Application Note: 52099

The Determination of Organotins in Water Using Triple Quadrupole GC-MS/MS

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Key Words

- Comparison of EI-SIM and EI-SRM
- Detection Limits
- Organotin
- PTV
- Timed-SRM

Introduction

The European Union Water Framework Directive seeks to lower detection and reporting limits for many contaminants.[1] One class of these is organotins. These include mono-, di-, tri- and tetrabutyl and triphenyl tin compounds. Tributyltin compounds are considered the most hazardous, and several studies have shown the effect on shell malformation of oysters, imposex of marine snails and reduced resistance to infections.[2,3] Exposure to these compounds has been reported to cause acute kidney and central nervous disorders in humans.

Organotins are used widely in industry for a variety of applications, including as antifouling agents on underwater structures for both tributyl and triphenyltin; and triphenyltin as a fungicide in crop protection. Mono- and dibutyltin have uses as stabilizers in plastics and catalysts in soft foam production.[1,2]

Concentration levels of organotin compounds in seawater are in the ppb to ppt range. Higher concentrations are found in sediments and biological samples. Organotin compounds are lipophilic and get absorbed into adipose tissue. They can also be adsorbed onto particulate matter. The toxicity of these compounds at low concentrations drives the requirement for accurate and sensitive analytical methods for their detection, quantitation and research for less-toxic replacements.[4,5,6]

The method described in this paper uses the Thermo Scientific TSQ Quantum XLS triple quadrupole GC-MS/MS system to provide detection and quantitation limits that go below regulatory requirements with the use of timed selected reaction monitoring (t-SRM).

Sample Preparation

Derivatization and extraction of organotin compounds from water samples:[7,8,9] From the water sample, 400 mL was taken and the pH was adjusted to 5 using a 1 M acetic acid/sodium acetate buffer prior to derivatization. For the ethylation of the organotin compounds, a 2% w/v sodium tetraethyl borate solution in 0.1 M NaOH was added.

Extraction was performed by adding pentane, followed by shaking for at least ten minutes. The organic phase was transferred and slowly evaporated to 400 µL. A 3 µL injection was made on the GC.

Method

All sample analyses were carried out using the TSQ Quantum XLS™ GC-MS/MS system, equipped with a Thermo Scientific TRACE GC Ultra gas chromatograph. The TRACE GC Ultra™ was configured with a programmable temperature vaporizer (PTV) injector. Sample introduction was performed using the Thermo Scientific TriPlus AS liquid autosampler. The capillary column was a Thermo Scientific TraceGOLD TG-5MS column (5% phenyl film) of 30 m length, 0.25 mm inner diameter and 0.25 µm film thickness. An uncoated 2 m DMTPS deactivated 0.53 mm ID pre-column was used as a guard column. Selected instrument parameters are shown in Table 1.

TRACE GC Ultra

Injection Volume:	3 µL injection
Liner:	Thermo Scientific SurfaSil treated glass liner p/n PTV straight liner: 45352054 p/n SurfaSil™: TS-42800 (*)
Carrier Gas:	He, constant flow, 1.4 mL/min
Column Type:	TraceGOLD™ TG-5MS column (5% phenyl film) of 30 m length, 0.25 mm inner diameter and 0.25 µm film thickness. p/n: 26099-1420
Oven Temperature:	Initial 45 °C, Hold 2 min, Ramp 55.0 °C/min – 175 °C, Ramp 35.0 °C/min – 300 °C Hold 2.0 min
Transfer Line:	300 °C

TRACE GC Ultra PTV Injector

Injector Temperature:	50 °C, hold 0.1 min, splitless injection
PTV Transfer:	8 °C/sec to 280 °C, hold 1 min
PTV Cleaning Step:	350 °C, 11 min, clean flow 50 mL/min

TSQ Quantum XLS Mass Spectrometer

Source Temperature:	250 °C, closed EI ion volume
Ionization:	EI, 70 eV
Emission Current:	50 A
Resolution:	0.7 Da Q1, Q3
Collision Gas:	Argon, 1.0 mTorr

Table 1: Selected instrumental conditions for the TRACE GC Ultra and TSQ Quantum XLS mass spectrometer

** Treating liners with SurfaSil is described in instructions on this website www.separatedbyexperience.com/literature/pierce_instructions.pdf*

