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Essential oils — Determination of water content — Karl Fischer method

Huiles essentielles — Détermination de la teneur en eau — Méthode de Karl Fischer

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

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Essential oils — Determination of water content — Karl Fischer method

1 Scope

This International Standard specifies a method for the determination of the water content of essential oils by the Karl Fischer method.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, this publication do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 760, *Determination of water content — Karl Fischer method (General method).*

3 Terms and definitions

For the purposes of this International Standard, the following term and definition apply.

3.1
water content
amount of water present in the essential oil considered, determined in accordance with the procedure specified in this International Standard

NOTE Water content is expressed as a mass fraction in percent [formerly designated as % (m/m)].

4 Principle

The water present in a test portion is absorbed with dried methanol. The water is allowed to react with the Karl Fischer reagent without pyridine, previously standardized by titration using a Karl Fischer apparatus. The endpoint of the reaction is obtained by an electrometric method.

5 Reactions

During the determination of water according to the Karl Fischer method, the water present in the sample reacts, in the presence of an amine and an alcohol, with iodine and sulfur dioxide:

$$\mathrm{H_2O + I_2 + SO_2 + ROH + 3R}_n\mathrm{NH}_{3-n} \rightarrow \mathrm{2R}_n\mathrm{NH}_{3-n}\mathrm{HI + R}_n\mathrm{NH}_{3-n}\mathrm{HSO_4R}$$

where R is an alkyl or alkoxyl group.

The endpoint of the reaction is obtained electrometrically by a surplus of iodine.

6 Reagents and materials

Use only reagents of recognized analytical quality and distilled or demineralized water or water of equivalent purity.

6.1 Methanol, containing not more than 0,05 % of water by mass. If the reagent contains more than this quantity of water, dry it by distillation in an inert atmosphere (nitrogen, helium etc.) with magnesium turnings activated with iodine. Collect the distillate in a flask protected from atmospheric moisture by means of a guard tube with a desiccant. Alternatively, use 2-methoxyethanol (6.2).

6.2 2-Methoxyethanol (ethylene glycol monomethyl ether or methylcellosolve), containing not more than 0,05 % of water by mass. If the reagent contains more than this quantity of water, dry it by distillation, rejecting the first few millilitres of the distillate which contains water.

6.3 Karl Fischer reagent,1) free from pyridine, having a titre lower than 4,0 mg/ml; one or two component system. The titre shall be determined daily.

If carbonyl compounds are present, an adapted Karl Fischer reagent shall be used.

6.4 Tartaric acid, dipotassium salt ($C_4H_4O_6K_2 \cdot ½H_2O$), or **water**.

7 Apparatus

See ISO 760.

All the glassware used shall be previously dried for 30 min in an oven maintained at approximately 130 °C, then stored in a desiccator containing a desiccant then allowed to cool to room temperature.

The automatic burettes should not be heated in an oven. They should be dried with absolute ethanol or acetone and a dry air stream.

Usual laboratory apparatus and, in particular, the following.

7.1 Titration apparatus

There is commercially available apparatus for the automatic determination of the water content according to the Karl Fischer method, which consists of the items given in 7.1.1 to 7.1.5.

7.1.1 Endpoint indicator, for titration according to the electrometric method.

7.1.2 Platinum double electrode.

7.1.3 Magnetic stirrer, fitted with a stirring rod covered with polytetrafluoroethylene, operating at a rotational frequency of 150 r/min to 300 r/min.

7.1.4 Titration vessel, of approximately 200 ml capacity, with at least three ground glass sockets.

Connect one of the ground glass sockets to the automatic burette. Place the platinum double electrode in the automatic burette, and the platinum double electrode in the second one, and use the third one to add the reagents and the sample. A discharge tap at the bottom of the vessel is an advantage. Connect it to the vessel with a capillary tube having a volume of not more than 0,5 ml. Close all ventilation sockets in the titration vessel either with drying tubes which have been charged with an effective drying agent or molecular sieves, or with drying receivers filled with the reagent (6.3) in order to avoid the influence of moisture from the air.

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1) Suitable products are commercially available.

7.1.5 Automatic burette, of 25 ml capacity, graduated in intervals of 0,05 ml, and reagent bottle and drying tubes.

The minimum interval of the burette depends on data from the manufacturer (e.g. 0,02 ml).

Protect the reagent bottle, the burette and the Karl Fischer reagent (6.3) from moisture and light.

7.2 Oven, regulated at 130 °C ± 5 °C, to dry the glassware.

8 Sampling

A recommended sampling method is given in ISO 212.

