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Note

Determination of butyltin species in water by gas chromatography with flame photometric detection

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Organotin compounds are used in three major ways, *viz.*, as thermal stabilizers for polyvinyl chloride, as catalysts in the production of polyurethane foams and as biocides[1]. The increasing annual usage of organotins raises the possibility of environmental pollution. Organotins are a class of compounds about which more information is sought under Canada's Environmental Contaminants Act[2] regarding toxicology and environmental fate. We chose to examine the aquatic environmental fate of bis(tri-*n*-butyltin) oxide (TBTO), and this article describes the method we have established for the determination of TBTO and some of its possible[1] de-alkylation products in natural waters.

Our method is a refinement of an earlier method[3] which involved (1) extraction of TBTO, Bu_2Sn^{2+}*, $BuSn^{3+}$ and Sn^{4+} from water, (2) derivatization with a methyl Grignard reagent to form the various $Bu_nMe_{4-n}Sn$ species, and (3) analysis by gas chromatography–mass spectrometry. This method is suitable for the parent TBTO; however, it is not suitable for Bu_2Sn^{2+}, $BuSn^{3+}$ and Sn^{4+} since the derivatives Bu_2Me_2Sn, $BuMe_3Sn$ and Me_4Sn are fairly volatile compared with solvents such as hexane and benzene, and appreciable quantities of the derivatives are lost during routine concentration procedures such as "rotary" and "vortex" evaporating of solvents. The same problem is encountered with (1) the series of ethyl derivatives, $Bu_nEt_{4-n}Sn$ when $n \leq 2$, and (2) the series of *n*-propyl derivatives, $Bu_nPr_{4-n}Sn$ when $n \leq 2$ (ref. 4).

Our approach is to make *n*-pentyl derivatives of TBTO and its de-alkylation products. The species $Bu_nPe_{4-n}Sn$ are all sufficiently non-volatile compared with hexane or benzene that none are lost in solvent "stripping", yet they are volatile enough to be analyzed by gas chromatography (GC). We used a modified flame photometric detector which has been shown to be sensitive to organotins[5–9].

EXPERIMENTAL

Materials

TBTO (97%), tetrabutyltin (97%), dibutyltin dichloride (96.5%), butyltin trichloride (95%), tin (99.99%), 48% HBr and *n*-pentylmagnesium bromide in diethyl

* Bu = *n*-butyl, Pe = *n*-pentyl, Me = methyl, Et = ethyl, Pr = *n*-propyl.

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ether were obtained from Ventron (Danvers, MA, U.S.A.); 2-hydroxy-2,4,6-cycloheptatrien-1-one (tropolone) was from Aldrich (Milwaukee, WI, U.S.A.), and was recrystallized from diethyl ether before use (m.p. 52°C, uncorr.). All organic solvents were pesticide grade from Caledon Labs., Georgetown, Ontario, Canada.

Preparation of $Bu_nPe_{4-n}Sn$ standards

$Bu_nPe_{4-n}Sn$ species where $n \geq 1$ were prepared according to the method of Meinema *et al.*[3] except that the derivatization was carried out under refluxing conditions. The derivatives were purified by passage through a 1 m × 2 cm I.D. column of 5% water-deactivated Florisil, with hexane as eluent. Fractions of 5 ml were collected and the presence of organotins confirmed by thin-layer chromatography with dithizone developer[3]. Appropriate fractions were pooled, dried with magnesium sulfate and stripped of solvent; standard solutions of the derivatives in hexane were prepared by weighing and subsequent decadic dilution. All standards were ≥98% pure by GC with electron capture (ECD), flame ionization (FID) and flame photometric detectors (FPD); the standards were stable in the dark at room temperature for at least six months.

For the synthesis of Pe_4Sn, solutions of Sn^{4+} were prepared by dissolution of Sn in hot concentrated HCl and subsequent dilution to an appropriate volume such that the final concentration of HCl was 10% (v/v). These aqueous solutions were extracted with freshly prepared solutions of 1% tropolone in benzene. This procedure ensured quantitative (100 ± 3%) extraction of Sn^{4+} from the aqueous phase as shown by the pyrocatechol violet assay for Sn[10]. The organic phase was then treated with Grignard reagent and Pe_4Sn was purified as described above.

Analysis for butyltins in water

Twenty-five ml of 10-ppm solutions of TBTO (Bu_3Sn^+) and its debutylated metabolites Bu_2Sn^{2+} (as dibutyltin dichloride), $BuSn^{3+}$ (as butyltin trichloride) and (acidified) Sn^{4+} in distilled water, tap water or Hamilton Harbour (Lake Ontario) water were acidified with 25 ml of 48% HBr. The acidified solutions were extracted (2 × 25 ml) with freshly prepared solutions of 1% tropolone in benzene, and the extracts were derivatized as described above. The analyses of each of the organotins, and of solutions of all the organotins together, were done five times to check the efficiency of extraction from water and the yields of the derivatization reactions.

