INTERNATIONAL STANDARD

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17353

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Water quality — Determination of selected organotin compounds — Gas chromatographic method

Qualité de l'eau — Dosage de composés organostanniques sélectionnés — Méthode par chromatographie en phase gazeuse

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Foreword

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ISO 17353 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

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

This International Standard describes a gas-chromatographic/organotin specific determination of organotin compounds after derivatization with sodium tetraethyl borate and liquid/liquid extraction.

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water 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.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the identification and quantification of organotin compounds and/ or cations as mentioned in Table 1 in drinking water, surface water and wastewater containing not more than 2 g/l of suspended material. The working range is 10 ng/l to 1 000 ng/l. The respective anions are not determined.

This method can also be applicable to other compounds such as R = methyl, n = 1 to 2 and R = phenyl, n = 1 to 2. This International Standard is also applicable to marine water.

Table 1 — Organotin compounds and cations determined using this International Standard

$R_nSn^{(4-n)+}$	R	n	Name	Acronym
$BuSn^{3+}$	Butyl	1	Monobutyltin cation	MBT
Bu_2Sn^{2+}	Butyl	2	Dibutyltin cation	DBT
Bu_3Sn^+	Butyl	3	Tributyltin cation	TBT
Bu_4Sn	Butyl	4	Tetrabutyltin	TTBT
$OcSn^{3+}$	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

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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design on sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

3   Terms and definitions

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

3.1
organotin compound
OTC
substance with at least one Sn-C bond

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

3.2
organotin cation
OC
part of the organotin compound that contains all Sn-C bonds (and which is formally loaded)

NOTE   In this International Standard, the abbreviation OC is also used for the non-dissociated tetrasubstituted organotin. OC therefore comprises the cations MBT, DBT, TBT, TTBT, MOT, DOT, TCyT, and TPhT.

4   Principle

Organotin compounds in water are alkylated with sodium tetraethylborate and extracted with hexane. The extract can be cleaned with silica. After concentration, the tetrasubstituted OTC are separated by capillary gas chromatography and detected with a suitable system such as MS (mass spectrometry), FPD (flame photometric detection), AED (atomic emission detection). The concentration is determined by calibration for the total procedure using an internal standard mixture.

5   Interferences

The reagents sometimes contain impurities of organotin compounds. It is absolutely essential to verify the blanks (see A.4.6).

6   Reagents

Use reagents of highest purity.

6.1   Water, free of substances causing interference with this method and complying with ISO 3696:1987, Grade 1.

6.2   Nitric acid, $\rho(HNO_3) = 1{,}4$ g/ml.

6.3   Acetic acid, CH_3COOH, glacial.

6.4   Sodium hydroxide solution, $c(NaOH) = 1$ mol/l.

6.5   Sodium acetate, CH_3COONa, anhydrous.

6.6   **Sodium sulfate**, Na_2SO_4, anhydrous.

6.7   **Silica**, grain size 0,2 mm to 0,063 mm (200 mesh to 63 mesh).

6.8   **Tetrahydrofurane**, C_4H_8O, free of peroxides and water.

6.9   **Acetone**, (propanone) $(CH_3)_2CO$.

6.10   **Methanol**, CH_3OH.

6.11   **Hexane**, C_6H_{14}.

6.12   **Sodium tetraethylborate**, $NaB(C_2H_5)_4$.

6.13   **Monobutyltin trichloride**, MBTCl, $C_4H_9SnCl_3$.

6.14   **Dibutyltin dichloride**, DBTCl, $(C_4H_9)_2SnCl_2$.

6.15   **Tributyltin chloride**, TBTCl, $(C_4H_9)_3SnCl$.

6.16   **Tetrabutyltin**, TTBT, $(C_4H_9)_4Sn$.

6.17   **Monooctyltin trichloride**, MOTCl, $C_8H_{17}SnCl_3$.

6.18   **Dioctyltin dichloride**, DOTCl, $(C_8H_{17})_2SnCl_2$.

6.19   **Triphenyltin chloride**, TPhTCl, $(C_6H_5)_3SnCl$.

6.20   **Tricyclohexyltin chloride**, TCyTCl, $(C_6H_{11})_3SnCl$.

6.21   **Monoheptyltin trichloride**, MHTCl, $C_7H_{15}SnCl_3$; (internal standard).

6.22   **Diheptyltin dichloride**, DHTCl, $(C_7H_{15})_2SnCl_2$; (internal standard).

6.23   **Tripropyltin chloride**, TPTCl, $(C_3H_7)_3SnCl$; (internal standard).

6.24   **Tetrapropyltin**, TTPT, $(C_3H_7)_4Sn$; (internal standard).

6.25   **Multicomponent solutions and prepared reagents**.

Since stability of multicomponent standard solutions is a matter of concern, it is recommended to prepare several solutions containing solely organotin compounds with the same degree of alkylation/arylation (e.g. four solutions respectively for mono-, di-, tri-, and tetrasubstituted compounds). Stability can be assessed by the absence of degradation products.

6.25.1   Multicomponent-standard solution in methanol, **Stock solution A**.

For the preparation of 1 mg/ml of organotin cation stock solution, weigh, to the nearest 0,1 mg, the amounts of organotin compounds specified in Table 2 into a 100 ml volumetric flask. Dissolve these compounds in a small amount of methanol (6.10). Then make up to volume with methanol and mix well.

If stored at 4 °C in the dark, the solution is stable for up to one year.

6.25.2   Solution of the internal standards in methanol, Stock solution B.

Weigh, to the nearest 0,1 mg, into a 100 ml volumetric flask, about:

— 120 mg of diheptyltin dichloride,

— 150 mg of monoheptyltin trichloride,

— 115 mg of tripropyltin chloride, and

— 100 mg of tetrapropyltin

and dissolve in a small amount of methanol (6.10). Make up to volume with methanol and mix well.

For the preparation of exactly 1 mg/ml of OC as specified in Table 2, weigh exactly 122,4 mg of diheptyltin dichloride, 148,8 mg of monoheptyltin trichloride, 114,3 mg of tripropyltin chloride and 100 mg of tetrapropyltin into the 100 ml volumetric flask and prepare as described above.

The solution is stable for three months when stored in the dark at 4 °C.

Table 2 — Amounts of organotin compounds and weighing factors for recalculation to organotin cations (for 100 % purity of the substances)

Substance	Weighing factor[a]	Mass[b] mg	Solution[c]
Monobutyltin trichloride	0,623	160,5	A
Dibutyltin dichloride	0,767	130,4	A
Tributyltin chloride	0,891	112,2	A
Tetrabutyltin	1,000	100,0	A
Monooctyltin trichloride	0,686	145,8	A
Dioctyltin dichloride	0,830	120,5	A
Triphenyltin chloride	0,908	110,1	A
Tricyclohexyltin chloride	0,912	109,6	A
Monoheptyltin trichloride	0,672	148,8	B
Diheptyltin dichloride	0,817	122,4	B
Tripropyltin chloride	0,875	114,3	B
Tetrapropyltin	1,000	100,0	B

[a]   Weighing factor = molar mass (OC)/molar mass (OTC).

[b]   If the mass weighed of the compound is different from that given in this table, use the weighing factor to calculate the actual concentration of the OTC.

[c]   A for multicomponent standard solution in methanol.

   B for the solution of the internal standards in methanol.

6.25.3   Multicomponent spiking solutions for reference solutions.

Prepare the spiking solutions as specified in Table 3 using pipettes. Pipette the respective starting volume specified in Table 3 of the (stock) solution into a 100 ml volumetric flask. Make up to volume with methanol and mix well. The final mass concentration of the resulting spiking solution shall be between 10 ng/ml and 1 000 ng/ml of organotin cations in methanol. Dilutions steps greater than 1:100 are not allowed.

