Method OIV-MA-VI-17 : R2000
Type IV method

Measurement of mercury content in vinegars (cold vapour method)

(OENO 68/2000)

1. Principle

Vinegar mineralization: is performed in an acidic environment, through a reflux heating method; complete mineralization with potassium permanganate.

Reduce unused permanganate with hydroxylamine hydrochloride.

Reduce the mercury II to metal mercury with tin (II) chloride.

Drive mercury with an air or argon current, at room temperature.

Measure mercury in a monoatomic vapour state with atomic absorption spectrometry.

2. Reagents

2.1. Ultra pure demineralized water with a 18.2 M resistivity

2.2. High purity 65% nitric acid

2.3. Sulphuric acid 20 = 1.84 mg/L

2.4. 5.6 M nitric acid solution: using a test-tube put 100 mL of nitric acid (2.2.) in a 250 mL flask; make up to the mark with demineralized water (2.1.).

2.5. 9 M sulphuric acid solution: using a test-tube put 100 mL of sulphuric acid (2.3.) in a 200 mL flask; cool, then make

up to the mark with demineralized water (2.1.).

2.6. Potassium permanganate

2.7. Potassium permanganate solution at 5%: dissolve 10 g of $KMnO_4$ (2.6) in a 100 mL cylindrical flask with demineralized water (2.1.); transfer in a 200 mL flask and make up to the mark.

2.8. Hydroxylamine hydrochloride

2.9. Hydroxylamine hydrochloride solution at 1.5%: dissolve 1.5 g of NH_4OCl (2.8.) in a 100 mL cylindrical flask with demineralized water (2.1.); transfer in a 100 mL flask and make up to the mark.

2.10. Tin II chloride

2.11. Tin chloride solution:

2.11.1. Cold vapours in closed circuit method:

Tin II chloride solution at 10%: dissolve 5 g of $SnCl_2$ .2 H_20 (2.10.) in a 100 mL cylindrical flask with the addition of 5 ml of H_2S0_4 (2.5.) in demineralized water (2.1.); transfer in a 50 mL flask.

2.11.2. Cold vapours in continuous flow method:

25% $SnCl_2$ in 20% HCl: to prepare this tin (II) chloride solution, add concentrated hydrochloric acid directly onto the solid tin (II) chloride and heat on a hotplate to dissolve, then add demineralized water (2.1).

2.12. Mother mercury solution at 1 g/L

2.13. Mercury solution at 10 mg/L: put 1 mL of the mother solution (2.12) in a 100 mL flask; make up to the mark with demineralized water (2.1.).

2.14. Mercury solution at 0.1 mg/L (or 100 □g/L): put 1 mL of the diluted solution (2.13.) in a 100 mL flask; make up to the mark with demineralized water (2.1.).

3. Devices and utensils

3.1. Glassware:

3.1.1. 50, 100, 200, 250 mL volumetric flasks (class A)

3.1.2. 1, 2, 3, 4, 5, 20, 50 mL calibrated pipettes (class A)

3.1.3. 5, 10 mLs calibrated pipettes (class A)

3.1.4. 100 mL calibrated test-tube

3.1.5. 100 mL cylindrical flask.

3.2. Circulation system of the mercury vapours in closed circuit:

3.2.1. Reaction tube

3.2.2. Mineralized sample

3.2.3. Tin (II) chloride

3.2.4. Air compressor

3.2.5. Mercury trap ($KMnO_4$)

3.2.6. Absorption cell

3.2.7. Drier ($CaCl_2$)

3.3. Circulation system of the mercury vapours in continuous flow

3.3.1. Argon

3.3.2. Flow controller

3.3.3. Reducing agent: 25% $SnCl_2$ in 20% HCl

3.3.4. Demineralized water

3.3.5. Mineralized sample

3.3.6. Peristaltic pump

3.3.7. Reagents mixing

3.3.8. To the sink

3.3.9. Gas / liquid separator

3.3.10. To the spectrophotometer

3.4. Atomic absorption spectrophotometer

3.4.1. 253.3 nm wavelength

3.4.2. Width of the aperture: 0.5 nm

3.4.3. Intensity of the lamp: 2.5 mA

3.4.4. Baseline correction with a deuterium lamp

4. Preparation of samples

4.1. Mineralization of vinegars: is performed in a pyrex-glass equipment made of three elements linked with spherical "rodages": a 250 mL flask, a recovery chamber with a cooling device on top.

