# OIV-MA-F1-07 Sulphur dioxide

**Type IV method**

## 1. Definitions

Free sulphur dioxide is defined as the sulphur dioxide present in the must in the following forms: $H_2SO_3$, $HSO_3^-$

The equilibrium between these forms is a function of pH and temperature:

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

$H_2SO_3$ represents molecular sulphur dioxide.

Total sulphur dioxide is defined as the total of all the various forms of sulphur dioxide present in the must, either in the free state or combined with its constituents.

## 2. Materials

Total sulphur dioxide is extracted from the previously diluted rectified concentrated must by entrainment at high temperature (approximately 100 °C).

2.1. Reagents

2.1.1. Phosphoric acid, 85 % ($H_3PO_4$) ($\rho_{20}$ = 1.71 g/ml).

2.1.2. Hydrogen peroxide solution, 9.1 g $H_2O_2$/litre (three volumes).

2.1.3. Indicator reagent:

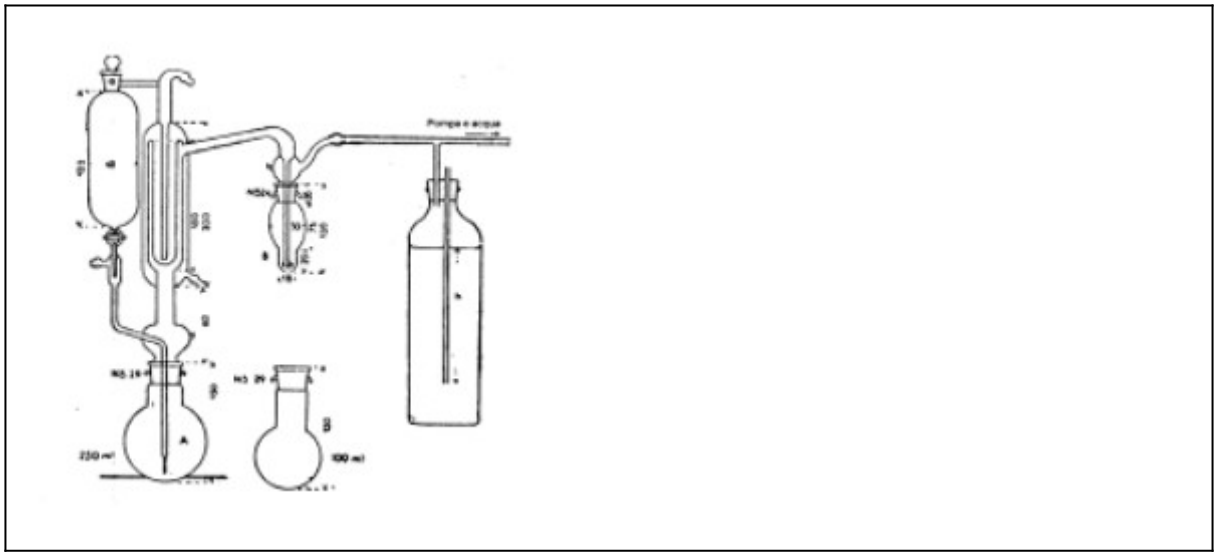
| | |
|---|---|
| methyl red | 100 mg |
| methylene blue | 50 mg |
| alcohol 50 % vol | 100 ml |

2.1.4. Sodium hydroxide solution (NaOH), 0.01 M.

2.2. Apparatus

2.2.1. The apparatus used should conform to the diagram shown below, particularly with regard to the condenser.

Fig. 1 The dimensions given are in millimetres. The internal diameters of the four concentric tubes forming the condenser are 45, 34, 27 and 10 mm.



The gas feed tube to the bubbler B ends in a small sphere of 1 cm diameter with 20 0.2-mm diameter holes around its largest horizontal circumference. Alternatively, this tube may end in a frit glass plate which 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 litres per hour. The bottle on the right of the diagram is intended to restrict the pressure reduction produced by the water pump to 20 to 30 cm of water. To regulate the vacuum to its correct value, a flowmeter with a semi-capillary tube should be installed between the bubbler and the bottle.

2.2.2. A microburette.

3. P**rocedur**e

1. For rectified concentrated musts, use the solution obtained by diluting the sample to be analysed to 40 % (m/v) as indicated in the chapter 'Total acidity', section 5.1. Introduce 50 ml of this solution and 5 ml of phosphoric acid (2.2.1) into the 250 ml flask A of the entrainment apparatus. Connect the flask to the apparatus.
2. Place 2 to 3 ml of hydrogen peroxide solution (2.2.2) in the bubbler B, neutralize with the 0.01 M sodium hydroxide solution (2.2.4) and bring the must in the flask A to the boil using a small flame of 4 to 5 cm height which should directly touch the bottom of the flask. Do not put the flask on a metal plate but on a disc with a hole of approximately 30 mm diameter in it. This is to avoid overheating substances extracted from the sample that are deposited on the walls of the flask.

Maintain boiling while passing a current of air (or nitrogen). Within 15 minutes the

total sulphur dioxide has been carried over and oxidized. Determine the sulphuric acid which has formed by titration with the 0.01 M sodium hydroxide solution (2.2.4).
Let n ml be the volume used.

4. C**alculation**

Total sulphur dioxide in milligrams per kilogram of total sugars (50 ml prepared test sample (3.1):

$$(1600 \times n)/P$$

(where P = percentage concentration (m/m) of total sugars

**5. Expression of results**

Total sulphur dioxide is expressed in mg/kg of total sugars.

**6. Characteristics of the method**

Repeatability (r)

- 50 ml test sample < 50 mg/l; r = 1 x 250/P mg/kg of total sugars

Reproducibility (R)

- 50 ml test sample < 50 mg/l; R = 9 x 250/P mg/kg of total sugars