Sulfur Dioxide

Sulfur dioxide in wine acts as an antioxidant and an inhibitor of microbial growth. Too little sulphur dioxide and the wine may suffer bacterial attack and may suffer from oxidation, thus affecting taste. Too much sulphur dioxide is evident to taste. In Australia the legal limit for the total sulphur dioxide level permitted is 250 mg/L.

When added to juice or wine most of the sulphur dioxide combines with aldehydes and ketones, (especially acetaldehyde or ethanal) and is not free to provide antimicrobial or antioxidative protection. The remainder of the sulphur dioxide, referred to as *free SO_2*, exists in solution as $SO\neq_{2\,(aq)}$, $HSO_3^-{}_{(aq)}$ or $SO_3^{2-}{}_{(aq)}$. The three forms are related by the equlibria,

$$SO_{2\,(aq)} + H_2O_{(l)} \longrightarrow H^+_{(aq)} + HSO_3^-{}_{(aq)} \longrightarrow 2\,H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$$

Most of the free sulphur dioxide exists in solution as the bisulfite ion, HSO_3^-. Clearly the pH of the juice/wine has a significant effect on the equlibria. At lower pH, i.e. more acid conditions more of the sulphur dioxide exists as $SO_{2\,(aq)}$, which is the form required for protection of the wine.

Experiments can be done to measure the amount of free sulphur dioxide, SO_2, HSO_3 and SO_3^{2-}, the bound SO_2 or the *total SO_2* depending on the method used.

Experiment 1 Determination of SO_2 by the Aspiration Method.

Note: This method is the industry standard and requires appropriate glassware. While “Quickfit” glassware is ideal, the apparatus can be fashioned from equipment more commonly found in school laboratories.

When a stream of air is passed through an acidified sample of juice or wine the free SO_2 is released. This is the passed through a hydrogen peroxide solution where the following reaction takes place

$$SO_{2\,(g)} + H_2O_{2\,(aq)} \longrightarrow H_2SO_{4\,(aq)}$$

The sulfuric acid formed is titrated with sodium hydroxide solution.

Part 1 Determination of *Free SO_2*

1. Set up the apparatus as shown in the photograph.
2. Fill a burette with 0.01 M NaOH solution.
3. To the side-arm test-tube add about 10 mL of 0.3% w/v hydrogen peroxide, H_2O_2, solution and 4 drops of the mixed indicator solution. Add 0.01 M NaOH from the burette to the solution in the test-tube until the solution turns a green colour which persists for 30 seconds.
4. Ensure that the end of the bubbler when inserted in the test-tube is clearly immersed in the solution in the flask.

5. Disconnect the round bottom flask and add about 10 mL of 25% v/v phosphoric acid, H_3PO_4, to the flask.
6. Pipette 20.0 mL of juice or wine into the round bottom flask. Reconnect the flask.
7. Turn on the air pump and aspirate the sample for 15 minutes. The flow rate of the air pump should be such that there is a steady stream of bubbles in the top flask, but this should not be excessively vigorous.
8. Turn off the air pump.
9. Record the initial burette reading.
10. Titrate the solution in the test-tube with 0.01 M NaOH to the olive green colour achieved before.
11. Record the final burette reading and calculate the volume of NaOH used.

Part 2 Determination of *Bound SO_2*

1. After completing the free SO_2 titration, empty the side-arm test-tube and prepare it again as described in step 3 of part 1.
2. Ensure that there is adequate airflow from the pump.
3. With the same round bottom flask and sample from part 1 in place ensure water is flowing through the condenser. Heat the round bottom flask to gently boiling with a small Bunsen burner and aspirate the solution for 15 minutes while gently boiling the solution.
4. Turn off the heat and the airflow from the pump and titrate the contents of the two-necked flask with NaOH, as before.
5. Record the final burette reading and calculate the volume of NaOH used.

