RESOLUTION OIV-OENO 591A-2018

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

WARNING: this resolution repeals the following method:
- *OIV-MA-AS323-05*

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 remove Method OIV-MA-AS323-05 from the Compendium of International Methods of Wine and Must Analysis, given that there is no longer reason to distinguish the specific case of grape juice,

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 free sulphur dioxide is modified as follows:

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

Type IV Method

1. Scope

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

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018

2. Definitions

Free sulphur dioxide is defined as the sulphur dioxide present in the must or wine in the following forms: H_2SO_3 and HSO_3^-, whose equilibrium is dependent on pH and temperature:

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

H_2SO_3 represents the molecular sulphur dioxide.

3. Principle

Sulphur dioxide is entrained by a current of air or nitrogen, and is fixed 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 quantity of sulphur dioxide entrained being strongly temperature dependent, the decision was made to work at room temperature (between 18 and 24 °C). This temperature, as for that of the currents of air or nitrogen, should be kept constant throughout the determination.

4. Reagents and products

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

4.2. Diluted phosphoric acid (~25.5%):

By way of example: Dilute 300 mL of phosphoric acid at 85% (4.1) in 1 L of water for analytical use

4.3. 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)
thanol (≥ 95%) (CAS no. 64-17-5)	50 mL

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018

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.

4.4. 1 M Sodium hydroxide (3.84%) or in anhydrous form (pellets) (CAS no. 1310-73-2)

4.5. 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.

4.6. Hydrogen peroxide solution in 3 volumes (= 9.1 g/L = 0.27 mol/L H_2O_2 H202), prepared or commercial (e.g. 30% H202: 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.

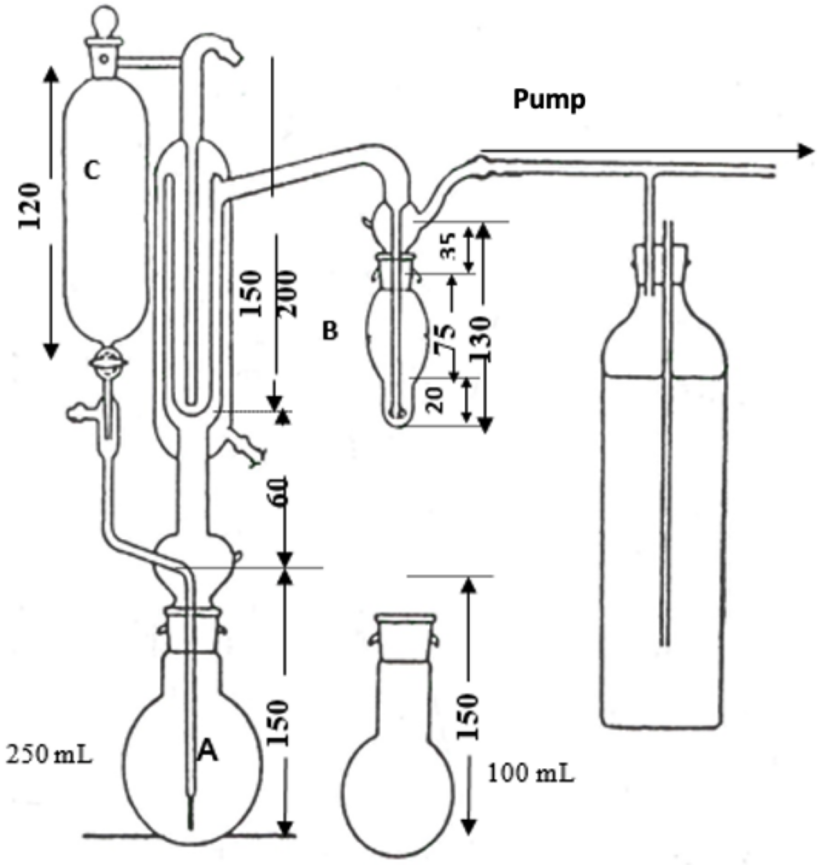
Flask A should be kept at a temperature of between 18 °C and 24 °C throughout aspiration. Each flask should consequently be temperature-controlled (e.g. using a

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018

thermostatic bath) if the room temperature of the laboratory is not within these limits or if 85% phosphoric acid is used, which can significantly increase the temperature in the flask during addition.

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



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.

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018

- Connect the water from the condenser.
- Control the laboratory temperature or stabilise the bath in advance (at between 18 °C and 24 °C).
- In bubbler B of the entrainment apparatus, introduce 2-3 mL hydrogen peroxide solution (4.6) and 2 drops of indicator reagent (4.3), and neutralise with the 0.01 M sodium hydroxide solution (4.5); 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).

- Adapt this bubbler to the apparatus.
- Transfer 50 mL of sample to the 250-mL flask A and attach it to the apparatus.
- Introduce 15 mL of diluted phosphoric acid (4.2) into bulb C.
- Note: If the expected concentration of free sulphur dioxide is higher than 50 mg/L, it is necessary to use phosphoric acid at 85% (4.1). However, ensure that the temperature in flask A does not increase during addition.
- Open the tap to add the acid to the sample while simultaneously starting the gas flow and setting the timer to 15 minutes. The entrained free sulphur dioxide is oxidised into sulphuric acid.
- After 15 minutes, take bubbler B out and rinse the gas supply tube in water (via the socket).
- Titrate the acid formed by the 0.01 M sodium hydroxide solution (4.5) up to the green bend.
- The number of millilitres used is expressed by n.

7. Calculation and expression of results

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

Calculation: Free sulphur dioxide in milligrams per litre: 6.4 n

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018

8. Bibliography

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

Certified in conformity Punta del Este, 23rd November 2018
The Director General of the OIV
Secretary of the General Assembly
Jean-Marie AURAND

© OIV 2018