BRITISH STANDARD

BS EN ISO
23161:2011

Soil quality — Determination of selected organotin compounds — Gas-chromatographic method

ICS 13.080.10

National foreword

This British Standard is the UK implementation EN ISO 23161:2011. It is identical to ISO 23161:2009. It supersedes BS ISO 23161:2009, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/5, Sludge characterization.

A list of organizations represented on this committee can be obtained on request to its secretary.

BSI, as a member of CEN, is obliged to publish EN ISO 23161 as a British Standard. However, attention is drawn to the fact that the UK committee voted against its approval as a European Standard and has strong reservations about endorsing its publication as a British Standard.

The UK committee believes that the reproducibility obtained in interlaboratory evaluation was not an adequate basis on which to support a reference method to measure the concentration of an analyte (or analytes) in a sample within the scope of the method. This could cause problems in the event of dispute or litigation.

The standard deviations of reproducibility in the interlaboratory validation trials of this method were poor and there is a low probability of getting the same result from two laboratories analysing the same sample. In the worst cases the standard deviation of reproducibility was about half the mean analysis (after rejection of outliers), for example agricultural soil mean 27,48 ngTPhT/g, S_R 14,33 ngTPhT/g; harbour sediment mean 3524,16 ngTBT/g, S_R 1018,88 ngTBT/g; and river sediment 219,72 ngMBT/g, S_R 135,27 ngMBT/g.

BSI technical committee EH/5 advises caution in the application of this standard. If it is used in cases of dispute, analytical data should be reviewed carefully and preferably should be obtained from more than one laboratory.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 October 2009

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30 November 2011	This corrigendum renumbers BS ISO 23161:2009 as BS EN ISO 23161:2011

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN ISO 23161

August 2011

ICS 13.080.10

English Version

Soil quality - Determination of selected organotin compounds - Gas-chromatographic method (ISO 23161:2009)

Qualité du sol - Dosage d'une sélection de composés organostanniques - Méthode par chromatographie en phase gazeuse (ISO 23161:2009)

Bodenbeschaffenheit - Bestimmung ausgewählter Organozinnverbindungen - Gaschromatographisches Verfahren (ISO 23161:2009)

This European Standard was approved by CEN on 14 July 2011.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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Ref. No. EN ISO 23161:2011: E

Foreword

The text of ISO 23161:2009 has been prepared by Technical Committee ISO/TC 190 “Soil quality” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 23161:2011 by Technical Committee CEN/TC 308 “Characterization of sludges” the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2012, and conflicting national standards shall be withdrawn at the latest by February 2012.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of ISO 23161:2009 has been approved by CEN as a EN ISO 23161:2011 without any modification.

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 23161 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably qualified staff.

It can be noted whether, and to what extent, particular problems will require the specification of additional boundary conditions.

Soil quality — Determination of selected organotin compounds — Gas-chromatographic method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a gas-chromatographic method for the identification and quantification of organotin compounds (OTCs) in soils as specified in Table 1. The method is also applicable to samples from sediments, sludges and wastes (soil-like materials). The working range depends on the detection technique used and the amount of sample taken for analysis. The limit of quantification for each compound is about 10 µg/kg.

Table 1 — Organotin compound, which can be determined in accordance with this International Standard

$R_nSn^{(4-n)+}$	R	n	Name	Acronym
Organotin cations[a]				
$BuSn^{3+}$	Butyl	1	Monobutyltin cation	MBT
Bu_2Sn^{2+}	Butyl	2	Dibutyltin cation	DBT
Bu_3Sn^{+}	Butyl	3	Tributyltin cation	TBT
$OcSn^{3+}$	Octyl	1	Monooctyltin cation	MOT
Oc_2Sn^{2+}	Octyl	2	Dioctyltin cation	DOT
Ph_3Sn^{+}	Phenyl	3	Triphenyltin cation	TPhT
Cy_3Sn^{+}	Cyclohexyl	3	Tricyclohexyltin cation	TCyT
Peralkylated organotin				
Bu_4Sn	Butyl	4	Tetrabutyltin	TTBT
[a] Organotin compounds are measured after derivatization.				

NOTE When applying this method to the determination of other organotin compounds not specified in the scope, its suitability is proven by proper in-house validation experiments, e.g. methyltin compounds. See Table 2. Methyltin cations are unlikely to evaporate from aqueous solvents, but peralkylated methyltin compounds are volatile and subject to losses (see C.3). Therefore, additional precautions are established.

Table 2 — Methyltin compounds

$R_nSn^{(4-n)+}$	R	n	Name	Acronym
$MeSn^{3+}$	Methyl	1	Monomethyltin cation	MMT
Me_2Sn^{2+}	Methyl	2	Dimethyltin cation	DMT
Me_3Sn^{+}	Methyl	3	Trimethyltin cation	TMT

Organotin cations can only be determined in accordance with this International Standard after derivatization. The anionic part bound to the organotin cation is mainly dependent on the chemical environment and is not determined using this method. The peralkylated organotin compounds behave in a completely different way from their parent compounds. Tetraalkylated organotin compounds which are already peralkylated, such as tetrabutyltin, are determined directly without derivatization.

The properties, such as particle size distribution, water content and organic matter content of the solids to be analysed using this International Standard vary widely. Sample pretreatment is designed adequately with respect to both the properties of the organotin compounds and the matrix to be analysed.

2 Normative references

The following referenced documents are indispensable for the application 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 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 16720, *Soil quality — Pretreatment of samples by freeze-drying for subsequent analysis*

ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
organotin compound
substance containing 1 to 4 Sn-C bonds

NOTE The number of Sn-C bonds is a measure for the degree of substitution.

3.2
organotin cation
part of the organotin compound (3.1) that contains all Sn-C bonds and is formally charged

3.3
organotin cation derivatives
non-dissociated tetrasubstituted organotin compounds which are produced by derivatization

3.4
solid
soil, sediment, sludge and waste (soil-like material)

4 Principle

For the ionic and the non-ionic organotin compounds (see Table 1), a different sample pretreatment and sample preparation are necessary. For the determination of organotin cations, laboratory samples are pretreated by freeze drying and grinding. This procedure enables homogeneity of the sample to be achieved. The determination of non-ionic TTBT cannot be carried out with freeze-dried materials due to evaporation losses, thus, it shall be determined in the field-moist sample. Organotin cations can only be determined after derivatization, whereas TTBT is already peralkylated and can be determined without derivatization (see the flowchart in Figure 1).

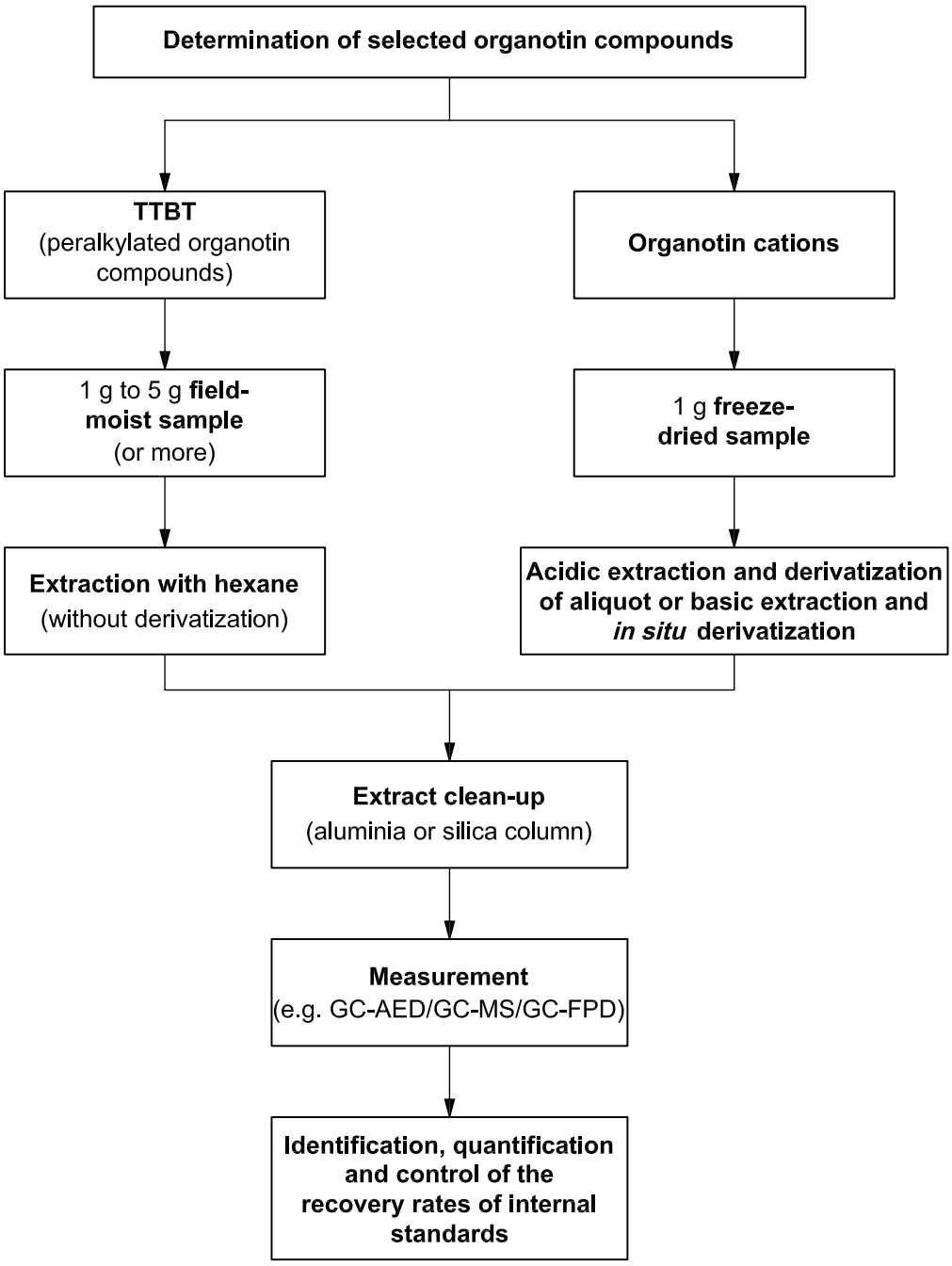


Figure 1 — Flowchart for the pretreatment and analysis of selected organotin compounds

For the determination of organotin compounds, two alternative extraction methods are given, both followed by *in situ* derivatization with a tetraethylborate compound and simultaneous extraction with hexane:

a) treatment with acetic acid;

b) treatment with methanolic potassium hydroxide.

NOTE 1 If it is necessary to take a large amount of sample, extraction and derivatization can be done in two steps. An aliquot of the extract can be taken for derivatization. This also applies for samples with high levels of OTC contamination.

NOTE 2 During *in situ* derivatization, the solid phase is still present. This supports the extraction by continuous changing of the polar organotin cations to the non-polar organotin cation derivates. *In situ* methods can improve the extraction efficiency, particularly for monoalkylated organotin compounds.

NOTE 3 Other extraction techniques can be applied if a comparable extraction efficiency is achieved.

NOTE 4 Treatment with potassium hydroxide provides some degree of digestion and is recommended especially when the solid contains high amounts of organic and biological materials.

The internal standard mix comprises four compounds representing four alkylation states in order to mimic the behaviour of the target compounds. After alkylation, they cover a wide range of volatility. A recovery of at least 80 % for derivatization/extraction and again 80 % for each clean-up step of the internal standard compounds should be achieved. (For more information, see A.3.) Tetraalkylborate is very reactive and will also alkylate other compounds in the matrix. Those compounds (and also boroxines) may interfere with the target compounds during gas chromatographic determination and influence detection. In order to protect the column and to reduce the interference in chromatography, it will be necessary to apply a precleaning step to most samples. Clean-up with silica or aluminium oxide is the minimum; further clean-up steps (e.g. aluminium oxide/silver nitrate, silica/silver nitrate, pyrogenic copper; see Annex B) may be applied if necessary.

