OIV-MA-AS321-02 Chlorides

Type II method

1. Principle

Chloride is determined directly in the wine by potentiometry using an Ag/AgCl electrode.

2. Apparatus

2.1. pH/mV meter graduated at intervals of at least 2 mV.
2.2. Magnetic stirrer.
2.3. Ag/AgCl electrode with a saturated solution of potassium nitrate as electrolyte.
2.4. Microburette graduated in 0.01 mL.
2.5. Chronometer.

3. Reagents

3.1. Standard chloride solution: 2.1027 g of potassium chloride, KCl (max. 0.005% Br), dried before use, by leaving in a desiccator for several days, is dissolved in distilled water and made up to one liter. 1 mL of this solution contains 1 mg Cl^-.

3.2. Silver nitrate solution: 4.7912 g of analytical grade silver nitrate, $AgNO_3$, is dissolved in ethanol solution, 10% (*v/v*) and made up to one liter. 1 mL of this solution corresponds to 1 mg Cl^-.

3.3. Nitric acid, not less than 65% ($\square_{20}$ = 1.40 g/mL).

4. Procedure

4.1. Place 5.0 mL of standard chloride solution (3.1) into a 150 mL cylindrical vessel placed on a magnetic stirrer (2.2), dilute with distilled water to approximately 100 mL and acidify with 1.0 mL of nitric acid (3.3). After immersing the electrode, add silver nitrate solution (3.2) with the microburette, with moderate stirring using the following procedure: begin by adding the first 4 mL in 1 mL fractions and read the corresponding millivolt values. Add the next 2 mL in fractions of 0.20 mL. Finally, continue the addition in fractions of 1 mL until a total of 10 mL has been added. After each addition, wait for approximately 30 sec before reading the corresponding millivolt value. Plot the values obtained on a graph against the corresponding milliliters of titrant and determine the potential corresponding to the equivalence point.

4.2. Place 5 mL of the standard chloride solution (3.1) in a 150 mL cylindrical vessel with 95 mL of distilled water and 1 mL of nitric acid (3.3). Immerse the electrode and titrate, while stirring, until the potential of the equivalence point is obtained. This determination is repeated until a good degree of agreement in the results is obtained. This check must be carried out before each series of measurements of chloride in the samples.

4.3. Place 50 mL of wine into a 150 mL cylindrical vessel. Add 50 mL of distilled water and 1 mL of nitric acid (3.3) and titrate using the procedure described in 4.2.

5. Expression of results

5.1. *Calculations*

If n represents the number of milliliter of silver nitrate titrant, the chloride content in the tested liquid, is given by:

- 20 x n expressed as milligrams Cl per liter
- 0.5633 x n expressed as milliequivalents per liter,
- 32.9 x n expressed as milligrams of NaCl per liter.

2. *Repeatability (r):*

- r = 1.2 mg Cl/L
- r = 0.03 mEq/L
- r = 2.0 mg NaCl/L

3. *Reproducibility* (R)

- R= 4.1 mg/L
- R= 0.12 mEq/L
- R= 6.8 mg NaCl/L

6. Note: For very precise determination.

Refer to the complete titration curve obtained during determination of the test liquid (4.2).

a) Measure 50 mL of the wine to be analyzed into a 150 mL cylindrical vessel. Add 50 mL of distilled water and 1 mL of nitric acid (3.3). Titrate using silver nitrate solution (3.2), adding 0.5 mL at a time and recording the corresponding potential in millivolts. Estimate from this first titration the approximate volume of silver nitrate solution (3.2) required.

b) Repeat the determination adding 0.5 mL of titrant at a time until the volume added is 1.5 to 2 mL less that the volume determined in (a). Thereafter add 0.2 mL at a time. Continue to add the solution beyond the estimated equivalence point in a symmetrical manner, i.e. by adding 0.2 mL and then 0.5 mL at a time.

The end point of the measurement and the exact volume of silver nitrate consumed are obtained:

- either by drawing the curve and determining the equivalence point;

or by the following calculation:

$$V = V' + \Delta V_i \frac{\Delta\Delta E_1}{\Delta\Delta E_1 + \Delta\Delta E_2}$$

Where:

V= volume of titrant at the equivalence point;

V'= volume of titrant before the largest potential change;

ΔV_i= constant volume of the increments of titrant, i.e. 0.2 mL;

ΔE_1= second difference in potential before the largest potential change;

ΔE_2= second difference in potential after the largest potential change.

Example:

Volume of AgNO_3 titrating solution	E potential in mV	Difference ΔE	Second difference ΔΔE

0	204	4 4 6 6 6 8 12 22 44 34 26 20	
0.2	208		0
0.4	212		2
0.6	218		0
0.8	224		0
1.0	230		2
1.2	238		4
1.4	250		10
1.6	272		22
1.8	316		10
2.0	350		8
2.2	376		6
2.4	396		

In this example, the end point of the titration is between 1.6 and 1.8 mL: the largest potential change (ΔE = 44 mV) occurs in this interval. The volume of silver nitrate titrant consumed to measure the chlorides in the test sample is:

$$V = 1.6 + 0.2\,\frac{22}{22 + 10} = 1.74 mL$$

Bibliography

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