Table 3 — Example for the dilution series for preparation of the spiked solutions

Starting solution	Concentration of OC in starting solution ng/ml	Volume of starting solution ml	Final volume ml	Final concentration of OC ng/ml	Designation of final solution
A	1 000 000	10	100	100 000	A1
A1	100 000	10	100	10 000	A2
A1	100 000	15	100	15 000	A3
A2	10 000	20	50	4 000	A4
A2	10 000	5	100	500	A5
A2 + A3	10 000/15 000	1 + 6	100	1 000	AH6
A2 + A3	10 000/15 000	1 + 5	100	850	AH5
A2 + A3	10 000/15 000	1 + 4	100	700	AH4
A2 + A3	10 000/15 000	1 + 3	100	550	AH3
A2 + A3	10 000/15 000	1 + 2	100	400	AH2
A2 + A3	10 000/15 000	1 + 1	100	250	AH1
A4	4 000	6	100	240	AM6
A4	4 000	5	100	200	AM5
A4	4 000	4	100	160	AM4
A4	4 000	3	100	120	AM3
A4	4 000	2	100	80	AM2
A4	4 000	1	100	40	AM1
A5	500	7	100	35	AL6
A5	500	6	100	30	AL5
A5	500	5	100	25	AL4
A5	500	4	100	20	AL3
A5	500	3	100	15	AL2
A5	500	2	100	10	AL1
Solutions AH1 to AH6 are used for calibration AH (higher working range).					
Solutions AM1 to AM6 are used for calibration AM (medium working range).					
Solutions AL1 to AL6 are used for calibration AL (lower working range).					
Solutions AH1 to AH6 are prepared from two Stock solutions A2 and A3.					

6.25.4 Spiking solutions containing internal standards.

Dilution steps greater than 1:100 are not allowed.

Pipette 1 ml of Stock solution B (see Table 4) into a 100 ml volumetric flask. Make up to volume with methanol (6.10) and mix well (Solution B1).

Pipette 1 ml of Solution B1 into a 100 ml volumetric flask. Make up to volume with methanol and mix well (Solution B2).

Use Solution B2 for all samples. The mass concentration of Solution B2 is about 100 ng/ml of organotin cation in methanol, depending on the original mass weighed according to 6.25.1 (Table 2).

**Table 4 — Example of a dilution series for the preparation
of the spiking solutions of the internal standards**

Starting solution	Concentration of OC in starting solution	Volume of starting solution	Final volume	Final concentration of OC	Designation of final solution
	ng/ml	ml	ml	ng/ml	
B	1 000 000	1	100	10 000	B1
B1	10 000	1	100	100	B2

6.25.5   Blank solution, consisting of 1 l of water (6.1) put into a 1 000 ml sampling bottle.

6.25.6   Reference solutions (aqueous multicomponent reference solution).

For each working range, prepare at least six reference solutions, distributed equidistantly over the chosen working range. The working range should not exceed one order of magnitude.

Add 1 000 ml of water (6.1) to each of six 1 000 ml sampling bottles. Under vigorous stirring, dip the tip of the pipette below the surface of the water and add 1 ml of the respective spiking solution (AH1 to AH6, AM1 to AM6, or AL1 to AL6, see Table 3) ensuring that the spiking solution is distributed evenly in the water. Stir for an additional 20 min.

Depending on the working range, the reference solutions shall contain the following mass concentration of OC in water:

— higher range: 1 000 ng/l, 850 ng/l, 700 ng/l, 550 ng/l, 400 ng/l and 250 ng/l;

— medium range: 240 ng/l, 200 ng/l, 160 ng/l, 120 ng/l, 80 ng/l and 40 ng/l; or

— lower range: 35 ng/l, 30 ng/l, 25 ng/l, 20 ng/l, 15 ng/l, and 10 ng/l.

6.25.7   Acetate buffer solution.

Dissolve about 1 mol of sodium acetate (equal to 82 g of anhydrous sodium acetate) (6.5) in 500 ml of water (6.1) into a 1 000 ml volumetric flask. Add sufficient glacial acetic acid (6.3) to reach a pH of 4,5. Make up to volume with water (6.1) and mix well.

6.25.8   Derivatization agent A (2 % mass concentration in water).

Weigh about 200 mg of sodium tetraethylborate (6.12) into a 10 ml volumetric flask and make up to volume with water (6.1).

This solution is not stable, and should be used immediately.

6.25.9   Derivatization agent B (20 % mass concentration in tetrahydrofurane).

Weigh about 2 g of sodium tetraethylborate (6.12) into a 10 ml volumetric flask and make up to volume with tetrahydrofurane (6.8).

This solution is stable for about three months if stored under an inert gas blanket. Its use is recommended for large series of samples.

6.25.10   Drying agent.

Place about 250 g to 300 g of powdered sodium sulfate (6.6) onto a quartz plate and dry for at least 4 h at a temperature of 180 °C. Add the dried sodium sulfate to a wide-necked bottle and allow to cool to room temperature in a desiccator. Remove the bottle from the desiccator and close tightly.

6.25.11   Silica for the clean-up column.

It is recommended to prepare batches of no more than 120 g per batch.

Heat silica (6.7) for at least 12 h at (500 ± 20) °C on a quartz plate in a muffle furnace (the temperature should not exceed 520 °C).

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

Check the homogeneity and the moisture content of the prepared silica by determining the moisture content of different portions of the prepared silica. The moisture content shall not vary by more than 0,1 %.

6.25.12   Clean-up column.

Ensure that the clean-up column is filled homogeneously, e.g. by using a hexane slurry of silica.

Add about 5 g of silica (6.25.11) to the column (see 7.6), and add about 3 g of drying agent (6.25.10). Rinse with 30 ml of hexane (6.11) and let the solvent pass through the column to the level of the upper surface of the column bed.

The column is then ready for use.

Commercially available pre-packed columns may be used.

6.25.13   Eluent for cleaning extract, acetone in hexane.

To ensure quantitative elution of all organotin from the clean-up column, use a mixture of *n*-hexane and acetone. Using an appropriate standard solution prior to applying the clean-up procedure, determine the percentage of acetone to be added to the *n*-hexane and the volume of the resulting mixture necessary for complete elution. Add the appropriate volume of acetone (6.9) to a 100 ml volumetric flask. Make up to volume with hexane (6.11) and mix well.

7   Apparatus

The glassware should be free of contamination (see A.4.5).

7.1   Volumetric flasks, of 10 ml, 50 ml, 100 ml and 1 000 ml capacities.

7.2   Pipettes, of 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 10 ml, 15 ml, 20 ml and 50 ml capacities.

7.3   Microlitre syringes, of 10 µl and 250 µl capacities.

7.4   Sampling bottle, of 1 000 ml capacity, made of amber glass, with straight shoulders and fitted with a glass stopper.

7.5   Separating funnel, 1 000 ml.

7.6   Glass column for clean up, for example of 15 cm length, 1 cm inner diameter, with a frit, but without a cock stop.

7.7   Beaker, of 150 ml and 5 l capacities.

7.8   Shaker.

7.9   Magnetic stirrer, for example with a stirring rate of 1 200 min^{-1}, and a magnetic bar, 60 mm × 4,5 mm, coated with polytetrafluoroethene.

7.10 **Round bottomed flasks**, fitted with a ground glass joint, of 100 ml and 250 ml capacities.

7.11 **Concentration apparatus**, for example a rotary evaporator.

7.12 **Muffle furnace**, capable of maintaining a temperature of 500 °C $\pm$ 20 °C.

7.13 **Drying oven**, capable of heating up to 180 °C.

7.14 **Quartz plate**, having a 12 cm diameter.

7.15 **Desiccator**.

7.16 **Separator**, for example a Schultze separator, see Figure 1.

7.17 **Gas chromatograph**, with suitable detector device (see 7.19).

7.18 **Injector**, split or splitless, preferably with automated sampling device.

7.19 **Detectors**, equipped with a suitable data processing system for acquisition and data evaluation.

7.19.1 **Flame photometric detector** (FPD), equipped with a cut-off filter of 590 nm or an interference filter of 610 nm or pulsed flame photometric detector equipped with a large bandpass filter working at 610 nm or 390 nm with time-selective acquisition.

7.19.2 **Mass spectrometer for electron impact (EI) mode**, with sufficient sensitivity.

7.19.3 **Atomic emission detector**.

8   Procedure

8.1   Sampling and sample storage

Carry out sampling in accordance with ISO 5667-1, ISO 5667-2, and ISO 5667-3.

For sampling of drinking water, surface water and wastewater, use 1 000 ml sampling bottles (7.4). Carry out all the following steps including the extraction (see 8.2.1) in the sampling bottle.

Mark a 1 000 ml sampling bottle with a 1 l mark. Fill the bottle to the mark. Keep cool and in the dark and pretreat within 24 h (see 8.2).

It is also appropriate to weigh prior to and after filling.

8.2   Derivatization and extraction

8.2.1   General

In cases where the concentration of organotin compounds in surface and wastewater exceeds the working range, the samples need the following further treatment.

