Journal of Chromatography, 475 (1989) 373–379
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 555

EXTRACTION OF BUTYLTIN SPECIES AND THEIR GAS CHROMATOGRAPHIC DETERMINATION AS CHLORIDES IN A SEDIMENT CERTIFIED REFERENCE MATERIAL FOR TRACE METALS, PACS-1[a]

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(Received April 6th, 1989)

SUMMARY

A gas chromatographic method has been developed for the determination of butyltin species in sediment. The butyltin species are separated as chlorides by using a DB-608 open tubular column after their extraction from the sediment using a combination of sonication in methanolic HCl and solvent extraction. Two extractants are possible: toluene–isobutyl acetate–tropolone and hexane–isobutyl acetate. The efficiencies for the first extractant are: tributyltin, 94.4 ± 4.7%; dibutyltin, 94.9 ± 2.2%; and monobutyltin, 86.3 ± 4.2%. The absolute detection limits are about 30 pg tin. Using a 1-g sample, the relative detection limits are about 30 ng tin per g sediment. These may be lowered to 3 ng tin per g by starting with a 4-g sample and adding a concentration step. The reference material PACS-1 was found to contain 1.08 ± 0.31 μg tin per g of tributyltin and 1.13 ± 0.30 μg tin per g of dibutyltin.

INTRODUCTION

Due to their significant environmental impact, the butyltin species are under intense scrutiny. Gas chromatography (GC) with flame photometric or electron-capture detection is often the analytical method of choice because of its speciation capability, high sensitivity and general availability. Although many versions of butyltin species extraction from complex environmental matrices have been developed, they almost always involve releasing and extracting the butyltin species into an organic solvent as chlorides and/or tropolone complexes[1–9]. It is general belief that the butyltin chlorides are not sufficiently volatile or inert for successful GC, and derivatization to more inert forms such as hydrides[3–6,9] and tetraalkyl forms[1,2] is necessary. This belief appears justified considering the proliferation of reports on hydridization and Grignard reactions[1–6,9].

Yet, some of the earliest work on the GC of organotin species was on the separation of organotin halides[10,11]. It was evident that organotin halides with alkyl

[a] NRCC 30230.

groups containing a few carbon atoms, such as butyltin halides, are volatile enough for GC. However, it was also quite apparent that on-column adsorption and degradation, particularly those of the more ionic mono- and dibutyltin chlorides, were appreciable. These effects could be minimized by extensive silylation/deactivation carried out frequently[11]. The GC of organotin halides took a quantum leap after the significance of hydrogen halide doping was realized[7,8,12,13]. Flinn and co-workers[12,13] added hydrogen halide, either in solution or gaseous form, into the carrier gas stream of the chromatograph. A hydrogen halide steady state established between the gas and liquid phases. Organotin compounds injected were derivatized, on-column, to the halides and eluted as such. Degradation of the organotin halides was minimized by the presence of a large excess of hydrogen halide which shifted the equilibrium in favour of organotin halides. This allowed the separation of sub-microgram amounts of mono-, di- and tributyltin halides and detection of 1 pg of tripropyltin and tributyltin chloride[12,13].

This study aims to: (1) test the chromatography of butyltin halides on the more inert and yet more delicate open tubular columns, (2) apply this chromatographic technique to the determination of butyltin species in a sediment sample, and (3) develop compatible extraction techniques for butyltin species.

EXPERIMENTAL

Instrumentation

A Varian VISTA 6000 gas chromatograph modified for megabore open tubular columns was used. Two columns were tried; these were DB-1 (J&W Scientific, 100% methylsilicone) and DB-608 (also from J&W Scientific, 40–45% phenyl-, 60–55% methylsilicone). Most work, however, was done on the DB-608 column. Nitrogen (Linde, ultra-high-purity grade) further purified by passing sequentially through a molecular sieve 5A trap and a heated oxygen scavenger unit (Supelco) was used as carrier gas at 16 ml/min. The injector temperature was 200°C. To separate the butyltin chlorides on the DB-608 column, the following temperature program was used: initial 80°C, hold 2 min; temperature ramp 10°C/min; final 135°C, hold 4 min. For the analysis of sediment extracts, a second temperature gradient of 10°C/min to 180°C for 4 min was added to elute concomitant sulphur compounds. The detector was the Varian dual-flame photometric detector. For tin detection, optimal response was obtained with single flame operation. In this mode, no air was supplied to the lower burner and only the upper burner was lit. The column effluent mixed with hydrogen (104 ml/min) at the base of the flame jet and burned in an atmosphere of air (154 ml/min). The red SnH emission was monitored using a 40-nm band pass filter centred on 600 nm (Ealing Optics). The photomultiplier current was processed by the Varian dual-flame photometric detector electrometer whose output was smoothed by a long-pass filter (Spectrum 1021A) before recorded by a strip-chart recorder (Fisher Recordall 5000).

