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Organotin Speciation in Environmental Samples by Capillary Gas Chromatography and Pulsed Flame Photometric Detection (PFPD)

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Pulsed flame photometric detection (PFPD) for gas chromatography was applied to organotin compounds as standards and in environmental samples. Ethylated organotin species (n-propyl-, n-butyl- and phenyl-) were extracted from spiked artificial seawater and from an environmental sample. Selectivity towards tin is shown in the analysis of highly polluted seawater samples from a commercial port where no significant interferences are found. The self-cleaning capability and long-term stability of PFPD is shown in this work during 140 days of continuous operation. The absolute limit of detection for this capillary GC–PFPD technique ranged from 0.2 to 0.4 pg (Sn) for tetraethyl- to tetraphenyl-tin, allowing determination of sub-nanogram/litre concentrations of organotin compounds. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Organotin compounds are used in a broad variety of industrial processes and products as accelerators, PVC stabilizers, coatings, polymers, cross-linking and as biocides.[1,2] One of the most species-specific toxic substances deliberately released to the marine environment is the organotin antifouling agent tri(n-butyl)tin (TBT), which is mainly used in the paints applied to subsurface areas of ships. The first effects on non-target organisms (oysters) were found by Alzieu and co-workers at the beginning of the 1980s.[3] TBT is toxic at approximately 1 ppt (ng l^{-1}) in seawater, and has caused a decline in dog whelks (*Nucella lapillus*) around the United Kingdom.[4–6] Recently effects arising from TBT in the open North Sea have been reported and related to shipping traffic intensities.[7]

The scope of this work was to implement an analytical method for the simultaneous determination of organotin species from ethyl to phenyl derivatives in environmental samples at concentration levels of ecological concern. Over the last two decades a large number of analytical techniques have been developed and applied to the determination of organotin compounds in environmental matrices. The separatory power of gas chromatography (GC) in combination with tin-selective and -sensitive detection methods such as flame photometry (FPD) is widely used.[2] Nevertheless, self-contamination of important parts of the photometer by tin oxides and other low-volatility and inert oxides is a major concern, especially when analysing environmental samples.[8] The detection of organotin compounds by GC–FPD can encounter interferences from sulphur- and phosphorus-containing compounds, that may be abundant in environmental samples, and therefore analysis of biota and harbour water samples requires a highly selective method. Interferences have been reduced using dual-channel FPD, but self-contamination still remains.[8]

Pulsed flame photometric detection (PFPD) is suggested to be self-cleaning by the pulsed flame propagation principle and, furthermore, may have better selectivity and higher sensitivity towards elemental tin detection as proposed by the developers Amirav and Jing).[9]

In this work PFPD has been successfully

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applied for organotin determination at ultra-trace levels in important environmental matrices.

EXPERIMENTAL

Reagents

Sodium tetraethylborate ($NaEt_4B$) was obtained as capsules from Fluorochem Ltd, UK, and made up to a 10% stock solution in methanol (LiChrosolv, Merck), and was dried with anhydrous Na_2SO_4 (Merck p.a.). The extraction solvent was n-pentane (Merck p.a.), redistilled at our laboratory; pH adjustment reagents were 30% HCl (Merck, Suprapur®), sodium acetate (NaAc) and sodium hydroxide (NaOH Merck, p.a.).

The standards used were tri(n-propyl)tin chloride, tetraethyltin, tetra(n-propyl)tin and tetraphenyltin, all from Johnson–Matthey and Alfa, Germany; di(n-butyl)tin dichloride, tri(n-butyl)tin chloride and tetra(n-butyl)tin were from Fluka Chemie, Buchs, Switzerland; mono(n-butyl)tin trichloride was from Ventron GmbH, Karlsruhe, Germany; triphenyltin chloride was obtained from Merck–Schuchhardt, Munich, Germany.

Standard preparation

Standards were dissolved (weight per volume) in methanol. Stock solutions of 1000 $mg\,l^{-1}$ level (as Sn) was diluted at a factor of 25–100 per step using glass precision flasks and full 1 ml pipettes with precision ±0.007 ml.

No ethylated standards were commercially available.

Instrumentation

The system consisted of a Varian 3500 gas chromatograph equipped with a Varian 1077 split/splitless injector and a pulsed flame photometer detector also from Varian Chromatography (Walnut Creek, CA, USA). The separation was performed on a fused silica capillary column type DB-5, from J & W Scientific (Folsom, CA, USA) of 20 m length, 0.25 mm i.d. and 0.25 μm film thickness. The prepared samples were introduced manually using hot needle injection into the 220 °C quartz frit splitter lined injector, operated splitless for 2 min. The detector was set 350 °C with a BG-12 colour filter and gas flow-rates of Air_1 to 17 ml min^{-1}, Air_2 to 10 ml min^{-1} and H_2 to 13.5 ml min^{-1} giving a pulse frequency of 2.6 Hz.

