# OIV-MA-AS323-04B Sulfur dioxide

**Type IV method**

## 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:

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

$H_2SO_3$ 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 determined by direct titration with iodine. The combined sulfur dioxide is subsequently determined by iodometric titration after alkaline hydrolysis. When added to the free sulfur dioxide, it gives the total sulfur dioxide.

2.2. *Rapid Method*

2.2.1. *Reagents*

2.2.1.1. EDTA: ethylenediaminetetraacetic acid, *di*-sodium salt

2.2.1.2. 4 M Sodium hydroxide solution (160 g/L).

2.2.1.3. Dilute sulfuric acid: 10% sulfuric acid (□20 = 1.84 g/mL) diluted 10% (*v*/*v*).

2.2.1.4. Starch solution, 5 g/L.

Mix 5 g starch with approx. 500 mL water. Bring to a boil stirring continuously and keep boiling for 10 minutes. Add 200 g of sodium chloride. Cool and make to 1 liter.

2.2.1.5. 0.025 M Iodine solution

2.2.2. *Free sulfur dioxide*

Place in a 500 mL conical flask place:

- 50 mL of wine
- 5 mL starch solution

- 30 mg EDTA
- 3 mL $H_2SO_4$

Immediately titrate with 0.025 M iodine, until the blue color persists clearly for 10 to 15 seconds. Let *n* mL be the volume of iodine used.

2.2.3. *Combined sulfur dioxide*

Add 8 mL of 4 M sodium hydroxide solution, shake the mixture once and allow to stand for 5 minutes. Add, with vigorous stirring and in one operation, the contents of a small beaker in which 10 mL of sulfuric acid have been placed. Titrate immediately with the 0.025 M iodine solution; let *n*' be the volume used.

Add 20 mL of sodium hydroxide solution, shake once and allow to stand for 5 minutes. Dilute with 200 mL of ice-cold water.

Add, while stirring vigorously and in one operation, the contents of a test tube in which 30 mL sulfuric acid has previously been placed. Titrate the free sulfur dioxide immediately with the 0.025 M iodine, and let *n*" be the volume of iodine used.

2.2.4. *Expression of the results*

2.2.4.1. Calculation

Free sulfur dioxide in milligrams per liter is given by:

$32 \cdot n$

Total sulfur dioxide in milligrams per liter is given by:

$32 (n + n' + n'')$

*Remarks:*

1. For red wines with low $SO_2$ concentrations, the 0.025 M iodine may be diluted (for example: 0.01 M). In this case, replace the coefficient 32 by 12.8 in the above formula.

2. For red wines, it is useful to illuminate the wine from below with a beam of yellow light from an ordinary electric light bulb shining through a solution of potassium chromate or from a sodium vapor lamp. The determination should be carried out in a dark room and the transparency of the wine observed: it becomes opaque when the starch endpoint is reached.

3. If the quantity of sulfur dioxide found is close to or exceeds the legal limit, the total sulfur dioxide should be determined with the reference method.

4. If the determination of free sulfur dioxide is specifically required, carry out a determination on a sample kept under anaerobic conditions for two days at 20 °C before analysis. Carry out the determination at 20 °C.

5. Because certain substances are oxidized by iodine in an acid medium, the quantity

of iodine used in this way must be assessed for more accurate determinations. To achieve this, combine the free sulfur dioxide in an excess of ethanal or propanal before beginning the titration with iodine.

Place 50 mL of wine into a 300 mL conical flask, add 5 mL of 7 g/L ethanol solution or 5 mL of a 10 g/L propanal solution.

Stopper the flask and allow to stand for at least 30 minutes. Add 3 mL of sulfuric acid and sufficient iodine, 0.025 M, to cause the starch to change color. Let $n'''$ mL be the volume of iodine used. This must be subtracted from $n$ (free sulfur dioxide), and from $n + n' + n''$ (total sulfur dioxide).

$n'''$ is generally small, from 0.2 to 0.3 mL of 0.025 M iodine. If ascorbic acid has been added to the wine, $n''$ will be much higher and it is possible, at least approximately, to measure the amount of this substance from the value of $n'''$ given that 1 mL of 0.025 M iodine will oxidize 4.4 mg ascorbic acid. By determining $n'''$, it is possible to detect quite easily the presence of residual ascorbic acid in amounts greater than 20 mg/L, in wines to which it has been added.

**Bibliography**

*Rapid method:*

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