Application Note: 40744

Determination of Butyltins in Waters and Leachates using GC Coupled with XSERIES 2 ICP-MS

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Key Words

- Butyltins
- GC
- ICP-MS
- Speciation
- Water

Introduction

Organotin compounds are commercially valuable industrial additives used in pesticides, fungicides, wood preservatives, glues and as stabilizers or catalysts in poly-vinylchloride (PVC) and other plastics. This widespread use and the increase in global demand, projected to be approximately 220 000 ty^{-1} in 2005, is of concern due the toxicity of organotins. The use of tributyltin (TBT) in anti-fouling paints for ships hulls is another major environmental concern. This use has resulted in global pollution of estuarine waters, causing shell deformations in oysters and imposex in female gastropod molluscs due to TBT toxicity.

The toxicity of organotin species depends on the extent of alkylation and the size of the alkyl group. In general, the greater the number of alkyl groups and the lower the alkyl homologue, the more toxic the compound.

As well as causing deformations in marine fauna, organotin compounds are known to attack white blood cells causing immunosupression and have adverse effects on the endocrine and nervous-system. Taking into consideration that nappies, clothes and some toys are reported to contain organotin compounds, this is of particular concern for young children where the immune system is still developing. As a result, both the European Union and the Agency for Toxic Substances and Disease Registry have classified tributyltin as a priority hazardous substance. The European Union Food Safety Authority has established a daily tolerable intake of 0.25 µg/kg body weight for TBT, dibutyltin (DBT), triphenyltin and di-n-octyltin.

Dimethyltins, dibutyltins or dioctyltins used as stabilizers in PVC, prevent thermal degradation during manufacture and light-induced degradation of the finished product. The use of PVCs and plastics in an ever increasing range of household products is a health concern for the general population. PVC pipes are used in water mains, sewers and drains in domestic water systems. Organotins will be found in the environment where the PVC pipes are manufactured but are also reported to leach into water in contact with the pipes. Anaerobic decomposition of PVC stabilizers and environmental cycling could lead to the presence of several organotin compounds in domestic water systems. Therefore it is important to determine the level of organotins that are likely to be encountered from leaching into potable water.

There are two current EPA protocols for the determination of organotins; the first concerns the analysis of marine and fresh water by solid-liquid extraction and GC-ECD (Method 282.3) and the other uses microliquid chromatography coupled to electrospray iontrap mass spectrometry (Method 8323). The latter uses 1L sample volumes which are often inconvenient to manipulate.

This application note describes the use of the GC-ICP-MS instrument package from Thermo Fisher Scientific to determine trace concentrations of butyltins in potable water and leachates from PVC tubing.

Instrument configuration

A Thermo Scientific FOCUS™ Gas Chromatograph and AS3000 autosampler were coupled to the Thermo Scientific XSERIES 2 ICP-MS using the new GC-ICP-MS Coupling Pack (P/N 4600503) and FOCUS GC Wiring Harness (P/N 4600510.) The coupling pack includes all the required components to establish electrical and analytical connections between the GC and ICP-MS instrumentation. A schematic of the GC and ICP-MS coupling is illustrated in Figure 1.

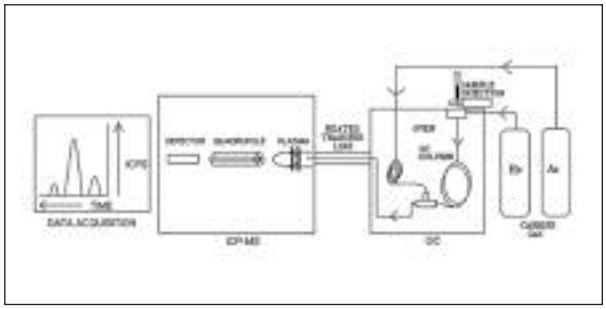

Figure 1: Schematic diagram for GC-ICP-MS coupling

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Samples were injected in splitless mode onto the GC column in a flow of He carrier gas to enable separation of derivatized tin species. The GC Transfer Line was connected from the outlet of the GC column to the torch of the XSERIES 2 ICP-MS via a 1/16-inch flexible transfer capillary located inside an insulated stainless steel capillary tube. A flow of heated Ar make-up gas was used to sheath the transfer capillary in the GC Transfer Line and sweep the species from the end of the transfer capillary to the ICP-MS. These instrument features ensure a uniform heating profile for the GC Transfer Line to prevent loss of species due to condensation and to aid transmission of the separated species to the ICP-MS detector. The GC Transfer Line can be heated isothermally to temperatures in excess of 300 °C and further technical details regarding the Thermo Scientific GC-ICP-MS Coupling Packs can be found in Product Specification Note PS40674 (available to download from www.thermo.com/XSERIES2).

