International Standard

ISO 16179

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

Chaussures — Substances critiques potentiellement présentes dans les chaussures et les composants de chaussures — Détermination des composés organostanniques dans les matériaux de chaussures

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Foreword

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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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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 second edition cancels and replaces the first edition (ISO/TS 16179:2012), which has been technically revised.

The changes are as follows:

— the technical specification becomes an ISO standard;

— GC-MS/MS technique added in 8.9.3 and in Clause B.2;

— new extraction solvent in Clause 4;

— new Table 1 (certain substances added) in Clause 4;

— change in the safety instructions at the preparation of the sodium tetraethylborate solution in Clause 8;

— sample preparation reference to ISO 21061 in Clause 7;

— new Table 2 (certain substances added) in 8.3.1;

— deletion of the need for duplicate determinations in Clause 7;

— new Annex B for mass spectroscopy;

— deletion of the reference to ISO 22744-1 in the Bibliography.

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.

Introduction

Certain organotin compounds have been identified as carcinogenic. Thus, several countries have restricted them in articles such as footwear, e.g. in the European Union by commission regulation (EU) 276/2010[1] amending regulation (EC) No 1907/2006[2].

Further organotin compounds are restricted by footwear brands in their restricted substances lists (RSL).

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

1 Scope

This document specifies a test method for the qualification and quantification of organotin compounds by applying gas chromatography coupled with mass spectrometry. This test method is applicable to all types of footwear materials except metal hardware (see ISO/TR 16178).

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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4787, *Laboratory glass and plastic ware — Volumetric instruments — Methods for testing of capacity and for use*

ISO 21061, *Footwear — Chemical tests — General principles on the preparation of samples*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

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

4 Principle

The organotin substances are extracted from the footwear material with methanol, in a medium-strength acidic condition, using tropolone as a complexing agent.

In the previous version of this test method, the extraction solvent was a mixture of methanol-ethanol. Comparisons have shown that methanol gives equivalent results to methanol-ethanol solution. It is still possible to use extraction with methanol-ethanol solution.

The polar and high-boiling organotin is then converted to the corresponding volatile alkyl derivative, by reaction with sodium tetraethylborate, $NaB(Et)_4$. Finally, it is detected and quantified by using a gas chromatograph fitted with a mass selective detector [gas chromatograph with a single quadrupole mass spectrometer (GC-MS) or gas chromatograph with a triple quadrupole mass spectrometer (GC-MS/MS)].

Table 1 indicates the list of target compounds which can be analysed with the method defined in this document. This document is also applicable for further organotin substances provided that the method is validated with the additional compounds.

Table 1 — List of target compounds and internal standards that can be analysed

Type of compound	Compound	CAS Registry Number® [b]
Monosubstituted	Internal standard: *n*-heptyltin trichloride	59344-47-7
	methyltin trichloride	993-16-8
	n-butyltin trichloride	1118-46-3
	n-octyltin trichloride	3091-25-6
	phenyltin trichloride	1124-19-2
Disubstituted	Internal standard: di-*n*-heptyltin dichloride	74340-12-8
	dimethyltin dichloride	753-73-1
	di-*n*-propyltin dichloride	867-36-7
	di-*n*-butyltin dichloride	683-18-1
	di-*n*-octyltin dichloride	3542-36-7
	diphenyltin dichloride	1135-99-5
Trisubstituted	Internal standard: tri-*n*-pentyltin chloride	3342-67-4
	trimethyltin chloride	1066-45-1
	tri-*n*-propyltin chloride	2279-76-7
	tri-*n*-butyltin chloride[a]	1461-22-9
	tri-*n*-octyltin chloride	2587-76-0
	triphenyltin chloride (or fentin chloride)	639-58-7
	tricyclohexyltin chloride	3091-32-5
Tetrasubstituted	Internal standard: tetra-*n*-propyltin	2176-98-9
	tetra-*n*-ethyltin	597-64-8
	tetra-*n*-butyltin	1461-25-2

[a] If bis(tri-*n*-butyltin) oxide (TBTO), CAS RN® 56-35-9, is present, it is detected as tri-*n*-butyltin.

