
**Textiles and textile products —
Determination of organotin
compounds —**

**Part 1:
Derivatisation method using gas
chromatography**

*Textiles et produits textiles — Détermination des composés
organostanniques —*

*Partie 1: Méthode de dérivation utilisant la chromatographie en
phase gazeuse*



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 the European Committee for Standardization (CEN) Technical Committee CEN/TC 248, *Textiles and textile products*, in collaboration with ISO Technical Committee ISO/TC 38, *Textiles*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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.

Textiles and textile products — Determination of organotin compounds —

Part 1: Derivatisation method using gas chromatography

WARNING — The use of this document involves hazardous materials. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of the document.

1 Scope

This document specifies a test method for the qualification and quantification 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 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 glassware — Volumetric instruments — Methods for testing of capacity and for use*

3 Terms and definitions

No terms and definitions are listed in this document.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Principle

The organotin substances are extracted from the material of a textile product with a methanol-ethanol mixture using tropolone as a complexing agent.

The polar and high-boiling organotin is then converted to the corresponding volatile alkyl derivative, by reaction with sodium tetraethylborate, $\text{NaB}(\text{Et})_4$. Finally, it is detected and quantified by using 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.

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 that can be analysed and internal standards

Type of compound	Compound	CAS ^a number
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 ^b	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 Chemical Abstract Service.		
^b If bis(tri-n-butyltin)oxide (TBTÖ), CAS number 56-35-9, is present, it is detected as tri-n-butyltin.		

5 Reagents

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

5.1 Water, grade 3 according to ISO 3696.

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

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

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

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

5.6 n-Heptyltin trichloride, CAS number: 59344-47-7 (internal standard).

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

5.8 Tri-n-pentyltin chloride, CAS number: 3342-67-4 (internal standard).

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

If the recovery rate of the internal standards ([5.6](#), [5.7](#), [5.8](#) and [5.9](#)) is low, alternative internal standards may be used (for example deuterated compounds) (see also [9.1](#)).

5.10 Hexane, CAS number: 110-54-3.

5.11 Inert gas, e.g. nitrogen or argon.

5.12 Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), CAS number: 533-75-5.

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

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

5.15 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).

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

6.5 Pipettes, 1 ml to 10 ml capacity.

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

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

6.8 Centrifuge.

6.9 Horizontal mechanical shaker.

NOTE Horizontal shaker with minimum frequency of 5 s⁻¹, path length 2 cm to 5 cm has been found suitable.

6.10 Volumetric flasks, 10 ml to 500 ml as required.

7 Preparation of the test piece

The test piece consists of a single material taken from the textile product, such as textile, coated material, polymer 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 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

8.1 General

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.

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 (5.4) into a 10 ml volumetric flask (6.10) and make up to volume with tetrahydrofuran (5.5).

This solution is stable for about three months if stored under an inert gas blanket (5.11).

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 as their chloride forms, but the mass concentration for the calibration curve and the result are expressed in mg/kg of organotin cations.

EXAMPLE 1 With dibutyltin dichloride, Bu_2SnCl_2 (dibutyltin dichloride) is the chloride form and $\text{Bu}_2\text{Sn}^{2+}$ 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		
Methyltin trichloride	0,557	179,5
n-Butyltin trichloride	0,623	160,5
n-Octyltin trichloride	0,686	145,8
Phenyltin trichloride	0,648	154,3
Dimethyltin dichloride	0,677	147,7
Di-n-propyltin dichloride	0,742	134,8
Di-n-butyltin dichloride	0,767	130,4
Di-n-octyltin dichloride	0,830	120,5
Diphenyltin dichloride	0,793	126,1
Trimethyltin chloride	0,821	121,8
Tri-n-propyltin chloride	0,875	114,3
Tri-n-butyltin chloride	0,891	112,2
^a These compounds have no chloride and therefore the weighting factor is 1,000.		

Table 2 (continued)

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
Tri-n-octyltin chloride	0,927	107,9
Triphenyltin chloride	0,908	110,1
Tricyclohexyltin chloride	0,912	109,6
Tetra-n-ethyltin ^a	1,000	100,0
Tetra-n-butyltin ^a	1,000	100,0
Internal standards		
n-Heptyltin trichloride	0,672	148,8
Di-n-heptyltin dichloride	0,817	122,4
Tri-n-pentyl chloride	0,906	110,4
Tetra-n-propyltin ^a	1,000	100,0
^a These compounds have no chloride and therefore the weighting factor is 1,000.		

The mass concentration of organotin cation is usually calculated using [Formula \(1\)](#):

$$\rho_{\text{Sn}} = \rho_{\text{Cl}} \times W_F \quad (1)$$

where

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

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

W_F is the weighting factor.

