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Simultaneous determination of organotin compounds in textiles by gas chromatography–flame photometry following liquid/liquid partitioning with *tert*-butyl ethyl ether after reflux-extraction

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ABSTRACT

A rapid and relatively clean method for determining six organotin compounds (OtC) in textile goods with a gas chromatograph equipped with a conventional flame photometric detector (GC-FPD) has been developed. After the reflux-extraction to use methanol containing 1% (v/v) of hydrochloric acid, five hydrophobic OtC (e.g. tributyltin: TBT) and slightly less hydrophobic dibutyltin (DBT) could be drawn out through partitioning between the methanolic buffer solution and *tert*-butyl ethyl ether instead of hazardous dichloromethane, of which usage is provided by the official-methods notified in Japan, and following the ethylation procedure to use sodium tetraethylborate, the OtC were determined with the GC-FPD. The recoveries of DBT, TBT, tetrabutyltin, triphenyltin, dioctyltin, and trioctyltin from textile products (cloth diaper, socks, and undershirt) were 60–77, 89–98, 86–94, 71–78, 85–109, and 70–79% respectively, and their coefficients of variation were 2.5–16.5%. Calibration curves for OtC were linear (0.01–0.20 μg as Sn mL^{-1}), and the correlation coefficients were 0.9922–1.0000. Their detection limits were estimated to be 2.7–9.7 ng as Sn g^{-1}. These data suggested that this method would be applicable to their simultaneous determination. Five retailed textile goods were analyzed by this proposed method, and 0.013–0.65 μg as Sn g^{-1} of OtC (e.g. DBT) were determined in three. Moreover, a possibility that various OtC including non-targeted species in textile would be specifically detected by applying the studying speciation-technique of controlling signal intensity-flame fuel gas pressures of the GC-FPD was found.

1. Introduction

Organotin compounds (OtC) widely used in industry [1] are frequently found out in human samples [2–5]. Tributyltin (TBT) is one of the endocrine disrupting chemicals, and the adverse effects through the retinoid X receptor and peroxisome proliferator-activated receptor gamma are being shed light on [6]. Dibutyltin (DBT) and dioctyltin (DOT) are immuno-toxic for mammals [7,8], and DBT also induces the genotoxicities in vitro assays [9–11].

In European Union and United States, the use of OtC (e.g. DOT) in plastic food packaging has been regulated because of the possibilities to migrate to the food, and it has been regarded that the consumption of contaminated fish would be the most relevant human exposure source [12]. However, their concentrations in aquatic environments are deduced to be showing a tendency to decrease, since usages of tri-OtC as antifouling agents for ships, boats, and fishing nets were banned in many countries. OtC (e.g. butyltin compounds) in seafood were recently surveyed from the point of view of health risks [13,14], and those data denoted that the daily intakes of OtC through seafood consumptions were below the tolerable daily intake.

Meanwhile, the occurrence of OtC in living environments might be concerned in human exposures. It was recently disclosed that mono- and di-OtC (e.g. DBT) were often found in house dust [15,16]. Furthermore, OtC have been detected in the clothes [17–21]. There are possibilities that the OtC might be absorbed from skin through putting on. The author [22–25] also reported that various OtC could be found in the textile goods such as underwear and sanitary goods for babies even of late years. However, the researches on the occurrence of OtC in textile samples are relatively sparse. Hence, investigating the actual conditions of contamination of OtC in textile goods further may also hold significance.

The residues of the most harmful TBT and/or triphenyltin (TPT) in 8 kinds of clothes (e.g. underwear; limits of detection: 1 μg as Sn g^{-1} each) are not permitted legally in Japan [26], and it has been notified that TBT and TPT are able to be drawn out through dichloromethane/the methanolic phosphate–citrate

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buffer solution partition following the reflux-extraction to use methanol containing 1% (v/v) of hydrochloric acid from the textile goods [26]. Moreover, it was presented that in addition to TBT and TPT, the other toxic OtC (e.g. DOT) were determinable through this extraction procedure to use dichloromethane [19,20]. For the reasons that in the liquid/liquid partition extraction step, the emulsification would be scarcely caused owing to the ionic strength of the methanolic buffer layer and the extraction would be able to be performed smoothly without centrifugation, it is considered that this notified method is very useful. However, the substitute solvent for dichloromethane is needed, because its hazardousness has been being acknowledged.

In this study, therefore, developing a clean method for extracting hydrophobic TBT, tetrabutyltin (TeBT), TPT, DOT, trioctyltin (TOT), and slightly less hydrophobic DBT, without using dichloromethane has first been undertaken. The diverse compounds, from which chlorinated compounds were excluded, for instance, cycloalkanes, ethers, and esters, were adopted as tested chemicals, and the organic solvent-species to be appropriate for the lipophilic solution/the buffer solution partition extraction was determined.

