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Speciation of organotin compounds released from poly(vinyl chloride) at increased temperature by gas chromatography with atomic emission detection

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Abstract

A method for sampling and analysis of airborne organotin compounds emitted from poly(vinyl chloride) (PVC) was developed and tested. The organotins originating from dibutyltin maleate, mono- and dioctyltin mercaptoacetate stabilizers were released from PVC under controlled conditions and recovered from the sorption part of a sampling tube. The composition of the sampling material in the tube was optimized to get a reproducible release and complete sorption of the target compounds and to simplify the extraction procedure. An optimized extraction procedure together with aqueous phase derivatization and determination by gas chromatography–atomic emission detection resulted in a selective and reproducible determination of the organotin compounds. Influences of different thermoplast temperatures, heating times, purge flow gases and purge flow rates on the release of organotins from PVC have been evaluated. Significant amounts of dibutyltin were found to be released from a PVC sample stabilized with dibutyltin maleate at temperatures of 108°C to 200°C. © 1997 Elsevier Science B.V.

Keywords: Sample handling; Derivatization, GC; Organotin compounds; Poly(vinyl chloride)

1. Introduction

Organotin compounds used as stabilizers for poly(vinyl chloride) (PVC) are applied in a large industrial scale. World consumption of organotins can be estimated to be about 25 000 tons per year [1,7]. These compounds are applied as additives to prevent dehydrochlorination of the polymer during processing and to strengthen the finished product against long-term degradation. Dialkyltin compounds are of the general structure R_2SnX_2 in which R usually corresponds to a methyl, *n*-butyl or *n*-octyl group; X may be a mercaptide or mercapto acid ester group or a carboxylate group such as maleate or laurate. Dialkyltins are esteemed because of their excellent thermostabilizing properties. In the case of elevated thermoplast temperatures which occur during the processing of the plastics like extrusion, milling, hot-wire cutting or bandsawing or in case of fire the stabilizers react with hydrochloric acid formed in the thermoplast to their corresponding dialkyltin dichlorides. These chemicals can therefore be expected to be present in environments where PVC is processed.

Organotin compounds have widely been applied in

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antifouling paints and as agrochemicals which has resulted in a substantial release of these substances into the aquatic environment. Due to the quantities involved and due to their toxicity to aquatic organisms, alkyltins are considered to be environmental pollutants [2–4]. Among them, tributyltin (TBT) and dibutyltin (DBT) have been included in the priority pollutant list of contaminants issued by the European Union [5]. Release of alkyltin compounds from other organotin-containing materials like PVC pipes has been suggested as a source of DBT and monobutyltin (MBT) in river water and effluents from sewage treatment plants [6–9]. Investigations on the occurrence of organotins in air have been made to a small extent [10,11]. Besides the simulation of the process of PVC combustion in an incineration plant [13], one work shows degradation products of dibutyltin mercaptide and dioctyltin mercaptide stabilizers detected in fumes released from PVC at 225°C [12]. References which specifically investigate organotin emissions from PVC into ambient air under various conditions and temperatures of plastics processing have not yet been published. Thus, the purpose of this study was to develop a method for quantitative determination of organotins released from PVC under controlled temperature and flow conditions.

In general, organotin compounds used as PVC stabilizers have not been found to be highly acutely toxic in toxicological investigations. On the other hand evidence was found for immunotoxic, genotoxic and teratogenic effects to rodents for dibutyltin dichloride and partly for dioctyltin dichloride [14,15]. Experiments which compared toxic effects of di- and tributylated tins on rodents state that an estimation of organotin toxicity should consider the toxicity of dibutyltin compounds beside the tributylated species [3]. For the present sufficient toxicological data are not available to evaluate their toxicity to mammalians.

Experimental parameters of this study have been chosen with consideration given to earlier results. Filters and adsorbents like Chromosorb 102, a set of two quartz fibre filters and charcoal filter as well as glass fibre filters were tested for sorption of alkyltins from ambient air or cooled PVC fumes [10–12]. However, the sorption efficiency of the materials was tested as retention efficiency of the materials spiked with pure organotins. In stability tests, the target compounds were shown to be stable for several weeks if stored on an adsorbent or a filter and kept at −20°C [3,11,16].

For the extraction of organotins from adsorbents and filters, from sediments or from polymers basically three procedures are used; extraction with solvents with or without a complexing agent, acid digestion followed by a solvent extraction or extraction by supercritical fluids. Dialkyltins can be quantitatively extracted from glass fibre filter (GFF) by hexane [12], whereas extraction of di- and trialkyltins from activated carbon fibre collection filter is difficult [11]. Acid digestion was found to be necessary for efficient extraction from particulate matter [2]. Diluted HCl (0.1 *M*) was found to be too weak, but on the other hand 2–8 *M* HCl caused degradation of the analytes [17]. One of the most often used extractants was methanolic HCl itself [3,4,11,18] or in combination with tropolone [6,19,20] or some other complexing agent [21]. While pure acetic acid was shown to be an inefficient extraction medium [22], methanolic acetic acid (0.5 *M*) used for the microwave assisted extraction of di- and tributyltins from sediments was proven to be successful [23]. Sonication was also found to be effective for extraction of organotins from sediment with 0.5 *M* HCl in MeOH [24]. On the other hand Soxhlet extraction using hexane–acetone was found to be an inappropriate method for DBT and MBT extraction from sediments [25]. Application of formic acid modified carbon dioxide for supercritical fluid extraction and chromatography of dimethyltin from PVC yielded complete extraction recoveries [26].

