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Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine dimethylformamide in footwear materials

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Chaussures — Substances critiques potentiellement présentes dans les chaussures et les composants de chaussures — Méthode d'essai pour déterminer quantitativement le diméthylformamide dans les matériaux de chaussures

ISO/FDIS 16189

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Contents

| | Page |
|--|----------|
| Foreword | iv |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Terms and definitions | 1 |
| 4 Principle | 1 |
| 5 Reagents | 1 |
| 6 Apparatus | 2 |
| 7 Preparation of sample | 3 |
| 7.1 Sampling | 3 |
| 7.2 Extraction | 3 |
| 8 Determination with GC-MS | 3 |
| 8.1 Calibration standard | 3 |
| 8.2 Examples of instrumental method | 3 |
| 9 Expression of results | 4 |
| 9.1 Calibration curve | 4 |
| 10 Performance of the method | 4 |
| 11 Test report | 4 |
| Annex A (informative) Suggested parameters for GC-MS determination of DMF | 5 |
| Bibliography | 6 |

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 216, *Footwear*, in collaboration with the European Committee for Standardization (CEN) – Technical Committee CEN/TC 309, *Footwear*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This first edition of ISO 16189 cancels and replaces ISO/TS 16189:2013, which has been technically revised.

The main changes compared to the previous edition are as follows:

- [5.4](#) updated;
- [5.5](#) updated;
- new clause 5.8;
- [7.1](#): new size of cut pieces.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine dimethylformamide in footwear materials

1 Scope

This document specifies a method to determine the amounts of dimethylformamide (DMF) in footwear and footwear components containing polyurethane (PU) coated material.

NOTE 1 In the footwear industry, when PU is injected (reaction moulded), this process does not require the use of DMF. For PU coated material, the use of DMF is possible.

NOTE 2 Several abbreviations can be used for dimethylformamide DMF, DMFa, DMFo. This document uses DMF.

ISO/TR 16178:2020, Table 1 defines which materials are concerned by this determination.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*
ISO/FDIS 16189
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3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Principle

The sample is cut in small pieces and extracted with methanol in a sealed vial at 70 °C in an ultrasonic bath for 1 h. An aliquot is then analysed using a gas chromatograph with mass selective detector.

5 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

5.1 Dimethylformamide (DMF), CAS Registry Number¹⁾ 68-12-2, highest available defined purity standard.

1) CAS Registry Number® (CAS RN®) is a trademark of CAS corporation. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.2 Dimethylformamide – d7 (DMF-d7), CAS RN® 4472-41-7, highest available defined purity standard.

5.3 Methanol, CAS RN® 67-56-1.

5.4 Internal standard

5.4.1 Internal standard – stock solution (1 000 mg/l)

10 mg of DMF-d7 (5.2) is weighed with an accuracy of 0,1 mg in a 10 ml volumetric flask and filled up to the mark with methanol. The content is further transferred in an amber 10 ml vial with PTFE stopcock. The stock solution shall be stored in a refrigerator at about 4 °C.

5.4.2 Internal standard – working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (5.4.1) with methanol (5.3). This solution shall be stored in a refrigerator at about 4 °C.

5.5 Target compounds solutions

5.5.1 Target compound – stock solution (1 000 mg/l)

10 mg of DMF (5.1) is weighed with an accuracy of 0,1 mg in a 10 ml volumetric flask and filled up to the mark with methanol. The content is further transferred in an amber 10 ml vial with PTFE stopcock. This solution shall be stored in a refrigerator at about 4 °C.

5.5.2 Target compound – working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (5.5.1) with methanol (5.3). This solution shall be stored in a refrigerator at about 4 °C.

6 Apparatus

The usual laboratory apparatus and amber laboratory glassware in accordance with ISO 4787 shall be used, in addition to the following.

6.1 Analytical balance with a precision of at least 0,1 mg.

6.2 Glass vial with screw cap that can be tightly sealed (e.g. volume of 20 ml).

6.3 Ultrasonic bath with adjustable temperature suitable for operation at 70 ± 5 °C.

6.4 PTFE-membrane filter pore width 0,45 µm.

6.5 GC vials capped (e.g. volume of 2 ml).

6.6 Amber glass vials with a screw cap that can be tightly sealed (e.g. volume of 10 ml).

6.7 Gas chromatograph with mass selective detector (GC-MS).

7 Preparation of sample

7.1 Sampling

Samples of PU coated materials are cut in pieces of about 3 mm to 5 mm edge length.

NOTE Up to three test specimens (of equal mass) of the same material classification (see ISO 21061) can be tested together, taking into consideration the limits of detection and quantification.