Although, HPLC is also applicable to the determination of OtC in textiles [18,27], a gas chromatograph equipped with a conventional flame photometric detector (GC-FPD) [14,19,20,22–25,28] and a pulsed GC-FPD [29,30], which have high selectivity, sensitivity, and robustness, are extensively employed for the analyses of various samples. To simplify the notified method to use atomic absorption spectrometer/thin-layer chromatography-instruments [26], a conventional GC-FPD was used for the determination of extracted OtC, to which the ethylation was performed with sodium tetraethylborate ($NaBEt_4$).

The applicability (e.g. sample matrix effects: recoveries) of the clean and rapid method, which has been developed to the analysis of residuary OtC in the textile goods was investigated, and then, the OtC contents of marketed products were also quantified by this method. Application of studying speciation technique of controlling signal intensity-flame fuel gas pressures of a GC-FPD to the sample analysis was also attempted in order to pinpoint the presences of various OtC more obviously.

2. Materials and methods

2.1. Preparation of samples

Five textile products in which the presence(s) of TBT and/or TPT are not allowed in Japan [26] were purchased at retail stores in Nagoya. These products were stored at room temperature in the dark until analysis. The purchased articles were cut to pieces below 1 cm × 1 cm individually, before each experiment.

2.2. Chemicals and reagents

Deionized and distilled water was employed. Methanol (Kanto Chemical Co., Inc.; Wako Pure Chemical Industries, Ltd) and *n*-hexane (Kanto Chemical Co., Inc.; Wako Pure Chemical Industries, Ltd) of the grade for pesticide residue analysis and PCB analysis were utilized. *tert*-Butyl ethyl ether (TBEE; >97%) was purchased from Tokyo Chemical Industry Co., Ltd.. $NaBEt_4$ was obtained from Wako Chemical, Ltd.. Ethylation was performed with 0.5% (w/v) of $NaBEt_4$ aqueous solution which was made freshly. Sodium acetate–acetic acid buffer (pH 5.5) which was used in the ethylation process was prepared through mixing 1500 mL of 0.5 M sodium acetate and 210 mL of 0.5 M acetic acid. The other reagents (e.g. phosphate–citrate buffer: pH 2.0) were prepared according to the notified official methods [26].

The standard solutions (1 mg mL^{-1}; toluene) of TBTCl, TPTCl, and tripentyltin chloride (TPentTCl) of the grade for water analysis were purchased from Kanto Chemical Co. Inc.. The other OtC of which purities were above 95% were employed. $DBTCl_2$, TeBT, $DOTCl_2$, and TOTH (trioctyltin hydride) were obtained from Wako Pure Chemical Industries, Ltd., Merck Schuchchardt, Wako Chemical, Ltd., and Tokyo Chemical Industry Co., Ltd. respectively. Methyltin trichloride ($MMTCl_3$), dimethyltin dichloride ($DMTCl_2$), and trimethyltin chloride (TMTCl) were purchased from Wako Pure Chemical Industries, Ltd., Sigma Aldrich Inc., and Tokyo Chemical Industry Co., Ltd. respectively. The other chemicals were all analytical grade.

Methyltin compounds were dissolved in water respectively, and 2000 mg L^{-1} of the stock solutions were prepared. The working standard solutions to be desired concentrations were made up through diluting these stock solutions with water. $DBTCl_2$, TeBT, $DOTCl_2$, and TOTH were dissolved in *n*-hexane individually, and 2000 mg L^{-1} of the stock solutions were prepared. The working standard solutions of these 4 compounds were made up through diluting the stock solutions with *n*-hexane. The working solutions of TBTCl, TPTCl, and TPentTCl were brought through diluting the purchased standard solutions with *n*-hexane.

For the recovery tests, *n*-hexane, which was the incipient solvent of the standard mixture of $DBTCl_2$, TBTCl, TeBT, TPTCl, $DOTCl_2$, and TOTH (concentration: 2 μg as Sn mL^{-1} each), was removed with N_2-gas stream, and it was substituted for TBEE. The solvent, *n*-hexane, of the standard solution of TPentTCl (concentration: 2 μg as Sn mL^{-1}) added to the samples in the analysis of the marketed textile goods was also replaced TBEE in the same manner. The standard substances and the standard solutions were stored in the dark at 4 °C.

2.3. Apparatus

OtC were determined with a GC-FPD (GC-14A; 611 nm, Shimadzu Co.).