Water sample preparation

The sample preparation step is an *in situ* ethylation followed by organic solvent extraction.[10,11] A seawater sample was collected in the commercial port of Copenhagen, acidified with HCl ($pH<2$) and stored in the dark at 4 °C until analysis. The sample was spiked with tri(n-propyl)tin chloride (TPrT) as internal standard at 50 ng Sn l^{-1}. For standardization, artificial 20% seawater was prepared using sea salt from Sigma, in Milli-Q filtered water and acidified with HC1 to $pH<2$ followed by spiking of various organotin species alone and in mixture.

All water samples were prepared as follows: a pH adjustment to 5.5 ± 0.5 (as described in detail elsewhere[12]) using 10% NaAc and 20% NaOH in Milli-Q aqueous solution. A 400 ml sample was loaded into a 500 ml separatory funnel and oxygen-stripped by argon gas over 20 min. The *in situ* ethylation was carried out by adding 500 μl of a 10% $NaEt_4B$ stock solution, mixing well, and allowing a reaction time of 10 min. Extraction into 10 ml n-pentane was carried out by vigorous shaking for 1 min. After allowing phase separation to occur (approx. 10 min), the organic phase was collected and dried with anhydrous Na_2SO_4. Samples with a low organotin content were preconcentrated under a flow of cool nitrogen.

RESULTS AND DISCUSSION

Chromatographic performance

The chromatographic separation of most of the environmentally relevant organotin substances is demonstrated in Fig. 1. The peak tailing of organotin compounds is believed not to originate from separation problems by the capillary column, but only from the combustion chemistry of tin compounds and troublesome tin-oxide formation as described by Au *et al.*[8] and by Müller.[13,14] This is supported by chromatograms with peaks not containing tin, where no tailing is found.

The chromatographic stability of this GC–PFPD system given by the retention times of the individual peaks has a relative standard deviation (RSD) of 0.4% in 18 repetitive manual injections

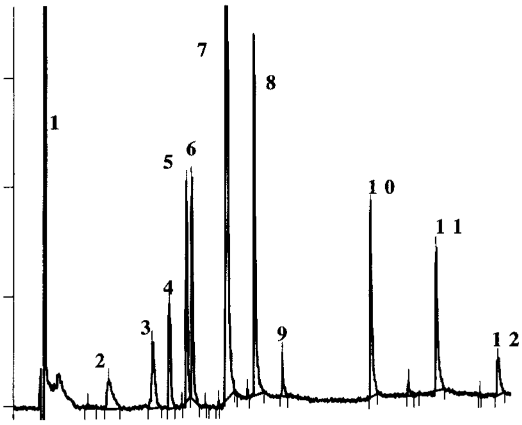

Figure 1 An ethylated organotin standard mix spiked to artificial seawater (concentration ranges from 1 to 200 μg l^{-1} as Sn): 1, solvent peak; 2, Sn(IV); 3, mono(n-butyl)tin; 4, tri(n-propyl)tin; 5, tetra(n-propyl)tin; 6, di(n-butyl)tin; 7, tri(n-butyl)tin; 8, tetra(n-butyl)tin; 9, diphenyltin; 10, triphenyltin; 11, tetraphenyltin; 12, tetraoctyltin.

ranging from 0.5 to 1000 μg l^{-1} as Sn, with no difference observed when injecting solutions with high concentrations of organotins. The peaks were verified on another GC under the same conditions, with detection using inductively coupled plasma mass spectrometry,[15] thus routine identification of peaks was possible from the retention times. The internal standard commonly used for quantification of butyltin species, tri(n-propyl)tin (TPrT), has traces of di(n-propyl)tin (DPrT). The ethylated DPrT might interfere with ethylated MBT due to an equal number of carbon atoms after the ethylation, but with these chromatographic conditions there is a time difference of 0.2 min that is enough for proper integration of both peaks. Furthermore, the TBT standard contains DBT at approximately 2%, which could lead to an underestimation of TBT concentrations in natural samples when calibration calculations are based on a 100% purity assumption on the available standards. There is no addition of diphenyltin, but this peak (as diethyldiphenyltin) also appears as a multiorganotin mixed chromatogram (Fig. 1), as an impurity in triphenyltin.

Tetra(organo)tin species were used in the instrumental calibration of the GC-PFPD as external standards because no ethylated organotin standards are commercially available at the present time. The correlation (r^2) ranges from 0.9991 to 0.9995 with a linear range of four orders of magnitude based on peak height. The same integration methods as for conventional FDP are considered to be appropriate due to the typical tin tailing and SnO_2 formation within the detector.[16]

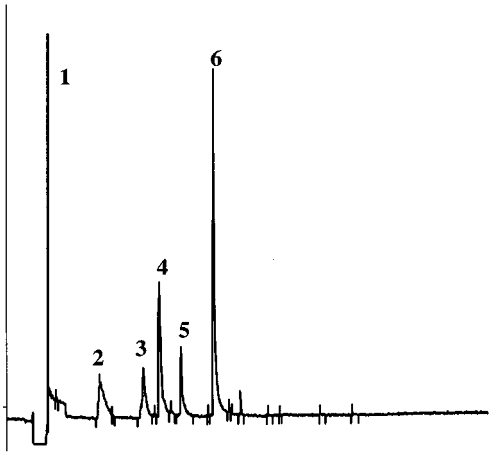

Figure 2 Ethylated seawater sample from the commercial port of Copenhagen. Concentrations as Sn: 1, solvent flame out; 2, Sn(IV) 5 ng l^{-1}; 3, mono(n-butyl)tin, 6 ng l^{-1}; 4, tri(n-propyl)tin (internal standard), 19 ng l^{-1}; 5, di(n-butyl) tin, 9 ng l^{-1}; 6, tri(n-butyl)tin, 46 ng l^{-1} as Sn.

