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# Gas chromatographic determination of airborne dialkyltin dichlorides as hydride derivatives

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## ABSTRACT

A sampling and analysis method for airborne dibutyltin and dioctyltin dichlorides was developed. The air samples were collected on glass-fibre filters. The chlorides were desorbed with *n*-hexane and converted into hydrides using sodium borohydride. The hydride derivatives were analysed by capillary gas chromatography with flame ionization detection (FID). The identity of dibutyltin and dioctyltin dihydrides in standard solutions was confirmed by gas chromatography–mass spectrometry (GC–MS) and GC–Fourier transform infrared spectrometry. The presence of tin compounds in the fumes released from heated PVC plastics (at 225°C) was shown by GC–MS. The detection limit of the method was 0.02 $\mu$g/ml (for tin), corresponding to a concentration of 0.0003 mg/m$^3$ in an air sample of 120 l. The sensitivity of the method was about 50 times better with FID compared with optimum electron-capture detection conditions. This method can also be applied to the determination of dimethyltin dichloride.

## INTRODUCTION

Organotin compounds are used as stabilizers for halogen-containing polymers such as poly(vinyl chloride) (PVC). They account for about 30% of the total stabilizer consumption. Dibutyltin and dioctyltin compounds are the most widely used, but methyltin compounds are also very effective. These disubstituted organotin compounds have the general formular $R_2SnX_2$, with X representing any of a number of chemical groups such as mercaptide, thioglycolate, maleate or carboxylate. The amount of the stabilizer in the plastics ranges from 0.5 to 5% of the polymer weight.

Organotin compounds act as stabilizers in several ways, but in all instances they slow down the dehydrochlorination of PVC. They function, for example, as HCl scavengers and as blocking agents on weak sites in the polymer molecules [1]. Dialkyltin dichlorides are formed in both of these reactions [2]. These compounds may volatilize into the workplace atmosphere during high-temperature processing (usually at 150–200°C). As alkyltin compounds with different substituents X give the same

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reaction product $R_2SnCl_2$, this can be used as an indicator of air impurity during the processing of tin-stabilized PVC.

Several methods have been used to measure organotin compounds, including spectrophotometry, atomic absorption spectrometry (AAS), polarography and gas chromatography (GC). In high-performance liquid chromatography (HPLC), detection has been carried out with AAS or with a fluorescence detector after post-column derivatization. In GC method the tin compounds have been analysed as hydrides or after alkylation with detection methods based on electron-capture detection (ECD), flame photometry, AAS, flame ionization detection (FID) or mass spectrometry (MS) [3].

To monitor the release of these dialkyltin dichlorides into the air, a sensitive and selective method of analysis utilizing common analytical instruments was required. GC equipment is commonly used in organic analytical chemistry, but these organotin chlorides are not very volatile and they are also adsorbed on the column [4]. Because hydride formation is a rapid and simple method of rendering these compounds volatile and non-adsorbing, GC after hydridation was chosen as the method for the analysis. The hydride derivatives have been detected with electron-capture [4] and flame ionization [5] detectors. In this study, the responses of alkyltin dihydrides in these two detection systems were compared. An air sampling method for dioctyl and dibutyltin dichlorides was also tested. In addition, the formation and release of dialkyltin dichlorides in air was elucidated by heating tin-stabilized PVC in a dynamic system.

## EXPERIMENTAL

### *Reagents*

Dioctyltin dichloride was purchased from Riedel-de Haën (Hannover, F.R.G.), dibutyltin dichloride from Aldrich-Chemie (Steinheim, F.R.G.) and dimethyltin dichloride from Merck-Schuchardt (Hohenbrunn, F.R.G.). Sodium borohydride ($NaBH_4$) was obtained from BDH (Poole, U.K.), *n*-hexane (HPLC grade) from Rathburn Chemicals (Walkerburn, U.K.) and *n*-heptane from J.T. Baker (Deventer, The Netherlands).