The fused silica capillary column which was DB-1 (100% dimethylpolysiloxane; 0.53 mm inner diameter, 30 m length, 1.5 μm film thickness: J&W Scientific Inc.) or DB-1701 ((14%-cyanopropyl-phenyl)-methylpolysiloxane; 0.53 mm inner diameter, 30 m length, 1.0 μm film thickness: J&W Scientific Inc.) was connected with the GC-FPD. The pressure of the carrier gas (N_2) was set to be 1.0 kg cm^{-2} at 260 °C (20 mL min^{-1}). The GC-FPD was run under the settled column oven temperature program [50 °C (for 4 min)-increase at 10 °C min^{-1}—120 °C-increase at 20 °C min^{-1}—260 °C(for 5 min)]. The temperatures in the injection-port and the detector-block were kept at 270 °C. The gas pressures of H_2 and air of the GC-FPD were controlled at 1.8 kg cm^{-2} and at 1.4 kg cm^{-2} respectively. The injection volume of tested solution was 5 μL.

2.4. Analytical procedure for the determination

2 μg as Sn of TPentTCl were first fortified to 2.0 g of the sample. Then, in line with the notified method [26], 75 mL of methanol containing 1% (v/v) of hydrochloric acid was added to the sample, and the mixture was refluxed at 70 °C for 30 min. After these processes, the methanol solution embracing the sample was filtered. Next, 50 mL of the phosphate–citrate-buffer (pH 2.0), 100 mL of water, and 30 mL of TBEE were appended to the filtrate, and the extraction was once carried out through shaking the mixture for 5 min. The upper TBEE-layer was concentrated to less than 2 mL below 40 °C with a rotary evaporator, and TBEE was finally eliminated with N_2-gas stream. After this procedure, 2 mL of *n*-hexane was added to the dried residues, and this solution was provided for the subsequent ethylation process.

Ethylation was carried out by adding 10 mL of sodium acetate–acetic acid buffer (pH 5.5) and 4 mL of 0.5% (w/v) $NaBEt_4$ to the *n*-hexane solution. This mixture was shaken for 2 min. After the elapse of 10 min, 5 mL of *n*-hexane was further added to this mixture, and this blend was shaken for 2 min. After 10 min, the upper organic layer was collected, and dehydrated with 5 g of anhydrous sodium sulfate. Furthermore, *n*-hexane was added to the dehydrated solution up to 10 mL, and this solution was injected into the GC-FPD.

The amount of each OtC in the sample was calculated from the peak area in the GC-FPD chromatogram.

2.5. Recovery tests

Three kinds of articles of clothing which were different from the products for the sample analyses were employed for the recovery tests. Before the tests, it was verified by the methods reported previously [22,23] that these articles did not include the targeted 6 OtC individually above 5% of the sample weight. These textile goods were segmented into smaller pieces than 1 cm^2 respectively. 1 mL of the standard mixture containing $DBTCl_2$, TBTCl, TeBT, TPTCl, $DOTCl_2$, and TOTH (2 μg as Sn mL^{-1} each) and 0.5 mL of the standard mixture containing $MMTCl_3$, $DMTCl_2$, and TMTCl (4 μg as Sn mL^{-1} each) were added to 2.0 g of the segmented article. TPentTCl was not appended to the sample. The fortified samples were analyzed through the rapid procedure recommended in this report.

2.6. Limits of detection

The standard mixture of ethylated 10 OtC (0.01 μg as Sn mL^{-1} each) was injected into the GC-FPD, and the peak heights of the OtC were measured. The peak heights of the background signals (noises) were also gauged. Each limit of detection was defined as the calculated amount of the OtC which corresponded to the average noise peak height + 3SD. Each limit of determination was defined as 3-fold amount of the limit of detection.

3. Results and discussion

3.1. Solvent appropriate for the liquid/liquid partition

To determine the lipophilic solvent species to be appropriate for the liquid/liquid partition extraction, the extraction efficiencies of OtC (MMT, DMT, TMT, DBT, TBT, TeBT, TPT, DOT, and TOT; sample=0 g; added OtC=2 μg as Sn each; $n=2$) were first examined with *n*-hexane solution (30 mL) containing 67% (v/v) of a tested chemical in the solvent extraction after the reflux-extraction. The experimental results are shown in Table 1.

Though 100% *n*-hexane was used for the extraction solvent in the liquid/the methanolic buffer solution partition in order to perform clean analysis without hazardous dichloromethane in the previous studies [22,23], the recoveries of DBT from a cloth diaper were lower than them of the lipophilic OtC (e.g. TBT).

