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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

Tetsuo Hamasaki *

Environmental Health Department, Nagoya City Public Health Research Institute, 1–11 Hagiyama-cho, Mizuho-ku, Nagoya 467-8615, Japan

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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

* Tel.: +81 52 841 1511; fax: +81 52 841 1514.
E-mail address: t.hamasaki.dr@city.nagoya.lg.jp

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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.