The determination of the tetrasubstituted organotin compounds is carried out after clean-up and concentration steps by separation with capillary gas chromatography and detected with a suitable system [mass spectrometer (MS), (MS/MS), flame photometric detector (FPD), atomic absorption spectrometer (AAS), atomic emission detector (AED), inductively coupled plasma/mass spectrometer ICP/MS]. The concentrations are determined by calibration over the total procedure using aqueous multi-component calibration standard solutions in accordance with 5.4.3.

5 Reagents

5.1 General

Use reagents of highest purity, typically of pesticide grade or better. The reagents may contain impurities of organotin compounds. It is absolutely essential to verify the blanks.

The water shall be free of interferences. Use water in accordance with Grade 3 of ISO 3696.

5.2 Chemicals

5.2.1 Acetic acid, CH_3COOH, glacial.

5.2.2 Sodium hydroxide solution, NaOH, 40 % (m/V).

5.2.3 Sodium acetate, CH_3COONa.

5.2.4 Sodium sulfate, Na_2SO_4, anhydrous.

5.2.5 Potassium hydroxide, KOH.

5.2.6 Silica gel, grain size 0,085 mm to 0,28 mm (63 mesh to 200 mesh).

5.2.7 Aluminium oxide, Al_2O_3, alkaline.

5.2.8 Tetrahydrofurane, C_4H_8O, free of peroxides, free of water.

5.2.9 Acetone, $(CH_3)_2CO$.

5.2.10 Hexane, C_6H_{14}.

NOTE Both *n*-hexane and 2-methylpentane (*i*-hexane) have been found to be suitable.

5.2.11 Tetraethylborate compound, e.g sodium tetraethylborate, $NaB(C_2H_5)_4$.

NOTE The active species during derivatization is the tetraethylborate anion. The choice of the cation is arbitrary. Sodium tetraethylborate was chosen since it is commercially available. In principle, any other tetraethylborate compound can be used for analysis, including complexes formed with tetrahydrofuran (THF). A simple and rapid synthesis of a suitable derivatization agent is described in A.1.

WARNING — Sodium tetraethylborate may contain traces of triethylboron, which may cause instantaneous combustion.

5.2.12 Methanol, CH_3OH.

5.2.13 Dichloromethane, CH_2Cl_2.

5.3 Standards

WARNING — Organotin compounds vary largely regarding toxicological properties towards mammals with respect to the alkylation stage and type of alkyl group. Cautious handling of reagents is mandatory at any time.

Table 3 lists the standards used for calibration of the target compounds (solution A), internal standards (solution B) and injection standard (solution C). Additional information is provided concerning weighing factors for calculation to organotin cations (for 100 % purity of the substances).

Table 3 — Standards and internal standards for calibration of target compounds

No.	Standard	Abbreviation	Formula	CAS-RN [a]	WF [b]	Solution [c]
5.3.1	Monobutyltin trichloride	MBTCl	$C_4H_9SnCl_3$	1118-46-3	0,623	A
5.3.2	Dibutyltin dichloride	DBTCl	$(C_4H_9)_2SnCl_2$	683-18-1	0,767	A
5.3.3	Tributyltin chloride	TBTCl	$(C_4H_9)_3SnCl$	1461-22-9	0,891	A
5.3.4	Tetrabutyltin	TTBT	$(C_4H_9)_4Sn$	1461-25-2	1,000	A
5.3.5	Monooctyltin trichloride	MOTCl	$C_8H_{17}SnCl_3$	3091-25-6	0,686	A
5.3.6	Dioctyltin dichloride	DOTCl	$(C_8H_{17})_2SnCl_2$	3542-36-7	0,830	A
5.3.7	Triphenyltin chloride	TPhTCl	$(C_6H_5)_3SnCl$	639-58-7	0,908	A
5.3.8	Tricyclohexyltin chloride	TCyTCl	$(C_6H_{11})_3SnCl$	3091-32-5	0,912	A
Internal standards						
5.3.9	Monoheptyltin trichloride	MHTCl	$C_7H_{15}SnCl_3$	59344-47-7	0,672	B
5.3.10	Diheptyltin dichloride	DHTCl	$(C_7H_{15})_2SnCl_2$	74340-12-8	0,817	B
5.3.11	Tripropyltin chloride	TPTCl	$(C_3H_7)_3SnCl$	2279-76-7	0,875	B
5.3.12	Tetrapropyltin	TTPT	$(C_3H_7)_4Sn$	2176-98-9	1,000	B
5.3.13	Tetrapentyltin	TTPeT	$(C_5H_{11})_4Sn$	3765-65-9	1,000	C

[a] Chemical Abstracts Registration Number.

[b] WF= Weighing factor = Molar mass of organotin cation/molar mass of organotin compound.

[c] A for the multicomponent-standard solution in methanol.
B for the solution of the internal standards in methanol.
C for the solution of the injection standards in hexane.

5.4 Preparation of reagents and solutions

5.4.1 General requirements

Prepare the following (see also Table 3):

— multicomponent standard stock solution A in methanol (e.g. 1 mg/ml);

— multicomponent standard spiking solutions for calibration, by diluting solution A with methanol;

— stock solution B of internal standards in methanol (e.g. 1 mg/ml);

— spiking solution of the internal standards, by diluting solution B with methanol (e.g. 100 ng/ml);

— stock solution C of the injection standard in methanol (e.g. 2 mg/ml);

— injection standard solution, by diluting solution C (e.g. 2 µg/ml).

5.4.2 Blank solution

Add 20 ml of water (5.1) to an Erlenmeyer flask with a ground joint or a screw-capped [polytetrafluoroethylene (PTFE) lined] vial.

5.4.3 Aqueous calibration solutions (multicomponent solution of organotin compounds in water)

For each working range, prepare at least 6 calibration solutions with appropriate concentration levels.

Add 20 ml of water (5.1) to an Erlenmeyer flask with a ground joint or a screw-capped (PTFE-lined) vial. While stirring vigorously, pipette an appropriate volume of the respective spiking solution underneath the surface and ensure that the spiking solution is well distributed in the water. Stir for an additional 20 min.

5.4.4 Methanolic potassium hydroxide solution

Prepare a solution of 25 % (m/V) potassium hydroxide (5.2.5) in methanol (5.2.12). This is the methanolic potassium hydroxide solution.

5.4.5 Acetate buffer solution

Dissolve about 1 mol of sodium acetate (equal to 82 g of anhydrous sodium acetate) (5.2.3) in 500 ml of water (5.1) in a 1 L volumetric flask. Add sufficient glacial acetic acid (5.2.1) to adjust to a pH of 4,5. Dilute to volume with water (5.1) and mix well.

5.4.6 Solvent mixture

Prepare a solvent mixture of acetic acid, methanol and water with a volume ratio of 1:1:1.

5.4.7 Derivatization agent

Prepare an approximately 10 % (m/V) solution of tetraethylborate compound (5.2.11) in tetrahydrofurane (5.2.8).

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

5.5 Clean-up

5.5.1 General requirements

A silica or aluminium oxide clean-up is the minimum requirement. Further clean-up steps (aluminium oxide/silver nitrate, silica/silver nitrate, pyrogenic copper) may be applied if necessary (see Annex B). A recovery of $>$ 80 % of the internal standards and target compounds shall be achieved for each clean-up step.

5.5.2 Silica gel for the clean-up column

Heat silica gel (5.2.6) for at least 12 h at (500 $\pm$ 20) °C on a quartz plate in a muffle furnace. Ensure that the temperature does not exceed 520 °C.

Allow the plate to cool in an oven to about 200 °C, transfer the silica to a wide-necked glass bottle and allow cooling to room temperature in a desiccator.

Add water to the cooled silica until a mass fraction of 3 % is reached. Close the bottle and homogenize the contents for 2 h on a shaker.

5.5.3 Aluminium oxide for the clean-up column

Activate aluminium oxide (5.2.7) by heating to 600 °C for a minimum of 24 h.

Allow to cool in the oven to about 200 °C, transfer the aluminium oxide to a wide-necked glass bottle and allow cooling to room temperature in a desiccator.

Add water to the cooled aluminium oxide until a mass fraction of 10 % is reached. Close the bottle and homogenize the contents for 2 h on a shaker.

5.5.4 Clean-up column

Add about 5 g of adsorbent (5.5.2 or 5.5.3) to one column, and add about 3 g of drying agent. Ensure that the clean-up column is filled homogeneously, for example, by using hexane as a moistening agent during the filling process.

Commercially pre-packed columns may be used as an alternative if the requirement for recovery is met.

5.5.5 Eluent for extract cleaning with silica gel

A mixture of hexane (5.2.10) with a more polar solvent can be used as an eluent to obtain a quantitative elution of all organotin compounds. In routine work, about 5 % of acetone (5.2.9) or 20 % of dichloromethane (5.2.13) was used successfully. The concentration of polar solvent in hexane and the volume of total eluent should be determined prior to application.

5.5.6 Eluent for extract cleaning with aluminium oxide

Generally, hexane (5.2.10) is used as the eluent. The volume of the eluent should be determined prior to application.

6 Apparatus

6.1 Requirements for glassware

Customary laboratory glassware shall be used.

All glassware and material that comes into contact with the sample or extract shall be thoroughly cleaned.

6.2 Sampling apparatus

Sampling devices shall not be a source of contamination. The use of stainless steel, glass or PTFE is recommended.

NOTE For example, poly(vinyl chloride) (PVC) can contain large amounts of organotin compounds.

Containers shall be inert and appropriate for storing and transport.

The size of the container shall be appropriate to ensure sampling of a suitable amount of solid to provide a representative sample and facilitate a determination in accordance with this International Standard within the calibrated working range.

6.3 Additional apparatus

Use ordinary laboratory apparatus and the following.

6.3.1 Centrifuge.

WARNING — The use of organic solvents in centrifuges needs to be assessed for safety reasons.

6.3.2 Glass column for clean-up, e.g. length 15 cm, inner diameter 1 cm, with frit, without a cock.

6.3.3 Shaker.

6.3.4 Ultrasonic bath or **horn-type transducer**.

6.3.5 Analytical balance, with suitable reading accuracy and range.

6.3.6 Concentration apparatus, e.g. rotary evaporator, Kuderna Danish.

6.3.7 Gas chromatograph, equipped with a high-resolution capillary column of suitable polarity and **Injector**, split or splitless, preferably with an automated sampling device (C.1).

6.3.8 Detectors (for typical detector configurations, see C.2). The following detector types may be used for the measurement of alkylated organotin compounds:

— atomic absorption spectrometer (AAS), quartz oven, tin(Sn) lamp;

— flame photometric detector (FPD), equipped with a cut-off filter of 590 nm or interference filter of 610 nm;

— pulsed flame photometric detector (PFPD) equipped with a large pass-band filter working at 610 nm or 390 nm with a time-selective acquisition;

— mass spectrometer (MS) for electron impact mode (EI-mode);

— atomic emission detector (AED);

— inductively coupled plasma/mass spectrometric detector (ICP/MS).

6.3.9 Data processing system, suitable for the respective detector for acquisition and data evaluation.

7 Procedure

7.1 Sampling and sample pretreatment

Sample pretreatment should be carried out according to ISO 14507 [4] or ISO 16720.

The use of, for example, stainless steel, PTFE and glass is recommended. Store the sample until pretreatment in a cool place.

If the storage time is less than 48 h, store the sample in a dark, cool place until pretreatment.

If the storage time exceeds 48 h, the sample shall be stored frozen (< –18 °C) in the dark.

The laboratory sample should represent the field sample. The amount of sample taken depends on homogeneity and on the resulting dry mass after preparation. If necessary, select coarse material and sieve to particle size < 2 mm. Stir with a metal spoon.

For the preparation of freeze-dried samples take, for example, 250 g of original field-moist sample and proceed with freeze drying in accordance with ISO 16720.

Grind the freeze-dried material, for example, in an agate centrifugal ball mill, to a homogeneous powdery consistency. Prevent high temperatures in the mill by grinding for a short time.

Determine the dry mass of the freeze-dried material in accordance with ISO 11465.

For the determination of organotin compounds in original field-moist material, take the sieved and stirred sample as described above. From this homogenized laboratory sample, suitable amounts of sub-samples (test samples) are taken for subsequent analysis for the determination of organotin compounds and dry mass in accordance with ISO 11465.

