OIV-MA-VI-09 Determination of the total sulfur dioxide content

Type IV method

1. Introduction

In the wine vinegars industry, the addition of sulfur dioxide or salts (E 220 - E 227) is authorized according to defined standards and doses. Accordingly, the applied doses must be checked, above all, their SO_2 contents.

2. Definition

Free sulfur dioxide is that found in the forms H_2SO_3, HSO_3 and SO_3^{2-}.

Combined sulfur dioxide is found in all other forms.

Total sulfur dioxide is the sum of the free sulfur dioxide and the combined sulfur dioxide.

3. Principle[1]

Free sulfur dioxide - Iodometric direct titling with subtraction of the other oxidizable substances by iodine.

Combined sulfur dioxide - iodometric titling after double alkaline hydrolysis of vinegar whose free sulfur dioxide has been oxidized during the previous determination.

Total sulfur dioxide - sum of the free sulfur dioxide content and the combined sulfur dioxide content.

4. Reagents

1. Sulfuric acid (p20 = 1.84 g/ml)
2. Sulfuric acid solution to 1/10 (1 + 9 of water by volume)
3. Solution of sodium hydroxide 4 M
4. Solution of iodine at 0.025 M
5. Disodic ethylene diamine tetracetate (EDTA.Na_2)

6. Starch solution at 5 g/l.

Dissolve 0.5 g of the soluble starch in a small amount of cold water in order to obtain a fluid base. Add to 100 ml of boiling water and maintain on the boil for 10 min. Allow to cool.

4.7. Ethanal solution at 7 g/l

4.8. Propanal solution at 10 g/l.

5. Equipment and utensils

Standard laboratory equipment.

6. Technique

6.1. Free sulfur dioxide

In a 500 ml conical flask, add 50 ml of vinegar, 3 ml of sulfuric acid solution (4.2), 5 ml of starch solution (4.6) and 30 mg of EDTA Na_2 (4.5).

Title immediately with the iodine solution (4.4) until the blue coloring, first fleeting, becomes persistent for 10 to 15 s.

6.2. Combined sulfur dioxide

To the aforementioned conical flask (6.1), add the solution of sodium hydroxide (4.3) up to pH 11-12 (approximately 18 ml), stir and leave in contact for 5 min. Add, in one go and while shaking thoroughly, 17 ml of sulfuric acid solution (4.2).

Title immediately with the iodine solution (4.4).

Then add 20 ml of sodium hydroxide solution (4.3), stir and leave in contact for 5 min. Dilute with 200 ml of water, as cold as possible, stir thoroughly and add in one go, 30 ml of sulfuric acid solution (4.2). Title the liberated sulfur dioxide immediately using the iodine solution (4.4).

6.3. Interference of other substances

Some other substances may be oxidized by iodine in the acid environment; therefore, it is necessary to determine the quantity of iodine used up by such oxidization.

To do this, it is necessary to combine the free sulfur dioxide by excess ethanal or propanal before iodometric titling. To do this, add 50 ml of vinegar to an Erlenmeyer flask of 300 ml and add 5 ml of ethanal solution or 5 ml of propanal solution. Stop and

allow to stand for at least 30 min. Add 3 ml of sulfuric acid solution (4.2) , 5 ml of starch solution (4.6) and the iodine solution (4.4) until a blue color is obtained.

7. Results

7.1. Calculation

Considering:

- **V** the volume in ml of the iodine solution used in 6.1
- $\mathbf{V_1}$ the volume in ml of the iodine solution used for the first titling of 6.2
- $\mathbf{V_2}$ the volume in ml of the iodine solution used for the second titling of 6.2
- $\mathbf{V_3}$ the volume in ml of the iodine solution used in 6.3

The total sulfur dioxide content expressed in milligrams of SO_2 per l of vinegar is:

$$32\,(V + V_1 + V_2 - V_3)$$

7.2. **Presentation**

Round off the results expressed in milligrams of SO_2 per liter, to the nearest unit.

8. Characteristics of the method

8.1. Repeatability of the iodometry method for determining SO_2 in vinegar

Seven red wine vinegars and five white wine vinegars were analysed in duplicate in order to determine the repeatability parameters (table 1).

Table 1:Total SO2 content in different vinegars in mg/l			
	Test 1	Test 2	Difference

Red wine vinegars	14	14	0
	23	27	-4
	64	61	3
	46	50	-4
	119	129	-10
	188	174	14
	38	37	1
White wine vinegars	61	65	-4
	85	85	0
	29	26	3
	96	91	5
	141	150	-9

Mean = 75.54 mg/l

Repeatability: standard deviation=4.4; r limit= 12.38 mg/l

Relative repeatability r = 15%

8.2. Recovery rate of added concentrations

Quantities of SO_2 were added to different vinegars in order to calculate the recovery rate of the iodometry determination method (table 2).

Table 2

Study of recovery rate of known concentrations added to different vinegars

Table 2: Study of recovery rate of known concentrations added to different vinegars				
	Initial concentration (mg/l)	Added concentration (mg/l)	Concentration recovered (mg/l)	Recovery rate

Red wine vinegars	5	25	11	**44%**
	5	50	49	**98%**
	38	100	76	**76%**
	38	150	133	**89%**
White wine vinegars	26	25	25	**100%**
	26	50	47	**94%**
	0	100	66	**66%**
	0	150	118	**79%**

The recovery rate varies from 44% to 100%: occasionally it is too low, but is nonetheless more acceptable than the rate noted for the method of drying under a nitrogen stream, which sometimes produces excessive values.

9. Important remark

After studying the application of the reference method for the determination of sulphur dioxide described in the *Compendium of International Methods of Analysis of Wine and Must* to vinegars, the results produced are unsatisfactory in terms of the recuperation rate of added SO_2 concentrations, which appears to be due to the very high concentration of acetic acid.

10. Bibliography

- Curvelo-Garcia A.S. and Godinho M.C., 1986. Determinação analítica do dióxido de enxofre em vinagres. Optimização das condições operatórias, *Ciência e Técnica Vitivinícola*, **5**(1): 25 - 29.
- FAO/OMS, Commission du Codex Alimentarius, 1982. Doc. CX/EURO 82/3, Partie II, Annexe I, Roma.

- B. Medina: Dosage du SO_2 dans les vinaigres de vin - comparaison de deux méthodes Document OIV, CII-SCMA 03.2006-13.5 - FV 1236

[1] The CPIV has described another method (determination of the absorbance at 550 nm of the solution colored with products from the reaction between sulfur dioxide, formaldehyde and p-rosaniline). The *Instituto da Vinha e do Vinho* (Portugal) has developed a continuous flow method based on the same principle.