Method	ISO/TS 16181:2011	ISO 16181-1:2021
Title	Footwear — Critical substances potentially present in footwear and footwear components — Determination of phthalates in footwear materials	Footwear — Critical substances potentially present in footwear and footwear components — Part 1: Determination of phthalates with solvent extraction
Scope	Applicable to all types of footwear materials such as leather, textile, polymer, coated materials or others.	Footwear and footwear components such as coated leather, textile, polymer, coated material or others. Note: A list of relevant materials potentially containing phthalates can be found in ISO/TR 16178:2012, Annex A or in CEN/TR 16417.
Principle	This method uses extraction apparatus with n- hexane / acetone as solvent. The total n-hexane/acetone extractable phthalate plasticizer content is calculated by weight with GC-MS detection to identify and quantify individual phthalates.	The test sample is extracted using toluene at 60 °C in an ultrasonic bath for 1 h. An aliquot is then analysed using a GC-MS.

Internal standard	Di-cyclohexyl phthalate (DCHP) (CAS# 84-61-7)	Bis (2-Ethylhexyl) phtalates- 3,4,5,6-D4 (CAS# 93951-87-2) OR Diphenylphthalate (CAS# 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# 358731-29-0).
Standards	Di-iso-nonyl phthalate (DINP) (CAS# 28553-12-0 or 68515-48-0)	Di-iso-nonyl phthalate (DINP) (CAS# 28553-12-0 or 68515-48- 0)

Di-(2-ethylhexyl) phthalate (DEHP) (CAS# 117-81-7)	Bis-(2-ethylhexyl) phthalate (DEHP) (CAS# 117-81-7)
Di-n-octyl phthalate (DNOP) (CAS# 117-84-0)	Di-n-octyl phthalate (DNOP) (CAS# 117-84-0)
Di-iso-decyl phthalate (DIDP) (CAS# 26761-40-0 or 68515-49-1)	Di-iso-decyl phthalate (DIDP) (CAS# 26761-40-0 or 89-16-7 or 68515-49-1)
Butyl benzyl phthalate (BBP) (CAS# 85-68-7)	Butyl benzyl phthalate (BBP) (CAS# 85-68-7)
Di-butyl phthalate (DBP) (CAS# 84-74-2)	Di-butyl phthalate (DBP) (CAS# 84-74-2)
Di-isobutyl phthalate (DIBP) (CAS# 84-69-5)	Di-isobutyl phthalate (DIBP) (CAS# 84-69-5)
/	Bis(2-methoxyethyl) phthalate (DMEP) (CAS# 117-82-8)

/	Diisopentyl phthalate (DIPP) (CAS# 605-50-5)
/	N-pentyl-isopentyl phthalate (PIPP) (CAS# 776297-69-9)
/	Di-n-pentyl phthalate (DNPP) (CAS# 131-18-0)
/	Diisohexyl phthalate (DIHxP) (CAS# 71850-09-4)
/	Di-n-hexyl phthalate (DNHP) (CAS# 84-75-3)
/	Butyl octyl phthalate (*) (BOP) (CAS# 84-78-6)
/	1,2-Benzenedicarboxylic acid, di- C6-8-branched alkyl esters, C7- rich (DIHP) (CAS# 71888-89-6)
/	Diisooctyl phthalate (*) (DIOP) (CAS# 27554-26-3)
/	Diundecyl phthalate (*) (DUP) (CAS# 3648-20-2)
/	1,2-Benzenedicarboxylic acid, dipentylester, branched and linear (DPP) (CAS# 84777-06-0)

/	1,2-Benzenedicarboxylic acid, dihexyl ester, branched and linear (DHP) (CAS# 68515-50-4)
/	1,2-Benzenedicarboxylic acid, di- C7-11-branched and linear alkyl esters (DHNUP) (CAS# 68515- 42-4)
/	1,2-benzenedicarboxylic acid, di- C6-10-alkyl esters; 1,2- benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters with ≥ 0.3% of dihexyl phthalate (CAS# 68515-51-5, 68648-93-1)
/	Diethylphthalate (*) (DEP) (CAS# 84-66-2)
/	Dimethylphthalate (*) (DMP) (CAS# 131-11-3)
/	Dicyclohexylphthalate (DCHP) (CAS# 84-61-7)
/	Di-n-propyl phthalate (*) (DPRP) (CAS# 131-16-8)
/	Dinonyl phthalate (*) (DNP) (CAS# 84-76-4)

Sampling	The test piece consists of a single material taken from the footwear, such as leather, textile, polymer, coated material or others. The preparation of the sample should involve removal of the individual materials from the footwear, and preparation of a test piece made of particles as small as possible (but of at least 4 mm). Note: It is possible to grind the sample.	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.
Sample size	as small as possible (but of at least 4mm)	3 mm to 5 mm edge length
Composite sample	/	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.

A. Ultrasonic extraction: 1. Weigh (2.0 ± 0.1) g of sample into a reaction vessel.

 Add 40 ml of nhexane/acetone (80/20) into the reaction vessel.
 Extract in an ultrasonic bath for 60 mins at 50°C.
 Cool down to room temperature.

5. Transfer the extract to a
50 ml volumetric flask after
filtration or centrifugation.
6. Mark up with n-hexane.

7. Transfer the organic pahse into a GC vial, add an appropriate volume of internal standard solution.
8. Perform GC-MS analysis.

A. Ultrasonic extraction: (a) Extraction with toluene 1. Weigh (1.0 ± 0.1) g of sample into a reaction vessel. 2. Add 10 ml of extraction solution (toluene with 50 µg/ml IS) into the reaction vessel, seal the vessel with a Telfon stopper. 3. Extract in an ultrasonic bath for (60 ± 5) mins at (60 ± 5) °C. 4. Cool down to room temperature.

5. Filter the solution into a GC vial through a PTFE membrane filter.

6. Perform GC-MS analysis.

(b) Extraction with THF for PVC materials

1. Weigh (0.5 ± 0.01) g of sample into a reaction vessel.

2. Add 10 ml of THF into the reaction vessel, seal the vessel with a Telfon stopper.

3. Extract in an ultrasonic bath for (60 ± 5) mins at (50 ± 5) °C. For samples that have not completely dissolved at this point, add an additional (120 ± 10) mins of extraction time and then proceed. 4. Add 20 ml n-hexane to precipitate the sample matrix. 5. Filter or centrifuge to obtain a transparent extraction solution.

Sample preparation

		 6. 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. 7. Transfer a known volume of organic phase into a GC vial, add an appropriate volume of IS in n-hexane. 8. Perform GC-MS analysis.
Instrumentation	GC-MS	GC-MS
Q lons (Quantifier / Qualifier) for analysis	DBP: m/z 149 / 223 /205 BBP: m/z 149 / 206 /238 DEHP: m/z 149 / 167 / 279 DNOP: m/z 149 / 279 / 261 DINP: m/z 293 / 149 / 127 DIDP: m/z 307 / 149 / 141 DIBP: m/z 149 / 223 / 205 DCHP (IS): m/z 149 / 167 / 249	refer to Table C.1 of ISO 16181- 1:2021
Quantification limit	/	50 mg/kg with toluene extraction 100 mg/kg with THF extraction 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.
No. of phthalates	7	26
Reference Standard	ISO/TR 16178:2012	ISO/TR 16178:2012
	EN 14372:2004	ISO 16181-2
	/	CEN/TR 16417