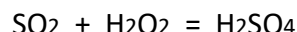


Aeration Oxidation Method of Determining Free Sulphur Dioxide in Wine

By Clem Joyce, Sept 2020

Let's have a quick look at the process and the theory behind it.

The process involves taking a sample of wine that supposedly has an amount of sulphur dioxide in solution; acidulating it to allow all the free SO₂ to be released. Air is then bubbled through the wine sample carrying the SO₂ gas over to a solution of hydrogen peroxide that traps the gas forming a sulphuric acid solution. The reaction formula looks like this:



The hydrogen peroxide solution has a colour indicator in it that turns purple when in an acidic state and Kelly green when in an alkaline state. Before the test procedure the hydrogen peroxide solution has been neutralized to a denim/teal colour, in between purple and green. The final titration of the hydrogen peroxide is done with a weak solution of sodium hydroxide (.01N). The amount of sodium hydroxide used is multiplied by 16 to give the free sulphite level of the wine in parts per million (ppm)

This method gives an accurate, easily read colour transition end point, unlike other methods.

The equipment needed.

The commercially available flasks currently cost over \$175, but they are not necessary. Here's an alternative.

- You will need a small aquarium air pump capable of about 1000cc air flow per minute. Most are. They cost about \$15.
- Also required are two preferably glass vessels approximately 100 mls volume, about one inch wide and 4-5 inches tall. I have found the caper jar, 100mls size to be perfect. Mark one **W** for wine and one **P** for peroxide
- You need two #6.5 rubber carboy bungs, they fit perfectly in the top. If you get the bung with the hole, you will need to seal the hole with the tubing going through it with a silicone sealer. If you can accurately drill a hole through a solid rubber bung, that will work too, but bung for flask **W** must seal perfectly.
- You will also need about 4-5 feet of 1/8th plastic flexible vinyl tubing available at your local hardware store. Cost is less than \$2. The tubing will undoubtedly be tightly coiled and need to be straightened. Place entire tubing in near boiling water for a few moments then lay flat to cool ensuring it stays straight. Cut a length off at 16-18 inches. The longest length will connect to the air pump and go through the bung marked **W**, to the bottom of the flask. The short length will also go through the bung marked **W**, but only about one inch maximum. This bung now needs to be sealed completely with a silicone sealant. The other end of the short length will go through the bung marked **P** to the bottom of the flask. It should be secured so it will stay at the bottom. This flask and bung also needs to be able to vent air out.
- I find the flasks somewhat unstable so placing each in short jar, ensures they do not tip over.
- Once you have your equipment prepared you can organize your chemicals.

Chemicals you will need.

1. Sodium Hydroxide solution

- Provided is a bottle of standardized 1N concentration sodium hydroxide. This will do 3000 tests, more than you will need in the near future, but it will gradually deteriorate and need to be replaced after a few years, which I will do.
- This strength of sodium hydroxide needs to be diluted to strength of .01N and made fresh periodically. Carefully fill your 1 ml syringe with 1N NaOH and put into your prepared bottle marked **.01N Sodium Hydroxide**. With a 50 ml syringe and accurately put a **total of 99mls** of steamed distilled water into your bottle. Only use stemmed distilled water for your water additions. Mix well. **You now have 100mls** of the strength you need. You can make it up fresh when you have used about 75mls of it, or about every 3 months. Keep this bottle well sealed. You can do duplicate tests with old and new to see how much if any, it has deteriorated.

2. Bottle of Colour Indicator for A/O test (Methylene Blue/ Methyl Red)

3. Hydrogen Peroxide solution.

- Hydrogen Peroxide is available in different concentrations: 30% from some suppliers as well as the common 3% (labeled 10 Volume) available from the drugstore. Both contain preservatives and when diluted, re-act exactly the same and give the same results.
- Take 3% drugstore hydrogen peroxide solution and make a 1% solution by diluting 1 part peroxide with 2 parts distilled water. Only use stemmed distilled water for your water additions. You can use a graduated cylinder or a syringe to measure your proportions. Place this in an appropriate marked bottle **1 % Hydrogen Peroxide**, with lid. If you have some left over, it keeps well for next time.
- You will use 10mls of this 1% solution per test so make enough for all the tests you will do short term. I keep my 10 ml syringe in my bottle of prepared 1% peroxide. Keep your syringes separate and marked so you don't cross contaminate anything.
- Once you have your 1% peroxide solution prepared, add a few drops of the Methylene Blue/ Methyl Red colour indicator solution. About 3-4 drops per 50 mls of peroxide solution. The solution will turn purple. This indicates the peroxide is slightly acid. The more drops you add, the darker the solution will get. It does not need to be very dark to see the colour change. You will get used to seeing the best colour that suites you.
- Now take your **.01N solution** of sodium hydroxide and draw up about 1ml into your 3ml syringe. Add this, a drop at a time to the 1% Peroxide purple solution mixing well between drops **until** the colour changed to a denim/teal colour, lacking any purple hue. You will see the colour gradually change. This is your neutral point
When you do your final titration of the test, this will be the sample colour you will want to come back to.
Adding more drops of the sodium hydroxide will cause the colour to change to green which is too far.

4. Phosphoric Acid, a 25% concentration.

An alternative acid is **Nitric Acid**. Add 40 mls of concentrated Nitric Acid to 1 litre of distilled water and mix well. The pH of the wine sample when the acid is added should be about pH 1.0 . You can test this with your pH meter after doing the A/O test.

You are now ready to do some tests.

The Aeration / Oxidation Test

In this order.

- Place 10 mls of the 1% hydrogen peroxide solution with the corrected colour into the flask marked **P**. Place the tubing and bung into the flask ensuring the tubing goes to the bottom.
- Take a 20 ml syringe of your wine sample and carefully add to flask marked **W**. **Do not aerate** when putting in. Take a 10 ml syringe of 25% Phosphoric or Nitric Acid and add to flask **W** with the wine. **Do not aerate**. Immediately place the tube and bung into flask **W** to ensure it is sealed.
- Record your time and turn on the air pump. Bubble air for 10 minutes. Ensure bubbles are coming only about half way up the flasks. Reduce air flow slightly if necessary. Within a few moments the colour should start to change to a purple colour. If it does not change to purple, there is no Sulphur Dioxide in the wine sample being tested.
- After 10 minutes, with the air still bubbling, remove the rubber bung and tube from flask **P**, so no solution stays in the tube. Now, turn off air pump.
- From your bottle of .01N NaOH, carefully fill your 3ml syringe with 3mls.
- Take your flask **P**, that is now a purple colour and slowly add the .01N NaOH until the colour changes back to the original denim/teal colour.
- Record the amount of .01N NaOH used and multiply by 16.
- This gives you the free sulphur dioxide level in your wine sample.
- If you were curious as to whether you removed all of the SO₂ out of the wine sample, you could put the flask **P** back in place with bung and tube, and bubble for another few minutes. If it doesn't change to a purple colour after 2-3 minutes, you know.
- Discard the contents of flask **W** and **P**, rinse well, remove excess water for next test.
- If you wanted to confirm that your wine and acid sample in flask **W** was acidified properly, you could test that sample with your pH meter before discarding. It should have a pH of about 1.0 or lower.