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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Foreword

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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: $1\,605 \times 0{,}623 = 1\,000$ 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: $1\,104 \times 0{,}830 = 916$ 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).

7.5.4 Add 8 ml of buffer solution pH 4,5 (7.4).

7.5.5 Add 1 ml of tropolone solution by pipette (5.6).

7.5.6 Add 100 µl sodium tetraethyl borate solution (7.1.9) and shake vigorously for 30 min.

7.5.7 Using a pipette (5.6), transfer 2 ml of isooctane (4.10) into the vessel and shake vigorously for 30 min.

7.5.8 Transfer the isooctane phase to the gas chromatograph for analysis.

7.6 Sample preparation

7.6.1 Use the analytical balance (5.2) to weigh (1,0 $\pm$ 0,1) g of sample (see Clause 6) into a tared empty vessel of volume 50 ml (5.4) and record the mass, m_1, with a precision to 0,1 mg.

7.6.2 Add 20 ml of methanol (4.13)/ethanol (4.2) mixture (80/20 in volume).

7.6.3 Add 100 µl of internal standard (ISTD) (7.2.2).

7.6.4 Add 1 ml of tropolone solution (7.3) by pipette (5.6).

7.6.5 Extract in an ultrasonic bath (5.9) for 1 h at 60 °C.

7.6.6 If required, centrifuge at 4 000 g for 5 min and transfer the clear solution into another vessel.

7.6.7 Add 8 ml of buffer solution pH 4,5 (7.4).

7.6.8 Add 100 µl sodium tetraethyl borate solution (7.1.9) and shake vigorously for 30 min using a mechanical shaker (5.13).

7.6.9 Using a pipette (5.6), transfer 2 ml of isooctane (4.10) into the vessel and shake vigorously for 30 min using a mechanical shaker (5.13).

NOTE For a better separation, centrifugation at 4 000 g can be used.

7.6.10 Transfer the isooctane phase to the gas chromatograph for analysis.

7.7 Preparation of the blank solution

Prepare the blank solution in the same way as the samples (see 7.6.2 to 7.6.10).

7.8 Gas chromatography

NOTE Refer to user instructions for the analytical equipment used (e.g. a protocol is given in Annex A).

7.8.1 General

When possible, duplicate determinations shall be performed on all samples, blank and standard solutions.

7.8.2 Identification

Identify the target compounds by comparing the retention times for samples and calibration. Retention times for samples have to be in a time window of ($T_r \pm 1$) % compared to the calibration.

Three diagnostic ions (one ion for quantification and the two others for qualification) and the full spectra are used for the detection of the target compounds (see Table 3 for the choice of the three diagnostic ions).

Use the mass spectrometer in simultaneous SIM/SCAN mode, or in SIM mode with SCAN confirmation in case of positive results.

The target compounds have to be quantified with an internal standard with the same degree of substitution.

Table 3 — Likelihood of diagnostic ions determining and quantifying the target compound, and their respective internal standard

Compound (as ethyl derivative)	Group 1	Group 2	Group 3
Internal standard: Monoheptyltriethyltin	**277/275**	**179/177**	**151/149**
n-butyltriethyltin	235/233	179/177	151/149
n-octyltriethyltin	291/289	179/177	151/149
Internal standard: Diheptyldiethyltin	**347/345**	**249/247**	**151/149**
Di-n-butyldiethyltin	263/261	179/177	151/149
Di-n-octyldiethyltin	375/373	263/261	151/149
Internal standard: Tripropylmonoethyltin	**249/247**	**235/233**	**193/191**
Tri-n-butylmonoethyltin	291/289	263/261	179/177
Tricyclohexylmonoethyltin	233/231	315/313	369/367
Triphenylmonoethyltin	351/349	197/195	—
Internal standard: tetra-n-propyltin	**249/247**	**165/163**	**207/205**
Tetra-n-butyltin	291/289	235/233	179/177
NOTE The monosubstituted target compounds are quantified under the monosubstituted internal standard. For example, n-butyltriethyltin and n-octyltriethyltin appear under the internal standard monoheptyltriethyltin.			

7.9 Quantification

7.9.1 Calculate the total peak areas of the standards, the internal standard, and each detected organotin species in the sample.

