

**ORTEP STABILIZER TASK FORCE (STF) ANALYTICAL METHOD -  
EXTRACTION OF ALKYL TIN CHLORIDES FROM WATER**

**SUMMARY**

Water samples are spiked with a multi-component internal standard and buffered to a pH of 4.5. Mono- and dialkyl (methyl, butyl, or octyl) tin chlorides are simultaneously derivatized and extracted using sodium tetraethylborate and hexane. The derivatized extract is washed with 2 M hydrochloric acid and transferred to an autosampler vial for analysis by gas chromatography.

**GENERAL INFORMATION**

--This method is intended for use in conjunction with the corresponding ORTEP Association (2006) method, *Gas Chromatographic Analysis of Derivatized Alkyltin Chlorides*.

--Reagents may contain organotin impurities. It is essential to verify the purity of reagents before use and monitor contamination by analyzing reagent blanks with each analytical batch.

--When pre-treating samples and calibration standards, an internal standard is needed for each degree of alkylation (i.e., the internal standard solution should contain a mono-, di-, tri-, and tetra-substituted compounds).

--While preparing the German Standard method (DIN 38407 F13), a round robin test was performed and significant singular deviations were observed. Therefore, it is important that two independent determinations of each sample be performed.

**I. Reagents and Solutions**

A. Chemicals

Acetic acid, CH<sub>3</sub>COOH (glacial), 99+%

Acetone, (CH<sub>3</sub>)<sub>2</sub>CO, HPLC Grade

Hexane, C<sub>6</sub>H<sub>14</sub>, HPLC Grade

Hydrochloric acid, HCl, 2 M

Naphthalene, C<sub>10</sub>H<sub>8</sub>, 98+%

Reagent water, Milli-Q or equivalent purity

Sodium acetate-Acetic acid buffer, pH 4.5

Sodium hydroxide solution, NaOH, 40% (m/v)

Sodium tetraethylborate (STEB), NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> – **Caution: STEB may spontaneously combust in air! Use appropriate safety measures when handling.**

Tetrahydrofuran (THF), C<sub>4</sub>H<sub>8</sub>O, 99+%, free of peroxides and water

Monomethyltin trichloride (MMTC), CH<sub>3</sub>SnCl<sub>3</sub>

Dimethyltin dichloride (DMTC), (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>


  
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Monobutyltin trichloride (MBTC),  $C_4H_9SnCl_3$   
 Dibutyltin dichloride (DBTC),  $(C_4H_9)_2SnCl_2$   
 Monooctyltin trichloride (MOTC),  $C_8H_{17}SnCl_3$   
 Dioctyltin dichloride (DOTC),  $(C_8H_{17})_2SnCl_2$   
 Monoheptyltin trichloride (MHTC),  $C_7H_{15}SnCl_3$  (internal standard)  
 Diheptyltin dichloride (DHTC),  $(C_7H_{15})_2SnCl_2$  (internal standard)  
 Tripropyltin chloride (TPTC),  $(C_3H_7)_3SnCl$  (internal standard)  
 Tetrapropyltin (TTPT),  $(C_3H_7)_4Sn$  (internal standard)

**B. Prepared Reagents and Solutions**

1. **Stock Solution A (Multi-component Standard Solution):** Prepare a 1 mg/mL organotin cation stock solution by weighing the organotin compounds of interest according to Table 1 (to an accuracy of  $\pm 0.1$  mg) into a tared 100 mL volumetric flask. Dissolve in a small amount of methanol, bring to volume with methanol, and homogenize.

*NOTE:* All standards should be labeled with actual concentrations (vs. theoretical). For example, if theoretically using 0.1 g/100 mL (0.001 g/mL), but actually used 0.11 g/100 mL (0.0011 g/mL), the solution should be labeled with the actual concentration of 0.0011 g/mL.

**Table 1. Masses of organotin compounds required for stock solutions A and B (@ 1.0 mg/mL) and weighing factors for recalculation to organotin cations (assuming 100% purity of the substances)**

Substance	Weighing Factor*	Mass** (mg)	Solution
Monomethyltin trichloride	0.557	179.5	A
Dimethyltin dichloride	0.677	147.7	A
Monobutyltin trichloride	0.623	160.5	A
Dibutyltin dichloride	0.767	130.4	A
Monoctyltin trichloride	0.686	145.8	A
Dioctyltin dichloride	0.830	120.5	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

\* - Weighing factor = molar mass organotin cation/ molar mass organotin compound

\*\* - In case of deviating masses, the actual concentration of the OTC is calculated using the weighing factor

Solution A = The multi-component stock standard solution (see Section I.B.1)

Solution B = The internal standard stock solution (see Section I.B.2)

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1. Stock Solution B (Internal Standards): Prepare a 1 mg/mL internal standard stock solution by weighing the appropriate propyltin or heptyltin compounds according to Table 1 (to an accuracy of  $\pm 0.1$  mg) into a tared 100 mL volumetric flask. Dissolve in a small amount of methanol, bring to volume with methanol, and homogenize.