7.2 Sample extraction

7.2.1 General

Add 1 g to 5 g of solid to a container that can be closed [e.g. an Erlenmeyer flask with a ground joint or a screw-capped vial, polytetrafluoroethylene (PTFE) lined]. It is recommended to choose two samples, varying in size at least by a factor of 2. Ensure that the mass of analytes in the samples is covered by the working range.

Pretreat samples of solids, blank solutions (5.4.2) and aqueous calibration solutions (5.4.3) as follows.

7.2.2 Acidic extraction and derivatization of an aliquot

Add an appropriate amount of internal standard mixture and of a solvent mixture of acetic acid:methanol:water (1:1:1) to the freeze-dried sample to obtain a sample slurry containing 20 % or less of solid material.

Sonicate for 30 min in an ultrasonic bath.

Transfer all the slurry to a centrifuge glass tube and then centrifuge to obtain a liquid/solid phase separation. The liquid phase is then transferred by a pipette to another container. The extraction procedure is repeated in the same way by adding half of the volume of extraction solvent mixture used for the first extraction step. The two extraction solutions are combined prior to derivatization.

For derivatization, add aqueous sodium hydroxide (5.2.2) to an appropriate aliquot (at least 5 ml) of the extraction solution obtained above and adjust to pH 4,5 using acetic acid (5.2.1). After the addition of 5 ml of hexane (5.2.10) and a 10 % solution of tetraethylborate compound (5.2.11) in tetrahydrofurane (5.2.8) (0,5 ml/g of sample taken), the solution is immediately shaken by hand for 1 min. Afterwards, the whole mixture is shaken for 20 min on a mechanical shaking machine. The procedure is then repeated. The hexane phases separated are combined and dried over sodium sulfate (5.2.4) and concentrated to 1 ml.

Blank solutions and aqueous calibration solutions (5.4.2 and 5.4.3) shall be treated in the same way as the samples.

7.2.3 Alkaline treatment and *in situ* derivatization

Add an appropriate amount of the internal standard solution and water (5.1) to the freeze-dried sample to obtain a sample slurry with 20 % or less of solid material.

Shake for about 20 min and ensure that the spiking solution is well distributed in the water or water/solid slurry.

Add methanolic potassium hydroxide solution (1,2 ml/g of sample taken) (see 5.4.4) and 20 ml of hexane (5.2.10). Heat to 70 °C for 1 h in a closed container (ensure the tightness). Choose a volume of methanolic potassium hydroxide solution to ensure that the slurry is alkaline. Instead of treatment at 70 °C for 1 h, ultrasonic treatment (e.g. for a few minutes followed by 1 h of shaking) or treatment overnight at ambient temperature may be applied.

Add acetic acid (5.2.1) to adjust to a pH of 4,5. Add 10 ml of acetate buffer solution (5.4.5) and shake for about 1 min. To the buffered solution, add the 10 % solution of tetraethylborate compound in tetrahydrofurane (see 5.4.6) (0,5 ml/g of sample taken). Shake for about 2 h. Repeat the derivatization procedure and shake for 1 h minimum. Ensure that the phases are well mixed.

Separate the phases using a centrifuge. Collect the hexane layer and dry it with sodium sulfate (5.2.4), and reduce the volume of the organic phase to 1 ml using a suitable apparatus, but avoid reduction to dryness in every case.

Blank solutions and aqueous calibration solutions (5.4.2 and 5.4.3) shall be treated in the same way as the samples.

7.2.4 Separate determination of TTBT in the field-moist sample

The determination of TTBT can be carried out by extraction of the field-moist sample with hexane without the derivatization step. Therefore, it is possible to take a larger amount of homogenized field-moist sample (5 g or more) and to use only tetrapropyltin as the internal standard.

7.3 Clean-up of the extract

7.3.1 General

If necessary, sample extracts shall be subjected to an adsorption chromatography clean-up. If the chromatographic measurements of the target compounds are disturbed by interferences, apply further appropriate clean-up procedures (see Annex B) provided a recovery of > 80 % of the internal compounds is achieved for each clean-up step. The reference and blank solutions shall be treated in the same way.

NOTE 1 Triphenyltin elutes later from the clean-up column than the other organotin compounds. If TPHT is not to be analysed, the clean-up efficiency can be improved by reducing the eluent volume, the water content of the adsorbent or the concentration of the polar solvent in hexane.

NOTE 2 Boroxins will be formed during derivatization, which can affect the gas chromatography (GC) column. These are eliminated by silica clean-up with hexane, but can be eluted if acetone is added to the eluent. An alternative separation method is to shake with sodium hydroxide (NaOH) solution; peralkylated organotin compounds are stable against NaOH solution.

7.3.2 Silica and aluminium oxide clean-up

Rinse the clean-up column, freshly prepared in accordance with 5.5.4 with 30 ml of hexane (5.2.10).

Transfer the concentrated extract in hexane to the clean-up column (5.5.4). After the extract has penetrated the top of the adsorbent layer, cautiously add the volume of eluant (5.5.5 or 5.5.6) found to be necessary.

Collect the eluate and reduce the volume of the organic phase to 1 ml using a suitable apparatus, but avoid reduction to dryness in every case.

If the chromatography turns out to be unacceptable, apply further clean-up procedures (see Annex B).

7.4 Determination of dry mass

Determine the fraction of dry mass gravimetrically in accordance with ISO 11465. The fraction of dry mass of original field-moist samples or of freeze-dried materials is expressed as a percentage.

NOTE The following standards can be used for other solids: EN 12880 for sediments or sludges; EN 14346 for wastes.

7.5 Measurement

7.5.1 Gas chromatographic separation

Optimize the instrument in accordance with the manufacturer's instructions. Ensure at least baseline separation of the target peaks of interest. Higher resolution is recommended to avoid co-elution of matrix compounds as far as appropriate (for typical gas chromatographic conditions, see C.1).

The resolution of triphenylethyltin and tricyclohexylethyltin should be at least 0,8.

Prepare injection solutions of blanks, references and samples by adding, for example, 50 µl of injection standard (see 5.4.1) to the final extract of 1 ml.

Inject an appropriate volume of the prepared sample extracts into the injection port of a gas chromatograph. Record retention times and the signal intensity of each compound.

Quantify the gas chromatographic signals either as peak areas or as peak heights. In the case of non-continuous detection (e.g. mass spectrometry), evaluation using peak areas is recommended.

NOTE In this International Standard, only the evaluation using peak areas is described as an example.

7.5.2 Detection and identification

Use an appropriate detector (see 6.3.8) for monitoring the target peaks.

Independent from the detection system, identify the analytes by comparison of the retention times for samples and references. Minimal requirements for identification are retention times within ± 0,02 min and relative retention times within ± 0,1 % over the total run of a chromatogram.

Following the retention time criteria, three identification points are necessary. For GC/MS, this procedure is described in ISO 22892; each individual mass meeting the criteria gives one identification point. Identification points for other detectors are described in Table 4. If the detector does not give three identification points, additional points can be obtained by, for instance, using a second column or by pattern recognition (see also ISO 22892).

Table 4 — Identification points

Detector	Number of identification points	Remarks
FPD, PFPD	2	
MS	1 for each individual mass	Refer to ISO 22892
MS/MS	2 for each mass transfer	
MS^n	1 for each mass transfer	
AED	3	Different spectral lines
ICP/MS	3	
AAS	3	

8 Calibration

Calibration is carried out by putting standards, including internal standards, through the whole procedure. The underivatized organotin compounds are added to water to give the aqueous calibration solutions (5.4.3). The whole procedure of derivatization, extraction, clean-up and concentration is carried out to establish calibration curves. At least six calibration solutions at different concentrations should be used to prepare the calibration curve.

For quantification of monobutyltin and monooctyltin compounds, use monoheptyltin trichloride (MHTCl) as the internal standard; for dibutyltin and dioctyltin compounds, use diheptyltin dichloride (DHTCl) as the internal standard; and for tributyltin, triphenyltin and tricyclohexyltin compounds, use tripropyltin chloride (TPTCl) as the internal standard. The recovery of the internal standards corresponding to each group of organotin compounds is to be checked to verify complete derivatization and extraction. For quantification of tetrabutyltin use tetrapropyltin (TTPT) as the internal standard.

Derive from the chromatograms, by integration, the peak areas of the organotin cation derivates, TTBT and the internal standards. Calculate, for each organotin cation and TTBT, a calibration curve according to Equation (1) for each working range, using the least-squares linear regression

$$y = a_1 \cdot x + a_0 \tag{1}$$

where

x is the ratio of the masses of organotin cation, respectively TTBT (m_i) and the corresponding internal standard (m_I) in the reference solution;

$$x = \frac{m_i}{m_\mathrm{I}} \tag{2}$$

a_1 is the slope of the calibration curve;

y is the ratio of the peak areas of organotin cation derivates or TTBT and the corresponding internal standard in the chromatograms of the calibration solutions;

a_0 is the intercept of the calibration curve.

9 Recovery rates of the internal standard compounds

The recoveries facilitate the recognition of bias caused by the procedure or by the matrix of the sample, allowing indications of the reliability of the procedure to be derived. Examples are shown in Annex A, Table A.1 (A – D) to assist in the assessment of possible causes and effects.

These recoveries are not to be used for the calculation of results. They should be at least 80 % for derivatization/extraction and again 80 % for each clean-up step, with a minimum of 50 % for the overall recovery.

The injection standard tetrapentyltin (TTPeT) is used as the internal standard for the calculation of the recovery rates of the other internal standards.

The ratios of the signal response of each of the four internal standards and the tetrapentyltin in the six calibration chromatograms (the relative response factors, RRF) are calculated according to Equation (3).

$$\mathrm{RRF} = \frac{A_\mathrm{I} \cdot m_\mathrm{TTPeT}}{A_\mathrm{TTPeT} \cdot m_\mathrm{I}} \tag{3}$$

where

A_{I} is the peak area of the internal standard, I;

m_{I} is the mass of the internal standard, I;

A_{TTPeT} is the peak area of the injection standard;

m_{TTPeT} is the mass of the injection standard.

The mean of the relative response factors for each internal standard is taken as the reference value of recovery = 100 %. The relative response factors of these internal standards have to be calculated in the same manner as for the sample materials and thus measure the recoveries of the four internal standards.

The recovery of a single internal standard (Rec) is calculated according to Equation (4).

$$\mathrm{Rec} = \frac{\mathrm{RRF_{I\ sample}}}{\mathrm{RRF_{I\ cal}}} \times 100 \tag{4}$$

where

$\mathrm{RRF_{I\ sample}}$ is the relative response factor of the internal standard, I, of the sample;

$\mathrm{RRF_{I\ cal}}$ is the mean relative response factor of the internal standard, I, of the calibration.

10 Quantification

Calculate the mass m_i of organotin cation or TTBT (analyte i) in the sample extract according to Equations (5) to (7).

$$x = \frac{y - a_0}{a_1} \tag{5}$$

$$m_i = x \cdot m_{\mathrm{I}} \tag{6}$$

$$y = \frac{A_i}{A_{\mathrm{I}}} \tag{7}$$

where

a_1 is the slope of the calibration curve;

a_0 is the intercept of the calibration curve;

A is the peak area of analyte i or of internal standard I in the sample chromatogram;

m is the mass of analyte i or of internal standard I in the sample taken;

y is the ratio of the peak areas of organotin cation derivates i or of TTBT and the corresponding internal standard I in the sample chromatograms.

Calculate the mass fraction of analyte i in the solid sample, in micrograms per kilogram (µg/kg) dry mass, according to Equation (8).

$$w_i = \frac{m_i}{E} \tag{8}$$

where

w_i is the mass fraction of the analyte i in the solid, in micrograms per kilogram (µg/kg) or nanograms per gram (ng/g), respectively;

m_i is the mass of analyte i in the pretreated sample portion, in nanograms (ng);

E is the dry mass of sample taken, in grams (g).

