TECHNICAL SPECIFICATION

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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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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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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.

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ISO/TS 16179 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in collaboration with ISO Technical Committee ISO/TC 216, *Footwear*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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

1 Scope

This Technical Specification specifies a test method for determining the presence of organotin compounds. This test method is applicable to all types of footwear materials.

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

2 Normative references

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

3 Principle

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

The polar and high-boiling organotin is then converted to the corresponding volatile tetra-alkyl derivative, by reaction with sodium tetraethylborate, $NaB(Et)_4$. Finally, it is detected by a gas chromatograph fitted with a mass selective detector (GC-MS).

Table 1 indicates the list of target compounds which can be analysed with this Technical Specification.

Table 1 — List of target compounds which can be analysed with this Technical Specification

Type of compound	Compound	CAS[a]
Monosubstituted	n-butyltin trichloride	1118-46-3
	n-octyltin trichloride	3091-25-6
Disubstituted	Di-n-butyltin dichloride	683-18-1
	Di-n-octyltin dichloride	3542-36-7
Trisubstituted	Tri-n-butyltin chloride	1461-22-9
	Triphenyltin chloride (or fentin chloride)	639-58-7
	Tricyclohexyltin chloride	3091-32-5
Tetrasubstituted	Tetra-n-butyltin	1461-25-2

[a] Chemical Abstract Service.

4 Reagents

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

4.1 Water, grade 3 according to ISO 3696.

4.2 Ethanol, GPR grade or industrial methylated spirit (IMS), CAS number: 64-17-5.

4.3 Glacial acetic acid, CAS number: 64-19-7.

4.4 Sodium tetraethylborate, CAS number: 15523-24-7.

4.5 Tetrahydrofuran (THF), stabilized, CAS number: 109-99-9.

4.6 n-heptyltin trichloride, CAS number: 59344-47-7 (internal standard).

4.7 Di-n-heptyltin dichloride, CAS number: 74340-12-8 (internal standard).

4.8 Tri-n-propyltin monochloride, CAS number: 2279-76-7 (internal standard).

4.9 Tetra-n-propyltin, CAS number: 2176-98-9 (internal standard).

4.10 Isooctane, CAS number: 540-84-1.

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

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

4.13 Methanol, of analytical grade, CAS number: 67-56-1.

4.14 Sodium acetate, CAS number: 127-09-3.

4.15 Organotin compounds listed in Table 1.

5 Apparatus and materials

5.1 GC-MS gas chromatograph fitted with a mass selective detector (MS).

5.2 Analytical balance, capable of measuring mass to an accuracy of 0,1 mg.

5.3 Glove bag, box or isolation chamber with built-in gloves that enables work to be carried out in a totally isolated and controlled environment and has side and front openings and means of sealing the openings, such as tape.

5.4 Sample tubes of polypropylene, with screw tops and a volume of 50 ml.

5.5 Micropipettes, 10 µl to 500 µl range, with disposable tips.

5.6 Pipette, 1 ml to 10 ml capacity.

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

5.8 Volumetric flasks of 10 ml, 25 ml and 100 ml.

5.9 Ultrasonic bath with adjustable temperature.

5.10 Disposable glass Pasteur pipettes.

5.11 Glass beaker.

5.12 Centrifuge.

5.13 Mechanical shaker, adjusted to a minimum frequency of 50 min^{-1}.

6 Preparation of the test piece

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 sample 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 diameter of 4 mm or less.

7 Procedure

SAFETY PRECAUTIONS — Sodium tetraethylborate solution shall be prepared in an inert atmosphere, as this material is air-sensitive and can spontaneously combust in the presence of air. The solution should be prepared in an empty fume cupboard, using the method provided, in order to minimize fire risks. Organotins are both toxic and known endocrine system disrupters; therefore, they should be treated with utmost care.

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

7.1 Preparation of the sodium tetraethylborate solution

7.1.1 Preparation shall be carried out in an inert environment.

7.1.2 Place the analytical balance inside the inert environment, taking the power cord through one of the small side openings, using tape to seal the opening around the cord.

7.1.3 Place the following items in the inert environment:

— a small beaker (5.11);

— a sealed bottle of sodium tetraethylborate (4.4);

— a large spatula, a small spatula and a small beaker containing THF (4.5);

— a disposable pipette (5.10).

7.1.4 Using an inert gas supply (4.11) connected through the side of the inert environment, fill the bag with gas, allowing mixed air and inert gases to be expelled through the front opening for several minutes. This will ensure that any remaining oxygen is of sufficiently low concentration not to support combustion.

7.1.5 Seal the front opening of the inert environment and turn off the inert gas supply.

7.1.6 Using the gloves in the side of the bag, weigh out 2,0 g sodium tetraethylborate (4.4) into the beaker (5.11), then add sufficient THF (4,5) to dissolve the borate (less than 10 ml).

7.1.7 Re-seal the top of the sodium tetraethylborate bottle.

7.1.8 Open the front of the bag and remove all of the items, leaving them inside the fume cupboard for later cleaning.

7.1.9 Transfer the sodium tetraethylborate solution from the beaker (5.11) into a 10 ml volumetric flask (5.8) and make up to the mark with THF (4.5). Store the reagent for a maximum of three months in a fridge, when not in use, to minimize evaporation of the solvent.