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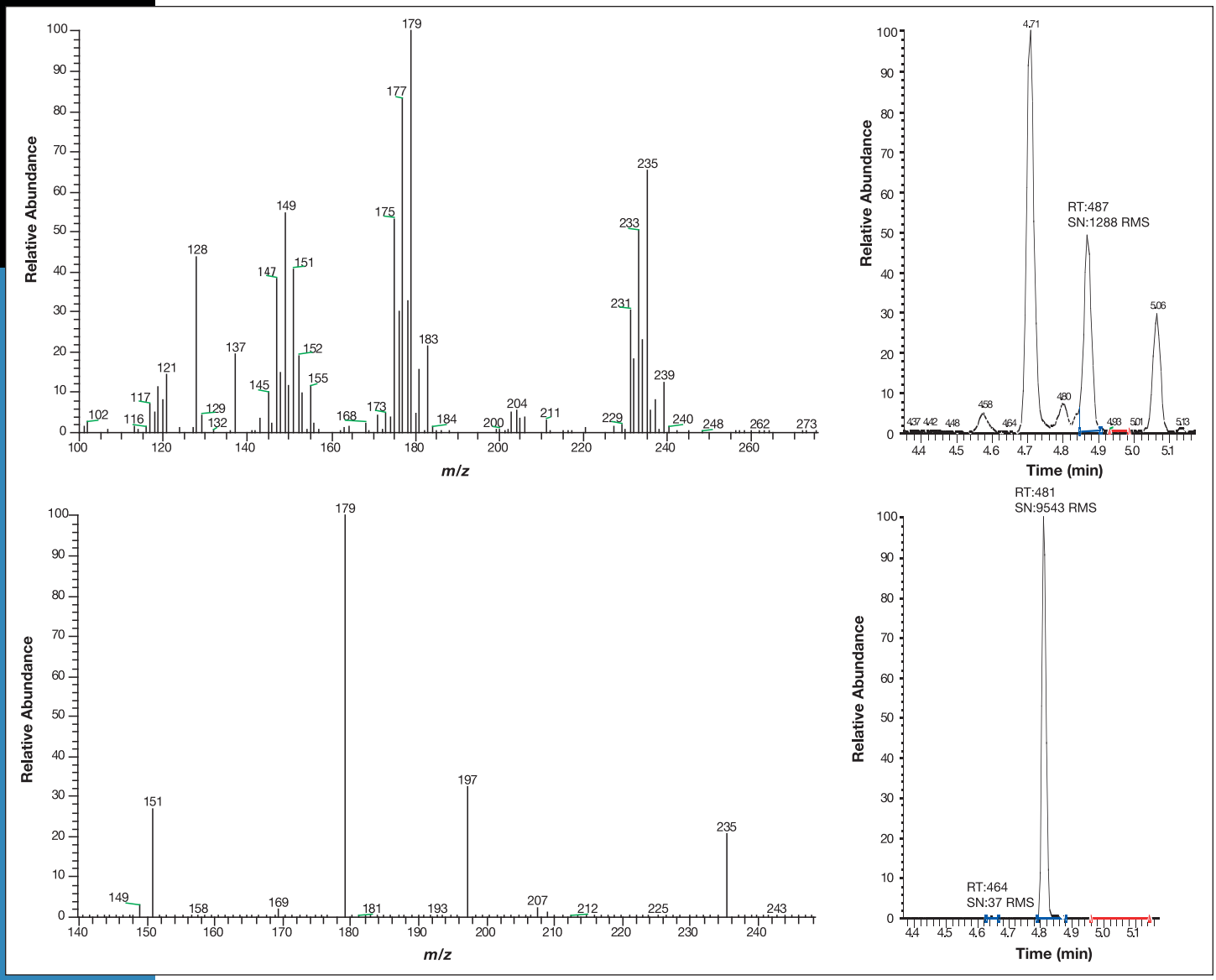

Figure 1: Clockwise: full scan spectrum of monobutyltin; S/N of *m/z* 235.08 in full scan mode; S/N of 235.08>178.95 in SRM mode; product spectrum of monobutyltin

EI-SRM Method Development

A higher-level standard was used for optimizing the transitions on the TSQ Quantum XLS operated in electron ionization (EI)-SRM mode. An example of one SRM optimization is given in Figure 1. The same procedure was followed for all organotin compounds, resulting in at least two transitions each.

The transitions that were found in the method development process were added to the t-SRM table, shown in Table 2. The start and stop times show partial overlap. This function of t-SRM allows the instrument to monitor SRM transitions more efficiently by only monitoring at the specific elution times for the compounds analyzed.