For GC analyses it is necessary to convert the dialkyltin dichloride species into fully alkylated derivatives. Among the available methods such as hydride generation [3,12], alkylation by Grignard reagents and direct aqueous phase ethylation using sodium tetraethylborate, the last method offers several advantages. Compared to hydride generation, alkyl derivatives obtained by direct aqueous phase ethylation or Grignard alkylation are more stable and can be stored for a limited time [7]. Direct aqueous phase ethylation [4] can be performed in a simple, fast way; solutions obtained by extraction of the derivatives into isooctane [23], pentane, or hexane [27] are directly applicable to GC. Ethylation of organotins in complex matrices is said not to suffer from interfer-

ences [24,28]. On the other hand, the yield of the ethylation reaction is influenced by the degree of alkylation and/or by the nature of the alkyl groups [28] of an organotin compound. The derivatization is also affected by pH, temperature of the solution, reaction time and concentration of the reagent [23,28].

An appropriate method for the determination of organotins consists in capillary GC with a selective detector. Several detectors used for the identification and the determination of organotins were compared in literature [21,25,29]. Most promising seems to be atomic emission detection (AED) with a microwave induced plasma. The advantages consist in multi-element and multi-channel detection, good linearity, selectivity and high sensitivity [17,21,30,31].

This work presents a sampling method for organotins released under controlled conditions from PVC at thermoplast temperatures between 108°C and 200°C and a method for their extraction from adsorbents, derivatisation by aqueous phase ethylation and determination by GC–AED.

2. Experimental

2.1. Apparatus

An adapted gas chromatograph Chrom 6 (Laboratory Works, Prague, Czech Republic) was used for sampling of organotins from heated PVC onto adsorbents. The instrument was provided with a high pressure (1.5 MPa) GC gas supply and a flow control. Using copper tubing the carrier gas output was connected to the sampling tube input near the bottom of the oven space. The sampling tube was fixed in a vertical position having the desorption part in the oven and protruding the injector chamber above the instrument box (Fig. 1). The adsorption part of the sampling tube was situated on top of the instrument. The sampling tube was isolated from the hot oven wall by a PTFE ring above which a round plastic bottle sealed in a fitting by silicone ring was placed round the sorption part of the sampling tube. The plastic bottle contained a water bath at 0°C.

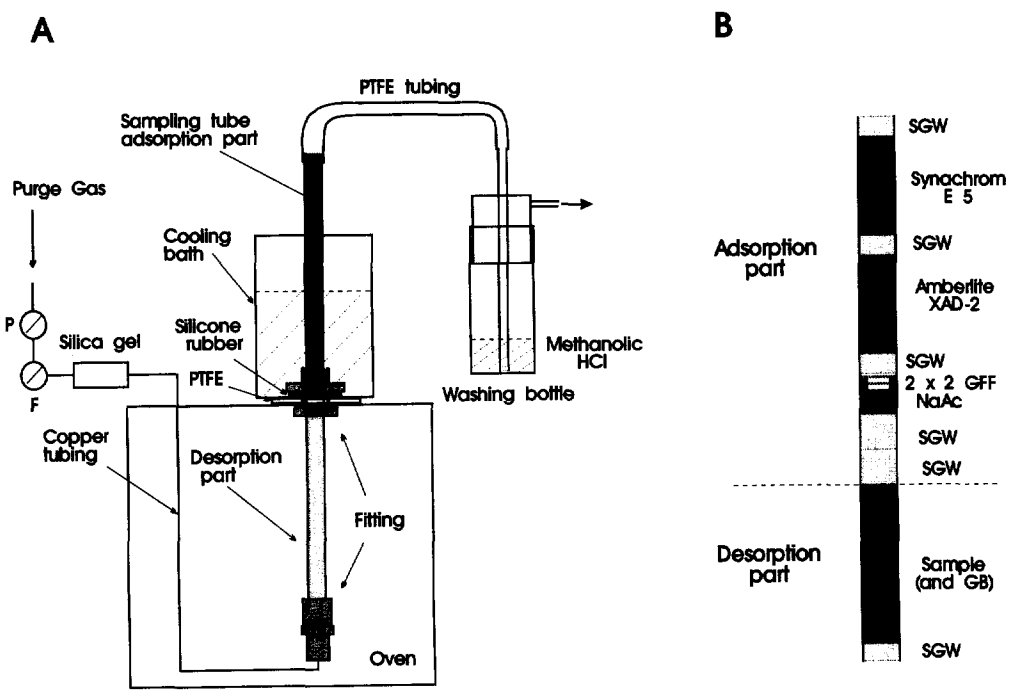

Fig. 1. Schematic diagram of the apparatus for sampling of organotin compounds (A) overwiew (B) composition of the sampling tube

Using a PTFE tubing the output of the sorption tube was connected to a washing bottle.

