

Determination of Organo-Tin Species in Sediment Extracts Using GC Coupled with X Series ICP-MS

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Introduction

The use of organo-tin compounds (OTCs) commenced at the end of the 19th century and almost 800 OTCs are now recognized today. The majority of these OTCs are derived exclusively from anthropogenic sources with the exception of methylated tin species which may be formed due to bio-methylation processes. The commercial use of OTCs commenced in the 1940's and to date one of the major industrial applications for OTCs include the addition of dialkyl tin derivatives as thermal and light stabilizers in polyvinyl chloride (PVC) materials. However, tributyl and triphenyl tin species have also been used widely in fungicides, biocides, rodent repellents, wood preservatives and as antifoulants on boats, ships, quays, buoys, crab pots and fishing nets. Industrial applications of OTCs have increased extensively since the mid 1950s and the annual consumption of these compounds is reported to have increased from $5,000 \text{ t y}^{-1}$ to $50,000 \text{ t y}^{-1}$ between 1955 and 1992. These increased anthropogenic activities have resulted in the increased release of OTCs to environmental systems.

Butylated OTCs such as tributyl tin (TBT) are highly stable and are resistant to natural degradation processes in water. These OTCs can accumulate readily in organisms as a result of their high solubility in fat and bio-concentration factors of up to 30,000 have been reported in field and laboratory-based investigations with molluscs, fish and micro-organisms. OTCs are broadly classified as endocrine disrupters and are known to inhibit oxidative phosphorylation and alter mitochondrial structure and function in biota. TBT is highly toxic to aquatic organisms such as marine molluscs when present at nano-molar concentrations and has been shown experimentally to affect shell deposition of growing oysters, gonadal development and gender of adult oysters, settlement, growth, and mortality of larval oysters and other bivalves. TBT is also known to cause imposex (the development of male characteristics) in female gastropods. To date TBT entering water from the hulls of boats and ships poses the greatest environmental concern for both freshwater and saltwater biota. However, there are growing concerns with regards to the increasing use of PVC pipes in drinking water distribution systems due to the potential for human toxicity resulting from the leaching of OTCs into the drinking water supply.

TBT is known to be absorbed readily from both the gut and the skin of mammals and can be transferred across the blood-brain barrier and from the placenta to the foetus.

Organisations such as the United States Environmental Protection Agency Office of Ground Water and Drinking Water (OGWDW) are beginning to recognize the potential for toxicity from selected OTCs and have registered monomethyl tin (MMT), dimethyl tin (DMT), monobutyl tin (MBT) and dibutyl tin (DBT) on the 1998 Contaminant Candidate List. However, there is increasing demand for the application of sensitive and selective analytical techniques to enable the reliable determination OTCs in waters, soils and sediments and a necessity for validation of these methods using certified reference standards.

The application of ICP-MS, as a stand alone technique, can enable highly sensitive determinations of total tin concentrations in environmental matrices. However, this analytical technique provides no mechanism for the on-line separation and determination of intrinsic tin species. An effective approach to the analysis of mixtures of OTCs can, however, be achieved by coupling chromatographic separation methodologies with sensitive mass specific ICP-MS detection. This application note describes use of the new GC-ICP-MS instrument package from Thermo Electron Corporation to determine trace concentrations of MBT, DBT and TBT species in sediment extracts. The analytical methodology is evaluated following analysis of a certified reference sediment sample, examination of instrument stability during prolonged periods of sample analysis and the calculation of method detection limits (MDLs).



Key Words

- GC
- ICP-MS
- Organo-Tin
- Speciation
- Transient TRA

Instrument Configuration

A Finnigan™ FOCUS™ Gas Chromatograph and AS3000 autosampler were coupled to the X Series ICP-MS using the new Thermo GC-ICP-MS Coupling Pack (P/N 4600503) and Finnigan FOCUS GC Wiring Harness (P/N 4600510). This coupling pack includes all the required components to establish electrical and analytical connections between the GC and ICP-MS instrumentation and an outline of the analytical coupling is shown below in Figure 1.

