Journal of Chromatography, 315 (1984) 341–349
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,180

DETERMINATION OF TRIALKYLTIN, DIALKYLTIN, AND TRIPHENYLTIN COMPOUNDS IN ENVIRONMENTAL WATER AND SEDIMENTS

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(First received July 9th, 1984; revised manuscript received August 27th, 1984)

SUMMARY

An analytical procedure for the determination of trialkyltin (tributyltin, tripropyltin), triphenyltin and dialkyltin (dibutyltin) compounds in environmental water and sediment was studied. Water samples were extracted into benzene with hydrochloric acid and sodium chloride. Sediment samples were extracted into methanolic hydrochloric acid and converted into benzene. Silica gel, which was impregnated with hydrochloric acid and activated, was used for clean-up of these compounds. These extracts of organotin chlorides were hydrogenated with an ethanol solution of sodium borohydride. Organotin hydrides were measured by gas chromatography with electron-capture detection. Recoveries of these compounds were *ca.* 70–95% from river water and sediment samples. The detection limits were 0.4–0.8 μg/l in water and 0.02–0.04 μg/g in sediment samples.

INTRODUCTION

Organotin compounds have been widely used during recent decades. The properties of organotin compounds (R_mSnX_{4-m}) depend on the number and the types of the organic groups (R). R_2SnX_2 and R_3SnX are mainly used in industry and agriculture. R_2SnX_2 as dibutyltin and dioctyltin compounds is used in large amounts as catalysts and poly(vinyl chlorides) stabilizers. Most of the R_3SnX compounds exhibit fungicidal activity. Tributyltin compounds are used for the mildew-resistant finishing of textiles, wood preservation and anti-fouling paints for ships' bottoms. Triphenyltin, tripropyltin, and tricyclohexyltin compounds are used mainly as pesticides in agriculture. These are most toxic. Environmental pollution from these compounds may be a serious problem when they are released. The elucidation of the environmental fate and pollution level of these compounds requires the establishment of a sensitive and accurate method for determination of these compounds.

Organotin compounds have been determinated with various methods, such as colorimetry[1,2], atomic absorption spectrometry[3–6], polarography[7], gas chromatography[8–12] and high-performance liquid chromatography[13]. Braman *et al.*[4] deter-

0021-9673/84/$03.00

mined methyltin compounds using atomic absorption spectrometry. Meinema *et al.*[9] and Maguire *et al.*[10] reported analytical methods for methyltin and butyltin compounds in sea and lake water. On the other hand, these compounds were alkylated with a Grignard reagent and measured by gas chromatography–mass spectrometry (GC–MS) or a gas chromatography–flame photometric detection (GC–FPD). Tetra- and trialkyltin compounds in biological materials were determined separately by gas chromatography–electron capture detection (GC–ECD) by Arakawa *et al.*[8]. But it is difficult to determine dialkyltin compounds by GC because they are adsorbed on the GC column packing. As organotin compounds are unstable, it is difficult to clean up environmental samples for their determination. Soderquist *et al.*[11] detected phenyltin compounds in water with GC–ECD by converting them into their hydrides with lithium aluminium hydride, but these authors did not apply their method to the analysis of environmental samples.

Reports concerning the determination of organotin compounds in environmental waters have been published by Braman *et al.*[4] and Maguire *et al.*[10]. Furthermore, few reports have been published concerning analytical methods that are applicable to both water and sediment samples.

We have determined trialkyltin, triphenyltin, and dialkyltin compounds in environmental water and sediment samples using GC–ECD after extraction and conversion into their hydride derivatives with sodium borohydride. Furthermore, an effective method for the clean-up of organotin compounds was studied.

EXPERIMENTAL

Apparatus and gas chromatography

Varian aerograph 2100 (d.c. operation mode) and 6000 type (constant current operation mode) gas chromatographs with an electron-capture detector (^{63}Ni, 8 mCi) were used. The glass column (2 m × 2 mm I.D.) was packed with 2% Silicone OV-17 on Gas Chrom Q (100–120 mesh). The column temperature was set at 70°C [for di-*n*-butyltin dihydride (Bu_2SnH_2) and tri-*n*-propyltin hydride (Pr_3SnH)], 100°C [for tri-*n*-butyltin hydride (Bu_3SnH)], and 190°C [for triphenyltin hydride (Ph_3SnH)]. The injector temperature was kept constant at 220°C, and the detector temperature was set at 320°C. Nitrogen was used as carrier gas at a flow-rate of 30 ml/min. Bu_2SnH_2, Pr_3SnH, and Bu_3SnH were determined with the 6000 type gas chromatograph, and Ph_3SnH with the 2100 type. A JEOL JMS-DX300 type gas chromatograph–mass spectrometer was operated at 70 eV electron energy. The ion source temperature and the separator temperature were 270°C and 250°C, respectively. Helium was used as carrier gas at a flow-rate of 30 ml/min.