Results and Discussion

A single-point calibration was used at a level of 10 ng/L. The concentration is calculated on the actual levels in the water sample, not in neat solutions. The result shown in Figure 2 demonstrates the instrument's capability to reach 0.05 ng/L of organotins in the water sample and below. This is four times lower than the annual average stated in the Water Framework Directive. The actual amount injected on column was 0.2 pg for each organotin compound. Calculations were performed using tripropyltin as an internal standard. The ratio deviation was calculated and is shown in Table 3.

Peak identification is a key element in mass spectrometry. In SRM mode, at least two product ion transitions for each compound are needed, with peaks positively identified if the ion ratios in standards and samples are the same. The deviation for the calculated ion ratios must therefore be established by running their respective standards. Demonstration of ion ratios is shown in Table 3.

Name	Parent Ion	Product Ion	Collision Energy (V)	Start Time (min)	Stop Time (min)
Monobutyltin	235.08	150.98	6	7.44	8.44
Monobutyltin	233.08	176.95	6	7.44	8.44
Monobutyltin	235.08	178.95	6	7.44	8.44
Tripropyltin internal standard	249.08	164.91	8	8.06	9.71
Tripropyltin internal standard	245.08	160.91	8	8.06	9.71
Tripropyltin internal standard	247.08	162.91	8	8.06	9.71
Tetrapropyltin internal standard	249.08	164.91	8	8.06	9.71
Tetrapropyltin internal standard	245.08	160.91	8	8.06	9.71
Tetrapropyltin internal standard	247.08	162.91	8	8.06	9.71
Dibutyltin	261.03	205.03	8	8.92	9.92
Dibutyltin	263.03	150.98	8	8.92	9.92
Dibutyltin	263.03	207.03	8	8.92	9.92
Monoheptyltin internal standard	178.95	150.98	8	10.05	11.05
Monoheptyltin internal standard	275.07	176.95	8	10.05	11.05
Monoheptyltin internal standard	277.07	178.95	8	10.05	11.05
Tributyltin	287.09	174.94	8	10.17	12.24
Tributyltin	291.08	235.08	8	10.17	12.24
Tributyltin	289.09	176.95	8	10.17	12.24
Monooctyltin	287.09	174.94	8	10.17	12.24
Monooctyltin	289.09	176.95	8	10.17	12.24
Monooctyltin	291.08	178.95	8	10.17	12.24
Tetrabutyltin	287.09	174.94	8	10.17	12.24
Tetrabutyltin	289.09	176.95	8	10.17	12.24
Tetrabutyltin	291.08	235.08	8	11.24	12.24
Diheptyltin internal standard	275.07	176.95	8	13.21	14.21
Diheptyltin internal standard	277.07	178.95	8	13.21	14.21
Diheptyltin internal standard	245.08	145.98	8	13.21	14.21
Dioctyltin	261.03	148.98	8	14.44	15.44
Dioctyltin	263.03	150.98	8	14.44	15.44
Dioctyltin	375.17	263.03	8	14.44	15.44
Triphenyltin	196.94	119.9	18	15.71	16.71
Triphenyltin	349.15	194.98	22	15.71	16.71
Triphenyltin	351.15	196.94	22	15.71	16.71
Tricyclohexyltin	233.08	150.98	8	15.78	16.78
Tricyclohexyltin	287.09	205.03	8	15.78	16.78
Tricyclohexyltin	315.04	150.98	8	15.78	16.78

Table 2: Transitions for EI-SRM

The peaks were all easily detected at the lowest level and confirmed on two transitions. A fast method was used to allow a large number of samples to be processed per day. Figure 2 displays extracted ion chromatograms for all quantifier peaks at the 0.2 pg injected level.

Injection	Ion Ratio in %
1	72.84
2	66.29
3	70.73
4	70.87
5	70.18
6	72.84
Average	**70.62**
Stdev	**2.40**
RSD	**3.4%**

Table 3: Ion ratio in percentage for monobutyltin at 10 ng/L; the ratio between 233.08>176.95 and 235.08>178.95 was calculated

Conclusion

This method demonstrates the ability of the TSQ Quantum XLS system to exceed the EU Water Framework Directive requirements for the detection and quantitation of organotins.[1,10] The t-SRM functionality gives the instrument the ability to automatically determine optimal SRM transition times, even allowing for partially overlapping SRM transitions. This method demonstrates detection and quantitation levels to 0.05 ng/L, exceeding the EU Directive's Annual Allowable average of 0.2 ng/L. The methodology provided here offers the operator an easier implementation of this method in the laboratory.

