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DETERMINATION OF BUTYLTIN COMPOUNDS IN SEDIMENTS USING AN IMPROVED AQUEOUS ETHYLATION METHOD

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Summary—We have determined tributyltin and dibutyltin species in various environmental sediment samples (marine, harbour and river sediment) using the *in situ* aqueous ethylation–gas chromatography–atomic absorption spectrometry method subsequent to extraction by methanol containing 0.5*M* HCl. The present technique provides a significantly lower detection limit than previous methods, so that tributyltin can for the first time be measured in some of the samples. Thus, the method described is well suited for the determination of tributyltin and dibutyltin compounds in sediments with low levels of butyltin species (*e.g.*, Main River, 1.7 ng of tributyltin as Sn/g dry sediment).

There is growing concern over the presence and impact of anthropogenic butyltin compounds in the environment. Butyltin compounds can enter the aquatic environment through antifouling paints used on boats and through municipal and industrial wastewaters.[1,2] Tributyltin (TBT) is extremely toxic to a wide variety of aquatic organisms.[3] TBT effectively inhibits the growth of fouling organisms that attach to boat hulls, but unfortunately also exhibits toxicity toward non-target organisms.[4,5] The first large-scale environmental effect of TBT was reported in an oyster-growing area in France in 1980.[6] Similar effects were also observed at other locations around the globe.[7] These observations eventually led many countries to legally constrain the use of TBT-containing antifouling paints.[5] As a result, TBT concentrations in marina and harbour waters and sediments have declined in some areas, for example, in San Diego Bay, California[8] and in certain United Kingdom estuaries.[9] In order to monitor decreasing TBT concentrations in the environment and to evaluate the remaining threat to ecosystems from reduced TBT concentrations (thus assessing the effect and appropriateness of legislation), the development of accurate and sensitive analytical methods for measuring butyltins at extremely low concentrations in varied environmental matrices is essential. Further, as a consequence of additional butyltin compounds usage for other purposes, the presence of butyltin residues in municipal wastewater and sewage has been confirmed.[2,10,11,12]

Several techniques to measure butyltin species in sediments have been reported. Many of these methods employ derivatisation and separation by standard chromatographic techniques, and subsequent determination by atomic absorption spectrometry (AAS),[13,14] mass spectrometry (MS),[15,16] flame photometry (FPD),[17–19] and atomic emission spectrometry (AES).[20,21] Two methods in particular have been used for the derivatisation of the relatively involatile organotin compounds bound to chlorides, oxides, hydroxides or to unknown counterions: (1) hydride generation[13,14,17,22] and (2) alkylation by Grignard reagents, *e.g.*, RMgX.[10,15,16] Both of these methods have disadvantages when applied to environmental samples. The hydride formation method using sodium borohydride ($NaBH_4$) is convenient for the derivatisation of organotin compounds, but often suffers from interference. For instance, the signal has been found to be suppressed in the presence of diesel oil and sulphides, both of which can occur at high levels in sediment samples.[23–25] The second method, alkylation by Grignard reagents, can only be performed on completely dry media. Thus organometallic species in aqueous

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samples, including water, sediment, *etc.*, have to be first extracted to an organic solvent and then dried prior to alkylation by Grignard reagents. The large number of handling steps required affect the accuracy and precision of the determination. Rapsomanikis *et al.* have introduced the use of sodium tetraethylborate ($NaBEt_4$) as a derivatisation reagent for the analysis of methyllead and methylmercury ionic compounds.[26,27] Recently, we developed the aqueous ethylation method for the determination of butyltin species in a river sediment.[29,30] It employs *in situ* ethylation of butyltin species in aqueous solution, followed by gas sparging, cryogenic trapping, separation, and subsequent detection by AAS. It requires no clean-up steps and no preconcentration. Foaming does not occur and high pressure does not build-up in the reaction vessel. The handling steps are kept to a minimum and the entire procedure takes place *in situ.*

Varying analytical interference may be encountered with different types of sediment. We carried out this study to assess the viability of this analytical method for the determination of butyltin species in variety of environmental sediments. Here we present the results of the investigation on tributyltin and dibutyltin species in marine, harbour and river sediments. Further, during the course of this work, we were also able to improve on previous analytical conditions.

