BS EN ISO 17226-3:2011

BSI Standards Publication

Leather — Chemical determination of formaldehyde content

Part 3: Determination of formaldehyde emissions from leather (ISO 17226-3:2011)

National foreword

This British Standard is the UK implementation of EN ISO 17226-3:2011.

The UK participation in its preparation was entrusted to Technical Committee TCI/69, Footwear, leather and coated fabrics.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Cuir - Dosage chimique du formaldéhyde - Partie 3: Dosage du formaldéhyde émis par le cuir (ISO 17226-3:2011)

Leder - Chemische Bestimmung des Formaldehydgehalts - Teil 3: Bestimmung der Formaldehydemissionen aus Leder (ISO 17226-3:2011)

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Foreword

This document (EN ISO 17226-3:2011) has been prepared by Technical Committee CEN/TC 289 “Leather”, the secretariat of which is held by UNI, in collaboration with the International Union of Leather Technologists and Chemists Societies.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2011, and conflicting national standards shall be withdrawn at the latest by November 2011.

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Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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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ISO 17226-3 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 289, *Leather*, in collaboration with Chemical Test Commission of the International Union of Leather Technologists and Chemists Societies (IUC Commission, IULTCS), in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

IULTCS, originally formed in 1897, is a world-wide organization of professional leather societies to further the advancement of leather science and technology. IULTCS has three Commissions, which are responsible for establishing international methods for the sampling and testing of leather. ISO recognizes IULTCS as an international standardizing body for the preparation of test methods for leather.

ISO 17226 consists of the following parts, under the general title *Leather — Chemical determination of formaldehyde content*:

— *Part 1: Method using high performance liquid chromatography*

— *Part 2: Method using colorimetric analysis*

— *Part 3: Determination of formaldehyde emissions from leather*

INTERNATIONAL STANDARD

ISO 17226-3:2011(E)
IULTCS/IUC 19-3:2011(E)

Leather — Chemical determination of formaldehyde content —

Part 3:
Determination of formaldehyde emissions from leather

1 Scope

This part of ISO 17226 specifies a method for determining the emission of formaldehyde from leathers. This method is based on high performance liquid chromatography (HPLC). It is selective and also allows the emission of other low molecular aldehydes and ketones to be observed.

This part of ISO 17226 deals with the release of formaldehyde to the gas phase. Therefore, the obtained results are not comparable with the results of methods described in ISO 17726-1 and ISO 17226-2 which are based on extraction with liquid water.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2418, *Leather — Chemical, physical and mechanical and fastness tests — Sampling location*

ISO 2419, *Leather — Physical and mechanical tests — Sample preparation and conditioning*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 4684, *Leather — Chemical tests — Determination of volatile matter*

3 Principle

A specimen with defined dimensions is held above demineralized water in a sealed bottle and is heated at constant temperature for a specific period. Afterwards, the bottle is cooled and the formaldehyde absorbed into the water is analysed. The water is mixed with 2,4-dinitrophenylhydrazine, whereby aldehydes and ketones react to give the respective hydrazones. These are separated by means of a reversed-phase HPLC method, detected at 360 nm and quantified.

4 Reagents

Use only reagents of recognized analytical grade, unless otherwise stated. The water shall be of grade 3 in accordance with ISO 3696:1987. All solutions are aqueous solutions.

4.1 Reagents for the formaldehyde stock solution

4.1.1 Formaldehyde solution, approximately 37 % (mass fraction).

4.1.2 Iodine solution, 0,05 mol/l, i.e. 12,68 g iodine/l.

4.1.3 Sodium hydroxide solution, 2,0 mol/l.

4.1.4 Sulfuric acid solution, 2,0 mol/l.

4.1.5 Sodium thiosulfate solution, 0,1 mol/l.

4.1.6 Starch solution, 1 %, i.e. 1 g in 100 ml water.

4.2 Reagents for the HPLC method

4.2.1 Dinitrophenylhydrazine (DNPH) solution, consisting of 0,3 g DNPH (2,4-dinitrophenylhydrazine) dissolved in 100 ml concentrated *o*-phosphoric acid (85 % mass fraction); (DNPH recrystallized from 25 % mass fraction, acetonitrile in water).

4.2.2 Acetonitrile.

5 Apparatus

Use usual laboratory equipment and, in particular, the following.

5.1 One (1) l polyethylene bottle with hook implement integrated in the lid (see Figure 1). Hook made of stainless steel with seals, positioned inside the lid of the test bottle.

