INTERNATIONAL STANDARD

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Essential oils — Determination of carbonyl value — Potentiometric methods using hydroxylammonium chloride

Huiles essentielles — Détermination de l'indice de carbonyle — Méthodes potentiométriques au chlorure d'hydroxylammonium

Reference number
ISO 1279:1996(E)

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 1279 was prepared by Technical Committee ISO/TC 54, *Essential oils.*

This third edition cancels and replaces the second edition (ISO 1279:1984), which has been technically revised.

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Essential oils — Determination of carbonyl values — Potentiometric methods using hydroxylammonium chloride

1 SCOPE

This International Standard specifies two methods for the potentiometric determination of the carbonyl value of essential oils which contain carbonyl compounds, either aldehydes or ketones.

Method I (see clause 5), is based on a cold oximation reaction with hydroxylammonium chloride. It applies to essential oils whose main constituents are easily oximable aldehydes and ketones, with the exception of citronellal which needs a low temperature to avoid cyclization phenomena and acetalization.

NOTE 1 In the case of citronellal the free hydroxylamine method described in ISO 1271 should be used.

NOTE 2 Examples of essential oils concerned are lemongrass, hesperydus and rue.

Method II (see clause 6), is based on a hot oximation reaction with hydroxylammonium chloride. It applies to essential oils whose main constituents are ketones which are in general oximable only with difficulty.

NOTE 3 Examples of essential oils concerned are vetiver, Dalmation sage and white artemisia which contain methylketones oximable only with difficulty.

The International Standard for a specific essential oil will specify the method to be used, whether this is the free hydroxylamine method described in ISO 1271 or another method.

2 NORMATIVE REFERENCES

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 212:1973, *Essential oils - Sampling.*

ISO 356:1996, *Essential oils - Preparation of test sample.*

ISO 1271:1983, *Essential oils - Determination of carbonyl value - Free hydroxylamine method.*

3 DEFINITION

For the purposes of this International Standard, the following definition applies.

3.1 carbonyl value (of an essential oil): Number of milligrams of potassium hydroxide, per gram of essential oil, required to neutralize the hydrochloric acid liberated in the oximation reaction with hydroxylammonium chloride.

4 SAMPLING

Sampling shall be carried out in accordance with ISO 212.

5 METHOD I: METHOD OF COLD OXIMATION OF ALDEHYDES WITH HYDROXYLAMMONIUM CHLORIDE

5.1 Principle

Conversion of the carbonyl compounds to oximes by reaction with hydroxylammonium chloride.

Potentiometric determination with standard potassium hydroxide solution of the hydrochloric acid liberated by this reaction.

5.2 Reagents

5.2.1 Potassium hydroxide, standard solution, c(KOH) ≈ 0,5 mol/l in 95 % (*V*/*V*) ethanol.

5.2.2 Potassium hydroxide, standard solution c(KOH) ≈ 0,1 mol/l in 95 % (*V*/*V*) ethanol.

5.2.3 Ethanol, 95 % (*V*/*V*).

5.2.4 Bromophenol blue, 2 g/l solution.

Heat 0,2 g of Bromophenol blue in 3 ml of ethanolic potassium hydroxide solution (5.2.2) and 10 ml of ethanol (5.2.3). After cooling, dilute to 100 ml with ethanol.

5.2.5 Hydroxylammonium chloride, 50 g/l solution.

Dissolve 50 g of hydroxylammonium chloride in 100 ml of water and add about 800 ml of ethanol (5.2.3). Neutralize with the ethanolic potassium hydroxide solution(5.2.1) in the presence of 10 ml of the Bromophenol blue solution (5.2.4) to the mid-green endpoint of the indicator (equivalence point of pH 3,4) and dilute to 1000 ml with ethanol.

NOTE: The neutralized solution is stable for 1 week at least.

5.3 Apparatus

Usual laboratory equipment and, in particular, the following.

5.3.1 Beaker, of capacity 100 ml, tall form.

5.3.2 Automatic burette

5.3.3 Recorder

5.3.4 pH-meter

5.3.5 Glass electrode

5.3.6 Printer

5.4 Procedure

5.4.1 Preparation of test sample

See ISO 356.