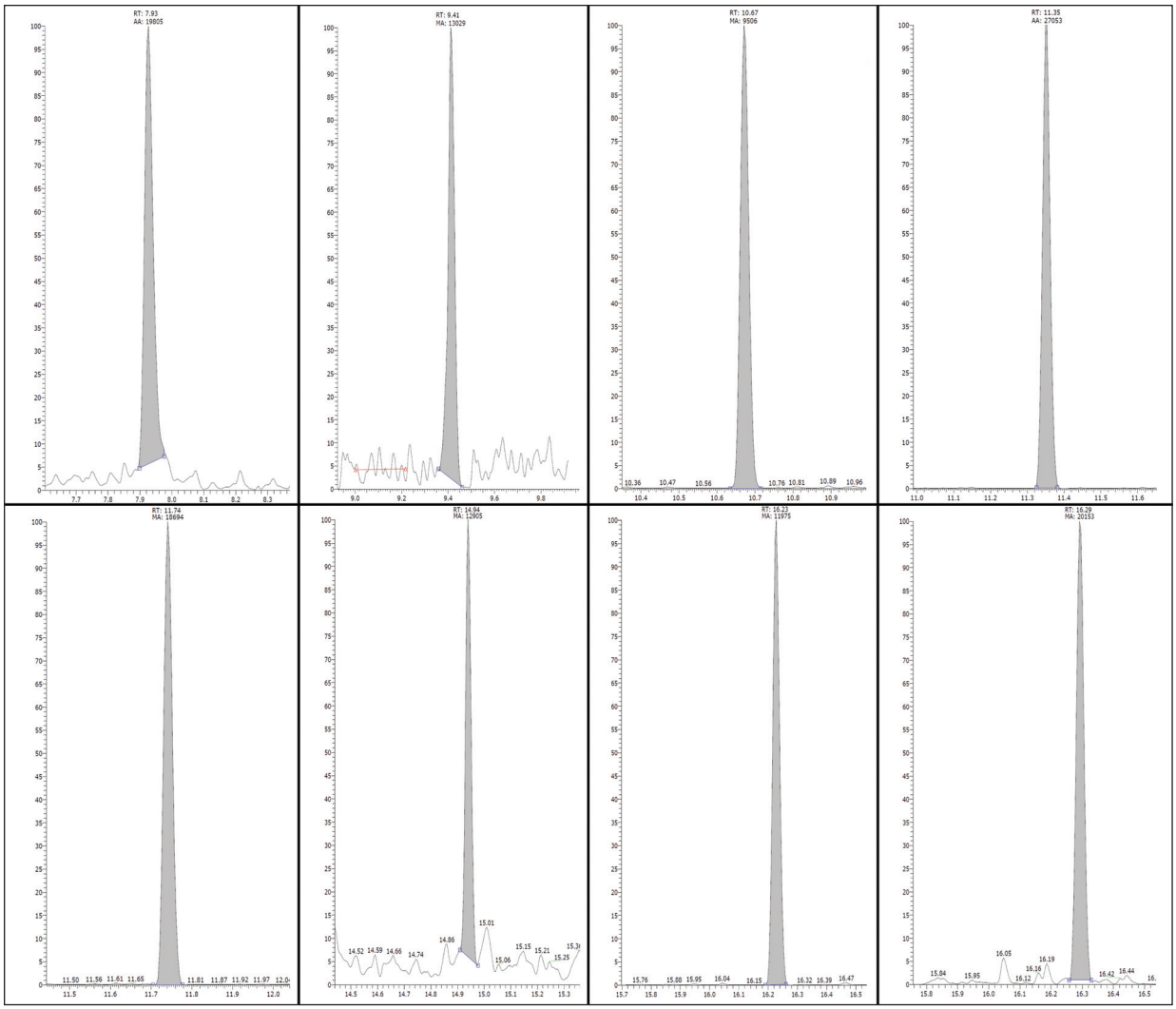

Figure 2: Compound peaks at 0.05 ng/L (0.2 pg on column). The peak names are listed in Table 4. Compounds 1 through 4 are on the top, compounds 5 through 8 are on the bottom (left to right).

	Compound	RT	Transition	Area	S/N
1	Monobutyltin	7.93	235.08>178.95	19805	103
2	Dibutyltin	9.42	263.03>207.03	13029	47
3	Tributyltin	10.67	289.09>176.95	9506	784
4	Monooctyltin	11.35	289.09>176.95	27053	2458
5	Tetrabutyltin	11.74	289.09>176.95	18694	1651
6	Dioctyltin	14.94	261.03>148.98	12905	80
7	Triphenyltin	16.23	351.15>196.94	11975	923
8	Tricyclohexyltin	16.29	233.08>150.98	20153	187

Table 4: Signal-to-noise ratio for all of the organotins at 0.05 ng/L

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