*NOTE:* As per Table 1, for the preparation of exactly 1 mg/ml of organotin cation internal standards, 148.8 mg of monoheptyltin trichloride, 122.4 mg of diheptyltin dichloride, 114.3 mg of tripropyltin chloride and 100.0 mg of tetrapropyltin are necessary.

2. Derivatization Agent: Prepare a solution containing 20% (w/v) of STEB in THF.

***NOTE:* This solution is stable for at least three months if stored under inert gas at 4°C, and out of direct light.**

3. Sodium Acetate-Acetic Acid Buffer, pH 4.5: Dissolve about 82 g of sodium acetate in 500 ml of water in a 1-L volumetric flask. Add sufficient glacial acetic acid to reach a pH of 4.5. Make up to volume with water and homogenize.

C. QA/QC Samples

1. Reference Solution Samples (Aqueous Multi-Component Reference Solutions): Using the same volume of reagent water as the samples, prepare at least 6 reference standard samples by spiking with various amounts of the reference standard solution described in Section I.B.1. Spiking should occur at (approximately) equidistant concentration levels surrounding the anticipated sample analyte concentrations (e.g., if expected final extract concentration = 10 ng/ml, then reference standards could be spiked to obtain final extracts at 1, 5, 10, 15, 20 and 25 ng/ml). A calibration range greater than one order of magnitude can be used, if linearity and repeatability can be demonstrated and only the upper 60–70% of the calibration curve is used. The lower end is adversely affected due to relatively high variation. Calibration points by factors (e.g. 0.1, 1, 10, 100) are not acceptable. In order to accomplish an appropriate precision, two calibrations should be performed: one covering the lower working range, and one covering the upper working range (e.g., working range is 40–1000 ng/ml in the final extract, divide into lower working range (40-240 ng/ml) and upper working range (250-1000) ng/ml. The internal standard concentration in the final extract should then be 100 ng/mL).

*NOTE:* For calculation of the amount of monoalkyl tin compounds, the peak area of MHTC is used as the internal standard. For calculation of the amount of dialkyl tin compounds, the peak area of DHTC is used. The other organotin internal standards (TPTC and TTPT) are not used for calculations, but as indicators to follow the quality of the extraction and analytical method.

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2. Method (Laboratory) Blank: For each analytical batch prepare a method blank of reagent water at the same volume as the samples being analyzed.
3. Matrix Spikes: For each analytical batch, prepare a matrix spike and a matrix spike duplicate using the appropriate volume of actual sample. Spike the samples with the compounds of interest at the approximate concentrations expected in the samples. A laboratory control spike (LCS) or “blank spike” can also be prepared using the same procedure, only using reagent water instead of actual sample.

## II. Apparatus

- A. GC autosampler vials, 2 mL (amber-colored, with PTFE-lined septum hole caps)  
Mechanical shaker  
Muffle furnace (up to 500°C ± 20°C)  
Quartz plate, 12 cm diameter  
Sample containers (e.g., 125 mL Polycarbonate bottles or 50 mL Corning tubes, depending on the sample volume used)  
Solvent evaporation apparatus (e.g., N-Evap, Turbovap, Rotary evaporator, etc.)  
Transfer pipettes (disposable)  
Volumetric flasks (varied volumes)  
Volumetric pipettes (varied volumes)
- B. Glassware: Use of PTFE, polycarbonate, or some form of disposable plastic containers/apparatus is an option, as organotins have been known to sorb to glass. Prior to using plastic containers however, verification that they do not leach tin at levels greater than analysis detection limits should be obtained (e.g., a leaching study should be performed, perhaps using total tin analysis).  
  
Cleaning of non-disposable apparatus should be performed after each analysis, and should include washing with a laboratory cleaner (e.g., Alconox™), followed by repeated rinsing with reagent water, acetone, and hexane prior to initiation of the next round of analyses. Examination of all non-disposable glassware for cross-contamination should be conducted frequently. If a batch of glassware is suspected of contamination due to exposure to high organotin concentrations, it is advisable to acid-rinse all glassware with high purity, 10 N nitric acid or equivalent. Acid rinsing removes even ultra-trace quantities of organotins adhering to glass surfaces.