### *Analysis procedure*

A 2-ml volume of dialkyltin dichloride–*n*-hexane solution and 1 ml of $NaBH_4$–ethanol solution were shaken in a test-tube and allowed to stand for 15 min. The $NaBH_4$ solution was prepared by adding 1 g of $NaBH_4$ to 40 ml of ethanol and shaking the mixture in an ultrasonic bath. This solution remained turbid. A 5-ml volume of water was added to the test-tube to remove the reagent. The *n*-hexane layer was separated and 1 $\mu$l was injected into the GC system.

The stabilities of the stock standard solution, of the untreated samples during storage and of the tin hydrides during storage were tested. The desorption efficiency, the reproducibility and the detection limits of the method were also tested. The identity of the hydrides in the standard solutions was confirmed with GC–MS and GC–Fourier transform infrared spectrometry (GC–FT-IR).

### *Gas chromatography*

The GC equipment consisted of a Hewlett-Packard Model 5790 gas chromatograph with a $^{63}$Ni electron-capture detector and a Hewlett-Packard Model 5890 gas chromatograph with a flame ionization detector. The injector temperature was 230°C for both instruments and the detector temperature was 280°C in the flame ionization apparatus. The gas flows were hydrogen 30, air 410 and make-up (helium) 26 ml/min. The optimum detector temperatures were tested for the EC detector. An argon–methane (5%) flow of 60 ml/min was used.

The column for the determination of dioctyl- and dibutyltin dihydrides ($Oc_2SnH_2$ and $Bu_2SnH_2$) was a fused-silica capillary column coated with a 0.17-$\mu$m film of HP-5 (25 m × 0.3 mm I.D.). The oven temperature programme was 50°C (held for 0.5 min), increased at 3.5°C/min to 75°C and then at 30°C/min to 200°C (held for 2 min) for $Bu_2SnH_2$ and 90°C (held for 0.5 min), increased at 4°C/min to 190°C and then at 30°C/min to 250°C (held for 2 min) for $Oc_2SnH_2$. The splitless injection mode was used with a splitless period of 0.5 min. The flow of the carrier gas (helium) was 4 ml/min. Dimethyltin dihydride ($Me_2SnH_2$) was analysed with a silica capillary column coated with a 5-$\mu$m film of DB-1 (30 m × 0.5 mm I.D.). The split injection mode (splitting ratio *ca.* 8:1) was used with a carrier gas flow-rate of 4.4 ml/min. The temperature programme was 30°C (held for 6 min), increased at 40°C to 200°C (held for 1 min).

### *GC–MS*

The mass spectrometer was a Hewlett-Packard 5970 A quadrupole mass-selective detector equipped with a Hewlett-Packard Model 5890 gas chromatograph. The electron impact spectra were achieved at an ionization potential of 70 eV and an emission current of 300 $\mu$A. The columns and the GC oven temperature programmes were as described above.

### *GC–FT-IR*

For IR analysis a Nicolet 20 SCX FT-IR spectrometer with an MCT detector, a GC light-pipe interface and a Hewlett-Packard Model 5890 gas chromatograph were used.

### *Degradation experiments and sampling tests*

The formation and release of dialkyltin dichlorides and the sampling procedures were tested by heating PVC plastics containing about 1.5% of dibutyl and dioctyltin mercaptides in a dynamic system at 225°C. The temperature chosen was close to the PVC processing temperatures, which are usually 150–200°C but may sometimes exceed 200°C. Slices of PVC film were placed in a glass tube (150 cm × 1.4 cm I.D.) in an even layer (0.3 g/cm). The tube was heated by a ring oven (10 cm × 1.8 cm I.D.), which was moved along the tube at a speed of 1.34 mm/min. The degradation products were conducted to a chamber [poly(methyl methacrylate), 32 × 50 × 70 cm] with an air flow of 0.5 l/min, this air flow being mixed with an air flow of 8 l/min immediately before the chamber to dilute and cool the fumes. The temperature of the air just before the inlet never exceeded 28°C.

