

Short Communication

Sampling method of organotin compounds in air using a quartz-fibre filter and an activated carbon-fibre filter for gas chromatographic determination

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ABSTRACT

A sampling method using quartz-fibre filters and an activated carbon-fibre filter was developed for gas chromatographic determination of organotin compounds in air. The organotin compounds investigated were dibutyltin chloride (DBTC), tributyltin chloride (TBTC), diphenyltin chloride (DPTC) and triphenyltin chloride (TPTC). The chlorides collected on filters were extracted ultrasonically with benzene and converted into propyl derivatives using propylmagnesium bromide. The derivatives were analysed by capillary gas chromatography (GC) equipped with a flame photometric detector adjusted for tin detection. The collection efficiencies and recoveries of the organotin compounds were quantitative. The minimum detectable concentrations were 0.2 ng/m³ for DBTC and TBTC, 0.3 ng/m³ for DPTC and 0.4 ng/m³ for TPTC. This method was successfully applied to the determination of organotin compounds in indoor air.

INTRODUCTION

Tributyltin and triphenyltin compounds have been used as antifouling agents for painting ship bottoms and fishing nets, and as wood preservatives; dibutyltin and diphenyltin compounds have been used as stabilizers for halogen-containing polymers. They are toxic to fish species and other aquatic animals, and exist as contaminants in water [1], sediment [2] and biota [3]. They are

not thought to exist in air because of their very low volatilities [4]. Therefore, there have been few investigations on their existence in the environmental air.

A few reports have described attempts to collect some organotin compounds from the working atmosphere for gas chromatographic determinations: chromosorb 102 resin collection for butyltin compounds [5] and glass-fibre filter collection for dialkyltin compounds [6]. However, these methods cannot be applied to the determination of organotin compounds in the environmental air because the detection limits of these methods are much higher than the mini-

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mum allowable environmental concentration levels.

We used a quartz-fibre filter and an activated carbon-fibre filter, which are effective in the collection of airborne pesticides [7–10], for the collection of organotin compounds in air, *i.e.* dibutyltin dichloride (DBTC), tributyltin chloride (TBTC), diphenyltin dichloride (DPTC) and triphenyltin chloride (TPTC). Some reports have shown that organotin compounds in water and biota can be analysed after propylation by gas chromatography (GC) coupled with flame photometric detection (FPD) with a tin filter [11,12]; this method is selective and sensitive. This report presents the results of organotin compound collection using quartz-fibre filter and activated carbon-fibre filter for GC–FPD determination after propylation.

MATERIALS AND METHODS

Apparatus and materials

An automated sequential air sampler, GS-10D (Tokyo Dylec, Tokyo, Japan), was used for sample collection. An ultrasonic apparatus, EN-20S-1A (Shimada, Tokyo, Japan), and a centrifugal apparatus, KN70 (Kubota, Tokyo, Japan), were used for the extraction procedure. The gas chromatograph used was a GC-7AG (Shimadzu) equipped with an FPD. A fused-silica HP-1 column (10 m × 0.53 mm I.D., coated with methylsilicone in 2.65 μm thickness) was purchased from Hewlett-Packard.

TPTC and 2 M propylmagnesium bromide (tetrahydrofuran solution) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). DPTC was obtained from Aldrich (Milwaukee, WI, USA). Other reagents were obtained from Wako (Osaka, Japan).

Quartz-fibre filters (Toyo Pallflex 2500 Qatup) and activated carbon-fibre filters (Toyobo KF Paper P-175) were shaped into circles of 47 mm diameter for sample collection.

