RESOLUTION OIV-OENO 591B-2018

TOTAL SULPHUR DIOXIDE – UPDATE TO METHOD OIV-MA-AS323-04A

WARNING: this resolution amends the following method:
- *OIV-MA-AS323-04A*

THE GENERAL ASSEMBLY,

IN VIEW OF Article 2, paragraph 2 iv of the Agreement of 3 April 2001 establishing the International Organisation of Vine and Wine,

AT THE PROPOSAL OF the "Methods of Analysis" Sub-Commission,

CONSIDERING the work carried out by the "Methods of Analysis" Sub-Commission on the revision of methods of analysis, and particularly the results of the questionnaire launched by the "Methods of Analysis" Sub-Commission in 2009 with the aim of collecting information on the application of OIV methods by laboratories responsible for the analysis of wine and musts,

DECIDES to modify and replace Method OIV-MA-AS323-04A in the Compendium of International Methods of Wine and Must Analysis, and to separate it into two different methods: the determination of free sulphur dioxide and the determination of total sulphur dioxide. The method for the determination of total sulphur dioxide is modified as follows:

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Type II method

1. Scope

This method is for the determination of total sulphur dioxide in wine and must.

2. Definitions

Total sulphur dioxide is defined as the sum of all of the different forms of sulphur

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dioxide present in the wine in free form or bound to the wine's constituents.

3. Principle

Sulphur dioxide is aspirated by a current of air or nitrogen, and is captured and oxidised by bubbling through a dilute and neutral solution of hydrogen peroxide. The sulphuric acid formed is determined by titration with a standard solution of sodium hydroxide.

The total sulphur dioxide is extracted from the wine by aspiration at high temperature (around 100 °C).

4. Reagents and products

4.1. Pure phosphoric acid at 85% (ρ_{20} = 1.71 g/mL) (CAS no. 7664-38-2)

4.2. Indicator reagent:

Methyl red (CAS no. 493-52-7)	100 mg (±1 mg)
Methylene blue (CAS no. 7220-79-3)	50 mg (±0.5 mg)
Ethanol (≥ 95%) (CAS no. 64-17-5)	50 mL

Make up to 100 mL with water for analytical use. Respect the proportions for the volumes that differ from 100 mL.

Commercial indicator reagents with the same composition may be used.

4.3. 1 M Sodium hydroxide (3.84%) or in anhydrous form (pellets) (CAS no. 1310-73-2)

4.4. 0.01 M Sodium hydroxide solution:

By way of example: Dilute 10.0 mL of 1 M sodium hydroxide (4.4) in 1 L of water for analytical use.

If necessary, check the titre of the solution regularly (correction factor to be applied) and keep it away from atmospheric CO_2.

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4.5. Hydrogen peroxide solution in 3 volumes (= 9.1 g/L = 0.27 mol/L H_2O_2), prepared or commercial (e.g. 30% H_2O_2: mixture with CAS no. 7722-84-1)

Note: A solution of 30% by mass corresponds to a titre of 110 volumes ($\rho_{20} \cong$ ▫ 1,11 g/mL), implying the volume of oxygen ideally released per litre of H_2O_2 under standard conditions of temperature and pressure, while a solution of 3% by mass ($\rho_{20} \cong 1$ g/mL) corresponds to a titre of 10 volumes (0.89 mol/L). The preparation thus depends on the commercial solution used, considering that in any case the volume used in the method will be in excess.

5. Apparatus

The apparatus to be used should conform to the diagram below, especially with regard to the condenser.

The gas supply tube to bubbler B ends in a small sphere of 1 cm in diameter with 20 holes of 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.