The XSERIES 2 was configured with Xs interface cones to enable enhanced instrument sensitivity, and was 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.

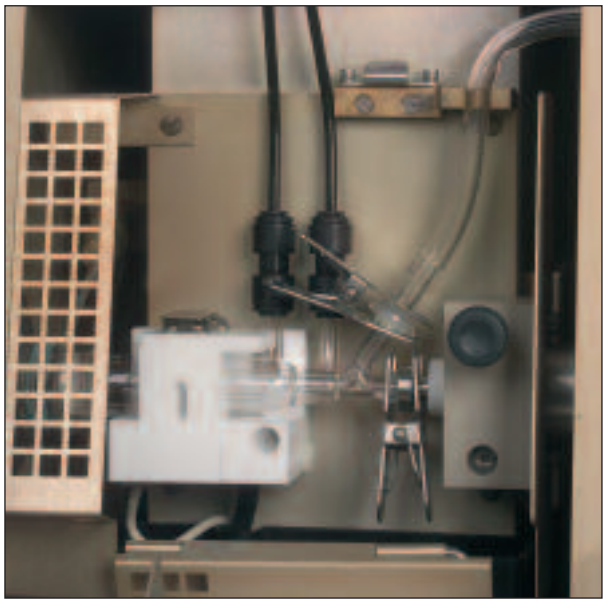

Figure 2: XSERIES 2 dual mode sample introduction for GC-ICP-MS

Analytical Conditions for GC

The FOCUS GC and AS3000 autosampler were programmed from the XSERIES 2 ICP-MS PC using ChromCard software to enable separation of the propylated tin species and the analytical conditions used for the GC and GC Transfer Line are shown in Table 1.

Column	100 % PDMS, 30 m x 0.53mm x 1 µm
Injection mode	Splitless
Injection port temperature	250 °C
Injection volume	1 µL
Carrier gas flow	He @ 25 mL min^{-1}
Make up gas flow*	Ar @ 400 mL min^{-1}
Splitless time	30 s
Transfer line temperature	300°C isothermal
Oven parameters	
Initial temperature	60 °C
Initial time	1 min
Ramp rate	50 °C min^{-1}
Final temperature	250 °C
Final time	1 min
Autosampler	
Injection depth	Standard
Vial depth	Bottom
Syringe rinse cycles	3
Preinjection syringe sample rinses	7
Post injection syringe rinses	5

Table 1. GC, GC Transfer Line and Autosampler conditions

*delivered via the XSERIES 2 Additional Mass Flow Controller

Analytical Conditions for ICP-MS

The XSERIES 2 ICP-MS was performance tested, tuned and optimized as required for GC-ICP-MS analysis using the automated PlasmLab Performance Test and Autotune facilities and analytical conditions for ICP-MS are shown in Table 2. An aqueous 1 µg L^{-1} Sb solution was aspirated continuously throughout the fully quantitative GC-ICP-MS analysis using the unique dual mode XSERIES 2 ICP-MS sample introduction system to allow correction for chromatographic baseline drift as required.

Forward Power	1350 W
Nebulizer Gas Flow	0.5 L min^{-1}
Auxilliary Gas Flow	0.9 L min^{-1}
Cool Gas Flow	14 L min^{-1}
Data Acquisition Mode	PlasmaLab Transient Time Resolved Analysis (TRA)
Isotopes and dwell times, ms	^{118}Sn, ^{120}Sn (50 ms) ^{121}Sb, ^{202}Hg, ^{208}Pb (20ms)
Channels per AMU	1
Timeslice duration	167 ms
Timeslice Internal Standard	Aqueous Sb solution (1 µg L^{-1}) pumped at 400 µL min^{-1}
Transient acquisition time	350 s
Spray chamber	Conical with impact bead
Nebulizer	Standard, pneumatic concentric
Cones	Xs

Table 2. ICP-MS conditions

Preparation of Organotin Standards

Individual stock solutions of MBT, DBT and TBT species (approx. 1000 mg L^{-1} as tin) were prepared by dissolving appropriate quantities of commercially available salts (ie. $BuSnCl_3$, Bu_2SnCl_2 and Bu_3SnCl respectively) in ultra-pure grade methanol. The stock solutions were diluted in 1 % HCl in 18.2 MΩ water to produce a mixed stock solution of 10 ng g^{-1}. Working calibration standards were then prepared in the range 0.1-2 ng Sn g^{-1} by derivatizing and diluting aliquots of the mixed stock solution.