5.2 Volumetric flasks, of capacities 10 ml, 500 ml and 1 000 ml.

5.3 Erlenmeyer flasks, of capacities 100 ml and 250 ml.

5.4 Pipettes, of capacities 5 ml and 50 ml.

5.5 Oven, capable of being maintained at (60 ± 2) °C.

5.6 Analytical balance, weighing to an accuracy of 1 mg.

5.7 HPLC system with UV detection, e.g. 360 nm.

5.8 Press knife, in accordance with ISO 2419, suitable for cutting specimens of (100 × 40) mm.

5.9 Hole punch for holes of 3 mm to 4 mm in diameter.

5.10 Membrane filter, polyamide, 0,45 µm.

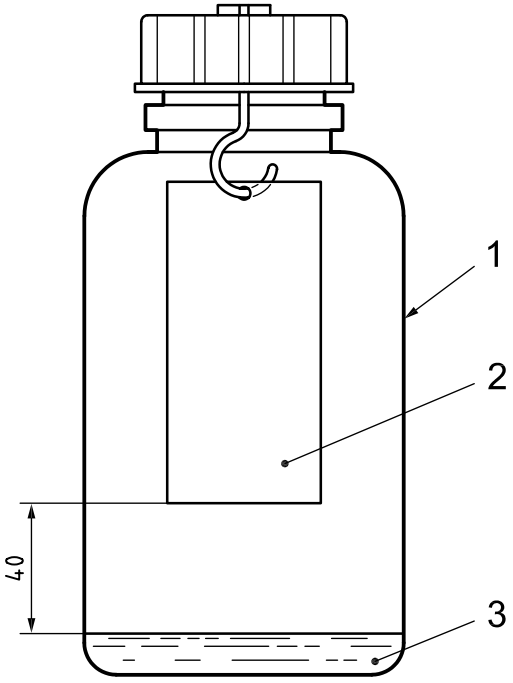
6 Methods

6.1 Procedure for the determination of formaldehyde in the stock solution

6.1.1 Preparation of the formaldehyde stock solution

Pipette 5 ml of the formaldehyde solution (4.1.1) into a 1 000 ml volumetric flask (5.2) which contains approximately 100 ml water, then fill the flask with demineralized water up to the mark. This solution is the formaldehyde stock solution.

Dimensions in millimetres



Key

1 polyethylene bottle
2 sample
3 water

Figure 1 — Polyethylene bottle with specimen and water

6.1.2 Determination

Pipette 10 ml from this solution into a 250 ml Erlenmeyer flask (5.3) and mix with the 50 ml iodine solution (4.1.2). Add sodium hydroxide (4.1.3) until it turns yellow. Allow it to react for 15 min ± 1 min at a temperature between 18 °C and 26 °C, then add 15 ml of sulfuric acid (4.1.4) while swirling.

After adding 2 ml of starch solution (4.1.6), titrate the excess iodine with sodium thiosulfate (4.1.5) until the colour changes. Make three individual determinations. Titrate at least two blank solutions in the same manner.

$$\rho_{FA} = \frac{(V_0 - V_1) \times c_1 \times M_{FA}}{2} \quad (1)$$

where

ρ_{FA} is the concentration of the formaldehyde stock solution, in milligrams per 10 ml (mg/10 ml);

V_0 is the volume of the thiosulfate solution for the blank solution, in millilitres (ml);

V_1 is the volume of the thiosulfate solution for the sample solution, in millilitres (ml);

M_{FA} is the relative molecular mass of formaldehyde, 30,02 g/mol;

c_1 is the concentration of the thiosulfate solution, in moles per litre (mol/l).

6.2 Procedure for the determination of formaldehyde emission by the HPLC method

6.2.1 Shipment and storage leather for this method

To avoid cross-contamination and loss of formaldehyde during shipment and storage, the leather samples should be sealed in an inert gastight plastic bag.

NOTE Multiple-layer polyethylene bags with a metal layer inside are appropriate.

6.2.2 Sampling

Sample six specimens of (100 × 40) mm, selecting them in accordance with ISO 2418 and applying the press knife (5.8) in accordance with ISO 2419. Use five of these specimens for the determination of formaldehyde emission. Use the sixth specimen for the determination of volatile matter.

To fasten specimens 1 to 5, punch a hole of 3 mm to 4 mm near the centre and 10 mm from the upper edge in each one.

6.2.3 Determination of volatile matter

If requested to calculate the result on the basis of dry substance, use the sixth specimen to determine the volatile matter in accordance with ISO 4684. Do not grind or cut the specimen.

6.2.4 Determination of formaldehyde emission

Weigh five of the specimens to 0,01 g.