EXPERIMENTAL

Apparatus

Analysis was performed using a method described in detail elsewhere.[29] Briefly, the procedure consists of the following steps: (a) the butyltin species in sediment extract are first reacted with $NaBEt_4$ in a glass reaction vessel to convert the ionic butyltin species to the corresponding butylethyltin; (b) the butylethyltins are stripped from solution by a helium stream and are cold trapped (using liquid nitrogen) on chromatographic packing; (c) the species are separated in order of increasing boiling points by heating the trap to $+200°$ and detected by an electrothermally heated quartz furnace in an atomic absorption spectrometer.

Reagents and standards

Monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), and monomethyltin (MMT), dimethyltin (DMT), trimethyltin chlorides (TMT) (Alfa-Ventron) and sodium tetraethylborate (Strem) were used without further purification. The methanol was analytical or "for liquid chromatography" grade. The hydrochloric acid, nitric acid, acetic acid and sodium acetate were "Suprapur" (Merck). All other chemicals were analytical grade or better.

The organotin stock solution was prepared at a concentration of approximately 1000 mg/l. as tin in methanol and was stored in the refrigerator at *ca.* $+4°$. The mixed organotin working solutions were prepared daily by diluting the stock solution with Millipore water to a range of 20–80 $\mu g/l.$ as tin. A fresh solution of approximately 1% (w/v) sodium tetraethylborate was prepared daily with deionised water, and stored in the refrigerator. The acetic acid–sodium acetate buffer, 1000 ml (pH 4.05) was prepared by mixing 800 ml of $0.2M$ acetic acid and 200 ml of $0.2M$ sodium acetate, and stored in a polyethylene bottle at room temperature.

Sediment sampling

Ten sediment samples were collected from marine, harbour and river environments. Four freeze-dried marine sediment samples were obtained from the Laboratoire de Chimie Analytique, Université de Pau, France. Three Hamburg harbour sediment samples obtained from the Institute of Chemistry, Forschungzentrum Geesthacht GmbH (GKSS), Germany, were freeze-dried upon arrival at our laboratory. River sediment samples were collected from the Schwarzbach to the east of Mainz and from the Main River adjacent to Großkrotzenberg, Germany, respectively, and were immediately freeze-dried upon arrival at the laboratory.

Sediment extraction

A 1.5-g amount of sediment sample was placed in a polycarbonate tube, and then a measured volume (25–100 ml) of methanol containing $0.5M$ hydrochloric acid was added. The sample was sonicated at 51 kHz for 2 hr and then the pH of the sample was adjusted to 4.2 with $2.0M$ sodium acetate. Subsequent to centrifugation for 20 min at 4000 rpm, the supernatant solution was decanted and stored in a polycarbonate bottle. The sediment was extracted and analyzed in duplicate using the ethylation–AAS method. This extraction procedure has produced the least interference in determining TBT and DBT in a Main River sediment sample.[29,30]

Analytical procedure

A 1-ml volume of HOAc–NaAc buffer and a Teflon-coated stirring bar were placed in the reaction vessel, then a measured volume of extract (0.1 ml–16 ml), concentrated acetic acid (1.0 ml–8.0 ml), and $NaBEt_4$ solution (130 μl–800 μl) were added. The amounts of acetic acid and $NaBEt_4$ solution added to the reaction vessel depended on the volume of extract used for the determination. The reaction vessel was closed and secured with a stainless steel clamp. The helium flow was switched to by-pass the reactor via a four-way valve, and the reaction was allowed to continue for 14 min under continuous stirring. The cold trap was cooled with liquid nitrogen to −196°, and then the four-way valve switched to pass helium through the reactor. After the solution was purged for 9 min, the helium flow was again switched to by-pass the reactor, the liquid nitrogen was removed and the temperature programme was initiated. At first, the variable transformer was set at 1.3 A for approximately 3.3 min to heat the column to 120°. The transformer was then turned up to 2.20 A so that the column reached a final temperature of 200°. The ethyl derivatives of methyltin and butyltin elute in approximately 4.0 min.

Quantitation

Peak areas were used for quantitative calculation. Peaks in the gas chromatograms were assigned to individual organotin compounds on the basis of retention time and were confirmed by standard addition. For the calculation of organotin concentrations in sediment extracts, three-point standard addition was performed to account for matrix interference. In the case of sediment samples with very low concentrations of tributyltin, one-point standard addition was used to compensate for the larger amounts of extract required to complete a single analysis. All analyses were carried out at least in duplicate.

