Method OIV-MA-AS323-04A Type II method

Sulfur dioxide

(Resolution Oeno 377/2009)

1. Definitions

Free sulfur dioxide is defined as the sulfur dioxide present in the must or wine in the following forms: H_2SO_3, HSO_3^-, whose equilibrium as a function of pH and temperature is:

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

H_2SO_3 represents molecular sulfur dioxide.

Total sulfur dioxide is defined as the total of all the various forms of sulfur dioxide present in the wine, either in the free state or combined with their constituents.

2. Free and Total Sulfur Dioxide

2.1 *Principle*

Free sulfur dioxide is carried over by a stream of air or nitrogen and is fixed and oxidized by bubbling through a dilute and neutral solution of hydrogen peroxide. The sulfuric acid formed is determined by titration with a standard solution of sodium hydroxide. Free sulfur dioxide is purged from the wine by entrainment at low temperature (10 °C).

Total sulfur dioxide is purged from the wine by entrainment at high temperature (approximately 100 °C).

2.2 *Method*

2.2.1 *Apparatus*

The apparatus to be used should conform to the diagram overleaf, especially with regard to the condenser (see Fig 1).

The gas supply tube to the bubbler B ends in a small sphere of 1 cm diameter with 20 holes 0.2 mm in diameter around its largest horizontal circumference. Alternatively, this tube may end in a sintered glass plate that produces a large number of very small bubbles and thus ensures good contact between the liquid and gaseous phases.

The gas flow through the apparatus should be approximately 40 L/h. The bottle situated on the right of the apparatus is intended to restrict the pressure reduction produced by the water pump to 20 – 30 cm water. In order to regulate the flow rate, a flow meter with a semi-capillary tube should be installed between the bubbler and the bottle.

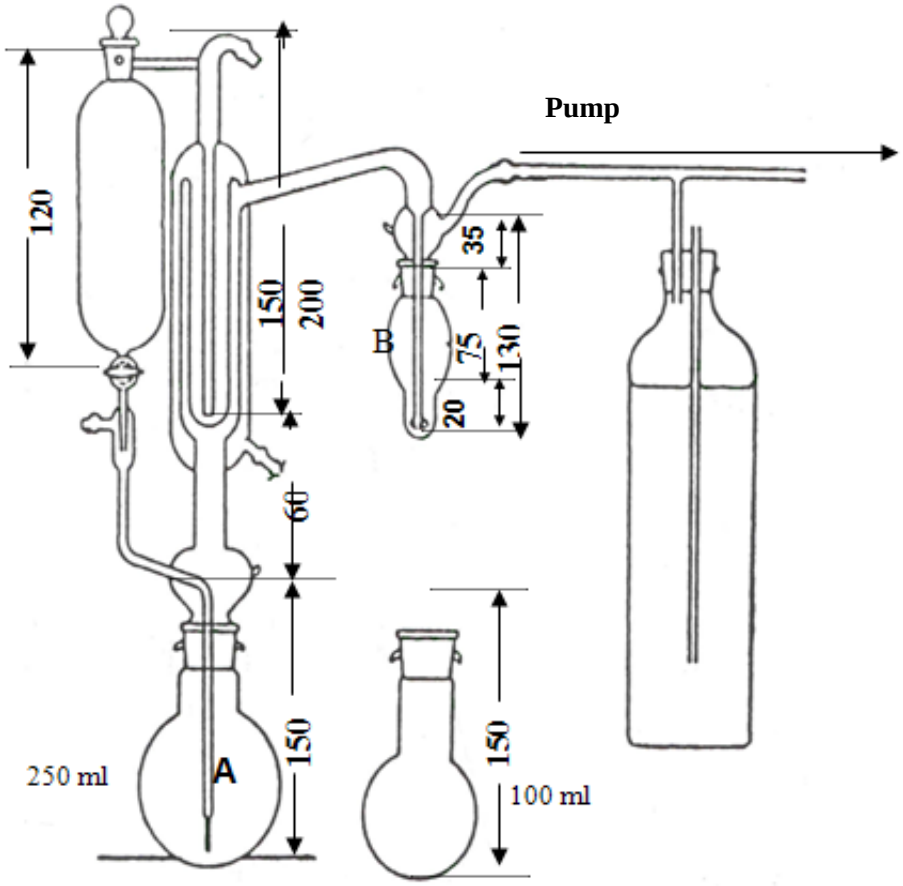

FIGURE 1: The dimensions are given in millimeters. The internal diameters of the 4 concentric tubes making up the condenser are: 45, 34, 27 and 10 mm.