Concentrations of 2–8 mg/m$^3$ for dibutyltin dichloride and up to 1 mg/m$^3$ for dioctyltin dichloride were measured in the chamber. The air samples were sucked through the holes in the chamber. Several sampling devices were connected in series, and these permitted separate GC analyses to test the breakthrough. The sampling tests were carried out with both glass-fibre filters and Tenax tubes, because preliminary tests showed that these samplers adsorbed both dioctyl and dibutyl dichlorides. The sampling recovery was not studied as it was not possible to produce constant, known concentrations of the chlorides in the air. The identities of the tin compounds found were confirmed by GC–MS.

## RESULTS AND DISCUSSION

### *Analysis*

The reproducibility of the method was good: the relative standard deviation was 3% for $Bu_2SnH_2$ and 2% for $Oc_2SnH_2$ at a concentration of 8 $\mu$g/ml ($n = 4$). The linearity was also good. The correlation coefficient was 0.9 for $Oc_2SnH_2$ and 1.0 for $Bu_2SnH_2$ for standard solutions in the range 0.02–100 $\mu$g/ml. The detection limit (calculated in terms of tin) was 0.02 $\mu$g/ml for $Bu_2SnCl_2$ and $Oc_2SnCl_2$ and 1.5 $\mu$g/ml for $Me_2SnCl_2$. These figures correspond to air concentrations of 0.0003 and 0.025 mg/m$^3$, respectively, for an air sample of 120 l.

The stock standard solutions (chlorides) were tested and found to be stable for at least 7 weeks. The $Bu_2SnH_2$ solution could be stored for at least 2 weeks, but the $Oc_2SnH_2$ derivative was stable for only 1 week. All of the solutions were stored in glass vials in a refrigerator at 4°C.

### *Gas chromatography*

The responses of the electron-capture and flame ionization detectors were compared by injecting the same amount of dialkyltin dihydrides under identical GC conditions into both gas chromatographs. The flame ionization detector showed a

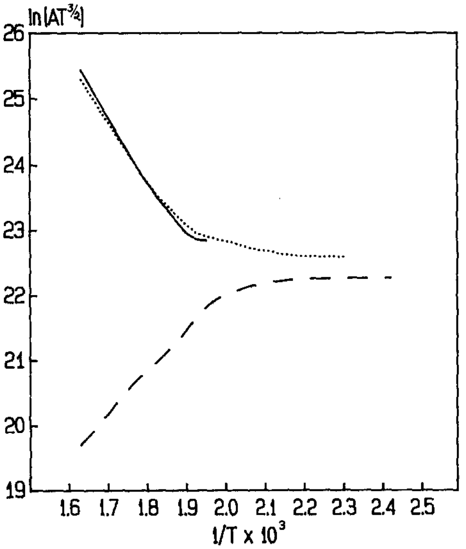

Fig. 1. ECD response of (—) dioctyltin dihydride, (...) dibutyltin dihydride and (---) dimethyltin dihydride.