RESULTS AND DISCUSSION

Butyltin concentrations in sediments

Previous results have shown that the variable-volume-extraction-method (VVEM) is a reliable procedure for the assessment of recoveries and true content of butyltins in sediment in the absence of suitable standard reference material.[14,29,30]

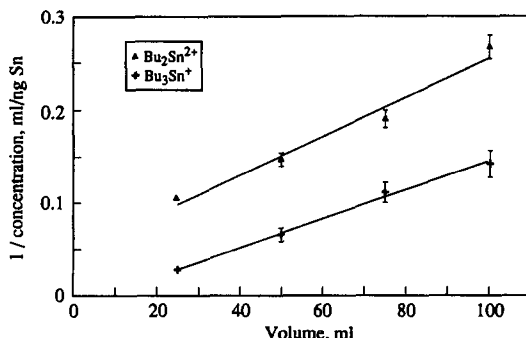


Fig. 1. Results of extraction experiments on Hamburg harbour sediment No. 1.

A series of different volumes of solvent were used to extract an aliquot of sediment and then the true content of compound was calculated from the slope of reciprocal concentration against the volume of solvent (*e.g.*, Fig. 1; see also Refs. 29 and 30). In the present work, 25, 50, 75 and 100 ml of methanolic HCl were employed to extract the majority of the sediment samples. However, because of the low concentration of TBT in Main River sediment, only 25 and 50 ml were used for this sediment extraction.

The analytical results of some sediment samples (one marine, one Hamburg harbour and the Schwarzbach sediment) are shown in Figs. 1, 2 and 3. For most of the sediment samples, the DBT and TBT results fit a linear relationship. For MBT, however, quantitative determination was not possible using this extraction and analytical method. This may be due to the loss of MBT during the centrifuge procedure where it may be coprecipitated with colloid material.[30] Thus, MBT is not discussed

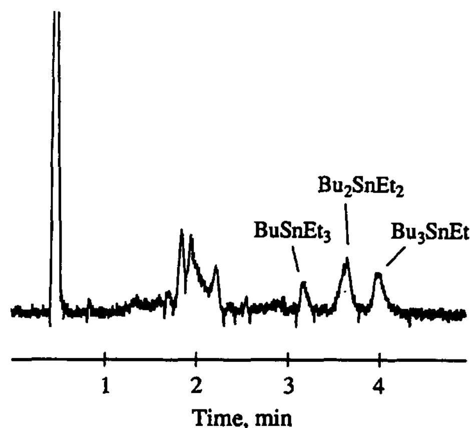


Fig. 2. Chromatogram of butyltin compound analysis in Main River sediment sample by ethylation method. 50 ml of extraction solution was used, 16 ml of which was analysed.

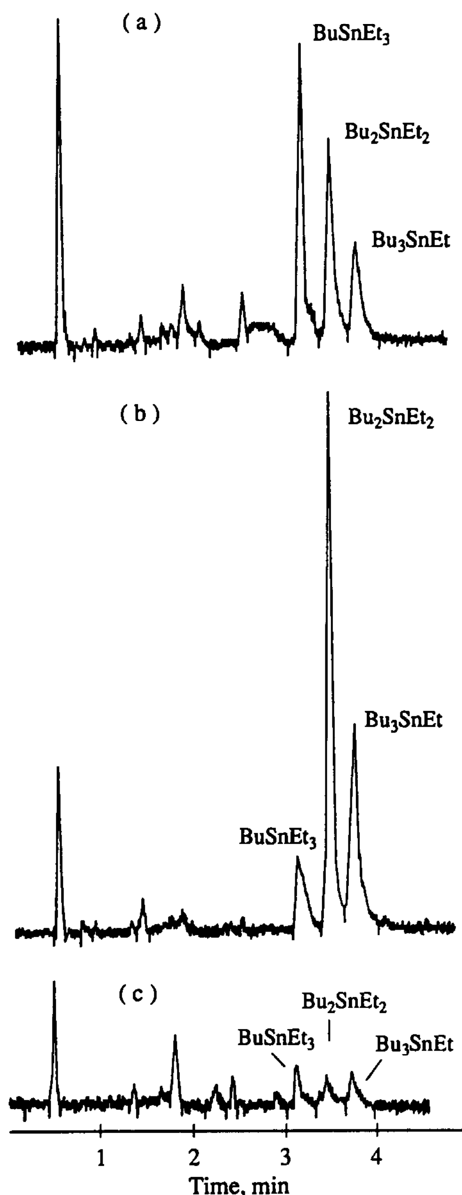


Fig. 3. Chromatograms of butyltin compound analysis in marine sediment C. 50 ml of extraction solution was used, 5 ml of which was analysed. (a) 4 ml acetic acid (pH: 2.6) and (b) 8 ml of acetic acid (pH: 2.3) were added. (c) The pH of reaction solution was adjusted to 2.3 by hydrochloric acid.

here. Concentrations calculated from linear equations for dibutyltin and tributyltin species in the sediment samples are presented in Table 1.

