OIV-MA-AS312-03B Methanol

Type IV method

1. Principle

The wine distillate is diluted to an ethanol content of 5% (*v/v*). Methanol is oxidized to formaldehyde (methanol) by potassium permanganate (acidified by phosphoric acid). The amount of formaldehyde is determined by the violet color formed by the reaction of chromotropic acid in a sulfuric medium. The intensity of the color is determined by spectrophotometry at 575 nm.

2. Method

2.1. Reagents

2.1.1. Chromotropic Acid

4,5□Dihydroxy□2,7□naphthalenedisulfonic acid, ($C_{10}H_8O_8S_2.2H_2O$), (MW 356.34 g)

White or light brown powder, soluble in water. The *di*-sodium salt of this acid that forms a yellow or light brown substance, and is very soluble in water can also be used.

Purification - The chromotropic acid must be pure and give a negligible color in the blank tests of reagents prepared with it. If this is not the case, proceed with purification using the following procedure:

Dissolve 10 g of chromotropic acid or its salt in 25 mL of distilled water. If the salt has been used, add 2 mL of concentrated sulfuric acid (□$_{□□}$ = 1.84 g/mL) to release the acid.

Add 50 mL of methanol, heat to boiling and filter. Add 100 mL of *iso*-propanol to precipitate the pure crystals of chromotropic acid, allow the crystals formed to drain and cold dry.

Reaction - The addition of ferric chloride (1 drop) to 10 mL of a 0.1 g/L solution should give a green color.

Sensitivity test - Dilute 0.5 mL of analytical grade formaldehyde to 1 L with water. To 5 mL of 0.05%chromotropic acid solution in sulfuric acid, 75% (*v/v*), add 0.1 mL of formaldehyde solution and heat to 70°C for 20 min. A violet color should be produced.

2.1.2. Chromotropic acid solution, 0.05%, in sulfuric acid solution, 75% (*v/v*).

Dissolve 50 mg chromotropic acid (2.1.1) or its sodium salt in 35 mL of distilled water. Cool this solution with iced water and add carefully 75 mL of concentrated sulfuric acid (□$_{□□}$ = 1.84 g/mL) in small portions, while mixing.

This solution must be prepared just before use.

2.1.3. Methanol, 5 g/L, standard solution in alcohol 5%, (*v/v*)

Pure methanol (E_{760} = 64.7 $\pm$ 0.2): 0.5 g

Absolute alcohol (without methanol): 50 mL

Distilled water to: 1 liter

2.1.4. Dilution solution

Absolute alcohol (without methanol): 50 mL

Distilled water to: 1 liter

2.1.5. Phosphoric acid solution, 50% (*m/v*)

2.1.6. Potassium permanganate solution, 5% (*m/v*)

2.1.7. Neutral sodium sulfite solution, 2% (*m/v*)

Solution rapidly oxidizes in air. Determine the exact strength by iodometric titration.

2.2. Procedure

Dilute the wine distillate (see chapter *Alcoholic strength*) to reduce the alcoholic strength to 5% vol.

Into a ground-glass stopper test tube place 0.5 mL of the diluted distillate, add 1 drop of phosphoric acid, 50%, 2 drops of potassium permanganate solution, 5%, shake and allow to stand for 10 minutes.

Decolorize the permanganate by adding a few drops, usually 4, of neutralized 2% sodium sulfite solution, (avoid any excess). Add 5 mL 0.05% chromotropic acid. Place in a water bath at 70°C for 20 min. Allow to cool.

Determine the absorbance As, at 570 nm, the zero of the absorbance being adjusted on the control sample prepared with 0.5 mL of the dilution solution.

Calibration curve

In a series of 50 mL volumetric spherical flasks, place 2.5, 5, 10, 15, 20, 25 mL respectively of the methanol, 0.5 g/L, solution in ethanol 5%. Make up to volume with a 5% ethanol solution. These solutions contain 25, 50, 100, 150, 200 and 250 mg of methanol per liter.

Treat simultaneously 0.5 mL of the dilution solution and 0.5 mL of each of the standard solutions, with the same technique as used to bring the wine distillate to an ethanol concentration of 5%.

Determine the absorbance of these solutions at 570 nm, in the conditions described above.

The graph of absorbance of the standard solutions as a function of concentration should be a straight line.

2.3. Calculations

Determine the methanol concentration, expressed in mg/L of the wine distillate brought to an alcoholic strength of 5% vol., and plotted as A_S on the calibration line.

Express the concentration in wine in mg/L taking into account the dilution performed to bring the strength to 5% vol.