Reagent

Tri-*n*-propyltin chloride (Pr_3SnCl) (Alfa Division), tri-*n*-butyltin chloride (Bu_3SnCl), triphenyltin chloride (Ph_3SnH), and di-*n*-butyltin dichloride (Bu_2SnCl_2) (Tokyo Chemical) were used. Organic solvents were pesticide analytical grade from Wako. Sodium sulphate (special grade) was washed with hexane and dried before use. Sodium borohydride (chemical analytical grade) (1 g) was added to 40 ml of ethyl alcohol in a glass-stoppered test-tube. The mixture was shaken, and dispersed with an ultrasonic wave. The precipitate was allowed to settle before use. A fresh

solution was prepared before use. Sodium chloride (special grade) was from Wako. Water was distilled and washed with hexane for hydrogenation. The silica gel used was Wako gel C-100; for trialkyltin chloride, it was impregnated with hydrochloric acid, air-dried, and activated for *ca.* 10 h at 120°C; for dialkyltin chloride, it was impregnated with hydrochloric acid, air-dried, and activated for *ca.* 4 h at 120°C.

Procedure

A 500-ml water sample was mixed in a separatory funnel with 2.5 ml of hydrochloric acid (sp. gr. 1.17) and 10 g of sodium chloride. The mixture was twice extracted with two portions of 100 ml of benzene, and the pooled extracts were dehydrated, concentrated to *ca.* 5 ml in a round-bottomed flask on a rotary evaporator at 40°C, transferred to a spitz test-tube and concentrated to *ca.* 0.5 ml and diluted with hexane to 10 ml. A sediment sample (10 g) was mixed in a flat-bottomed flask with 50 ml of conc. HCl–methanol (5:95) solution. The mixture was refluxed for 30 min in a water bath (70–80°C) fitted with a reflux condenser, cooled, and then filtered with washing by methanolic hydrochloric acid solution. The extract wass mixed with 100 ml of water and 10 g of sodium chloride, and then twice extracted with two aliquots of benzene (50 ml). The pooled extracts were dehydrated, and concentrated in the same way as for the water sample.

Column clean-up

The glass column (30 × 1 cm I.D.) used for clean-up of the trialkyltin compounds was packed with 8 g of silica gel for trialkyltin and *ca.* 1 cm of sodium sulphate. The column was prewashed with hexane. When the liquid level just reached the top of the sodium sulphate, 5 ml of sample extract was introduced, followed by two portions of 1 ml of hexane. With the sample well on to the column, 50 ml of hexane were added and the eluate was discarded. When the hexane level just reached the column bed, 50 ml of 20% (v/v) ethyl acetate–hexane were added. The eluate was collected and concentrated to *ca.* 0.5 ml by rotary evaporator at 40°C.

The glass column (30 × 1 cm I.D.) used for clean-up of the dialkyltin compounds was packed with 5 g of silica gel and *ca.* 1 cm of sodium sulphate. The column was prewashed with hexane. When the liquid level just reached the column bed, another 5 ml of sample extract were introduced, followed by two portions of 1 ml of hexane. With the sample well on to the column, 50 ml of hexane were added and the eluate was discarded. When the hexane level just reached the column bed, 50 ml of 33.3% (v/v) ethyl acetate–hexane were added; the eluate was collected, and concentrated to 0.5 ml by rotary evaporator at 40°C.

Hydrogenation

The cleaned-up extract was placed in a 25-ml glass-stoppered test-tube and made up to 5 ml with hexane. It was mixed with 2 ml of sodium borohydride–ethanol solution, shaken gently and allowed to stand for 15 min. It was then mixed with 10 ml of water, shaken well, and allowed to stand. The first hexane layer was transferred to another test-tube, and 5 ml of hexane were added to the water layer for a further extraction. The pooled hexane extracts were made up to 10 ml and dehydrated with anhydrous sodium sulphate.

