TECHNICAL SPECIFICATION

ISO/TS 16181

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Footwear — Critical substances potentially present in footwear and footwear components — Determination of phthalates in footwear materials

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

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Foreword

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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 document:

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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order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn.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again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.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 16181 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in collaboration with Technical Committee ISO/TC 216, *Footwear*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Introduction

Phthalates are commonly used as plasticizers in polymers. Toxicological concern has arisen due to their potential effect as endocrine disruptors and some of the listed phthalates are toxic in reproduction. The level of media publicity will ensure that their use continues to be of concern to consumers.

Phthalates are controversial because high doses of many phthalates have shown hormonal activity in rodent studies. Studies on rodents involving large amounts of phthalates have shown damage to the liver, the kidneys, the lungs, and the developing testes.

This Technical Specification calls for the use of substances and/or procedures that can be injurious to health if appropriate precautions are not observed. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

Footwear — Critical substances potentially present in footwear and footwear components — Determination of phthalates in footwear materials

SAFETY PRECAUTIONS — Persons using this Technical Specification should be familiar with normal laboratory practice. This Technical Specification does not claim to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this Technical Specification be carried out by suitably trained staff.

1 Scope

This Technical Specification specifies a test method to determine the presence of phthalate compounds. This test method is applicable to all types of footwear materials.

NOTE 1 This test method can also be used to determine plasticizers other than those listed in 3.2, subject to validation.

NOTE 2 ISO/TR 16178 defines which materials are concerned by this determination.

2 Principle

The aim of the method is to extract phthalates in footwear materials such as leather, textile, polymer, coated materials or others. 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 gas chromatography-mass spectrometry (GC-MS) detection to identify and quantify individual phthalates.

3 Apparatus and reagents

3.1 Apparatus

3.1.1 Scales, resolution of 1 mg.

3.1.2 Flask, 50 ml.

3.1.3 Water-cooled condenser.

3.1.4 Spark-proof heating mantle/water bath.

3.1.5 Ultrasonic bath.

3.1.6 Microwave extractor.

3.1.7 Steam bath or **rotary evaporator**.

3.1.8 Calibrated volumetric flasks of suitable volume.

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0,1 N nitric acid and finally with acetone, acetone/methanol and/or cyclohexane. Dry at 110 °C for 1 h.

WARNING — The vapour of the organic solvents are highly flammable, especially at high temperature. Allow glassware to cool down before use.

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

3.2 Reagents

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

3.2.1 Water, distilled or of equivalent purity.

3.2.2 *n*-Hexane, CAS[1)] number: 110-54-3.

3.2.3 Di-iso-nonyl phthalate (DINP), CAS number: 28553-12-0 or 68515-48-0.

3.2.4 Di-(2-ethylhexyl) phthalate (DEHP), CAS number: 117-81-7.

3.2.5 Di-*n*-octyl phthalate (DNOP), CAS number: 117-84-0.

3.2.6 Di-iso-decyl phthalate (DIDP), CAS number: 26761-40-0 or 68515-49-1.

3.2.7 Butyl benzyl phthalate (BBP), CAS number: 85-68-7.

3.2.8 Di-butyl phthalate (DBP), CAS number: 84-74-2.

3.2.9 Di-cyclohexyl phthalate (DCHP), CAS number: 84-61-7, internal standard.

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

3.2.11 Mixture of *n*-hexane/acetone, 80 %/20 % volume fraction.

3.2.12 Di-isobutyl phthalate (DIBP), CAS number: 84-69-5.

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.

1) CAS: Chemical Abstract Service.

5 Test procedure

5.1 Preparation of solutions

5.1.1 Preparation of the internal standard solution

Prepare a 500 µg/ml stock solution of the internal standard in *n*-hexane.

5.1.2 Standard solution

Prepare a series of individual stock standard solutions of the individual phthalate in *n*-hexane, as shown in Table 1.

Table 1 — Stock solutions

Phthalate	DIDP	DINP	DBP	BBP	DNOP	DEHP	DIBP
Concentration, µg/ml	1 000	1 000	200	200	200	200	200

From the stock standard solutions, prepare appropriate phthalate calibration solutions in *n*-hexane.

Use at least five appropriate dilutions of the calibration sets to create calibration graphs, add to each an appropriate amount of internal standard and perform GC-MS analysis.

NOTE DIDP and DINP overlap in the chromatogram; the target ions to be chosen are indicated in Annex A.

