INTERNATIONAL STANDARD

ISO 16181-1

First edition
2021-03

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 par extraction au solvant

Reference number
ISO 16181-1:2021(E)

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Published in Switzerland

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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).

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*, 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 16181-1, together with ISO 16181-2, cancels and replaces ISO/TS 16181:2011, which has been technically revised.

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

— addition of number of phthalates from 7 to 26;

— addition of new Clause 2 and Clause 3, and renumbering of subsequent clauses;

— replacement of “n-hexane/acetone” with “toluene” and alternative “tetrahydrofuran” as extraction solution;

— splitting of former Clause 3 into Clauses 5 and 6, with technical modification;

— technical revision of Clauses 4 and 5;

— deletion of 5.2.4;

— addition of Clause 9;

— addition of Annex D.

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 —

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 document to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of the document, and to determine the applicability of regulatory limitations for this purpose.

1 Scope

This document specifies a test method to determine the qualitative and quantitative presence of phthalate compounds (see Annex A) in footwear and footwear components.

NOTE 1 A list of relevant materials potentially containing phthalates can be found in ISO/TR 16178:2012, Annex A or in CEN/TR 16417.

NOTE 2 This test method can also be used to determine phthalates other than those 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 4787:2010, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

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 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 (GC) with a mass selective detector (MS).

All the abbreviations of phthalates used are given in Annex A.

When compared with ISO 16181-2, the two analytical methods should give similar trends but not necessarily the same absolute result. Therefore, in cases of dispute, the method in this document shall be used in preference to ISO 16181-2.

5 Reagents

5.1 Chemicals

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

5.1.1 Toluene, Chemical Abstract Service Registry Number®[1] (CAS RN®): 108-88-3.

5.1.2 Internal standard

Either of the following chemicals can be used as internal standard:

— Bis (2-Ethylhexyl) phtalates-3,4,5,6-D4 (CAS RN®: 93951-87-2);

— Diphenylphthalate (CAS RN® 84-62-8)

NOTE 1 Diphenylphthalate gives appropriate results in case of DEHP <1 %. In case of DEHP >1 % the results of all other phthalates can be affected because of poor resolution between DEHP and Diphenylphthalate.

NOTE 2 Other internal standards have been found convenient as Di-n-propylphthalate-3-4-5-6 D4 (CAS RN®: 358731-29-0).

5.1.3 Phthalates, see Annexes A and B.

5.1.4 Acetone, CAS RN®: 67-64-1.

5.1.5 Methanol, CAS RN®: 67-56-1.

5.1.6 Cyclohexane, CAS RN®: 110-82-7.

5.1.7 Tetrahydrofurane (THF), CAS RN®: 109-99-9.

5.1.8 n-hexane, CAS RN®: 110-54-3.

5.2 Standard solutions

5.2.1 Target phthalates — Stock solution

Based on its tasks a laboratory shall decide which phthalates from Table A.1 need to be determined.

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

Prepare, for example, standard stock solutions with concentrations of 1 000 µg/ml, weigh 50,0 mg of each phthalate depending on the purity (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 that 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 5.2.1.

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1) CAS Registry Number (CAS RN) is a registered trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named.

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) respectively in n-hexane (5.1.8).

An examples of calibration solutions are shown in Table 1 and 2.

Table 1 — Example of calibration solutions extraction (8.1.1)

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

Table 2 — Example of calibration solutions with THF extraction (8.1.2)

Standard	L1	L2	L3	L4	L5
Concentration of phthalate (µg/ml)	1,0	3,0	15	30	90
Volume of the phthalate stock solution (µl) (5.2.1)	10	30	150	300	900
Volume of the internal standard stock solution (µl) (5.2.2)	500				
Concentration of the internal standard (µg/ml)	50				
Volume of n-hexane (µl) (5.1.8) (completed to 10 ml)	9 490	9 470	9 350	9 200	8 600

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 4787:2010, 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, for example 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, for example 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 mm 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 three test specimens of equal mass and the same material type can be tested together, taking into consideration the limit of quantification and the limit given by the applicable regulations.

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 (Clause 7) 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 a Teflon stopper. If the test specimen is not sufficiently immersed in the extraction solution, add more solvent and report the final volume (V) for calculation of the 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) shall be added in order to get the same concentration of internal standard as in the calibration solutions.

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 procedure for PVC materials

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

a) Weigh accurately (0,5 ± 0,01) g of the pieces of a representative specimen (Clause 7) into a 50-ml glass flask fitted with a Teflon stopper. Add 10 ml of THF to wet the entire specimen.

b) Extract the phthalates in the ultrasonic bath for 1 h ± 5 min at (50 ± 5) °C. For samples that have not completely dissolved at this point, add an additional 2 h ± 10 min of extraction time and then proceed.

c) Add 20 ml n-hexane to precipitate the sample matrix, 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 F includes the results of a comparison of phthalates extraction 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 (6.6) and seal with a cap.

Determinate the phthalates extracted in 8.1 by GC-MS (6.7). An example of chromatographic conditions for GC-MS analysis of target phthalates are given in Annex C. An example of chromatogram is given in Annex E.

In 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), add an appropriate volume of internal standard solution.

9 Expression of results

9.1 Calibration curve

Set up the linear regression function by using the ratios (A_s/A_{is}) and (C_s/C_{is}) according to 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 (C_{ss}, 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

9.2.1 For each phthalate

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 Formula (3) as a percentage, *P*.

$$P = \frac{V \times (C_{ss} - C_b)}{m \times 10\,000} \quad (3)$$

Alternatively, it can be expressed as a mass fraction, *W*, in mg/kg using Formula (4).

$$W = \frac{V}{m} \times (C_{ss} - C_b) \quad (4)$$

where

V is the final volume as given in 8.1.1 or 8.1.2 d), in ml;

m is the specimen mass as given in 8.1.1 or 8.1.2 a), 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, determined by Formula (2).

9.2.2 When a sum of phthalates is requested

In certain cases, a final requested result can be expressed as a sum of different phthalates.

All the phthalates included in the sum shall be clearly identified.

The results of the identified phthalates (as obtained in 9.2.1) are added to give the result of the sum. If the result for a single phthalate is lower than the limit of quantification of the test method (see 9.3), this result is considered as zero and is not included in the sum.

9.3 Performance of the test method

The results of the interlaboratory test is given in Annex D.

This method is able to quantify Phthalates listed in Table A.1 with a limit of quantification (LOQ) of

— 50 mg/kg with toluene extraction (8.1.1)

— 100 mg/kg with THF extraction (8.1.2)

NOTE For complex matrix (for example, leather, rubber, materials with high amount of paraffins), these limits of quantification might be difficult to achieve. That is possible for phthalates that yield a single peak. If a phthalate yields several peaks, it will be difficult to achieve this LOQ.

10 Test report

The test report shall include at least the following:

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

b) a reference to this document, i.e. ISO 16181-1:2021;

c) the method used (solvent of extraction);

d) the amount determined for each phthalate that was requested to be tested in mg/kg or in percentage by mass of each listed phthalate in the tested material;

e) any deviation by agreement or otherwise from the procedure specified;

f) any unusual features observed;

g) the date of the test.