OIV-MA-AS4-02C Detection of preservatives and fermentation inhibitors

Type IV method

1. Detection of the monohalogen derivatives of acetic acid

1.1. Principle

The monohalogen derivatives of acetic acid are extracted with ether from acidified wine. The ether is then extracted using a 0.5 M sodium hydroxide solution. The extraction solution must have the alkalinity maintained between 0.4 and 0.6 M. After the addition of thiosalicylic acid, the synthesis of the thioindigo is implemented by the following steps:

a) Condensation of the monohalogen derivative with thiosalicylic acid and formation of *ortho*-carboxylic phenylthioglycolic acid;

b) Cyclization of the acid formed in a heated alkaline medium, with the formation of thioindoxyl;

c) Oxidation of the thioindoxyl with potassium ferricyanide in an alkaline medium with formation of thioindigo, soluble in chloroform, in which it gives a red color.

1.2. Apparatus

Water bath at 100°C.

Mechanical stirrer.

Oven with a temperature of 200 ± 2°C.

1.3. Reage*nts*

Diethyl ether.

Hydrochloric acid solution diluted to 1/3 (v/v). Mix one part pure hydrochloric acid, □$_{20}$ = 1.19 g/mL, with 2 parts of distilled water.

Anhydrous sodium sulfate.

Thiosalicylic acid solution: thiosalicylic acid 3 g in 100 mL sodium hydroxide solution, 1.5 M.

Sodium hydroxide solution, 0.5 M

Potassium ferricyanide solution containing 2 g of $K_3Fe(CN)_6$ per 100 mL of water.

Chloroform.

1.4. Procedure

Place 100 mL of test wine in an extraction flask with a ground glass stopper; add 2 mL hydrochloric acid (1.3.2) and 100 mL diethyl ether (1.3.1). Shake the contents vigorously for a few seconds by hand, then for 1 h with a mechanical stirrer (1.2.2). Transfer to a separating funnel, allow to separate and recover the ether layer.

Shake the ether extract with 8 to 10 g of anhydrous sodium sulfate (1.3.3) for a few seconds.

Transfer the extract to the separating funnel, add 10 mL sodium hydroxide solution, 0.5 M (1.3.5); shake for 1 min. Allow to settle.

Remove 0.5 mL of the alkaline extract and check, by titration with sulfuric acid, 0.05 M, so that the strength falls between 0.4 and 0.6 M. Transfer the alkaline extract contained in the separating funnel into a test tube containing 1 mL of thiosalicylic acid solution. Adjust, if necessary the strength of the alkaline extract in order to bring it to the limits indicated, using a stronger sodium hydroxide solution of known strength. Shake the contents of the test tube for 30 seconds and transfer to an evaporating dish.

Place the dish on a water bath at 100°C blowing its surface with a current of cold air. Maintain the dish on the water bath at 100°C for exactly 1 hour; the residue may become practically dry in a shorter amount of time. If a crust forms on the surface of the residue during the evaporation, it is advisable to break or grind it up with a thin glass rod to facilitate the evaporation.

Place the dish in an oven maintained at 200 ± 2°C for exactly 30 minutes. After cooling, recover the contents of the dish with 4 mL of water; transfer into a separation funnel, add to the dish 3 mL of potassium ferricyanide solution to fully dissolve any remaining residue and add to the separating funnel. Shake for 30 seconds to facilitate oxidation. Add 5 mL chloroform, mix using 3 to 4 inversions. Allow to separate.

A pink or red color (according to the quantity of thioindigo formed) indicates the presence of monohalogen derivatives of acetic acid.

Sensitivity - The method allows detection of 1.5 to 2 mg monochloroacetic acid per liter of wine and corresponding quantities of the other derived monohalogens. Since the yield of miscellaneous extractions is not quantitative, this method cannot be used for determining the amount of these monohalogen derivatives in the wines.

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