In this study, water-soluble methyltin compounds were also used as tested compounds, but they were hardly extracted in all experimental conditions. The *n*-hexane solutions containing the alcohol or methyl acetate generally induced a little loss in the extraction efficiencies of TBT, TeBT, TPT, DOT, and TOT in comparison with the efficiency value obtained with 100% *n*-hexane. However, the other solvent species caused little loss in the extraction efficiencies of those 5 compounds, and additionally, they improved the efficiencies of DBT and TMT.

The average extraction efficiency of DBT was 8.4% in the experiments to use 100% *n*-hexane. However, the efficiency values were appreciably enhanced by utilizing TBEE, diethyl ether, ethyl acetate, which possess oxygen atom in their molecules and are comparatively less hydrophilic than alcohols. In the experiments to utilize TBEE, the efficiency value of DBT run into 27.5%, and 1.9% of TMT could be also extracted.

It was speculated that the coordination compounds (e.g. DBT $[Sn]\delta^{+}\ldots[O]\delta^{-}$TBEE; DBT$[H]\delta^{+}\ldots[O]\delta^{-}$TBEE) might be formed by weak intermolecular forces between the OtC (e.g. DBT; TMT) and TBEE, and consequently, their extraction efficiencies would be improved.

Moreover, it was presumed that the poor solubility of TBEE ($\log P_{ow}=1.9$) in water would be closely concerned in the increase in the extraction efficiencies of DBT and TMT of which $\log P_{ow}$ values are lower than hydrophobic OtC (e.g. TBT). The volumes of the upper layer containing *n*-hexane were also measured to estimate the mechanisms of partition of OtC between the hydrophobic liquid and the methanolic buffer solution. The upper layers varied in volume from 9.5 to 29 mL (Fig. 1). The volume of TBEE dissolved in aqueous layer was much smaller (6 mL) than that of diethyl ether (16.8 mL). The extraction efficiencies of TMT and DBT acquired by utilizing TBEE were higher than those by utilizing diethyl ether. Conversely, their extraction efficiency values of hydrophobic OtC (e.g. TOT) were analogous. Thus, it has been thought that the 5 lipophilic OtC and the 2 possibly formed coordination compounds would show a tendency to coexist with the solvent of low polarity, and that they would be readily distributed to the *n*-hexane layer.

Table 1
Extraction of organotin compounds from the methanolic buffer layer by the solvent extraction to employ *n*-hexane-solution containing 67% (v/v) of a tested chemical.

Chemical[a]	Extraction efficiency (%)[b]								
	MMT	DMT	TMT	DBT	TBT	TeBT	TPT	DOT	TOT
2-Propanol	0.0	0.0	0.0	4.9	105.3	103.3	72.2	126.1	120.9
1-Butanol	0.0	0.0	0.0	3.0	81.2	88.3	45.1	95.9	100.9
2-Methyl-2-butanol	0.0	0.0	0.0	4.7	90.7	96.1	68.2	114.9	114.6
Diethyl ether	0.0	0.0	0.38	20.4	92.8	91.5	85.6	108.9	105.6
tert-Butyl ethyl ether	0.0	0.0	1.9	27.5	89.3	86.3	86.9	103.3	105.3
Methyl acetate	0.0	0.0	0.0	7.6	84.1	86.4	67.2	106.7	100.5
Ethyl acetate	0.0	0.0	0.0	19.7	92.5	92.7	91.6	118.0	111.2
Cyclopentane	0.0	0.0	0.0	16.1	92.6	91.2	84.1	104.9	96.6
Cyclohexane	0.0	0.0	0.0	12.4	81.0	79.8	87.8	91.3	96.6
Cycloheptane	0.0	0.0	0.0	17.2	87.5	87.9	81.7	92.6	86.5
n-Pentane	0.0	0.0	0.0	4.0	96.5	98.0	88.3	107.1	104.9
n-Hexane[c]	0.0	0.0	0.0	8.4	103.6	105.7	108.1	125.0	125.5

[a] Volume of a tested chemical (organic solvent) added to 10 mL of *n*-hexane: 20 mL.
[b] Sample: 0 g. Organotin compound added to the methanolic solution for the reflux: 2 μg as Sn each. Average. ($n=2$).
[c] *n*-Hexane: 100% (30 mL).

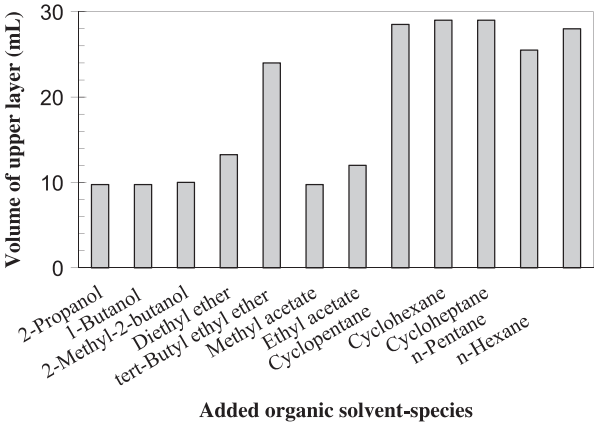

Fig. 1. Effect of added organic solvent species on volume of upper layer containing *n*-hexane. Average. ($n=2$).