Standard solution

A mixed solution of Pr_3SnCl, Bu_3SnCl, Ph_3SnCl, and Bu_2SnCl_2 (2 μg/ml in each) was prepared in hexane. A 2-ml volume of sodium borohydride–ethanol solution was added to 5 ml of the mixed organotin chloride solutions, which contained 0.8–3.2 μg of these organotin chlorides. Hydrogenation was accomplished as previously described. These standard solutions for calibration were prepared for each analysis.

RESULTS AND DISCUSSION

Gas chromatogram

Trialkyltin chlorides, *e.g.* Bu_3SnCl and Pr_3SnCl, can be separately analysed on 20% DEGS-HG (Chromosorb W AW-CMDS) or Silicone OV-1 (Gas Chrom Q), which is silanized. Various stationary phases were investigated for the elution of dibutyltin dichloride; however, it did not elute through any stationary phase when the concentration was low because it was either adsorbed or decomposed. Dibutyltin dihydride, which is virtually non-polar, can be analysed on 2% Silicone OV-17 on Gas Chrom Q (100–120 mesh); it can also be determined on 2% Silicone OV-1 on Gas Chrom Q, which was silanized. Fig. 1 shows gas chromatograms of dibutyltin dihydride, tripropyltin hydride, tributyltin hydride, and triphenyltin hydride. As is often the case during d.c. operation of the electron capture detector, a negative dip was observed in the peak of Ph_3SnH. However, it did not interfere with quantitative analysis of Ph_3SnH. These hydrides were identified by GC–MS.

Hydrogenation

The correlation between hydride generation and reaction time is shown in Fig.

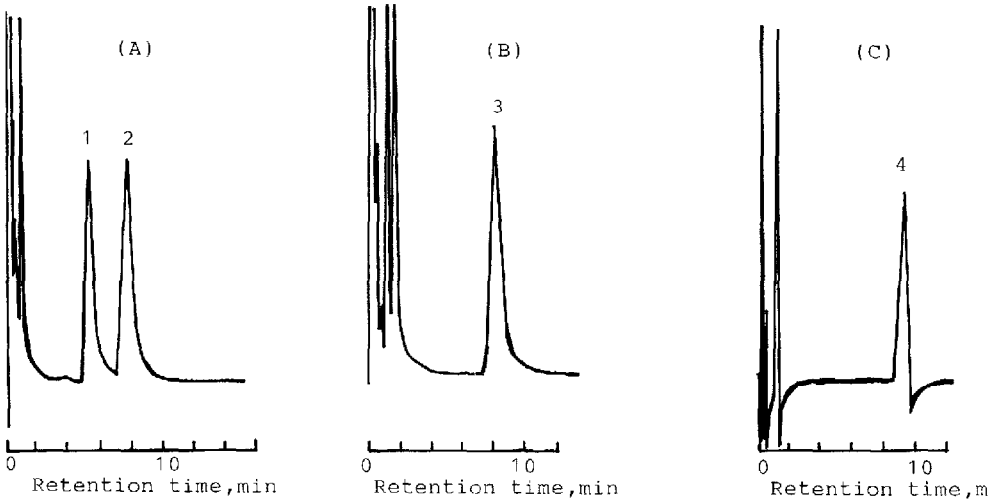

Fig. 1. Gas chromatograms of standard solutions of Bu_2SnH_2 (1), Pr_3SnH (2), Bu_3SnH (3), and Ph_3SnH (4). Column: 2% OV-17, Gas-Chrom Q (100–120 mesh), 2 m × 2 mm I.D. Column temperature: 65°C (A), 100°C (B), 190°C (C). Detector temperature, 320°C; injector temperature, 220°C. Apparatus: Varian 5000 type GC (A, B); Varian 2100 type GC (C).

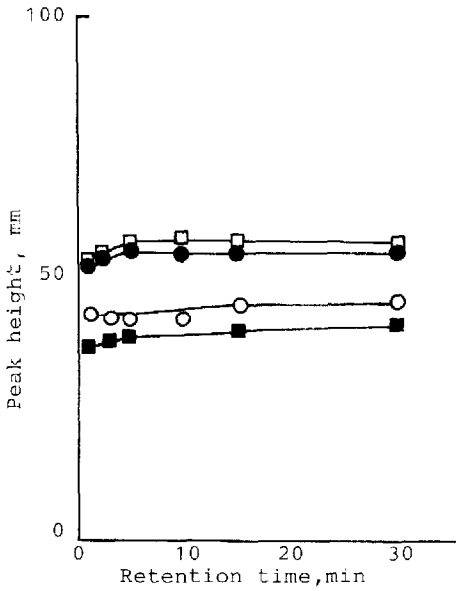

Fig. 2. Hydrogenation of organotin chlorides. (●) Bu_2SnH_2; (○) Pr_3SnH; (□) Bu_3SnH; (■) Ph_3SnH.