A Bransonic B 220 ultrasonic bath with an output power of 50 W was used to increase the mass transfer during the extraction and the derivatization of the organotins.

Separation of ethylated organotin species was performed using an HP Model 5890 Series II gas chromatograph (Hewlett–Packard, Avondale, PA, USA) coupled to an HP 5921A atomic emission detector. The GC system was equipped with an HP 7673 A automatic sample injector and an HP on-column injection inlet. This was fitted with a deactivated retention gap (HP, 0.3 m×0.53 mm I.D.) connected in series to a DB-1 fused-silica column (20 m×0.25 mm I.D., 0.1-μm film, J&W Scientific, Folsom, CA, USA). The GC column was connected directly to the AED cavity. Helium of 99.9999% purity was used as a carrier gas at a linear velocity 0.30 m s^{-1}. The GC–AED system was controlled by an HP 9000 CHEMSTATION. The AED response of the atomic emission detector was optimized to get the best selectivity and linearity. Optimal conditions were similar to those described in the literature [17,21,31]. The carbon channel at 248 nm was monitored together with the tin selective line at 271 nm. No interferences were noticed on the tin selective channel.

An Incos 50 quadrupole mass spectrometer (Finnigan MAT, San Jose, CA, USA) connected to a Varian 3400 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a DB-5-MS column (30 m×0.25 mm I.D., 0.25-μm film, J&W Scientific) was used for complementary solute identification.

2.2. Reagents

Dibutyltin dichloride was obtained from Fluka (Buchs, Switzerland), dioctyltin dichloride from Riedel-de Haën (Hannover, Germany), dimethyltin dichloride from Merck–Schuchardt (Hohenbrunn, Germany), dicyclohexyltin dibromide from Alfa (Karlsruhe, Germany), monobutyltin trichloride and tetrabutyltin from Aldrich (Milwaukee, WI, USA). They were all used as standards. Sodium tetraethylborate was obtained from Strem Chemicals (Bischheim, France). The chemicals were used without further purification. Isooctane and methanol as well as acetic acid and sodium acetate (all from Merck) were of analytical grade. Hydrochloric acid (Merck) was of suprapure quality. Silane treated glass wool and Amberlite XAD-2 were obtained from Supelco (Bellefonte, PA, USA), Whatman glass fibre filters type GF/B were used (Whatman, Maidstone, UK) and regular glass beads, 80–120 mesh, were from Applied Science Labs. (State College, PA, USA). All other chemicals were of suprapure quality and were obtained from Lachema (Brno, Czech Republic).

2.3. PVC samples

Two different PVC samples were applied. Sample 1 consisted of pellets containing a mixture of di-*n*-octyltin di(2-ethylhexyl-mercaptoacetate) and mono-*n*-octyltin tris(2-ethylhexyl-mercaptoacetate) at a content of 0.21% Sn. Sample 2 was a powder containing dibutyltin di(methylmaleate) at a content of 0.62% Sn. Both samples were obtained from Hydroplast (Helsingborg, Sweden).

2.4. Procedure

2.4.1. Sampling

Sampling of the organotins released at elevated temperatures from the PVC samples was achieved by using a glass tube (0.30 m×7 mm I.D.), consisting of a desorption part filled with a PVC sample and immersed in the GC oven, as shown in Fig. 1, and a cooled sorption part packed with filters and adsorbents. Regular glass beads were in some cases mixed with the PVC sample 1 in order to prevent clogging of the tube. The optimal set-up of the sorption part corresponding to 1.5 g of PVC in the desorption part consisted of 0.2 g of sodium acetate, two couples of Whatman GF/B glass fibre filters, 0.8 g of Amberlite XAD-2 and 0.6 g of Synachrom E5. Each layer was separated from the upper and the lower layer with a small plug of silylated glass wool. Twice the amount of the silylated glass wool was placed in between the desorption and adsorption part of the glass tube. The glass fibre filters were fixed in the glass tube by PTFE-coated rings cut out from a GC inlet septa. The washing flask connected with the outlet of the sorption part of the glass tube was filled with 25 ml of 1 *M* HCl in methanol. A flow of