4.1.1. Water circulation

4.1.2. Cooling device with balls

4.1.3. Reflux

4.1.4. Flask heater

4.1.5. Vinegar + H_2SO_4 + HNO_3

Put 20 mL of vinegar in a 250 mL flask with a pipette; assemble the mineralization equipment. Add very slowly 5 mL of H_2SO_4 (2.3.) and 10 mL of $HN0_3$ (2.4.). Heat slowly with reflux. Recover the condensed vapours in the reaction flask. Leave to cool; rinse with demineralized water (2.1.). Add some $KMn0_4$ (2.7.) until the colour is lasting. Make the $Mn0_2$ precipitate soluble with NH_40CI (2.9.). Transfer the solution in 100 mL flask and make up to the mark with demineralized water. Make a blank without vinegar.

5. Measurements

5.1. Range of standard solutions:

5.1.1. Cold vapours in closed circuit method:

- Range of standard solutions: 0; 0.1; 0.2; 0.3; 0.4; 05 µg of mercury.
- Put successively 1, 2, 3, 4, 5 mL of the mercury solution at 100 µg/L (2.14.) in the reaction tube; add two drops of $KMnO_4$ (2.7.), 2.5 ml of HNO_3 (2.4.), 2.5 mL of H_2S0_4 (2.5.) and 2.5 mL of NH_40CI (2.9.); make up to a constant volume (70 ml) with demineralized water (2.1.).
- Add 2.5 mL of $SnCl_2$ (2.11.); start immediately the bubbling process. Read the maximal optical densities. Then trap the mercury in $KMn0_4$ (2.7.).

5.1.2. Cold vapours in continuous flow method:

- Range of standard solutions: 0; 2.5; 5; 10 µg/L of mercury.
- Put in 4 100 mL flasks: 0; 2.5; 5; 10 mL of the 100 µg/L diluted mercury solution (2.14.); make up to the mark with demineralized water. The peristaltic pump will suck the reducing solution (25% $SnCl_2$ in 20% HCI), the demineralized water and the standard solution.

5.2. samples:

5.2.1. Cold vapours in closed circuit method:

- Transfer the mineralized sample to the reaction tube with a 50 mL pipette. Make up to a 70 mL constant volume with demineralized water (2.1.). Add 2.5 mL of $SnCI_2$ (2.11.); start immediately the bubbling process. Read the maximal optical densities. Then trap the mercury in the permanganate (2.7.).

5.2.2. Cold vapours in continuous flow method:

- The mineralized sample is sucked by the peristaltic pump together with the tin (II) chloride and the water.

5.3. Results:

5.3.1. Cold vapours in closed circuit method:

- 50 mL of mineralized sample are equivalent to 10 mL of vinegar.
- The concentration given by the software of the device should therefore be multiplied by 100 to have the mercury content of the vinegar in □g/L.

5.3.2. Cold vapours in continuous flow method:

- 20 mL of mineralized vinegar are collected in a 100 mL flask. The software of the device gives the result in µg/L; therefore, to have the mercury content of the vinegar in µg/L, one should multiply the result by 5.

6. Quality control

Quality control is achieved by regularly interposing a reference material of in-house quality control every 10 samples, or, at the most, one after the standard solution, one in the middle and one at the end of the measurements.

A tolerance of two standard variations of the known value is accepted.

7. Bibliography

1. CayroI M. & Brun S., 1973. Sur le dosage du mercure (On the measurement of mercury), *Ann. Fats. Exp. Chim.*, 66 (709): 135-142.
2. Varian, 1986. *Spectra AA-10/20. Operation Manual.*

3. Varian, 1994. Instruments at Work, Vapor Generation Accessory VGA-77.