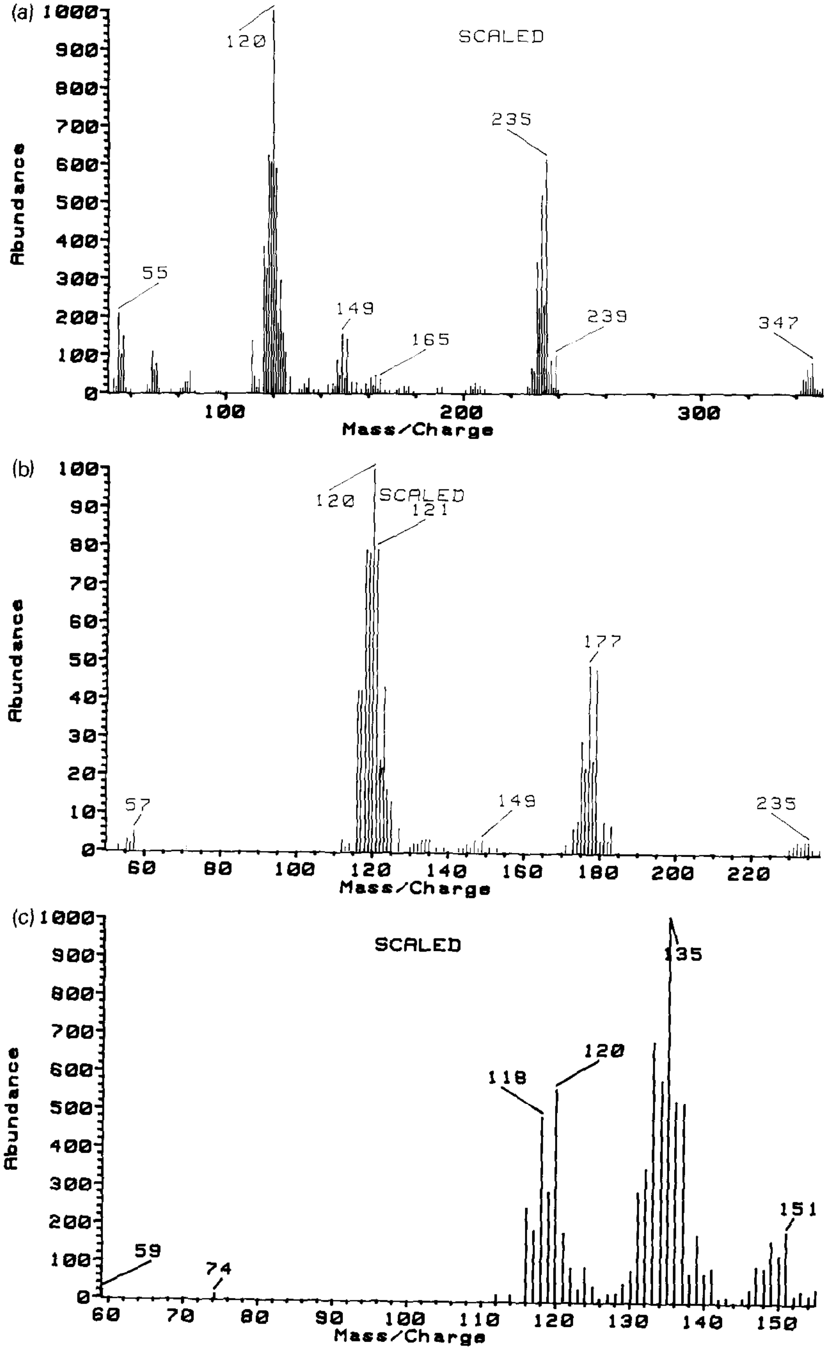

Fig. 2. Mass spectra of (a) dioctyltin dihydride, (b) dibutyltin dihydride and (c) dimethyltin dihydride.

greater sensitivity for all three compounds. The FID response of $Oc_2SnH_2$ and $Bu_2SnH_2$ was about 50 times that using ECD (340°C), or 10 times in the case of $Me_2SnH_2$ (at a detector temperature of 170°C). The retention times were 19.1, 6.2 and 5.1 min for the octyl, butyl and methyl compounds, respectively, under the conditions described above. Because the methyl derivative was not separated from the *n*-hexane solvent, it was prepared in *n*-heptane. Using split injection a sharp peak eluting before the solvent was obtained.

Because the response of the electron-capture detector is markedly temperature dependent, the optimum operating temperatures for the electron-capture detector were determined by plotting the Ln $AT^3/^2$ against $1/T$ for the dialkyltin dihydrides (Fig. 1), where $A$ is the peak area for a fixed mass of dialkyltin dihydride injected at the different detector temperatures $T$ (K). For $Bu_2SnH_2$ and $Oc_2SnH_2$ the optimum temperature was 340°C ($10^3/T = 1.63$). The mechanism of the response appeared to be dissociative, as indicated by the negative slope. For $Me_2SnH_2$ the response was highest below 190°C ($10^3/T = 2.16$), and the positive slope indicated a non-dissociative mechanism.