Dilute surface water and wastewater samples with water (6.1) to meet the working range (10 ng/l to 1 000 ng/l). If necessary, carry out a screening procedure in order to determine the approximate concentration of organotin in the sample. Mark a 1 l sampling bottle with a 1 l mark. Add the appropriate amount of surface water or wastewater, respectively. Make up with water to the mark. Note the surface water and wastewater volume, respectively, used for analysis in order to calculate the final result.

Dimensions in millimetres (approximate)
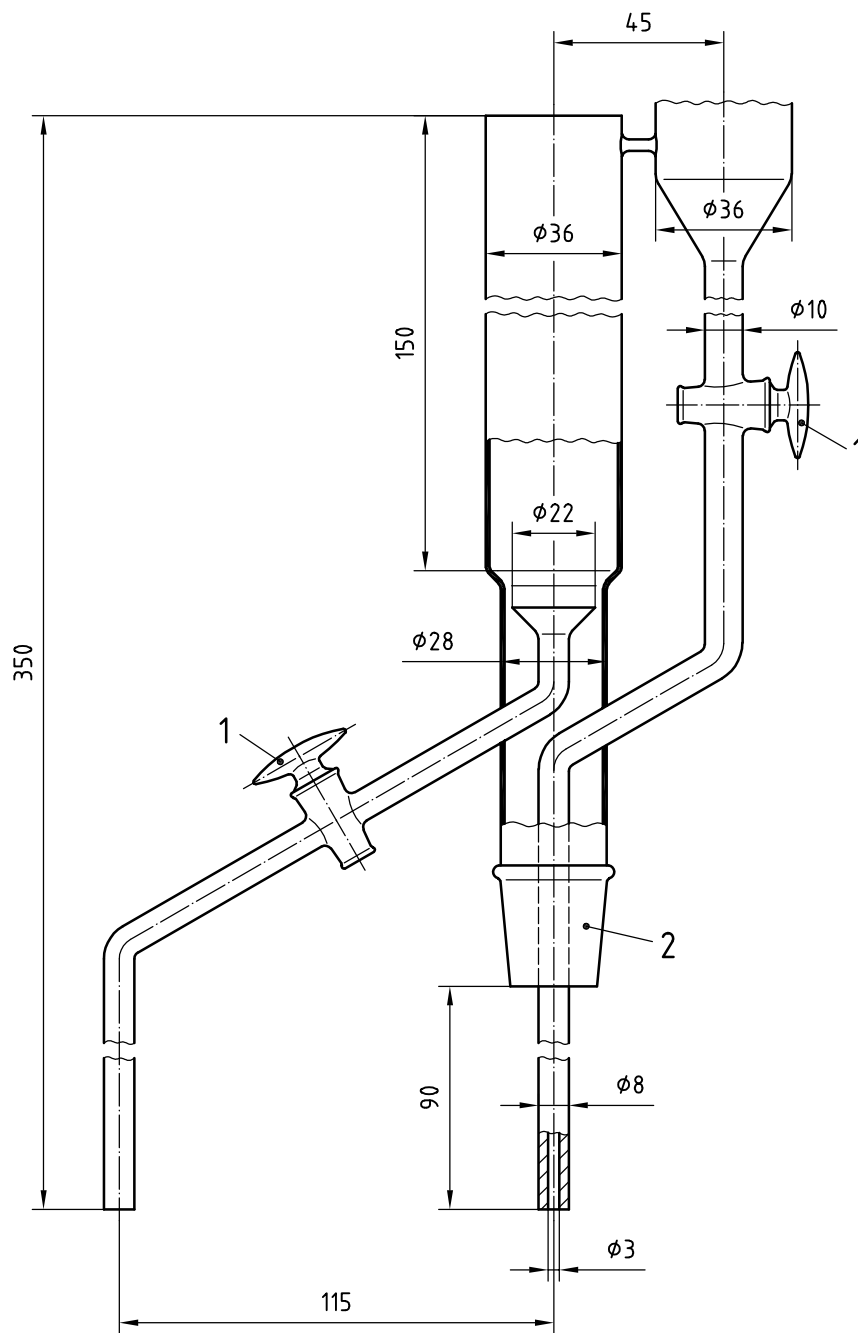
Key

1 stopcock

2 ground glass joint

Figure 1 — Schultze separator

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Pretreat samples of drinking water, surface water and wastewater and aqueous reference samples (6.25.6) and blanks (6.25.5) as follows.

Add 10 ml of acetate buffer solution (6.25.7) and shake for about 1 min. Check the pH and, if necessary, adjust to pH 4,5 using glacial acetic acid (6.3) or sodium hydroxide solution (6.4).

While stirring the samples using a magnetic stirrer (about 1 200 min^{-1}) with a bar (7.9), dip the tip of the pipette below the surface of the water sample and add 1 ml of the spiking Solution B2 (6.25.4) to it. Stir for a further 20 min.

The volume of the sample for screening may be reduced; in which case the added volumes will need to be reduced to meet the same analysis conditions.

It is recommended to carry out analyses in duplicate.

8.2.2 Derivatization and extraction procedure

To the buffered solution (8.2.1), add 5 ml of the Derivatization agent A (6.25.8) or 0,5 ml of the Derivatization agent B (6.25.9). Add 20 ml of hexane (6.11) and shake for about 1 min. Check the pH and, if necessary, adjust to pH 4.5 using glacial acetic acid (6.3) or sodium hydroxide solution (6.4). Stir for 20 min or shake vigorously, ensure that the phases are well mixed.

Allow the phases to separate using a separator (7.16) by adding water (6.1). Transfer the hexane layer to a 100 ml flask and dry with 2 g of sodium sulfate (6.6).

Reduce the volume of the organic phase to about 1 ml using a suitable apparatus (7.11), but take care to avoid reduction to dryness.

For evaporation of the solvent to the final volume of 1 ml, the extract may be transferred to a smaller flask.

When using a rotary evaporator, it is recommended to adjust the water bath to about 40 °C to 50 °C and to allow for a constant pressure of about 30 kPa to 45 kPa.

It may be advisable to check the efficiency of the ethylate solutions. This may be done, for example by adding triethyltin to the standard solutions containing mono-, di- and trisubstituted tin compounds and by adding tetraethyltin to the standard solutions containing the tetrasubstituted tin. By this procedure, the derivatization yield may be determined for (at least) one compound and a proper limit value may be set.

8.3 Clean up of the extract

In the case of low polluted samples, the clean-up step may be omitted. Treat the reference solutions in the same way as the samples.

Transfer the concentrated extract to the clean-up column (6.25.12). After the extract has reached the silica surface, add cautiously 1 ml of eluent (6.25.13) onto the column. After penetration of the eluent, elute with the appropriate amount of eluent (6.25.13), and collect the eluate in a 100 ml round-bottomed flask.

Reduce the volume of the eluate to about 1 ml, using a suitable apparatus (7.11), but take care to avoid reduction to dryness.

For evaporation of the solvent to the final volume of 1 ml, the extract may be transferred to a smaller flask.

When using a rotary evaporator, it is recommended to adjust the water bath to about 40 °C to 50 °C and to allow for a constant pressure of about 30 kPa to 45 kPa.

It may be advisable to check the efficiency of the ethylate solutions. This may be done, for example by adding triethyltin to the standard solutions containing mono-, di- and trisubstituted tin compounds and by adding tetraethyltin to the standard solutions containing the tetrasubstituted tin. By this procedure, the derivatization yield may be determined for (at least) one compound and a proper limit value may be set.

8.4   Measurement

Optimize the instrument according to the manufacturer's instructions. Quantify the gas chromatographic signals either as peak areas or as peak heights. In the case of non-continuous detection (e.g. mass spectrometry), the evaluation using peak areas is recommended.

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

The injection sequence is as follows:

⎯   hexane;

⎯   blank extract;

⎯   extracts of the reference solutions in ascending mass concentration (calibration solutions);

⎯   hexane;

⎯   sample extracts.

For procedure control, it is advantageous to analyse a blank extract and a reference solution extract after about every six injections (recalibration). If the control value for the blank does not match with the original blank value or the recalibration does not allow values within the precision data, repeat the last series of measurements. If necessary, check the procedure.

9   Identification

9.1   Minimum requirement for identification

Independent from the detection system, identify the analytes by comparison of the retention times for samples and references. Minimum requirement for identification are retention times within $\pm$ 0,05 min, respectively relative retention times within $\pm$ 0,2 % over the total run of a chromatogram.

9.2   Identity check

9.2.1   General

The identity is checked in several steps.

If the retention times or the relative retention times for samples and references, respectively, from one capillary column are in agreement, the identity in respect to a specific detection is probable.