Derivatization of the calibration standards was achieved by adding 0, 10, 25, 50, 100 and 200 µL of the 10 ng g^{-1} stock solution to 5 mL acetate/acetic acid buffer (0.1 M) at pH 4.9, adding 1 mL isooctane and 1 mL 1 % $NaBPr_4$ (in 18.2 MΩ water) and agitating the mixture for approximately 5 minutes. The two liquid phases were allowed to separate in the vial and the derivatized standards were isolated for analysis by transferring a portion of the top organic layer to a 2 mL, amber GC vial.

Preparation of Water and PVC Leachate Samples

Sample preparation:

A 1m length of PVC tubing (approx. 3 cm I.D.) was sealed at one end and filled with tap water (the tube held approximately 500 mL). The tube was kept stationary at room temperature during leaching and was agitated for 1 min prior to sub-sampling. 10 mL aliquots were sub-sampled at t = 0, 0.5, 1.5, 3.5, 5, 10, 15, 36, 60 and 84 h and transferred to clean Teflon®-capped vials for derivatization.

Derivatization of samples:

5mL aliquots of acetic acid/Na acetate buffer (0.1 M) at pH 4.9 were added to the 10 mL PVC leachate samples and the pH was adjusted by adding small amounts of acetic acid (puriss.). 1 mL of isooctane was then added and the propylation was performed by adding 1 mL of aqueous 1 % $NaBPr_4$ solution. The tube was capped immediately and shaken by hand for 5 min. After phase separation the upper, organic layer containing the derivatized organotins was transferred to a 2 mL amber GC vial. Derivatized samples were stored in the dark at –18 °C until measurement.

Results and Discussion

The three butylated tin species were analyzed using the GC-ICP-MS methodology as described above. Chromatographic data is displayed automatically in the PlasmaLab software package following analysis and an example of the chromatographic separation of derivatized butyltin species is shown in Figure 3 (a).

The GC parameters allowed baseline separation of MBT, DBT and TBT at 247, 258 and 269 seconds respectively. The small peak eluting at 232 s is inorganic Sn and occurs due to degradation of the butylated species during derivatization. Calibrants containing approximately 0.1, 0.25, 0.5, 1 and 2 ng Sn g^{-1} as MBT, DBT and TBT were integrated using the PlasmaLab software package to enable fully quantitative determinations of the butyltins in water samples. The calibration curves for MBT, DBT and TBT are shown in Figure 4.

Leachates from the PVC tubing were analyzed using the same GC parameters as described above. Five peaks were observed in the leachates where t is greater than 15h, at retention times of 168, 203, 233, 246, 258 and 269 s. The latter three peaks match the retention times of MBT, DBT and TBT respectively and the PVC leachate at t = 60 h, spiked with approximately 0.1 ng Sn g^{-1} of each of the butyltin species is presented in Figure 3(b). The peak at 233 s corresponds to inorganic tin, due to degradation of the butyltin species. The peaks eluting at 168 and 203 s (represented as U_A and U_B in Fig. 3(b)) are presently uncharacterized. The species concentrations found in the derivatized aliquot were converted to ng Sn L^{-1}. The concentrations of MBT and DBT at the end of the leaching experiment were calculated as 3.1 and 2.1 ng Sn L^{-1} respectively and the leaching pattern of MBT and DBT from the PVC pipes is shown in Figure 5. The concentrations determined in the sample aliquots were blank corrected. TBT was found at a concentration below the limit of quantification, as were the uncharacterized species U_A and U_B.

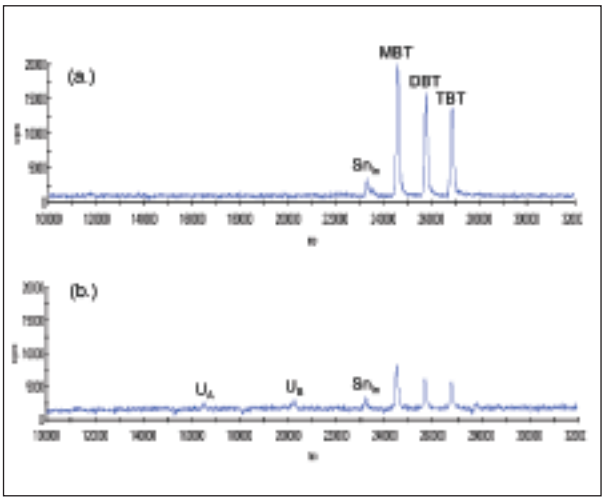

Figure 3 a). Chromatogram of derivatized MBT, DBT and TBT at concentrations of 0.4, 0.37 and 0.39 ng Sn g^{-1} respectively. Figure 3 b.) PVC leachate, t = 60 h spiked with 0.112, 0.098, 0.101 ng Sn g^{-1} of MBT, DBT and TBT respectively

