GC/MS Analysis of Organotin Compounds in the Environment

GC/MS

Varian Application Note
Number 31

Joan a. Stäb, Bert van der Horst, Joris van Kesteren,
Gerard Stroomberg, Ivo Freriks, Wim Cofino
Institute for Environmental Studies, Amsterdam, The Netherlands

Key Words: *Saturn, Organotin, Environmental, Derivative*

Introduction

Triorganotin compounds and their degradation products (OTs) enter the environment as a result of the use of OT's as biocides and in anti-fouling paints. Analysis of OTs in environmental samples is a considerable challenge for several reasons. Analytical methods have to be very sensitive and selective to be able to detect concentrations at the low environmental target values for triphenyltin and tributyltin. In most European countries environmental quality targets of 10 ng/l for water samples and 1-2 ng/g for sediments are now implemented[1]. For di- and mono-OTs, that will be formed through degradation and metabolization of triorganotin compounds, no legal standards have been established. But in view of their toxicity, it is desirable to incorporate these compounds in new analytical methods.

Discussion

In order to determine the fate of organotin compounds, several samples were analyzed. These samples included sediment, liver and muscle tissue (fillet)of predator fish (Pike) and liver samples of birds (Grebe) that feed on the fish. Table 1 shows some typical concentrations of the various OTs in the fish and birds. The extremely high concentration of dibutyltin in relation to the tributyltin in the Pike liver indicates that the tributyltin is being metabolized in the liver to produce more dibutyltin. The ratio of these two compounds in the fillet is comparable to the ratio in sediments (indicating little metabolism/ degradation). The same elevated level of dibutyltin is found in the liver of the Grebe.

The large increase in signal intensity for the liver samples demonstrates how the organotin compounds are concentrated and metabolized in the liver of the fish and birds.

Table 1: Concentrations of Organotin (µg/Kg wet weight) found in fish and birds.

	PIKE		GREBE
COMPOUND	**FILLET**	**LIVER**	**LIVER**
MONOBUTYLTIN	1.6	305	14
DIBUTYLTIN	4.6	2799	149
TRIBUTYLTIN	31	69	14
MONOPHENYLTIN	0.2	14	19
DIPHENYLTIN	28	257	22
TRIPHENYLTIN	143	460	11

Figure 1 shows a typical calibration standard for the six organotin compounds. The large unlabeled peaks in Figure 1 are the internal standards. Figures 2 and 3 show the typical total ion chromatograms and mass chromatograms that are obtained for Pike fillet and liver samples. The differences in retention time represent the occasional changing of the guard column as it becomes contaminated. Figure 4 shows the total ion chromatogram for a typical sediment sample. The matrices are extremely complex yet low picogram measurements are possible using various background ion ejection techniques such as elevated RF storage or Wave~Board ion isolation. Figure 5 shows the linear internal standard calibration curves that are obtained using the Saturn GC/MS.

Experimental

Organotin standards and samples were derivatized with Pentyl Magnesium Bromide Grignard reagent to convert the OH group to a pentyl group. The procedure is described in detail by J. Stäb et al[2]. Internal standards and surrogates were added for quantitation and recovery measurements. The following are typical retention times for the analytes.

Compound	Ret. Time (min.)
Butyltin-tripentyl	17.53
Dibutyltin-dipentyl	15.82
Tributyltin-pentyl	14.12
Phenyltin-tripentyl	22.31
Diphenyltin-dipentyl	25.51
Triphenyltin-pentyl	28.79

Gas Chromatograph	
Column:	0.25 mm x 0.25 μm with a 2 meter DB-5 30M x retention gap of deactivated fused silica 0.53 mm
Flow rate:	1 mL/min
Oven program:	70°C hold for 1 min then program at 30°C to 120°C with no hold. Program at 5°C to 260°C with no hold. Program at 30°C to 285°C and hold until matrix elutes.
SPI injector:	70°C hold for 1 min then program at 40°C per minute to 285°C and hold for 5 min.
Injection volume:	7.5 μL
Injection rate:	1.5μL/sec
Mass Spectrometer	
Mass range:	segment 1, 280-325u segment 2, 275-355u segment 3, 390-462u
Scan rate:	100 scans/min
Multiplier delay:.	11 min
Threshold:	0
Filament:	40 μamps
Background mass:	150u
Target:	5000
Ion trap:	220°C