NOTE   In this International Standard only specific detections are described.

The identity is regarded as confirmed, if on a second capillary column of different polarity, the retention times or the relative retention times, respectively, for samples and references are also in agreement. Furthermore, the identity is confirmed if the retention times or the relative retention times, respectively, from one column matches sufficiently (see 9.2.2) with the mass spectrum of a reference substance, or, if in case of single ion monitoring, the characteristic masses of the isotope clusters occur and the following criteria are met.

9.2.2   Special criteria for the mass spectrometric identification

The ratios of peak areas of the respective isotope clusters of a compound may be mass-portion dependent and may differ due to the parameter setting and type of the mass spectrometric system used. From the chromatograms of the extracts of the reference solutions and the sample extracts, the peak areas of the chosen four masses from Table 6 (A_{Mh1}, A_{Mh2}, A_{Ml1} and A_{Ml2}).

The ratios F_h (higher cluster) and F_l (lower cluster) are determined.

$$F_h = \frac{A_{Mh1}}{A_{Mh2}} \qquad (1)$$

$$F_l = \frac{A_{Ml1}}{A_{Ml2}} \qquad (2)$$

where

F_h is the ratio of the peak areas of the higher isotope cluster (subscript h) in the chromatograms;

F_l is the ratio of the peak areas of the lower isotope cluster (subscript l) in the chromatograms;

A_{Mh1} is the peak area of the higher mass (subscript 1) in the higher isotope cluster (subscript h);

A_{Mh2} is the peak area of the lower mass (subscript 2) in the higher isotope cluster (subscript h);

A_{Ml1} is the peak area of the higher mass (subscript 1) in the lower isotope cluster (subscript l);

A_{Ml2} is the peak area of the lower mass (subscript 2) in the lower isotope cluster (subscript l).

Table 5 — Characteristic masses for identification and evaluation

Substance	Cluster a1 / a2	Cluster b1 / b2	Cluster c1 / c2
Monobutyltriethyltin	235,1 / 233,0	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
Triphenylmonoethyltin	351,0 / 349,0	197,0 / 195,0	—
Tricyclohexylmonoethyltin	233,0 / 231,0	315,1 / 313,1	369,2 / 367,2
Monoheptyltriethyltin	277,1 / 275,1	179,0 / 177,0	151,0 / 149,0
Diheptyldiethyltin	347,2 / 345,2	249,1 / 247,1	151,0 / 149,0
Tripropylmonoethyltin	249,1 / 247,1	235,1 / 233,0	193,0 / 191,0
Tetrapropyltin	249,1 / 247,1	165,0 / 163,0	207,0 / 205,0
If two clusters of masses (from a, b, c) have been chosen, use the following nomenclature: — Mhn = cluster of the higher masses, n = 1st or 2nd mass in the cluster; — Mln = cluster of the lower masses, n = 1st or 2nd mass in the cluster.			

Assuming that the cluster ions in the chromatograms of the extracts from the reference solutions are not affected by interferences, the peak area ratios are calculated (F_{hc} and F_{lc}) and compared with the respective peak area ratios (F_{hs} and F_{ls}) from the chromatograms of the sample extracts. The identity of an analyte is confirmed if one of the following criteria (3), (4), or (5) is met:

$$\frac{F_{hc}}{F_{hs}} = 1,00 \pm a \quad \text{and} \quad \frac{F_{lc}}{F_{ls}} = 1,00 \pm b \tag{3}$$

$$\frac{F_{hc}}{F_{hs}} = 1,00 \pm c \quad \text{and} \quad \frac{F_{lc}}{F_{ls}} = 1,00 \pm b \tag{4}$$

$$\frac{F_{hc}}{F_{hs}} = 1,00 \pm a \quad \text{and} \quad \frac{F_{lc}}{F_{ls}} = 1,00 \pm d \tag{5}$$

where

F_{hc}, F_{lc} is the peak area ratio of the higher (subscript h), respectively lower (subscript l), isotope cluster in the chromatograms of the reference solutions (subscript c);

F_{hs}, F_{ls} is the peak area ratio of the higher (subscript h) , respectively lower (subscript l) isotope cluster in the chromatograms of the sample extracts (subscript s);

a, b, c, d are the mass portion and matrix dependent tolerances of the peak area ratios (see Table 6).

If criterion (3) is fulfilled, both isotope clusters are regarded as not undergoing interference. If criterion (4) is fulfilled, the lower cluster is regarded as not undergoing interference. If criterion (5) is fulfilled, the higher cluster is regarded as not undergoing interference. In other cases, both clusters undergo interference and the identity is not confirmed.

Calculate the apparatus and possibly mass portion dependent ratios (F_{hc} and F_{lc}) by injection of the reference solution extract which is the nearest to the expected mass ratio of the sample.

Table 6 — Mass portion and matrix dependent tolerances (a, b, c, d) of the peak area ratios

Tolerances	Working range		
	10 ng/l to 35 ng/l	40 ng/l to 240 ng/l	250 ng/l to 1 000 ng/l
a	0,3	0,1	0,05
b	0,3	0,1	0,05
c	0,5	0,25	0,15
d	0,5	0,25	0,15

10 Calibration

Calibrate with the internal reference standard over the total procedure using a calibration curve. To establish a calibration curve, measure the extracts of at least six reference solutions (6.25.6). For quantification of the monoalkylated compounds, use monoheptyltin trichloride (MHTCl) as internal standard, for quantification of dialkylated compounds, use diheptyltin dichloride (DHTCl) as internal standard, for quantification of trialkylated compounds, use tripropyltin chloride (TPTCl) as internal standard, and for the quantification of the tetralkylated compounds, use tetrapropyltin (TTPT) as internal standard.

The specific, intralaboratory relative responses, related to an internal reference standard (subscript I), e.g. diheptyltin (DHT) are determined using three additional internal standards (subscript k) of different degrees of alkylation. They are taken from the extract chromatograms of the reference solution. The mean is compared to the relative response calculated from the chromatograms of sample extracts.

If diheptyltin (DHT) is chosen as internal reference standard (subscript I), use subscript k subsequently for each of the other three internal standards monoheptyltin (MHT); tripropyltin (TPT) and tetrapropyltin (TTPT) in Equation (6).

Calculate the relative response as follows:

$$R_{f,Ikcj} = \frac{A_{Icj} \times m_{kcj}}{A_{kcj} \times m_{Icj}}$$ (6)

where

$R_{f,Ikcj}$ is the relative response of the internal standard k, in relation to the internal reference standard I in the calibration c, mass portion step j;

A_{Icj} is the peak area of the internal reference standard I in the calibration c, mass portion step j;

m_{kcj} is the mass, expressed in nanograms, of the internal standard k in the calibration c, mass portion step j;

A_{kcj} is the peak area of the internal standard k in the calibration c, mass portion step j;

m_{Icj} is the mass, expressed in nanograms, of the internal reference standard I in the calibration c, mass portion step j;

Derive the typical, specific intralaboratory relative response for the degree of alkylation by calculation of the mean value from all mass portion steps:

$$R_{f,Ikc} = \frac{1}{j} \sum_{j=1}^{j} R_{f,Ikcj}$$ (7)

where

$R_{f,Ikc}$ is the mean relative response of the internal standard k, related to the internal reference standard I in the calibration c over all mass portion steps j;

$R_{f,ikcj}$ is the relative response of the internal standard k related to the internal reference standard I in the calibration c for mass portion step j.

Calculate the standard deviation of the typical, specific intralaboratory relative response for the degree of alkylation as follows:

$$s_{R_{f,Ikc}} = \sqrt{\frac{\sum(R_{f,Ikc} - R_{f,Ikcj})^2}{j - 1}}$$ (8)

where

$s_{R_{f,Ikc}}$ is the standard deviation of the mean relative response of the internal standard k related to the internal reference standard I in the calibration c over all mass portion steps j;

$R_{f,Ikc}$ is the mean relative response of the internal standards k related to the internal reference standard I in the calibration c over all mass portion steps j;

$R_{f,Ikcj}$ is the relative response of the internal standard k related to the internal reference standard I in the calibration c, of the mass portion step j;

j is the mass portion step.

and successively the relative standard deviation S_{rel}:

$$S_{rel} = \frac{s_{R_{f,Ikc}}}{R_{f,Ikc}} \times 100 \qquad (9)$$

where

S_{rel} is the relative standard deviation, expressed in percent, of the mean relative response of the internal standard k related to the internal reference standard I in the calibration c over all mass portion steps j;

$s_{R_{f,Ikc}}$ is the standard deviation of the mean relative response of the internal standard k related to the internal standard I in the calibration c over all mass portion steps j;

$R_{f,Ikc}$ is the mean relative response of the internal standard k related to the internal reference standard I in the calibration c over all mass portion steps j.