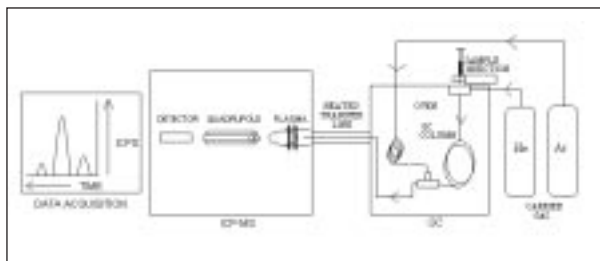


Figure 1: Schematic diagram for GC-ICP-MS coupling

Samples were injected onto the GC column in a flow of He carrier gas to enable separation of the required elemental species. These species were then swept through the GC Transfer Line to the ICP-MS detector in a flow of Ar make-up gas. The GC transfer line was connected from the outlet of the GC column to the torch of the X Series ICP-MS via a 1/16 inch flexible transfer capillary located inside an insulated stainless steel capillary tube. The stainless steel capillary was heated using the external power supply unit and the transfer capillary was also sheathed by a flow of heated Ar gas inside the steel capillary. These instrument features ensure a uniform heating profile for the Transfer Line to prevent the loss of species due to condensation and aid transmission of the separated species to the ICP-MS detector. The transfer line can be heated isothermally to temperatures in excess of 300 °C and further technical details regarding the Thermo GC-ICP-MS coupling packs can be found in Product Specification Note PS40674 (available to download from www.thermo.com/elemental).

The X Series ICP-MS was configured with HPI interface cones to enable enhanced instrument sensitivity and was also configured with the unique dual mode sample introduction system to facilitate simultaneous introduction of both liquid and gaseous samples. This dual sample introduction system allowed connection of the GC transfer line to the torch through the orifice used for standard mode sample introduction. A quartz concentric nebulizer and impact bead spray chamber arrangement was then mounted above the GC transfer line and connected to the third leg of the GC-ICP-MS torch as shown in Figure 2.



Figure 2: X Series dual mode sample introduction for GC-ICP-MS

Analytical Conditions For GC

The Finnigan FOCUS GC and AS3000 autosampler were programmed from the X Series ICP-MS PC using ChromQuest software to enable separation of the butylated tin species and the analytical conditions used for the GC and GC Transfer Line are shown below in Table 1.

Column	Restek MXT-1, 30 m, df 1 µm, 0.53 mm i.d., PDMS 100 %
Injection Mode	Splitless
Injection Port Temp	250 °C
Injection Volume	1 µl
Carrier Gas Flow	He @ 25 ml min ⁻¹
Make-Up Gas Flow*	Ar @ 300 ml min ⁻¹
Transfer Line Temp	250°C isothermal
Initial Oven Temp	70 °C
Initial Oven Hold	1 min
Oven Ramp Rate	50 °C min ⁻¹
Final Oven Temp	250°C
Final Oven Hold	1 min

Table 1. GC and Transfer Line conditions

* delivered via the X Series Additional Mass Flow Controller

Analytical Conditions For ICP-MS

The X Series ICP-MS was performance tested, tuned and optimized as required for GC-ICP-MS analysis using the automated PlasmaLab Performance Test and Autotune facilities and analytical conditions used for the ICP-MS are shown below in Table 2. An aqueous Sb solution was aspirated continuously throughout the fully quantitative GC-ICP-MS analysis (PlasmaLab Timeslice Internal Standard) using the unique dual mode X Series ICP-MS sample introduction system to allow correction for chromatographic baseline drift.

