all affect the result. The sample should be at 20ºC or lower to prevent dissociation of weakly bound $SO_2$. If room temperatures are high, consider placing an ice bath around the round bottomed flask during the aspiration.
- Ensure all seals are tight to prevent loss of $SO_2$ gas during the aspiration
- The titre in this method is generally only 1 – 3mL as typically levels of $SO_2$ in wine, so best results are usually obtained using a 10mL micro burette which allows drop wise addition of the titrant. However accurate results can be obtained using a 25mL burette with care.
- Be consistent in judging the indicator colour change at the endpoint of the titration. Always titrate to the same shade of green that was started with.

- Note when testing red wines that the $FSO_2$ result will be slightly overstated as the added strong acid will cleave sulphite-anthocyanin binding. There is no correction available for this error as free anthocyanin levels vary in red wines.

**References:**

Zoeckein, Fugelsang, Gump & Nury, *Production Wine Analysis*, Van Nostrand Reinhold, 1990

Iland, Ewart, Sitters, Markides & Bruer, *Techniques for chemical analysis and quality monitoring during winemaking*, Patrick Iland Wine Promotions, 2000

http://www.monashscientific.com.au/SO2.htm