11 Expression of results

Report the mass fraction, in micrograms of analyte i (organotin cation or TTBT) per kilogram of dry solid (µg/kg), to the nearest whole number and with two significant digits.

12 Precision

Precision data of four soil and soil-like materials are included in Annex E.

13 Test report

The test report shall contain the following details:

a) a reference to this International Standard;

b) a complete identification of the sample;

c) information on sampling, storage and pretreatment;

d) a detailed description of the procedure (e.g. extraction method, extract cleaning, type of detector);

e) the results of the determination;

f) the determined recoveries of the internal standards;

g) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Information about the procedure

A.1 Derivatization agent

A simple and rapid synthesis of a suitable derivatization agent is published in Reference [13] in the Bibliography.

Attach a stirrer, reflux condenser and a dropping funnel with inert-gas supply to a three-necked round-bottomed flask. Add 14,19 g of BF_3OEt_2, 9,72 g of Mg and 75 ml of THF to the round-bottomed flask. Add, by means of the dropping funnel, 43,59 g of ethylchloride while stirring. Stir for 2 h. Let the phases separate.

The resulting supernatant is about 1,33 mol/l of tetraethylborate. Accompanying salts, such as MgFBr, do not interfere with the derivatization reaction.

Tetraethylborate solutions are stable for about three months if they are stored under an inert-gas blanket.

A.2 Stability of stock solutions (A, B, C) and spiking solutions

Since the stability of the organotin compound in the multicomponent stock solution cannot be assessed, it is recommended to prepare separate stock solutions of each substitution grade. Stability can than be assessed by the absence of compounds of lower substitution grade.

The organotin compounds in the stock solutions (1 mg/ml organotin cation in methanol) are stable for at least one year if stored at 4 °C in a refrigerator in the dark.

The organotin compounds in the spiking solutions are stable for at least 6 months if stored at 4 °C in a freezer in the dark; however, it is recommended to prepare a fresh batch after 3 months.

The stability of the concentration of the solution is dependent on the use of appropriate containers. Measures of control have to be established in each laboratory.

A.3 Internal standards

The use of multiple internal standards serves to ensure the accuracy of the procedure. The internal standards used will not only represent compounds of each substitution grade but also check for definite procedural steps.

— Tetrapropyltin (TTPT) as aperaklylated compound will not be derivatized; it therefore indicates extraction efficiency.

— Tripropyltin (TPT) is the most volatile internal standard. It indicates losses during evaporation; however, as far as methyltin compounds are concerned, the indication is limited.

— Monoheptyltin (MHT) is the internal standard that needs to be derivatized three times to be peralkylated. It indicates the completeness of derivatization.

— Diheptyltin (DHT) is the least volatile internal standard and indicates whether gas chromatographic effects (e.g. discrimination) occur.

— Tetrapentyltin (TTPeT) is added prior to injection. It is therefore not influenced by derivatization, extraction and clean-up. It indicates detector sensitivity and may be used to determine recovery rates of the other internal standards. If there are no interferences during detection, recovery rates are independent of the detection mode used [mass spectrometric detection (MSD), flame photometric detection (FPD), atomic emission spectrometric detection (AESD), etc.] The recovery rates may also be used to assess the procedural performance with respect to derivatization, extraction and evaporation.

If the recovery rates of the internal standards are calculated in accordance with Clause 9, indications on the reliability of the procedure may be derived. Examples are shown in Table A.1 (A – D) to assist in assessing possible causes and effects.

Table A.1 — Selected examples of interpretation to recognize analytical problems using recovery rates of internal standards related to the injection

Example	Recovery rates of internal standards related to tetrapentyltin, %			
	A	B	C	D
TPT	51	158	43	70
TTPT	55	151	46	91
MHT	60	142	41	12
DHT	96	105	48	34
TTPeT	100	100	100	100
Cause	Selective loss due to evaporation	Selective loss in calibration due to evaporation	Equal distributed loss due to non-quantitative separation of organic phase	Selective loss due to non-quantitative derivatization
Possible effect	False quantification on volatile organotins	False quantification	Elevated limit of detection (e.g. factor of 2)	False quantification, especially of monoalkylated and dialkylated organotins

Alternatively, for MS detection, tin-isotope enriched, deuterated or ^{13}C-marked standards can be used.

A.4 Volume reduction of extracts

When using a rotary evaporator, a water-bath temperature of about 40 °C is recommended and a constant pressure of about 300 hPa to 450 hPa is allowed.

Experience has shown that losses will not occur if solvent reduction is stopped at 1 ml.

Annex B
(informative)

Additional clean-up procedures

B.1 Clean-up with silica/silver nitrate

B.1.1 Supplementary reagents

Silver nitrate, $AgNO_3$.

B.1.2 Silica/silver nitrate adsorbent for the clean-up column

Add 90 g of dried silica to a 250 ml Erlenmeyer flask with a ground joint. Dissolve about 10 g of $AgNO_3$ in 40 ml of water in a beaker. Add the $AgNO_3$ solution to the silica. Mix well for about 2 h on a shaker and let stand for about 30 min. Place in an oven at 70 °C and raise the temperature within 5 h, stepwise at 10 °C per hour to 120 °C. Activate at 120 °C for a further 15 h. Allow to cool in a desiccator to room temperature. Store the adsorbent in a closed amber glass bottle with a ground joint. The efficiency will decline over a period of several months.

B.1.3 Silica/silver nitrate clean-up

The adsorption properties of silica/silver nitrate are different from silica. Phenyltin compounds will not elute quantitatively from silica/silver nitrate.

Transfer the reduced extract in hexane (5.2.10) to a clean-up column (5.5.4) prepared with silica/silver nitrate (B.1.2). After the extract has penetrated, cautiously add the volume of hexane that was found to be necessary.

Collect the eluent and reduce the volume of the organic phase to 1 ml using a suitable apparatus, but avoid reduction to dryness.

B.2 Clean-up with aluminium oxide/silver nitrate

B.2.1 Supplementary reagents

Silver nitrate, $AgNO_3$.

B.2.2 Aluminium oxide/silver nitrate adsorbent for the clean-up column

Add, to 10 g of aluminium oxide (5.2.7), 4 ml of acetone (5.2.9) and 0,75 ml of 50 % silver nitrate solution, for example, made from 1 g of water and 1 g of silver nitrate. Remove the acetone by means of rotary evaporation (e.g. at 50 °C and 300 hPa). Store the adsorbent in a closed amber glass bottle with a ground joint. The efficiency will decline over a period of several months.

B.2.3 Aluminium oxide/silver nitrate clean-up

The adsorption properties of aluminium oxide/silver nitrate are different from those of aluminium oxide. Phenyltin compounds will not elute quantitatively from aluminium oxide/silver nitrate.

Transfer the reduced extract in hexane (5.2.10) to a clean-up column (5.5.4) prepared with aluminium oxide/silver nitrate (B.2.2). After the extract has penetrated, cautiously add the volume of hexane that was found to be necessary.

Collect the eluent and reduce the volume of the organic phase to 1 ml using a suitable apparatus, but avoid reduction to dryness.

B.3 Pyrogenic copper

B.3.1 Supplementary reagents

B.3.1.1 **Copper(II) sulfate pentahydrate**, $CuSO_4 \cdot 5H_2O$.

B.3.1.2 **Hydrochloric acid**, HCl, $c = 2$ mol/l.

B.3.1.3 **Zinc granules**, Zn, particle size 0,3 mm to 1,4 mm (14 mesh to 50 mesh ASTM).

B.3.1.4 ***n*-Dodecane-1-sulfonic acid, sodium salt**, $CH_3(CH_2)_{11}SO_3Na$.

B.3.2 Pyrogenic copper for clean-up column

WARNING — Pyrogenic copper is spontaneously inflammable. Suitable precautions must be taken.

In a 1 000 ml beaker, dissolve 45 g of copper(II) sulfate pentahydrate (B.3.1.1) in 480 ml of water containing 20 ml of 2 mol/l hydrochloric acid (B.3.1.2).

To another 1 000 ml beaker, add 15 g of zinc granules (B.3.1.3) and then 25 ml of water and one drop of anionic detergent aqueous solution [e.g. 35 % m/V *n*-dodecane-1-sulfonic acid, sodium salt (B.3.1.4)].

Stir with a magnetic stirrer at a high speed to form a slurry. Whilst stirring at this high speed, carefully add the copper(II) sulfate solution drop by drop using a glass rod.

Hydrogen is liberated and elemental pyrogenic copper is precipitated (red-coloured precipitate).

Continue stirring until the hydrogen generation almost ceases and the precipitated copper is allowed to settle. The supernatant water is carefully removed and the product washed with deoxygenated water three times to eliminate residual salts.

Then the water is carefully replaced with 250 ml of acetone (5.2.9) (whilst continuously stirring the mixture). This operation is repeated twice more to ensure elimination of water.

The above procedure is repeated three times with 250 ml of hexane (5.2.10) to ensure elimination of the acetone.

Carefully transfer the copper with hexane into an Erlenmeyer flask and store under hexane. Seal the flask to prevent ingress of air and store in an explosion-proof refrigerator at 2 °C to 8 °C.

The shelf-life of the pyrogenic copper is at least two months. The clean-up efficiency will then decline. The copper will change colour as the clean-up efficiency decreases.

B.3.3 Pyrogenic copper clean-up column

Pyrogenic copper is useful if the extract is not heavily contaminated. It does not affect phenyltin compounds.

Add about 100 mg of pyrogenic copper to the extract and treat in an ultrasonic bath for 2 min to 3 min. Centrifuge for 5 min at 3500 min^{-1}. Separate the supernatant, rinse the copper with some hexane and combine the hexane with the supernatant.

Reduce the volume of the organic phase to 1 ml using a suitable apparatus, but avoid reduction to dryness.

Annex C
(informative)

Information about typical instrumental conditions [1)]

C.1 Example of common gas chromatographic conditions

Injection:	splitless for 60 s, injection volume: 1 µL, autosampler: HP 7673
Injection temperature:	280 °C
Carrier:	helium (He), constant flow: 2,5 ml/min = 40 cm/s
Capillary column:	length 30 m, internal diameter (ID) = 0,32 mm, d_f = 0,25 µm, phase HP-5
Temperature program:	40 °C for 3 min, then 10 °C/min increments to 220 °C, held for 5 min, then 20 °C/min increments to 300 °C, held for 2 min (HP 5890 Series II)

C.2 Examples of common detection conditions

C.2.1 Atomic absorption spectrometric detection

Transfer line:	250 °C
Quartz oven:	minimum constant temperature > 650 °C, e.g. 750 °C
Gases:	hydrogen (H_2),145 ml/min; air, 15 ml/min
Excitation:	tin(Sn)-lamp, e.g. electrodeless discharge lamp (EDL) or hollow cathode lamp (HCL)
Wavelengths:	286,3 nm (224,6 nm, 235,5 nm) e.g. excitation/wavelength: EDL, 286,3 nm
Slit:	0,7 nm

C.2.2 Flame photometric detection

C.2.2.1 Continuous flame

Detector temperature:	180 °C, detector base 300 °C
Gases:	H_2, He, synthetic air, inert gas (e.g. nitrogen, N_2)
Filter:	If interferences are suspected, use a cut-off filter with a cut range below 590 nm or an interference filter at 610 nm transmissible in the range 610 nm ± 5 nm

(The flame should be as hydrogen-rich as possible in order to allow the formation of Sn-H* species. The synthetic air level should be kept as low as possible in order to avoid a high background; however, it should be sufficient to prevent the extinction of the flame when passing the solvent peak.)

1) The instruments mentioned in this Annex are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO or IEC of these products.