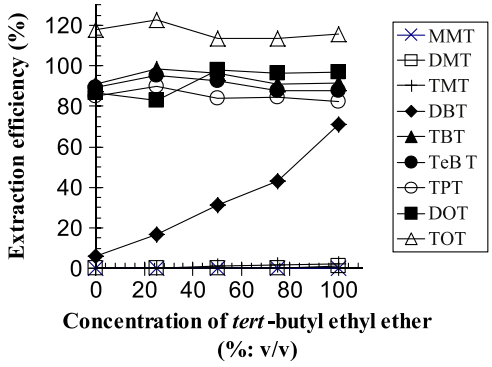

Fig. 2. Effects of amount of added *tert*-butyl ethyl ether on extraction efficiencies of organotin compounds. Average. ($n=2$).

In these experimental results, it was suggested that TBEE would be useful for the partition extraction of several hydrophobic OtC and slightly less hydrophobic OtC such as DBT from the methanolic buffer layer.

3.2. Utilization of TBEE for the extraction

The effects of the amount of added TBEE on the extraction of OtC from the buffer solution layer were also investigated. The proportions of the volume of TBEE to total volume (30 mL) of organic solvent containing *n*-hexane were varied from 0 to 100%, and the extraction efficiencies of 9 OtC (sample=0 g; OtC=2 μg as Sn each; $n=2$) were determined (Fig. 2).

The increases in the extraction efficiencies of TMT and DBT were found according to the rise in the amount of TBEE. The efficiencies of 5 OtC of comparatively high log P_{ow} values rarely decreased. 71% of DBT could be drawn out with 100% TBEE. This extraction efficiency value was 8.5 times as high as that obtained with 100% *n*-hexane. It was estimated from these results that by utilizing 100% TBEE in the place of hydrophobic *n*-hexane [23,25], DBT, TBT, TeBT, TPT, DOT, and TOT would be able to be extracted concurrently without large loss.

3.3. Recoveries

The results of recovery tests are summarized in Table 2. Small losses of five lipophilic OtC were observed. Although methyltin compounds could not be generally recovered, the recoveries of DBT surpassed 60%. The average recoveries of DBT, TBT, TeBT, TPT, DOT, and TOT from textile products (socks, undershirt, and cloth diaper) were 60–77, 89–98, 86–94, 71–78, 85–109, and 70–79% ($n=4$) respectively, and the coefficients of variation were less than 16.5%.

Table 2
Recoveries of organotin compounds added to textile-products.[a]

Organotin compound[c]	Diaper[b]		Socks[b]		Undershirt[b]	
	Recovery[d] (%)	C.V.[e] (%)	Recovery[d] (%)	C.V.[e] (%)	Recovery[d] (%)	C.V.[e] (%)
MMT	0.0	ND	0.0	ND	0.0	ND
DMT	0.0	ND	0.0	ND	0.0	ND
TMT	1.0	9.1	1.2	14.6	1.3	39.5
DBT	60.2	16.5	70.7	10.9	77.3	10.2
TBT	88.7	10.6	91.8	4.0	97.6	8.6
TeBT	85.8	10.6	85.5	4.0	94.1	9.2
TPT	73.9	9.2	70.9	0.8	78.3	9.4
DOT	92.2	11.3	85.4	2.5	109.0	8.1
TOT	72.1	11.8	69.9	5.0	79.0	9.5

[a] Proposed reflux extraction-solvent extraction (100% *tert*-butyl ethyl ether: 30 mL)-ethylation method.
[b] Materials; Socks: Cotton (Co), acryl (Ac), nylon, and polyurethane. Undershirt: Co; Diaper: Ac and Co.
[c] Organotin compound added to the sample (2 g): 2 μg as Sn each.
[d] Average. ($n=4$).
[e] Coefficient of variation. ND: Not determined.

Though the average recovery of DBT from the cloth diaper in the previous tests to employ 100% *n*-hexane for the liquid/liquid partition extraction solvent was below 10% [23], 7.0-fold increase in the recovery from the same product was found in this extraction method to use 100% TBEE. Slightly more rapid analysis could be also realized by reducing the number of times (from twice to once) of the liquid/liquid partition extraction than the analysis by the method [26] notified in Japan. It was suggested by these results that this modified method would be applicable to the simultaneous determination of DBT, TBT, TeBT, TPT, DOT, and TOT in textile goods.