The relative standard deviation, S_{rel}, shall not exceed 10 %.

When using a mass spectrometer, the detection may be based either on the peak area for the mass of highest intensity (base peak) from a cluster without interference (9.2.2; preferably the higher cluster) of OTC i or on the sum of the peak areas for this cluster ($A_{Mh1} + A_{Mh2}$ respectively $A_{Ml1} + A_{Ml2}$). Derive one of these sums from the chromatograms by integration of the peak areas A of the OTC i and for the internal reference standard I and for each OTC i. Calculate a calibration curve according to Equation (7) for each working range.

$$y = a_1 x + a_0 \qquad (10)$$

where

y is the mass of OTC i in a calibration of one working range;

a_1 is the slope of calibration curve;

x is the value calculated from peak area and mass of internal reference standard (subscript I) and peak area of OTC i;

a_0 is the intercept of calibration curve.

Calculate the coefficients of Equation (10) according to Equations (11) and (12).

$$a_1 = \frac{\sum (x_{ij} - \bar{x}_i)(y_{ij} - \bar{y}_i)}{\sum (x_{ij} - \bar{x}_i)^2} \qquad (11)$$

where

$$\bar{x}_i = \frac{1}{j} \sum_{j=1}^{j} x_{ij};$$

$$\bar{y}_i = \frac{1}{j} \sum_{j=1}^{j} y_{ij};$$

$$x_{ij} = \frac{A_{icj}}{A_{Icj}} \times m_{Ic}$$

$$a_0 = \bar{y}_i - a_1 \bar{x}_i \tag{12}$$

where

a_1 is the slope of calibration curve;

a_0 is the intercept of calibration curve;

y_{ij} is the mass of OTC i in a calibration c of one working range, mass portion step j $(= m_{icj})$;

x_{ij} is the value calculated from peak area and mass of internal reference standard (subscript I) and peak area of OTC i in a calibration c of one working range, for mass portion step j;

A_{Icj} is the peak area of internal reference standard I in a calibration c of one working range, for mass portion step j;

A_{icj} is the peak area of OC i in a calibration c of one working range, mass portion step j;

m_{Ic} is the mass, expressed in nanograms, of internal reference standard I in a calibration c of one working range;

$\bar{x}_i$ is the mean of all x_{ij} in a calibration of one working range for one OTC i;

$\bar{y}_i$ is the mean of all y_{ij} in a calibration of one working range for one OTC i.

Derive from the chromatograms by integration of the peak areas A of the OTC i and for the internal reference standard I and for each OTC i the mass portion dependant response factors $R_{f,icj}$.

$$R_{f,icj} = \frac{A_{Icj} \times m_{ic}}{A_{icj} \times m_{Ic}} \tag{13}$$

where

$R_{f,icj}$ is the response factor for the OC i during calibration c, mass portion step j;

A_{Icj} is the peak area for the internal reference standard I in the calibration c, mass portion step j;

m_{ic} is the mass, expressed in nanograms, of the OC i in the calibration c;

A_{icj} is the peak area for the OTC i in the calibration c, for mass portion step j;

m_{Ic} is the mass, expressed in nanograms, of the internal reference standard I in the calibration c.

11 Calculation

11.1 Mass concentrations

Calculate from the chromatograms of the calibration solutions the specific, intralaboratory relative response for the degree of alkylation [Equation (7)] of the internal standards related to the internal reference standard, e.g. diheptyltin (DHT) and its response and the respective standard deviation [Equation (8)]. Calculate the relative

response of the internal standards related to the reference standard [Equation (6)] from the chromatograms of the sample extracts and compare it to the specific, intralaboratory relative response for the degree of alkylation. Depending on the degree of alkylation and the sample, state the relative response in the calibration including the respective standard deviation and the relative response in the test report.

Calculate the mass m_i of OTC i in the sample extract using Equation (14):

$$m_i = a_1 \times \frac{A_i m_I}{A_I} + a_0 \tag{14}$$

where

m_i is the mass, expressed in nanograms, of the OC i in the pretreated sample extract;

A_i is the peak area of OTC i in the sample measurement;

m_I is the mass, expressed in nanograms, of the internal reference standard I in the pretreated extract as OC;

A_I is the peak area for the internal reference standard I in the sample measurement;

a_1, a_0 are the coefficients calculated from Equation (10).

If the OC i is to be quantified by the "adjusted-single-reference-calibration", use as a basis the response factor $R_{f,icj}$ for the mass portion step j, which is nearest to the peak area A_{ic} for the measured value A_i.

Calculate the mass m_i of the OC i in the pretreated sample extract according to Equation (15):

$$m_i = \frac{R_{f,icj} \times A_i \times m_I}{A_I} \tag{15}$$

where

m_i is the mass, expressed in nanograms, of the OC i in the pretreated sample extract;

$R_{f,icj}$ is the mean response factor OC i at the mass portion step j;

A_i is the peak area OTC i in the sample measurement;

m_I is the mass, expressed in nanograms, of the internal reference standard I in the pretreated extract as OC;

A_I is the peak area for the internal reference standard I in the sample measurement.

The mass concentration w_i of the OC i in the water sample is calculated according to Equation (16).

$$\rho_i = \frac{m_i}{V_s} \tag{16}$$

where

ρ_i is the mass concentration, expressed in nanograms per litre, for the OC i in the water sample;

m_i is the mass, expressed in nanograms, of the OC i in the pretreated sample portion;

V_s is the volume, expressed in litres (8.1), of the water sample used for analysis.

11.2 Expression of results

Report the mass concentration in nanograms of OC per litre (ng/l) without decimals and to two significant digits.

Report the mass concentration higher than 1 000 ng/l in micrograms of OC per litre (μg/l) to two significant digits.

12 Precision

Precision data from an interlaboratory study are given in Annex B.

13 Test report

The test report shall contain the following information:

a)   reference to this International Standard (ISO 17353:2004);

b)   identity of the water sample;

c)   information on sampling and sample pretreatment (transport and storage);

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

e)   procedure during identification and quantification of the single components (statement of calibration and calculation mode);

f)   statement of results as specified in 11.2;

g)   any deviation from the procedure and statement of all circumstances that may have influenced the result;

h)   relative response from the calibration and the sample solutions.

Annex A
(informative)

Gas chromatographic conditions

A.1 Examples of common gas chromatographic conditions

A.1.1 Example 1

Injection conditions:	split/splitless
Injection temperature:	250 °C
Carrier:	helium
	flowrate: 0,61 ml/min at 60 °C
	flowrate: 0,42 ml/min at 160 °C
Capillary column:	length 25 m
	0,22 mm inner diameter
	film thickness 0,11 µm
	phase OV1[1] (methyl silicone)
Oven temperature programme:	60 °C → 4 °C/min → 240 °C → 6 °C/min → 270 °C

A.1.2 Example 2

Injection conditions:	cold injection system
	120 s splitless
	split 30 ml/min
Injection temperature programme:	60 °C → 10 °C/s → 300 °C
Carrier:	helium
	pre-pressure 70 kPa
	flowrate about 1 ml/min
Capillary column:	length 25 m
	0,25 mm inner diameter
	film thickness 0,4 µm
	phase CP-Sil 8 CB[1]
Oven temperature programme:	60 °C → 15 °C/min → 260 °C → 16,7 min → 260 °C

A.1.3 Example 3

Injection conditions:	cold injection system, split 4 ml/min
Injection temperature programme:	50 °C → 10 °C/s → 290 °C
Carrier:	helium
	flowrate 1 ml/min
Capillary column:	length 25 m
	0,25 mm inner diameter
	film thickness 0,33 µm
	phase HP-1[1]
Oven temperature programme:	140 °C → 5 °C/min → 220 °C → 11 °C/min → 290 °C → 2 min → 290 °C

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1) OV1, CP-Sil 8 CB and HP-1 are examples of suitable phases available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this/these products. Equivalent products may be used if they can be shown to lead to the same results.

