

# Quantification of Organotin Compounds Using S/SL Injection and LVI-GC-MS

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## Keywords

Organotin; GC-MS, DSQ, large volume injection.

## SUMMARY

Due to the toxicity of organotin compounds, there is a need for a wide dynamic range methodology for the quantification of these compounds. Consequently, two different injection techniques were evaluated: The first one was a splitless injection technique GC-MS (SIM mode): good results were obtained in the identification and quantification of organotin compounds from 1 ppb to 100 ppb. The second injection technique was Large Volume Injection (LVI) using a PTV injector and GC-MS (SIM mode). This technique was found adequate for the separation, identification and quantification of organotin compounds from 100 ppt to 500 ppb.

## INTRODUCTION

Organotin compounds have been employed in industry as catalysts, biocides, stabilizing agents, as well as protective paint coatings applied to ships' hulls. Triphenyltin (TPhT) for example, has a high bioaccumulation potential and the ecotoxicological impact of TBT has been documented; in addition TBT is considered an endocrine disrupter **1,2**. Considerable concentrations of these compounds and their metabolites were detected in environmental samples **3**: In water, trisubstituted organotin compounds decompose in a stepwise manner to less substituted compounds, down to inorganic tin. The concentration levels of organotin compounds in seawater are in the ppb to ppt range, and it is found in higher concentrations in sediments and biological samples. Organotin compounds are lipophilic and get absorbed into adipose tissue; they can also be adsorbed onto particulate matter, where sediment is their final sink. The recognition of their toxicity at low concentration has stimulated the development of accurate and sensitive analytical methods for their determination **3,4**. Two different GC-MS approaches to their quantification are exposed: splitless injection technique in the range between 1 ppb to 100 ppb and LV-PTV injection technique to reach down to 100 ppt.

## EXPERIMENTAL

### *Materials and Reagents*

Analytical grade reagent chemicals obtained from Merck (Darmstadt, Germany) were used unless otherwise stated. Sodium tetraethylborate was obtained from Strem Chemicals (Bischheim, France). Organotin compounds were extracted with tropolone in hexane/ethyl acetate. Derivatization with NaBEt<sub>4</sub> was performed as described by Ceulemans *et al.* **5**.

### *Gas Chromatography- Mass Spectrometry*

For both techniques a Trace GC in combination with a double stage quadrupole (DSQ) mass spectrometer were used (ThermoFinnigan, Austin, Tx, US). After having run the standards in full scan mode, the spectra and the ions to measure in single ion monitoring (SIM) mode were selected (see **Table 1**). All calculations were performed by the Xcalibur software (ThermoFinnigan, US), using external standard calibration.

**Table 1. List of organotin compounds with their retention times and the ion fragments ( $m/z^+$ ) used for their detection and quantification.**

Compound	Nomenclature	$m/z^+$ (Th)	$R_t$ (min)
butyltriethyltin	MBT	179, 233, 235	6,55
dibutyldiethyltin	DBT	207, 261, 263	7,59
phenyltriethyltin	MPT	197, 255	8,27
tributylethyltin	TBT	205, 207, 263	5,53
octyltriethyltin	MOT	289, 291	9,04
diphenyldiethyltin	DPT	275, 301, 303	10,76
dioctyldiethyltin	DOT	261, 263, 375	11,76
triphenylethyltin	TPT	197, 349, 351	12,82

### Splitless injection technique

Column: CPSil-8-MS 20 m L x 0,15 mm ID x 0,15  $\mu$ m  $d_f$  (Varian, Middelburg, the Netherlands). He carrier gas flow set at 0,8 ml/min -constant flow-. Hot needle injection of 2  $\mu$ L into a split/splitless injector at 240 °C. Oven programme: 50 °C (1 min) @ 20 °C/min to 280 °C @ 120 °C/min to 300 °C.

