OIV-MA-AS322-01 Ammonium

Type IV method

1. Principle

Retention of the ammonium cation on a weak cation exchange resin, elution using an acidic solution, distillation of the eluent and determination of the ammonia in the distillate by titration with a standardized solution of hydrochloric acid.

2. Apparatus

2.1. *Cation exchange resin column*

A 50 mL burette with a glass stopcock fitted with a glass wool plug containing 25 g of weak cation exchange resin (e.g. Amberlite IR□50, 80□100 mesh).

Wash alternately with 1 M sodium hydroxide solution and 1 M hydrochloric acid solution. Wash the resin with distilled water until a negative reaction of chloride ion with silver nitrate is obtained. Pass 50 mL of neutral buffer slowly through the glass column, rinse with distilled water until phosphates begin to elute as detected using a saturated solution of lead acetate.

2.2. *Distillation apparatus*

Use the apparatus described in the chapter on *Alcoholic Strength 3.1*

The condensate is transferred to the conical flask through a drawn□out tube touching the bottom of the vessel.

Alternatively, it is possible to use the steam distillation apparatus used in the chapter on *Volatile Acidity 4.1* or other apparatus that can be used for the following experiments which check the purity of the reagents.

1. Place 40-45 mL of 30 % sodium hydroxide solution (*v/v*), 50 mL of water and 50 mL hydrochloric acid, 1 M, in the distillation flask. Distil half the volume and collect the distillate in 30 mL of boric acid solution, 40 g/L to which 5 drops of methyl red have been added. Adjust the color to pink by the addition of 0.1 mL of 0.1 M hydrochloric acid.

2. A test (similar to that described in a) is conducted using, 10 mL 0.05 M ammonium sulfate solution, containing 3.55 g/L of anhydrous ammonium sulfate, $(NH_4)_2SO_4$. In this case, between 10 and 10.1 mL 0.1 M hydrochloric acid must be used to obtain the change of color of the indicator.

3. Reagents

3.1. Hydrochloric acid solution, 1 M.

3.2. Sodium hydroxide, 1 M.

3.3. Neutral solution to wash the resin:

- *di*-sodium hydrogen phosphate $Na_2PO_4 12H_2O$: 15 g
- potassium *di*-hydrogen phosphate KH_2PO_4 : 3.35 g
- water to 1000 mL

Verify pH is 7 ± 0.2

3.4. Sodium hydroxide solution, 30% (*m/m*), □ = 1.33 g/mL

3.5. Hydrochloric acid solution, 0.1 M.

3.6. Phenolphthalein solution, 1% (*m/v*), in neutral ethanol, 96% (*V/V*)

3.7. Bromocresol green solution, 1% (*m/v*):

- bromocresol green 1 g
- dissolve in 0.1 M sodium hydroxide solution, 14 mL
- water to 100 mL

8. Methyl red ethanol/water solution, 0.2% (*v/v*):

- methyl red 0.2 g
- alcohol, 95% (*vol)* 60 mL
- water to 100 mL

9. Boric acid solution

- Boric acid 40g
- Water to 1000mL

Boric acid usually contains a small quantity of alkaline impurities and it is possible to correct this by adding 5 drops of indicator to this solution and adjusting to a pink color by means of few drops of 0.1 M hydrochloric acid (1 mL at most).

4. Procedure

Transfer 50 mL of the sample to be analyzed into a 250 mL beaker. Add a quantity of sodium hydroxide, 1 M, equal to half of (n□0.5) mL, where n is the volume sodium hydroxide solution, 0.1 M, used in the total acidity titration on 10 mL of wine. Pass this mixture through the cation exchange column (2.1) at a rate of one drop every two seconds. The eluent pH should lie between 4 and 5. Rinse the column with 50 mL of distilled water at the same flow rate.

Ammonium and other cations are quantitatively retained on the column. Amides, oligopeptides and nearly all amino acids are eluted by the washing procedure.

Elute the cations retained on the resin with 50 mL of 1 M hydrochloric acid, (3.1) and rinse with 50 mL distilled water.[*] The eluate and the water washings are combined in a 1 liter round bottom distillation flask.

Add one drop of phenolphthalein, 1% (*m/v*), and sufficient quantity of 30% sodium hydroxide solution (*m/v*)(3.4), to obtain a true alkaline reaction, constantly cooling the flask during this addition.

Distil about half the volume of the liquid from the distillation flask, into 30 mL of 4% boric acid (*m/v*)(3.9).

The distillate is titrated with 0.1 M hydrochloric acid (3.5), in the presence of bromocresol green or methyl red. Record the volume of hydrochloric acid used (n).

5. Expression of results

The content of ammonium (NH_4) ions is expressed in milligrams per liter to the nearest

whole number.

5.1. *Calculation*

The content of ammonium ions, expressed in milligrams per liter is:

- 36 x n

When wines with low ammonium content are analyzed, the determination is conducted using 100 mL of wine. In this case the quantity of ammonium is given by:

- 18 x n

Bibliography

Usual Method:

- Jaulmes P., *Analyse des vins,* 1951, 220, Montpellier
- Kourakou Mme S., *Ann. Fals. Exp. Chim.*, 1960, **53**, 337.

[*]* The column should be washed with 50 mL of neutral buffer solution and rinsed with water before using the column for another determination.