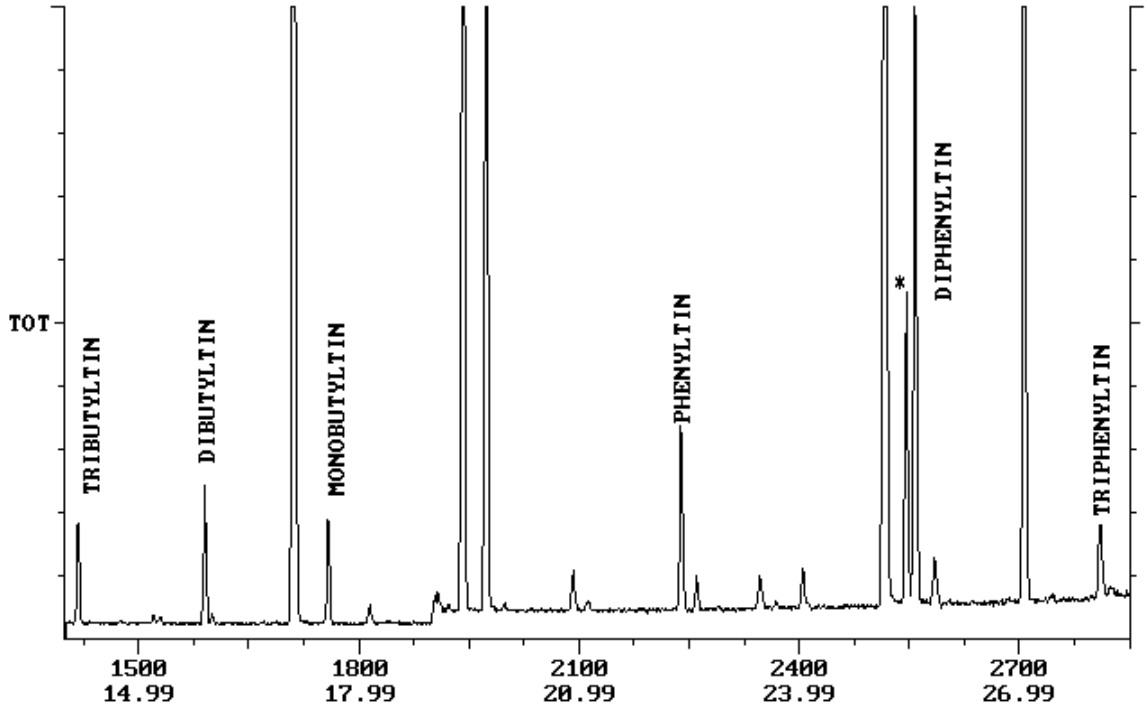

Figure 1: Total ion chromatogram of organotin standards

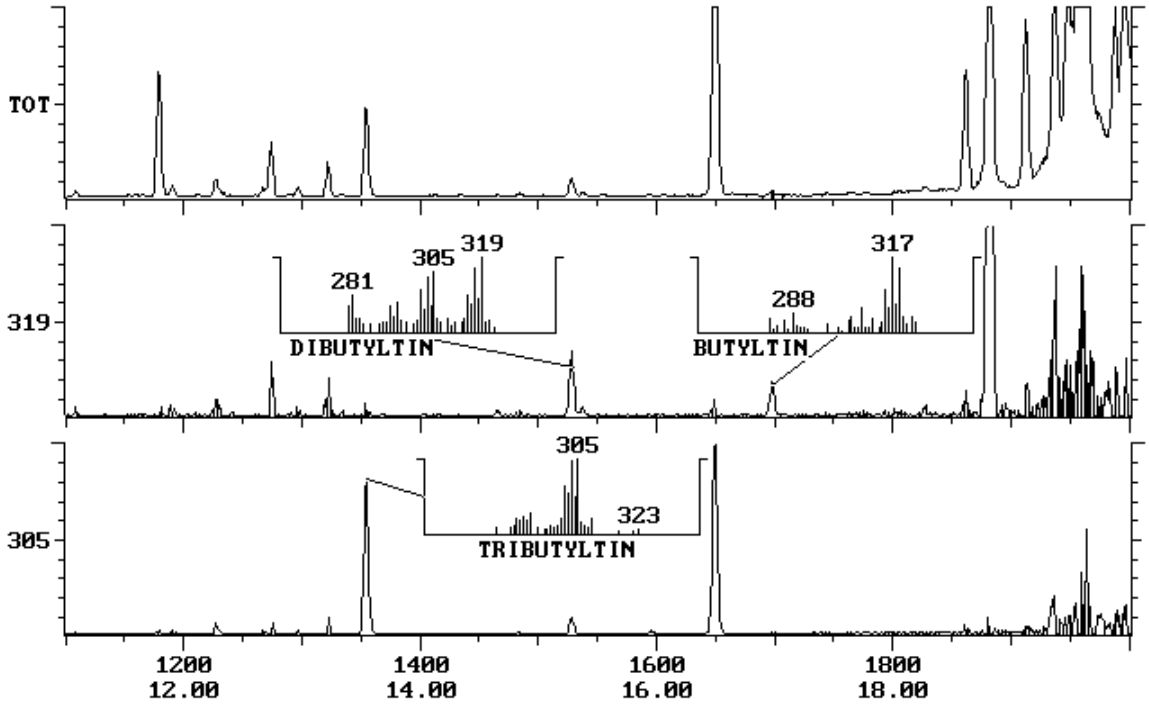