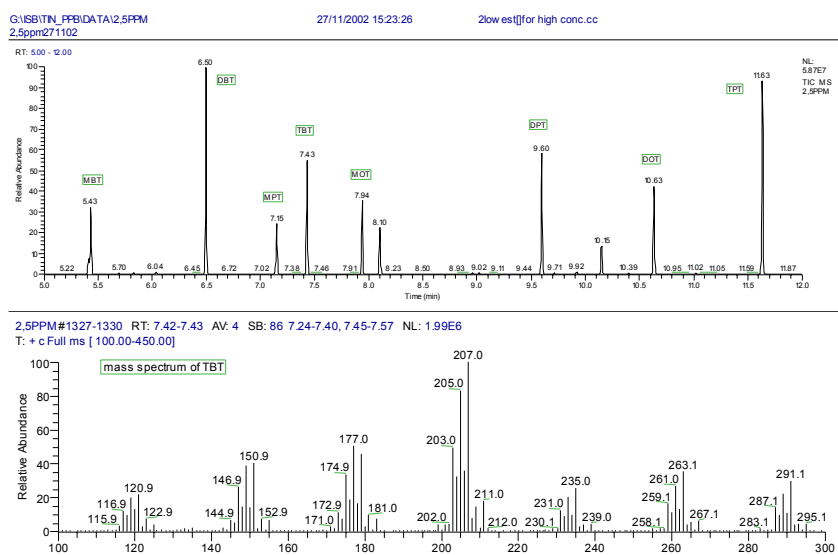
### LV-PTV injection technique

Column RTX5-MS 30 m L x 0,25 mm *i.d.* x 0,25  $d_f$  (Restek, US). He carrier gas flow set at 1,5 mL/min -constant flow-. Oven programme: 35 °C (1 min) @20 °C/min to 280 °C @ 120 °C/min to 300 °C. 50  $\mu$ l were injected into a LV-PTV injector using a CombiPal autosampler (CTC Analytics, Switzerland).

## RESULTS AND DISCUSSION

### Method 1: Splitless injection

In **Figure 1** a TIC of organotin compounds listed in **Table 1** (top) and a spectrum of TBT is shown. Good chromatographic and spectral quality was observed for all concentrations studied.



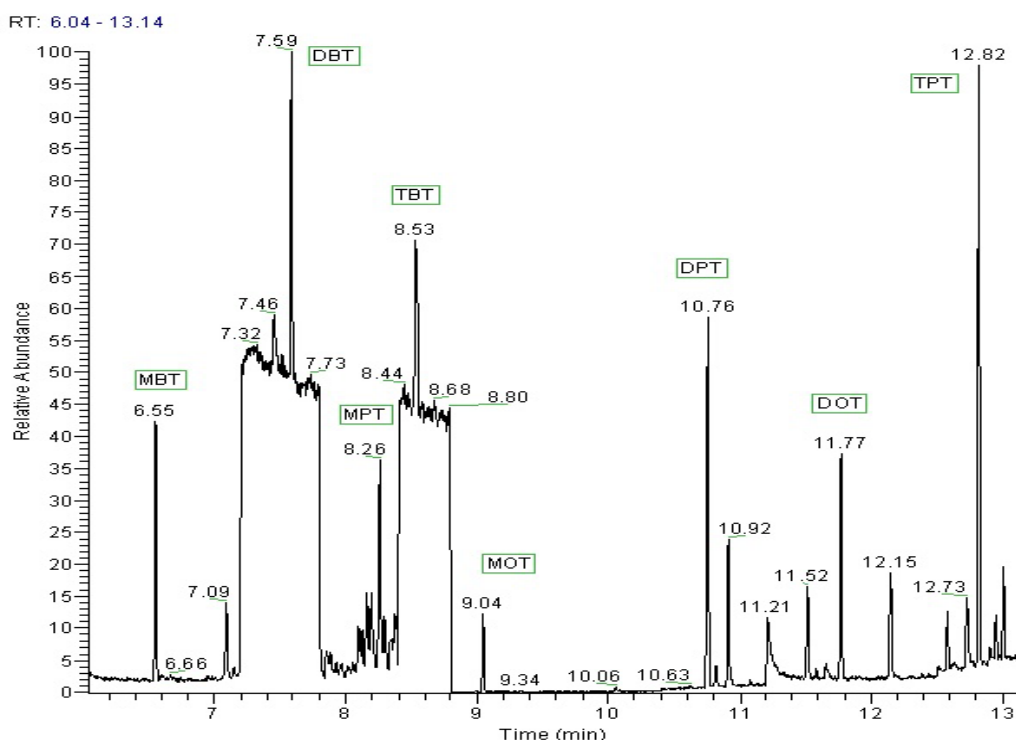
**Figure 1. TIC of the organotin compounds and a FS spectrum of TBT.**

One can see the characteristic isotopic masses belonging to  $^{118,69}\text{Sn}$  that has 10 stable isotopes, where the most abundant isotopes are:  $^{116}\text{Sn}$  (14,7%),  $^{117}\text{Sn}$  (7,7%),  $^{118}\text{Sn}$  (24,3%),  $^{119}\text{Sn}$  (8,6%),

$^{120}\text{Sn}$  (32,4%),  $^{122}\text{Sn}$  (4,6%) and  $^{124}\text{Sn}$  (5,6%) [6]. Calibration curves were obtained for all compounds, showing good linearity in the range of 1 to 100 ppb.