Forward Power	1300 W
Nebulizer Gas Flow	0.56 L min ⁻¹
Auxilliary Gas Flow	0.80 L min ⁻¹
Cool Gas Flow	13.0 L min ⁻¹
Data Acquisition Mode	PlasmaLab Transient Time Resolved Analysis (TRA)
Isotopes and Dwell Times	¹¹⁸ Sn, ¹²⁰ Sn (40 ms) ¹²¹ Sb, ¹²³ Sb (10 ms)
Channels per AMU	1
Timeslice Duration	150 ms
Timeslice Internal Standard	Aqueous Sb solution (5 ng mL ⁻¹) pumped at 400 μL min ⁻¹
Run Duration	280 s

Table 2. ICP-MS conditions

Preparation of Calibration Standards

Individual stock solutions of MBT, DBT and TBT species (approximately 1000 mg L⁻¹ as tin) were prepared by dissolving appropriate quantities of commercially available salts (i.e. BuSnCl₃, Bu₂SnCl₂ and Bu₃SnCl respectively) in ultra-pure grade methanol. These stocks were diluted further as required with 1% HCl in 18.2 MΩ water to produce a mixed stock solution of MBT, DBT and TBT species at approximately 100 ng mL⁻¹ (as tin). Working calibration standards were then prepared in the 0-10 ng mL⁻¹ concentration range by derivatizing and diluting aliquots of the mixed stock solution. The derivatisation was achieved by adding 0, 20, 100 and 200 μL of the mixed stock solution, respectively, to a mixture of 5 mL of 0.1 mol L⁻¹ acetate/acetic acid buffer (pH 4.9), 2 mL of isooctane, 1 mL of 1% NaBEt₄ (in 18.2 MΩ water) and then agitating the mixture for a 5 minute period. The two liquid phases were allowed to separate in the vial and the derivatized standards were then isolated for analysis by transferring the top organic layer (i.e. the isooctane solvent layer) to 2 mL amber GC vials.

Preparation of Sediment Samples

A dry homogenous certified reference sediment sample (Marine Sediment PACS II, National Research Council Canada) was analyzed to verify the GC-ICP-MS performance. However, the sediment was first digested and the OTCs extracted and derivatized prior GC-ICP-MS analysis. Sample digestion was achieved by adding 5 mL of analytical grade acetic acid and 5 mL of 18.2 MΩ water to 0.2 g of the sediment sample in a microwave digestion vessel fitted with an air cooled condenser. The sample was then irradiated for 2 minutes at 40 W using an open focused microwave extraction system and allowed to cool to room temperature before being transferred to Teflon-capped vial. The digested sample was centrifuged for 5 minutes at 2,500 rpm and the supernatant transferred quantitatively to a clean glass vial. 0.2 mL of the supernatant extract were added to 5 mL of 0.1 mol L⁻¹ acetate/acetic acid buffer (pH 4.9) in a clean Teflon-capped vial and the extracted species then derivatized, isolated and transferred to 2 mL amber GC vials prior to analysis using the methodology described previously for the calibration standard solutions.

Fully Quantitative Data

Calibration standards were analyzed using the GC-ICP-MS methodology as described above. The chromatographic data is displayed automatically in the PlasmaLab software package following analysis and an example of the calibration standard chromatography is shown below in Figure 3.

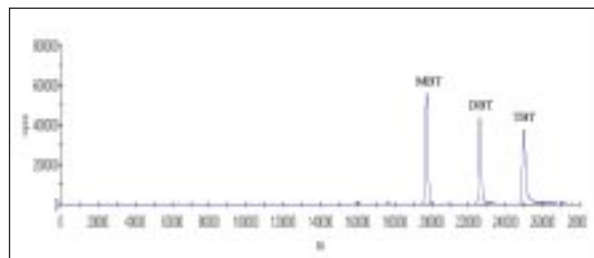


Figure 3. Calibration standard chromatography for MBT, DBT and TBT at 11.6, 10.0 and 9.5 ng mL⁻¹ respectively

The methodology enabled baseline resolution of the three butylated tin species in less than 260 seconds (4.3 mins) and the MBT, DBT and TBT species were eluted as sharp chromatographic peaks with retention times of 197, 226 and 250 seconds respectively. The calibration standard chromatography was integrated using the PlasmaLab software package to enable fully quantitative speciation analysis and the resultant calibration curves for these species are shown below in Figures 4-6.