A.1.4 Example 4

Injection conditions:	large volume system, 25 µl
Injection temperature programme:	15 °C → 2 °C/s → 25 °C → 12 °C/s → 260 °C held for 60 s
Carrier:	helium
	column head pressure 130 kPa
Capillary column:	length 25 m
	0,32 mm inner diameter
	film thickness 0,17 µm
	phase HP-1[2)]
Oven temperature programme:	45 °C → held for 2 min → 20 °C/min → 280 °C → held for 1 min

A.2 Examples of common detection conditions

A.2.1 Flame photometric detection, FPD

A.2.1.1 Continuous flame

Detector temperature:	180 °C, detector base 300 °C
Gases:	flame gases: H_2, synthetic air
	carrier gas: for example N_2, He
Filter:	cut-off filter 590 nm or interference filter 610 nm

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

Where interferences are suspected, use filters. Cut-off filters shall cut the range below 590 nm. Interference filters should be transmissible in the range (610 ± 5) nm.

A.2.1.2 Pulsed flame

Detector temperature:	350 °C, detector base 300 °C
Gases:	flame gases: H_2, synthetic air
	carrier gas: for example N_2, He
Filter:	large bandpass filter working at 610 nm or 390 nm with a time selective acquisition
Combustor:	3 mm

A.2.2 Mass spectrometric detection, MSD

Transfer line:	290 °C
Electron impact:	70 eV
Electron multiplier:	2 000 V
Selected ion monitoring	

The isotope cluster of the organotin compounds is formed by 10 natural tin isotopes (see Table A.1).

In case of analysis with GC/MS, each fragment ion containing tin will be split in an isotope cluster referring to tin. Choose two of the most intensive non-interfered fragment ions (9.2.1) with preferably high mass. Ensure to record two of the most intensive cluster ions of each fragment (see Table 5).

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2)   HP-1 is an example of a suitable phase available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this/these products. Equivalent products may be used if they can be shown to lead to the same results.

Table A.1 — Masses and abundance of natural tin isotopes

Mass	Abundance	Relative abundance
amu	%	%
112	0,95	2,88
114	0,65	1,97
115	0,34	1,03
116 [a]	14,24	43,19
117	7,57	22,96
118 [a]	24,01	72,82
119	8,58	26,02
120 [a]	32,97	100,00
122	4,71	14,29
124	5,98	18,14
NOTE See Reference [1].		
[a] These isotopes are preferred for mass spectrometric detection.		

A.2.3 Atomic emission spectrometric detection, AES

Transfer line:	280 °C
Cavity temperature:	280 °C
He flowrate:	240 ml/min (measured at the cavity vent)
Wavelength:	303,419 nm (270,651 nm)
H_2	350 kPa
O_2	500 kPa

A.2.4 Atomic absorption spectrometric detection AAS

Although not used in the interlaboratory trial, AAS has been successfully applied to the analysis of organotin compounds. Typical instrument settings are:

Transfer line:	250 °C
Quartz furnace:	constant temperature > 650 °C, e.g. 750 °C
Gases:	H_2, flowrate 145 ml/min air, flowrate 15 ml/min
Excitation:	Sn-lamp, for example electrodeless discharge lamp (EDL) or hollow cathode lamp (HCL)
Wavelength:	286,3 nm (224,6 nm, 235,5 nm)
Slit:	0,7 nm

A.3 Examples of analyses

A.3.1 Identity check (see 9.2) and calculation (see Clause 11)

Table A.2 — Identity check (ascertained identity with mass spectrometry)

Extract analysed	Measured peak areas in arbitrary units			
	A_{Mh1}	A_{Mh2}	A_{Ml1}	A_{Ml2}
Calibration extract 1 000 ng/l	2 825	1 965	2 054	1 436
Calibration extract 550 ng/l	565	393	411	287
Sample extract 1st sample	1 392	962	998	728
Sample extract 2nd sample	1 392	1 089	998	728
Sample extract 3rd sample	1 392	962	1 193	728
Sample extract 4th sample	1 531	817	1 098	622

When calculating according to the method of the "adjusted-single-reference-calibration" use data of calibration extract 550 ng/l (see Table A.3).

**Table A.3 — Calculation of peak area ratios for calibration extract**

Extract analysed	F_{hc}	F_{lc}
Calibration extract 550 ng/l	1,44	1,43

The identity of the samples is checked by making the calculations given in Table A.4.

Table A.4 — Calculation of peak area ratios for sample extracts

| Sample extract	Calculation				Conclusion
	F_{hs}	F_{ls}	F_{hc}/F_{hs}	F_{lc}/F_{ls}	
1st sample	1,45	1,37	$1,00 \cong 1,00 \pm 0,05$	$1,04 \cong 1,00 \pm 0,05$	Criterion (3) is met; identity is confirmed, no interference occurs in either cluster.
2nd sample	1,28	1,37	$1,13 \cong 1,00 \pm 0,15$	$1,04 \cong 1,00 \pm 0,05$	Criterion (4) is met; identity is confirmed, no interference occurs in the lower cluster.
3rd sample	1,45	1,64	$1,00 \cong 1,00 \pm 0,05$	$0,87 \cong 1,00 \pm 0,15$	Criterion (5) is met; identity is confirmed, no interference occurs in the higher cluster.
4th sample	1,87	1,77	0,77	0,81	Criteria are not met; identity is not confirmed, both clusters undergo interference.

A.3.2 Typical chromatogram
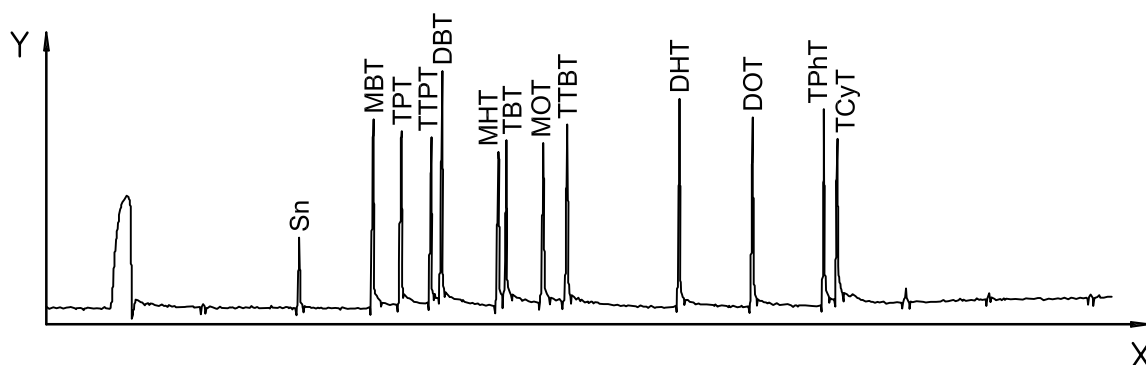
Key

X   retention time, min

Y   intensity

Operating conditions

Injection:	Open hot split, 3 µl, split 1,5 ml to 2 ml
Carrier:	Helium, pre-pressure 90 kPa, about 1 ml/min
Capillary column:	CP-SIL 8 CB-MS, 5 % phenyl-95 % dimethylpolysiloxane, length 25 m, 0,32 mm inner diameter, film thickness 0,25 µm
Column temperature programme:	50 °C, 1 min → 12 °C/min → 150 °C → 8 °C/min → 300 °C → 7 min
Detection:	FPD, 200 °C, Range 2
Gases:	22 ml/min helium
	95 ml/min air
	180 ml/min hydrogen
Internal standards:	MHT, DHT, TPT, TTPT: 100 ng/l
Other OC:	100 ng/l

