# Organotins in Sediment/Soil by GC with MS Detection - PBM

**Parameter**

Tributyltin*
Dibutyltin*
Monobutyltin

**CSR-regulated analyte (soils)*

**Analytical Method**

Solvent Extraction, Derivatization, GC with MS detection

**Introduction**

Tributyltin compounds such as bis(tributyltin) oxide have seen widespread historical use as biocides in antifoulant marine paints to prevent growth of organisms such as barnacles, mussels, algae, tubeworms, etc., which has caused contamination and toxic effects to marine and freshwater ecosystems worldwide. TBT substances and other organotins are also commonly used as PVC stabilizers and for other pesticidal uses such as fungicidal wood preservatives and disinfectants.

Organotin compounds have a backbone of the tetravalent tin IV molecule. When fully alkylated, that is for tetrabutyltin and tributyltin oxide (TBT-O-TBT), TBT acts like a typical organic compound and is easy to extract into solvent. However, as the molecule becomes less organic, as in dibutyltin, it develops a stronger inorganic affinity for water and is difficult to extract. Monobutyltin exhibits very little organic tendencies and is not extractable from aqueous media with solvent alone. Monobutyltin can be solvent-extracted with the addition of tropolone (2-hydroxy-2,4,6-cycloheptatriene-l-one) as a ligand. Adjacent hydroxy-ketone functional groups on the seven-member tropolone ring bind with tin molecules through hydrogen bonding. Tropolone also improves extraction efficiency for dibutyltin.

**Method Summary**

Soil or sediment samples are extracted with tropolone-spiked diethyl ether:hexane (80:20) prior to derivatization (ethylation) with sodium tetraethyl borate. The extract is cleaned up with a silica gel column prior to instrumental analysis.

Instrumental analysis is by gas chromatography with mass spectrometric detection (GC/MS, GC/MS/MS, GC/HRMS, or GC/ICPMS may be used). Selected ion monitoring (SIM) may be required with some instrumental techniques to achieve detection limit requirements. Refer to listed references for details on recommended instrumental analysis techniques.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

**MDL(s) and EMS Analyte Codes**

| Analyte | CAS No. | Approx. MDL (ug/L) | EMS Analyte Code |
|---|---|---|---|
| Tributyltin | 36643-28-4 | 0.001 | TRSN |
| Dibutyltin | 14488-53-0 | 0.001 | DISN |
| Monobutyltin | 78763-54-9 | 0.001 | MNSN |

**EMS Method Code(s)**

***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

**Matrix**

Soil, sediment, sludge

**Interferences and Precautions**

Interferences may result from contaminants in solvents, reagents, glassware and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Matrix interferences may be caused by contaminants that could be co-extracted from the sample. The extent of the matrix interferences will vary from source to source.

MBT and DBT are used as stabilizers in a variety of plastics (e.g. PVC). MBT is also used as a precursor for tin oxide coatings in glass products.

**Sample Handling and Preservation**

**Container:** Glass jars with Teflon-lined cap or PTFE or HDPE (opaque).

**Preservation:** None.

**Stability**

**Holding Time:** Extract samples within 28 days after sampling (hold time may be extended to 1 year with freezing to ≤ -10°). Extracts may be held up to 40 days before instrumental analysis. Derivatize within 3 days of extraction.

**Storage:** Sample temperature should be chilled to ≤ 10°C immediately after sampling and during transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C.

