OIV-MA-AS323-06 Determination of mercury in wine by vapour generation and atomic spectroglurimeter

Type IV method

1. Field of application

This method applies to the analysis of mercury in wines with a concentration range between 0 to 10 ug/l.

2. Description of technique

2.1. Principle of the method

2.1.1. Mineralisation of wine takes place in an acid environment: heating under reflux; mineralisation is achieved with a potassium permanganate.

2.1.2. Reduction of non-consumed permanganate by hydroxylamine hydrochlorate

2.1.3. Reduction in mercury II (metal mercury by stannous chloride (II).

2.1.4. Mercury pick up by an argon current at ambient temperature

2.1.5. Dosage of mercury in monoatomic vapour state by atomic flourescence spectometre with wavelength of 254 nm. Mercury atoms are excited by a mercury vapour lamp; the atoms thus excited emit a radiation called flourescent which allows the quantification of mercury present using a photonics detector to obtain good linearity while eliminating memory effects.

2.2. Principle of analysis (figure 1)

The peristaltic pump absorbs the stannous chloride solution, the blank solution (demineralised water containing 1% nitric acid) and the sample of mineralised wine.

The mercury metal is taken up in a gas-liquid separator by a current of argon. After going through a drying tube, the mercury is detected by florescence. Then, the gaseous current goes through a permanganate potassium solution in order to capture the mercury.

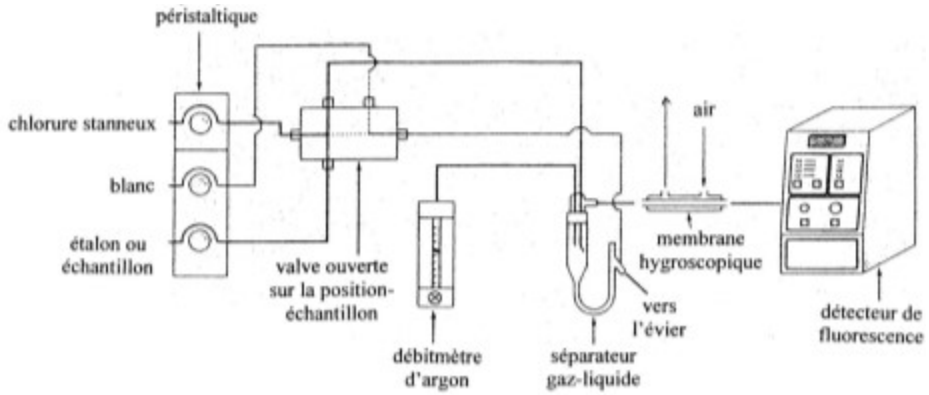


Figure n°1. Chaîne analytique pour doser le mercure

3. Reagents and preparation of reactive solutions

3.1. Ultra-pure demineralised water

3.2. Ultra-pure 65% nitric acid

3.3. White: demineralised water (3.1) containing 1% of nitric acid (3.2)

3.4. Nitric acid solution 5.6 M (3.1):

Put 400 ml of nitric acid (3.2) into a 1000 ml flask; fill with demineralised water (3.1).

3.5. Sulphuric acid (d= 1.84)

3.6. Sulphuric acid solution 9M:

Put 200 ml of demineralised water (3.1), 50 g of potassium permanganate (3.7) into a 1000 ml flask; fill with demineralised water (3.1).

3.7. Potassium permanganate $KMnO_4$

3.8. 5% Potassium permanganate solution:

Dissolve 50 g of potassium permanganate (3.7) with demineralised water (3.1), in a 1000 ml flask. Fill with demineralised water (3.1).

3.9. Hydroxylamine hydrogen chloride NH_2OH, HCl

3.10. Reducing solution:

Weigh 12g of hydroxylamine hydrogen chloride (3.9) and dissolve in 100 ml of demineralised water (3.1).

3.11. Stannous chloride ($SnCl_2, 2 H_2O$)

3.12. Concentrated hydrochloric acid

3.13. Stannous chloride solution:

Weigh 40 g of stannous chloride (3.11) and dissolve in 50 ml of hydrochloric acid (3.12). Fill with 200 ml of demineralised water (3.1).

Mercury standard solution at 1g/l prepared by dissolving 1708 g of Hg (NO_3). H_2O in an aqueous nitric acid solution at 12% prepared from metal mercury.

Reference mercury solution at 10 mg/l :

Place 1 ml of mercury standard solution (3.14) in a 100 ml volumetric flask, add 5 ml of nitric acid, fill will demineralised water (3.1)

Mercury solution at 50 mg/l:

Place 1 ml of 10 mg/l (3.15) solution in a 200 ml flask. Add 2 ml of nitric acid (3.2). Fill with demineralised water (3.1).