Figure 2: TIC and mass chromatogram for Pike fillet.

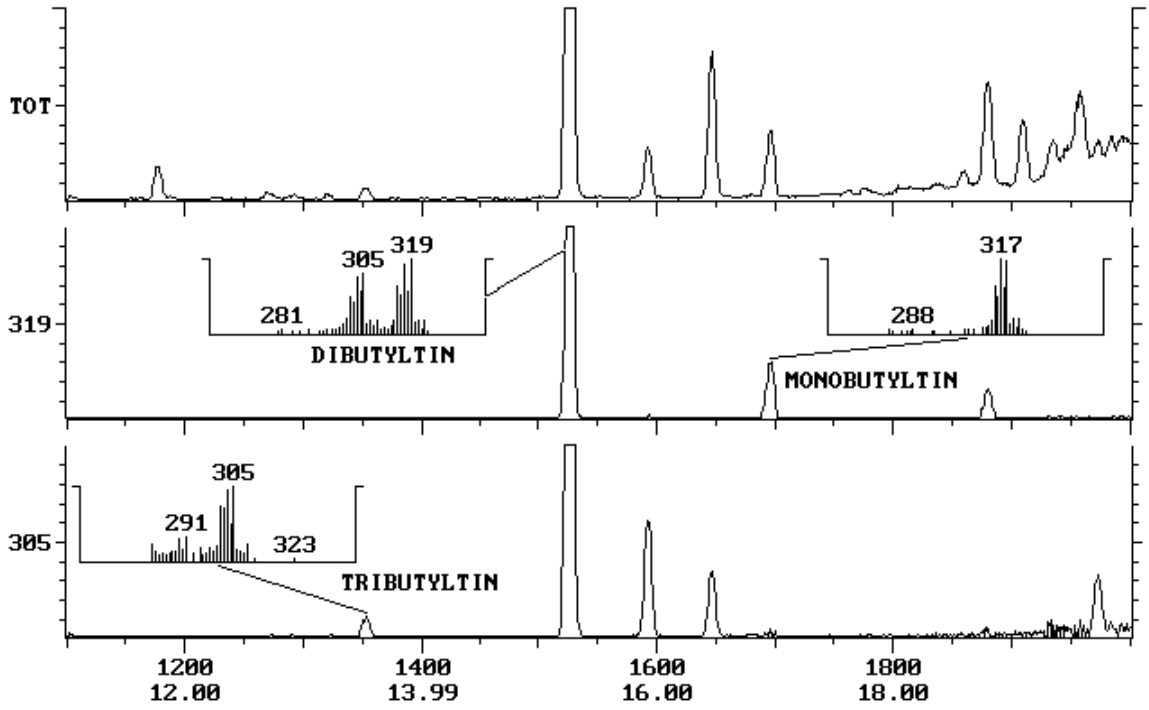

Figure 3: TIC and mass chromatogram for pike liver.