NOTE Attention is drawn to the fact that the method given in ISO 356 cannot be used to prepare the test samples as it specifies that the sample has to be dried.

9 Procedure

9.1 Preparation of the titration apparatus

Prepare the titration apparatus (7.1) in accordance with the manufacturer's instructions and lubricate every joint. The air-tightness of the titration vessel is of special importance.

Place 25 ml of the dried methanol (6.1) or of the 2-methoxyethanol (6.2) in the titration vessel (7.1.4). Be sure that the metallic parts of the platinum double electrode (7.1.2) are completely immersed. Start the automatic titration (7.1.3).

Add Karl Fischer reagent (6.3) to enable a reaction to take place with the traces of water in the methanol. The titration and the recognition of the endpoint is controlled automatically by the apparatus.

9.2 Standardization of the Karl Fischer reagent

Prepare the titration apparatus as indicated in 9.1.

Weigh, to the nearest 0,000 1 g, approximately 0,300 g of the potassium bitartrate (6.4). Introduce quantitatively and as fast as possible, the mass (m_1) of the bitartrate to the titration vessel (7.1.4).

Titrate the known amount of water introduced in the vessel by the dipotassium salt of tartaric acid, with the Karl Fischer reagent to perform the standardization. The titration and the endpoint are controlled automatically by the apparatus.

Record the volume (V_1) of the reagent used with the bitartrate.

Standardization of the reagent may also be carried out with a known mass of pure water (m_2), approximately 0,040 g, measured to the nearest 0,000 1 g.

Record the volume (V_2) of the reagent used with the water.

Carry out several titrations without changing the titration vessel. Use the arithmetic mean of the results for the calculation of the water equivalent of the reagent (10.1).

9.3 Determination

Prepare the titration apparatus as indicated in 9.1.

Depending on the expected water content of the sample, take a portion (V_0 ml) of the sample (10,0 ml if the water content is $< 3\%$ or 25,0 ml if the water content is $< 1\%$) and place it very quickly in the titration vessel at a temperature below 25 °C, as slurring and dissolution may occur.

Start the automatic titration while stirring with the magnetic stirrer (7.1.3). The titration and the recognition of the endpoint are controlled automatically by the apparatus.

Record the volume (V_3) of the reagent used.

Carry out three titrations on each sample and use the arithmetic mean of the results for the calculation (10.2).

10 Expression of results

10.1 Water equivalent of the Karl Fischer reagent

The calculation of the water equivalent, T, of the Karl Fischer reagent (6.3), expressed in milligrams of water per millilitre of reagent, is given by one of the formulae:

$$T = \frac{m_1}{V_1} \times \frac{0{,}5 \times 18}{235{,}28} \quad \text{or} \quad T = \frac{m_2}{V_2}$$

where

m_1	is the mass, in milligrams, of the dipotassium salt of tartaric acid (6.4) introduced when this reagent is used for standardization (9.2);
V_1	is the volume, in millilitres, of the reagent (6.3) used for the standardization;
0,5	is the number of water moles per mole of dipotassium salt of tartaric acid;
18	is the relative molecular mass of water;
235,28	is the relative molecular mass of dipotassium salt of tartaric acid;
m_2	is the mass, in milligrams, of the known pure water (6.4), if water is used for standardization;
V_2	is the volume, in millilitres, of the Karl Fischer reagent (6.3) used for the standardization.

10.2 Water content of the essential oil

The water content of the essential oil, W_w, expressed as a mass fraction in percent, is given by the formula:

$$W_w = \frac{V_3 \times T}{V_0 \times \rho \times 10}$$

where

V_0	is the volume, in millilitres, of the test portion (9.3);
ρ	is the density of the sample, in grams per millilitre, at 20 °C;
V_3	is the volume, in millilitres, of the Karl Fischer reagent (6.3) used for the determination (9.3);
T	is the water equivalent, in milligrams of water per millilitre of the Karl Fischer reagent (6.3), calculated in accordance with 10.1.

To calculate the density of the essential oil, multiply the value obtained for the relative density by the density of water at 20 °C, that is 0,998 23 g/ml.

11 Test report

The test report shall specify:

- the method used,
- the test result obtained;
- any operating details not specified in this International Standard, or regarded as optional, as well as any circumstances that may have influenced the test result.

The test report shall include all information required for the complete identification of the sample.

Bibliography

[1] ISO 212, *Essential oils — Sampling.*

[2] ISO 356, *Essential oils — Preparation of test samples*.