One of the initial objectives of our work was to assess the viability of the *in situ* aqueous ethylation method for the determination of butyltin compounds in different kinds of sediments. TBT and DBT were found in all sediment samples in a concentration ranging from 1.7 (Main River sediment) to 460 (Hamburg harbour sediment sample 1) ng TBT as Sn/g dry mass, and from 3.1 (marine sample B) to 319 (Hamburg harbour sediment sample 1) ng DBT as Sn/g dry mass. The Hamburg harbour area is subject to strong contamination from butyltins (levels ranging from 110 to 460 ng Sn/g dry mass for TBT, and from 50 to 319 ng Sn/g dry mass for DBT). The lowest concentration of TBT was found in the Main River sediment sample.

Here we emphasize that the *in situ* aqueous ethylation–AAS method achieves low concentration detection limits in the determination of butyltin compounds, especially for TBT, in sediment samples. We have established that the detection limit for TBT in Main River sediment is 0.44 ng Sn/g dry sediment. Prior to the development of the ethylation–AAS method, several sediment samples used in the present work had been analysed using hydride generation–atomic absorption spectrometry (HG–AAS) method which did not show TBT in Main River sediment and Schwarzbach sediment samples.[31] When a sample with a low concentration of analyte is analysed, a large amount of extract must be analysed in a single measurement. For the HG–AAS method, however, the amount is limited by analytical interference and foaming. The concentration detection limit is therefore affected because only small amounts of extract can be added to the reaction vessel. The ethylation method overcomes these disadvantages,[30] and a larger amount of sediment extract can be used in the analytical procedure. Hence the detection limit for butyltin species in sediment is significantly improved. A typical chromatogram of butyltin species in Main River sediment using the ethylation method is displayed in Fig. 2.

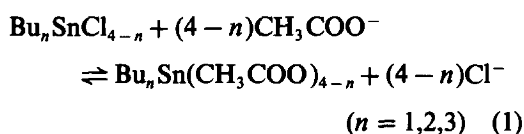
Table 1. Dibutyltin and tributyltin concentrations in sediment samples (ng Sn/g dry mass)

	Bu_2Sn^{2+}	Bu_3Sn^+
Marine sediments		
A	4 ± 2	69 ± 21
B	3 ± 1	19 ± 2
C	128 ± 6	103 ± 21
D	5 ± 1	47 ± 2
Hamburg Harbour		
1	319 ± 35	460 ± 23
2	50 ± 12	110 ± 29
3	246 ± 14	401 ± 90
Main River sediment	11 ± 7	2 ± 0.2
Schwarzbach sediment	84 ± 19	23 ± 4

Ethylation procedure

During the development of the analytical procedure, we found that the ethylation efficiency can be improved significantly by adding a suitable volume of concentrated acetic acid into the reaction vessel before $NaBEt_4$ is added. Initially, the resulting change in pH was suspected to be the cause of this improvement because the addition of acetic acid resulted in the pH of the reaction solution decreasing from 4.1 to approximately 3.0. To test this hypothesis, hydrochloric acid instead of acetic acid was used, following a similar experimental procedure. Figure 3 shows that the pH of the reaction solution was not the main cause of the improvement in the analytical results and that acetic acid and hydrochloric acid have pronounced, but different effects on the ethylation procedure.