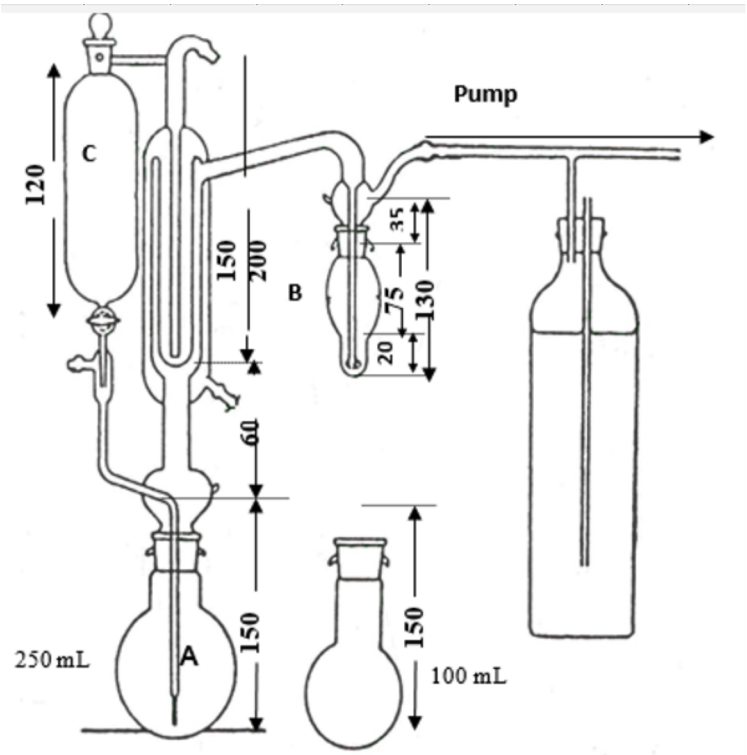
The gas flow through the apparatus should be approximately 40 L/h. The bottle situated on the right of the apparatus is intended to restrict the pressure reduction produced by the water pump to 20-30 cm water. In order to regulate the pressure reduction to achieve the proper flow rate, it is preferable to install a flow meter with a semi-capillary tube between the bubbler and the bottle. For the determination of total sulphur dioxide, using a burner (with a 4-5 cm high flame or infrared) allowing for boiling point to be reached very quickly is preferable. Do not place a wire gauze under flask A, but rather a deflector with a 2-4 cm orifice. The pyrogenation of non-volatile matter in the wine on the flask walls is thus avoided.

Use a 250-mL flask for a 50 mL sample and a 100-150 mL flask for a 20 mL sample.

Figure 1 – The dimensions are indicated in millimetres. The internal diameters of the 4 concentric tubes that make up the condense are 45, 34, 27 and 10 mm.

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6. Procedure

Air- or nitrogen-rinsing the apparatus before each new determination (e.g. for 5 minutes) is recommended. If a blank test is carried out, the colour of the indicator in the neutralised hydrogen peroxide solution at the exit of the gas-supply tube should not change.

- Connect the water from the condenser.
- In bubbler B of the entrainment apparatus, introduce 2-3 mL hydrogen peroxide solution (4.5) and 2 drops of indicator reagent (4.2), and neutralise with the 0.01 M sodium hydroxide solution (4.4); a neutral pH = green colour.

Note: For large sample series, it is also possible to prepare an already neutralised H_2O_2 solution before introducing it into the flask. Adapt the concentrations and volumes accordingly, bearing in mind that the oxidative power of the solution must be maintained (reduced shelf life).

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- Adapt this bubbler to the apparatus.
- Transfer 50 mL of sample to flask A if the presumed total SO_2 content in the sample is < 50 mg/L, and 20 mL of sample if the presumed total SO_2 content is ≤ 50 mg/L and attach it to the apparatus.
- Introduce 15 mL of phosphoric acid (4.1) into bulb C if the presumed total SO_2 content of the sample is < 50 mg/L and 5 mL phosphoric acid (4.1) if the presumed total SO2 content of the sample is ≥ 50 mg/L.
- Open the tap to add the acid to the sample and activate the heat source, while simultaneously starting the gas flow and setting the timer to 15 minutes. Maintain at boiling point for the duration of the gas flow. The entrained total sulphur dioxide is oxidised into sulphuric acid.
- After 15 minutes, turn off the heat source, take bubbler B out, and rinse the gas supply tube (via the socket) with water.
- Titrate the acid formed by the 0.01 M sodium hydroxide solution (4.4) up to the green bend.

The number of millilitres used is expressed by n.

7. Calculations and expression of results

The total sulphur dioxide is expressed in milligrams per litre (mg/L), in whole numbers.

Calculations:

- Samples low in sulphur dioxide (50 mL sampling): 6.4 n
- Other samples (20 mL sampling): 16 n

8. Precision

8.1. Repeatability (r)

Content < 50 mg/L (50 mL sampling), r = 1 mg/L

Content ≥ 50 mg/L (20 mL sampling), r = 6 mg/L

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8.2. Reproducibility (R)

Content < 50 mg/L (50 mL sampling), R = 9 mg/L
Content ≥ 50 mg/L (20 mL sampling), R = 15 mg/L

9. Bibliography

1. Paul, F., Mitt. Klosterneuburg, Rebe u. Wein, 1958, ser. A, 821.

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