ANALYSIS OF SEDIMENT SAMPLES FOR SELECTED ORGANOTIN COMPOUNDS

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Five marine sediments supplied by EPS Vancouver were analysed for tri-, di- and monobutyltin compounds. Extracts were split and analysed independantly by Seakem using GC/MS/SIM and Dr. Jim McGuire of Canada Centre for Inland Waters using GC/FPD. Triphenyltin compunds and free tin (IV) were also determined by GC/MS and GC/FPD respectively. Two samples were extracted and analysed in duplicate by GC/MS.

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1. METHODS

The sediments were extracted by a method based closely on that of Dr. James McGuire (1) of Canada Centre for Inland Waters (CCIW). One half of the extract was shipped to CCIW for analysis and one half retained and analysed at Seakem by GC/MS/SIM as described by Meinema et al. (2).

1.1 Materials

Solvents (benzene, hexane and ether) were of distilled in glass 'pesticide' grade (Burdick and Jackson or BDH Omnisolv). Silica gel was activated by heating to 350oC for 12 h in a forced air oven. Sulphuric acid (ultra-pure grade, double distilled in quartz, Seastar Chemicals) was diluted to 0.5 M and serially extracted with dichloromethane then hexane before use. Tropolone (2-hydroxy-cyclohepta 2,4,6 trienone, Sigma Chemicals) was used as received.

The Grignard reagent, n-pentymagnesium bromide, was prepared as required using redistilled n-pentyl bromide (BDH Chemicals), magnesium turnings, and pesticide grade diethyl ether dried by double distillation off sodium metal.

Glassware and metal items were cleaned by detergent wash, distilled water rinse, then air dried and baked at 350°C overnight. Nonbakeable items were solvent rinsed (acetone, benzene then hexane) before use. Procedural blanks were carried through the method before and during analysis to determine blank levels, which were found to be undetectable for the four GC/MS target compounds.

GC/MS response calibration standards were prepared by derivation of bis-tributyltin ether, tributyltin chloride, dibutyltin dichloride, and butyltin trichloride (Aldrich Chemicals) with n-pentyl magnesium bromide by the following procedure. Approximately 200 mg of each precursor (0.3 - 0.8 millimoles) were weighed out accurately and taken up in sodium dried ether (25 mL) in a separatory funnel (100 mL). Pentylmagnesium bromide (10 mL of 1-6 Molar solution in ether, 16 millimoles) were added, allowed to stand 15 minutes, sulphuric acid added (25 mL of 0.5M, pre-extracted), shaken and the ether layer separated. The aqueous phase was extracted with 3 x 10 mL ether, the combined extracts washed with water (3 x 100 mL), dried over anhydrous sodium sulphate, quantitatively transferred and made up to 100 mL with benzene in a volumetric flask. Tin compound concentrations were calculated in µg tin per gram of dried sediment.

1.2 Extraction

The frozen sediment sample was allowed to thaw and a 30 g subsample taken and air dried at 20°C for 24 h. Approximately 10 g of dried sediment were accurately weighed into a 500 mL flask; 100 ml benzene and 1 g tropolone were added and the sample refluxed for 2 h. The benzene extract was decanted off and dried through an anhydrous sodium sulphate column (1.8 x 15 cm, granular Na_2SO_4). Pentyl magnesium bromide solution (1.6 M in diethyl ether, 12 mL) was added and refluxed for 1 h, cooled and shaken with 100 mL of 0.5 M sulphuric acid. The benzene layer was separated and washed by shaking with distilled water, separated and dried by standing over anhydrous sodium sulphate. The dried extract was taken down by vacuum rotary evaporation to 2 mL and cleaned up by elution through a silica gel column (1.8 x 15 cm, 3-70 mesh, 100% activated) with 100 mL hexane. The extract was taken down to 4 mL by vacuum rotary evaporation. If colour was still present the extract was further cleaned by repetition of the silica gel column chromatography. The extracts were accurately split into two equal 2.0 mL samples for GC/MS and GC/FPD analysis. One half of each sample was sealed into a 8 mL ampule and shipped to Dr. James McGuire (National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario) for GC/FPC analysis for butyl tin compounds. An internal standard (2.0 µg d_{10}anthracene) was added to the remaining extract which was blown down to 100 µL by dry nitrogen for GC/MS analysis at Seakem.

1.3 Instrumental Analysis

The samples were analysed using a Finnigan 9500/3200 gas chromatograph/mass spectrometer with a Finnigan G100 interactive data system. Butyltin and triphenyltin compounds present as the pentyl derivatives were detected using the selected ion monitoring (SIM) mode, set to monitor three abundant and charactristic ions of $(pentyl)_n(butyl)_{n-4}tin$, i.e., 121, 179 and 193 at 120, 193 and 351 for triphenylpentyltin. The parent ion of the internal standard, d_{10}anthracene was monitored at 188.

The following conditions were used:

Column:	SGE BP-5, 25 m x 0.22 mm bonded phase
Carrier:	helium at 14 psi (split), 38 psi (splitless) flow rate, 2 mL·min^{-1}
Injector:	Grob type, splitless for 1 minute. Flow rate 60 mL·min-, split into 30:1.
Temperature Program:	200C 2 minutes, 100oC for 4 minutes then 100.min^{-1} to 280oC and cool.
Column/MS Interface:	Direct insertion of column up to MS source.
Temperatures:	Injector: 250oC Interface: 270oC Analyser: 100oC
MS Source:	emission current 0.50 mA electron impact at 40 V
MS Scan Rate:	4 selected ions·sec^{-1}
Selected Ions:	188 (Internal Std.); 120, 121, 179 193 and 351
Data:	acquired on hard disc and archived on magnetic tape cartridge.

