

Organotins in Water by GC with MS Detection - PBM

Parameter	Tributyltin* Dibutyltin* Monobutyltin Tricyclohexyltin* Triethyltin* Triphenyltin* <i>*CSR-regulated analyte (waters)</i>			
Analytical Method	Solvent Extraction, Derivatization, GC with MS detection			
Introduction	<p>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.</p> <p>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. As such, this method calls for in-situ derivatization prior to extraction.</p>			
Method Summary	<p>Waters are acidified to pH 4.5, derivatized in-situ with sodium tetraethyl borate and subsequently liquid-liquid extracted with dichloromethane (DCM)-</p> <p>Once extracted into solvent, organotins must be fully alkylated before they are chromatographable on a GC. Organotin substances are reacted with sodium tetraethyl borate and are derivatized (ethylated) to ethyl-butyltins or to other tetraalkylated organotin substances. Interfering compounds may be removed by columning on silica gel.</p> <p>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.</p> <p>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.</p>			
MDL(s) and EMS Analyte Codes	<u>Analyte</u>	<u>CAS No.</u>	<u>Approx. MDL</u> <u>(ug/L)</u>	<u>EMS Analyte Code</u>
	Tributyltin	36643-28-4	0.001	TRSN
	Dibutyltin	14488-53-0	0.001	DISN
	Monobutyltin	78763-54-9	0.001	MNSN
	Tricyclohexyltin	n/a	0.01	Defined on request
	Triethyltin	n/a	0.01	Defined on request
	Triphenyltin	668-34-8	0.01	Defined on request
EMS Method Code(s)	***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.			
Matrix	Fresh water, marine water, wastewater			
Interferences and Precautions	<p>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.</p> <p>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.</p>			

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.

Organotin reference standards can be subject to degradation over time (to lesser alkylated analogs). ISO 17353 and ISO 231671 indicate that multi-component methanolic stock standards are stable for up to 1 year and working solutions are stable for up to 6 months when stored at 4°C in the dark, but more frequent preparation is recommended. Verification of calibration standard integrity versus second source standards is required for this method.

Sodium tetraethylborate ethylation reagent solutions are stable for up to 3 months when stored under inert gas (ISO 231671), but are unstable when exposed to air. Immediate use after preparation or after exposure to air is recommended.

Sample Handling and Preservation

Container: Amber glass bottle with Teflon-lined cap or PTFE or HDPE (opaque). 1 L samples are typically used (contact laboratory for required sample volume).

Preservation: Preserve samples with glacial acetic acid (5-10 mL per litre) within 3 days of sampling.

Stability

Holding Time: Extract preserved samples within 14 days after sampling (may optionally be extended to 28 days if frozen to $\leq -10^{\circ}\text{C}$). If unpreserved, hold time is reduced to 3 days. Extracts may be held up to 40 days before instrumental analysis. Derivatize in-situ at time of extraction, or within 3 days of extraction.

Storage: Store in dark (use of amber or opaque containers is sufficient). Sample temperature should be chilled to $\leq 10^{\circ}\text{C}$ immediately after sampling and during transit to the laboratory. In the laboratory, samples must be refrigerated at $\leq 6^{\circ}\text{C}$. If samples are frozen to extend hold times, use care to prevent sample breakage.

Procedure

Reagents:

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

Extraction:

- a) Quantitatively transfer an accurately measured portion (approximately 0.5 L) of the sample from the bottle into a 1 L glass separatory funnel.
- b) Add 10 mL of 5M NaOAc buffer (adjusted to pH 4.5 by adding AcOH). Shake to mix.
- c) Add 200 μL of 0.25 ppm TBT-d27 (and/or suitable amounts of other organotin internal standard / surrogate compounds).
- d) Add 1-2 mL of 1% sodium tetraethylborate solution and gently shake to mix.
- e) Wait 1 hour and then add another 1 mL of 1% sodium tetraethylborate solution. Gently shake to mix.
- f) Add 50 mL of dichloromethane, cap and shake for 1 minute.
- g) Collect the solvent extract by filtering through a bed of precleaned anhydrous sodium

sulfate and glass wool into a 250 mL boiling flask.

- h) Repeat the process two more times with 50 mL of dichloromethane per L of sample.
- i) Concentrate the entire sample extract to 2 mL.
- j) If necessary (yellow solution, or if interferences are observed), 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. Add 2 x 2 mL of hexane to the boiling flask to rinse and transfer to the column. Elute column with 50 mL of hexane, collecting the hexane into a 60 mL vial.
 - Concentrate extract to 2 mL and transfer to a 15 mL conical disposable test tube.
 - Concentrate the solution to 2 mL by passing a gentle stream of nitrogen over the solvent.
- k) Add 50 μL of 1.0 $\mu\text{g}/\text{mL}$ 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	$\text{SnC}_8\text{H}_{19}^+$	235.0509	233.0503
Dibutyltin	$\text{SnC}_{10}\text{H}_{23}^+$	263.0822	261.0816
Tributyltin	$\text{SnC}_{10}\text{H}_{23}^+$	263.0822	261.0816
Tetrabutyltin	$\text{SnC}_{12}\text{H}_{27}^+$	291.1135	289.1129
Tricyclohexyltin	$\text{SnC}_8\text{H}_{17}^+$	233.0352	231.0346
Triethyltin	$\text{SnC}_6\text{H}_{15}^+$	207.0196	205.0190
Triphenyltin	$\text{SnC}_{18}\text{H}_{15}^+$	351.0196	349.0190
Tri-n-propyltin	$\text{SnC}_9\text{H}_{21}^+$	249.0665	247.0659
Tri-n-pentyltin	$\text{SnC}_{15}\text{H}_{33}^+$	333.1604	331.1598
Tetra-n-propyltin	$\text{SnC}_9\text{H}_{21}^+$	249.0665	247.0659
Tributyltin-d27	$\text{SnC}_{10}\text{D}_{18}\text{H}_5^+$	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 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) – 2 nd 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% 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)	One per batch (max 20 samples)	TBT 60-140% 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, tripropyltin, 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. Ikonou, 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 17353, Water Quality – Determination of selected organotin compounds – Gas chromatographic method, 2004.
3. ISO 23161, Soil Quality – Determination of selected organotin compounds – Gas chromatographic method, 2018 (analytical elements including reference for GC-ICPMS analysis).

Revision History

July 21, 2020 Draft method for public comment.