[b] CAS Registry Number® (CAS RN®) is a 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. Equivalent products may be used if they can be shown to lead to the same results.

5 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade and certified reference standards.

5.1 Water, grade 3 according to ISO 3696.

5.2 Glacial acetic acid, CAS RN®: 64-19-7.

5.3 Sodium tetraethylborate, CAS RN®: 15523-24-7.

5.4 Tetrahydrofuran (THF), stabilized, CAS RN®: 109-99-9.

5.5 Internal standards

Alternative internal standards (such as deuterated compounds) to those listed may be used.

5.5.1 *n*-heptyltin trichloride, CAS RN®: 59344-47-7 (internal standard).

5.5.2 Di-*n*-heptyltin dichloride, CAS RN®: 74340-12-8 (internal standard).

5.5.3 Tri-*n*-pentyltin chloride, CAS RN®: 3342-67-4 (internal standard).

5.5.4 Tetra-n-propyltin, CAS RN®: 2176-98-9 (internal standard).

5.6 *n*-Hexane, CAS RN®: 110-54-3.

5.7 Inert gas, e.g. nitrogen, helium or argon.

5.8 Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), of laboratory grade, CAS RN®: 533-75-5.

5.9 Methanol, CAS RN®: 67-56-1.

NOTE If methanol-ethanol solution is used, ethanol, GPR grade or industrial methylated spirit (IMS), CAS RN®: 64-17-5.

5.10 Sodium acetate anhydrous, CAS RN®: 127-09-3.

5.11 Organotin compounds listed in Table 1.

6 Apparatus and materials

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

6.1 Gas chromatograph with a mass selective detector (GC-MS or GC-MS/MS).

6.2 Analytical balance, with a resolution of 0,1 mg.

6.3 Glass vessel, with screw tops and a volume of, for example, 50 ml.

6.4 Micropipettes, of required volumes.

6.5 Pipettes, of required volumes.

6.6 Calibrated pH-meter with a glass combination electrode and range of 0 to 14.

6.7 Volumetric flasks of required volumes.

6.8 Ultrasonic bath with adjustable temperature suitable for operation at about 60 °C.

6.9 Centrifuge.

6.10 Horizontal shaker, with a minimum frequency of 5 s^{-1}.

NOTE Horizontal shaker with minimum frequency of 5 s^{-1}, path length from 2 cm to 5 cm has been found suitable.

6.11 GC vial with PTFE cap, for example 2 ml.

7 Preparation of the sample

Prepare the test specimen in accordance with ISO 21061.

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

from the footwear and the preparation of a test piece, which results in particles with a maximum edge length of 4 mm.

NOTE Up to three test specimens (of equal mass) of the same material type can be tested together taking into consideration the limits of detection and quantification.

8 Procedure

SAFETY PRECAUTIONS — Sodium tetraethylborate is air-sensitive and can spontaneously combust in the presence of air. The solution should be prepared in a fume cupboard without the presence of flammable substances or under inert gas atmosphere. Organotins are both toxic and known endocrine system disrupters; therefore, they should be treated with utmost care.

8.1 General

All the chemicals that are stored below room temperature should be allowed to reach room temperature before an aliquot is taken.

8.2 Preparation of the sodium tetraethylborate solution

Weigh about 2 g of sodium tetraethylborate (5.3) into a 10 ml volumetric flask (6.7) and make up to volume with tetrahydrofuran (5.4).

This solution is stable for approximately three months if stored under an inert gas blanket (5.7), in refrigerator at approximately 4 °C and preferably in an amber container.

NOTE Pre-weighed tetraethylborate or commercial solutions are available on the market.

8.3 Preparation of standard solutions

8.3.1 General

The organotin compounds are available on the market under their chloride forms, but the mass concentration for the calibration curve and the result are expressed in mg/kg of organotin cations. Certified standard solutions are available on the market.

EXAMPLE 1 With dibutyltin dichloride, Bu_2SnCl_2 (dibutyltin dichloride) is the chloride form and Bu_2Sn^{2+} is the cation form.

Table 2 gives the amount of organotin chloride and the weighting factor for recalculation of organotin cations (for 100 % purity of the chloride form).