Figure A.1 — Example of an FPD chromatogram of ethylated organotin compounds

A.3.3 Mass spectra
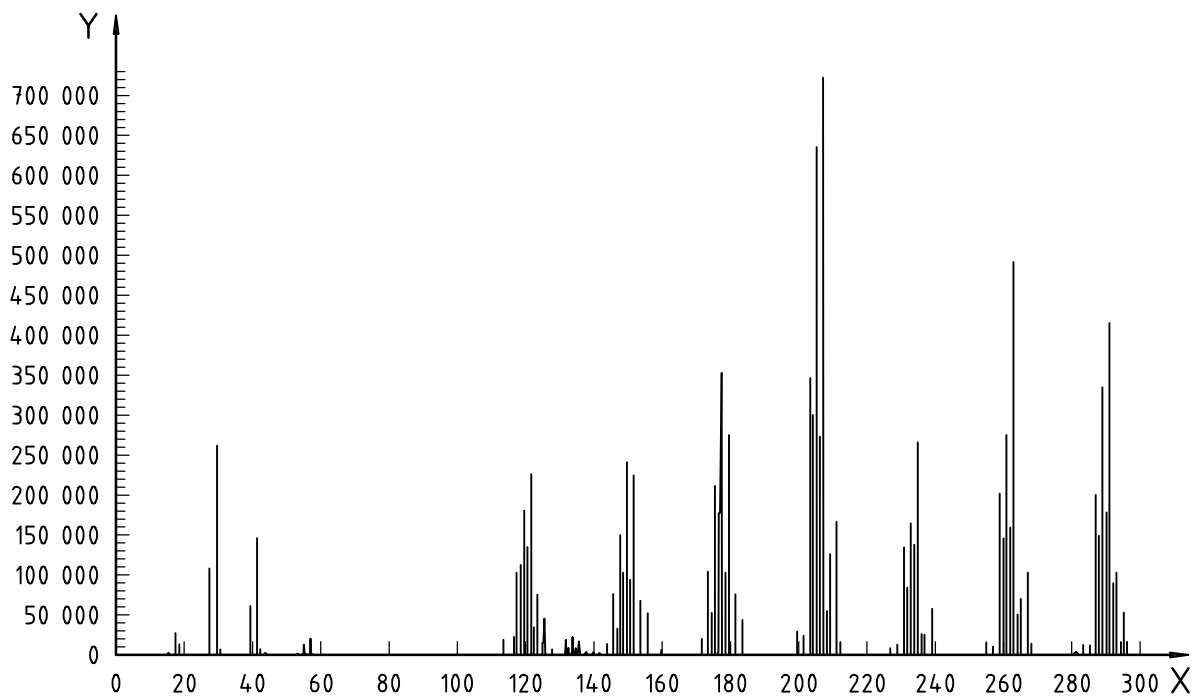
Key

X   *m/z*

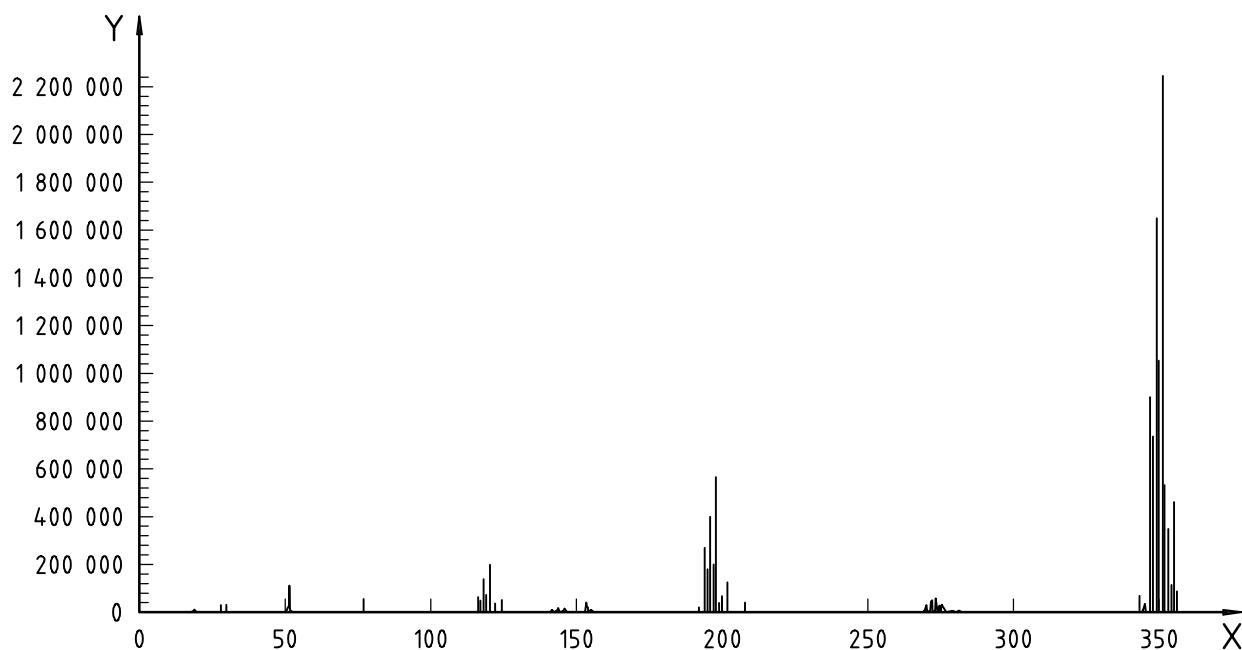Y   abundance

Operating conditions

Transfer line: 290 °C
Electron impact: 70 eV
Mass range: 10 amu to 400 amu

Figure A.2 — Example of mass spectrum of tributylethyltin

Key

X   *m/z*

Y   abundance

Operating conditions

Transfer line: 290 °C

Electron impact: 70 eV

Mass range: 10 amu to 400 amu

Figure A.3 — Example of mass spectrum of triphenylethyltin

A.4 General considerations

A.4.1 Chromatography and detection modes

The most critical step of this type of analysis is the extraction/derivatization step. Once an extract is obtained that is ready for injection, the determination using gas chromatography followed by suitable detection is not a problem.

The basic requirement for chromatography is to obtain sufficient resolution. This can be achieved using different columns. However, care need be taken to apply appropriate temperature profiles so as to obtain proper separation. The choice of the injection system should be based upon the requirements of the detector and its sensitivity. This choice does not influence the accuracy of the determination, unless the amount injected is too small to be detected by the chosen detector. Within this International Standard, a variety of instrumentation is described in A.2 with detailed examples described in A.3.

The method of detection shall fulfil at least the requirement that it be sensitive to tin and sufficiently selective. AED, FPD, PFPD, AAS (as described below) are specific to tin (if adjusted accordingly). Mass spectrometry is specific to tin-containing fragments (if adjusted accordingly). Combined with the retention time, this is an appropriate way to identify organotin-containing compounds.

For confirmation, additional proof is required that the obtained signal is due to an organotin compound. This can be achieved by

— performing a second gas chromatographic separation using a column of different polarity (9.2.1);

— examining a second characteristic fragment characteristic to the respective organotin compound (9.2.2) when using mass spectrometry.

Detection using mass spectrometry overcomes the problems related to distinguishing coeluting substances at a level of specificity almost impossible to be achieved using optical detection methods. This is the reason why, when using spectrometric detection, verification by a second emission or adsorption wavelength cannot be regarded as sufficient confirmation.

A.4.2 Hexane

Most of the work establishing the test method was performed using *n*-hexane. An interlaboratory trial revealed that 2-methylpentane may be used as well.

A.4.3 Precision

A.4.3.1 Remarks for data obtained for spiked drinking water and surface water

The precision data obtained for dibutyltin spiked in drinking water and surface water need to be addressed. The recovery in drinking water was 202 %. Closer examination of the source data shows that three laboratories were responsible for increasing the mean value. However, this does not account for the high recovery.

The institute organizing the interlaboratory trial stated that it is unlikely that an error occurred during spiking, for example by adding this compound twice to the spiking mixture.

Although there was a time frame given for analysis, some of the laboratories did not respond in time giving rise to the possibility that analyses were carried out at a later date. Therefore it is not clear whether wall adsorption effects may have played a factor.

Some, but not all questionable results could be recognized by the intralaboratory precision. Some laboratories were very precise while being very inaccurate. The reason may be that accuracy is chiefly affected by day-to-day variance.

Therefore it is recommended that two independent analyses be performed on two different days.

A.4.3.2 Reasons for laboratory failure accounting for high percentage of outliers

A.4.3.2.1 Possibility A: Laboratories not meeting the required range

The range of application for this method is clearly indicated in Clause 1. One laboratory (out of 12) presented data that were outside of this range of application for five of seven compounds in surface water and for five of eight compounds in wastewater. In the preparation of this interlaboratory trial, all participants were informed as to the approximate amounts of substances to spike (for example for wastewater this range was 0,1 µg/l to 10 µg/l). Considering this information, one laboratory (out of 12) presented data that were outside of the range of application for five of seven compounds in surface water and for five of eight compounds in wastewater. This laboratory has been identified as an outlier each time contributing 8,3 % to the percentage of outliers.

A.4.3.2.2 Possibility B: Laboratories not meeting the goal due to intralaboratory variances

Presumably most of these could have been recognized if the analyses were split to different days.