5.2 Extraction procedures

5.2.1 General

Prepare the appropriate amount of internal standard solution.

5.2.2 Blank

For each series of tests, a blank shall be prepared. For the preparation of the blank, the complete procedure (extraction either 5.2.3 or 5.2.4 and GC-MS analysis) shall be done in a 50 ml glass flask (3.1.2) without the sample.

5.2.3 Ultrasonic extraction

Weigh accurately (2,0 ± 0,1) g of the pieces of a representative specimen into a 50 ml glass flask (3.1.2) fitted with teflon stopcock. Add 40 ml of *n*-hexane/acetone (3.2.11) to wet the entire specimen.

Extract the phthalate in the ultrasonic bath (3.1.5) for 1 h at 50 °C and transfer the extract to a 50 ml volumetric flask (3.1.8) after filtration or centrifugation.

Fill to the mark with *n*-hexane.

Transfer a known volume of organic phase into a suitable GC sampling vial, add an appropriate volume of internal standard solution and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of internal standard solution.

5.2.4 Microwave extractor

Weigh accurately (2,0 ± 0,1) g of the pieces of a representative specimen into a polytetrafluoroethylene (PTFE) vessel. Add a sufficient quantity of the *n*-hexane/acetone mixture (3.2.11) to wet the whole specimen.

Extract the phthalate in the microwave extractor. The following parameters could be used as a basis for optimizing the extraction:

— power: 600 W;

— time: 15 min;

— temperature: 100 °C;

— pressure: 10 bars (1 MPa).

Transfer the extract into a 50 ml volumetric flask. Fill to the mark with *n*-hexane.

Transfer a known volume into a suitable GC sampling vial, add an appropriate volume of internal standard solution and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of internal standard solution.

5.3 Calculation of results

From the calibration graph, determine the content of each phthalate, P, expressed as a percentage, corrected for the internal standard peak area, and interpolate the concentration of the phthalate in micrograms per millilitre, correcting for any dilutions. Subtract the blank concentration (see 5.2.2) from the specimen concentration, according to Equation (1).

$$P = \frac{V \times (c_s \times c_b)}{m \times 1000} \quad (1)$$

where

V is the volume of the volumetric flask, in millilitres;

m is the corrected mass of the specimen, in grammes;

c_b is the concentration of the individual phthalate of blank solution, in micrograms per millilitre;

c_s is the concentration of the individual phthalate of the specimen solution, corrected for any dilutions, in micrograms per millilitre.

6 Test report

The test report shall include at least the following:

a) a reference to this Technical Specification, i.e. ISO/TS 16181:2011;

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

c) a description of the extraction apparatus;

d) the percentage by mass of each listed phthalate in the plasticized material or tested material;

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

Annex A
(informative)

Suitable gas chromatography-mass spectrometry (GC-MS) apparatus, method and precision data for determination of phthalate plasticizers

A.1 General

The following equipment, column and operating conditions have been found suitable:

Equipment: 6890 gas chromatograph (GC) mass-selective device (MS), quadrupole.

Column: 5 % phenyl methyl siloxane for MS; length 30 m; 0,32 mm interior diameter and 0,25 µm film thickness.

Carrier gas: helium.

Flow rate: 2,0 ml/min.

Injector temperature: 250 °C, mode splitless or split.

Injection volume: 1,0 µl.

Temperature programme:
150 °C for 1 min.
up to 250 °C at 8 °C/min.
up to 290 °C at 3 °C/min.
isothermal 5,00 min.
Total programme time: 34 min.

Transfer line temperature: 290 °C.

MS mode: Electron impact.

Typical quantification ions for phthalate plasticizers are shown in Table A.1.

Table A.1 — Typical quantification ions for phthalate plasticizers

Phthalate plasticizers	Target ion	Q1	Q2
Di-butyl phthalate (DBP)	149	223	205
Butyl benzyl phthalate (BBP)	149	206	238
Di-(2-ethylhexyl) phthalate (DEHP)	149	167	279
Di-*n*-octyl phthalate (DNOP)	149	279	261
Di-iso-nonyl phthalate (DINP)	293	149	127
Di-iso-decyl phthalate (DIDP)	307	149	141
Di-cyclohexyl phthalate (DCHP) (internal standard)	149	167	249
Di-isobutyl phthalate (DIBP)	149	223	205

Depending on the type of equipment used, the appropriate operating conditions may need to be established.