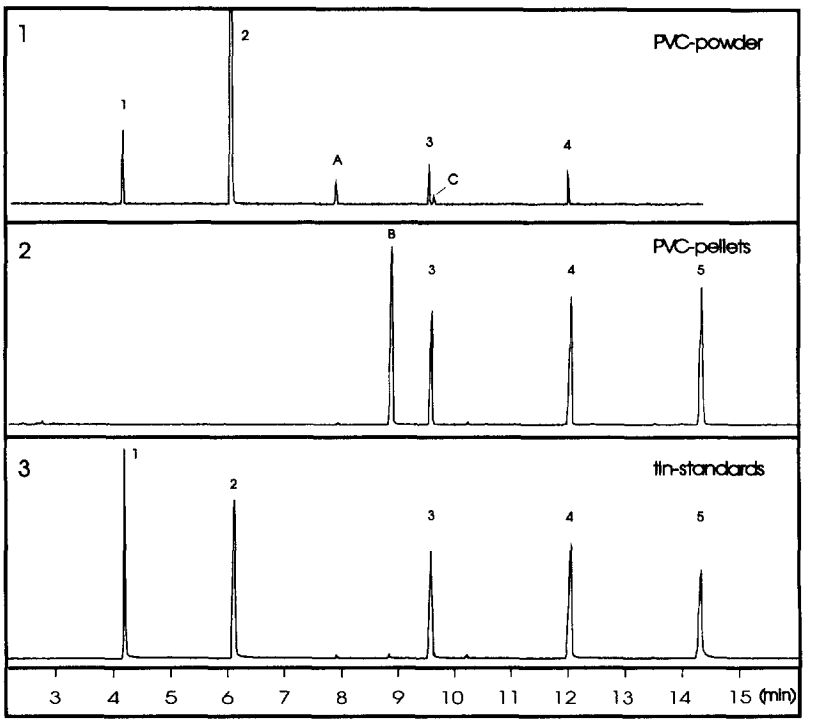

Fig. 2. Gas chromatographic separation of organotin compounds using the tin-selective channel at 271 nm emission wavelength for detection. Chromatograms 1 and 2: organotin compounds released from PVC (conditions: temperature 200°C, purge gas air, 2 h sampling) compound A=tributyltin chloride, B=monooctyltin trichloride, C=octylbutyltin dichloride, other peaks correspond to chromatogram 3. Chromatogram 3: standard compounds: 1=monobutyltin trichloride, 2=di-butyltin dichloride, 3=tetrabutyltin (I.S.), 4=dicyclohexyltin dibromide (spiked), 5=dioctyltin dichloride.

nitrogen or air was precleaned by passing through a tube with a dry silica gel prior to entering the glass sampling tube and the GC oven was heated up to the desired temperature for a particular time. Each experiment was done twice. The sampling tubes were stored at −20°C for about 6 weeks before the analyses.

2.4.2. Leaching and derivatization

The adsorption part of the sampling tube including the glass wool between the desorption and adsorption part was cut into pieces and transferred into a screw-capped extraction tube. Each sample was spiked with dicyclohexyltin dibromide as internal standard and extracted with 6 ml of 0.01 *M* HCl or 1 *M* acetic acid in methanol under sonication for 90 min. After each 30 min, 4 ml of the extraction solution was exchanged for new solvent. The direct aqueous phase derivatization was performed similarly to a procedure described in the literature [23,28]. The pH of the collected extraction solution was adjusted to between 4.5 and 5.0 by an acetic acid–acetate buffer. A 1-ml volume of a freshly prepared solution of sodium tetraethylborate ($NaBEt_4$) in Milli-Q water (25 mg ml^{-1}) giving about a 20-fold molar excess to an assumed maximum quantity of 2 mg dialkylated tin compound was given to each extract at room temperature. After standing for 2–3 min the second internal standard, tetrabutyltin (TeBT) was added in 2 ml of isooctane. After being vigorously shaken for 5 min the mixture was left to separate and the organic phase containing the ethylated derivatives was exchanged with pure isooctane. This was repeated twice. The collected isooctane phase was directly analyzed by GC–AED.

GC–AED analysis: A 1-μl volume of sample was injected on-column at an initial oven temperature of 80°C. The temperature was held for 1 min, then

raised at a rate of 10°C min^{-1} to 220°C and further at a rate of 40°C min^{-1} to 300°C and kept there for 2 min.

