Method OIV-MA-VI-13 : R2000
Type II method

Measurement of the copper content in vinegars

(OENO 64/2000)

1. Introduction

The presence of copper in vinegars mainly has its origin in contaminations from contact materials during the different phases of their manufacture. Relatively high copper content can cause hazes or even serious alterations in the colour, hence the importance of this measurement.

2. Principle

Direct measurement by atomic absorption spectrophotometry.

3. Reagents

3.1. copper metal

3.2. concentrated nitric acid 65% (p_{20} = 1.38 g/ml).

3.3. diluted nitric acid 1:2 (v/v).

3.4. acetic acid solution 5% (v/v).

3.5. standard solution of copper 1.000 g per L.

Weigh 1.000 g of copper metal, and transfer it entirely into a 1000 ml volumetric flask. Add diluted nitric acid (3.3) in strictly sufficient quantity to dissolve the metal, then add 10 ml of concentrated nitric acid and make up to the mark with doubled distilled

water.

This solution can be purchased ready-made.

3.6. standard solutions of copper, from 1 to 10 mg/L.

Prepare standard solutions of 1 to 10 mg/L by diluting the solution (3.5) with the acetic acid solution (3.4).

4. Devices and utensil

Standard laboratory material, plus:

4.1. atomic absorption spectrophotometer

4.2. copper ion hollow cathode lamp

5. Preparation of the sample

Shake the sample to homogenize and filter if necessary.

6. Technique

Select a 324.7 nm wavelength. Adjust the absorbence scale to zero with the acetic acid solution (3.4). Suck the vinegar sample directly into the burner of the spectrophotometer, then successively the standard solutions (3.6). Read the absorbencies. The measurements should be done at least twice.

7. Results

7.1. Calculation

Draw the absorbence variation curve according to the copper concentration of the standard solutions. Write down the absorbencies middle value of the vinegar sample and measure the copper content, expressed in milligrams per L of the sample.

7.2. Presentation

Round the results, expressed in milligrams of copper per L, to the first decimal place.

8. Remarks

For very low copper concentrations in the sample, and to improve the precision and exactness of the measurements, either the method of standard additions, or the method of prior ashing of the sample, should be used. Both are described by OIV (1990) for the measurement of copper content in wine.

Most devices give the concentration of samples directly.

9. Inter-laboratory validation (Hitos et al, 00)

Units: mg/L

Sample	r	S_r	RSD_r	R	S_R	RSD_R	RSD_R (Horwitz)	HORRAT Index
1 - 0.22 mg/L	0.0678	0.024	10.89	0.1905	0.068	30.61	20.10	1.52
2 - 0.03 mg/L	0.0210	0.008	21.82	0.0567	0.020	58.89	27.12	2.17
3 - 0.58 mg/L	0.0895	0.032	5.48	0.3187	0.114	5.48	17.37	0.32
4 - 0.11 mg/L	0.0493	0.018	16.77	0.1567	0.056	53.31	22.31	2.39

5 - 2.78 mg/L	0.2589	0.092	3.33	1.1809	0.422	15.17	13.72	1.11

10. Method of standard additions

10.1. Principle

Copper is measured in vinegar by flame atomic absorption spectrometry (method of standard additions).

10.2. Reagents

10.2.1. ultra pure demineralized water

10.2.2. 1 g/L standard copper solution, ready to use

10.2.3. nitric acid 65% *suprapur*

10.2.4. 10 mg/L copper solution: put 2 mL of the 1 g/L copper solution (10.2.2) in a 200 ml flask; add 1 ml of nitric acid (10.2.3); make up to volume with demineralized water (10.2.1).

10.2.5. to adjust the position of the burner of the spectrophotometer, prepare a standard of copper at 0.4 mg/L: 2 mL of the 10 mg/L copper solution (10.2.4) in a 50 mL volumetric flask; make up to volume with demineralized water (10.2.1).

10.3. Devices and utensils

10.3.1. Glassware

10.3.1.1. 50, 200 ml volumetric flasks (class A)

10.3.1.2. 2, 5 and 10 ml calibrated pipettes (class A)

10.3.1.3. 10 ml cylindrical flasks

10.3.1.4. 200 µl automatic micropipette

10.3.1.5. Atomic absorption spectrophotometer (air-acetylene oxidizing flame, 324.7 nm wavelength, width of the aperture: 0.5 nm, intensity of the hollow cathode lamp: 3.5 mA).

10.4. Preparation of samples

10.4.1. addition of 0.2 mg/L of copper: place 5 ml of vinegar in a cylindrical flask; add a 10 mg/L copper solution with the 100 µl micropipette.

10.4.2. addition of 0.4 mg/L of copper: place 5 ml of vinegar in a cylindrical flask; add a 10 mg/L copper solution with the 200 µl micropipette.

10.4.3. dilution of the vinegar: a dilution of vinegar with demineralized water is only necessary if the copper concentration is higher than 0.5 mg/L.

10.5. Measurements

Make two absorbance readings, each of 10 seconds, for, successively, the blank (demineralized water), vinegar with the added 0.2 mg/L of copper, vinegar with the added 0.4 mg/L of copper (4.2.), and vinegar as is, without addition of copper. The software draws the graph of the standard additions and gives the vinegar's copper content directly in mg/L. The dilutions resulting from the additions are negligible.

10.6. Quality control

The measurements by flame atomic absorption spectrometry are made manually.

Quality control is achieved by regularly interposing a reference material every 5 measurements, or one after the standard solution, one in the middle and one at the end of the measurements.

A tolerance of two standard variations from the known value of the reference material is acceptable.

11. Bibliography

1. Anonymous, 1993. *Métodos Oficiales de Anàlisis*, (Official Analytical Methods) Tomo II (Part II) Ministério de Agricultura, Pesca y Alimentación, (Ministry for Agriculture, Fishing and Food) Madrid, Spain.
2. EEC, 1990. Méthode de référence de dosage de cuivre dans le vin (Reference method for copper measurement in wine), *Journal Officiel des Communautés Européennes* (Official Newspaper of the European Communities), L272,: 145 - 146.
3. Hitos P., Pons A., Martin de la Hinojosa I., Gomez R., Hernandez A. and Muñoz J., 00. Validation des méthodes d'analyse pour l'acidité totale, fixe et volatile, les substances réductrices non volatiles, le cuivre et le zinc dans les vinaigres de vin (Validation of analytical methods for the total acidity, fixed and volatile, the non volatile reducing substances, the copper and zinc in wine vinegars), *Feuillet Vert de l'OIV* (OIV Green Leaflet) no 1115.
4. Llaguno C. and Polo M.C., 1991. *El Vinagre de Vino* (The Wine Vinegar) Consejo Superior de Investigaciones Cientificas (High Council of Scientific Research) Madrid, Spain.
5. OIV, 1990. *Recueil des méthodes Internationales d'analyse des vins et des moûts* (Compilation of the international methods of analysis of wines and musts) OIV Paris, France.
6. Varian Techtron, 1972. *Analytical methods for flame spectroscopy.*