1.4 Quantification

The GC/MS retention time and response of the pentyltin derivatves relative to the perdeuterated anthracene internal standard was determined using a calibration standard containing pentyltributyltin, dipentyldibutyltin, tripentylbutyltin, pentyltriphentyltin and the internal standard (2.0 ng· μL^{-1}). The mass chromatogram peak areas for the internal standard (188+ ion) and characteristic ion for the organotins were determined on the 6100 data system by manually controlled integration at the appropriate retention time window.

The quantification is based on the ratio of the 179+ ion peak area to the 188+ ion peak area, and in conjunction with retention times the ratio of 179 to the other characteristic ions is used as a confirmation of the assignment of the compound, as described in the quality assurance section. Sediment concentrations are calculated on a dry weight basis as μg·g^{-1} tin.

1.5 Quality Control/Quality Assurance

Throughout this sample suite, steps were taken to verify the analyses were being conducted in a state of analytical control with includes the following:

1) Procedural blanks indicated interference or contamination levels were below the limit of detection.

2) Replicate instrument calibration before and after sample analysis.

3) Linearity of GC/MS method confirmed over three orders of magnitude including the concentration range encountered in these samples.

4) The identify of the derivatised organotins were confirmed by continuous scan GC/MS.

5) Relative retention time of inferred organotin peak required to be within ± 1% of that expected from the standards.

6) Relative intensity ratios of the primary characteristic ion to the characteristic ions required to be within 20% of the mean found for authentic compound in the calibration standard.

7) Independent analysis of extracts by separate labs and different instrumental methods.

1.6 Characteristic Ion Selection

Organotin precursors and the pentyl derivatives were analysed individually by continuous scan GC/MS to determine the retention time, characteristic ions and parity of each. All starting compounds appeared to be 99%+ pure and the derivatisation proceeded quantitatively with no detectable precursor in the derivatised product. All mass spectra were assigned and were consistent with structures. Characteristic ions were 121^+ (SnH^+, from alkyl tins), 179^+ ($BuSn^+$ from butyltin compounds), 193^+ ($PnSn^+$ from pentyltin compounds, 351^+ (Ph_3Sn^+, from triphenyltin compounds), 120^+ (Sn^+ from triphenyltin compounds), 155^+ ($ClSn^+$ from

chlorotin compounds) and 55+ (butenyl fragment from butyltin compounds). The latter two ions were only monitored initially to confirm quantitative derivatisation to the pentyltin compounds.

2. DISCUSSION

The concentrations of selected organotin compounds in the five sediments are given in Table 1. There is generally good agreement between values determined by GC/FPD and GC/MS, with the conspicuous exception of sample 85-43-04, Pacific Plastics, storm sewer. For this sample, the GC/FPD value for tributyltin is approximately twenty times that found by GC/MS. However the characteristic ion ratios of the compound detected by GC/MS within the expected retention time window indicates that the compound is probably not tributyltin and the GC/MS reported value is an over-estimate. The relative retention times and a characteristic ion ratio for the tributyltin derivative are given for all samples in Table 2. The GC/MS data indicates negligible tributyltin in this sample. The mass chromatograms for this sample indicate other compounds eluting in this region including a compound eluting 28 seconds before the retention time for tributyltin. This compound gives rise to a prominent 121^+ peak (Sn-H^+ from an alkyl tin) and a 193^+ peak (Sn-pentyl$^+$ from the pentyltin derivative), but no 179^+ peak (Sn-butyl$^+$). This compound may account for the disparity between the tin sensitive GC/FPD method and the GC/MS.

Two samples (85-43-02 and -04) were analysed in duplicate and the results are presented in Table 1. Based on this limited set, the coefficient of variation by GC/MS is less than 15%.

3. REFERENCES

1) McGuire, J. personal communication.

2) Meinema, H.A., T. Burger-Weimma, G. Versluis-de Haan and E. Ch. Gevers. 1978. Determination of trace amounts of butyltin compounds in aqueous systems by Gas Chromatography/Mass Spectrometry. Analytical Chemistry, 12, 288.

Table 1.

Sediment Concentration of Organotin Compounds and Tin
($\mu g \cdot g^{-1}$, dry weight)

Sample No.	Description	Bu_3Sn GC/FPD	Bu_3Sn GC/MS	Bu_2Sn GC/FPD	Bu_2Sn GC/MS	BuSn GC/FPD	BuSn GC/MS	Sn GC/FPD	Ph_3Sn GC/M
85-43-01	Blackball Ferry 1112 Organic No. 3 July 11/85	0.049	0.10	0.20	0.035	0.007	0.010	3.4	0.001
85-43-02	Esquimalt Harbour Site No. 6, Organics No. 2 July 11/85	3.7	1) 3.0 2) 4.1	0.56	0.78 1.32	0.11	0.082 0.28	0.017	0.001 0.02
85-43-03	Marine Centre 1103, Organics No. 3 July 11/85	0.40	0.45	0.38	0.39	0.007	0.064	0.007	0.001
85-43-04	Pacific Plastics Storm Sewer Nov. 28/85	5.1	1) 0.22 2) 0.27	0.007	0.0073 0.013	0.007	0.56 0.39	3.3	0.001 0.001
85-43-05	Seaspan No. 1 1151, Organics No. 3 July 11/85	0.72	0.54	0.52	0.17	0.007	0.025	0.65	0.001

Table 2.

Comparison of Relative Retention Time and 179/121 Ion Ratios of Calibration Standards and Samples for Tributylpentyltin

Sample	Relative Retention Time[a]	179/121
pentyltributyltin	0.925	2.0
85-43-01	0.925	2.5
85-43-02	0.932	2.1
85-43-03	0.935	2.1
85-43-04	0.918	0
85-43-05	0.926	2.5

a) Tributyltin compound relative to d_{10}anthracene.