### *GC–MS*

GC–MS was used to confirm the presence of dialkyltins in the standard solutions and in the degradation products of the PVC plastics. The mass spectra showed a typical tin pattern (Fig. 2) of ten isotopes of tin, $^{120}Sn$ being the most abundant. Fragmentation of $Bu_2SnH_2$ and $Oc_2SnH_2$ began principally with the loss of the alkyl group. Ions of *m/z* 347 and 235 could also be found, indicating a loss of hydrogen before the loss of the alkyl groups. However, the abundances were much lower than those of the fragments $[BuSnH_2]^+$ and $[OcSnH_2]^+$. No obvious peak of molecular ions could be observed. In the mass spectrum of $Me_2SnH_2$ the molecular ion was also absent or negligible, but the fragment $[Me_2SnH]^+$ of *m/z* 151 was found. The mass spectra indicated that fragmentation may begin in different ways, with loss of either hydrogen or the methyl group. The base peak was *m/z* 150, $[MeSn]^+$, but *m/z* 120 $[Sn]^+$ in the case of butyl of octyl hydrides.

### *GC–FT-IR*

The GC–FT-IR spectra of $Oc_2SnH_2$ and $Bu_2SnH_2$ are shown in Fig. 3. A strong absorption band (stretching) from the tin–hydrogen bond of the butyl compound could be seen with a wavenumber of 1840 $cm^{-1}$. In the literature this band is reported to be between 1832 and 1845 $cm^{-1}$ [6]. The tin–hydrogen band of the octyl hydride was at 1839 $cm^{-1}$, compared with 1830–1836 $cm^{-1}$ reported in the literature [6].

### *Sampling and degradation experiments*

Sampling was performed with glass-fibre filters (SKC 225L-16, diameter 13 mm) with an air flow of 2 l/min. After sampling the filters could be stored in test-tubes in a refrigerator for 2 weeks without any loss of the chlorides. The desorption efficiency was found to be >99% for the octyl compound and >98% for the butyl compound when the desorption liquid was 2 ml of *n*-hexane and the desorption time was 1 h. These test samples were prepared at a concentration of 8 µg/ml (calculated as hydrides) by spiking filters with the standard solutions. The filters for desorption tests were analysed immediately after drying at room temperature.

