
**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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Contents

Page

| | |
|--|-----------|
| Foreword | iv |
| Introduction..... | v |
| 1 Scope | 1 |
| 2 Normative references | 2 |
| 3 Terms and definitions | 2 |
| 4 Principle..... | 2 |
| 5 Reagents..... | 4 |
| 5.1 General | 4 |
| 5.2 Chemicals..... | 4 |
| 5.3 Standards | 5 |
| 5.4 Preparation of reagents and solutions..... | 6 |
| 5.5 Clean-up | 7 |
| 6 Apparatus | 7 |
| 6.1 Requirements for glassware | 7 |
| 6.2 Sampling apparatus..... | 8 |
| 6.3 Additional apparatus..... | 8 |
| 7 Procedure..... | 8 |
| 7.1 Sampling and sample pretreatment | 8 |
| 7.2 Sample extraction..... | 9 |
| 7.3 Clean-up of the extract..... | 10 |
| 7.4 Determination of dry mass..... | 11 |
| 7.5 Measurement | 11 |
| 8 Calibration..... | 12 |
| 9 Recovery rates of the internal standard compounds | 12 |
| 10 Quantification | 13 |
| 11 Expression of results | 14 |
| 12 Precision..... | 14 |
| 13 Test report..... | 14 |
| Annex A (informative) Information about the procedure | 15 |
| Annex B (informative) Additional clean-up procedures..... | 17 |
| Annex C (informative) Information about typical instrumental conditions | 20 |
| Annex D (informative) Information about GC/MS identification..... | 31 |
| Annex E (informative) Validation data | 33 |
| Bibliography..... | 37 |

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*.

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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.

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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

| $R_n\text{Sn}^{(4-n)+}$ | R | n | Name | Acronym |
|--------------------------------------|------------|-----|-------------------------|---------|
| Organotin cations^a | | | | |
| BuSn ³⁺ | Butyl | 1 | Monobutyltin cation | MBT |
| Bu ₂ Sn ²⁺ | Butyl | 2 | Dibutyltin cation | DBT |
| Bu ₃ Sn ⁺ | Butyl | 3 | Tributyltin cation | TBT |
| OC ₈ Sn ³⁺ | Octyl | 1 | Monooctyltin cation | MOT |
| OC ₂ Sn ²⁺ | Octyl | 2 | Diocetyl tin cation | DOT |
| Ph ₃ Sn ⁺ | Phenyl | 3 | Triphenyltin cation | TPhT |
| Cy ₃ Sn ⁺ | Cyclohexyl | 3 | Tricyclohexyltin cation | TCyT |
| Peralkylated organotin | | | | |
| Bu ₄ Sn | 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

| $R_n\text{Sn}^{(4-n)+}$ | R | n | Name | Acronym |
|----------------------------------|--------|-----|----------------------|---------|
| MeSn ³⁺ | Methyl | 1 | Monomethyltin cation | MMT |
| Me ₂ Sn ²⁺ | Methyl | 2 | Dimethyltin cation | DMT |
| Me ₃ Sn ⁺ | 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*

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3 Terms and definitions

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

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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).