C.2.2.2 Pulsed flame

Detector temperature:	350 °C, detector base 300 °C
Gases:	H_2, He, synthetic air, inert gas (e.g. N_2)
Filter:	large pass-band filter working at 610 nm or 390 nm with a time-selective acquisition

C.2.2.3 Pulsed flame photometric detection

Instrument:	Varian GC 3800
Injection:	splitless, injection volume: 5 µl, autosampler: CTC Analytics CombiPal
Injector temperature:	220 °C
Carrier gas:	N_2 constant flow 2 ml/min
Capillary column:	length 30 m, ID = 0,32 mm, d_f = 0,25 µm
Factor four Varian:	VF-1 ms
Temperature program:	70 °C for 1 min, then 10 °C/min increments to 120 °C, held for 2 min; then 20 °C/min increments to 190 °C, held for 2 min; then 30 °C/min increments to 300 °C
Detector temperature:	350 °C
Gas flows:	H_2: 30,0 ml/min, air 1: 22,0 ml/min, air 2: 25,0 ml/min
Filter:	Large pass-band filter working at 610 nm or 390 nm with a time-selective acquisition
Selective acquisition for 610 nm filter:	gate delay 3,5 ms, gate width 2,0 ms

C.2.3 Atomic emission spectrometric detection

Instrument:	HP 5921A
Transfer line:	HP-5 capillary, 280 °C
Cavity temperature:	280 °C
Wavelength for Sn:	271 nm or 303 nm
Elevated helium make-up	270 ml/min
Gas flow:	measured at cavity vent
Gas for spectrometer:	2 L nitrogen/min
Solvent back flush:	0,1 min to 4 min
Hydrogen (purity 5.6):	50 psi (3,5 bar)
Oxygen (purity 4.8):	14 psi (1 bar)

C.2.4 ICP/MS detection

Instrument: HP 6890/HP 4500/HPICP-MS Chemstation (Hewlett-Packard)

Power: 1 300 W

Sampling depth: 7 mm

Carrier-gas flow rate: 1 500 ml/min

Auxiliary-gas flow rate: 1,0 L/min

Plasma-gas flow rate: 15,0 L/min

Sampling cone: nickel

Skimmer cone: nickel

Acquisition mode: time-resolved analysis; 1 point per spectral peak

Table C.1 — Proposed masses of tin and possible interferences

Element	Isotope	Abundance	Potential interferences	Interference with practical relevance	Preference	Reason
		%	Inter-element	Polyatomic ions		
Sn	118	24,2	U	MoO, RuO, PdO	X	Least interference
	120	32,6	Te	RuO, PdO		

Scan time Sn: 30 ms; Xe: 5 ms

Transfer line: 250 °C

Gas chromatograph column: FSOT (fused-silica open tubular), 30 m, ID = 0,25, d_f = 0,25 µm methylsilicone

Injection technique: splitless

Injection temperature: 250 °C

Purge time: 1 min

Temperature program: 60 °C (for 1 min) → 45 °C/min → 250 °C (for 1 min)

Carrier gas/inlet pressure: Xe/H_2 (0,1/99,9 mixture); 30 psi

Pressure control: constant pressure mode: 30 psi

C.2.5 Mass spectrometric detection

Instrument: Agilient 6890 / 5973 Quadrupole GC-MS

MSD transfer-line temperature: 300 °C

Acquisition mode: single-ion monitoring (SIM)

Detected ions:	see Annex D
Ionization voltage:	70 eV
Source temperature:	230 °C
Quadrupole temperature:	150 °C

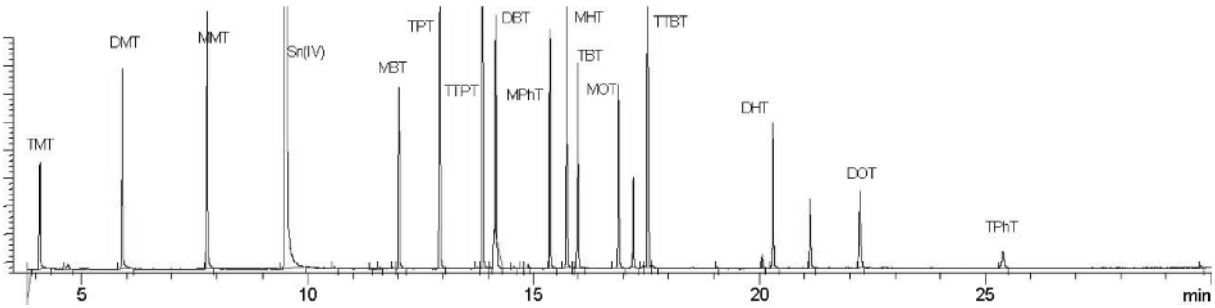
C.2.6 GC/MS^n detection

Instrument:	Saturn 2200, Varian	
Ion-trap:	Transfer-line temperature:	270 °C
	Temperature	220 °C
	Ionization voltage	70 eV
	Emission current	100 µA
	Multiplier voltage	elevated by 300 V
MS^n-conditions:	See Table C.2	

Table C.2 — MS^n-conditions

Precursor-ion *m/z*	Isolation-window *m/z*	Wave mode	Amplitude of excitation V
122	3	Non-resonant	80
121	7	Resonant	1
120	3	Resonant	1,5

C.3 Example of a chromatogram

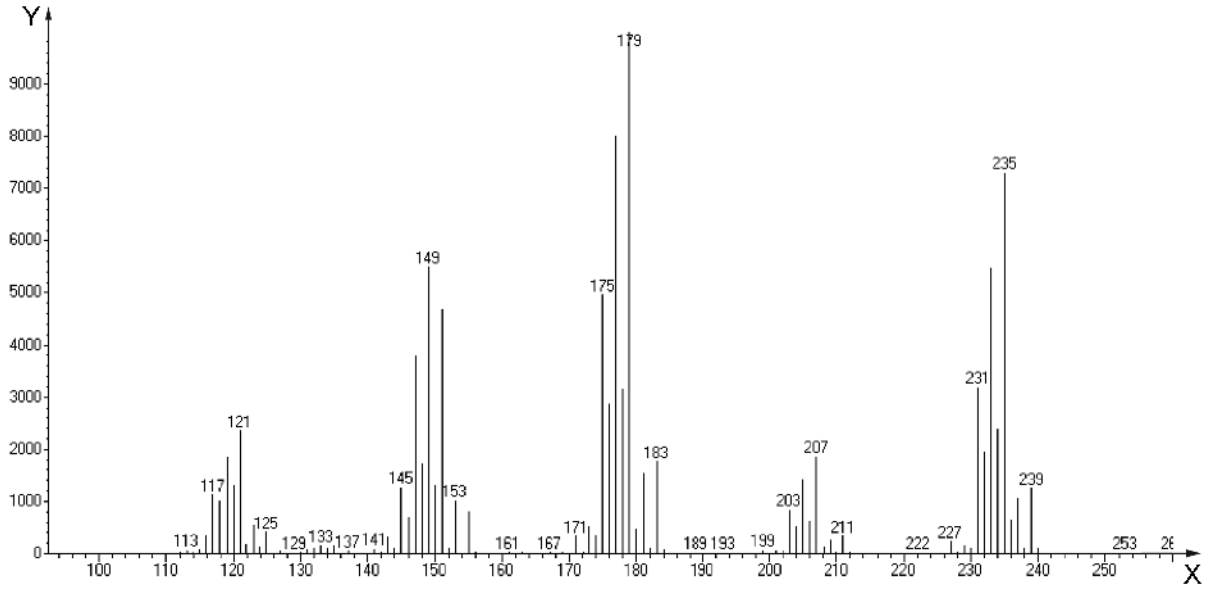


The retention time of tetrapentyltin would be at 20,82 min and the retention time of tricyclohexylethyltin would be at 25,10 min. The gas chromatographic (GC) conditions are given in C.2.3.

Figure C.1 — Example of a chromatogram using GC-AED

C.4 Examples of mass spectra (for MS conditions, see C.2.5)