Sample collection and determination

Air was sampled through two quartz-fibre collection filters at the front and through an activated carbon-fibre collection filter at the rear at 5 l/min for 24 h using the automated sequen-

tial air sampler. Each sampled filter was extracted ultrasonically with 10 ml of 1 M HCl–methanol for 10 min followed by centrifugation at 1700 g for 10 min, and the supernatant was decanted. The extraction was repeated with 10 ml of 1 M HCl in methanol and then twice with 2.5 ml of benzene. The extracts were combined, washed with 15 ml of 10% NaCl, dried over Na₂SO₄ and concentrated to 1 ml by blowing with nitrogen gas. A 1-ml volume of 2 M propylmagnesium bromide was added to the sample, shaken and allowed to stand for 30 min in a water bath at 40°C. A 10-ml volume of 0.5 M H₂SO₄ was added to decompose excess propylmagnesium bromide, then 10 ml of methanol were added. The resulting solution was extracted twice with 2.5 ml of *n*-hexane. The combined organic phases were concentrated to 0.5 ml by blowing with nitrogen gas. The solution was analysed by GC. GC conditions were as follows: column temperature, 110°C (held for 2 min) to 250°C (held for 2 min) increasing at 8°C/min; injector and detector temperature, 280°C; injection mode, direct injection; carrier gas flow-rate, 10 ml/min; detector, FPD with tin filter (λ = 611.1 nm).

RESULTS AND DISCUSSION

Extraction solvent

Extraction efficiencies for the organotin compounds from the quartz-fibre collection filter and the activated carbon-fibre collection filter were determined by adding known amounts of organotin compounds (25 μg of DBTC and TBTC and 75 μg of DPTC and TPTC) to each filter as an ethanolic solution. The filter was allowed to stand for 20 min in order to evaporate the ethanol, then the organotin compounds were extracted from the filter as described above by using ten different solvents. All organotin compounds were extracted quantitatively from the quartz-fibre collection filter by each extraction solvent; for example, 96 ± 5.9% DBTC, 92 ± 4.2% TBTC, 99 ± 3.6% DPTC and 95 ± 4.9% TPTC (*n* = 4) were extracted with benzene. On the other hand, it was hard to extract quantitatively the organotin compounds from the activated carbon-fibre collection filter. As shown in

TABLE I

EXTRACTION EFFICIENCIES FOR ORGANOTIN COMPOUNDS FROM ACTIVATED CARBON-FIBRE COLLECTION FILTER

Solvent	Extraction efficiency (%)			
	TBTC	TPTC	DBTC	DPTC
<i>n</i> -Hexane	34	11	19	0.6
<i>n</i> -Hexane-ethanol (4:1, v/v)	49	14	30	0.6
Dichloromethane	46	60	73	1.8
Dichloromethane-ethanol (4:1, v/v)	49	63	96	3.6
Benzene-ethanol (4:1, v/v)	50	84	78	11
Toluene	55	86	53	6.0
Toluene-ethanol (4:1, v/v)	45	95	81	14
Xylene	45	73	32	2.4
Xylene-ethanol (4:1, v/v)	39	84	83	20
Benzene	99 ± 38 ^a	93 ± 1.7 ^a	68 ± 5.1 ^a	26 ± 3.8 ^a
Benzene ^b	92 ± 12 ^a	91 ± 4.2 ^a	66 ± 3.3 ^a	21 ± 0.9 ^a

^a Mean ± standard deviation (*n* = 4).^b Added: 1 μg of DBTC, 1 μg of TBTC, 3 μg of DPTC and 3 μg of TPTC.

Table I, TBTC and TPTC were extracted quantitatively from the filter by benzene, and DBTC by dichloromethane-ethanol (4:1, v/v), but DPTC could not be extracted by any solvent investigated. However we need not consider the low extraction efficiencies of DBTC and DPTC by benzene from the activated carbon-fibre collection filter, because both compounds can be collected by the quartz-fibre collection filters, as described later. The extraction efficiencies for 1–3 μg of the organotin compounds were almost equal to those for 25–75 μg of the compounds, as shown in Table I. Therefore, benzene was chosen as the best solvent.

Retention efficiencies

It is difficult to determine the collection efficiencies of filters for organotin compounds, because it is impossible to prepare air samples containing known amounts of organotin compounds [6]. Hence, we estimated the collection efficiency from the retention efficiency [13,14].