The $Bu_nPe_{4-n}Sn$ derivatives were detected with a Tracor 550 gas chromatograph equipped with a Melpar FPD and a Spectra-Physics 4000 integrator. The FPD was modified in three ways: (i) for maximum photomultiplier response to tin, the interference filter was replaced with a round sheet of metal foil[5] which had a 0.5 cm diameter hole half way between the center and the top of the foil, (ii) the detector inlet ports for hydrogen and air were reversed to avoid solvent flameout[11] with no change in sensitivity or linearity of response and (iii) copper tubing was wound around the photomultiplier tube to allow thermostating at 25°C. A 2 m × 2 mm I.D. glass column containing 3% OV-225 on Chromosorb WHP (80–100 mesh) was used under the following conditions: inlet and outlet temp., 220°C; detector temp., 240°C; nitrogen carrier, hydrogen and air flow-rates of 25, 100 and 80 ml/min, respectively (these flow-rates were optimal for the FPD in the reversed configuration[11], and a separate supply of oxygen was not required). Optimal column temperatures were

TABLE I

ANALYSES OF BUTYLTINS IN WATER BY FPD

Species	*% Extraction from water*			*% Yield of derivatization*	*Minimum detectable amount (pg)*	*Linear response range (pg)*
	Distilled	*Tap*	*Hamilton Harbour*			
Bu_3Sn^+	98 ± 5	101 ± 6	96 ± 4	100 ± 3	1.5×10^2	1.5×10^2–3.0×10^4
Bu_2Sn^{2+}	100 ± 3	95 ± 7	97 ± 6	96 ± 6	1.2×10^2	1.2×10^2–3.0×10^4
$BuSn^{3+}$	96 ± 8	99 ± 5	103 ± 8	95 ± 7	1.0×10^2	1.0×10^2–2.0×10^4
Sn^{4+}	94 ± 9	104 ± 6	98 ± 7	99 ± 4	6.0×10^1	6.0×10^1–2.5×10^4

Initial organotin concentration in water, 10 ppm.

135°C for Bu_3PeSn, 145°C for Bu_2Pe_2Sn, 155°C for $BuPe_3Sn$ and 165°C for Pe_4Sn. Ten aliquots of each butyltin solution, at each concentration tested, were injected to check for (i) reproducibility of injections, (ii) active sites on the column which would necessitate "priming" and (iii) detector poisoning.

Determinations of the purity of the $Bu_nPe_{4-n}Sn$ derivatives were also made with an ECD and an FID mounted on the same gas chromatograph, and under the same general conditions. Mass spectra of the derivatives were obtained with a Finnigan 3200 gas chromatograph–mass spectrometer equipped with a Ribermag 1000 data system.

RESULTS AND DISCUSSION

Table I shows the results of the butyltin analyses. The extractions are quantitative no matter the source of the water. Extractions of each butyltin and Sn^{4+} from aqueous solutions of all four species together were also quantitative. It is important to prepare the tropolone–benzene solution immediately before extraction of the aqueous phase (we recommend less than 5 min). We have noted, for example, that a tropolone–benzene solution prepared 18 h earlier extracted only 20% of Sn^{4+} from a 10-ppm solution. We have also noted that poor extraction efficiencies for Sn^{4+} were obtained if the tropolone were added to the aqueous phase before extraction with benzene, rather than the reverse. Not all the butyltins required tropolone for extraction. For example, TBTO can be quantitatively extracted from water into benzene or hexane alone; however, in the interests of documenting a general method we recommend the use of tropolone for all butyltin species.

The yields of the derivatization reactions were also quantitative, even in the case in which all four tin species are together. TBTO can be quantitatively pentylated at room temperature, but $BuSn^{3+}$ and Sn^{4+} require refluxing for quantitative reaction.

Fig. 1 shows a chromatogram of all four derivatives. The minimum detectable amounts injected were about 100 pg with linear responses over concentration ranges of at least 100. These detection limits could probably be improved significantly with different instrumentation; for example, using a modified version of a newer commercially available FPD, Aue and Flinn[9] were recently able to detect as little as 0.04 pg of

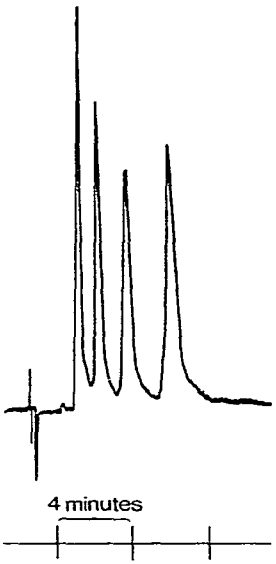

Fig. 1. Isothermal chromatogram (135°C) of about 4 ng each of, in order of elution, Bu_3PeSn, Bu_2Pe_2Sn, $BuPe_3Sn$ and Pe_4Sn. FPD conditions as described in the text.