A chromatogram from the commercial port of Copenhagen is shown in Fig. 2 and gives no evidence of interfering substances although this port is generally expected to be highly polluted due to intense commercial shipping activities.

Instrumental limits of detection

The chromatogram of a low-concentration injection standard solution is shown in Fig. 3. The limit of detection is determined by the formula:

$$\text{Limit of detection} = t(\text{dF})_{0.995} \cdot s(n)$$

where t is the Student t-distribution and dF denotes degrees of freedom, in the case $10 - 1 = 9$; s is the standard deviation of each compound peak and n the number of independent repetitions.

The limits of detection (LOD) for propylated and butylated tins are presented in Table 1. These concentrations are similar to or better than those listed in a recent review.[2]

Long-term stability

The determination of organotin compounds by flame photometry is influenced by the formation of tin oxide and fouling on vital photometric parts, such as quartz surfaces. Repetitive injec-

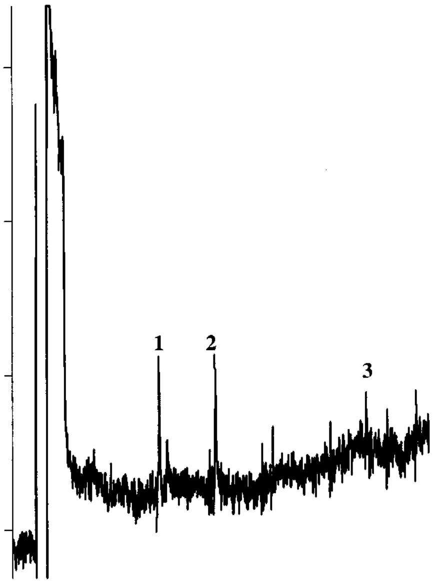

Figure 3 Chromatogram of an injection near the limit of detection. Injected amounts were (as Sn): 1, 0.62 pg tetra(n-propyl)tin; 2, 0.70 pg tetra(n-butyl)tin; 3, 0.36 pg tetraphenyltin.

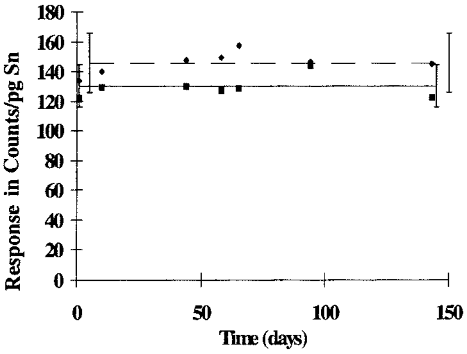

Figure 4 Time stability of PFPD over 140 days of operation for tetra(n-propyl)tin (■) and tetra(n-butyl)tin (◆). The mean and 95% confidence limits are shown for both species: ——, tetra(n-propyl)tin; ———, tetra(n-butyl)tin.

tions of high concentrations of tin-containing compounds have been shown to be a major problem in the detection of organotin compounds using conventional flame detectors for gas chromatography.[16] To test the self-cleaning capability of PFPD on the assumption that contamination of the quartz surfaces would lead to a decline in the tin signal a standard mixture, i.e. a control mixture of low-concentrations of tetra(n-propyl)tin (12.4 $\mu g\, l^{-1}$ as Sn) and tetra(n-butyl)tin (13.9 $\mu g\, l^{-1}$ as Sn), was injected frequently over a 140-day period of organotin analysis, including changes of the capillary column. The results are presented in Fig. 4, where the variance of 5% for both substances is within the precision of the manual injection; thus, no evidence of decline in tin response using GC–PFPD was found in this study. The theory of the self-cleaning capability of PFPD, as emphasized by Amirav and Jing,[17,18] is therefore strongly supported by our work.

Table 1 The instrumental (absolute) limits of detection for organotin compounds

	Injected amount (pg Sn)	LOD (pg Sn)
Tetra(n-propyl)tin	0.62	0.3
Tetra(n-butyl)tin	0.70	0.2
Tetraphenyltin	0.36	0.4

CONCLUSION

This study demonstrates that PFPD is a stable, sensitive and selective detection method in the speciation of organotin compounds in environmental samples. Specially important for tin determination are the self-cleaning capability and the linear dynamic range which make the pulsed flame detector appropriate in the routine analysis of tin-containing compounds in complex matrices.

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