TECHNICAL SPECIFICATION

ISO/TS 16189

First edition
2013-07-15

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

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

Reference number
ISO/TS 16189:2013(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword ... **iv**

1 Scope ... **1**

2 Normative references ... **1**

3 Method principle ... **1**

4 Reagents and solvents ... **1**
4.1 Reagents ... 1
4.2 Stock solutions ... 1

5 Equipment ... **2**

6 Preparation of sample ... **2**
6.1 Sampling ... 2
6.2 Extraction ... 2

7 Determination with GC-MS ... **3**
7.1 Calibration standard ... 3
7.2 Examples of instrumental method ... 3

8 Quantification ... **3**
8.1 Calibration curve ... 3

9 Performance of the method ... **4**

10 Test report ... **4**

Annex A (informative) **Suggested parameters for GC-MS determination of DMFo** ... **5**

Bibliography ... **6**

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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 16189 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in collaboration with ISO Technical Committee ISO/TC 216, *Footwear*, in accordance with the agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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

1 Scope

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

NOTE In the footwear industry, when PU is injected (reaction moulded), this process does not require the use of DMFo. DFMo can be used for PU coated material.

2 Normative references

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

ISO/TR 16178:2012, *Footwear — Critical substances potentially present in footwear and footwear components*

3 Method principle

The sample is cut into small pieces and extracted with methanol in a sealed vial at 70 °C in an ultrasonic bath. An aliquot of the extract is analysed with GC-MS in SIM mode.

ISO/TR 16178:2012, Table 1 defines which materials are concerned by this determination.

4 Reagents and solvents

4.1 Reagents

The substances are given in Table 1.

Table 1 — Reagents

Number	Substances	CAS Number [a]	Purity
1	Dimethylformamide (DMFo)	68-12-2	Certificated standard
2	Dimethylformamide-d7 (DMFo-d7)	4472-41-7	Certificated standard
3	Methanol	67-56-1	Analytical grade

[a] CAS: Chemical Abstract Service.

4.2 Stock solutions

4.2.1 Internal standard — Stock solution (1 000 mg/l)

10 mg of DMFo-d7 is weighted 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 and keep at 4 °C.

4.2.2 Internal standard — Working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (4.2.1) with methanol.

4.2.3 Target compound — Stock solution (1 000 mg/l)

10 mg of DMFo is weighed with an accuracy of 0,1 mg in 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 and keep at 4 °C.

4.2.4 Target compound — Working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (4.2.3) with methanol.

5 Equipment

Usual laboratory equipment, in addition to the following.

5.1 **Analytical balance** (precision at least 0,1 mg).

5.2 **Glass vial** which can be tightly sealed, 20 ml.

5.3 **Ultrasonic bath** with adjustable temperature.

5.4 **PTFE-membrane filter** pore width 0,45 µm.

5.5 **2 ml sample vials** with PTFE-capped.

5.6 **Volumetric flask,** 10ml.

5.7 **Amber vessels**.

5.8 **Micropipettes,** 20 µl to 10 ml.

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

6 Preparation of sample

6.1 Sampling

Samples of PU coated materials are cut into pieces up to 3 mm edge length.

A maximum of three PU coated materials (equal in mass) can be mixed together.

6.2 Extraction

A test sample of 1 g ± 0,001 g is weighed (m_S) with the analytical balance (5.1) in a 20 ml glass vial (5.2). Then 9 ml of methanol and 1 ml of the internal standard working solution (4.2.2) are added and the vial is sealed.

The sample is extracted at 70 °C for 1 h in an ultrasonic bath.

After cooling to room temperature the solution is filtered (if necessary) through a PTFE membrane filter (5.4). An aliquot of the extract is transferred to a GC-MS vial and sealed with a PTFE-cap (5.5).

7 Determination with GC-MS

7.1 Calibration standard

Six calibration points are used to establish the calibration curve. They are all prepared in 10 ml volumetric flasks, as given in Table 2.

Table 2 — Preparation of calibration

Standard	L1	L2	L3	L4	L5	L6
Volume of target compound working solution (4.2.4)	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 (4.2.2)	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
NOTE Filled to the mark with methanol.						

7.2 Examples of instrumental method

An example is given in Annex A.

8 Quantification

8.1 Calibration curve

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

$$\left(\frac{A_e}{A_{is}}\right) = a \times \left(\frac{C_e}{C_{is}}\right) + b$$

where

A_e is the area of the peak of dimethylformamide;

A_{is} is the area of the peak of dimethylformamide-D7;

C_e is the concentration of dimethylformamide in the calibration standard in milligrams per litre (mg/l);

C_{is} is the concentration of dimethylformamide-D7 in the calibration standard in milligrams per litre (mg/l);

a is the slope of the linear function;

b is the ordinate intercept of the calibration curve (the units depend on the evaluation).

The content of DMFo is calculated according to the following equation 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

W is the content of the dimethylformamide in the specimen (mg/kg);

V is the volume of the solvent used for the extraction (ml) (in most cases this value will be equal to 10 ml);

m is the mass of the tested specimen (g);

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_{is} is the concentration of dimethylformamide-D7 in the sample in milligrams per litre (mg/l);

a is the slope of the linear function;

b is the ordinate intercept of the calibration curve (the units depend on the evaluation).

9 Performance of the method

This quantification limit of this test method is 5 mg/kg of DMFo in PU coated materials.

10 Test report

The test report shall include at least the following:

a) reference to this test method;

b) date of the test;

c) all details necessary for complete identification of the sample tested;

d) condition of storage before the test, if available;

e) the amount determined of the extracted dimethylformamide in mg/kg;

f) any deviation from the present standard.

Annex A
(informative)

Suggested parameters for GC-MS determination of DMFo

A.1 Measuring method

A.1.1 Measuring parameter

The DMFo is analysed 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 m

Internal diameter: 250 µm

Film thickness: 0,5 µm

Carrier gas: Helium

Oven:

60 °C for 2 min

250 °C at 20 °C/min

250 °C for 2 min

Injector: 240 °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 amu and 200 amu.

The SIM mode focus on the following ions:

Compounds	Ions
DMFo	73 (quantifier)
	44 (qualifier)
DMFo-d7	80 (quantifier)