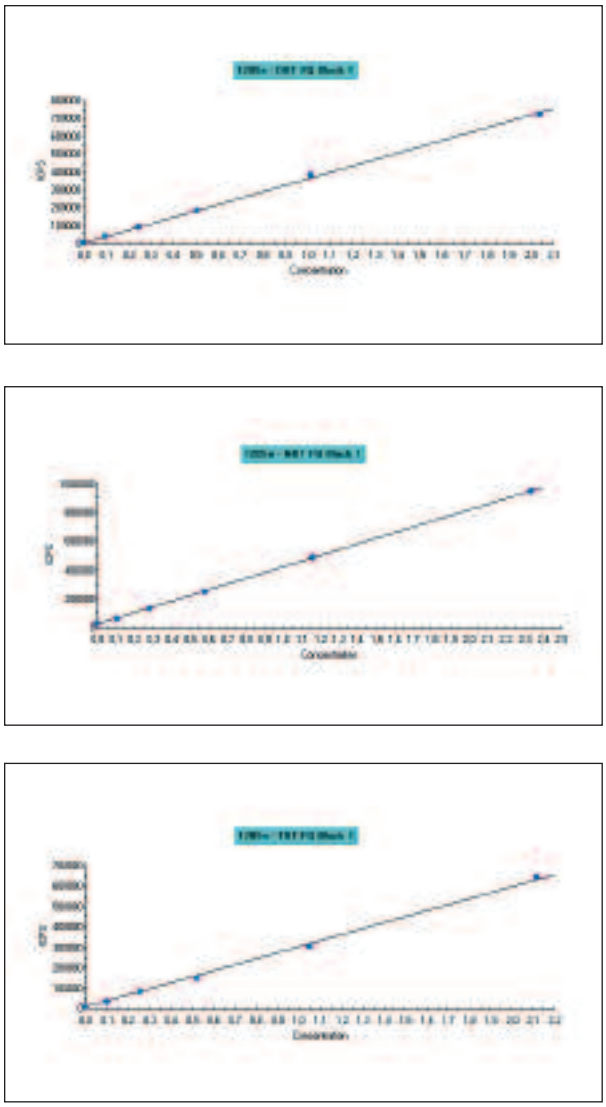

Figure 4. PlasmaLab calibration curves for MBT, DBT and TBT

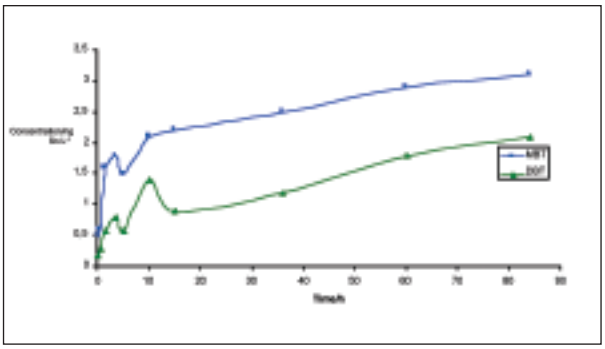

Figure 5. Leaching profile of MBT and DBT into tap water from a PVC pipe over a period of 3.5 days.

Recovery of the butyltin compounds was determined from the spike of an aliquot of the PVC leachate sample taken at t = 60 h with the butylated tin species at a concentration of 1 ng Sn g^{-1}. Table 3 presents the recovery data of between 92 and 97 % for the butyltin compounds. The good recovery demonstrates the suitability of the analytical methodology.

Detection limits for butyltin species were determined in accordance with the 3s model following fully quantitative analysis of the calibration blanks (n=6) and this data is presented in Table 3.

	MBT	DBT	TBT
Recovery (%)	94	97	92
Limit of Detection (pg Sn g^{-1})	3.0	3.0	1.7

Table 3. Recovery data for PVC leachate spiked with approximately 0.1 ng Sn g^{-1} of MBT, DBT and TBT and limits of detection for the butylated tin species

Summary

The Thermo Scientific GC-ICP-MS instrument package offers a complete instrument solution for the sensitive and accurate determination of tin-containing compounds in waters. The unique PlasmaLab software features and external trigger card facility enable increased productivity and permit failsafe automated instrument operation for routine speciation applications.

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