INTERNATIONAL STANDARD

ISO 22744-2

First edition
2020-08

Textiles and textile products — Determination of organotin compounds —

Part 2: Direct method using liquid chromatography

Textiles et produits textiles — Détermination des composés organostanniques —

Partie 2: Méthode directe utilisant la chromatographie en phase liquide

Reference number
ISO 22744-2:2020(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 22744 series can be found on the ISO website.

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 2:
Direct method using liquid 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 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 compounds are extracted from the material of a textile product with a methanol-ethanol mixture using tropolone as a complexing agent. The mono- and di-organotin-tropolone complexes and tri-organotin cations formed in the extraction procedure are directly analysed by a liquid chromatograph with a tandem mass spectrometer (LC-MS/MS). This method does not require additional derivatization step.

Table 1 indicates the list of organotin compounds which can be analysed with this document.

This document is also applicable for further organotin compounds provided that the method is validated with the additional compounds.

Table 1 — List of organotin compounds that can be analysed and internal standards

Type of compound	Compound	CAS[a] number
Monosubstituted	Internal standard: n-Heptyltin trichloride	59344–47–7
	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
	Di-n-butyltin dichloride	683–18–1
	Di-n-octyltin dichloride	3542–36–7
	Diphenyltin dichloride	1135–99–5
Trisubstituted	Internal standard: 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

[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, analytical grade chemicals, especially relevant for liquid chromatography (5.1 to 5.5) shall be used.

5.1 Water.

5.2 Methanol.

5.3 Ethanol.

5.4 Ammonium formate.

5.5 Formic acid.

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

5.7 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 Analytical balance, with resolution of 0,1 mg.

6.2 Glass vessel, with screw cap, e.g. 40 ml.

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

6.4 Disposable syringe and syringe filter, with 0,45 µm pore size or less.

6.5 Glass vial, with septum cap for LC, e.g. 2 ml.

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

6.7 Pipettes, 1 ml to 10 ml capacity.

6.8 Liquid chromatograph with tandem mass spectrometer (LC-MS/MS).

NOTE C18 reverse phase column for liquid chromatography has been found suitable for the analysis.

7 Preparation of the test sample

The test sample 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.

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 — Organotin compounds 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 extraction solvent (250 mg/l of tropolone in methanol/ethanol mixture)

For example, use the analytical balance (6.1) to measure 0,125 g of tropolone (5.6) into a glass beaker and dissolve in approximately 20 ml of methanol (5.2)/ethanol (5.3) mixture (80/20 in volume). Dilute to 500 ml with the same methanol (5.2)/ethanol (5.3) mixture in a volumetric flask to obtain a 250 mg/l solution of tropolone.

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

8.3 Preparation of standard solution

8.3.1 General

Commercial solutions are available on the market for use in preparing the internal standards working solution and standards working solution. Be mindful of the concentration and the species (chloride or cation forms) of the commercial solution. The mass concentration for the calibration curve and the result are expressed as organotin cations.

EXAMPLE With the Di-n-butyltin dichloride (Bu_2SnCl_2) is the chloride form and Bu_2Sn^{2+} is the cation form.

8.3.2 Internal standards — Stock solution (1 000 mg/l of organotin cation)

Internal standards are available commercially as certified solutions. Alternatively, a solution of internal standards can be made. Three internal standards shall be used as solutions in methanol (5.2).

To prepare an internal standard solution, use the analytical balance (6.1) to weigh the appropriate amount of Tri-n-propyltin chloride, Di-n-heptyltin dichloride and n-Heptyltin trichloride. Dissolve them together in methanol (5.2) in a single volumetric flask 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.

8.3.3 Internal standards — Working solution (2 mg/l of organotin cation)

Use a micropipette (6.6) to transfer an appropriate volume of the internal standard stock solution (see 8.3.2) into a volumetric flask and make the solution up to volume with methanol (5.2) to create a 2 mg/l solution of each organotin cation.

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

Standards are available commercially as certified solutions. Alternatively, a solution of standards may be made.

Use the analytical balance (6.1) to weigh the appropriate amount of each organotin compounds (see Table 2). Dissolve each of them (separately) in methanol (5.2) in an appropriate volumetric flask 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 Standards — Working solution (10 mg/l of organotin cation)

Use a micropipette (6.6) to transfer an appropriate volume of each standard stock solution (see 8.3.4) into an appropriate volumetric flask and make the solution up to volume with methanol (5.2) to create a 10 mg/l solution of organotin cation.