3. Results and discussion

3.1. Optimization of the determination of organotins

3.1.1. Extraction efficiency

The effect of the extraction time and type of extractant on the extraction yield of the expected main decomposition products (dibutyltin dichloride, dioctyltin dichloride) from organotin stabilizers used in the PVC samples was estimated for the sorption materials applied in the sampling tube. For this, sodium acetate, glass fibre filter and Amberlite XAD-2 at an amount of 0.5 g as well as blanks were spiked with equal amounts of dibutyltin and dioctyltin dichlorides, each at a level of 0.33 mg total tin per gram adsorbent. Following extraction, derivatization and quantitation with internal standard were carried out in the same way for both the adsorbents and blanks. Recoveries from the adsorbents were related to blank recoveries. Two different extractants, 0.01 *M* HCl in methanol and 1 *M* acetic acid in methanol were applied at 3 different extraction times (15, 30 and 90 min). More concentrated methanolic HCl was avoided with respect to possible salt precipitations during the buffering process before the aqueous phase ethylation. While dibutyltin dichloride was quantitatively recovered from all adsorbents after 15 min of extraction with any of the extractants applied, 90 min extraction time was necessary for good recovery of dioctyltin dichloride from glass fibre filters and from XAD-2 adsorbent. The results for 90 min extraction time are summarized in Table 1. Both applied extractants showed almost equal abilities to extract the dialkytins. Methanolic HCl was selected for further experiments due to slightly better recoveries of dioctyltin (DOT) from Amberlite XAD-2. To enhance the extraction, the solution was exchanged with fresh extractant every 30 min. A lowered recovery for DOT from Amberlite XAD-2 indicates the need for a bit less polar extraction reagent to achieve an efficient extraction. Preliminary experiments showed that the more polar species monobutyltin could be fully sorbed and extracted from the sodium acetate layer applied in this study. In this way incomplete extraction of this compound reported can be overcome [3,4].

3.2. Derivatization

The choice of parameters for the ethylation procedure was adopted from experimental results described in [23,28]. The somewhat lower recoveries of DOT were shown to originate from the extraction step by blank experiments in which both dicyclohexyltin (DCyHT) and DOT showed the same complete derivatisation as DBT. The aqueous phase ethylation of the extracted ionic organotin species was compared to a direct in situ ethylation. In the later case the solution of sodium tetraethylborate was added directly onto the Amberlite XAD-2 adsorbent spiked with the organotin mixture and suspended in buffered methanolic HAc (pH 5.0). The extraction/derivatization was performed for 15 min and then the ethylated species reextracted into isooctane containing TeBT as the internal standard, similarly as with the direct aqueous phase ethylation. The results summarized in Table 2 show much lower recoveries for in situ derivatization. Therefore, the two-step procedure was used in this work. It must be noted that the in situ derivatization has been successfully

Table 1
Extraction recoveries (%) of organotin species from sorption materials used in the sampling tube

	Sorbent/Extractant				
	NaAc/HAc	GFF/HCl	GFF/HAc	XAD-2/HCl	XAD-2/HAc
DBT	109	108	94	94	93
DOT	110	99	99	80	68

NaAc, sodium acetate; GFF, glass fibre filter; XAD-2, Amberlite; HAc, acetic acid.
Extraction time 90 min.

Table 2
Organotin recoveries (%) from Amberlite XAD-2 by a two-step procedure of extraction and derivatization compared to one-step in situ derivatization

	Procedure	
	Two-step	One-step in situ
DBT	104	72
DOT	72	<10

Extraction time 15 min.

used for the determination of organotin compounds in tissues, however, at a cost of a strong increase in the consumption of the reagent [17].

3.3. GC determination and evaluation

Fig. 2 shows tin-specific chromatograms from the GC–AED analysis of the alkyltin compounds released from PVC samples using air as purge gas. The peaks were identified with the help of standards using GC–AED and from GC–MS analyses. The main tin containing decomposition products released from PVC were considered to be the chloride derivatives of the original monooctyltin, dioctyltin and dibutyltin stabilizers. While DOT was not proven to dealkylate to MOT dealkylation of DBT to MBT was found when using air as purge gas. Other minor tin components tentatively identified (tributyltin and butyloctyltin species) were considered to be a biostabilizer of the plast and a contaminant respectively.

Only a few tin-free compounds were found among the decomposition products in the extract of the adsorbents from the sampling tube as shown for sample 2 in Fig. 3. This documents a selective sorption and a selective extraction of the organotin species from the adsorbents.

The minimum detectable amount of tin released from PVC by the procedure was estimated from a spiking experiment. The glass wool placed between the desorption part, packed with a raw, tin-free PVC sample, and the trapping part of the sampling tube was spiked with 6.2 mg tin as DBT. The sampling tube was heated to 200°C for 4 h which was found sufficient to release all DBT from the glass wool. The minimum detectable level based on a ratio of DBT response to noise level equal three (peak

