Method OIV-MA-VI-16 : R2000
Type IV method

Measurement of lead content in vinegars

(OENO 67/2000)

1. Introduction

As for the other metals, the presence of lead in vinegars mainly has its origin in contaminations from contact materials during their manufacture, and of course the lead of the wine itself from which the vinegar has been made.

2. Principle

Direct measurement of lead content in the vinegar by atomic absorption spectrometry without flame, (electrothermal atomization).

3. Reagents

3.1. ultra pure demineralized water, for example: pre-purification through inverse osmosis; filter to eliminate all particles > 0.22 □m; control of the purified water resistivity (18.2 M□)

3.2. nitric acid at 65%: high quality acid

3.3. ammonium dihydrogen-phosphate ($NH_4H_2PO_4$)

3.4. ready-made standard lead solution at 1 g/L

3.5. tantalum powder: > 99.7 % purity

3.6. fluorhydric acid

3.7. anhydrous oxalic acid

3.8. hydrogen peroxide at 30%

4. Devices and utensils

Standard laboratory material, including:

4.1. atomic absorption spectrophotometer

4.2. lead ion hollow cathode lamp

4.3. 50 and 100 mL volumetric flasks (class A).

4.4. calibrated pipettes (class A).

Decontaminate the glassware: rinse with demineralized water, soak for at least 24 hours in a bath of nitric acid at 5% and rinse twice with demineralized water.

5. Preparation of the sample

Shake the sample to homogenize and filter if necessary.

6. Technique (example only using a particular type of equipment)

6.1. Test parameters (atomic absorption spectrometry)

6.1.1. 283.3 nm wavelength

6.1.2. width of the aperture: 0.5 nm

6.1.3. intensity of the hollow cathode lamp: 5 mA

6.1.4. base line correction by the Zeeman effect

6.1.5. introduction of standard solutions and samples when warm in the graphite oven with an automatic feeder (1 drop of Triton in 500 mL of rinsing water)

6.1.6. reading of signal: when highest

6.1.7. length of reading: 1 s.

6.1.8. number of readings per standard solution or sample: 2.

6.2. Pyrolytic graphite tube

6.2.1. pyrolytic graphite oven with a tantalum treated platform of L'Vov

6.2.2. tantalum treatment of a platform: put the platform inside a graphite or used pyrolytic graphite tube, and fit the whole lot onto the atomization unit of the spectrophotometer. Inject 10 µl of the tantalum solution on the platform with an automatic sample feeder. Set the temperature cycle as follows: drying for 40 s at 100° C, mineralization for 60 s at 900° C, atomization at 2 for 2.5 s at 600° C. Use argon for inert gas.

6.2.3. oven parameters: as per Table 1.

The atomization of lead is performed without a mineralization procedure.

6.3. Preparation of solutions

6.3.1. tantalum solution at 6%: put 3 g of tantalum powder (3.5) in a 100 mL teflon cylindrical flask; add 10 mL of fluorhydric acid (3.6) diluted (1+1), 3 g of anhydrous oxalic acid (3.7) and 0.5 mL of hydrogen peroxide at 30% (3.8); heat carefully to dissolve the metal; add some hydrogen peroxide when the reaction slows down; when the dissolution is complete, add 4 g of oxalic acid (3.7) and approximately 30 mL of demineralized water (3.1); dissolve the acid and make to the mark to 50 mL; store this solution in a plastic flask.

Table I. Oven parameters

temperature (°C)	Duration (s)	gas flow (mL/min)	gas type	reading
150	10.0	3.0	argon	no
150	35.0	3.0	argon	no
150	1.5	0	argon	no
2250	1.1	0	argon	yes
2250	1.5	0	argon	yes
2600	1.5	3.0	argon	no
1250	10.0	3.0	argon	no
75	10.0	3.0	argon	no

6.3.2. matrix modifier ($NH_4H_2PO_4$ at 6%): put 3 g of ammonium dihydrogen-phosphate (3.3) in a 50 mL flask; dissolve and make up with demineralized water (3.1).

6.3.3. lead solution at 10 mg/L: put 1 mL of the 1 g/L lead solution (3.4) in a 100 mL flask; add 1 mL of nitric acid (3.2); make up to the mark with demineralized water (3.1). This solution keeps 1 month at +4° C in a polypropylene flask.

6.3.4. lead solution at 0.l mg/L (100 µg/L): put 1 mL of the 10 mg/L lead solution to (6.3) in a 100 mL flask; add 1 mL of nitric acid (3.2); make up to the mark with demineralized water (3.1). This solution keeps 2 days at +4° C in a polypropylene flask.

6.3.5. range of standard solutions: can be achieved using the automatic feeder cycle with the 100 µg/L lead solution (Table II). These standard lead solutions have the following final concentrations: 0; 16.6; 33.3; 50.0 and 66.6 µg of lead per litre.

6.4. Operating instructions

6.4.1. samples need not be prepared; they are put directly into the pots of the automatic device. The analytical blank is made up of demineralized water with 1% of nitric acid (3.2).

Table II. Automatic sampler parameters

	injected volumes in µL		
	100 µg/L solution	blank	matrix modifier
Blank		5	1
Standard sample n° 1	1	4	1

Standard sample n° 2	2	3	1
Standard sample n° 3	3	2	1
Standard sample n° 4	4	1	1
vinegar sample	2	3	1

6.4.2. measurements: the spectrophotometer software draws the standard sample graph (absorbance according to the lead concentration in the standard solutions) and gives the lead concentration reading of the samples (6.4.1) in µg/L.

6.4.3. results: multiply by 3 the reading given by the software of the device to deduct the lead concentration in the vinegar (2 µL of sample injected in the oven for an end volume of 6 µL). Take into account a possible dilution of the vinegar. The result is expressed in micrograms of lead by litre of vinegar.

7. Detection and quantification limits

7.1. detection limit: set according to a series of 20 analytical blank results of the white and is equal to 3 standard variations.

7.2. quantification limit: equal to 3 times the detection limit.

8. In house quality control

8.1. reference material: a vinegar sample with a carefully measured lead content should be used for quality control.

8.2. in-house quality control mode of use: the lead content of the reference material is measured directly after calibration. If the reading is within a satisfactory bracket (+/- 15% on average), go on with the analysis. Otherwise, the device should be calibrated again. A control quality sample is interposed every 5 pots.

8.3. graphite-oven measurements: some spectrophotometers are equipped with an automatic quality control software. 5 standard solutions, including blank, are used for calibration.

8.4. control card: a control card is drawn up for the reference material. Warning limits are +/-1.96.s_R and control limits +/- 2.58.s_R.

9. Bibliography

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4. ZATKA V., 1978. Tantalum treated graphit atomizer tubes for atomic absorption spectrometry, *Analytical Chemistry*, 50 (3).