2. The peak heights of these hydrides reached a maximum within 15 min, so the standard solutions for calibration and sample solutions were hydrogenated for 15 min. The calibration curves were prepared by plotting peak heights *vs.* the amount of standard solution injected, converted into organotin chlorides, from which the concentrations of the sample solutions could be determined. Detection limits of these compounds were 79 pg (Bu_2SnH_2), 85 pg (Pr_3SnH), 74 pg (Bu_3SnH), and 31 pg (Ph_3SnH) as Sn (based on three times the noise signal). Meinema *et al.*[9] and Maguire *et al.*[10] reported analytical methods for methyltin and butyltin compounds that had been alkylated with Grignard reagents and measured with GC–MS and GC–FPD. Our analytical method shows similar sensitivity for these compounds, but our derivatization method is simpler than the others.

Extraction

It is well known that organotin compounds (R_mSnX_{4-m}) are transformed into organotin chlorides (R_mSnCl_{4-m}) by reaction with hydrochloric acid. Trialkyltin chlorides can be extracted with hexane, but dialkyltin dichloride was extracted with hexane below the recovery of 50%. Both trialkyltin and dialkyltin chloride were extracted from water into benzene with hydrochloric acid and sodium chloride at recoveries of 90–100%.

Column clean-up

Dialkyltin dichloride is more polar than trialkyltin chloride, and is strongly adsorbed on column packings such as silica gel. Dibutyltin dihydride (10 μg) was applied to three kinds of column: (i) *ca.* 4 g of anhydrous silica gel; (ii) 10% hydrated silica gel; (iii) aluminium oxide coated with H_3PO_4 (10% hydrated). But it did not elute from any column with 50 ml of 50% (v/v) hexane–ethyl acetate mixture because

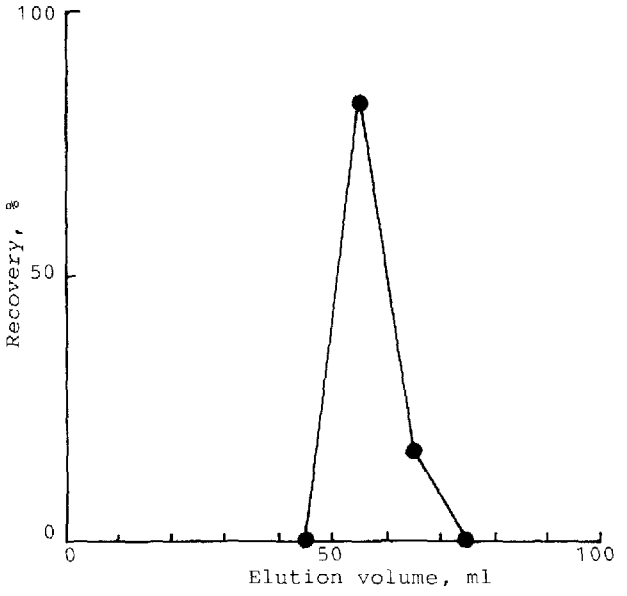

Fig. 3. Elution pattern of dibutyltin dichloride. Column: 5 g of Wako gel C-100, impregnated with hydrochloric acid, activated for 4 h at 120°C. Eluent, hexane (0–50 ml), 33.3% (v/v) ethyl acetate–hexane (50–100 ml).

