COEI-2-MERCUR Determination of mercury by the generation of vapour and atomic fluorescence spectrometry

1. Field of application

This method is applied to the analysis of mercury in oenological products in the concentration range of 0 to 10 µg/l.

2. Description of the technique

2.1. Principle of the method

2.1.1. Mineralisation by the wet process of the oenological product to be analysed.

2.1.2. Reduction of the permanganate not consumed by hydroxylamine hydrochloride.

2.1.3. Reduction of mercury(II) into metal mercury by tin chloride (II).

2.1.4. Entrainment of mercury by a current of argon at room temperature.

Detremining mercury in the state of monoatomic vapour by atomic fluorescence spectrometry, with the wave length at 254 nm: the mercury atoms are excited by a mercury vapour lamp; the atoms thus excited reemit fluorescent radiation that enables to quantify the mercury present using a photonic detector placed at 90° in relation to excitation beam; detection by atomic fluorescence enables to obtain good linearity and eliminates memory effects.

2.2. Principle of the analysis (figure n°1)

The peristaltic pump draws up the tin chloride (II) solution, the blank (demineralised water containing 1% nitric acid) and the mineralised sample or calibration.

The metal mercury is entrained in the gas-liquid separator by a current of argon.

After going through the membrane of a dessicator, the mercury is detected by fluorescence.

Then the gaseous current goes through a potassium permanganate solution in order to trap the mercury.

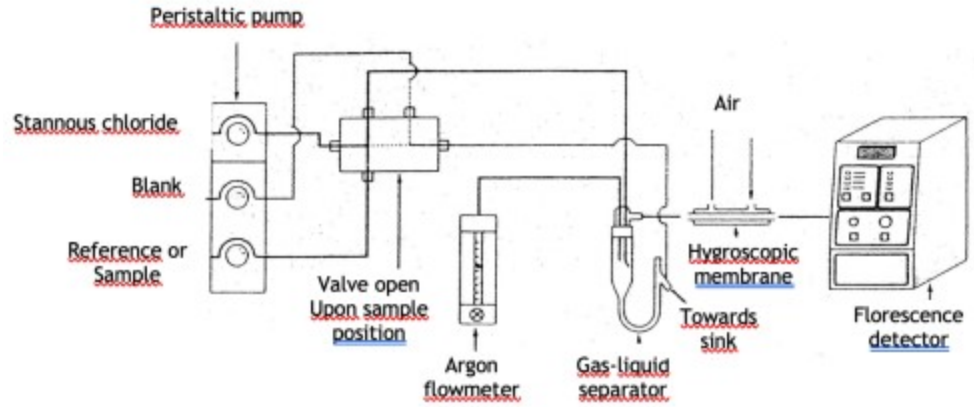


Figure n°1. Analytic Chain for dosage of mercury

3. Reagents and preparation of reagent solutions

3.1. Ultra-pure demineralised water

3.2. Ultra-pure nitric acid at 65%

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

3.4. Nitric acid solution 5.6 M: introduce 400 ml of nitric acid (3.2.) into a 1000 ml flask; complete to volume with demineralised water (3.1.).

3.5. Sulphuric acid (d = 1.84)

3.6. Sulphuric acid solution 9 M: introduce 200 ml of demineralised water (3.1.) in a 1000 ml flask, then 500 ml of sulphuric acid (3.5.); after cooling, complete to volume with demineralised water (3.1.).

3.7. Potassium permanganate $KMnO_4$

3.8. Potassium permanganate solution at 5%: dissolve with demineralised water (3.1.), 50 g of potassium permanganate (3.7.) in a 1000 ml flask; complete to volume with demineralised water (3.1.).

3.9. Hydroxylamine hydrochloride NH_2OH,HCl

3.10. Reducing solution: weigh 12 g of hydroxylamine hydrochloride (3.9.) and dissolve in 100 ml of demineralised water (3.1.).

3.11. Tin chloride II ($SnCl_2$,2 H_2O)

3.12. Concentrated hydrochloric acid

3.13. Tin (II) chloride solution: weigh 40 g of tin chloride (3.11.) and dissolve in 50 ml of

hydrochloric acid (3.12.); complete to 200 ml with demineralised water (3.1.).

