SCHNEYDER & VLCEK
MODIFIED RIPPER TITRAMETRIC DETERMINATION OF SULFUR DIOXIDE

In the traditional Ripper procedure, standard iodine solution is used to titrate free sulfur dioxide (and, with additional steps, total sulfur dioxide as well). This is a well established and popular quick method to determine free and total SO_2 in wines or musts.

The Ripper procedure involves an inherent limitation in relying on a standard iodine solution for the titration. Iodine solutions oxidize appreciably over short periods of time, and so must be checked regularly and restandardized as required with standard sodium thiosulfate. This may be required biweekly or even more frequently, and is both inconvenient and time-consuming. In the modified procedure presented here, potassium iodate, a strong but stable oxidizing agent, is utilized in place of an iodine solution. In the presence of an excess of iodide and acid in the system employed, iodine is produced during the titration:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$
iodate iodide acid iodine water

As long as SO_2 is present, the iodine is immediately reduced to colorless iodide ion. The titration reaction is totally equivalent to that of Ripper's SO_2 determination, and proceeds to an intense blue-purple starch-iodine end point upon subsequent elimination of any SO_2 present.

EQUIPMENT

1. 250 ml Erlenmeyer flask (with proper size rubber stopper if doing total SO_2)
2. 10 ml burette
3. 25 ml volumetric pipette (suggest wide tipped for faster delivery, less plugging)
4. High intensity light source
5. Magnetic stirrer and bar

REAGENTS

1. Potassium iodate standard solution (0.01N): In a 1L volumetric flask, dissolve 356.7 mg (0.3567 gm) of *dried* (24 hrs @ 110°C) reagent grade potassium iodate in approximately 800 ml distilled or de-ionized (d / d) water. Add 50 ml of 1+3 sulfuric acid with mixing and dilute to volume with same.
2. Potassium iodide-starch solution: In a 1L volumetric flask, dissolve 10 grams soluble reagent grade starch in approximately 800 ml d / d water. Heat as necessary (140-200°F) for the solution to give an intense blue-purple color in the presence of free iodine; confirm before proceeding. Cool solution to room temperature, then add and dissolve 10 grams of potassium iodide. Bring to volume with d / d water.
3. Sulfuric acid (1+2): Very carefully and slowly add one volume concentrated acid to two volumes d / d (refrigerated if possible) water. Use heat resistant (borosilicate or similar) glass for mixing container.
4. Sulfuric acid (1+3): Very carefully and slowly add one volume concentrated acid to three volumes d / d (refrigerated if possible) water. Use heat resistant (borosilicate or similar) glass for mixing container.
5. Sodium hydroxide (1N): In a 1-L volumetric flask, dissolve 40 grams reagent grade sodium hydroxide in approximately 800 ml d / d water. Bring to volume with additional d / d water.
6. Sodium bicarbonate.

PROCEDURE: FREE SULFUR DIOXIDE

1. Volumetrically transfer 25 ml of wine or must to a clean 250 ml Erlenmeyer flask. (Note: if working with red wines, these may be diluted as required with d/d water to give lighter solutions. But, always start with a full 25 ml of straight wine in the flask, and then dilute as required. This may take 100+ ml of d/d water to give a readable endpoint; experience will quickly determine amount required. No dilution water is required for white, rosé or blush wines).
2. Add approximately 5 ml (amount NOT critical) iodide-starch and a pinch of bicarbonate.
3. Add approximately 5 ml 1+2 sulfuric acid.
4. Using a 10 ml burette, *rapidly* titrate with standard iodate solution to a blue/purple end point that is stable for a minimum of 20 seconds. A high intensity light source behind the sample is useful for end point detection in red wines. The use of a magnetic stirrer with stirrer bar adds convenience for all titrations.
5. Calculate the free SO_2 concentration (in mg/L):

$$SO_2 = \frac{(\text{ml iodate})(N \text{ iodate})(32)(1000)}{\text{ml wine sample}}$$

PROCEDURE: TOTAL SULFUR DIOXIDE

1. Volumetrically transfer 25 ml of wine sample to a clean 250 ml Erlenmeyer flask. (See remarks in Section 1. above if working with red wines).
2. Add 25 ml of 1N sodium hydroxide, swirl, and stopper. Allow 10 minutes for hydrolysis reactions to occur.
3. Add approximately 5 ml (amount NOT critical) iodide-starch solution and a pinch of bicarbonate.
4. Add approximately 10 ml of 1+3 sulfuric acid.
5. Using a 10 ml burette, *rapidly* titrate with standard iodate solution to a blue/purple end point that is stable for a minimum of 20 seconds. A magnetic stirrer with stirrer bar adds convenience for all titrations, and a high intensity light source behind the sample is useful for end point detection in red wines.
6. Calculate the free SO_2 concentration (in mg/L) using the same formula as above.

NOTE:
In the above procedures, it is intended that titrations be carried out promptly after acidification (addition of sulfuric acid). Due to complex reactions taking place within the acidified wine, titration delays will tend to give increasingly high results for red wines and inconsistent results for white wines. Titrations should be completed ideally within 1-2 minutes of acidification, though 3-4 minute periods should still be acceptable.

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8/04 (revised 4/05)

Questions or comments may be directed to the author. Consult the WVAVS membership list for contact information.