SLOVENSKI STANDARD
oSIST prEN ISO 16181-2:2019

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Obutev - Kritične snovi, ki so lahko v obutvi in sestavnih delih obutve - 2. del: Ugotavljanje ftalatov brez ekstrakcije s topilom (ISO/DIS 16181-2:2019)

Footwear - Critical substances potentially present in footwear and footwear components - Part 2: Determination of phthalate without solvent extraction (ISO/DIS 16181-2:2019)

Schuhe - Möglicherweise in Schuhen und Schuhbestandteilen vorhandene kritische Substanzen - Teil 2: Bestimmung von Phthalaten ohne Lösemittelextraktion (ISO/DIS 16181-2:2019)

Chaussures - Substances critiques potentiellement présentes dans les chaussures et les composants des chaussures - Partie 2: Détermination des phtalates sans extraction par solvant (ISO/DIS 16181-2:2019)

Ta slovenski standard je istoveten z: **prEN ISO 16181-2**

ICS:

61.060	Obuvala	Footwear

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

Part 2:
Determination of phthalate without solvent extraction

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

Partie 2: Détermination des phtalates sans les solvants d'extraction

ICS: 61.060

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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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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 16181-1 cancels and replaces ISO/TS 16181:2013, which has been technically revised.

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

Part 2: Determination of phthalate without solvent extraction

1 Scope

This international standard specifies a method for the determination of the content of specific phthalates (Annex A) by pyrolyzer/thermal desorption gas chromatography-mass spectrometry (Py/TD-GC-MS). This international standard is applicable to all types of footwear materials except textiles.

NOTE ISO/TR 16417:2017 defines which phthalates are concerned by this determination.

2 Normative references

There are no normative references in this document.

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

This test method is designed to specify procedures for qualitative and quantitative of specific phthalates in footwear materials by pyrolyer/thermal desorption gas chromatography-mass spectrometry(Py/TD-GC-MS). The sample is directly introduced into pyrolyzer, thermally extract phthalates under a specific heat zone and then transferred to the gas chromatograph. Phthalate compounds are separated by gas chromatographic capillary column and detected by mass spectrometer.

5 Apparatus

5.1 Analytical balance capable of measuring accurately to 0,000 01 g (0,01 mg)

5.2 cryogenic grinding/milling mill with liquid N_2 cooling

5.3 nipper (a hand tool for cutting samples)

5.4 micro spatula

5.5 tweezers

5.6 cutter

5.7 file

5.8 micro puncher

5.9 deactivated glass wool

5.10 micro syringe or automated pipettes

5.11 sample cup

5.12 Volumetric flasks 10 mL and 100 mL

5.13 gas chromatograph - mass spectrometer equipped with pyrolyzer:

— Pyrolyzer/thermal desorption accessory:

A temperature rise of 1 °C to 100 °C per minute should be possible across a temperature range from 40 °C to 500 °C. The sample cup should be treated for chemical stability, and should be capable of accommodating both liquid and solid samples. It should be possible to maintain the interface between the thermal pyrolysis unit and the gas chromatograph inlet up to 400 °C.

6 Reagents and materials

All reagent chemicals shall be tested for contamination and blank values prior to application as follow:

6.1 n-Hexane for preparing the phthalates standard solution, GC grade or higher

6.2 Phthalates (Annex A)

6.3 Helium (purity greater than a volume fraction of 99,999 %)

6.4 Calibrants:

a) Prepare stock solutions containing 100 mg/L of each phthalate(Annex A) in n-hexane(6.1) respectively.

NOTE A commercially available CRM is polypropylene resin pellet containing BBP, DBP DEHP and DNOP (National Metrology Institute of Japan, NMIJ CRM 8151-a), PVC containing BBP, DBP DEHP and DNOP (Korean Research Institute for Standards and Science, KRISS CRM 113-03-006), or polyethylene containing BBP, DBP, DEHP, DEP (Diethyl phthalate), DIDP, DINP, DMP (Dimethyl phthalate) and DNOP (SPEX CertiPrep, US, CRM-PE001).

6.4.1 Stock solution of phthalates, 10 000 mg/L

100 mg of the respective phthalate are dissolved in different 10 mL volumetric flasks (5.12) with n-hexane (6.1) and filled up to the mark.

6.4.2 Standard solution for calibration curve of phthalates, 100 mg/L

Add 1 mL of each stock solution of phthalates (6.4.1) into a 100 mL volumetric flasks (5.12) and filled up to the mark with n-hexane (6.1).

6.5 Blank material (no phthalate compounds shall be included).

7 Sampling

Definition of the sampling need to be done.

In the footwear, all types of footwear materials except textiles shall be tested.

If the sample consists of homogeneous materials, the sample can either be cut into small pieces using a cutting tool(5.6~5.8).

If the sample consists of heterogeneous materials (multi-layer materials), the sample shall be ground to pass through a 500 µm sieve before extraction. Cryogenic grinding/milling with liquid N2 cooling(5.2) is strongly recommended. More detail procedure described in annex B.

8 Test procedure

8.1 Test sample preparation

Place approximately 0,5 mg of the cut or powdered sample into a pre-weighed sample cup using a micro spatula(5.4) or tweezers(5.5). Record the total weight of the cup with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample cup from the total weight. Place an appropriate amount of deactivated glass wool into the sample cup to ensure that the sample powder will not spill out.