2.2.2 *Reagents*

2.2.2.1 Phosphoric acid: phosphoric acid 85% (ρ_{20} =1.71 g/mL),

2.2.2.2 Hydrogen peroxide solution, 9.1 g H_2O_2/L (3 volumes)

2.2.2.3 Indicator reagent:

Methyl Red ..... 100 mg
Methylene Blue ..... 50 mg
Ethanol 50% (*v/v*) ..... 100 mL

2.2.2.4 0.01 M Sodium hydroxide solution

2.2.3 *Determination of free sulfur dioxide content.*
The wine must be maintained at 20°C in a full and stoppered flask for 2 days before determination.

2.2.3.1 Procedure
- Place 50 mL of the sample and 15 mL of phosphoric acid (2.2.2.1) into the 250 mL flask (A) of the entrainment apparatus. Connect the flask into the apparatus.
- In the bubbler (B), place 2 or 3 mL of hydrogen peroxide solution (2.2.2.2), two drops of the indicator reagent (2.2.2.3) and neutralize the hydrogen peroxide solution with the 0.01 M sodium hydroxide solution. (2.2.2.4) Connect the bubbler to the apparatus.

Bubble air (or nitrogen) through the apparatus for 15 minutes. Free sulfur dioxide carried over is oxidized to sulfuric acid. Remove the bubbler from the apparatus and titrate the acid which has formed with the 0.01 M sodium hydroxide solution (2.2.2.4).
Let *n* mL be the volume used.

2.2.3.2 Expression of results
The liberated sulfur dioxide is expressed in mg/L to the nearest whole number.
2.2.3.2.1 Calculation
If *n* is the number of mL of 0.01 M sodium hydroxide solution, used, the amount of free sulfur dioxide in milligrams per liter is given by: 6.4 *n*

2.2.4 Determination of total sulfur dioxide content.
2.2.4.1 Procedure
• Samples having a SO_2 content ≤50 mg/L of total SO_2:
Place 50 mL of the sample and 15 mL of phosphoric acid (2.2.2.1) into the 250 mL round-bottom vacuum flask (A). Connect the flask to the apparatus.
Remark: In the case of must, proceed with the method of operation described in the 1978 edition of the Compendium (see page 367).
• Samples with a content ≥ 50 mg/L of total SO_2:
Place 20 mL of the sample and 5 mL phosphoric acid (2.2.2.1) into the 250 mL round-bottom vacuum flask A. Connect the flask to the apparatus.
Place in the bubbler B, 2 or 3 mL of the hydrogen peroxide solution (2.2.2.2), neutralized as before, and bring the wine in the flask A to a boil using a small flame of 4 or 5 cm height which should directly touch the bottom of the flask. Do not place the flask on a metal cloth, but on a mantle with a hole 30 mm in

diameter in it. This is to avoid overheating substances extracted from the wine that are deposited on the walls of the flask.
Maintain boiling while passing a current of air (or nitrogen). Within 15 minutes the total sulfur dioxide is carried over and oxidized. Determine the sulfuric acid formed by titration with 0.01 M sodium hydroxide solution. (2.2.2.4).
Let *n* be the volume used.

2.2.4.2 Expression of results.

2.2.4.2.1 Calculation

Total sulfur dioxide in milligrams per liter:

- Samples low in sulfur dioxide (50 mL test sample): $6.4 \cdot n$
- Other samples (20 mL test sample): $16 \cdot n$

2.2.4.3 Repeatability (r):

(< 50 mg/L) 50 mL test sample, r = 1 mg/L
(> 50 mg/L) 20 mL test sample, r = 6 mg/L

2.2.4.4 Reproducibility (R):

(< 50 mg/L) 50 mL test sample, R = 9 mg/L
(> 50 mg/L) 20 mL test sample, R = 15 mg/L

BIBLIOGRAPHY

Reference method
PAUL F., *Mitt. Klosterneuburg, Rebe u. Wein,* 1958, ser. A, 821.