3.4. Linearity

The standard-mixture containing DBT, TBT, TeBT, TPT, DOT, and TOT (concentration of each OtC: equivalent; concentration: 0.01; 0.05; 0.2 μg as Sn mL^{-1}) were utilized, and the correlation coefficients were calculated ($n=4$) by the linear least-squares regression method to plot the peak area against the concentration. Adequate linearities (0–0.2 μg as Sn mL^{-1}) were discerned, and the correlation coefficients were 0.9922–1.0000.

3.5. Limits of detection

The absolute limits of detection of DBT, TBT, TeBT, TPT, DOT, and TOT were 4.9, 3.3, 3.4, 3.9, 2.7, and 9.7 pg as Sn ($n=4$: average) respectively. It was estimated from these data that 2.7–9.7 ng as Sn g^{-1} of the OtC would be detectable in real sample. The blank tests (sample=0 g) were performed twice, and 0.039 μg as Sn mL^{-1} of DOT and 0.0041 μg as Sn mL^{-1} of TOT (average concentration each) were detected in the tested solutions for GC-FPD analysis. The concentrations of these detected DOT and TOT were similar to the levels perceived in the former studies [23,25].

3.6. Determination of OtC in marketed textile goods by the developed method

6 OtC in the marketed textile goods were determined by the developed method to employ 100% TBEE for the extraction solvent in the organic solution/methanolic buffer solution partition following the reflux-extraction. The results are summarized in Table 3. The large interference peaks by which purification was

Table 3
Organotin compounds determined in textile goods.

Sample	Content (μg as Sn g^{-1})[a]						Material(s)[b]
	DBT	TBT	TeBT	TPT	DOT	TOT	
Baby socks	ND[c]	ND	ND	ND	ND	ND	Co, Ac, Ny, Pu
Diaper	ND	ND	ND	ND	ND	ND	Co
Diaper cover	0.24	ND	0.013	ND	0.65	0.051	Pe
Drawers	0.24	ND	ND	ND	ND	ND	Co, Ac, Pe, Pu, Ra
Girdle[d]	0.05	ND	0.017	ND	ND	ND	Co, Ny, Pu

[a] Average. ($n=2$).
[b] Co: Cotton, Ac: Acrylic, Ny: Nylon, Pe: Polyester, Pu: Polyurethane, Ra: Rayon.
[c] ND: Not determined.
[d] Chinese product. The other textile goods were made in Japan.

required for the determination of targeted OtC did not appear in the GC-FPD chromatograms originated from samples. These phenomena may be attributed to the extraction to use *n*-hexane in the ethylation step in addition to the liquid/liquid partition extraction to employ TBEE. It is thought that the hydrophilic contaminants to originate in the samples would be removed from the test solution for the gas chromatography.

Moreover, it was appraised that in these experiments, reflux-extraction, liquid/liquid partition extraction, and ethylation were carried out accurately, since the average recoveries of 1 μg g^{-1} as Sn of TPentT which was fortified to baby socks, cloth diaper, diaper cover, drawers, and girdle were 62.8, 96.8, 88.5, 80.0, 75.6% respectively.

TBT and TPT were not detected in the textile goods. These results suggested that those compounds were not used for the tested textile goods as biocides.

On the other hand, 0.65 μg g^{-1} as Sn of DOT were detected in the diaper cover. The residue of DOT in textile goods is not regulated in Japan [26]. However, this compound is also harmful to mammals [7,31,32]. Approximately twenty years ago, Nakashima et al. [18] clarified that high DOT contents of retailed diaper covers were found by the method to employ the HPLC, and Yamada et al. [19,20] revealed that the analogous facts were discerned by the method which comprised of the notified extraction procedure to employ dichloromethane [26], the propylation to utilize *n*-propyl magnesium bromide, and gas chromatography. The author [22,23,25] also reported in recent years that DOT above 100 μg as Sn g^{-1} were occasionally discovered in baby diaper covers by the method to use a conventional GC-FPD.

DOT has been being utilized as the catalyst in the production of silicone. It was considered that the high DOT contents of the retailed products in the prior studies [22,23,25] would arise from waterproofing with silicone coating agents containing DOT. The DOT content of the diaper cover which was determined in this study was below 1 μg g^{-1} as Sn. Accordingly, it was thought that this analyzed diaper cover did not receive the treatment for the waterproofness.

