OIV-MA-AS313-08 Citric acid (Chemical method)

Type IV method

1. Principle

Citric acid is fixed with other wine acids onto an anion exchange column. The citramalic acid is obtained by fractionating the elute.

The citric acid is oxidized to acetone, which is separated by distillation. The acetaldehyde (ethanol) is oxidized to acetic acid and acetone is determined by iodometry.

2. Apparatus

2.1. Anion exchange column

In a 25 mL burette with tap, place a glass wool plug and pour 20 mL of Dowex resin 1 x 2.

Initially the resin goes through two complete regeneration cycles with alternate passages of hydrochloric acid solution, 1 M, and sodium hydroxide solution, 1 M. Rinse with 50 mL distilled water [(1)]. Saturate the resin with acetate ions by adding 250 mL acetic acid solution, 4 M. Wash with 100 mL distilled water.

The sample is passed through a column conforming to the description below. After the elution of the acids, rinse with 50 mL of distilled water and proceed once more to saturate the resin with acetic acid solution, 4 M. Rinse with 100 mL water. The resin is then ready for re-use.

2.2. Oxidation apparatus

The use of a distillation apparatus with oxidation round bottom flask, see drawing Fig. 1 facilitates the introduction of potassium permanganate, with a very regular flow.

If unavailable, use a 500 mL round bottom flask and a funnel fitted with a tap and a tapered end, to ensure that there is as regular flow of potassium permanganate as possible.

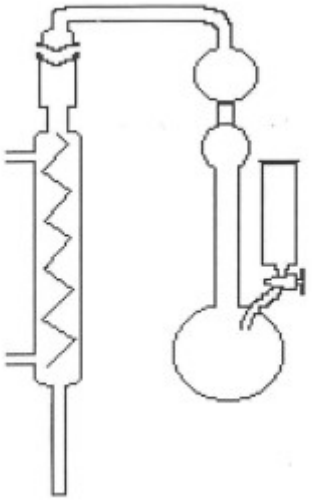

Fig. 1 : The oxidation and distillation apparatus for the determination of citric acid

3. Reagents

Dowex resin 1 x 2 (50 □ 100 mesh)
Acetic acid solution, 4 M
Acetic acid solution, 2.5 M
Sodium hydroxide solution, 2 M
Sulfuric acid (□20 = 1.84 g/mL) diluted $^{1}/_{5}$ (*v*/*v*)
Buffer solution of pH 3.2 □ 3.4
Potassium *di*-hydrogen phosphate KH_2PO_4: 150 g
Concentrated phosphoric acid ($□_{20}$ = 1.70 g/mL): 5 mL
Water to:1000 mL
Manganese sulfate solution, $MnSO_4H_2O$:50 g/L
Pumice stone
Potassium permanganate solution, 0.01 M
Sulfuric acid (□20 = 1.84 g/mL) diluted $^{1}/_{3}$ (*v*/*v*)
Potassium permanganate solution, 0.4 M

Iron (II) sulfate, $FeSO_4 7H_2O$, 40% (*m/v*)

Sodium hydroxide solution, 5 M

Iodine solution, 0.01 M

Sodium thiosulfate solution, 0.02 M

Thiodene or starch

4. Method

4.1. Separation of citramalic and citric acids

Pass 25 mL wine through the ion exchange Dowex 1 x 2 resin column (in an acetate form) at a flow rate of 3 mL every 2 minutes. Rinse the column three times with 20 mL distilled water. Elute the acids with 200 mL acetic acid solution, 2.5 M, at the same flow rate. This eluate fraction contains succinic, lactic, galacturonic, citramalic acids and nearly all of the malic acid.

Proceed with the elution of citric and tartaric acids by passing 100 mL sodium hydroxide solution, 2 M, through the column. Collect the eluate in the oxidation flask.

4.2. Oxidation

In the flask containing this second eluate, add sulfuric acid diluted 1/5 (about 20 mL) to bring the pH to between 3.2 and 3.8. Add 25 mL of pH 3.2-3.4 buffer solution, 1 mL of manganese sulfate solution and few grains of pumice stone.

Bring to the boil and distil over 50 mL, which is discarded.

Put the potassium permanganate solution, 0.01 M, in the funnel and introduce at 1 drop per second into the boiling eluate. The distillate is collected in a 500 mL ground glass stoppered flask containing few millimeters of water. The oxidation is carried on until a brown coloration of the liquid appears indicating an excess of permanganate.

4.3. Separation of the acetone

If the volume of the distillate is less than 90 mL, make up with distilled water, add 4.5 mL of sulfuric acid diluted $^1/_3$, and 5 mL potassium permanganate solution, 4.4 M. If the collected distillate largely exceeds this volume, complete to 180 mL and double the amounts of the reagents.

Under those conditions (i.e. sulfuric acid, 0.25 M, and potassium permanganate, 0.02 M), acetaldehyde (ethan0l) is oxidized into acetic acid while acetone remains intact.

The stoppered flask is left to rest for 45 minutes at room temperature. After which the excess of permanganate is destroyed by addition of iron (II) sulfate solution.

Distillate and collect about 50 mL of distillate in a ground glass stoppered flask

containing 5 mL sodium hydroxide solution, 5 M.

4.4. Determination of acetone

Add 25 mL iodine solution, 0.01 M, to the flask [*]. Leave for 20 minutes. Add 8 mL of sulfuric acid diluted 1/5. Titrate the excess of iodine by sodium thiosulfate, 0.02 M, in the presence of thiodene or starch, *n* mL.

Under the same conditions make a blank determination replacing 50 mL of distillate by 50 mL of distilled water.

n' mL of thiosulfate used.

5. Calculations

1 mL iodine, 0.01 M, corresponds to 0.64 mg of citric acid.

Under the same given conditions, the quantity of citric acid in milligrams per liter corresponds to:

$(n' - n) \times 25.6$

6. Expression of results

The concentration of citric acid is expressed in milligrams per liter.

Bibliography

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[(1)] The passage of the sodium hydroxide causes a contraction that, followed by a swelling during washings, stops the flow. It is recommended to stir the resin as soon as the first few mL of water pass through the column to stop the resin from sticking to the bottom of the burette.

[*] This amount is suitable for citric acid contents not exceeding 0.5 to 0.6 g/L. For higher contents the volume of the iodine solution prescribed is not sufficient and the solution does not take a yellow color which is typical of an iodine excess. In this case double or triple the quantity of iodine until the solution becomes really yellow. However, in exceptional cases where the amount of citric acid in wine exceeds 1.5 g/L, it is recommended to restart the analysis on 10 mL of wine.