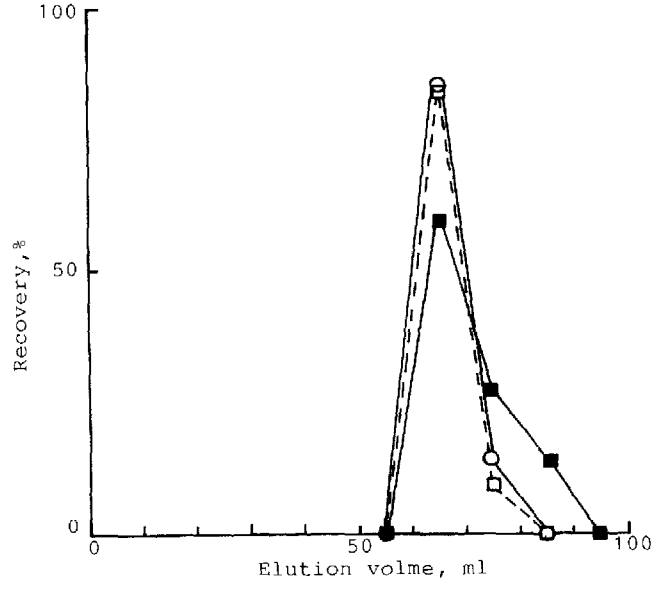

Fig. 4. Elution patterns of trialkyltin chlorides. (○) Pr_3SnCl; (□) Bu_3SnCl; (■) Ph_3SnCl. Column: 8 g of Wako gel C-100, impregnated with hydrochloric acid, activated for 10 h at 120°C. Eluent, hexane (0–50 ml), 20% (v/v) ethyl acetate–hexane (50–100 ml).

of adsorption or decomposition. When the silica gel was impregnated with hydrochloric acid was used, dibutyltin dichloride eluted from the column at a recovery of almost 90–100%. Fig. 3 shows the elution pattern of dibutyltin dichloride from silica gel impregnated with hydrochloric acid. Dibutyltin dichloride was eluted with 30 ml of 33.3% (v/v) ethyl acetate–hexane, and also through 2 g of silica gel coated with 10% aqueous potassium chloride solution. When the column is saturated with chloride ion, the chemical form of dibutyltin dichloride is not changed, hence there is no loss on elution through these columns. If excessive activation is achieved, the concentration of chloride ion decreases and the recovery of dibutyltin dichloride from the column becomes low. Clean-up of trialkyltin chloride was accomplished with anhydrous silica gel (Nakarai no. IIA), but the recovery was low. When silica gel impregnated with hydrochloric acid was used for clean-up, the recovery was also *ca.* 100%. It was necessary to control the elution range of trialkyltin chlorides by adjusting the activation time of silica gel impregnated with hydrochloric acid. Fig. 4 shows the elution pattern of trialkyltin chlorides. They almost eluted with 30–40 ml of 20% (v/v) ethyl acetate–hexane. Most non-polar compounds were removed from the sample extract by this clean-up. Moreover, polar compounds were also removed when organotin hydrides were extracted with hexane from water, because they are virtually non-polar. The effect on hydrogenation of the amount of ethyl acetate is shown in Fig. 5. When the amount of ethyl acetate in 5 ml of hexane solution was above 1 ml, hydrogenation was suppressed. As ethyl acetate was used as the eluent for clean-up, the solution eluted from the column must be concentrated to *ca.* 0.5 ml and adjusted to 5 ml with hexane.

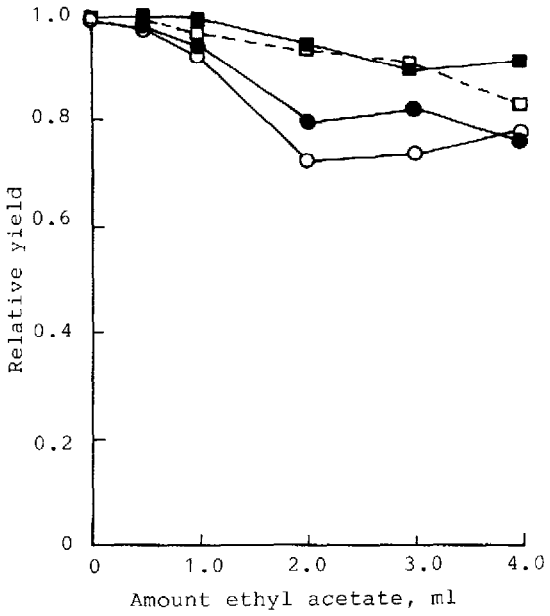

Fig. 5. Effect of amounts of ethyl acetate on hydrogenation. (●) Bu_2SnH_2; (○) Pr_3SnH; (□) Bu_3SnH; (■) Ph_3SnH.

TABLE I

RECOVERIES OF TRIALKYLTIN, DIALKYLTIN AND TRIPHENYLTIN COMPOUNDS FROM WATER AND SEDIMENT SAMPLES

Four organotin chlorides (5 μg and 20 μg of each) were added to 500 ml of river water and four organotin chlorides (20 μg of each) were added to river sediment sample. Then they were subjected to this method. Each result is the average of four determinations (mean ± standard error).