**Method 2: LV-PTV injection**

After optimising the large volume parameters of the PTV injector, adequate sensitivity and selectivity were achieved to quantify the compounds listed in **Table 1**. A volume of 50  $\mu\text{l}$  (hexane/isooctane 90/10) was slowly injected into a silicosteel unpacked liner at a temperature below the solvent's boiling point, producing a thin film from where the solvent was evaporated by the carrier gas stream, while the split valve was opened. In **Figure 2** a TIC of the 500 ppt standard is shown. In **Table 2** an overview is given of the calibration curves' quantitative ( $R^2$ ) results for the different compounds listed in **Table 1**. The signal to noise (S/N) calculation is given for the lowest standard measured (100 ppt).

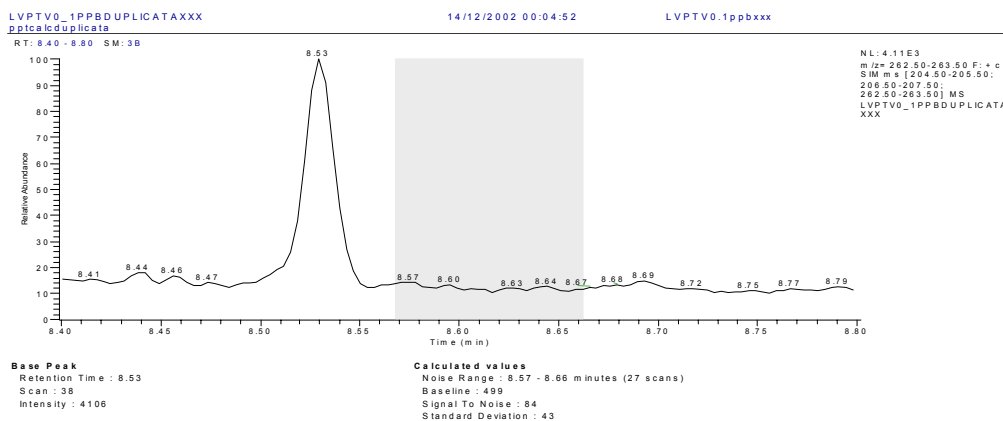
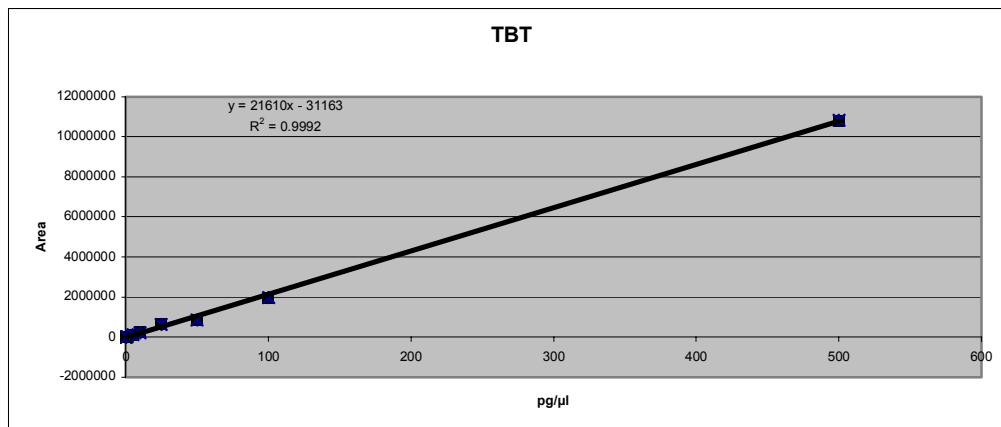


**Figure 2.** TIC of 0.5 ppb organotin compounds standard using LV-PTV injection.

**Table 2.** Correlation coefficients (linear regression plots) and S/N for the 100 ppt standard (Listed in increasing  $R_i$ , see Table 1).

Compound	Acronym	Splitless Injection ( $R^2$ )	LVI-PTV ( $R^2$ )	S/N (100 ppt) PTV-LVI
butyltriethyltin	MBT	0.9998	0.9995	47
dibutyldiethyltin	DBT	0.9905	0.9995	19
phenyltriethyltin	MPT	0.9997	0.9993	34
tributylethyltin	TBT	0.9989	0.9992	84
octyltriethyltin	MOT	0.9997	0.9985	333
diphenyldiethyltin	DPT	0.9963	0.9996	193
dioctyldiethyltin	DOT	0.9980	0.9996	591
triphenylethyltin	TPT	0.9990	0.9992	250

**Figure 3** shows the calibration curve from 0.1-500 ppb, as well as, the signal to noise calculation (100 ppt standard) for TBT.



**Figure 3.** Calibration curve of TBT using LV-PTV injection (top) and signal to noise calculation for the 100 ppt standard (bottom).

## CONCLUSIONS

In this study the quantification of organotin compounds was achieved using two different injection techniques in combination with GC-MS. Splitless injection (from 1ppb to 100 ppb) showed good linearity for all compounds, while LV-PTV injection (from 100 ppt to 500 ppb) showed good linearity throughout the dynamic range.

## REFERENCES

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