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

OTC	OC	Acronym[a]	Weighting factor[b]	Mass[c] mg
Standards				
n-Butyltin trichloride	n-Butyltin cation	MBT	0,623	160,5
n-Octyltin trichloride	n-Octyltin cation	MOT	0,686	145,8
Phenyltin trichloride	Phenyltin cation	MPhT	0,648	154,3
Di-n-butyltin dichloride	Di-n-butyltin cation	DBT	0,767	130,4
Di-n-octyltin dichloride	Di-n-octyltin cation	DOT	0,830	120,5
Diphenyltin dichloride	Diphenyltin cation	DPhT	0,793	126,1
Tri-n-butyltin chloride	Tri-n-butyltin cation	TBT	0,891	112,2
Tri-n-octyltin chloride	Tri-n-octyltin cation	TOT	0,927	107,9

[a] Acronyms correspond organotin chlorides (OTC) and organotin cations (OC).

[b] Weighting factor = molar mass (OC)/molar mass (OTC).

[c] If the mass of the compounds weighed is different from that given in this table, use the weighting factor to calculate the actual concentration of the OC.

Table 2 *(continued)*

OTC	OC	Acronym[a]	Weighting factor[b]	Mass[c] mg
Triphenyltin chloride	Triphenyltin cation	TPhT	0,908	110,1
Tricyclohexyltin chloride	Tricyclohextyltin cation	TCyT	0,912	109,6
Internal Standards				
n-Heptyltin trichloride	n-Heptyltin cation	MHT	0,672	148,8
Di-n-heptyltin dichloride	Di-n-heptyltin cation	DHT	0,817	122,4
Tri-n-propyltin chloride	Tri-n-propyltin cation	TPT	0,875	114,3

[a] Acronyms correspond organotin chlorides (OTC) and organotin cations (OC).

[b] Weighting factor = molar mass (OC)/molar mass (OTC).

[c] If the mass of the compounds weighed is different from that given in this table, use the weighting factor to calculate the actual concentration of the OC.

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

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

where

ρ_{Sn} is the mass concentration of organotin cation, in mg/l;

ρ_{Cl} is the mass concentration of organotin chloride, in mg/l;

W_F is the weighting factor.

EXAMPLE 1 If you weigh 160,5 mg of n-Butyltin trichloride ($BuSnCl_3$), into 100 ml solvent, you have a solution of 1 605 mg/l of n-Butyltin trichloride, which corresponds to a concentration of: 1 605 × 0,623 = 1 000 mg/l of n-Butyltin cation ($BuSn^{3+}$).

EXAMPLE 2 If you weigh 110,4 mg of Di-n-octyltin dichloride[$(C_8H_{17})_2SnCl_2$], into 100 ml solvent, you have a solution of 1 104 mg/l of Di-n-octyltin dichloride, which correspond to a concentration of: 1 104 × 0,830 = 916 mg/l of Di-n-octyltin cation[$(C_8H_{17})_2Sn^{2+}$].

8.4 Sample extraction

8.4.1 Use the analytical balance (6.1) to weigh 1 g of sample (see Clause 7) into a glass vessel (6.2) and record the mass, m_1.

8.4.2 Add 9,5 ml of extraction solvent (8.2) and 0,5 ml of the internal standard working solution (see 8.3.3).

8.4.3 Extract in an ultrasonic water bath (6.3) at (60 ± 5) °C for 1 h ± 5 min.

8.4.4 Cool the extract down to room temperature and filter approximately 1 ml to 2 ml of extract into a glass vial (6.5) using a disposable syringe and a syringe filter (6.4).

8.4.5 Close the glass vial (see 8.4.4) with cap immediately for analysis.

8.5 Sample analysis

Qualitative and quantitative analysis of organotin compounds is performed using LC-MS/MS.

Example of suitable chromatographic conditions is given in Annex A.

9 Expression of results

9.1 Calibration curve

Prepare a calibration curve of the response against the known standards concentration with at least three calibration points. From the calibration curve, the concentration of organotin cation (OC) in mg/l is determined.

Extraction solvent (see 8.2) shall be used during preparation of calibration standards. The example of calibration preparation is given in Annex B.

NOTE Concentration ranges for the calibration standards are subject to change upon the need of each laboratory and equipment used.

For quantification, the calibration curve shall have a correlation coefficient greater than 0,995 (R^2 greater than 0,990).