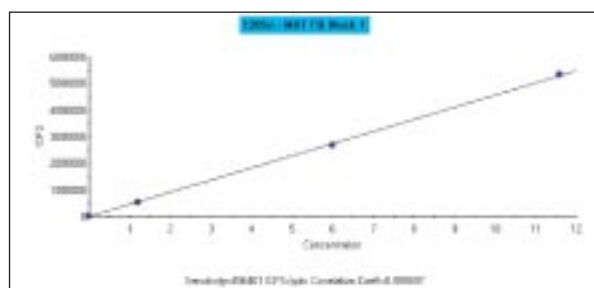


Figure 4. PlasmaLab calibration curve for MBT

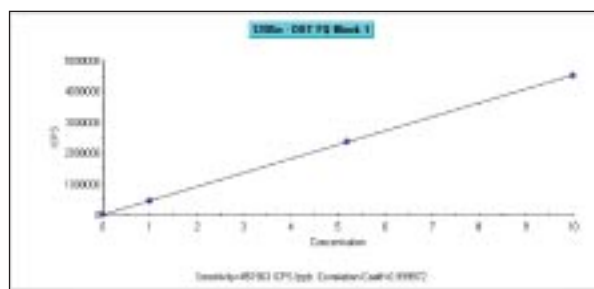


Figure 5. PlasmaLab calibration curve for DBT

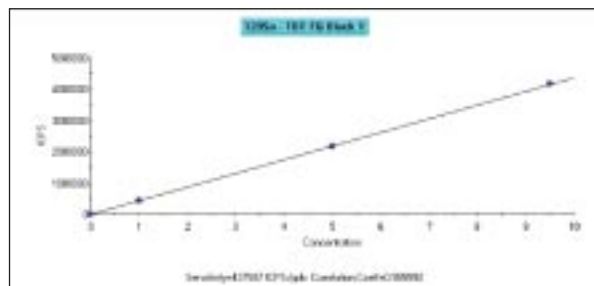


Figure 6. PlasmaLab calibration curve for TBT

Calibration curves derived from the MBT, DBT and TBT species show excellent linearity with correlation coefficients in the range of 0.999897-0.999992 and use of the sensitive element specific ICP-MS detector enabled similar sensitivities (i.e. 437587-456401 Integrated Counts Per Second/ppb Sn) for each butylated tin species. The PACS II reference sediment sample is certified for concentrations of MBT, DBT and TBT species and this sample was extracted, derivatized and analyzed fully quantitatively to verify the GC-ICP-MS methodology. An example of the sample chromatography for PACS II is shown below in Figure 7.

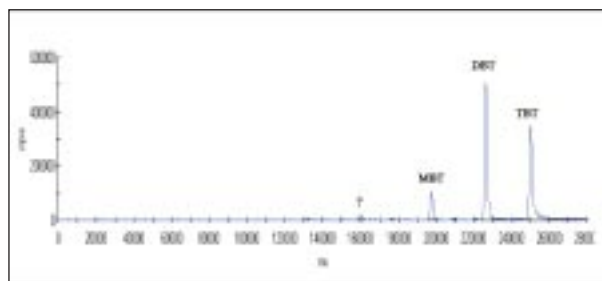


Figure 7. Chromatograph for PACS II reference sediment sample

Four chromatographic peaks were observed in the sample chromatograph as shown above. However, MBT, DBT and TBT species were clearly identified through their correlation with the calibration standard chromatography (Figure 3). The remaining peak showed no correlation with the peaks in the calibration standard chromatography and was subsequently unidentified in this analysis. However, semi-quantitative analysis may still be performed on this peak if required by using the response curve derived from the fully quantitative analysis of MBT, DBT and TBT species. This unique analytical feature is enabled through the inclusion of chromatographic data processing facilities in the X Series PlasmaLab software. Table 3 presents the fully quantitative data for the MBT, DBT and TBT species in this analysis and compares measured values with the certified values for MBT, DBT and TBT in the PACS II sediment sample.

