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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 par chromatographie en phase liquide

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Foreword

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This document was prepared by Technical Committee ISO/TC 38, *Textiles*.

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Textiles and textile products — Determination of organotin compounds —

Part 2:
Direct method using liquid chromatography

WARNING — The use of this standard 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 standard to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

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

ISO/TS 16179, *Footwear — Critical substances potentially present in footwear and footwear components — Determination of organotin compounds in footwear materials*

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 http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1 Organotin cations (OC)

Part of the organotin compound that contains all Sn-C bonds

Note In this document, the abbreviation OC comprises the cations; MBT, DBT, TBT, MOT, DOT, TOT, TCyT and TPhT.

3.2 Organotin Compounds (OTC)

Substance with at least one Sn-C bond

4 Principle

The organotins are extracted from textile test samples with a methanol-ethanol mixture, in a medium-strength acidic condition using tropolone as a complexing agent. The mono- and di-organotin-tropolone complexes and tri-organotins formed in the extraction procedure are directly analyzed by

a liquid chromatograph with a tandem mass spectrometer (LC-MS/MS). This method does not require additional derivatization step.

5 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

5.1 Organotin compounds

5.1.1 n-butyltin trichloride, CAS number: 1118-46-3.

5.1.2 n-octyltin trichloride, CAS number: 3091-25-6.

5.1.3 Di-n-butyltin dichloride, CAS number: 683-18-1.

5.1.4 Di-n-octyltin dichloride, CAS number: 3542-36-7.

5.1.5 Tri-n-butyltin chloride, CAS number: 1461-22-9.

5.1.6 Triphenyltin chloride, CAS number: 639-58-7.

5.1.7 Tricyclohexyltin chloride, CAS number: 3091-32-5.

5.1.8 Tri-n-octyltin chloride, CAS number: 2587-76-0.

5.1.9 n-heptyltin trichloride, CAS number: 59344-47-7 (internal standard).

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

5.1.11 Tri-n-propyltin monochloride, CAS number: 2279-76-7 (internal standard).

5.2 Water (HPLC grade).

5.3 Methanol (HPLC grade).

5.4 Ethanol (HPLC grade).

5.5 Ammonium formate (HPLC grade).

5.6 Formic acid (HPLC grade).

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

6 Apparatus

6.1 Apparatus and auxiliaries for preparing the sample

6.1.1 Analytical balance with resolution of 0,001 g.

6.1.2 Glass vial with screw cap (for sample pre-treatment, e.g. 40 ml).

6.1.3 Ultrasonic water bath with adjustable temperature suitable for operation 60 °C.

6.1.4 Disposable syringe and syringe filter (with 0,45 µm pore size or less).

6.1.5 Glass vial (with septum cap for HPLC, e.g. 2 ml).

6.1.6 Volumetric flask (of 10 ml, 100 ml and 500 ml).

6.1.7 Glass beaker.

6.1.8 Micropipette (of 10 µl to 1 000 µl range and 1 000 µl to 5 000 µl range, with disposable tips).

6.2 Chromatographic equipment

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

6.2.2 C18 reverse phase column for liquid chromatograph.

7 Preparation of the test samples

The test sample 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 5 mm.

8 Procedure

8.1 Preparation of the extraction solvent (250 mg/l of tropolone in methanol/ethanol mixture)

Use the analytical balance (6.1.1) to weigh 0,125 g of tropolone (5.7) into glass beaker and dissolve in approximately 20 ml of methanol (5.3)/ethanol (5.4) mixture (80/20 in volume). Dilute to 500 ml in a volumetric flask. For other volume, make the extraction solvent with same concentrations.

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

8.2 Preparation of standard solutions

8.2.1 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.

8.2.2 Internal standards – stock solution (1 000 mg/l of organotin cation)

Use the analytical balance (6.1.1) to weigh the appropriate amount of tri-n-propyltin chloride (5.1.11), di-n-heptyltin dichloride (5.1.10) and n-heptyltin trichloride (5.1.9). Dissolve them together with methanol (5.3) in a 100 ml volumetric flask up to the marked volume.

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.

8.2.3 Internal standards – working solution (2 mg/l of organotin cation)

Use the micropipette (6.1.8) to transfer 0,2 ml of stock solution (8.2.2) into a 100 ml volumetric flask and make it up to the marked volume with methanol (5.3).

This corresponds to 2 mg/l working solution for the three internal standards.

8.2.4 Standards – stock solution (1 000 mg/l of organotin cation)

Use the analytical balance (6.1.1) to weigh the appropriate amount of organotin compounds specified in Table 1. Dissolve them together with methanol (5.3) in a 100 ml volumetric flask up to the marked volume.

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.

8.2.5 Standards – working solution (10 mg/l of organotin cation)

Use the micropipette (6.1.8) to transfer 1,0 ml of stock solution (8.2.4) into a 100 ml volumetric flask and make it up to the marked volume with methanol (5.3).

Table 1 — Amounts of organotin compounds and weighing factor for recalculation to organotin cations (for 100 % purity of the compounds)

OTC	OC	Acronym [a]	Weighing 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
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
Tri-n-butyltin chloride	Tri-n-butyltin cation	TBT	0,891	112,2
Tri-n-octyltin chloride	Tri-n-octyltin cation	TOT	0,929	107.6
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-hepytltin cation	DHT	0,817	122,4
Tri-n-propyltin chloride	Tri-n-propylrin cation	TPT	0,875	114,3

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

[b] Weighing 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 weighing factor to calculated the actual concentration of the OC.

EXAMPLE 1 If you weigh 160,5 mg of n-butyltin trichloride ($BuSnCl_3$), you have a solution of 1 605 mg/l of n-butyltin trichloride, which corresponds to a concentration of: 1 605 x 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[$(C_8H_{17})_2SnCl_2$], you have a solution of 1 104 mg/l of di-n-octyltin dichloride, which correspond to a concentration of: 1 104 x 0,830 = 916 mg/l of di-n-octyltin 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 weighing factor.

8.3 Sample preparation

The test specimen is cut into pieces with the maximum dimension of 5 mm and pieces are mixed homogeneously. The specimen is weighed 1 g to the nearest 0.01 g with analytical balance (6.1.1) and put into the 40 ml glass vial (6.1.2) for extraction.

8.4 Sample extraction

9.5 ml of extraction solvent (8.1) and 0.5 ml of the internal standard working solution (8.2.3) are added to sample vial (see 8.3) and then extraction is performed in ultrasonic water bath (6.1.3) at (60 ± 5) °C for (60 ± 5) min. Afterwards the extract is cooled down to room temperature, approximately 1 ml to 2 ml of extract is filtered into a HPLC sample vial (6.1.5) using a disposable syringe and a syringe filter (6.1.4). The HPLC sample vial is closed with cap immediately for further analysis.

8.5 Sample analysis

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

Guidelines for suitable chromatographic conditions are 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 (8.1) must 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 organotin standards, internal standards and each detected organotin compound in the sample.