4. Apparatus

4.1. Glass ware

4.1.1. Volumetric flasks 100, 200, and 1000 ml (class A*)*

4.1.2. Volumetric pipette 0.5,1.0, 2.0, 5, 10 and 20 ml (class A)

4.1.3. *Precautionary action: Before using, the glass ware must be washed with 10% nitric acid, leave in contact 24 hours, then rinse with demineralised water.*

4.2. Mineralisation apparatus (figure 2)

4.3. Temperature controlled heating mantle

4.4. Squeeze pump

4.5. Cold vapour generator

4.5.1. Liquid gas separator

4.6. Desiccant (Hygroscopic membrane) covered by an air current (supplied from a compressor) and placed before the detector

4.7. Spectrofluorimeter

4.7.1. *M*ercury vapour lamp regulated to 254 nm wave length

4.7.2. Atomic fluorescence specific detector

4.8. Computer

4.8.1. *S*oftware which regulates the parameters of the vapour generator and the atomic fluorescence detector and enables calibration and usage of the results.

4.8.2. Printer which stores results

4.9. Neutral gas bottle (argon)

5. Preparation of calibration solutions and samples

5.1. Set of calibration solutions: 0; 0.25; 0.5; and 1.0 ug/L

Introduce : 0; 0.5; and 1.0 and 2.0 ml of the mercury solution to 50 ug/l (3.16.) in 4 100 ml flasks; add 1 % nitric acid (3.2.); fill with demineralised water (3.1.).

5.2. Preparation of samples (figure 2)

Wine is mineralised in a glass pyrex apparatus made up of three parts joined by spherical honing: a 250 ml balloon, a vapour recuperation chamber, a refrigerant.

Using a pipette put 20 ml of wine in a 250 ml reaction flask; assemble the mineralisation apparatus.

Add 5 ml of sulphuric acid (3.6.) and 10 ml of nitric acid (3.4.) slowly; leave overnight.

Heat slowly under reflux until the nitrous vapours disappear ; leave to cool. Recover the condensed vapours in the reaction flask. Rinse the recipient with demineralised water. Pour the contents of the reaction flask into a 100 ml volumetric flask. Add potassium permanganate solution (3.8.) until the colour remains. Solubilize the precipitate (MnO_2) with a reducing solution (3.10.). Fill with demineralised water (3.1.).

Carry out a blank test on demineralised water.

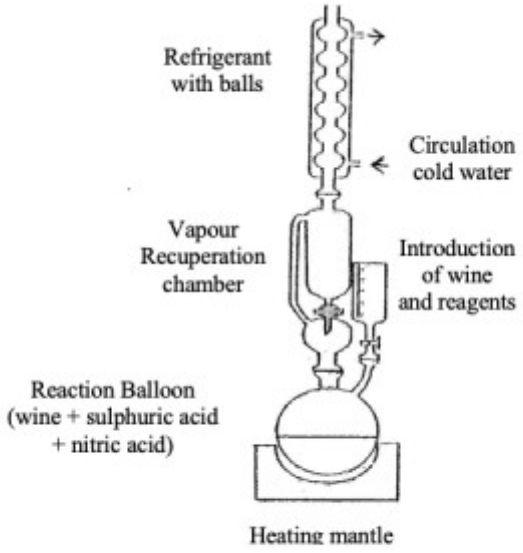


Figure n°2. Mineralisation apparatus

6. Operating procedure

6.1. Analytical measurement

Turn on the fluorimeter; the apparatus is stable after 15 minutes. The squeeze pump

absorbs the white (3.3), the stannous lead II (3.13) and the sample calibrations (5.1) or (5.2.) Verify that bubbling occurs in the liquid gas separator. Present the calibration samples successively (5.1); set off the vapour generator program. The computer software establishes a calibration curve (percentage of fluorescence according to concentration of mercury ug/l). Then present the samples (5.2).

6.2. Automatic checks

A blank analysis and a calibration are analysed every five tests to correct any possible spectrofluorimeter derivitives.

7. Expression of results

Results are provided by the computer software and expressed in ug/l. Deduct the mercury concentration in wine in ug/l keeping into account 1/5 dilution.

8. Checking results

Quality control is carried out by placing reference material in which the mercury content is known, following the set of calibrations and every 5 samples. Following the analytical series, the reference material is red wine, dry white wine or sweet white wine.

The check card is set for each reference material used. The check limits are set at: +/- $2S_R$ intra ($2S_R$ intra : reproducibility spread-type)

The uncertainly calculation, carried out on check cards, resulted in a red wine reference of: 3.4 +/- 0.8 ug/l and for reference dry white wine : 2.8+/-0.9 ug/l.

9. Bibliography

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