7.9.2 Using the data from the organotin standards, calculate the detector response factor, DRF, for each tin compound at each tin concentration using Formula (2):

$$DRF = \frac{CS_{\mathrm{Sn}} \times AR_{\mathrm{is}}}{AS_{\mathrm{Sn}} \times CR_{\mathrm{is}}} \quad (2)$$

where

CS_{Sn} is the concentration of organotin cation in the standard, in µg/l;

AR_{is} is the peak area of the relevant internal standard;

AS_{Sn} is the peak area of organotin cation in the standard;

CR_{is} is the concentration of the relevant internal standard (500 µg/l).

7.9.3 For each compound, calculate an average with all the DRF obtained at each level of concentration using Formula (3):

$$DRF_{\mathrm{a}} = \frac{1}{n}\sum_{\mathrm{i}=1}^{n} DFR_{\mathrm{i}} \tag{3}$$

Theoretically, the DRF values for a particular tin compound should be exactly the same, but slight differences are seen.

7.9.4 This average DRF value, DRF_{a}, is used to calculate the concentration of organotins in the sample using Formula (4):

$$C_{\mathrm{Sn}} = \frac{A_{\mathrm{Sn}} \times DRF_{\mathrm{a}} \times C_{\mathrm{is}}}{A_{\mathrm{is}}} \tag{4}$$

where

C_{Sn} is the concentration of organotin cation in the sample, in µg/l;

A_{Sn} is the peak area of organotin;

C_{is} is the concentration of the corresponding internal standard (500 µg/l);

A_{is} is the peak area of the corresponding internal standard.

7.9.5 Using Formula (5), convert C_{Sn}, whose units are expressed in µg/l, into µg/kg:

$$M_{\mathrm{Sn}} = \frac{C_{\mathrm{Sn}} \times V}{m_1} \tag{5}$$

where

M_{Sn} is the amount of tin, in µg/kg;

C_{Sn} is the concentration of organotin cation in the sample, in µg/l;

V is the volume of isooctane aliquot taken in 7.6.9 (2 ml);

m_1 is the mass of the sample obtained in 7.6.1, in g.

7.10 Detection limit and quantification limit

The detection limit shall be 50 µg/kg and the quantification limit shall be 200 µg/kg.

8 Test report

The test report shall include, at least, the following:

a) a reference to this Technical Specification, i.e. ISO/TS 16179;

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

c) the temperature at which the test was carried out;

d) the test result (in organotin cation) as recorded in 7.9;

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

Annex A
(informative)

Suggested gas chromatography-mass spectrometry (GC-MS) conditions for organotin analysis

Column length: 25 m, internal diameter 0,22 mm. A BPX5 column (SGE) or equivalent is suitable. No retention gap column should be used.

Carrier gas: helium, flow rate 0,76 ml/min, linear velocity 33,5 cm/s.

Injector temperature: 240 °C, mode splitless, splitless time 2,0 min.

Injection volume: 1,0 µl.

Temperature programme:	60 °C for 4 min.	
	Up to 300 °C at 20 °C/min.	
	300 °C for 6 min.	
	Total programme time: 22 min.	
Analyser temperatures:	Transfer line:	280 °C.
	Ion source:	180 °C (approximately).
	Quadrupole:	140 °C (approximately).
	Electron multiplier:	65 °C (approximately).
Selected ion monitoring (SIM) parameters:		
Time interval 1	Ions selected for detection:	179,00 amu, 235,00 amu, 263,00 amu, 291,00 amu, 375,00 amu.
	Dwell time per ion:	100 ms.
	Ion selection change at:	14,8 min.
Time interval 2	Ions selected for detection:	197,00 amu, 233,00 amu, 315,00 amu, 351,00 amu, 369,00 amu.
	Dwell time per ion:	100 ms.

Annex B
(informative)

Reliability of the method

The data in Table B.1 were obtained in a collaborative correlation trial carried out by five laboratories.

Table B.1 — Results of correlation trial

Organotin compound	Expected result µg/kg	Laboratory results								Average value	Standard deviation	RSD %
		1	2	3	4	5	6	7	8			
MBT[a]	1 000	1 545	868	1798	1 590	1 610	1 700	1 950	2 140	1 650	375	23
DBT[b]	1 000	786	786	760	690	710	840	800	760	767	48	6
TBT[c]	500	348	415	484	400	490	490	440	600	458	76	17

[a] Mono-butyl.

[b] Di-butyl.

[c] Tri-butyl.

Bibliography

[1] ISO/TR 16178, *Footwear — Critical substances potentially present in foot wear and footwear components*

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