Compound	*Amount added (μg)*	*Sample*	*Recovery (%)*	*C.V. (%)*
Bu_2SnCl_2	5	Water	74.1 ± 2.6	3.5
	20	Water	73.6 ± 3.4	4.6
	20	Sediment	76.1 ± 4.0	5.3
Pr_3SnCl	5	Water	66.6 ± 6.5	9.8
	20	Water	75.5 ± 5.2	6.9
	20	Sediment	93.5 ± 3.1	3.4
Bu_3SnCl	5	Water	95.1 ± 2.7	2.9
	20	Water	93.6 ± 3.6	3.8
	20	Sediment	93.3 ± 2.4	2.6
Ph_3SnCl	5	Water	86.2 ± 1.7	1.9
	20	Water	79.6 ± 4.0	5.0
	20	Sediment	68.2 ± 0.7	1.1

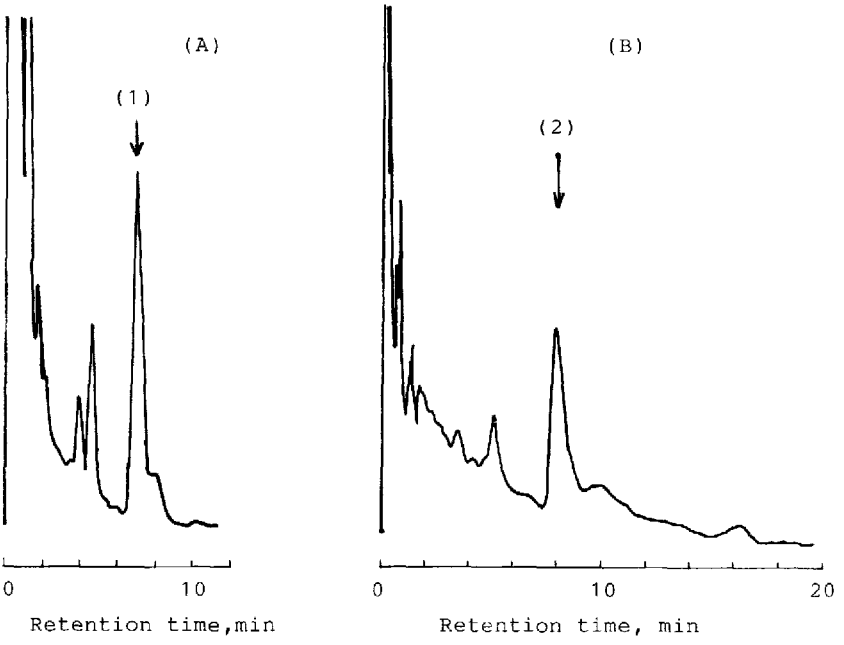

Fig. 6. Gas chromatograms of extract from a sediment sample. (A) Column temperature, 60°C; peak 1 = Bu_2SnH_2. (B) Column temperature, 100°C; peak 2 = Bu_3SnH.

Recovery of organotin compounds from aqueous and sediment samples

The analytical procedure was applied to the determination of individual organotin compounds in aqueous and sediment samples. Recovery tests were conducted on both river water and river sediment samples, to which were added 5 μg and 20 μg of individual organotin compounds (Table I). Average recoveries of trialkyltin and dialkyltin compounds ranged from 67% to 95% for river water samples and from 68% to 93% for river sediment samples, respectively. Detection limits of Bu_2SnCl_2, Pr_3SnCl, Bu_3SnCl, and Ph_3SnCl throughout this analytical procedure were 0.8, 0.8, 0.8, and 0.4 μg/l in water and 0.04, 0.04, 0.04, and 0.02 μg/l in sediment samples.

Determination of organotin compounds in a river sediment sample

Organotin compounds of the river sediment sample in Osaka Prefecture were analysed. Gas chromatograms of the organotin compounds in this sample are shown in Fig. 6. Tributyltin hydride and dibutyltin hydride were detected in this sample. The concentrations of dibutyltin compound (as Bu_2SnCl_2) and tributyltin compound (as Bu_3SnCl) were 0.47 μg/g and 1.13 μg/g, respectively.

ACKNOWLEDGEMENTS

The authors thank Dr. K. Oda and Dr. T. Yamamoto of Osaka City Institute of Public Health and Environmental Sciences and T. Okumura, K. Imamura, and H. Kitamura of Environmental Pollution Control Center of Osaka Prefecture for their helpful advice.

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