C.4.1 Butyltriethyltin

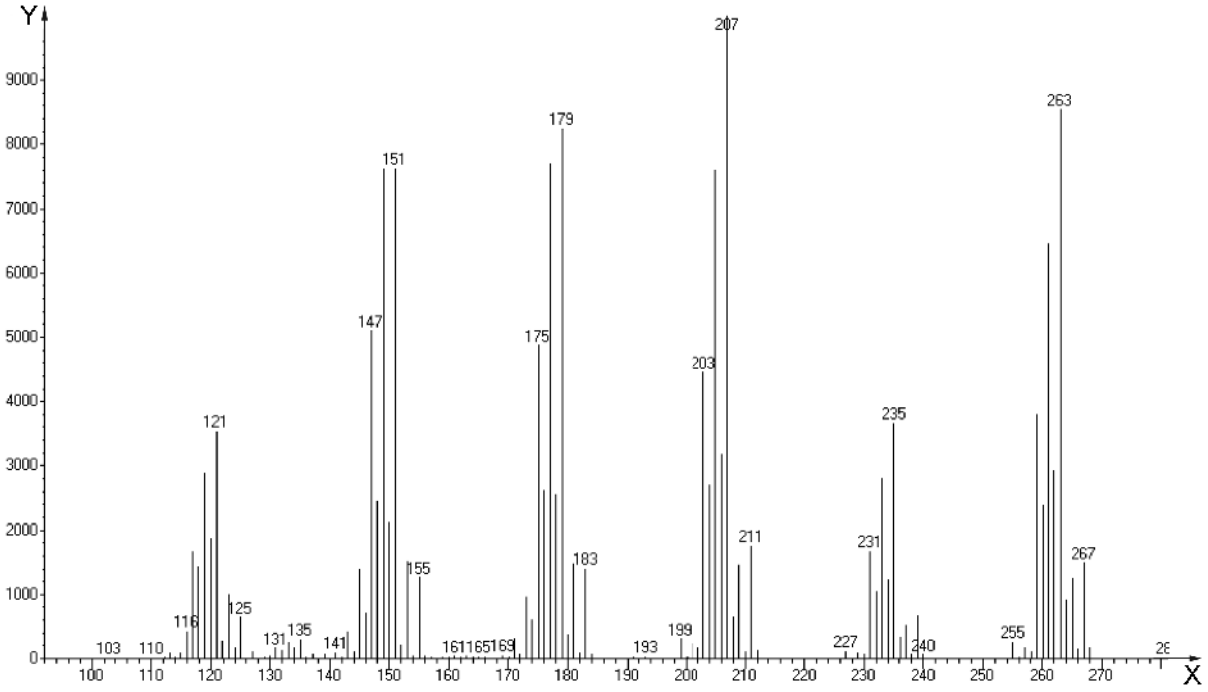


Key

X *m/z*

Y abundance

C.4.2 Dibutyldiethyltin

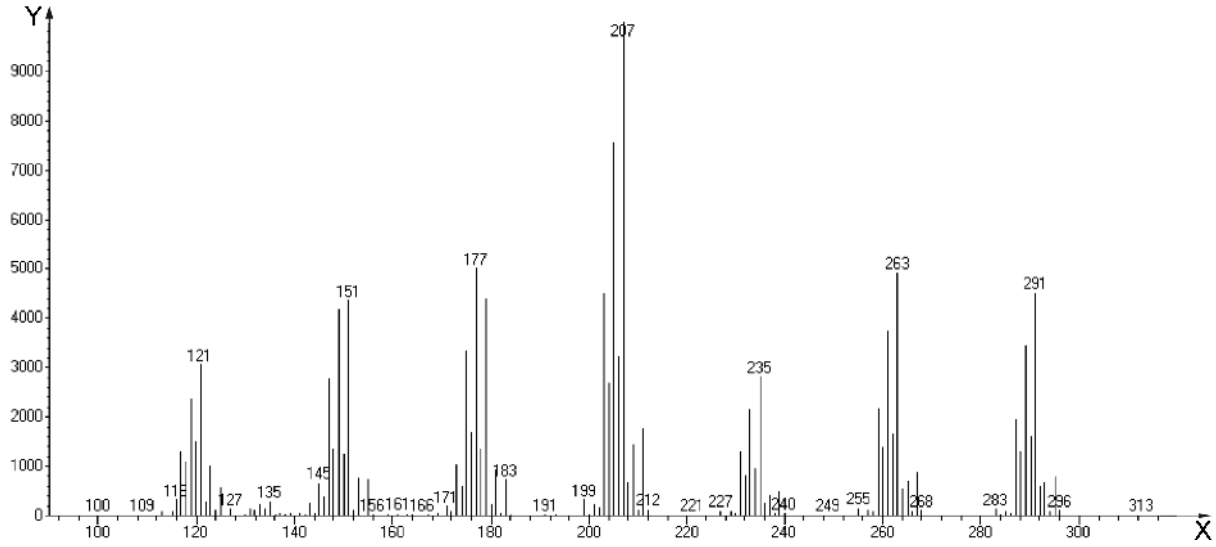


Key

X *m/z*

Y abundance

C.4.3 Tributylethyltin

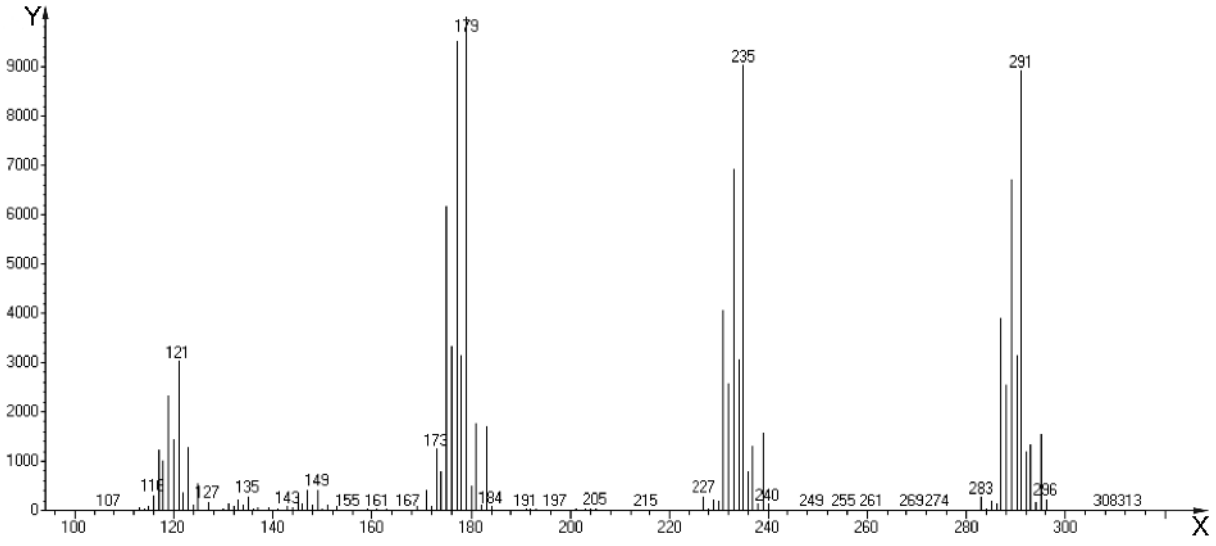


Key

X *m/z*

Y abundance

C.4.4 Tetrabutyltin

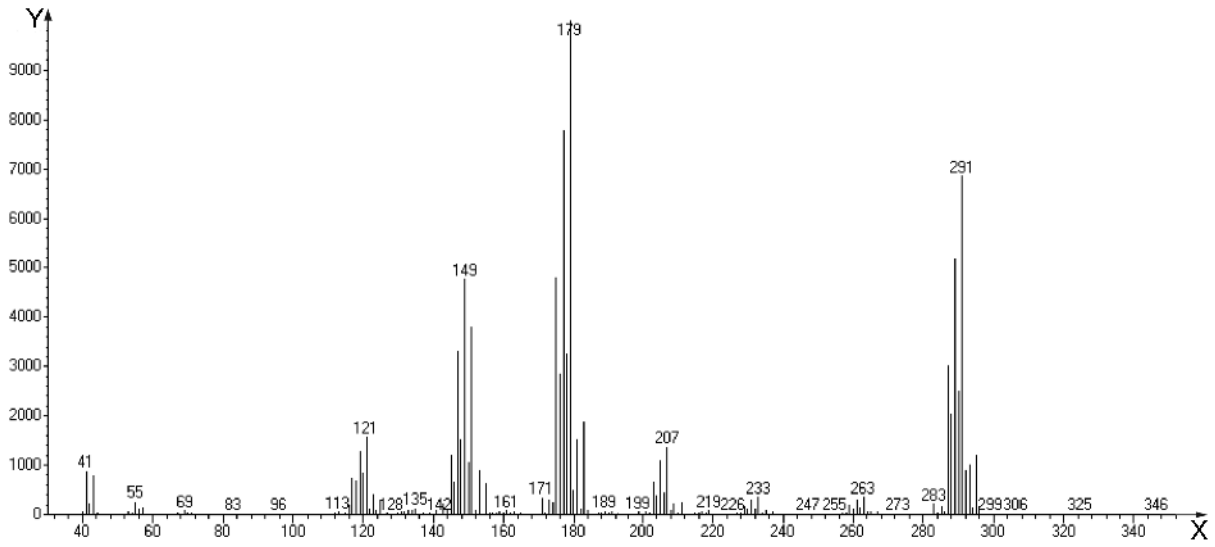


Key

X *m/z*

Y abundance

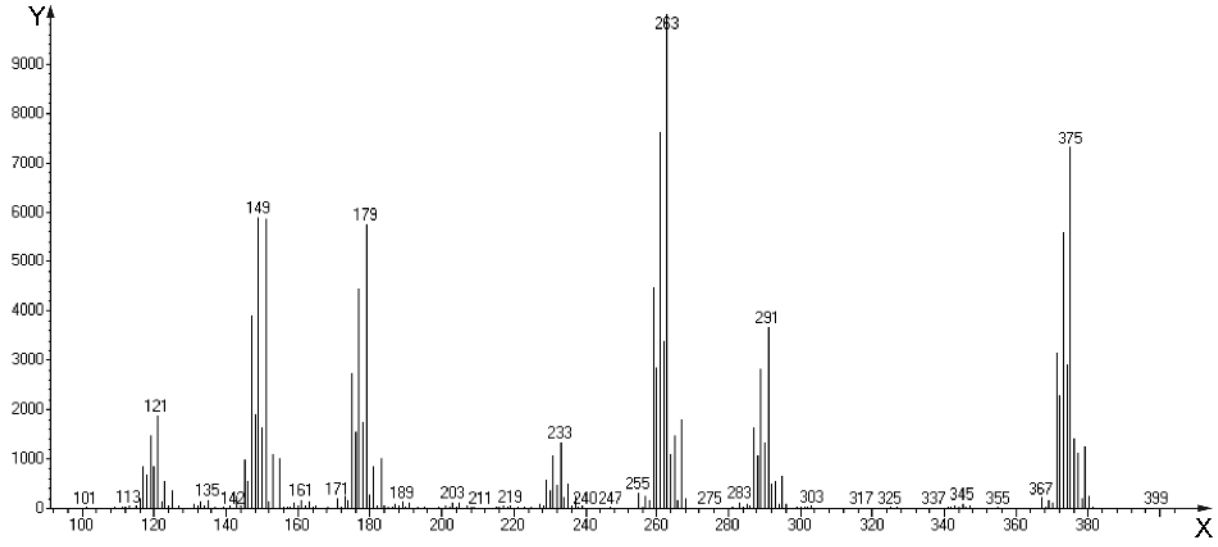
C.4.5 Octyltriethyltin



Key

X *m/z*
Y abundance

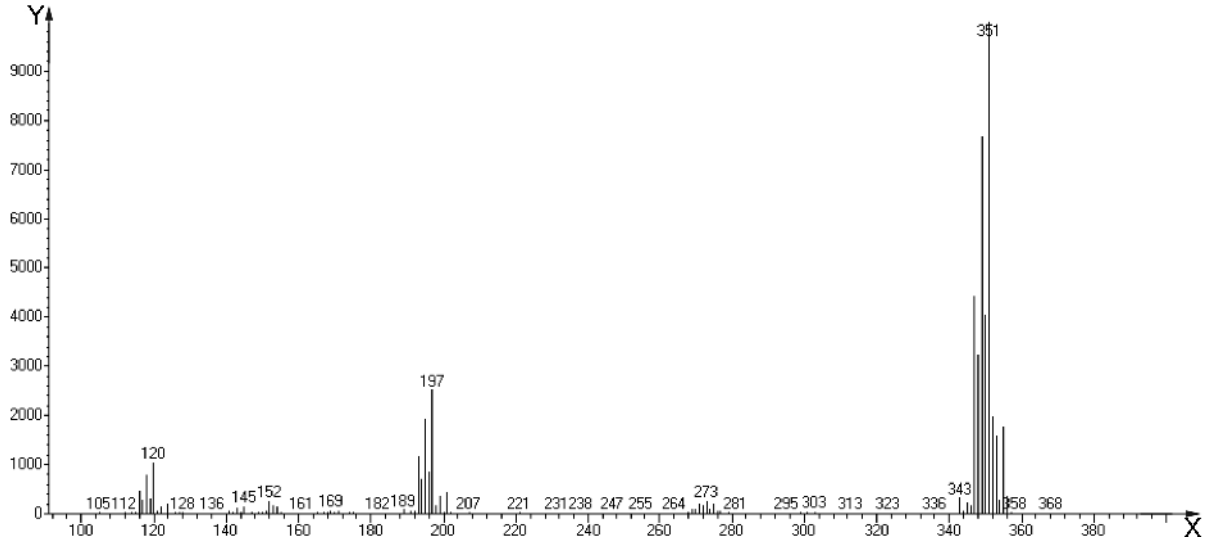
C.4.6 Dioctyldiethyltin



Key

X *m/z*
Y abundance

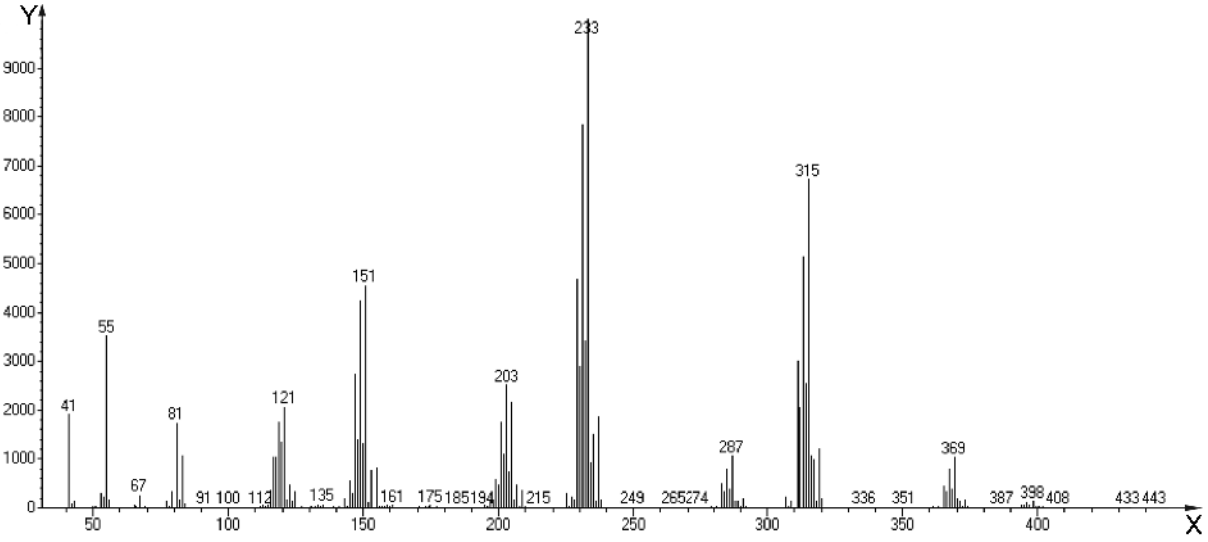
C.4.7 Triphenylethyltin



Key

X *m/z*
Y abundance

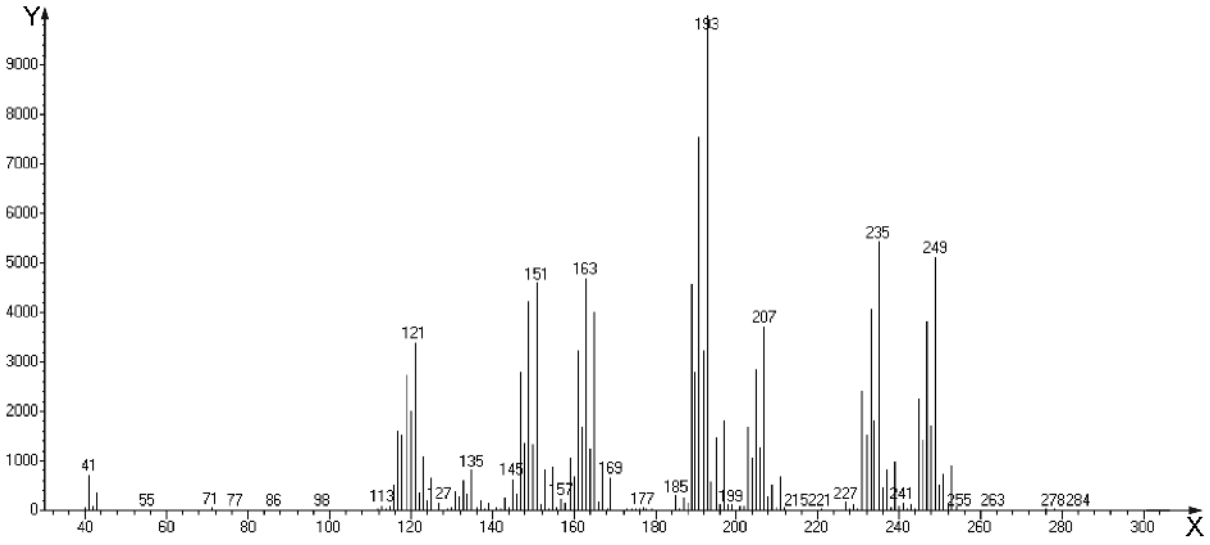
C.4.8 Tricyclohexylethyltin



Key

X *m/z*
Y abundance

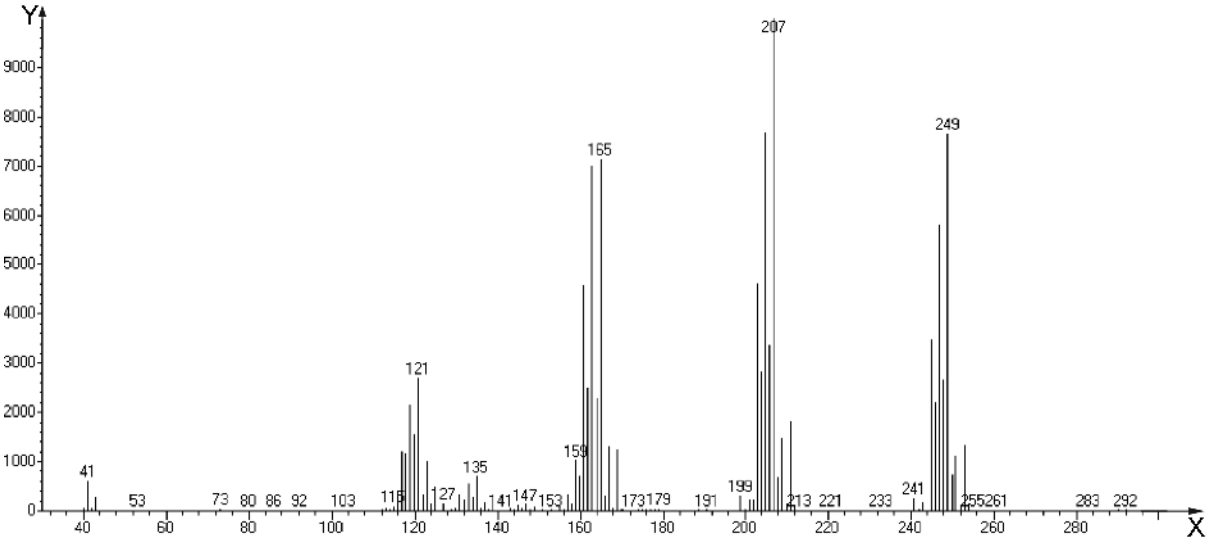
C.4.9 Tripropylethyltin



Key

X *m/z*
Y abundance

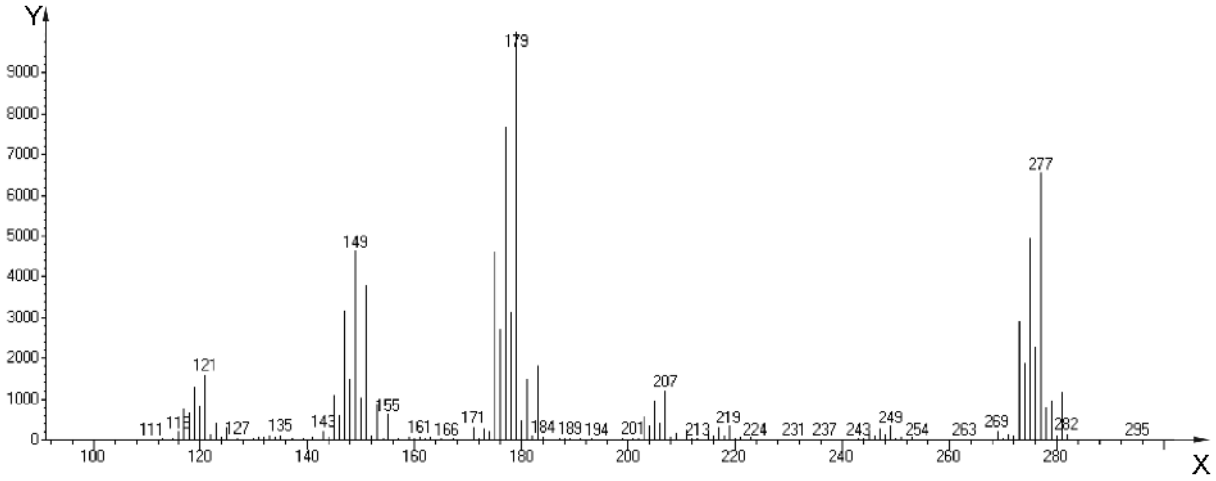
C.4.10 Tetrapropyltin



Key

X *m/z*
Y abundance

C.4.11 Heptyltriethyltin

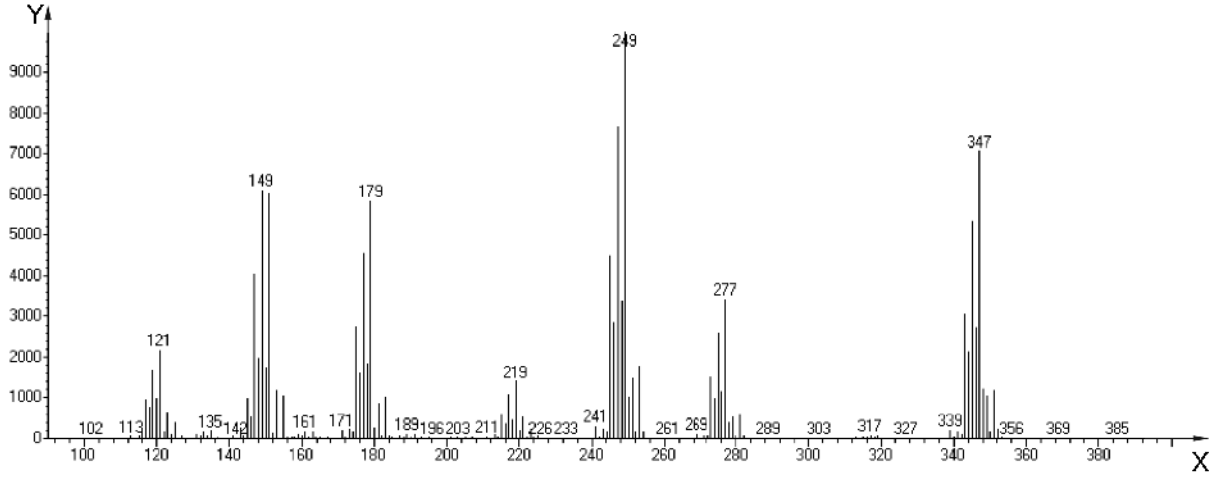


Key

X *m/z*

Y abundance

C.4.12 Diheptyldiethyltin

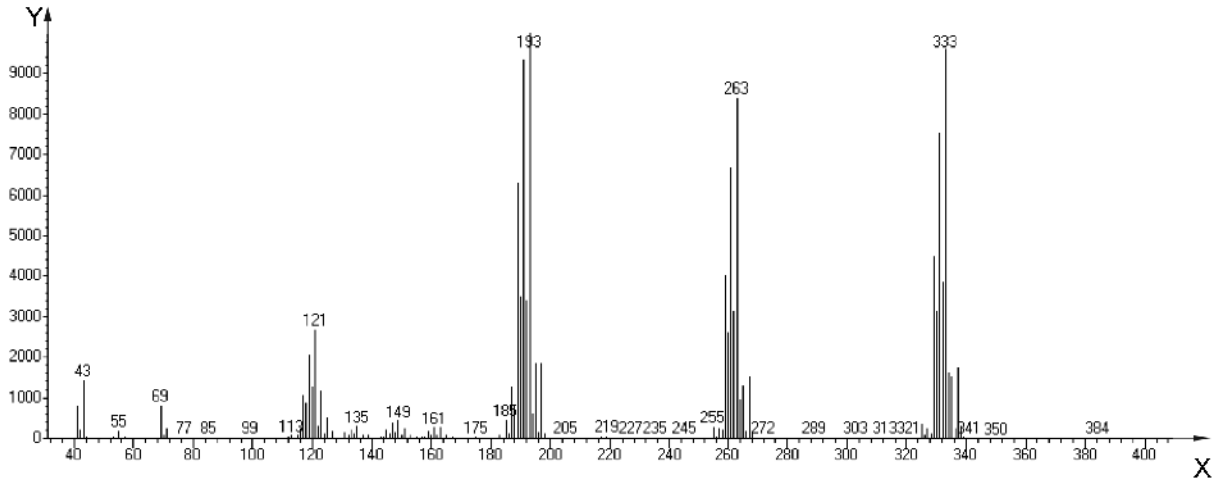


Key

X *m/z*

Y abundance

C.4.13 Tetrapentyltin



Key

X *m/z*

Y abundance

Annex D
(informative)

Information about GC/MS identification

D.1 Characteristic masses for mass spectrometric detection

The isotope cluster of the organotin compounds is formed by 10 natural tin isotopes:

Table D.1 — Masses and abundance of natural tin isotopes (see Reference [14] in the Bibliography)

Mass amu	Abundance %	Relative abundance %
112	0,97	2,98
114	0,66	2,03
115	0,34	1,04
116	14,54	44,63
117	7,68	23,57
118 [a]	24,22	74,34
119	8,59	26,37
120 [a]	32,58	100,00
122	4,63	14,21
124	5,79	17,77

