SLOVENSKI STANDARD
oSIST prEN ISO 16181-1:2019

01-november-2019

Obutev - Kritične snovi, ki so lahko v obutvi in sestavnih delih obutve - 1. del: Ugotavljanje ftalatov z ekstrakcijo topila (ISO/DIS 16181-1:2019)

Footwear - Critical substances potentially present in footwear and footwear components - Part 1: Determination of phthalate with solvent extraction (ISO/DIS 16181-1:2019)

Schuhe - Möglicherweise in Schuhen und Schuhbestandteilen vorhandene kritische Substanzen - Teil 1: Bestimmung von Phthalaten mit Lösemittelextraktion (ISO/DIS 16181-1:2019)

Chaussures - Substances critiques potentiellement présentes dans les chaussures et les composants des chaussures - Partie 1: Détermination des phtalates dans les solvants d'extraction (ISO/DIS 16181-1:2019)

Ta slovenski standard je istoveten z: **prEN ISO 16181-1**

ICS:

61.060	Obuvala	Footwear

oSIST prEN ISO 16181-1:2019 **en,fr,de**

DRAFT INTERNATIONAL STANDARD

ISO/DIS 16181-1

ISO/TC **216**

Secretariat: **UNE**

Voting begins on:
2019-09-19

Voting terminates on:
2019-12-12

Footwear — Critical substances potentially present in footwear and footwear components —

Part 1:
Determination of phthalate with solvent extraction

Chaussures — Substances critiques potentiellement présentes dans les chaussures et les composants des chaussures —

Partie 1: Détermination des phtalates dans les solvants d'extraction

ICS: 61.060

This document is circulated as received from the committee secretariat.

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/DIS 16181-1:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 216 *Footwear*.

This document together with ISO 16181-2 cancels and replaces ISO/TS 16181:2013, which has been technically revised.

Footwear — Critical substances potentially present in footwear and footwear components —

Part 1: Determination of phthalate with solvent extraction

WARNING — The use of this document can involve hazardous materials, operations and equipment. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this standard to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

1 Scope

This part of ISO 16181 specifies a test method to determine the qualitatively and quantitatively presence of phthalate compounds (Annex A) in footwear and footwear components.

NOTE 1 A list of relevant materials can be found in ISO/TR 16178, Annex A.

NOTE 2 This test method can also be used to determine phthalates other than listed in Annex A subject to validation.

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

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 http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The test sample is extracted using toluene at 60 °C in an ultrasonic bath for 1 h. An aliquot is then analysed using a gas chromatograph with mass selective detector.

5 Reagents

5.1 Chemicals

Unless otherwise specified, use only reagents of recognized analytical grade.

5.1.1 Toluene, CAS[1)] number: 108-88-3.

5.1.2 Bis (2-Ethylhexyl) phtalates-3,4,5,6-D4 (CAS number: 93951-87-2)

5.1.3 Phthalates, see Annex 1.

5.1.4 Acetone, CAS number: 67-64-1.

5.1.5 Methanol, CAS number: 67-56-1.

5.1.6 Cyclohexane, CAS number: 110-82-7.

5.1.7 Tetrahydrofurane (THF), CAS number: 109-99-9

5.1.8 n-hexane, CAS number: 110-54-3

5.2 Standard solutions

5.2.1 Target Phthalates - stock solution

Based on its tasks a laboratory shall decide which phthalates out of Table A.1 needs to be determined.

Based on this decision standard stock solution for each phthalate shall be available either as commercially available certified mixes or individual components in solution or as self-prepared individual standard stock solutions of each phthalate in toluene (5.1.1).

EXAMPLE For standard stock solutions with concentrations of 1000 µg/ml, weigh 50,0 mg of each phthalate (Table A.1) into 50 ml volumetric flasks, fill the volumetric flasks up to the mark with toluene (5.1.1) and mix thoroughly to dissolve completely the substance.

5.2.2 Internal standard – stock solution

Prepare an internal standard stock solution which is in the same concentration range as the standard stock solutions (5.2.1) by dissolving the internal standard (5.1.2) in toluene (5.1.1) according to the example in 5.2.1.

5.2.3 Calibration solutions

Prepare at least five appropriate phthalate calibration solutions, each containing an equal amount of the target phthalates (5.1.3) and an amount of internal standard (5.1.2) in toluene (5.1.1).

Example for calibration solutions, see Table 1.

Table 1 — Example of calibration solutions

Standard	L1	L2	L3	L4	L5
Concentration of phthalate (µg/ml)	**2,5**	**25**	**50**	**75**	**100**

1) CAS: Chemical Abstract Service.

Table 1 *(continued)*

Standard	L1	L2	L3	L4	L5
Volume of the phthalate stock solution (µl) (5.2.1)	25	250	500	750	1 000
Volume of the internal standard stock solution (µl) (5.2.2)	500				
Concentration of the internal standard (µg/ml)	50				
Volume of toluene (µl) (5.1.1) (completed to 10ml)	9 475	9 250	9 000	8 750	8 500

5.2.4 Extraction solution with internal standard (optional)

Prepare the extraction solution with the same concentration of an internal standard as in the calibration solutions (e.g. 50 µg/ml) by diluting internal standard working solution (5.2.2) with toluene (5.1.1).