0.050–0.24 μg g^{-1} as Sn of DBT were determined in 3 textile goods. The residue of noxious DBT [8–11,31] in them is not regulated in Japan [26]. DBT has been being used as the catalyst in the production of polyurethane. DBT was detected in the drawers and the girdle which included polyurethane as the material for the production. In the other studies [20,22,23,25], DBT was found out frequently in the textile goods containing polyester. In this study, DBT was also determined in two samples which include polyester as the ingredient.

Smaller amounts of TeBT than those of DBT were determined in the diaper cover and girdle. It was thought that the TeBT would be the by-product in the production of DBT. Di-OtC was considered to be the main OtC species detected in the samples. In these experimental results, it was thought that these OtC might remain as the impurities coexisting with the materials (e.g. polyurethane) of the textile goods.

It is presumed that in these days, tri-OtC is not probably utilized as the bactericides or the fungicide in the processing of the textile goods for household commodities. However, there is a possibility that determining the other OtC, for instance, di-OtC and/or tetra-OtC in the textile goods for babies and ladies at trace amount levels would be significant to investigate the deleterious influences of the exposures hereafter. DOT induces the developmental toxicity in mice [32]. Tetraalkyltin compounds are dealkylated by the cytochrome P-450 systems, and consequently the most toxic trialkyltin compounds are able to be formed [31].

3.7. Speciation by the method of controlling signal intensity-flame fuel gas pressures

The method of controlling signal intensity-flame fuel gas pressures [22–25,33,34] is a speciation technique to be being studied to identify targeted OtC more accurately with a GC-FPD. In this scrutiny, the detected peak (chemical) is characterized on the basis of the change in the signal intensity accompanied by altering the fixed flame fuel gas pressures.

In the determination of toxic OtC, for instance, TBT, which is a kind of endocrine disrupting chemicals, it is assumed to be preferable that in general, the GC-FPD would be set to be the highest sensitivity for tin compounds. In the environmental analyses to utilize a GC-pulsed FPD, Bancon-Montigny et al. [29] performed the optimization of the gas pressures of H_2 and air under considering the resolutions between the detected peaks. Because in my experimental GC-conditions (e.g. column oven temperature program), the targeted OtC peaks were able to be separated respectively, by reference to the previous data [33,34], the flame fuel gas pressures of H_2 and air for the determination were correspondingly adjusted at 1.8 kg cm^{-2} and at 1.4 kg cm^{-2} so as to acquire the maximum sensitivities.

A few small peaks which did not correspond to targeted OtC appeared in the GC-FPD chromatogram to originate from the diaper cover sample. Accordingly, on the basis of the data obtained in the previous studies [22–25,33,34], the gas pressures of H_2 and air of the GC-FPD were further regulated at 0.6 kg cm^{-2} and at 0.8 kg cm^{-2} respectively. The results are shown in Fig. 3 (10 OtC: 0.05 μg as Sn mL^{-1} each) and Fig. 4 (diaper cover sample).

The author formerly reported that by modulating this condition, flame extinguishing would not be caused by the injection of test solution, and the conspicuous decrease in the peak areas of the OtC would be also observed [22–25,33,34]. By this modification of the flame fuel gases condition, significant reductions in the signal intensities of standard OtC were discerned. The GC peak areas of targeted OtC (Fig. 4: Peaks 1, 2, 4, and 5) also decreased in a similar manner. To the contrary, the peak areas of *n*-hexane not including tin atom in the molecule slightly increased. It is considered that the shape of the response curve plotting the signal intensity versus the fuel gas pressures would be characteristic of the chemical species detected in the GC-FPD [22–25,33,34]. Therefore, it was thought to be verified more evidently by applying this technique that the peaks 1, 2, 4, and 5 would be DBT, TeBT, DOT, TOT, respectively. Moreover, it was suggested that the unknown substances (e.g. the peak of just prior to peak-5 in Fig. 4) peaks would be the compounds including tin atom(s) in their molecules. Hence, a possibility that various OtC containing non-targeted species in textile goods would be picked out more specifically by the studying speciation-approach of controlling signal intensity-flame fuel gas pressures of a GC-FPD was also found out.