5.4.2 Test portion

Weigh, to the nearest 0,001 g, between 1 g and 1,5 g of the essential oil.

NOTE: If the test sample should be larger, this will be stated in the appropriate International Standard for the oil concerned.

5.4.3 Determination

Add to the test portion (5.4.2) 25 ml of the hydroxylammonium chloride solution (5.2.5) and mix well. Add 3 drops of Bromophenol blue (5.2.4) and mix well. Dip the glass electrode (5.3.5) into the solution. Titrate with the potassium hydroxide solution (5.2.1) and mix the contents until the pH is lower than 4,20. It is important that the pH value does not exceed 4,20 during the determination.

Allow to stand for 15 min. Titrate with potassium hydroxide solution (5.2.1) to the equivalence point [the green to blue colour change of the Bromophenol blue (5.2.4)]. The equivalence point on pH is around a value of 3,4.

5.4.4 Expression of results

5.4.4.1 The content of carbonyl compounds, expressed as a percentage by mass, of the reference aldehyde specified is given by the formula:

$$\frac{M_r \times V \times c}{10m}$$

where

M_r is the relative molecular mass of the aldehyde specified in the standard specific to the essential oil concerned;

V is the volume, in millilitres, of potassium hydroxide solution (5.2.1) used in the titration;

c is the exact concentration, in moles per litre, of the potassium hydroxide solution;

m is the mass, in grams, of the test portion.

5.4.4.2 The carbonyl value, expressed in milligrams of potassium hydroxide per gram of essential oil, is given by the formula:

$$56{,}1\,\frac{V \times c}{m}$$

where the symbols are as given in 5.4.4.1.

6 METHOD II: METHOD OF HOT OXIMATION OF KETONES WITH HYDROXYL-AMMONIUM CHLORIDE

6.1 Principle

Conversion of the carbonyl compounds to oximes by reaction with hydroxylammonium chloride.

Determination with potassium hydroxide solution of the hydrochloric acid liberated by the reaction.

6.2 Reagents

Use the reagents given in 5.2.

6.3 Apparatus

Usual laboratory equipment and, in particular, the following.

6.3.1 Automatic burette, 50/0,1/B.

6.3.2 Beakers, of capacity 100 ml, tall form.

6.3.3 Flask, of capacity 100 ml, with reflux tube.

6.3.4 pH-meter

6.3.5 Glass electrode

6.3.6 Heater with magnetic stirrer

6.4 Procedure

6.4.1 Preparation of test sample

See ISO 356.

6.4.2 Test portion

Weigh, to the nearest 0,001 g, between 2 g and 2,5 g of the essential oil in the flask (6.3.3). See note to 5.4.2.

6.4.3 Determination

Add to the test portion (6.4.2) 25 ml of the hydroxylammonium chloride solution (5.2.5). Insert the glass electrode (6.3.5). Titrate with potassium hydroxide (5.2.1) until the pH is lower than 4,2. Add the reflux tube to the flask. Place the flask on the heater (6.3.6)and heat with stirring to a temperature sufficient to keep a constant reflux.

After 10 min, cool, add 3 drops of Bromophenol blue (5.2.4) and slowly titrate with the potassium hydroxide solution (5.2.1) to a pH lower than 4,22. It is important that the pH value does not reach or exceed 4,22 during the determination. Stop when the colour begins to change. Put the flask back on the heater.

Repeat this operation every 10 min, as many times as necessary, until the addition of a supplementary drop of solution is enough to pass the equivalence point.

NOTE: The determination time is usually 2 h, but for certain fragrances this is not enough. In this case, go on until the inflexion curve.

6.4.4 Expression of results

Trace the pH curve as a function of the volume V of potassium hydroxide (5.2.1) used in the titration:

$$pH = f(V)$$

Note the equivalence point.

Calculate the content of carbonyl compounds using the formula given in 5.4.4.1.

Calculate the carbonyl value using the formula given in 5.4.4.2.

7 TEST REPORT

The test report shall include the method used and the results obtained. It shall also mention any operating details not specified in this International Standard or regarded as optional, together with details of any incidents which might have influenced the results.

The test report shall include all details necessary for the complete identification of the sample.

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