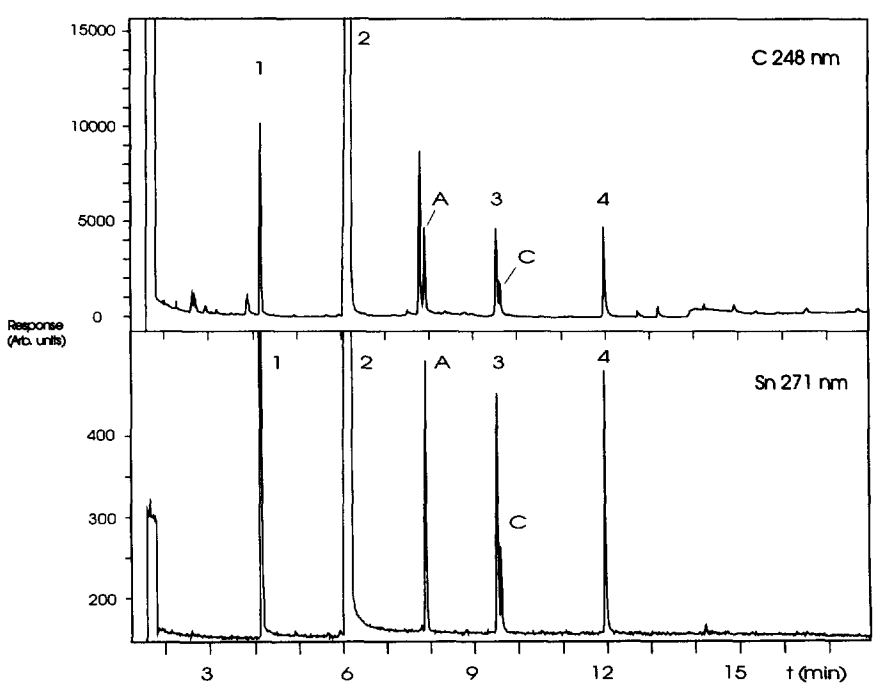

Fig. 3. Carbon and tin specific chromatograms of the derivatised extract from sample 2; conditions and solute identification as in Fig. 2

heights measured) was estimated to 20 ng tin per gram PVC.

Two internal standards were used for the evaluation. Quantification of DBT was done by help of TeBT added after the derivatization. DCyHT was shown to exhibit complete recovery and was used for quantification of DOT.

The linearity of GC–AED was about 3 orders of magnitude from the minimum detectable level using peak heights and even better when peak areas were used. However, this was not enough for estimation of low concentrations of some decomposition products at the same time as high concentrations of the main released organotins, especially of DBT. In this case one level of I.S. concentration was not applicable. Therefore, the amount of I.S. added before GC–AED analysis was selected to fit to minor components and the major components were determined from a diluted sample by the method of standard addition of the I.S. In this way, the absolute AED response overcame the lack of linearity for the major components. Peak heights were used for the peak evaluation, as they were shown to give slightly more precise results for small peaks when using GC–AED [32]. The relative standard deviation of the solute amount estimated by the above described procedure using different dilution was mostly below 10%.

3.4. Sampling of organotins released from the PVC samples

A set-up for controlled heating and release of organotin compounds from a PVC sample has been designed and tested at different temperatures and purge gas flows for different geometrical shapes of the sample. At the temperature interval applied, it was possible to maintain a constant purge gas flow through sample 2 (PVC powder containing dibutyltin methylmaleate). The pellets of the sample 1 were much more prone to stick together and therefore their mixing with an inert material was necessary together with an increased pressure of the purge gas at the sampling tube inlet to maintain a constant flow. Glass beads, 80–120 mesh, proved to serve well for this purpose at 65% of the PVC mass. An increased amount of glass beads had no effect on the release of the organotin compounds from the PVC sample.

Preliminary experiments using an atomic absorption spectrometer were aimed at determining a possible breakthrough of organotins into methanolic HCl, placed after the sorption system, as shown in Fig. 1. The collection efficiency of the set-up of filters and adsorbents was over 99.5% for gas volumes up to 200 l (3 experiments). Higher gas volumes were not investigated. A washing bottle with the methanolic HCl was placed behind the sorption part of the sampling tube in all experiments. In selected cases the content of the washing bottle was analyzed for tin species. In these cases tin compounds were proved to be absent. All the materials used for the sorption part of the sampling tube as well as the glass tube, glass wool and the glass beads were proved to be tin-free.

The sorption part of the sampling tube (Fig. 1) was designed to retain quantitatively organotins from both the vapor and particulate phase and to provide a sufficient retention capacity. The sorption ability of the different adsorbent layers and of the glass fiber filters was tested with a basic set of conditions (temperature at 200°C, gas purge flow at 100±20 ml min^{-1} and 4 h of heating).

Additionally, the organotins should be protected from decomposition when being stored for several weeks. Heated PVC releases hydrochloric acid, which possibly could increase the elution power of the purge gas and thus spread the organotins over the entire sorbing system or even decrease the recovery. Furthermore, the stability of organotin compounds under strongly acidic conditions has been questioned [18]. For this reason the first layer in the sorption part consisted of sodium acetate. As shown in Table 3 omitting this layer resulted in incomplete recovery.

Table 3
Dibutyltin amounts in different sorption layers of the sampling tube

Sample	1 (mg g^{-1})	2 (mg g^{-1})	3 (mg g^{-1})	4 (mg g^{-1})
NaAc	2.18	Na	Na	[a]
GFF	1.54	0.46	Na	[a]
XAD	0.43	2.36	2.41	[a]
Total	4.15	2.82	2.41	4.36

[a] The layer was applied in the sorption part, the amount of DBT was estimated from all sorption layers together.
Na=not applied.
Purge flow gas nitrogen.