[a] These isotopes are preferred for mass spectrometric detection.

With GC/MS analysis, each ion fragment containing tin will be split in an isotope cluster. Choose two of the most intensive clusters. Record two of the most intensive ion fragments for each of the two clusters (see Table D.2).

Table D.2 — Recommended characteristic masses for identification and evaluation

Substance	Cluster a		Cluster b		Cluster c	
	mass a_1	mass a_2	mass b_1	mass b_2	mass c_1	mass c_2
Monomethyltriethyltin	193,0	191,0	165,0	163,0	134,9	132,9
Dimethyldiethyltin	179,0	177,0	151,0	149,0	134,9	132,9
Trimethyldiethyltin	165,0	163,0	151,0	149,0	134,9	132,9
Monobutyldiethyltin	235,1	233,1	179,0	177,0	151,0	149,0
Dibutyldiethyltin	263,1	261,1	179,0	177,0	151,0	149,0
Tributylmonoethyltin	291,1	289,1	263,1	261,1	179,0	177,0
Tetrabutyltin	291,1	289,1	235,1	233,0	179,0	177,0
Monooctyltriethyltin	291,1	289,1	179,0	177,0	151,0	149,0
Dioctyldiethyltin	375,2	373,2	263,1	261,1	151,0	149,0
Monophenyltriethyltin	255,0	253,0	227,0	225,0	197,0	195,0
Diphenyldiethyltin	303,0	301,0	275,0	273,0	197,0	195,0
Triphenylmonoethyltin	351,0	349,0	197,0	195,0	—	—
Tricyclohexylmonoethyltin	233,0	231,0	315,1	313,1	369,2	367,2
Monoheptyltriethyltin (IS)	277,1	275,1	179,0	177,0	151,0	149,0
Diheptyldiethyltin (IS)	347,2	345,2	249,1	247,1	151,0	149,0
Tripropylethyltin (IS)	249,1	247,1	235,1	233,0	193,0	191,0
Tetrapropyltin (IS)	249,1	247,1	165,0	163,0	207,0	205,0
Tetrapentyltin (IS)	333,2	331,2	263,1	261,1	193,0	191,0

The ratios of peak areas of the respective isotope clusters of a compound may be mass-proportion dependent and may differ due to the parameter setting and type of the mass spectrometric system used.