NOTE The measure of sample weight using a balance may be unstable at digit of 0.01 mg. To check the accuracy of weighting sample, it is recommend to check reproducibility of weighting sample. If the reproducibility of five times weighting of one sample is below 10 %, it is possible to use the average value as the sample weight.

8.2 Calibration

1, 2, 5 and 10 µL of 100 mg/L phthalates standard solution (6.4.2) were put into sample cups, respectively.

Table 1 — Calibration standard solution of phthalates

No.	**Concentration of each phthalate standard solution,** mg/L	**Volume of each phthalate standard solution, µL**	**Final Concentration,** µg
1	100	1	0.1
2	100	2	0.2
3	100	5	0.5
4	100	10	1

8.3 Chromatographic analysis

8.3.1 The chromatography parameters for gas chromatograph — mass spectrometer equipped with pyrolyzer

Different conditions may be necessary to optimize a specific Py/TD-GC-MS system to achieve effective separation of each phthalate and meet the quality control (QC) and method detection limits (MDL) requirements. An example of chromatography parameters and the total ion current chromatogram are shown in annex C and E.

8.3.2 Qualitative and quantitative analysis by gas chromatograph — mass spectrometer equipped with pyrolyzer

5 µL of mixed standard working solution (6.4.2) for the calibration and the test sample (8.1) directly introduce into the sample cup. The sample cup introduce into the pyrolyzer, thermally extracted

phthalates in specific heat zone are separated in column for determination of phthalates. If one or more peaks in the chromatogram of test ample and standard working solution appear at the same retention time, analyze qualitatively by comparing the characteristic ions (Table A.1) of these peaks in the chromatogram of test sample and standard working solution, and analyze quantitatively by external standard calibration method through selected ion.

According to the content of the target phthalate in test sample, select the standard working solution with a similar concentration, and analyze the equal volume of standard working solution and test sample. The response value of each of the phthalates in standard working solution and in the test sample should be in the linear range of detector.

NOTE 1 If the response value of test solution is out of the calibration curve range, reduce the sample weight or adjust the split ratio appropriately before measurement.

NOTE 2 Under the above analysis conditions, GC-MSD total ion chromatogram of 18 kinds of phthalate standards is given in Annex D.

9 Calculation of phthalate compounds in the sample

The content of each phthalate in the sample is calculated by the formula (1)

$$X_i = \frac{A_i - A_0}{m} \quad (1)$$

where

X_i is the content of phthalate in the sample, in μg/g;

A_i is the concentration of phthalate in the test sample, in μg;

A_0 is the concentration of phthalate in the blank sample, in μg;

m is mass of the sample (see 8.1), in g.

10 Detection limit

The detection limit of phthalates by this method is below 30 μg/g. Results below 30 μg/g should be reported as not detected.

11 Test report

The test report shall include at least the following information:

a) a reference to this International Standard ;

b) all information necessary for complete identification of the sample tested;

c) test results;

d) any deviation from this standard.

Annex A
(informative)

The list of phthalates specified in CEN/TR 16417

A.1 Names of 21 kinds of phthalates

Table A.1 — The list of phthalates determined by this standard

No.	Substance a	Abbreviation	CAS No.
1	Dibutyl phthalate	DBP	84-74-2
2	Benzyl butyl phthalate	BBP	85-68-7
3	Bis (2-ethyl(hexyl)phthalate)	DEHP	117-81-7
4	Di-n-octyl phthalate	DNOP	117-84-0
5	Diisononyl phthalate	DINP	28553-12-0 68515-48-0
6	Diisodecyl phthalate	DIDP	26761-40-0 89-16-7 68515-49-1
7	Diisobutyl phthalate	DIBP	84-69-5
8	Bis(2-methoxyethyl) phthalate	DMEP	117-82-8
9	Diisopentyl phthalate	DIPP	605-50-5
10	N-pentyl-isopentyl phthalate	PIPP	776297-69-9
11	Di-n-pentyl phthalate	DNPP	131-18-0
12	Diisohexyl phthalate	DIHxP	71850-09-4
13	Di-n-hexyl phthalate	DNHP	84-75-3
14	Butyl octyl phthalate (*)	BOP	84-78-6
15	1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich	DIHP	71888-89-6
16	Diisooctyl phthalate (*)	DIOP	27554-26-3
17	Diundecyl phthalate (*)	DUP	3648-20-2
18	1,2-Benzenedicarboxylic acid, dipentylester, branched and linear	DPP	84777-06-0
19	1,2-Benzenedicarboxylic acid, dihexyl ester, branched and linear	DHP	68515-50-4
20	1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters	DHNUP	68515-42-4
21	1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters; 1,2-benzenedicarboxylic acid, mixed decyl and hexyl and octyl di-esters with ≥ 0.3% of dihexyl phthalate	–	68515-51-5 68648-93-1
22	Diethylphthalate (*)	DEP	84-66-2
23	dimethylphthalate (*)	DMP	131-11-3
24	dicyclohexylphthalate	DCHP	84-61-7
25	Di-n-propyl phthalate (*)	DPRP	131-16-8
26	Dinonyl phthalate (*)	DNP	84-76-4

Key

[a] See ISO/TR 16178, CEN/TR 16417 for detailed information.