On the other hand, when included, the main part of the released organotins was found in the sodium acetate layer. Almost equal total amounts of collected dibutyltin species were obtained from two comparable sampling tubes, of which the first one was analyzed partially layer by layer, the other in one analysis of all adsorbents together. Though the particulate phase which may contain the polar organotin compounds might be sorbed as well on the applied adsorbent (XAD-2), the best way to collect it consists in sorption on a GFF. Therefore, two sets of GFF were included after the sodium acetate layer. When using the standard set-up (see Fig. 1), including sodium acetate, glass fibre filters, XAD-2 and Synachrom E5 in series, the last layer of Synachrom E5 did not contain any organotin compounds sorbed. It was therefore excluded. The distribution of all alkyltins in the applied sorption system when using air as purge gas is shown in Table 4. The sampling tubes containing sodium acetate were found applicable for storage up to two months at −20°C. This was proved by spiking experiments which showed complete recovery of the spiked amounts.

Both nitrogen and air were used as purging gases to consider inert processing atmosphere as well as thermal stressing by air. While the released organotin species and their composition did not differ for different purge gases for the octyltin mixture, a slightly increased release of dibutyltin and decomposition to its monoalkylated form was found for the dibutyltin stabilizer (Table 5) when using air as purge gas. Taking literature data [1] into account, an almost equal release of DBT for different purge gases indicates the possibility for a release of the stabilizer itself beside the derivative from the decomposition process. A release of MBT indicates a dealkylation of the stabilizer in the presence of oxygen. DBT accounted for up to 98% of all released organotins from sample 2, while MBT contributed about 0.8%. The amounts of other minor components present in the sample 2 as TBT and BOT were similar irrespective of the purge gas applied.

Table 5
Comparison of the release of organotin compounds from PVC samples using nitrogen and air as a purge gas

Purge gas	MBT (mg g^{-1})	DBT (mg g^{-1})	MOT (mg g^{-1})	DOT (mg g^{-1})
N_2	0.06	4.15	0.29	0.60
Air	0.27	4.35	0.25	0.60

3.5. Effect of temperature, heating time and purge gas flow on the release of organotin compounds

3.5.1. Temperature

The amounts of released dibutyl- and octyltin compounds from commercially available PVC at temperatures of 110°C, 150°C and 200°C at different heating times are shown in Fig. 4 and Table 6. For thermoplast temperatures of 200°C high quantities of both target compounds could be determined. At 150°C the release of the less volatile octyltins is significantly decreased and occurs only for heating times above 8 h. At this temperature dibutyltin is still emitted with quantities of milligram per gram PVC. When the temperature is reduced to 108°C only DBT is detectable. At a sampling time of 32 h an increased DBT-release could be observed in the range of microgram DBT per gram PVC. A decrease

Table 4
Alkyltin distribution in the applied sorption system

Sorbent	MOT (mg g^{-1})	DOT (mg g^{-1})	MBT (mg g^{-1})	DBT (mg g^{-1})	TBT (mg g^{-1})	BOT (mg g^{-1})
NaAc	0.12	0.27	0.25	0.95	0.00	0.08
GFF	0.01	0.44	0.00	3.08	0.09	0.00
XAD	0.12	0.00	0.00	0.32	0.04	0.00
Total	0.25	0.71	0.25	4.35	0.13	0.08
AAT	0.32	0.62	0.25	4.43	0.10	0.05

Conditions: temperature 200°C, purge gas flow 100 ml min^{-1} air, sampling time 4 h.
AAT: all sorption layers analyzed together.

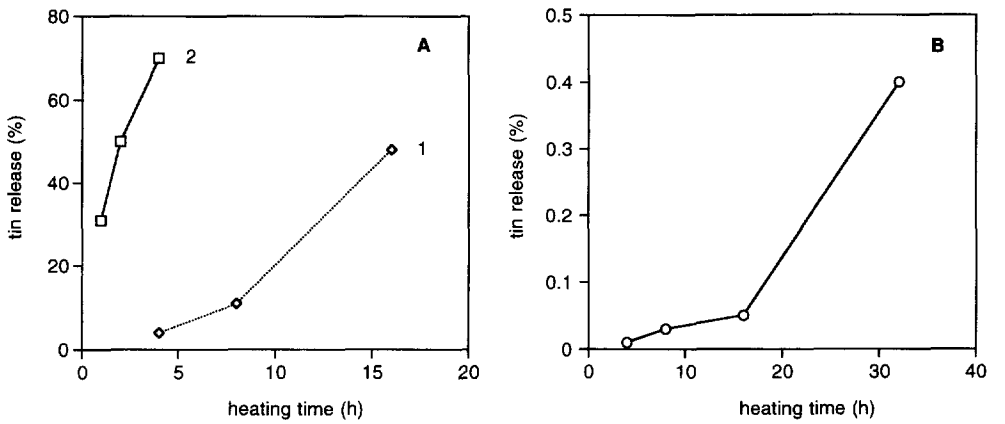

Fig. 4. Time dependence of the release of dibutyltin dichloride from PVC. (A) At a temperature of (1) 150°C and (2) 200°C; (B) at 110°C (unit: percent of total tin-content in the thermoplast)

of the release of MBT with decreasing temperature was found to be much more profound than for DBT, which indicates that MBT is formed to a lower extent at lower temperatures. This effect could not be seen for MOT and DOT.