Annex E
(informative)

Validation data

E.1 Design of the study and description of the sample materials

In 2008, an interlaboratory comparison was organized by the Federal Institute for Materials Research and Testing (BAM), Germany. For details, see Reference [16] in the Bibliography.

All the original field-moist solid samples were freeze-dried, ground, homogenized and put in bottles.

Five sample materials were distributed to the laboratories for this validation study. The participants were strongly advised to follow the attached instructions in the handling of the samples.

— One bottle of river sediment (river Elbe, Germany) (approximately 40 g) referred to as **RSED** with the natural contamination of the different OTC target compounds in the range of 5 µg/kg Sn to 700 µg/kg Sn. The freeze-dried ground material was sieved to less than 125 µm and homogenized and bottled in the Federal Institute for Materials Research and Testing (BAM).

— One bottle of harbour sediment from France (approximately 8 g), referred to as **HSED,** provided by Patrick Thomas from the Pasteur-Institute, Lille, with the natural contamination of the different target compounds in the range of 20 µg/kg Sn to 4 000 µg/kg Sn. The freeze-dried ground material was sieved to less than 100 µm and sent to BAM, where homogenization and bottling was done.

— One bottle of sewage sludge from Paris, France (20 g), referred to as **SLUDGE,** provided by Patrick Thomas from the Pasteur-Institute, Lille, with natural contamination in the range of 5 µg/kg Sn to 100 µg/kg Sn to check for the fitness for the purpose of the standard for application by CEN/TC 308, *Characterization of sludges*. This sample contains large amounts of sulfur. Therefore, the additional clean-up step for sulfur was recommended.

Two sample materials for quality-control purposes and plausibility checks of the analytical procedures applied in the laboratories, as follows.

— (One spiked sample) four bottles of ground and sieved agricultural soil (3 g each), referred to as **AGRICULTURAL SOIL,** were spiked with all the target OTCs given in this International Standard (including TTBT) in the range of 10 µg/kg Sn to 100 µg/kg Sn in the Federal Institute for Materials Research and Testing (BAM). The participants were instructed to take the whole sample to ensure homogeneity aspects.

— 1 vial of standard solution of OTC compounds (1 ml), prepared in the Federal Institute for Materials Research and Testing (BAM). The participants were instructed that an aliquot of this standard solution (100 µl) is to be added to a specific volume (1 000 ml of own laboratory water, with a checked blank value). The related measurements were referred to as **WATER** in the performance evaluation. This sample material is intended for the quality control and plausibility check for the calibration and derivatization steps without solid extraction step.

Tables E.1 to E.4 contain the results of this interlaboratory comparison. It should be noted that all results are expressed as amounts of Sn in nanograms per gram (Table E.1) or amounts of Sn in nanograms per litre (Tables E.2 to E.4). Data were calculated according to both ISO 5725-2 [1] and DIN 38402-45 [6].

Table E.1 — Validation data of agricultural soil

Agricultural soil															
Compound	ISO 5725-2								DIN 38402-45						**Reference value** ng/g
	l	n	n_{AP}	$\bar{x}$	s_R	η	CV_r	CV_R	l	$\bar{x}$	s_R	η	CV_r	CV_R	
MBT	8	20	10,0	32,61	6,00	97,59	7,32	17,96	12	36,57	13,70	109,46	4,87	41,00	33,41
DBT	10	25	4,0	37,27	8,10	94,72	8,13	20,59	13	36,08	7,07	91,68	7,40	17,97	39,352
TBT	10	26	0,0	20,62	2,68	97,11	9,74	12,60	13	20,73	3,33	97,65	8,55	15,66	21,232
TTBT	9	22	0,0	36,46	5,04	89,70	4,82	12,40	12	38,00	10,03	93,49	6,64	24,68	40,648
MOT	6	16	6,3	29,73	8,41	94,56	14,26	26,76	10	48,43	24,75	154,05	6,67	78,73	31,438
DOT	7	18	0,0	31,97	6,48	77,75	4,69	15,77	10	38,76	15,23	94,26	6,37	37,04	41,116
TPhT	10	26	0,0	27,48	14,33	56,50	12,60	29,47	13	28,38	16,04	58,35	5,78	32,99	48,631
TCyT	6	14	7,1	20,30	7,16	65,53	2,90	23,13	10	28,50	20,79	92,01	4,74	67,11	30,979

l is the number of laboratories

n is the number of results used for data evaluation

n_{AP} is the percentage (%) of outliers

$\bar{x}$ is the mean value, in nanograms per gram (ng/g)

s_R is the standard deviation of reproducibility, in nanograms per gram (ng/g)

η is the recovery rate = mean values $\bar{x}$ /reference value, in percent (%)

CV_r is the relative repeatability standard deviation, in percent (%)

CV_R is the relative reproducibility standard deviation, in percent (%)

Table E.2 — Validation data of harbour sediment (HSED)

Harbour sediment												
Compound	ISO 5725-2							DIN 38402-45				
	l	n	n_{AP}	$\bar{x}$	s_R	CV_r	CV_R	l	$\bar{x}$	s_R	CV_r	CV_R
MBT	8	21	0,0	576,19	226,31	9,14	39,28	11	649,08	285,36	6,62	43,96
DBT	9	24	0,0	1097,66	170,98	5,57	15,58	12	1109,81	199,33	5,12	17,96
TBT	9	24	0,0	3524,16	1018,88	8,37	28,91	12	3987,97	1873,89	9,99	46,99
TTBT	4	10	10,0	7,57	1,22	15,02	16,13	8	19,30	20,89	14,42	108,27
TPhT	4	10	10,0	13,71	2,52	11,68	18,39	7	26,29	17,82	67,80	67,80

l is the number of laboratories

n is the number of results used for data evaluation

n_{AP} is the percentage (%) of outliers

$\bar{x}$ is the mean value, in nanograms per litre (ng/l)

s_R is the standard deviation of reproducibility, in nanograms per litre (ng/l)

CV_r is the relative repeatability standard deviation, in percent (%)

CV_R is the relative reproducibility standard deviation, in percent (%)

Table E.3 — Validation data of river sediment (RSED)

River sediment												
Compound	ISO 5725-2							DIN 38402-45				
	l	n	n_{AP}	$\bar{x}$	s_R	CV_r	CV_R	l	$\bar{x}$	s_R	CV_r	CV_R
MBT	9	25	0,0	219,72	135,27	12,18	61,56	12	249,61	161,26	7,30	64,60
DBT	7	19	15,8	229,28	22,80	7,32	9,94	13	237,14	79,58	7,30	33,56
TBT	9	25	4,0	540,96	125,33	12,40	23,17	13	586,64	217,68	6,49	37,11
TTBT	6	16	6,3	3,48	1,24	13,94	35,50	9	3,71	2,53	11,52	68,17
MOT	6	17	0,0	6,77	4,65	17,55	68,64	9	8,25	7,30	13,04	88,47
DOT	5	14	7,1	7,09	4,41	5,39	62,12	9	8,91	5,49	7,70	61,57
TPhT	5	15	0,0	6,09	3,65	23,79	59,90	7	9,15	5,63	21,54	61,53

l is the number of laboratories

n is the number of results used for data evaluation

n_{AP} is the percentage (%) of outliers

$\bar{x}$ is the mean value, in nanograms per litre (ng/l)

s_R is the standard deviation of reproducibility, in nanograms per litre (ng/l)

CV_r is the relative repeatability standard deviation, in percent (%)

CV_R is the relative reproducibility standard deviation, in percent (%)

Table E.4 — Validation data of sewage sludge

Sewage sludge												
Compound	ISO 5725-2							DIN 38402-45				
	l	n	n_{AP}	$\bar{x}$	s_R	CV_r	CV_R	l	$\bar{x}$	s_R	CV_r	CV_R
MBT	8	22	0	99,16	38,45	9,51	38,77	11	94,47	71,40	5,44	75,57
DBT	9	25	0	32,65	8,12	13,69	24,87	12	32,07	13,18	10,45	41,09
TBT	6	16	0	4,82	1,39	7,36	28,76	9	5,20	4,05	14,68	77,98
MOT	6	16	0	34,45	13,25	5,33	38,46	8	37,61	29,55	7,03	78,58
DOT	6	16	0	13,47	3,21	3,79	23,81	9	17,87	10,00	5,02	55,99

l is the number of laboratories

n is the number of results used for data evaluation

n_{AP} is the percentage (%) of outliers

$\bar{x}$ is the mean value, in nanograms per litre (ng/l)

s_R is the standard deviation of reproducibility, in nanograms per litre (ng/l)

CV_r is the relative repeatability standard deviation, in percent (%)

CV_R is the relative reproducibility standard deviation, in percent (%)

E.2 Remarks on validation results and improvement of performance

During development and validation of the method described in this International Standard, it was found that laboratories need to gain experience in dealing with the complexity of the compounds and the determination method. The validation data given in this Annex represent the state of the art in the participating laboratories. It can be expected that the performance of laboratories applying this method frequently will quickly improve. Annex A gives suggestions to support laboratories in this improvement. The application of this method, including the use of reference materials as well as the participation in laboratory proficiency studies, is strongly recommended.

Bibliography

[1] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[2] ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

[3] ISO 10381-4:2003, *Soil quality — Sampling — Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites*

[4] ISO 14507, *Soil quality — Pretreatment of samples for determination of organic contaminants*

[5] DIN 19744, *Identification and qualitative determination of organic stannic compounds in solid materials (soils, sediments, wastes)* (now withdrawn)

[6] DIN 38402-45, *German standard methods for the examination of water, waste water and sludge — General information (group A) — Part 45: Interlaboratory comparisons for proficiency testing of laboratories (A 45)*

[7] DIN 38407-3, *German standard methods for the determination of water, waste water and sludge — Jointly determinable substances (group F) — Part 3: Determination of polychlorinated biphenyls (F 3)*

[8] DIN 38414-1, *German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S); sampling of sludges (S 1)*

[9] DIN 38414-11, *German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S); sampling of sediments (S 11)*

[10] EN 12880:2000, *Characterization of sludges — Determination of dry residue and water content*

[11] EN 13137, *Characterization of waste — Determination of total organic carbon (TOC) in waste, sludges and sediments*

[12] EN 14346, *Characterization of waste — Calculation of dry matter by determination of dry residue or water content*

[13] BROWN, H. C. and RACHERIA, U. S. *Organometallics*, Vol 5, No. 2, 1986, pp. 391-394

[14] CRC-Handbook, 1986, Wiley Interscience

[15] LEERMAKERS, M., NUYTTENS, J. and BAEYENS, W. (2005), Organotin analysis by gas chromatography – pulsed flame-photometric detection (GC–PFPD), *Analytical and Bioanalytical Chemistry*, Volume 381, No 6, March 2005, pp. 1272-1282

[16] THOMAS SOMMERFELD, ANDREAS BUCHHOLZ, TIN WIN and DETLEF LÜCK, *Report on the "Interlaboratory Comparison for the validation of a Draft International Standard ISO DIS 23161 for the determination of organotin compounds in soil and soil-like materials"*, Bundesanstalt für Materialforschung und Prüfung, BAM, Berlin, September 2008

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