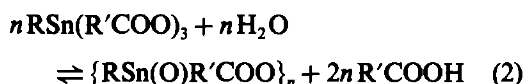
We used $0.5M$ HCl in methanol as extraction solvent. Butyltin species can be expected to exist in $Bu_nSnCl_{(4-n)}$ forms in this solution. During analysis, an aliquot of extract was added to 10 ml of NaOAc–HOAc buffer. Further addition of acetic acid should promote the reaction of butyltin chloride complexes with acetic acid to form the corresponding butyltin carboxylates.[32]



$$Bu_nSnCl_{4-n} + (4-n)CH_3COO^- \rightleftharpoons Bu_nSn(CH_3COO)_{4-n} + (4-n)Cl^- \quad (n = 1,2,3) \quad (1)$$

From the experimental results, it appears that the ethylation reaction is more efficient on butyltin carboxylate than on butyltin chloride complexes. Thus, the addition of acetic acid to the reaction solution promotes a higher yield during ethylation of butyltin species by $NaBEt_4$. In contrast, adding hydrochloric acid to the reaction solution shifts the equilibrium from carboxylate to chloride as a dominant ligand and thus causes butylethyltin yields to decrease (Fig. 3).

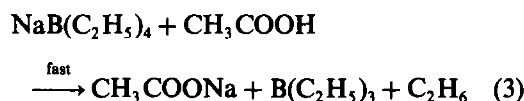
Comparing the results in Fig. 3, we find that a better analytical result was obtained using 4 ml rather than 8 ml of acetic acid in the determination of monobutyltin. Dibutyltin and tributyltin, however, show different behaviour. An explanation for this could be that the chlorides in the monoorganotin trichloride are not easily substituted by other ligands.[32,33] One or two chlorides may remain complexed with tin. This difference in behaviour may also originate from the differential hydrolytic stability of butyltin carboxylates.[32] Most triorganotin carboxylates are hydrolytically stable, whereas the diorganotin derivatives undergo partial hydrolysis to form the dimeric distannoxanes $R_2Sn(R'COO)OSnR_2(R'COO)$ and $R_2Sn(R'COO)OSnR_2OH$. The monoorganotin tricarboxylates are readily hydrolysed to form the monoorganotin oxycarboxylates (Reaction 2).



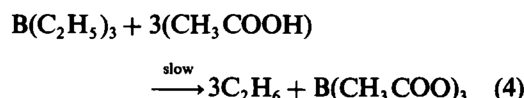
$$nRSn(R'COO)_3 + nH_2O \rightleftharpoons \{RSn(O)R'COO\}_n + 2nR'COOH \quad (2)$$

Mössbauer and infrared data suggest that the monoorganotin oxycarboxylates exist as polymers or oligomers in the solid state with Sn-O-Sn bridges and chelating carboxyl groups. Clearly, polymers or oligomers are not expected to react efficiently with $NaBEt_4$ to form butyltriethyltin.

On the other hand, the amount of acetic acid used in the analytical procedure must be kept within limits due to the instability of sodium tetraethylborate in acid solution. Excessive addition of acetic acid promotes the hydrolysis of sodium tetraethylborate.[34]



$$NaB(C_2H_5)_4 + CH_3COOH \xrightarrow{\text{fast}} CH_3COONa + B(C_2H_5)_3 + C_2H_6 \quad (3)$$



$$B(C_2H_5)_3 + 3(CH_3COOH) \xrightarrow{\text{slow}} 3C_2H_6 + B(CH_3COO)_3 \quad (4)$$

In this work, satisfactory analytical results were achieved when 4–8 ml of acetic acid was added to the reaction solution (pH 2.5–3.0).

It should be noted that we have previously shown that for the extraction of butyltin compounds from sediments, acetic acid alone is not an efficient extraction solvent.[35] In other words, acetic acid improves the ethylation of butyltin species by $NaBEt_4$, but it is not appropriate for the extraction of butyltins from sediment samples. Further, calculation of the true ethylation yields would require the synthesis of ultrapure butyltin ethyl derivatives and comparison of calibration graphs made from these standards with calibration graphs from ionic butyltin standards ethylated in aqueous sediment matrix. Hence, although we notice the improvement in the ethylation yields, we cannot claim that in real sediment extracts, acetic acid assists to achieve quantitative yields.

CONCLUSIONS

Tributyltin and dibutyltin species were analysed in marine, harbour and river sediment samples. The results show that the *in situ* aqueous ethylation–AAS method presents a highly suitable analytical technique for the determination of TBT and DBT in environmental sediments. This is especially true for sediments with lower levels of butyltin species because of lower concentration detection limits and reduced interference offered by the present analytical procedure. The ethylation reaction yields of butyltin with sodium tetraethylborate can be enhanced by adding a suitable volume of acetic acid to the reaction solution. It is reasonable to assume that the reaction yields, during the aqueous ethylation with sodium tetraethylorate, are higher for butyltin acetates than for their corresponding chlorides.

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