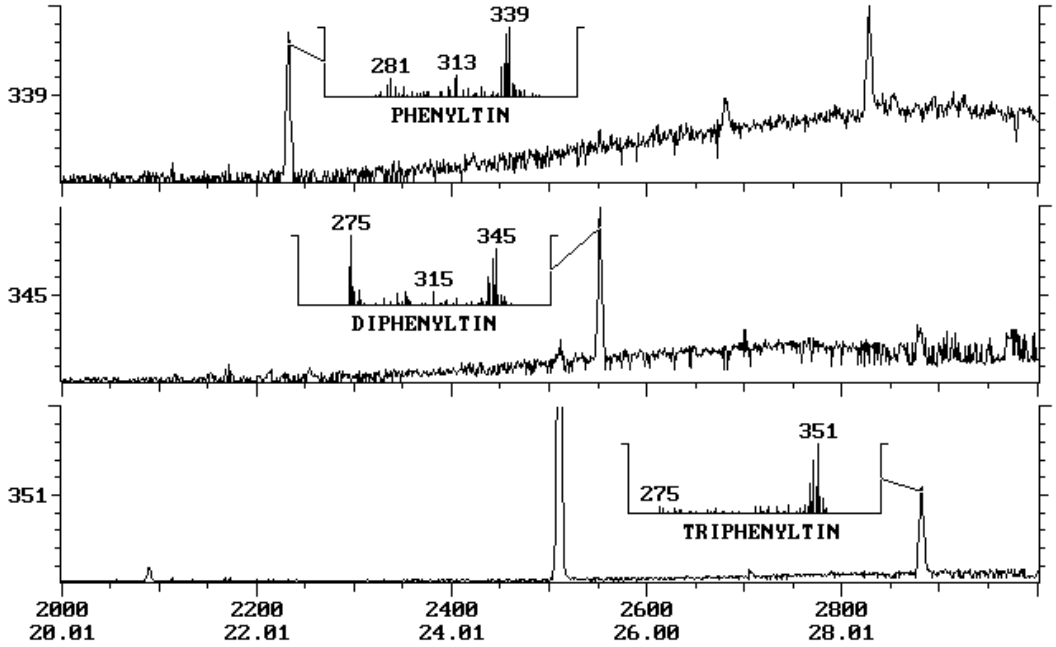

Figure 4: Mass chromatograms for a sediment sample.

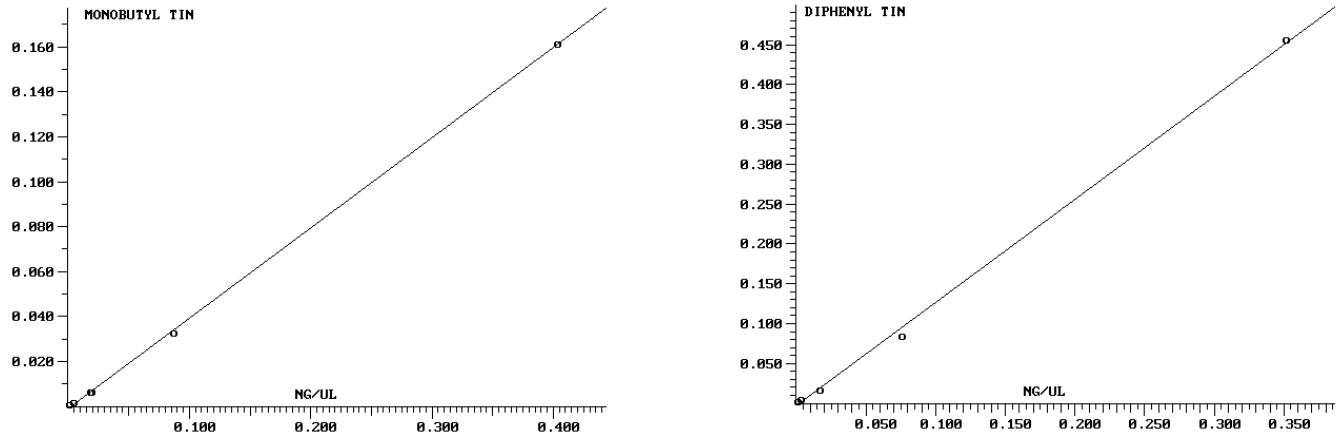

Figure 5: Typical internal standard calibration curves.

Conclusion

An analytical procedure for the analysis of organotin compounds has been developed. The procedure uses the Saturn ion trap mass spectrometer for quantitation and identification of the organotin compounds. Ultra trace levels of these compounds can be measured successfully in animal tissue and sediments.

References

1. Stäb, J A, Cofino, W P, Hattum B van, Brinkman, U A Th, Fresenius. J. Anal. Chem. 1993, 347: 247

2. Stäb, J A, Cofino, W P, Hattum B van, Brinkman, U A Th, Analytica Chimica Acta 286, (1994) 335-341.

Acknowledgment

We wish to thank Carl Feigel of Varian Chromatography Systems for his assistance in writing this manuscript.

These data represent typical results.
For further information, contact your local Varian Sales Office.