7.2 Extraction

Weigh $(1,00 \pm 0,10)$ g of the sample with the analytical balance (6.1) in a glass vial (6.2), record the mass to the nearest 1 mg, add 1 ml of the internal standard working solution (5.4.2) and 9 ml of methanol (5.3), and seal the vial.

Extract the sample at (70 ± 5) °C for (60 ± 5) min in an ultrasonic bath.

After cooling to room temperature, the solution is filtered (if necessary) through a PTFE membrane filter (6.4).

Transfer an aliquot of the extract to an GC-MS vial (6.5) and seal with a PTFE-cap.

8 Determination with GC-MS

8.1 Calibration standard

At least 4 calibration points shall be used to establish the calibration curve. Examples of calibration solutions are given in Table 1.

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Table 1 – Examples of calibration solution

| Standard | L1 | L2 | L3 | L4 | L5 | L6 |
|--|----------|----------|----------|----------|----------|----------|
| Volume of target compound working solution (5.5.2) | 25 µl | 50 µl | 100 µl | 250 µl | 500 µl | 1 000 µl |
| Concentration of target compound in the calibration solutions (mg/l) | 0,5 | 1 | 2 | 5 | 10 | 20 |
| Volume of the methanol working solution of internal standard (5.4.2) | 1 000 µl | 1 000 µl | 1 000 µl | 1 000 µl | 1 000 µl | 1 000 µl |
| Concentration of the internal standard (mg/l) | 20 | 20 | 20 | 20 | 20 | 20 |
| Filled to the 10 ml mark with methanol | | | | | | |

8.2 Examples of instrumental method

Examples are given in Annex A.

9 Expression of results

9.1 Calibration curve

Set up the linear regression function by using the following ratio (A_e/A_{is}) and (C_e/C_{is}) with the help of the following:

$$\frac{A_e}{A_{is}} = a \times \frac{C_e}{C_{is}} + b$$

The content of DMF is calculated according to the following as a mass fraction w in mg/kg:

$$w = (V / m) \times \frac{\left(\frac{A_{ech}}{A_{is}} - b \right)}{a} \times C_{is}$$

where

- V is the volume of the solvent use for the extraction (ml) (in most case this value will be equal to 10 ml);
- m is the mass of the tested specimen (g);
- A_e is the area of the peak of Dimethylformamide in the calibration standard
- A_{ech} is the area of the peak of Dimethylformamide in the sample;
- A_{is} is the area of the peak of Dimethylformamide-d7 in the sample;
- C_e is concentration of Dimethylformamide in the calibration standard in microgram per liter;
- C_{is} is concentration of Dimethylformamide-d7 in the sample in microgram per liter;
- a is the slope of the linear function;
- b is the ordinate intercept of the calibration curve. The units depend of the evaluation.

10 Performance of the method

This method is able to detect DMF with a limit of quantification of 5 mg/kg or lower in PU coated materials.

11 Test report

The test report shall include at least the following:

- a) reference to this document, i.e. ISO 16189:—;
- b) date of the test;
- c) all details necessary for complete identification of the sample tested;
- d) condition of sample receipt and storage before the test;
- e) the amount determined of the extracted dimethylformamide in mg/kg;
- f) any deviation from the given procedure.

Annex A (informative)

Suggested parameters for GC-MS determination of DMF

A.1 Measuring method

A.1.1 Measuring parameter

The DMF is analyzed by gas chromatography/mass spectrometry on a single quad/MS use in a simultaneous SIM/SCAN mode.

A.1.2 Chromatographic conditions

Column:

Polar stationary phase based on Polyethylene Glycol

Length: 30 meters

Internal diameter: 250 μm

Film thickness: 0,5 μm

Carrier gas: Helium

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60 °C during 2 min

230 °C at 15 °C/min

230 °C during 4 min

Injector: 230 °C in splitless mode with an injection volume of 1 μl

A.1.3 Detection conditions

Transfer line: 240 °C

The single quad MS work in simultaneous SIM/SCAN mode.

The mass SCAN range is between 40 to 200 m/z.

The SIM mode focus on the following ions:

| Compounds | Ions |
|-----------|-----------------|
| DMF | 73 (quantifier) |
| | 44 (qualifier) |
| DMF-d7 | 80 (quantifier) |
| | 50 (qualifier) |

Bibliography

- [1] ISO/TS 16189, *Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine dimethylformamide in footwear materials*
 - [2] EN 17131, *Textiles and textile products — Determination of dimethylformamide (DMF), method using gas chromatography*
 - [3] EN 16778, *Protective gloves — The determination of Dimethylformamide in gloves*
 - [4] ISO 3696, *Water for analytical laboratory use — Specification and test methods*
 - [5] ISO 21061, *Footwear — Chemicals tests — General principles on the preparation of samples*
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