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

Qualité du sol — Dosage d'une sélection de composés organostanniques — Méthode par chromatographie en phase gazeuse

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 23161:2009), which has been technically revised.

The main changes compared to the previous edition are as follows:

- note in Clause 1 (converted to normal text) and Table 2 have been moved to Clause 4;
- former Note 4 in Clause 4 has been changed to normal text and moved above Note 1;
- other pretreatment procedures allowed in Clause 4 and in 7.1;
- former second sentence in 5.5.5 has been changed to Note;
- storage conditions has been changed to be consistent with ISO 5667-15;
- the Bibliography has been updated.

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.

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

WARNING — Persons using this document should be familiar with usual laboratory practice. This document 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.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this document, 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.

1 Scope

This document specifies a gas-chromatographic method for the identification and quantification of organotin compounds (OTCs) in soils as specified in Table 1.

This document 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 compounds

$R_nSn^{(4-n)+}$	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.

Organotin cations can only be determined in accordance with this document 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 document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 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.

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/

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

Note 1 to entry: 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 to achieve homogeneity of the sample. 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).

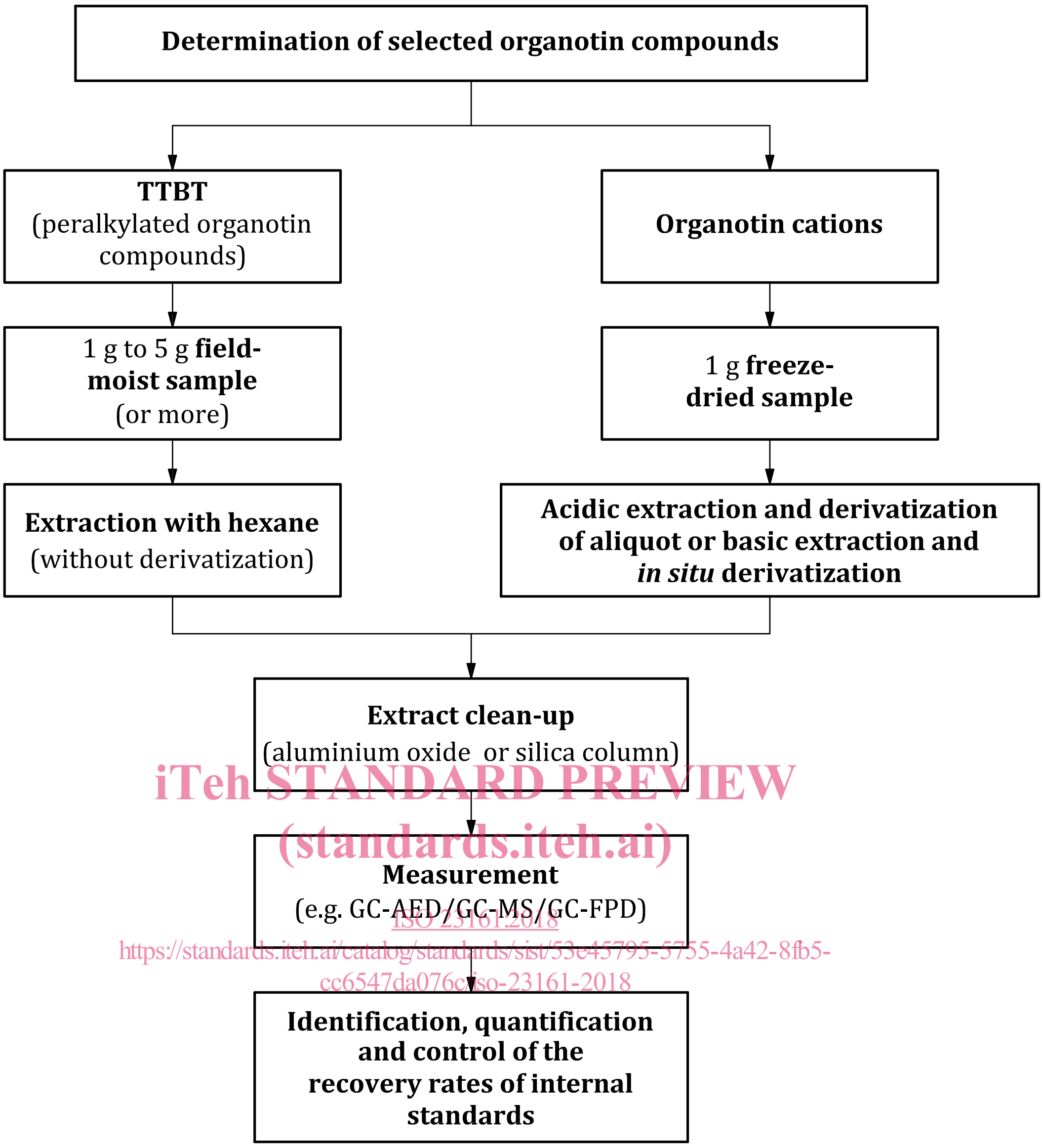

Figure 1 — Flowchart for the pretreatment and analysis of selected organotin compounds

Beside freeze drying, other pretreatment procedures can be carried out, if the suitability has been proven.

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.

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

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 contamination by organotin compounds.

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 derivatives. *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.

When applying this method to the determination of other organotin compounds not specified in the scope, its suitability has to be 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