Retention efficiencies for organotin compounds of quartz-fibre collection filters were determined by adding known amounts of the organotin compounds (125 μg of DBTC and TBTC and 175 μg of DPTC and TPTC) to a quartz-fibre collection filter as an ethanolic solu-

tion. Air was passed at 5 l/min for 24 h through the filter (F₁) with back-up from another two quartz-fibre collection filters (F₂ and F₃) at room temperature. The retention efficiencies of DBTC, DPTC and TPTC were quantitative, but TBTC evaporated from the quartz-fibre collection filters by passing air, suggesting the need for another back-up filter (F₃). Some experiments were carried out by adding the activated carbon-fibre collection filter as a back-up filter (F₃). The results are shown in Table II. Retention efficiencies of the organotin compounds were quantitative.

TABLE II

RETENTION EFFICIENCIES OF ORGANOTIN COMPOUNDS

Collection filter ^a	Retention efficiency ^b (%)			
	DBTC	TBTC	DPTC	TPTC
F ₁	86 ± 2.2	18 ± 5.7	93 ± 8.5	94 ± 4.5
F ₁ + F ₂	95 ± 3.4	67 ± 4.4	96 ± 8.4	98 ± 4.4
F ₁ + F ₂ + F ₃	96 ± 3.3	91 ± 5.7	96 ± 8.4	98 ± 4.4

^a F₁ and F₂ = quartz-fibre collection filters; F₃ = activated carbon-fibre collection filter.^b Mean ± standard deviation (*n* = 4).

The minimum detectable concentrations with signal-to-noise ratio of 3 based on peak height were 0.2 ng/m^3 for DBTC and TBTC, 0.3 ng/m^3 for DPTC and 0.4 ng/m^3 for TPTC. These values were about 100–2000 times lower than those achieved with previous methods.

Stabilities of organotin compounds on the collection filters

The storage stabilities of the organotin compounds on the collection filters were investigated. The collection filters with $50 \mu\text{g}$ of DBTC and TBTC and $150 \mu\text{g}$ of DPTC and TPTC added were stored for a known period. The results are shown in Table III. The organotin compounds were more stable on the collection filters at -20°C than at 15°C . DBTC, DPTC and TPTC remained almost unchanged in quantity for at least 7 days on the collection filters during storage at -20°C ; under the same conditions, TBTC was stable for at least 7 days on the quartz-fibre filter, and for at least 4 days on the activated carbon-fibre collection filter. Therefore, the collection filters should be stored at -20°C and be analysed within 4 days after sampling.

Application to environmental samples

This sampling and analytical method was applied to organotin compounds in air in houses. TPTC was detected in some samples in concentrations ranging from 0.4 to 0.6 ng/m^3 . No

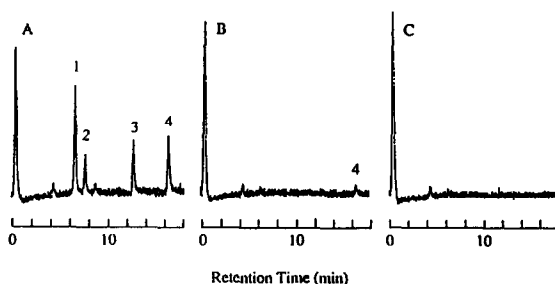


Fig. 1. GC-FPD chromatograms of organotin compounds. (A) Standard. (B) Sample. (C) Procedural blank. 1 = Dibutyldipropyltin; 2 = tributylpropyltin; 3 = diphenyldipropyltin; 4 = triphenylpropyltin.

TPTC was detected from the second quartz-fibre filter (F_2) or the activated carbon-fibre filter (F_3). Hence, TPTC in air was collected quantitatively by the first quartz-fibre filter (F_1). The detected TPTC came from wood preservatives applied to timber used in building the houses. Typical gas chromatograms of standards, a sample and a procedural blank are shown in Fig. 1. The organotin compounds could be analysed without interferences.

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TABLE III
STABILITIES OF ORGANOTIN COMPOUNDS ON COLLECTION FILTERS

Collection filter	Storage temperature ($^\circ\text{C}$)	Storage time (days)	Recovery ^a (%)			
			TBTC	TPTC	DBTC	DPTC
Quartz fibre	15	4	88	91	86	90
		7	85	90	76	87
	-20	4	99	96	90	92
		7	92	98	88	93
Activated carbon fibre	15	4	49	33	87	85
		7	41	30	63	76
	-20	4	92	92	98	94
		7	73	80	94	92

^a Mean ($n = 2$).

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