Twelve laboratories participated in the interlaboratory trial; three compartments were assessed with eight parameters each. Therefore each laboratory was asked to report 24 results. Outliers were coded as follows:

a) Code A: deviation from the intralaboratory mean resulting in rejection of one value;

b) Code B: deviation from the interlaboratory mean resulting in rejection of the entire data set of four measurements;

c) Code C: deviation from intralaboratory standard deviation from the interlaboratory standard deviation resulting in rejection of the entire data set of four values.

One of the laboratories had 15 outliers Code B. One laboratory had two outliers Code B and three laboratories had one outlier Code B. One of the latter had additionally one outlier Code C. There were 18 outliers Code A occurring in only four laboratories. The laboratory itself could have detected this, however, the laboratories were asked to provide all data without any internal rejection.

In the specific case of DBT in surface water, an unexpected high number of outliers (two outliers Code A, two outliers Code B and one outlier Code C) had to be taken into account as well as a reduced database due to one laboratory reporting only two values.

Table A.5 — Outlier laboratories in interlaboratory trial

Laboratory code number	Drinking water			Surface water			Wastewater		
	Outlier code			Outlier code			Outlier code		
	A	B	C	A	B	C	A	B	C
MBT	—	84	—		77, 91	—	76	77	—
DBT	84, 87	—	—	84,85	77, 91	92	87	77	—
TBT	78, 84	—	—	—	77	—	76	77	—
TTBT	84	85	—	—		—	84	77	—
MOT	84	—	—	—	77	—	—	77,92	—
DOT	—	—	—	85	77	—	—	77	—
TcyT	—	77	—	76		—	—	77	—
TPhT	84	—	—	76	77, 87	—	84, 87	77	—
Participating laboratory codes: 76, 77, 78, 80, 81, 82, 84, 85, 87, 88, 91, 92									

A.4.4 Stability of standard Stock solutions A and B

Standard stock solutions in methanol were stored at 4 °C in the refrigerator for more than one year without any adverse effects to stability.

Working solutions (AH, AM, AL, B2) (see Table 3) were stable for almost six months, it is recommended to prepare fresh working solutions after four months.

A.4.5 Cleaning of glassware

If the glassware becomes contaminated, the following appropriate cleaning procedures are to be applied.

Fill flasks and vials completely with 10 % (volume fraction) nitric acid solution. In an appropriate beaker (1 l to 5 l), completely immerse all other glassware, i.e. pipettes, glass column and separator, in the same nitric acid solution and close thoroughly. Decontaminate overnight and rinse three times with deionized water.

If the contamination is persistent, it is advisable to clean the glassware in the vapour phase with concentrated nitric acid as follows.

a)   Fill a 5 l beaker to a depth of about 5 cm with concentrated nitric acid.

b)   Place the glassware upside down in the beaker.

c)   Cover the beaker with a watch glass.

d)   Heat the beaker for about 6 h on a hotplate at low heat.

e)   Ensure that the nitric acid does not boil.

f)   Cool to room temperature.

g)   After cooling, remove the glassware from the beaker and rinse the glassware subsequently with blank free water and acetone followed by drying with air.

A.4.6 Blanks

The reagents sometimes contain impurities of organotin compounds. It is absolutely essential to verify the blanks.

A.4.7 Triphenyltin ions

During clean-up with silica, triphenyltin ions are not eluted with hexane from silica. Therefore, for elution of these ions, acetone is added to hexane and the volume of the eluent is increased in order to achieve a quantitative elution of triphenyltin ions. The amount of acetone in the eluent and the volume of eluent depend on the activity of the silica used. Both of these need to be determined in separate trials prior to application of the clean-up to calibration, blanks and samples.

A.4.8 Clean up

In order to avoid interferences, restrict the amount of silica and of eluent to the least amount possible. For low polluted samples with a background interference from reagents, the amount of silica and of eluent may be reduced to 1:10, provided the size of the column is reduced accordingly.

A.4.9 Emulsions

In cases where emulsions are formed during extraction, the total emulsion should be separated and treated with suitable measures (e.g. vigorous shaking, freezing, addition of Na_2SO_4, addition of Ca^{2+} or Mg^{2+} ions, centrifuging, reduced pressure in case of included gas bubbles).

A.4.10 Extraction efficiency

The extraction yield may be influenced by both the mass of suspended solids and the organic load.

Annex B
(informative)

Precision data

An interlaboratory trial, carried out in Germany in 1998, resulted in the values given in Tables B.1 to B.3, calculated according to ISO 5725-2.

Table B.1 — Precision data for drinking water, spiked

Spiked compound	l	n	o %	x_{true} ng/l	$\bar{x}$ ng/l	η %	s_r ng/l	CV_r %	s_R ng/l	CV_R %
Monobutyltin	10	40	9,1	18,0	17,6	97,9	2,71	15,4	5,35	30,4
Dibutyltin	11	42	12,5	15,0	28,2	188,2	3,75	13,3	16,9	59,9
Tributyltin	11	42	12,5	8,0	10,1	126,2	1,41	13,9	2,35	23,3
Tetrabutyltin	11	43	10,4	7,0	7,36	105,1	1,24	16,9	3,85	52,3
Monooctyltin	12	47	2,1	17,0	14,9	87,9	3,26	21,8	8,74	58,5
Dioctyltin	11	44	8,3	11,0	10,6	96,4	1,87	17,6	6,04	57,0
Triphenyltin	11	43	2,3	12,0	16,9	141,0	2,56	15,2	3,61	21,4
Tricyclohexyltin	9	36	18,2	20,0	23,4	116,7	2,37	10,2	6,92	29,7

Explanation of symbols

l is the number of laboratories

n is the number of measurements

o is the percentage of outliers

x_{true} is the conventional true value (spiked value)

$\bar{x}$ is the total mean

η is the recovery rate

s_r is the standard deviation of repeatability

CV_r is the coefficient of variation of repeatability

s_R is the standard deviation of reproducibility

CV_R is the coefficient of variation of reproducibility

Table B.2 — Precision data for surface water, spiked

Spiked compound	l	n	o %	x_{true} ng/l	$\bar{x}$ ng/l	η %	s_r ng/l	CV_r %	s_R ng/l	CV_R %
Monobutyltin	9	34	19	142,5	175,0	81,4	17,04	12,0	56,65	39,7
Dibutyltin	8	28	39,1	201,9	210,0	96,1	11,92	5,9	53,48	26,5
Tributyltin	10	40	16,7	390,0	398,5	102,2	38,99	9,8	83,54	21,0
Tetrabutyltin	9	36	25,0	80,0	67,6	84,5	5,60	8,3	10,94	16,2
Monooctyltin	10	40	16,7	445,0	267,1	60,0	28,97	10,8	112,5	42,1
Dioctyltin	10	39	18,8	315,0	231,8	73,6	18,21	7,9	75,28	32,5
Triphenyltin	10	39	18,8	285,0	320,4	112,4	67,48	21,1	83,13	25,9
Tricyclohexyltin	11	43	2,3	70,0	61,7	88,1	9,51	15,4	25,39	41,1
For definitions of symbols see Table B.1.										

Table B.3 — Precision data for wastewater, spiked

Spiked compound	l	n	o %	x_{true} µg/l	$\bar{x}$ µg/l	η %	s_r µg/l	CV_r %	s_R µg/l	CV_R %
Monobutyltin	11	43	10,4	6,5	5,51	84,7	0,929	16,9	1,318	23,9
Dibutyltin	9	35	27,1	2,2	1,72	78,0	0,112	6,5	0,528	30,8
Tributyltin	11	43	10,4	1,1	1,27	115,6	0,135	10,6	0,242	19,0
Tetrabutyltin	10	39	18,8	8,7	6,53	75,0	0,509	7,8	1,765	27,0
Monooctyltin	9	36	25,0	1,3	1,09	83,6	0,113	10,4	0,263	24,2
Dioctyltin	10	40	16,7	2,6	1,96	75,3	0,143	7,3	0,602	30,8
Triphenyltin	10	38	20,8	9,4	10,0	106,7	0,954	9,5	1,641	16,4
Tricyclohexyltin	11	44	8,3	4,9	3,55	72,5	0,760	21,4	1,398	39,4
For definitions of symbols see Table B.1.										

Bibliography

[1]   *CRC Handbook of Chemistry and Physics*, 1986, Wiley Interscience Publishers

[2]   *German standard methods for the examination of water, waste water and sludge — Jointly determinable substances (group F) — Part 13: Determination of selected organotin compounds by gas chromatography* (F 13), Beuth Verlag, Berlin, 2001

[3]   Abalos et al., *J. Chromatogr.*, **788** 1997, pp. 1-49

[4]   ISO 5725-2, *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*

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