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

7.2 Preparation of standard solutions

7.2.1 General

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

EXAMPLE 1 With the 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).

Table 2 — Amount of organotin chloride and weighting factor for recalculation of organotin cations

Compound	Weighting factor	Amount of organotin chloride required to have a solution of 1 000 mg/l of organotin cation (in a 100 ml flask) mg
Target compounds		
n-butyltin trichloride	0,623	160,5
n-octyltin trichloride	0,686	145,8
Di-n-butyltin dichloride	0,767	130,4
Di-n-octyltin dichloride	0,830	120,5
Tri-n-butyltin chloride	0,891	112,2
Triphenyltin chloride	0,908	110,1
Tricyclohexyltin chloride	0,912	109,6
Tetra-n-butyltin	1,000	100,0
Internal standards		
n-heptyltin trichloride	0,672	148,8
di-n-heptyltin dichloride	0,817	122,4
tri-n-propyltin monochloride	0,875	114,3
tetra-n-propyltin	1,000	100,0

EXAMPLE 2 If you weigh 160,5 mg of monobutyltin trichloride ($BuSnCl_3$), you have a solution of 1 605 mg/l of monobutyltin trichloride, which corresponds to a concentration of: 1 605 × 0,623 = 1 000 mg/l of monobutyltin cation ($BuSn^{3+}$).

EXAMPLE 3 If you weigh 110,4 mg of dioctyltin dichloride $(C_8H_{17})_2SnCl_2$), you have a solution of 1 104 mg/l of dioctyltin dichloride, which corresponds to a concentration of: 1 104 × 0,830 = 916 mg/l of dioctyltin cation $[(C_8H_{17})_2Sn^{2+}]$.

The concentration of organotin cation is usually calculated using Formula (1):

$$C_{Sn} = C_{Cl} \times WF \quad (1)$$

where

C_{Sn} is the concentration of organotin cation (mg/l);

C_{Cl} is the concentration of organotin chloride (mg/l);

WF is the weighting factor.

7.2.2 Internal standards – stock solution (1 000 mg/l of organotin cation)

Use the analytical balance (5.2) to weigh the appropriate amount of tripropyltin hydrochloride (4.8), monoheptyltin trichloride (4.6), diheptyltin dichloride (4.7) and tetrapropyltin (4.9). Dissolve them together in methanol (4.13) in a single volumetric flask (5.8) of at least 100 ml to obtain the concentration of 1 000 mg/l for each substance.

Store the standard solution for a maximum of one year in a fridge, when not in use, to minimize evaporation of the solvent.

7.2.3 Internal standards – working solution (10 mg/l of organotin cation)

Use the pipette (5.6) to transfer 1,0 ml of the internal standard solution (7.2.2) into a 100 ml volumetric flask (5.8). Make the solution up to volume with methanol (4.13).

This corresponds to a 10 mg/l working solution for the four internal standards.

7.2.4 Target compounds – stock solution (1 000 mg/l of organotin cation)

Use the analytical balance (5.2) to weigh the appropriate amount of each target compound (see Table 1). Dissolve them together in methanol (4.13) in a single volumetric flask (5.8) of at least 100 ml to obtain the concentration of 1 000 mg/l for each substance.

Store the standard solution for a maximum of one year in a fridge, when not in use, to minimize evaporation of the solvent.

7.2.5 Target compounds – working solution (10 mg/l of organotin cation)

Use the calibrated pipette (5.6) to dispense 1,00 ml of the target compound stock solution (7.2.4) into a 100 ml volumetric flask (5.8). Make the solution up to volume with methanol (4.13).

This corresponds to a 10 mg/l solution for the target compound working solution.

NOTE Commercial solutions are available on the market for use in preparing the internal standards working solution and the target compound working solution. Be mindful of the concentration and the species (chloride or cation forms) of the commercial solution. Use an appropriate solvent and dilution factor to have working solution at 10 mg/l of organotin cation in a water-miscible solvent.

7.3 Preparation of the tropolone solution

Use the analytical balance (5.2) to measure 0,500 g of tropolone (4.12) into a glass beaker (5.11) and dissolve in approximately 20 ml of methanol (4.13). Dilute to 100 ml in a volumetric flask (5.8).

This solution can be used for up to one month from preparation and stored in a fridge at approximately 4 °C.

7.4 Preparation of the buffer solution

Prepare a 0,2 M sodium acetate solution, for example by weighting 16,4 g of sodium acetate (4.14) in 1 l of water (4.1) and adjust the pH to 4,5 with acetic acid (4.3).

7.5 Calibration

7.5.1 As a guide, choose standards of concentration 100 µg/l, 200 µg/l, 300 µg/l, 400 µg/l and 500 µg/l.

7.5.2 These are added as 20 µl, 40 µl, 60 µl, 80 µl and 100 µl aliquots by micropipette (5.5) of the target compounds working solution (7.2.5) to individual vessels containing 20 ml of methanol (4.13)/ethanol (4.2) mixture (80/20 in volume).

7.5.3 Add 100 µl of internal standard (ISTD) (7.2.3).