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 pre-cleaning step. 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 and the glassware can contain impurities of organotin compounds. It is absolutely essential to verify the blanks.

5.1.1 Water, in accordance with grade 3 of ISO 3696, the water shall be free of interferences.

5.2 Chemicals

5.2.1 Acetic acid, CH_3COOH, glacial.

5.2.2 Sodium hydroxide solution, NaOH, approximately 400 g/l (aqueous solution).

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	$C_4H_9SnCl_3$	1 118–46–3	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	$(C_4H_9)_3SnCl$	1 461–22–9	0,891	A
5.3.4	Tetrabutyltin	TTBT	$(C_4H_9)_4Sn$	1 461–25–2	1,000	A
5.3.5	Monooctyltin trichloride	MOTCl	$C_8H_{17}SnCl_3$	3 091–25–6	0,686	A
5.3.6	Dioctyltin dichloride	DOTCl	$(C_8H_{17})_2SnCl_2$	3 542–36–7	0,830	A
5.3.7	Triphenyltin chloride	TPhTCl	$(C_6H_5)_3SnCl$	6 39–58–7	0,908	A
5.3.8	Tricyclohexyltin chloride	TCyTCl	$(C_6H_{11})_3SnCl$	3 091–32–5	0,912	A
Internal standards						
5.3.9	Monoheptyltin trichloride	MHTCl	$C_7H_{15}SnCl_3$	59 344–47–7	0,672	B
5.3.10	Diheptyltin dichloride	DHTCl	$(C_7H_{15})_2SnCl_2$	74 340–12–8	0,817	B

[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.

Table 3 *(continued)*

No.	Standard	Abbreviation	Formula	CAS-RN[a]	WF[b]	Solution[c]
5.3.11	Tripropyltin chloride	TPTCl	$(C_3H_7)_3SnCl$	2 279–76–7	0,875	B
5.3.12	Tetrapropyltin	TTPT	$(C_3H_7)_4Sn$	2 176–98–9	1,000	B
5.3.13	Tetrapentyltin	TTPeT	$(C_5H_{11})_4Sn$	3 765–65–9	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.

Internal standards other than those given in Table 3 may be used, if suitability has been proven. Examples of suitable internal standards are:

- Monobutyltin-D9 for monobutyltin;
- Tripropyltin for dibutyltin and tributyltin;
- Monoheptyltin for monooctyltin;
- Diheptyltin for tetrabutyltin, dioctyltin and tricyclohexyltin;
- Triphenyltin-D15 for triphenyltin.

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 PTFE lined vial.

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

For each working range, prepare at least six 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 additional 20 min.

5.4.4 Methanolic potassium hydroxide solution

Dissolve 25 g potassium hydroxide (5.2.5) in 100 ml 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 a solution of approximately 10 g tetraethylborate compound (5.2.11) in 100 ml 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 ± 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 3 % mass fraction 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 10 % mass fraction 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.