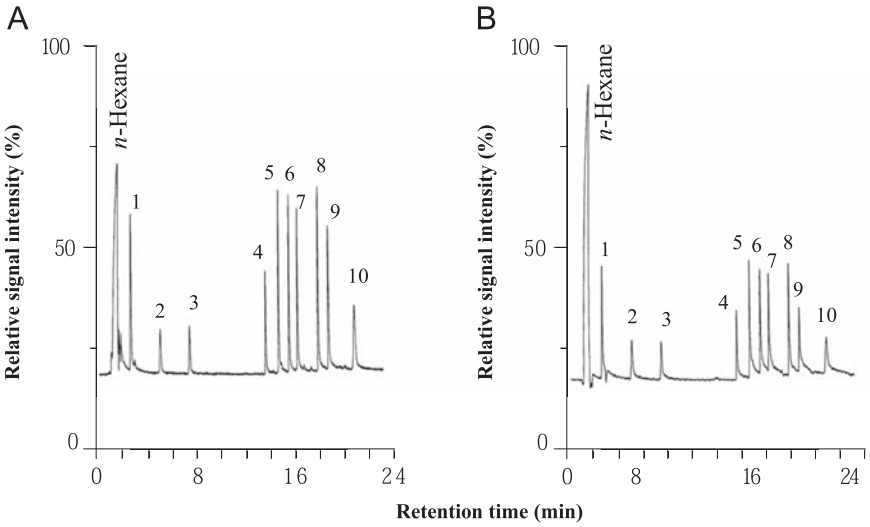

Fig. 3. GC-FPD Chromatograms of ten organotin compounds. Flame fuel gas pressures (kg cm^{-1}) (A): H_2=1.8, Air=1.4. (B): H_2=0.6, Air=0.8. Column: The DB-1 (J&W). GC-peak; 1: TMT, 2: DMT, 3: MMT, 4: DBT, 5: TBT, 6: TeBT, 7: TPentT 8: DOT, 9: TPT, 10: TOT. Ethylation was performed. 250 pg as Sn each.

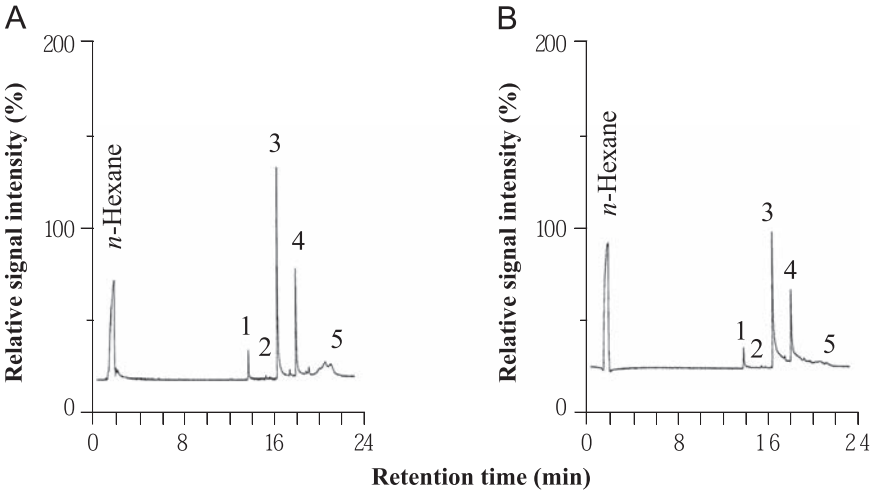

Fig. 4. GC-FPD Chromatograms of the extract from a diaper cover. Flame fuel gas pressures (kg cm^{-1}) (A): H_2=1.8, Air=1.4. (B): H_2=0.6, Air=0.8. Column: The DB-1 (J&W). GC-peak; 1: DBT, 2: TeBT, 3: TPentT (standard substance fortified to the sample for checking analytical condition), 4: DOT, 5: TOT. The proposed method was applied to the sample analysis.

4. Conclusions

In this study, it has been revealed that with a conventional GC-FPD, the five lipophilic OtC (e.g. TBT) and slightly less lipophilic DBT in textile goods would be able to be determined simultaneously by applying the developed method to utilize TBEE for the extraction solvent, in place of hazardous dichloromethane, in the liquid/methanolic buffer partition following the reflux extraction. The prominent characteristics of TBEE in extracting the OtC through the liquid/buffer solution partition were uncovered in comparison with those of the other organic solvents. Small losses of the OtC in the recovery tests suggested that this recommended method would be applicable to real textile sample analysis. It is estimated that 0.01 μg as Sn g^{-1} levels of DBT, TBT, TeBT, TPT, DOT, and TOT in those products would be capable of being determined satisfactorily by this method. These estimated levels were 100-fold lower than the detection limit(s) of TBT and/or TPT notified in the Japanese official method(s). By the developed method, five marketed textile goods were analyzed, and 0.013–0.65 μg as Sn g^{-1} of OtC were determined in three. Found out DBT, TeBT, DOT, and TOT were considered to be the impurities coexisting with the materials (e.g. polyurethane) of the textile goods. Moreover, it has been shown that in the analysis to utilize the GC-FPD, diverse OtC might be able to be detected more specifically and comprehensively through applying the studying speciation-technique of controlling signal intensity-flame fuel gas pressures.

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