3.14. Mercury reference solution at 1 g/l prepared by dissolution of 1.708 g of $Hg(NO3)_2.H_2O$, in 1 l of HNO_3 solution at 12% (m/n).

3.15. Mercury calibration solution at 10 mg/l, containing 5 % of nitric acid and prepared from the reference solution at 1 g/l (3.14).

3.16. Mercury solution at 50 µg/l: place 1 ml of the solution at 10 mg/l (3.14.) in a 200 ml flask; add 2 ml of nitric acid (3.2.); complete to volume with demineralised water (3.1.).

4. Apparatus

4.1. Glassware:

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

4.1.2. graduated pipettes 0.5; 1.0; 2.0; 5; 10 and 20 ml (class A)

4.1.3. precautions: before use, the glassware must be washed with nitric acid at 10%, left in contact for 24 hours, then rinsed with demineralised water.

4.2. Mineralisation apparatus (see Compendium of international methods of analysis of wines and musts)

4.3. Thermostatic heating mantle

4.4. Peristaltic pump

4.5. Cold vapour generator

4.5.1. gas-liquid separator

4.6. Dessicator (hygroscopic membrane) covered by an air current (supplied by a compressor) and placed before the detector

4.7. Spectrofluorimeter:

4.7.1. mercury vapour lamp, adjusted to the wave length of 254 nm

4.7.2. specific atomic fluorescence detector

4.8. PC:

4.8.1. software that adjusts the parameters of the vapour generator and atomic fluorescence detector and allows calibration and the analysis of results.

4.8.2. printer that archives results

4.9. Bottle of neutral gas (argon)

5. Preparation of the set of calibration solutions and samples

5.1. Set of calibration solutions: 0; 0.25; 0.5 and 1.0 µg/l

Introduce 0; 0.5; 1.0; 2.0 ml of the mercury solution at 50 µg/l (3.15.) in 4 100 ml flasks;

add 1% nitric acid (3.2.); complete to volume with demineralised water (3.1.).

5.2. Samples

Mineralise the samples by wet process The test sample is introduced into the round-bottomed flask in borosilicate glass placed on a disc with a hole. The neck is inclined.

Add 5 ml of concentrated sulphuric acid (R) and 10 ml of concentrated nitric acid (R) and gently heat. When the mixture starts to turn brown, add a small quantity of nitric acid while continuing to heat and so forth until the liquid remains colourless and that the atmosphere of the flask fills with white smoke of SO3. Allow to cool, take 10 ml of distilled water and heat again to allow the nitrous fumes to escape until the release of the white smoke. This operation is repeated; after a third time, boil an instant, cool, stabilise with several drops (about 10) of potassium permanganate (aqueous sol.) at 5% (m/m) and add water to the liquid to reach 40 ml.

Filter on filters without cinders. Introduce 10 ml of filtrate into a 50 ml flask. Add potassium permanganate (3.8.) until persistence of coloration. Solubilise the precipitate (MnO_2) with the reducing solution (3.10.). Complete to volume with demineralised water (3.1.).

Do a blank test with demineralised water.

6. Procedure

6.1. Analytical determination

Turn on the fluorimeter; the apparatus is stabilised after 15 minutes.

The peristaltic pump draws up the blank solution (3.3.), the tin chloride (II) solution (3.13.) and the calibrations or samples (5.1.) or (5.2.).

Check if there is a bubbling in the gas-liquid separator.

Present successively the calibration solutions (5.1.); start the programming of the vapour generator. The computer software sets up the calibration curve (percentage of fluorescence depending on the concentration of mercury in µg/l).

Then present the samples (5.2.).

6.2. Self-check

Every five determinations, an analytical blank solution and a calibration are analysed in order to correct a possible drift of the spectrofluorimeter.

7. Expression of results

The results are given by the computer software and are expressed in p.p.b. (or µg/l).

The concentration of mercury in oenological products is calculated according to the

test sample and the dilution of the mineralisate. It is expressed in µg/kg.

8. Control of results

The quality control is performed by placing, after the set of calibration solutions and all five samples, a reference material whose mercury content is known with certainty.

A control card is set up for each reference material used. The control limits are set at: +/- $2S_R$ intra (S_R intra: standard deviation for reproducibility).

9. Bibliography

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