9.2 Calculation

9.2.1 Calculate the total peak areas of the standards, internal standards and each detected organotin compound in the sample.

9.2.2 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):

$$D_{RF} = \frac{\rho_{\mathrm{St,Sn}} \times A_{\mathrm{St,is}}}{A_{\mathrm{St,Sn}} \times \rho_{\mathrm{St,is}}} \tag{2}$$

where

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

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

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

$\rho_{\mathrm{St,is}}$ is the mass concentration of the relevant internal standard, in mg/l.

NOTE The abbreviation St refers to Standard.

9.2.3 For each compound, calculate an average with all the D_{RF}, obtained at each level of 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 organotin compound should be exactly the same, but slight differences are seen. Therefore, the average is calculated.

9.2.4 This average D_{RF} value, D_{RFa}, is used to calculate the concentration of organotin compounds in 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 mg/l;

A_{Sn} is the peak area of organotin;

ρ_{is} is the mass concentration of the corresponding internal standard, in mg/l;

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

9.2.5 Using Formula (5), convert ρ_{is}, whose units are expressed in mg/l, into mg/kg.

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

where

w_{Sn} is the mass fraction of organotin cation, in mg/kg;

ρ_{Sn} is the mass concentration of organotin cation in the sample, mg/l;

V is the volume, in ml;

m_1 is the mass of the sample, in g.

9.3 Reliability of the method

See Annex C.

10 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 22744-2:2020;

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

c) the test result (in organotin cation) as recorded in 9.2.5 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.

Annex A
(informative)

Example of chromatographic condition

A.1 Preliminary remark

As the instrumental equipment of the laboratories can vary, no generally applicable instructions can be provided for chromatographic analyses. The following parameters have been successfully tested and used.

A.2 LC conditions

Mobile Phase 1: 10 mmol/l ammonium formate water with 0,01 % tropolone (by volume)

Mobile phase 2: Methanol with 1 % Formic acid

Column: C18 column, (2,7 µm), (4,6 × 100) mm

Column temperature: 40 °C

Flow rate: 0,5 ml/min

Injection volume: 5 µl

Detector: Tandem mass spectrometer (MS/MS)

Gradient:	Time [min]	Mobile phase 1 [%]	Flow [ml/min]
	0,00	30,0	0,5
	3,00	5,0	0,5
	13,00	5,0	0,5
	15,00	30,0	0,5
	23,00	30,0	0,5

A.3 MS/MS conditions

Ionization mode:	Atmospheric Pressure Ionization – Electro Spray (API-ES)
Polarity:	Positive
Desolvation temperature:	300 °C
Desolvation gas flow (N_2):	11 l/min
Nebulizer:	45 psi (i.e. 310 kPa)
Sheath gas flow rate:	11 l/min

Sheath gas temperature: 350 °C

Capillary voltage: 3 500 V

Acquisition mode Multiple Reaction Monitoring (MRM) mode, see Table A.1 for MRM

Table A.1 — MRM condition in LC-MS/MS

Compounds	Q1 *m/z*	Q3 *m/z*	Collision energy eV
Internal standard: MHT	461	241	28
MBT	419	241	32
MOT	475	241	34
MPhT	439	241	34
Internal standard: DHT	439	241	30
DBT	355	241	20
DOT	467	241	40
DPhT	395	241	34
Internal standard: TPT	249	123	18
	249	165	12
TBT	291	179	10
	291	123	30
TPhT	351	197	26
	351	120	28
TCyT	369	205	12
	369	81	30
TOT	459	235	18
	459	123	40

NOTE The mono-substituted organotin compounds are quantified using mono-substituted internal standard. For example, MBT and MOT are quantified using internal standard MHT.

Annex B
(informative)

Example of calibration preparation

Table B.1 shows the example of the 5-point calibration. The standards are all prepared in 10 ml volumetric flasks.

Table B.1 — Example of calibration preparation

Standards	L1	L2	L3	L4	L5
Concentration of standards, in mg/l	0,05	0,1	0,5	1	2
Volume of standards - working solution (see 8.3.5), in µl	50	100	500	1 000	2 000
Concentration of internal standards, in mg/l	0,1	0,1	0,1	0,1	0,1
Volume of internal standards - working solution (see 8.3.3), in µl	500	500	500	500	500
NOTE Filled to the marked volume with extraction solvent (see 8.2).					