OIV-MA-AS321-01 Total bromide

Type IV method

1. Principle

The wine is ashed at 525 oC in presence of an excess of soda lime. A solution of the residue (at pH 4.65) is treated with chloramine T to liberate bromide. The bromide is reacted with phenolsulfonephthalein to form phenoltetra-bromophthalein-3'-3"-disulfonic acid, which is determined by spectrophotometer at 590 nm.

2. Apparatus

2.1. Boiling water□bath 100□C

2.2. Temperature□controlled electric furnace

2.3. Spectrophotometer capable of measuring absorbance at wavelengths between 300 and 700 nm

3. Reagents

3.1. Sodium hydroxide solution, 50% (*m/m*)

3.2. Calcium hydroxide suspension containing 120 g of CaO per liter

3.3. Phenolsulfonephthalein solution:

0.24 g of phenolsulfonephthalein (phenol red) are dissolved in 24 mL sodium hydroxide solution, 0.1 M, and made up to the liter with distilled water.

3.4. pH 4.65 buffer solution:

Acetic acid, 2 M	500 mL
Sodium hydroxide, 2 M	250 mL
Distilled water to	1 L

3.5. Oxidizing solution:

Chloramine T	2 g
Distilled water to	1 L

Prepare this solution 48 hours before use

Storage: two weeks at ± 4 oC

3.6. Reducing solution:

Sodium thiosulfate	25 g/L
Distilled water to	1 L

3.7. Sulfuric acid, 10%(*v/v*): sulfuric acid (ρ_{20} = 1.84 g/mL) diluted 1/10.

3.8. Sulfuric acid, 1%(*v/v*): sulfuric acid (ρ_{20} = 1.84 g/mL) diluted 1/100.

3.9. Potassium bromide solution corresponding to 1 g of bromide per liter. 1.489g of potassium bromide, KBr, is dissolved in distilled water and made up to one liter.

4. Procedure

4.1. How to obtain ash and ash solution

Place 50 mL of wine in a silica dish of 7 cm diameter, add 0.5 mL 50% sodium hydroxide solution, (3.1), and 1 mL calcium hydroxide suspension (3.2). Check that the pH is at least pH 10. Leave the dish covered with a watch glass for 24 hours. Evaporate the liquid until dry on a boiling water bath. To accelerate the evaporation, a hot air current can be used in the final stages.

Ash as follows: place the dish 30 minutes in a furnace (2.2) at 525°C. After cooling, mix the residue with a little distilled water. Evaporate on the boiling water-bath. Ash again at 525°C. Repeat the operation until the ash is gray/white.

Mix the residue with 5 mL boiling distilled water. Add using a burette: first 10% sulfuric acid (3.7), then sufficient 1% sulfuric acid (3.8) to bring the pH to between 4 and 5 as measured by indicator paper. Let X mL = the volume added of sulfuric acid (3.7 & 3.8). Add 10.2 - (X+5) mL of distilled water. Crush the precipitated calcium sulfate with a glass rod. Transfer the content of the dish to a centrifugation tube. Centrifuge for 10 min. Place 8 to 9 mL of the clear supernatant into a test tube.

4.2. Qualitative test

This test is performed to determine if the bromide content of the wine is between 0 and 1 mg/L, which would enable the determination to be performed on the undiluted ash solution.

Place in a small test tube:

- 1 mL of ash solution
- 1 drop of pH 4.65 buffer solution

- 1 drop of phenolsulfonephthalein solution
- 1 drop of chloramine T solution

After exactly 1 minute, stop the reaction by adding 1 drop of sodium thiosulfate solution.

If the coloration obtained is yellow, brownish yellow or greenish yellow, the ash solution can be used undiluted.

If the obtained coloration is blue, purple or violet, the wine contains more than 1 mg of bromide per liter and the ash solution must be diluted 1/12 or 1/5 until the coloration obtained corresponds to the conditions above.

4.3. *Quantitative method*

Place in a test tube:

- 5 mL of ash solution, diluted or undiluted, add:
- 0.25 mL of pH 4.65 buffer solution
- 0.25 mL of phenolsulfonephthalein solution
- 0.25 mL T chloramine solution

Wait exactly 1 minute and add:

- 0.25 mL of sodium thiosulfate

Measure using a spectrophotometer set at 590 nm with a 1 cm cell, the difference in absorbance between the sample and the blank obtained by adding the same quantities of reagents to 5 mL of distilled water.

Note: When the bromide content is low (yellow coloration, slightly greenish) determine the absorbance in a cell of 2 cm optical path.

4.4. *Preparation of the calibration curve*

At the time of use, prepare a solution containing 10 mg of bromine per liter by making 2 successive dilutions (1/10) of standard potassium bromide solution, 1 g/L.

In a set of 8 test tubes, place 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 2.00 and 2.50 mL respectively of bromide standard, 1g/L (3.9) and make up to 5 mL with distilled water. (The solutions are equivalent to 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80 and 1 mg of bromine per liter of wine without dilution of the ash solution). Continue as in 4.3 using the calibration solutions instead of the ash solution. Determine the absorbance of these solutions and a blank, as in 4.3, using 5 mL of distilled water in the blank solution. The absorbance obtained corresponding to the bromide concentration is

plotted on a line that curves slightly towards the origin.

5. Expression of results

5.1. Calculations

The bromide content in wine is obtained by plotting on the calibration curve, the net absorbance of the ash solution (taking into account the thickness of the cell used and any dilution of the ash solution) and interpolating the bromide concentration. The total bromide content is expressed in milligrams per liter (mg/L) to two decimal places.

Bibliography

- DAMIENS A., *Bull. Sci. Pharmacologiques*, 1920, 27, 609; Ibid, 1921, 28, 37, 85 et 105.
- BALANTRE P., *J. Pharm. Chem.*, 1936, 24, 409.
- PERRONET M., ROCQUES Mme S., *Ann. Fals. Fraudes*, 1952, 45, 347.
- CABANIS J.-C., *Le brome dans les vins*, Thèse doct. Pharm., Montpellier, 1962.
- JAULMES P., BRUN Mme S., Cabanis J.-C., *Chim anal.*, 1962, 327.
- STELLA C., *Riv. Viticolt. Enol.*, Conegliano, 1967, 5.