**Procedure**

**Reagents:**

a) Dichloromethane (DCM), hexane, acetone, methanol, diethylether - distilled in glass or equivalent.
b) Sodium sulfate, ACS granular, anhydrous.
c) Activated Silica Gel, 35-70 mesh (200-500 µm).
d) Activated Silica Gel, 70-230 mesh (60-200 µm).
e) Sodium tetraethylborate (STEB), ~97% purity or better.
f) Glacial Acetic Acid (AcOH), ACS grade or better.
g) Sodium Acetate (NaOAc, ~99.995% or better).
h) TBT Standards. 1.0 mL mix of TBT chloride, DBT dichloride, MBT trichloride and Tetrabutyltin at 2,000 µg/mL in DCM is commercially available.
i) Tri-n-butyltin Chloride d-27, 1.2 mL at 100 µg/mL in DCM.
j) Tetra-n-propyltin Recovery Standard, 1 mL at 2,000 µg/mL in DCM.
k) Tri-n-propyltin Chloride, 1 mL at 2,000 µg/mL in DCM.
l) Tri-n-pentyltin Chloride, 1 mL at 2,000 µg/mL in DCM.

**Extraction:**

a) Accurately weigh out 10-15 g of wet soil into a 60 mL vial.
b) Add 1.0 mL of 0.25 ppm TBT-d27 (and/or suitable amounts of other organotin internal standards / surrogate compounds).
c) Add 3 mL of glacial acetic acid, 2 mL of 1 M NaOAc buffer (pH 4.5) and 5 mL of 30% w/v NaCl(aq).
d) Add 5 mL of 80:20 Diethyl Ether:Hexane containing 0.2% tropolone. Cap the vial and shake for 1 hour on a mechanical shaker.
e) Transfer the organic layer to a 15 mL test tube.
f) Repeat the extraction with a further 5 mL of 80:20 Diethyl Ether:Hexane containing 0.2% tropolone.
g) Transfer the organic layer to the same 15 mL test tube as in (e) above.
h) Concentrate the solution to 2 mL.
i) Add 1 mL of 1% STEB in methanol. Cap the vial and shake (vortex).
j) Add 0.5 mL of 1% STEB in methanol. Shake sample.
k) Add 2 mL of 2M KOH. Add 5 mL of 20:80 Diethyl Ether:Hexane and shake for 1 minute.
l) Allow the layers to separate and transfer the solvent layer to a second test tube.
m) Repeat the extraction with a second aliquot of 20:80 Diethyl Ether:Hexane.
n) Allow the layers to separate and transfer the solvent layer to a second test tube.
o) Concentrate the solution to 2 mL.
p) Prepare a silica gel column as follows:
    - Place a glass wool plug into the bottom of a 15 mm o.d. glass column.
    - Add 5 g of 100 % activated silica gel (60-200 µm) and top with 1 cm of anhydrous sodium sulphate. Elute 25 mL of hexane through the column and discard.
    - Transfer extract onto the silica gel column.
    - Elute column with 50 mL of hexane (collect).

q) Concentrate the solution to 2 mL.

r) Add 25 µL of 10.0 µg/mL Tetrapropyltin recovery standard to the sample.

**Instrumental Analysis:**

Detailed instrumental procedures are not provided with this method. Gas chromatography with mass spectrometric detection is required. Single quadrupole, triple quadrupole, high resolution magnetic sector MS, or ICPMS are all acceptable, provided the instrument is capable of meeting the detection limit requirements of the method.

A minimum five-point calibration over the desired working range is required.

Continuing calibration verifications are required at the beginning and end of every run and every 12 hours of continuous operation.

At least two ions for each measured substance must be monitored. Their ratio must be within 25% of theoretical, or within 15% of the ratio determined by continuing calibration.

*Recommended Monitoring Ions (exact), for GC/MS, GC/MS/MS, GC/HRMS **

| *Analyte* | *Ion* | *Quantitation* | *Qualifier* |
|---|---|---|---|
| Monobutyltin | $SnC_8H_{19}$+ | 235.0509 | 233.0503 |
| Dibutyltin | $SnC_{10}H_{23}$+ | 263.0822 | 261.0816 |
| Tributyltin | $SnC_{10}H_{23}$+ | 263.0822 | 261.0816 |
| Tetrabutyltin | $SnC_{12}H_{27}$+ | 291.1135 | 289.1129 |
| Tri-n-propyltin | $SnC_9H_{21}$+ | 249.0665 | 247.0659 |
| Tri-n-pentyltin | $SnC_{15}H_{33}$+ | 333.1604 | 331.1598 |
| Tetra-n-propyltin | $SnC_9H_{21}$+ | 249.0665 | 247.0659 |
| Tributyltin-d27 | $SnC_{10}D_{18}H_5$+ | 281.1952 | 279.1946 |

