INTERNATIONAL STANDARD ISO 3794

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Essential oils (containing tertiary alcohols) — Estimation of free alcohols content by determination of ester value after acetylation

Huiles essentielles (contenant des alcools tertiaires) — Évaluation de la teneur en alcools libres par détermination de l'indice d'ester après acétylation

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3794 was drawn up by Technical Committee ISO/TC 54, *Essential oils,* and was circulated to the Member Bodies in February 1975.

It has been approved by the Member Bodies of the following countries :

Belgium	Italy	Sri Lanka
Canada	Netherlands	Turkey
France	Portugal	Yugoslavia
Germany	South Africa, Rep. of	
India	Spain	

No Member Body expressed disapproval of the document.

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Essential oils (containing tertiary alcohols) — Estimation of free alcohols content by determination of ester value after acetylation

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for estimating the free alcohols content of essential oils, by determination of ester value after acetylation.[1)]

This method is applicable to essential oils containing an appreciable proportion of tertiary alcohols, namely of linalol and terpineol, ISO/R 1241 not being applicable to those oils.

This method is not applicable to essential oils containing appreciable proportions of phenols, anthranilates, lactones and aldehydes, as stated in ISO/R 1241.

2 REFERENCES

ISO 212, *Essential oils — Sampling.*

ISO 356, *Essential oils — Preparation of test sample.*

ISO/R 709, *Determination of ester value and calculation of ester content of essential oils.*

ISO/R 1241, *Essential oils — Estimation of free alcohols content by determination of ester value after acetylation.*

3 DEFINITION

ester value after acetylation : The number of milligrams of potassium hydroxide which are required to neutralize the acids liberated by the hydrolysis of the esters contained in 1 g of the acetylated oil.

4 PRINCIPLE

Acetylation of the essential oil by acetyl chloride and acetic anhydride, in the presence of dimethylaniline. Isolation and drying of the acetylated oil. Determination of the ester value after acetylation. Calculation of the free alcohols content taking into account the ester value of the same but non-acetylated essential oil.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

5.1 Acetyl chloride.

5.2 Dimethylaniline, freshly distilled and free from monomethylaniline and aniline.

5.3 Acetic anhydride, concentration not less than 98 %.

5.4 Anhydrous magnesium sulphate or sodium sulphate, recently desiccated and powdered.

5.5 Sodium sulphate (Na_2SO_4), 100 g/l solution.

5.6 Hydrochloric acid solution.

Dilute 5 parts of hydrochloric acid (ρ_{20} 1,19 g/ml) to 100 parts by volume with the sodium sulphate solution (5.5).

5.7 Sodium hydrogen carbonate solution.

Dissolve 50 g of sodium hydrogen carbonate in 1 l of the sodium sulphate solution (5.5).

5.8 Potassium hydroxide, 0,1 N aqueous solution.

5.9 Potassium hydroxide, 0,5 N standard volumetric solution in 95 % (*V*/*V*) ethanol.

5.10 Hydrochloric acid, 0,5 N standard volumetric solution.

5.11 Litmus paper.

5.12 Phenolphthalein, 2 g/l solution in 95 % (*V*/*V*) ethanol.

6 APPARATUS

Ordinary laboratory equipment, and

6.1 Acetylation apparatus, comprising a 100 ml round-bottomed acetylation flask connected by a ground glass joint to a glass tube at least 1 m long and with an inside diameter of about 10 mm, to act as an air condenser, and a ground glass stopper to fit the flask.

Both the round-bottomed flask and the condenser shall be carefully dried before use.

1) This method is usually known as the "Fiore method".

6.2 Measuring cylinders, capacity 10 ml.

6.3 Measuring cylinders, capacity 50 ml.

6.4 Melting ice bath.

6.5 Water bath, set at 40 ± 1 °C.

6.6 Boiling water bath.

6.7 Separating funnel, capacity at least 250 ml.

6.8 Saponification flask, capacity 250 ml, made of alkali-resistant glass and to which can be fitted a reflux condenser.

6.9 Calibrated burettes, capacity 50 ml, graduated in 0,1 ml.

7 SAMPLING

See ISO 212.

8 PROCEDURE

8.1 Preparation of test sample

See ISO 356.

8.2 Determination of ester value before acetylation

Determine the ester value before acetylation in accordance with ISO/R 709.

8.3 Acetylation

Measure, with a cylinder (6.2) 10 ml of the test sample and pour into the round-bottomed flask (6.1). Add 20 ml of the dimethylaniline (5.2), mix thoroughly and cool in the melting ice bath (6.4).

Then add, keeping the round-bottomed flask in the melting ice bath, 8 ml of the acetyl chloride (5.1) and 5 ml of the acetic anhydride (5.3). Remove the round-bottomed flask from the melting ice bath and allow it to stand at room temperature for 30 min. Place the flask in the water bath (6.5) at a temperature of 40 ± 1 °C and let it remain for 16 h.

Cool to room temperature and pour the liquid into the separating funnel (6.7), then wash the acetylated oil as follows :

a) twice with 75 ml of the sodium sulphate solution (5.5);

b) at least five times with 50 ml portions of the hydrochloric acid solution (5.6), until the washings are free from dimethylaniline[1];

c) twice with 25 ml of the sodium hydrogen carbonate solution (5.7);

d) twice with 25 ml of the sodium sulphate solution (5.5);

After each addition, shake vigorously for 30 s and allow to settle until the two layers are clearly separated. During the last separating operation, check the neutral condition of the aqueous layer with the litmus paper (5.11).

Transfer the oily layer into a flask, dry over anhydrous magnesium sulphate or sodium sulphate (5.4) and filter.

8.4 Determination of ester value after acetylation

Determine the ester value in accordance with ISO/R 709.

9 EXPRESSION OF RESULTS

The free alcohols content, expressed as a percentage by mass, is given by the formula

$$\frac{M\,(\text{E.V.}_2 - \text{E.V.}_1)}{561 - 0{,}42\ \text{E.V.}_2}$$

The combined alcohols content, expressed as a percentage by mass, can be calculated from the ester value, using the formula

$$\frac{M \times \text{E.V.}_1}{561}$$

The total alcohols content, expressed as a percentage by mass, is obtained by adding the two previous percentages.

In the above formulas,

M is the molecular mass of the reference alcohol specified in the International Standard for the essential oil being tested;

E.V._1 is the ester value of the oil before acetylation (8.2), determined according to ISO/R 709;

E.V._2 is the ester value of the oil after acetylation (8.4), determined according to ISO/R 709.

10 TEST REPORT

The test report shall state the method used and the result obtained. It shall also mention any operating conditions not specified in this International Standard, or regarded as optional, as well as any circumstances that might have influenced the result.

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

1) Test as follows for the absence of dimethylaniline : add to 15 ml of the hydrochloric washing 2 drops of a saturated solution of potassium permanganate. Shake vigorously. If an orange-yellow colour appears in less than 15 s, dimethylaniline is present.