DRAFT INTERNATIONAL STANDARD

ISO/DIS 22744-1

ISO/TC **38**

Secretariat: **SAC**

Voting begins on:
2018-08-02

Voting terminates on:
2018-10-25

Textiles and textile product — Critical substances potentially present in components of textile product materials — Determination of organotin compounds —

Part 1:
Method using gas chromatography

Titre manque —

Partie 1: Titre manque

ICS: 59.080.01

This document is circulated as received from the committee secretariat.

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/DIS 22744-1:2018(E)

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Published in Switzerland

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European foreword

This document (TC 248 WI 619) has been prepared by Technical Committee CEN/TC 248 “Textiles and textile products”, the secretariat of which is held by BSI.

This document is currently submitted to the CEN Enquiry.

This document is adapted from ISO/TS 16179, 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). The adaptation is based on the extension of the scope to textile products.

Textiles and textile product — Critical substances potentially present in components of textile product materials — Determination of organotin compounds —

Part 1: Method using gas chromatography

1 Scope

This document specifies a test method for determining the presence of organotin compounds. This test method is applicable to all types of materials of textile products.

NOTE CEN/TR 16741 defines which materials are applicable to this determination.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Principle

The organotin substances are extracted from the material of a textile product with a methanol-ethanol mixture, in a medium-strength acidic condition, using sodium diethyldithiocarbamate (NaDDC) as a complexing 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 document.

Table 1 — List of target compounds which can be analysed

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

[a] Chemical Abstract Service.

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

Table 1 *(continued)*

Type of compound	Compound	CAS[a]
Trisubstituted	Tri-n-butyltin chloride[b]	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.

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

4 Reagents

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

4.1 Water, grade 3 according to **EN 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 Sodium diethyldithiocarbamate (NaDDC), CAS number: 148-18-5.

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

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

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

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

5.5 Pipette, 1 ml to 10 ml capacity.

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

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

5.8 Centrifuge.

5.9 Horizontal 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 textile product, such as textile, coated material, polymer, leather or other. The preparation of the sample should involve the removal of the individual materials from the textile product and the preparation of a test piece, which results in particles with a maximum diameter of 4 mm or less.

7 Procedure

SAFETY PRECAUTIONS — As sodium tetraethylborate is air-sensitive and can spontaneously combust in the presence of air, the solution using it shall be prepared in a high-volume fume hood. 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

Weigh about 2 g of *sodium tetraethylborate* (4.4) into a 10 ml volumetric flask and make up to volume with *tetrahydrofuran* (4.5).

This solution is stable for about three months if stored under an inert gas blanket.

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):

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

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 refrigerator at about 6 °C, 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 refrigerator at about 6 °C, 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. 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 NaDDC solution

Use the *analytical balance* (5.2) to measure 0,600 g of *NaDDC* (4.12) into a glass beaker (5.11) and dissolve in approximately 20 ml of *ethanol* (4.2). Dilute to 100 ml in a volumetric flask.

This solution can be used for up to one month from preparation and stored in a refrigerator at about 6 °C.

7.4 Preparation of the buffer solution

Prepare a 0,2 M sodium acetate solution, for example by weighing 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 NaDDC solution by *pipette* (**5.6**).

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