3.5.2. Heating time

The dependence of the release of all detected organotins on heating times between 1 and 4 h was determined. The results are summarized in Fig. 5 and Table 7. A comparable speed of tin release was found for both PVC samples, the amounts of release were quite different. The differences consisted of increased volatility of DBT and highly differing surface areas of both materials. The number of measurements is too limited to be able to suggest kinetic data of the release.

Table 6
Alkyltin emission quantities (mg g^{-1} PVC) depending on PVC-temperature and heating time

Temperature (°C)	Heating time (h)	MBT	DBT	TBT	MOT	DOT
200	4	0.270	4.350	0.14	0.250	0.710
150	4	Nd	0.223	0.10	0.003	Nd
150	8	Da	0.680	0.16	0.003	Da
150	16	0.002	3.000	0.19	0.004	0.007
110	16	Nd	0.003	0.06	Nd	Nd
110	32	Nd	0.024	0.06	Nd	Nd

Nd=not detected.
Da=detectable amount.

3.5.3. Purge gas flow

The release of organotins consists of the transport inside the PVC bulk material, transfer into the gas phase, and transport in the gas phase. A purge gas velocity of about 60 mm s^{-1} was used in this study. This was supposed to be sufficient to sweep out the released organotins. Small fluctuations of the purge gas flow should not influence the results because diffusion inside the bulk material limits the release process. The effect of the purge gas flow on the amount of the organotins released from PVC sample 2 is shown in Table 8. It is possible to conclude that the differences in the estimated amount of released DBT at different purge gas flows are insignificant.

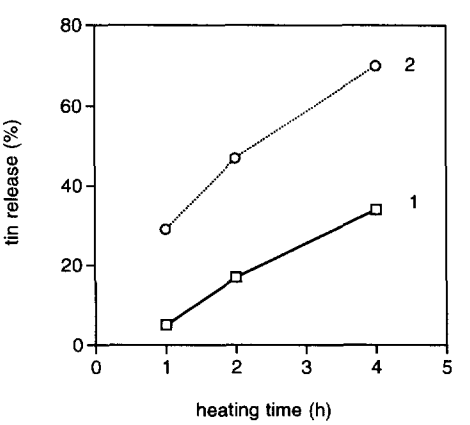

Fig. 5. Time dependence of the release of the main organotin compounds from PVC samples at a temperature of 200°C. (1) DOT, (2) DBT.

Table 7
Dependence of the release of alkyltin chlorides on the heating time

Time	MOT		DOT		MBT		DBT		TBT		BOT	
	mg g^{-1}	% Sn	mg g^{-1}	% Sn	mg g^{-1}	% Sn	mg g^{-1}	% Sn	mg g^{-1}	% Sn	mg g^{-1}	% Sn
1 h	0.18	9	0.10	5	0.08	1	1.94	31	0.07	1	0.00	
2 h	0.40	19	0.34	16	0.18	3	3.11	50	0.11	1	0.03	
4 h	0.25	12	0.60	30	0.25	4	4.35	70	0.13	1	0.08	1

Conditions: temperature 200°C, purge gas flow 100 ml min^{-1} air.

However, the amount of released MBT shows a tendency to increase with an increasing purge gas flow. This might be explained by an increased air exchange which, as shown above, could promote the decomposition of the DBT carbonate type of stabilizer into monobutyltin chloride. The fluctuations of the purge gas flow at our set-up did not exceed 20% which could not affect the obtained results at these amounts.

4. Conclusions

This work shows that organotin compounds are released from PVC at elevated temperatures. Using the described experimental set-up, a reproducible release of the target compounds was achievable. The choice of the adsorption layers was found to be important for complete retention and effective extraction. The amounts of released dibutyltin stabilizer might possibly imply a need to monitor the work environment where PVC is processed and installed. Further investigations in this direction should consider diverse surface characteristics of differing PVC materials. Of additional interest could be a monitoring of organotin emissions from PVC at temperatures below 100°C and the development of a matching analytical method for this purpose to determine possible long-term emissions from thermally stressed thermoplasts. The GC–AED technique provides excellent determination capabilities for this purpose.

Table 8
Dependence of the release of butyltin compounds on the gas flow-rates

Flow-rate (ml min^{-1})	MBT (mg g^{-1})	DBT (mg g^{-1})	TBT (mg g^{-1})
50	0.33	4.68	0.14
100	0.27	4.35	0.14
200	0.60	4.96	0.10

Conditions as in Table 4

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