Pipette 50 ml aliquots of demineralized water into each of the 1 l polyethylene bottles which have to be clean and dry. Attach a specimen to each hook and seal the 5 bottles.

Pipette 50 ml aliquots of demineralized water into an additional clean 1 l polyethylene bottle. Seal the bottle without a specimen. Use this bottle for a blank test.

As soon as the bottles have been sealed, store them for (180 ± 15) min in a heated oven at (60 ± 2) °C.

Remove the bottles from the oven and allow them to cool at room temperature for approximately 1 h. Then remove the leather specimens from the bottles and immediately analyse the formaldehyde absorbed in the water as described in 6.2.5.

6.2.5 Reaction with DNPH

Pipette 4,0 ml of acetonitrile (4.2.2), a 5,0 ml aliquot of water from the polyethylene bottle (5.1) and 0,5 ml of DNPH solution (4.2.1) into a 10 ml volumetric flask (5.2). Fill the volumetric flask with demineralized water up to the mark and shake it briefly by hand to mix the components. Allow it to stand at least 60 min, but not more than 180 min. After filtering through a membrane filter (5.10), analyse the sample using HPLC. If the concentration is out of the calibration range, take smaller aliquots.

6.2.6 HPLC conditions

These conditions are only recommendations. The method used should be verified using the recovery rate determination.

The chromatographic system should be checked every day, preferably using a sample containing 2 mg formaldehyde/l, in order to determine the recovery rate. The content of the sample should be determined according the procedure described for the calibration.

Flow rate: 1,0 ml/min

Mobile phase: acetonitrile/water, 60:40

Separation column: C18 reversed-phase column with precolumn (1 cm, RP18)

UV detection wavelength: 360 nm

Injection volume: 20 µl

6.2.7 Calibration of HPLC

Pipette 0,5 ml of the formaldehyde stock solution obtained in 6.1.1, with an exactly known formaldehyde content, into a 500 ml volumetric flask (5.2), pre-filled with approximately 100 ml water. Mix together and fill to the mark with water, and mix again. This solution is the standard solution for calibration purposes, i.e. the standard solution is approximately 2 µg formaldehyde/ml.

In each of six 10 ml volumetric flasks (5.2), add 4 ml acetonitrile (4.2.2), then add a concentration series of 0,25 ml; 0,5 ml; 1,0 ml; 2,0 ml; 3,0 ml; 5,0 ml, respectively, of the standard solution. Immediately after adding the formaldehyde solution, mix each flask and add 0,5 ml DNPH solution (4.2.1). Fill the flasks up to the mark with demineralized water and mix. After at least 60 min, but not more than 180 min, analyse the samples using HPLC after filtration through a membrane filter (5.10). Effect the calibration through plotting a graph of the formaldehyde derivative peak area versus the concentration in µg/10 ml.

6.2.8 Calculation of the formaldehyde content in leather samples

$$w_{FA} = \frac{(A_{sample} - A_{blank}) \times 10}{m \times b} \times D \qquad (2)$$

where

w_{FA} is the amount of emitted formaldehyde, in milligrams per kilogram (mg/kg), rounded to 0,1 mg/kg;

A_{sample} is the area of the leather sample determined by HPLC with UV detection;

A_{blank} is the area of the blank determined by HPLC with UV detection;

b is the slope of the calibration curve (10 ml/µg);

D is the dilution factor, in millilitres (ml), usually 1; dilution is necessary if the determined area of the sample is out of the range of the calibration curve;

m is the mass of leather weighed, in grams (g).

7 Expression of results

Express the formaldehyde concentration to the nearest 0,1 mg/kg based on the mass of leather sample tested.

If the results are to be reported on the basis of dry substance, multiply the results above by the factor $100/(100 - w)$, where w is the moisture content, expressed as a percentage, according to ISO 4684. If the results are presented on the basis of dry substance, clearly mention this in the test report.

If a single value differs by more than 20 % from the mean value, test two additional specimens.

8 Test report

The test report shall include the following:

a) a reference to this part of ISO 17226 (i.e. ISO 17226-3);

b) type, origin and designation of the leather sample analysed;

c) mean value for the formaldehyde emission, in milligrams per kilogram, to the nearest 0,1 mg/kg;

d) if requested, mean value for the formaldehyde emission, in milligrams per kilogram, to the nearest 0,1 mg/kg, calculated on dry substance and volatile matter as a percentage;

e) number of specimens tested;

f) any deviations from the analytical procedure, in particular any additional steps performed;

g) date of the test;

h) if the results are determined on the basis of the dry substance, this and the dry substance shall be reported.

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