Calculations and Questions

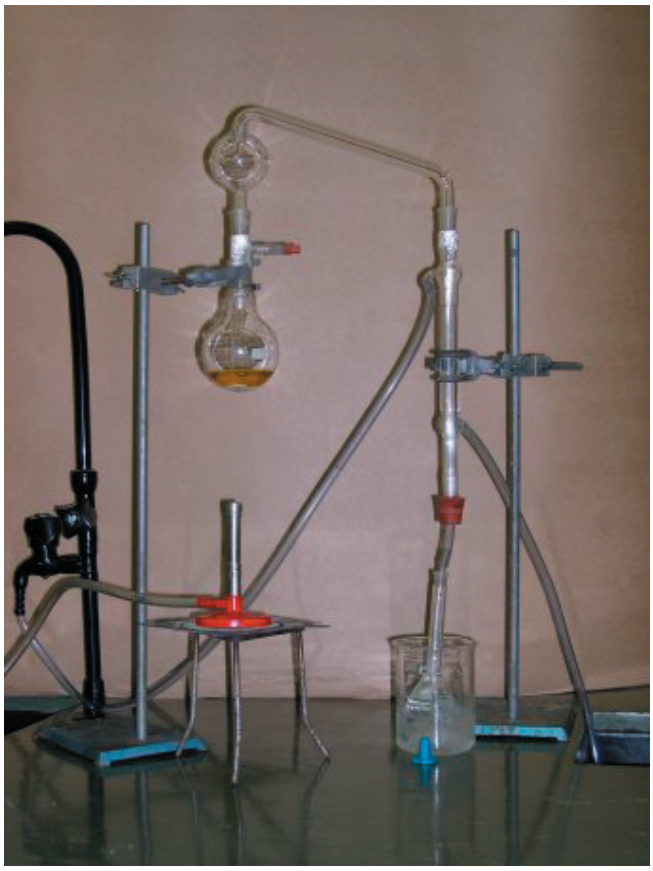
For Part 1

1. Write a balanced equation for the reaction between NaOH and H_2SO_4.
2. From the volume of NaOH used calculate the amount (in mol) used.
3. Calculate the amount of acid produced in the reaction between SO_2 and H_2O_2, hence determine the amount of SO_2.
4. Calculate the concentration of free SO_2 in the wine (in mol L^{-1}).
5. Express the concentration of free SO_2 in mg L^{-1}.

For Part 2

6. Using the same approach as in part 1 calculate the concentration of bound SO_2 .
7. What is the total SO_2 concentration? How does this compare with the legal limit?
8. To save repetitive calculations industry references quote a simple algorithm for calculating the SO_2 concentration (in mg L^{-1}). It is concentration = titre value x 16. Show how this algorithm can be derived.

Apparatus



The apparatus shown in the photograph is a combination of quickfit apparatus and other pieces fashioned to suit. A two-necked pear-shaped flask of the quickfit variety is available and is commonly used in industry. The apparatus photographed uses a side-arm test-tube in its place. This will suffice but is not as elegant and simple to use as the two-necked flask.

Distillation flask

Condenser

Bubbling apparatus
An aquarium pump was used. The flow rate needs to be about 1 litre of air per minute.

Glass and rubber delivery tubing

Clamp

Side-arm test tube or other suitable flask with inlet and outlet.

Burette

Reagents

Prepared accurately

0.01 M NaOH solution
N.B. the NaOH should be standardised by first titrating it against a suitable primary standard such as potassium acid phthalate However, standard 0.1 M HCl can be purchased and is used to standardise 0.1 M NaOH. Accurate dilution of the standardised 0.1 M solution will give the 0.01 M solution required.

Prepared approximately

0.3% v/v hydrogen peroxide solution

25% v/v phosphoric acid solution

methylene blue/methyl red mixed indicator solution

wine or juice

Experiment 2 Determination of SO_2 by the Ripper Method.

This method is based on the redox reaction that takes place when sulfur dioxide is reacted with iodine.
The reaction can be represented by the equation

$$SO_{2\,(aq)} + I_{2\,(aq)} + 2\,H_2O_{\,(l)} \longrightarrow 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\,I_{\,(aq)}$$

For *free* SO_2, the wine is acidified and titrated directly, whereas for *total* SO_2 first sodium hydroxide is added to the wine to break down complexes containing the bound SO_2 then it is acidified and titrated. The endpoint, shown by the reaction of iodine with starch, is difficult to observe accurately with red wines.

Part 1 Determination of *free* SO_2

1. Pipette 50.0 mL of wine into a 250 mL conical flask.
2. Add approximately 5 mL of 25% v/v sulfuric acid solution and 2 to 3 mL of starch solution.
3. Fill a burette with 0.01 M iodine solution. Record the initial burette reading.
4. Titrate the wine solution with iodine until the first appearance of a deep blue colour , which persists for about 1 minute.
5. Record the final burette reading and calculate the volume of iodine used.

Part 2 Determination of *total* SO_2

1. Pipette 20.0 mL of wine into a 250 mL conical flask.
2. Using a measuring cylinder, measure then add about 25 mL of 1 M NaOH solution to the wine.
3. Shake the flask to ensure thorough mixing then stopper the flask and leave the solution to stand for 15 minutes.
4. Add 10 mL of 25% v/v sulfuric acid and titrate with iodine solution as above.
5. From the initial and final burette readings calculate the volume of iodine used.

Calculations and Questions

For Part 1

1. From the volume of I_2 used calculate the amount (in mol) used.
2. Using the equation for the reaction calculate the amount of free SO_2.
3. Calculate the concentration of free SO_2 in the wine (in mol L^{-1}).
4. Express the concentration of free SO_2 in mg L^{-1}.

For Part 2

5. Using the same approach as in part 1 calculate the concentration of total SO_2 .
6. What is the bound SO_2 concentration?
7. How does the total SO_2 concentration compare with the legal limit?
8. If the same wine is analysed using the aspiration method different answers are obtained. Suggest some reasons for the difference.
9. To save repetitive calculations industry references quote simple algorithms for calculating the free and total SO_2 concentration (in mg L^{-1}).

   They are Free SO_2 concentration = titre value x 12.8

   Total SO_2 concentration = titre value x 32

   Show how these algorithms can be derived.

Apparatus

250 mL conical flasks

stoppers to suit flasks

burette

20.0 and 50.0 mL volumetric pipettes

Reagents

Prepared accurately

0.01 M I_2 solution

Accuracy not essential

25% v/v H_2SO_4 solution

0.2% w/v starch solution

1 M NaOH solution

wine or juice