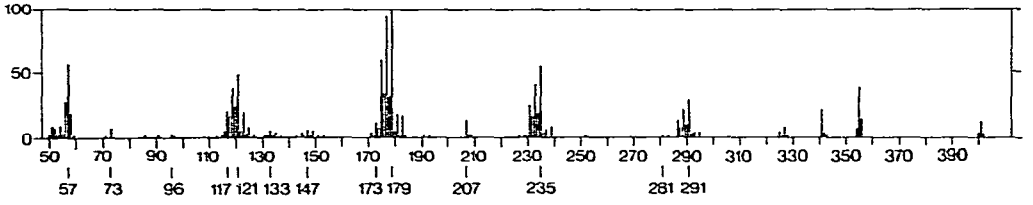

Fig. 2. Mass spectrum of tetrabutyltin, Bu_4Sn.

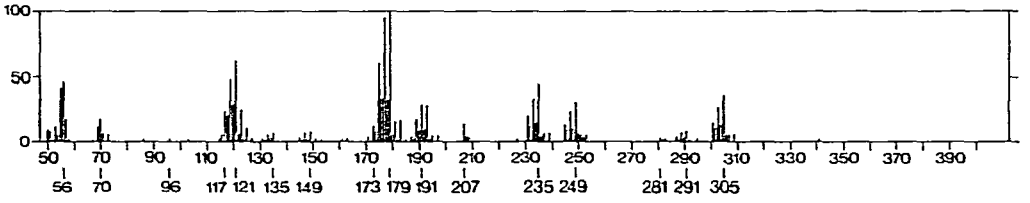

Fig. 3. Mass spectrum of tributylpentyltin, Bu_3PeSn.

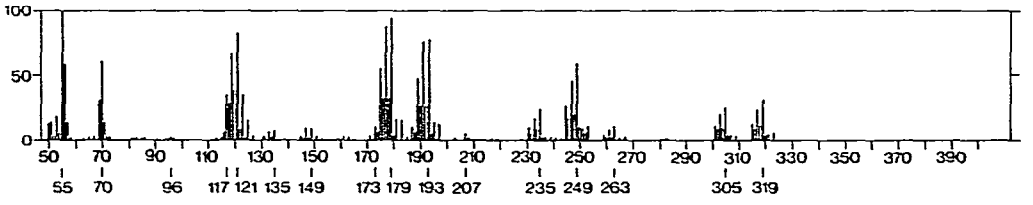

Fig. 4. Mass spectrum of dibutyldipentyltin, Bu_2Pe_2Sn.

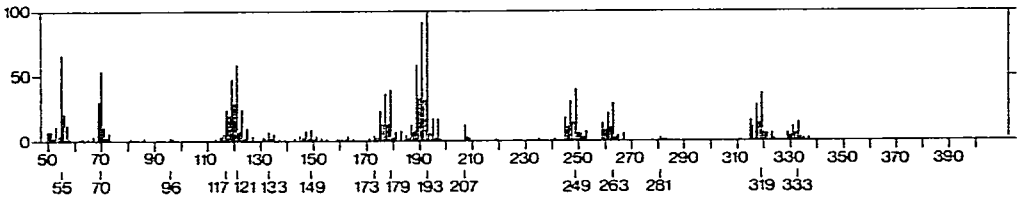

Fig. 5. Mass spectrum of butyltripentyltin, $BuPe_3Sn$.

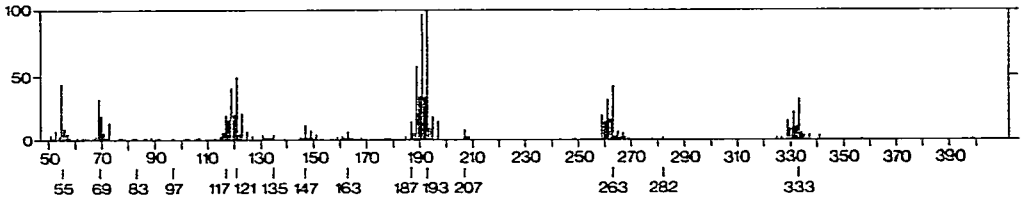

Fig. 6. Mass spectrum of tetrapentyltin, Pe_4Sn.

tetrapropyltin. Our FPD can be poisoned by injections of more than 10^2 ng, but does recover slowly with time. Tailing of organotin peaks such as seen in Fig. 1 has been ascribed to the detector rather than the column[6]; our results support this contention in that priming the OV-225 column with $Bu_nPe_{4-n}Sn$ standards did not reduce the tailing. The reproducibility of peak area with multiple injections was excellent.

Figs. 2–6 are mass spectra of the four derivatives and tetrabutyltin which is shown for comparison. Mass spectra could be obtained with about 25 ng of derivative. The typical tin cluster is evident as are losses of butyl and pentyl groups, but the striking feature is the disappearance of the cluster centered at *m/e* 179 ($BuSnH_2^+$) and the appearance of the cluster centered at *m/e* 193 ($PeSnH_2^+$) as *n* decreases in the series $Bu_nPe_{4-n}Sn$.

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