6 Apparatus

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

Glassware, after washing, should be given an extra rinse with 0,1 N nitric acid and finally with acetone, acetone/methanol and/or cyclohexane.

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

6.2 Flask with Teflon stopper, e.g. 20 ml.

6.3 Ultrasonic bath with adjustable temperature, suitable for operation at 60 °C.

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

6.5 Volumetric flasks of suitable volume.

6.6 GC vials, e.g. 2 ml

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

7 Sampling

The test piece consists of a single material taken from the footwear, such as coated leather, textile, polymer, coated material or others. The preparation of the sample should involve removal of the individual materials from the footwear.

Each material type is cut into pieces of about 3 to 5 mm edge length.

In order to avoid cross-contamination, the cutting device shall be cleaned with acetone after cutting of any individual material.

Up to 3 test specimens of equal mass, of the same material type could be tested together taking into consideration the limit of quantification and the limit given by the regulation.

8 Test procedure

8.1 Extraction

8.1.1 Ultrasonic extraction

Weigh accurately (1,0 ± 0,1) g of the pieces of a representative specimen, into a glass flask (6.2), record the mass (*m)*to the nearest 10 mg. Add 10 ml of extraction solution (5.2.4) to wet the entire specimen, and seal the flask with Teflon stopper. If the test specimen is not sufficiently immersed in the extraction solvent, add more solvent and report the final volume (V) for calculation of phthalate amount.

Alternatively, toluene (5.1.1) can be used for extraction. In this case an appropriate amount of internal standard solution (5.2.2) in order to get the same concentration of internal standard as in the calibration solutions has to be added.

Extract the phthalate in the ultrasonic bath (6.3) for 1 h ± 5 min at (60 ± 5) °C.

After cooling to room temperature, filter this solution through a PTFE membrane filter (6.4).

8.1.2 Alternative extraction procedures for PVC materials

For a PVC sample, tetrahydrofuran (THF) can also be used as extraction solvent, the following alternative extraction procedure may be applied.

a) Weigh accurately (0,5 ± 0,01) g of the pieces of a representative specimen into a 50 ml glass flask fitted with Teflon stopper. Add 10 ml of THF to wet the entire specimen.

b) Extract the phthalate in the ultrasonic bath for 1 h ± 5 min at (50 ± 5) °C. For samples without completely dissolving, and an additional 2 h ± 5 min to mixing time and then proceed.

c) Add 20 ml n-hexane to precipitate the sample matrix, and then filter or centrifuge to obtain a transparent extraction solution.

d) Transfer the extract to a 50 ml volumetric flask; fill to the mark with a mixture of THF and n-hexane at a volume ratio of 1:2.

e) Transfer a known volume of organic phase into a suitable GC sampling vial, add an appropriate volume of internal standard solution in n-hexane and perform GC-MS analysis.

NOTE Annex D includes the results for phthalates by using THF/toluene.

8.1.3 Preparation of a method blank

For each series of tests, a method blank shall be prepared. For the preparation of the blank, the complete procedure (extraction 8.1.1 or 8.1.2 and GC-MS analysis 8.2) shall be done in a 20 ml glass flask (6.2) without a sample.

8.2 Determination with GC-MS

Transfer an aliquot of the extract with internal standard into a suitable GC sampling vial, seal with a cap.

Determinate the phthalates extracted in 8.1 by GC-MS (6.6). An example of a programme and the parameters for GC-MS analysis of target phthalates are given in Annex B.

In some cases when the phthalates level is very high, prepare further diluted solutions using the original solution and repeat the analysis. In the case of toluene (5.1.1), adding appropriate volume of internal standard solution.

9 Expression of results

9.1 Calibration curve

Set up the linear regression function by using the following ratio (A_s/A_{is}) and (C_s/C_{is}) with the help of Formula (1):

$$\frac{A_s}{A_{is}} = a \times \left(\frac{c_s}{c_{is}} \right) + b \tag{1}$$

where

A_s is the area of the target phthalate based on the target ions;

A_{is} is the area of the peak of internal standard based on the target ions;

C_s is the concentration of the target phthalate in the calibration standard, in µg/ml;

C_{is} is the concentration of internal standard in the calibration standard, in µg/ml;

a is the slope of the linear function;

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

Calculate the concentration of each phthalate in the sample (Css, in µg/ml) using formula (2)

$$C_{ss} = \frac{C_{is}}{a} \times \left[\left(\frac{A_s}{A_{si}} \right) b \right] \tag{2}$$

9.2 Determination of the phthalates content

From the calibration graph, determine the content of each phthalate, corrected for the internal standard peak area, and interpolate the concentration of the phthalate in µg/ml, correcting for any dilutions. Subtract the blank concentration (see 8.1.3) from the specimen concentration.

The content of phthalate is calculated according to Equation (3) as a percentage, P:

$$P = \frac{v \times (c_{ss} - c_b)}{m \times 10\,000} \tag{3}$$

Alternatively, Expressed as a mass fraction W in mg/kg using Formula (4):

$$W = \frac{v}{m} \times (c_{ss} - c_b) \tag{4}$$

where

V is the final volume as given in 8.1.1, in ml;

m is the specimen mass as given in 8.1.1, in g;

C_b is the concentration of the individual phthalate of blank solution, in µg/ml;

C_{ss} is the concentration of the individual phthalate of the specimen solution, corrected for any dilutions, in µg/ml, determinated by formula (2).