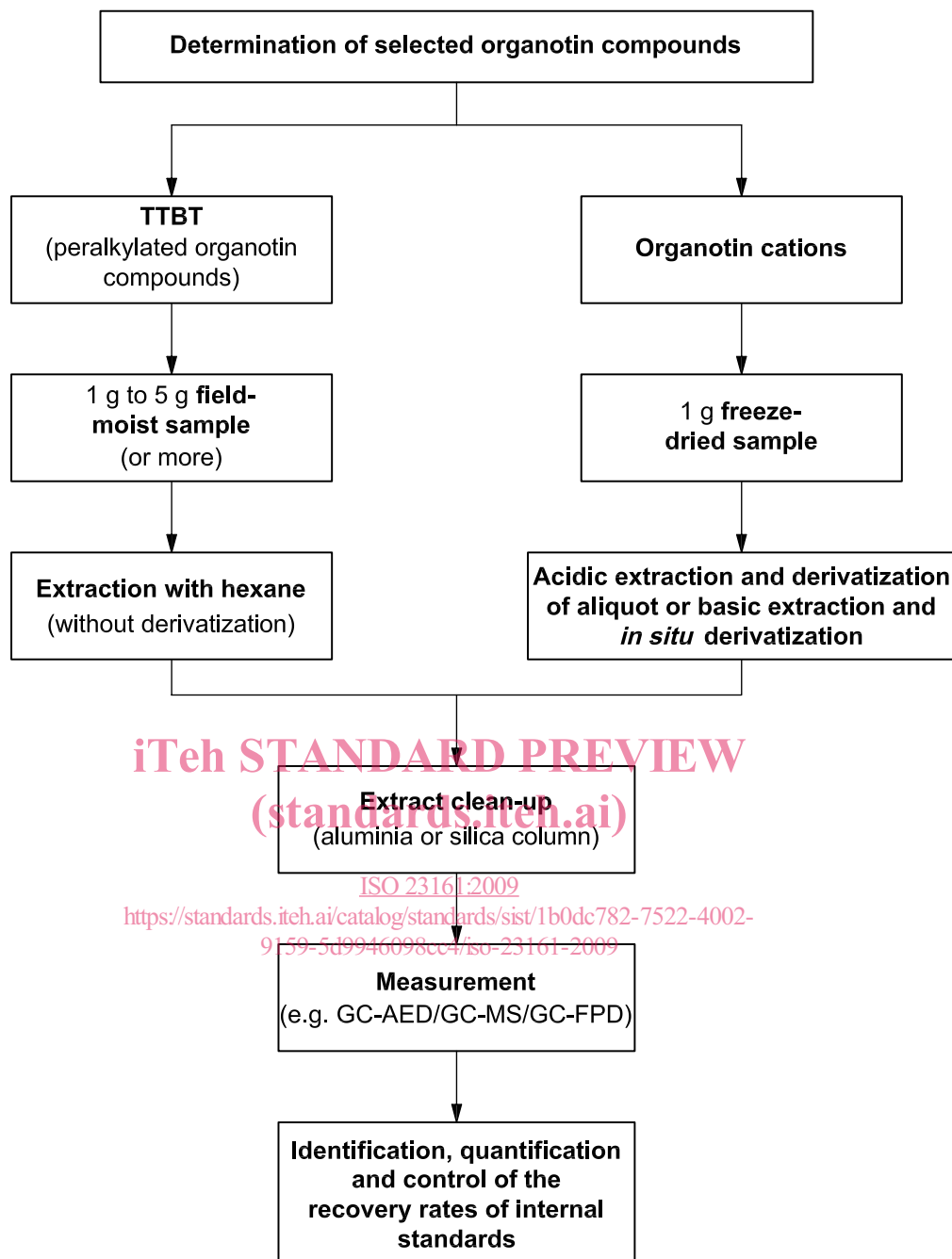


Figure 1 — Flowchart for the pretreatment and analysis of selected organotin compounds

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 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.

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.

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5.2 Chemicals

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5.2.1 **Acetic acid**, CH₃COOH, glacial.

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

5.2.3 **Sodium acetate**, CH₃COONa.

5.2.4 **Sodium sulfate**, Na₂SO₄, 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**, Al₂O₃, alkaline.

5.2.8 **Tetrahydrofurane**, C₄H₈O, free of peroxides, free of water.

5.2.9 **Acetone**, (CH₃)₂CO.

5.2.10 **Hexane**, C₆H₁₄.

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(C₂H₅)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, CH₃OH.

5.2.13 Dichloromethane, CH₂Cl₂.

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 | MBTCI | C ₄ H ₉ SnCl ₃ | 1118-46-3 | 0,623 | A |
| 5.3.2 | Dibutyltin dichloride | DBTCI | (C ₄ H ₉) ₂ SnCl ₂ | 683-18-1 | 0,767 | A |
| 5.3.3 | Tributyltin chloride | TBTCI | (C ₄ H ₉) ₃ SnCl | 1461-22-9 | 0,891 | A |
| 5.3.4 | Tetrabutyltin | TTBT | (C ₄ H ₉) ₄ Sn | 1461-25-2 | 1,000 | A |
| 5.3.5 | Monooctyltin trichloride | MOTCI | C ₈ H ₁₇ SnCl ₃ | 3091-25-6 | 0,686 | A |
| 5.3.6 | Diocetyl tin dichloride | DOTCI | (C ₈ H ₁₇) ₂ SnCl ₂ | 3542-36-7 | 0,830 | A |
| 5.3.7 | Triphenyltin chloride | TPhTCI | (C ₆ H ₅) ₃ SnCl | 639-58-7 | 0,908 | A |
| 5.3.8 | Tricyclohexyltin chloride | TCyTCI | (C ₆ H ₁₁) ₃ SnCl | 3091-32-5 | 0,912 | A |
| Internal standards | | | | | | |
| 5.3.9 | Monoheptyltin trichloride | MHTCI | C ₇ H ₁₅ SnCl ₃ | 59344-47-7 | 0,672 | B |
| 5.3.10 | Diheptyltin dichloride | DHTCI | (C ₇ H ₁₅) ₂ SnCl ₂ | 74340-12-8 | 0,817 | B |
| 5.3.11 | Tripropyltin chloride | TPTCI | (C ₃ H ₇) ₃ SnCl | 2279-76-7 | 0,875 | B |
| 5.3.12 | Tetrapropyltin | TTPT | (C ₃ H ₇) ₄ Sn | 2176-98-9 | 1,000 | B |
| 5.3.13 | Tetrapentyltin | TTPeT | (C ₅ H ₁₁) ₄ Sn | 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 tetrahydrofuran (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 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.