EXAMPLE 2 If you weigh 160,5 mg of monobutyltin trichloride (BuSnCl_3), into 100 ml solvent, you have a solution of 1 605 mg/l of monobutyltin trichloride, which corresponds to a mass 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 $[(\text{C}_8\text{H}_{17})_2\text{SnCl}_2]$, into 100 ml solvent, you have a solution of 1 104 mg/l of dioctyltin dichloride, which corresponds to a mass concentration of: $1\,104 \times 0,830 = 916$ mg/l of dioctyltin cation $[(\text{C}_8\text{H}_{17})_2\text{Sn}^{2+}]$.

8.3.2 Internal standards — Stock solution (100 mg/l of organotin cation)

Internal standards are available commercially as certified solutions, or a solution of internal standards can be made. Four internal standards shall be used as solutions in methanol ([5.13](#)).

To prepare an internal standard solution use the analytical balance ([6.2](#)) to weigh the appropriate amount of n-heptyltin trichloride ([5.6](#)), di-n-heptyltin dichloride ([5.7](#)), tri-n-pentyltin chloride ([5.8](#)) and tetra-n-propyltin ([5.9](#)). Dissolve them together in methanol ([5.13](#)) in a single volumetric flask ([6.10](#)) to obtain the mass concentration of 100 mg/l for each organotin cation.

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.

8.3.3 Internal standards — Working solution (10 mg/l of organotin cation)

Use a pipette ([6.5](#)) to transfer an appropriate volume of the internal standard solution ([8.3.2](#)) into a volumetric flask ([6.10](#)) and make the solution up to volume with methanol ([5.13](#)) to create a 10 mg/l solution of each organotin cation.

8.3.4 Target compounds — Stock solution (1 000 mg/l of organotin cation)

Target compounds are available commercially as certified solutions, or a solution of target compounds may be made.

Use the analytical balance (6.2) to weigh the appropriate amount of each target compound (see Table 1). Dissolve each of them (separately) in methanol (5.13) in an appropriately sized volumetric flask (6.10) to obtain the mass concentration of 1 000 mg/l for each organotin cation.

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.

8.3.5 Target compounds — Working solution (10 mg/l of organotin cation)

Use a pipette (6.5) to dispense an appropriate volume of each target compound stock solution (see 8.3.4) into an appropriately sized volumetric flask (6.10) and make the solution up to volume with methanol (5.13) to create a 10 mg/l solution of organotin cation.

8.4 Preparation of the tropolone solution

For example, use the analytical balance (6.2) to measure 0,500 g of tropolone (5.12) into a glass beaker and dissolve in approximately 20 ml of methanol (5.13). Dilute this solution to 100 ml, with methanol, in a volumetric flask (6.10), to obtain a 5 g/l solution of tropolone.

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

8.5 Preparation of the buffer solution

Prepare a 0,2 mol/l sodium acetate solution, for example by weighing 16,4 g of sodium acetate (5.14) in 1 l of water (5.1) and adjust the pH to 4,5 with glacial acetic acid (5.3).

8.6 Preparation of the calibration solutions

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

8.6.2 These are added as 20 µl, 40 µl, 60 µl, 80 µl and 100 µl aliquots by micropipette (6.4) of the target compounds working solutions (see 8.3.5) to individual vessels containing 20 ml of methanol (5.13)/ethanol (5.2) mixture (80/20 in volume).

8.6.3 Add an appropriate amount of internal standard working solution (ISTD) (see 8.3.3).

8.6.4 Add 8 ml of buffer solution pH 4,5 (see 8.5).

8.6.5 Add 1 ml of tropolone solution by pipette (6.5).

8.6.6 Add 100 µl sodium tetraethylborate solution (see 8.2) and shake vigorously for 30 min using a mechanical shaker (6.9).

8.6.7 Using a pipette (6.5), transfer 2 ml of hexane (5.10) into the vessel and shake vigorously for 30 min using a mechanical shaker (6.9).

8.6.8 Transfer the hexane phase to a GC-MS vial for analysis.

If necessary (to get a clear hexane layer) centrifuge (6.8) for 5 min.

8.7 Sample preparation

8.7.1 Use the analytical balance (6.2) to weigh $(1,0 \pm 0,1)$ g of sample (see [Clause 7](#)) into a vessel of volume 50 ml (6.3) and record the mass, m_1 , with a precision of 0,1 mg.

8.7.2 Add 20 ml of methanol (5.13)/ethanol (5.2) mixture (80/20 in volume).

8.7.3 Add an appropriate amount of internal standard working solution (ISTD) (see 8.3.3).

8.7.4 Add 1 ml of tropolone solution (see 8.4) by pipette (6.5).

8.7.5 Extract in an ultrasonic bath (6.7) at (60 ± 5) °C for $1 \text{ h} \pm 5 \text{ min}$.

8.7.6 If required, centrifuge for 5 min and transfer the clear solution into another vessel.

8.7.7 Add 8 ml of buffer solution pH 4,5 (see 8.5).

8.7.8 Add 100 µl sodium tetraethylborate solution (see 8.2) and shake vigorously for 30 min using a mechanical shaker (6.9).

8.7.9 Using a pipette (6.5), transfer 2 ml of hexane (5.10) into the vessel and shake vigorously for 30 min using a mechanical shaker (6.9).