** Recommended Ions above are for ethylated derivatives, except for tetra-alkyl tin substances. Refer to ISO 23161 for mass spectra of relevant example organotin species.*

**Reporting:**

Report organotin substances as cation concentrations for direct comparison to CSR standards (e.g. as tributyltin cation, not as tributyltin chloride).

**Performance Requirements**

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

**Accuracy Requirement:** Laboratories must demonstrate method accuracy (measured as average recovery) of 75-125% for tributyltin, and 60-130% for dibutyltin and other regulated organotin substances, for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

**Precision Requirement:** Laboratories must demonstrate method precision equal to or better than 20% RSD for tributyl tin, and 30% RSD for other regulated organotin substances, for clean matrix spikes at concentrations above ten times the MDL.

**Sensitivity Requirement:** Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

**Quality Control**

| Summary of QC Requirements | | |
|---|---|---|
| **QC Component** | **Minimum Frequency** | **Minimum Data Quality Objectives** |
| Calibration Verification Standard (CVS) – 2nd source | 1 per initial calibration | 70-130% |
| Continuing Calibration Verification (CCV) | At least every 12 hours (max 20 samples), and at end of each run | 70-130% for mid-level standards |
| Method Blank (MB) | One per batch (max 20 samples) | Less than reported DL |
| Lab Control Sample (LCS) | One per batch (max 20 samples) | TBT 70-130%<br>Other regulated organotins: 50-130% |
| Lab Duplicate (DUP) | One per batch (max 20 samples) | 50% RPD [or within 2x reported DL for low level results] |
| Matrix Spike (MS) or Reference Material (RM) | One per batch (max 20 samples) | TBT 60-140%<br>Other regulated organotins: 40-140% |

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

**Surrogate Compounds:** At least four organotin surrogate compounds have been identified in literature as being suitable for this method: tripropyltin, tripentyltin, dipropyltin, and tetrapentyltin (as chlorides). Reporting of one or more surrogates are recommended (required for GC-ICPMS if isotope dilution for TBT using TBT-d27 is not conducted, with 50-150% recovery limits).

**Prescribed Elements**

The following components of this method are mandatory:

1. Analysis must be by gas chromatography with mass spectrometric detection (i.e. GC/MS, GC/MS/MS, GC/HRMS, or GC/ICPMS). At least 1 qualifier ion per analyte must be monitored.
2. Initial calibrations must include at least 5 points.
3. All Performance Requirements and Quality Control requirements must be met.
4. Quantitation by isotope dilution or by use of suitable extracted organotin internal standards is required. If using GC/MS techniques (other than GC-ICPMS), isotope dilution for TBT is required using TBT-d27, with reporting of absolute recovery of TBT-d27 correction standard (10-150% recovery limits). If GC-ICPMS is used, recovery of a suitable organo-tin surrogate must be reported.
5. Derivatization is required (e.g. with sodium tetraethyl borate or a suitable Grignard reagent).

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

**References**


1. Ikonomou, M.G.; Fernandez, M.; He, T.; Cullon, D. A Gas Chromatography - High Resolution Mass Spectrometry (GC-HRMS) Based Method For The Simultaneous Determination Of Nine Organotin Compounds In Water, Sediment And Tissue. J. Chrom. A, 2002, 975(2), 319-333.
2. ISO 23161, Soil Quality – Determination of selected organotin compounds – Gas chromatographic method, 2018.


**Revision History**

July 21, 2020 Draft method for public comment.