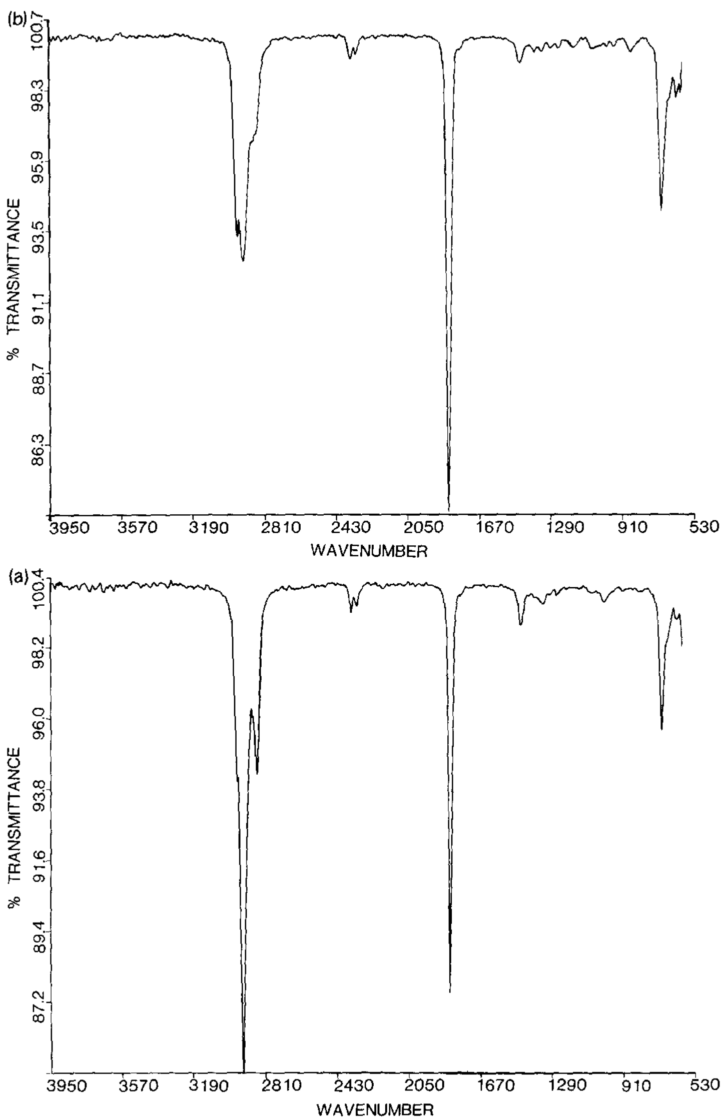

Fig. 3. GC–FT-IR spectra of (a) dioctyltin dihydride and (b) dibutyltin dihydride.

The glass-fibre filter was shown to have a considerably better sampling efficiency than the Tenax tube, which may indicate that the chlorides were in the aerosol phase. Usually filters are used for the collection of aerosols and solid adsorbents (such as Tenax) for the collection of gas-phase compounds. In the filter sampling, after a sampling time of 1 h, the breakthrough was <5% for the butyl compound; for the octyl compound it was 1.1% after 2 h. The breakthrough was calculated as the ratio of the amount found in the second filter to the sum of the amounts in the first and second filters.

The samples from the degradation experiments analysed by GC–MS revealed the same mass spectra of tin compounds as the standard solutions. A typical GC–FID

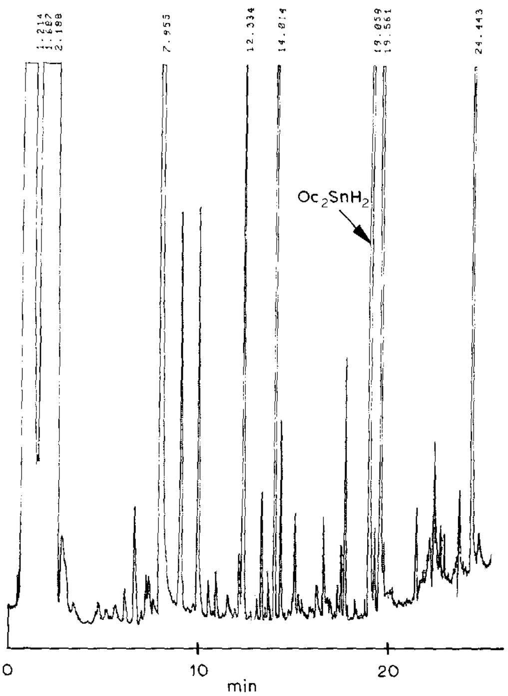

Fig. 4. GC–FID of the fumes of tin-stabilized PVC heated at 225°C.

trace originating from PVC fumes is shown in Fig. 4. The other peaks were well separated from the tin compounds and no interfering substances were eluted at the same time as the tin compounds. The ECD trace of these fumes was more complex than obtained with FID, indicating that the selectivity of ECD is not useful for the determination of organotins in these kinds of matrices. It is also possible that the sample contains interfering compounds at such low concentrations that they are not found by GC–MS (or GC–FID), despite having a high ECD response. Therefore, although the ECD method is not insensitive, FID is preferable for the fumes studied here.

This GC–FID application was shown to be simple and sensitive for the measurement of low air concentrations of tin compounds in the complex mixtures formed during thermal processing of PVC plastics. With this method concentrations substantially lower than the current hygienic standard for organic tin compounds in the working atmosphere (0.1 mg/m$^3$, calculated as tin) [7] can be measured.

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