8.7.10 If required (to get a clear hexane layer), centrifuge (6.8) for 5 min.

8.7.11 Transfer the hexane phase to a GC-MS vial for analysis.

8.8 Preparation of the blank solution

Prepare the blank solution in the same way as the samples (see 8.7.2 to 8.7.11).

8.9 Gas chromatography

NOTE Refer to user instructions for the analytical equipment used (a protocol is given in [Annex A](#) as an example).

Identify the target compounds by comparing the retention times for samples and 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 shall be quantified with an internal standard with the same degree of substitution.

Table 3 — Recommended ions for determining and quantifying the target compounds, and their respective internal standard

Compound (as ethyl derivative)	Group 1 <i>m/z</i> u	Group 2 <i>m/z</i> u	Group 3 <i>m/z</i> u
Internal standard: Monoheptyltriethyltin	277/275	179/177	151/149
Methyltriethyltin	193/191	165/163	—
n-Butyltriethyltin	235/233	179/177	151/149
n-Octyltriethyltin	291/289	179/177	151/149
Phenyltriethyltin	255/253	227/225	197/195
Internal standard: Di-n-heptyldiethyltin	347/345	249/247	151/149
Dimethyldiethyltin	179/177	151/149	—
Di-n-propyldiethyltin	235/233	193/191	151/149
Di-n-butyldiethyltin	263/261	179/177	151/149
Di-n-octyldiethyltin	375/373	263/261	151/149
Diphenyldiethyltin	303/301	275/273	197/195
Internal standard: Tri-n-pentylmonoethyltin	333/331	291/289	221/219
Trimethylmonoethyltin	165/163	179/177	151/149
Tri-n-propylmonoethyltin	249/247	235/233	193/191
Tri-n-butylmonoethyltin	291/289	263/261	179/177
Tri-n-octylmonoethyltin	459/457	375/373	263/261
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-ethyltin	179/177	151/149	207/205
Tetra-n-butylin	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.

9 Expression of results

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

NOTE If the recovery of the internal standard is suspected to be lower than the expected value (due to matrix effects or unknown reasons), increasing the amount of sodium tetraethylborate can lead to a better recovery.

9.2 Using the data from the organotin standards, calculate the detector response factor, D_{RF} , for each tin compound at each tin mass concentration using [Formula \(2\)](#):

$$D_{RF} = \frac{\rho_{St,Sn} \times A_{St,is}}{A_{St,Sn} \times \rho_{St,is}} \quad (2)$$

where

$\rho_{St,Sn}$ is the mass concentration of organotin cation in the standard, in $\mu\text{g/l}$;

$A_{St,is}$ is the peak area of the relevant internal standard;

$A_{St,Sn}$ is the peak area of organotin cation in the standard;

$\rho_{St,is}$ is the mass concentration of the relevant internal standard (e.g. 500 $\mu\text{g/l}$).

NOTE The abbreviation St refers to Standard.

9.3 For each compound, calculate an average with all the D_{RF} obtained at each level of mass concentration using [Formula \(3\)](#):

$$D_{RFa} = \frac{1}{n} \sum_{i=1}^n D_{RFi} \quad (3)$$

Theoretically, the D_{RF} values for a particular tin compound should be exactly the same, but slight differences are seen. Therefore, the average is calculated.

9.4 This average D_{RF} value, D_{RFa} , is used to calculate the mass concentration of organotins in the sample using [Formula \(4\)](#):

$$\rho_{Sn} = \frac{A_{Sn} \times D_{RFa} \times \rho_{is}}{A_{is}} \quad (4)$$

where

ρ_{Sn} is the mass concentration of organotin cation in the sample, in $\mu\text{g/l}$;

A_{Sn} is the peak area of organotin;

ρ_{is} is the mass concentration of the corresponding internal standard (500 $\mu\text{g/l}$);

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

9.5 Using [Formula \(5\)](#), convert ρ_{Sn} , whose units are expressed in $\mu\text{g/l}$, into $\mu\text{g/kg}$:

$$w_{Sn} = \frac{\rho_{Sn} \times V}{m_1} \quad (5)$$

where

w_{Sn} is the mass fraction of organotin cation, in $\mu\text{g/kg}$;

ρ_{Sn} is the mass concentration of organotin cation in the sample, in $\mu\text{g/l}$;

V is the volume of hexane aliquot taken in [8.7.9](#) (2 ml);

m_1 is the mass of the sample obtained in [8.7.1](#), in g.

9.6 Detection limit and quantification limit

With this method it is feasible to reach detection limits of 50 $\mu\text{g/kg}$ and quantification limits of 200 $\mu\text{g/kg}$.

10 Test report

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

- a) a reference to this document, i.e. ISO 22744-1:2020;
- b) all details necessary for complete identification of the sample tested;
- c) the test result (as organotin cation) as recorded in [9.5](#) or in mg/kg;
- d) any deviation, by agreement or otherwise, from the procedure specified;
- e) any unusual features observed;
- f) the date of the test.

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