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# 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

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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).

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# 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, $NaB(Et)_4$. 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 (TBTO), 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 $Bu_2Sn^{2+}$ 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** | | |
| 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):

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

where

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

$\rho_{Cl}$ 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 × 0,623 = 1 000 mg/l of monobutyltin cation ($BuSn^{3+}$).

EXAMPLE 3 If you weigh 110,4 mg of dioctyltin dichloride [$(C_8H_{17})_2SnCl_2$], 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 × 0,830 = 916 mg/l of dioctyltin cation [$(C_8H_{17})_2Sn^{2+}$].

### 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 ± 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 h ± 5 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<br>*m/z*<br>u | Group 2<br>*m/z*<br>u | Group 3<br>*m/z*<br>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-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.



## 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 µg/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 µg/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):

$$D_{RF\mathrm{a}} = \frac{1}{n}\sum_{i=1}^{n} D_{RFi} \tag{3}$$

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):

$$\rho_{Sn} = \frac{A_{\mathrm{Sn}} \times D_{RFa} \times \rho_{is}}{A_{\mathrm{is}}} \tag{4}$$

where

$\rho_{Sn}$ is the mass concentration of organotin cation in the sample, in µg/l;

$A_{\mathrm{Sn}}$ is the peak area of organotin;

$\rho_{is}$ is the mass concentration of the corresponding internal standard (500 µg/l);

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

**9.5** Using Formula (5), convert $\rho_{\mathrm{Sn}}$, whose units are expressed in µg/l, into µg/kg:

$$w_{\mathrm{Sn}} = \frac{\rho_{\mathrm{Sn}} \times V}{m_1} \tag{5}$$

where

$w_{\mathrm{Sn}}$ is the mass fraction of organotin cation, in µg/kg;

$\rho_{\mathrm{Sn}}$ is the mass concentration of organotin cation in the sample, in µg/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 µg/kg and quantification limits of 200 µg/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.