Sn SPECIES	MEASURED CONCENTRATION (ng/mL)					CERTIFIED	
	Sample 1	Sample 2	Sample 3	Mean	% RSD	Value	% Recovery
MBT	425	389	414	409	4.5	450	90.9
DBT	1128	1126	1042	1099	4.5	1090	101
TBT	964	941	969	958	1.5	980	97.7

Table 3. Fully quantitative data for the PACS II reference sediment sample

The fully quantitative data derived from sediment sample analysis (e.g. Figure 7 & Table 3) shows that the DBT species is present at the highest concentrations followed by the TBT and MBT species and that recoveries are achieved for the MBT, DBT and TBT species in the range of 90.9 - 101 % of the certified values. This analytical data demonstrates both the suitability of the sediment sample preparation methodology and the accuracy of the GC-ICP-MS technique.

Method Detection Limits

Method detection limits (MDLs) were determined in accordance with the 3σ model following fully quantitative analysis of the calibration blanks and standards ($n = 10$) and the associated data is shown below in Table 4. The methodology is shown to enable highly sensitive determinations of these OTCs with absolute detection limits of 4.9, 3.8 and 3.8 fg for MBT, DBT and TBT species respectively.

OTC	3σ LOD (fg)
MBT	4.9
DBT	3.8
TBT	3.8

Table 4. MDL data for OTCs

Long term Stability

The extracted PACS II sediment sample was analyzed repeatedly over a period of 7 hours in three analytical runs without the use of internal standards to examine the long term stability of the GC-ICP-MS system and the normalized analytical data is shown below in Figure 8.

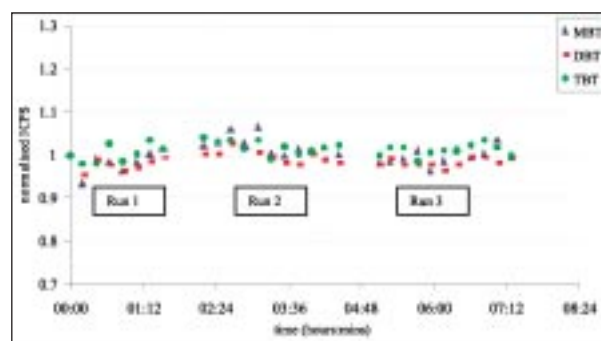


Figure 8. Long Term Stability Data

The GC-ICP-MS system demonstrated excellent long term stability throughout the 7 hour analysis period without the necessity for drift correction using internal standards and the signals derived from MBT, DBT and TBT in the PACS II sample were found to stabilize well within the normalized range of 0.9 to 1.1.

Conclusions

The X Series ICP-MS is easily coupled to GC accessories to enable sensitive elemental speciation analysis in liquid samples and the Thermo GC-ICP-MS speciation package offers a complete instrument solution to this analytical technique. The unique dual mode sample introduction system of the X Series ICP-MS enables a simple automated regime for GC-ICP-MS tuning, optimization and performance testing using aqueous solutions and also enables aspiration of an aqueous standard during GC-ICP-MS analyses to correct for chromatographic baseline drift. A rapid GC separation method is utilized in conjunction with the intelligent productivity enhancing features of the X Series PlasmaLab software and External Trigger card to enable fully automated, quantitative analysis of butylated tin species. This instrument methodology is shown to facilitate high sample throughput capability, excellent long term stability and achieves highly sensitive detection limits in the range of 3.8-4.9 fg for butylated tin species.

Parts List

GC-ICP-MS Coupling Pack (P/N: 4600503)

- Advantech PCI Trigger Card
- 7/02 Electrical Wire (2.0 m)
- 37 Pin D-Type Male Connector
- X Series dual sample introduction system
- GC Transfer Line
- Power Supply/Temperature Control Unit
- Transfer Capillary MXT Guard Column (0.28 mm id)
- 3/16 wrench tool for MXT connection
- Ferrules/Reducing Unions for analytical connections
- Coiled SS Capillary, 1/16" od, 1.0 mm id

Finnigan FOCUS GC Wiring Harness (P/N: 4600510)

Finnigan TRACE GC Wiring Harness (P/N: 4600509)

Generic GC Wiring Harness (P/N: 4600494)

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