### III. Water Extraction Procedure

1. Water samples are kept in 1-L amber glass or opaque PTFE/polycarbonate/ plastic bottles with PTFE-lined caps and are stored at 4°C for a holding time of no more than 24 hours. Samples should be frozen if storage is to be prolonged. Holding time studies may be performed to evaluate this issue further.
2. Use the appropriate volume of sample for the expected analytical range; measure and note the volume of sample extracted in order to calculate the final results. Method validation samples were prepared using 100 mL sample volume for analyte concentrations greater than 10 mg/L, and 10 mL sample volume for concentrations less than 10 mg/L. Prepare the necessary QC samples as appropriate (i.e., reference standards, method blank, matrix spike, matrix spike duplicate – see Section I.C.).
3. Transfer all samples, blanks, QC spikes, and reference standards to the appropriate sample container and treat each as follows:
  - a) Add 10 mL of acetate buffer solution and shake well to mix.
  - b) Check the pH and adjust it to pH 4.5 (use acetic acid to lower the pH or 40% NaOH solution to raise it).
  - c) Add an appropriate amount of internal standard solution (see Sections I.B.2 and I.C.1). Shake well to mix.
  - d) Add 0.5 mL of the derivatization solution (20% STEB in THF).
  - e) Add 10 mL of hexane (containing ~0.1 mg/L naphthalene to check the injection of the sample into the GC instrument). Cap each container and shake for 45 minutes (intensity ~225 rpm).
  - f) Allow the phases to separate, remove approximately 4 mL of the hexane (upper) layer, and wash it with approximately 4 mL of 2 M HCl.
  - g) Transfer an aliquot of the hexane top layer into an amber-colored GC autosampler vial and store at 4°C, in the dark, until analysis. Extracts may be stored for at least 1 week.

*NOTE:* In case of emulsions formed during extraction, the total emulsion should be separated and treated with suitable measures (e.g., vigorous shaking, freezing, addition of Na<sub>2</sub>SO<sub>4</sub>, addition of Ca<sup>2+</sup> or Mg<sup>2+</sup> ions, centrifuging, or reduced pressure).

### IV. Extract Cleanup

Depending on the source of the samples being analyzed, extract cleanup may be required prior to analysis (make sure that calibration and QC samples are treated accordingly). Commercially pre-packed silica gel columns may be used or cleanup columns may be prepared using the following steps. Both commercial and lab-packed columns should be tested for contamination prior to use, and to ensure that appropriate recoveries can be achieved.

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*(Please note, this procedure was not attempted during the method validation study)*

1. Add approximately 120 g of silica (grain size 63-200 nm) to a quartz plate and heat in a muffle furnace at 500°C ( $\pm$  20°C) for at least 12 hours. Make sure that the temperature does not exceed 520°C. Let the plate cool in the oven to about 200°C, pour the silica gel into a wide-necked glass bottle, and let cool to room temperature. Add water equivalent to 3% of the silica gel mass, to the cooled silica gel. Stopper the bottle and homogenize the contents for 2 hours on a shaker.

Check the homogeneity and the moisture content of the prepared silica gel by determining the moisture content gravimetrically in three different samples. The moisture content should not vary more than 0.1%.

Evenly add approximately 5 g of prepared silica gel to the column and top with approximately 3 g of sodium sulfate (dried for 4 hours at about 180°C). After rinsing with 30 mL of hexane, the column is ready for use.

*NOTE:* Hexane may be used as a moistening agent during the filling process.

2. After the 2 M HCl wash, add 1.0 mL of the separated extract to the head of a silica gel cleanup column.
3. Slowly add 1 mL of hexane (containing ~0.1 mg/L naphthalene) onto the column. After penetration of the solvent, add 20 mL hexane (containing ~0.1 mg/L naphthalene) solution and collect the eluent in a container suitable for solvent reduction.
4. Reduce the volume of the organic phase to 1.0 mL using a suitable apparatus. Avoid reducing the extract to dryness.

*NOTE:* Evaporation step should be performed slowly; if done too quickly there will be a loss of target compounds (esp. methyltins).

## V. Analysis

See the ORTEP Method “Gas Chromatographic Analysis of Derivatized Organotin Chlorides” for details of the GC-MS, GC-FPD, or GC-AED analysis.

## VI. Calculations

See the ORTEP Method “Gas Chromatographic Analysis of Derivatized Organotin Chlorides” for details of analytical calculations and data reporting.

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**VII. References**

de Wolf, J.M., R. Schilt, and H.A. Meinema. 2004. Validation of analysis of organotin chlorides MMTC, DMTC, MBTC, DBTC, MOTC and DOTC in water. TNO Report V4766. Study conducted by TNO Nutrition and Food Research, Analytical Sciences for the ORTEP Association Stabilizer Task Force. Zeist, The Netherlands.

DIN Deutsches Institut für Normung e.V. 2001. DIN 38407 – 13:2001-03 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 (F13). Beuth Verlag, 10772 Berlin, Germany.

ORTEP. 2006. ORTEP Stabilizer Task Force (STF) Analytical Method - Gas Chromatographic Analysis of Derivatized Alkyltin Chlorides. Revision 3.0. January 2006.