Reagents

Butyltin compounds were purchased (from Alfa). Their purity was confirmed by high-performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC–ICPMS). Solutions of these were usually made up in methanol and

refrigerated when not in use. Sediment samples were certified reference materials PACS-1 and MESS-1 (National Research Council of Canada). PACS-1 was collected from Esquimalt Harbour in British Columbia, while MESS-1 was from the Miramichi River estuary in New Brunswick.

Extraction of sediment samples

A 1-g amount of sediment plus any butyltin chloride spikes was sonicated with 2 ml of 10 *M* hydrochloric acid and 1 ml of methanol for 1 h. The suspension was then extracted with 1 ml of hexane–isobutyl acetate (80:20), or 1 ml of toluene–isobutyl acetate (80:20) containing 1.5% (w/v) tropolone after addition of 7 ml of water. Both extractions required vigorous mechanical shaking. Maximum transfer of butyltin chlorides required about 10 min of shaking for hexane–isobutyl acetate while 1 h for toluene–isobutyl acetate–tropolone. The phases were separated by centrifugation at about 700 *g* for 10 min. A 1 μl volume of the water immiscible phase was injected into the chromatograph.

HCl doping

Hydrochloric acid was introduced into the GC system by either discrete injections of 0.5 *M* HCl in methanol or continuous doping of a few ml/min of 1% HCl gas in nitrogen. For HCl solution injections, the gas chromatograph was conditioned by a daily 3-μl injection prior to analysis. To ensure proper butyltin chloride elution, 1 μl of HCl solution was co-injected with every sample injection.

RESULTS AND DISCUSSION

GC of butyltin chlorides

Fig. 1 shows a typical separation of butyltin trichloride, dibutyltin dichloride and tributyltin chloride, each containing 2 ng of tin, using the more polar DB-608 column. The DB-1 column yields a comparable pattern. Without HCl treatment, tributyltin chloride, the most covalent species, elutes with no apparent degradation; the dibutyltin dichloride peak exhibits significant tailing and is about 50% its normal

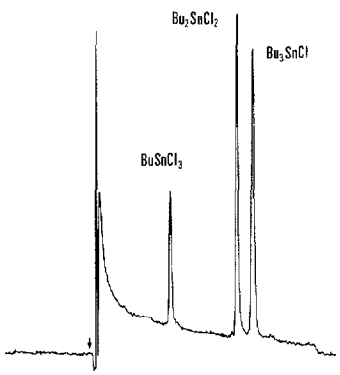

Fig. 1. Temperature programmed separation of butyltin trichloride, dibutyltin dichloride and tributyltin chloride standards, each containing 2 ng of tin (Bu = butyl). The arrow indicates the point of injection. Conditions are given in the Experimental section.

height on the DB-608 column, while only about 10% on the DB-1 column; butyltin trichloride does not elute on either column. With HCl, all species elute as almost symmetrical peaks.

The butyltin chloride peaks as eluted by using temperature programming are expected to be similar in height in the absence of degradation or irreversible adsorption assuming that their carbon quenching effects on the tin emission are comparable. The fact that the butyltin chloride peak is only about 50% of the dibutyltin dichloride and tributyltin chloride peaks, which are comparable, indicates that some degradation and/or irreversible adsorption of that species takes place even with HCl doping. This percentage is variable and has been seen to change from 30 to 100%. Generally, it is higher when the column is new and presumably more inert, and becomes progressively lower as the column ages. As well, it also appears somewhat influenced by the sample matrix. The magnitude of these effects, however, are deemed tolerable for quantitation of relatively high concentrations of butyltin trichloride using standard additions method.

The effectiveness of gas phase and solution phase HCl doping are rated similar. However, in HCl solution introduction, no hardware modification is necessary. Further, the acid is only added with each sample injection resulting in less overall stress on the GC system. The open tubular columns hold well in the presence of HCl. Our last DB-608 column withstood approximately 2000 injections over a span of six months. As well, the gas chromatograph exhibits no ill-effects from HCl use.

The flame photometric detector is a sensitive detector for tin. Our detection limit (signal to noise = 2, SnH emission centred on 600 nm) is about 30 pg tin. Optimal sensitivity was obtained under single flame operation. An attempt to improve the detection limit by using a more red sensitive photomultiplier tube (Hamamatsu R928) was unsuccessful, indicating that the limiting noise arose from the flame. No efforts were made to use the more sensitive but less reproducible blue tin emission[14].

Extraction of butyltin species as chlorides from sediments

In the earlier phases of this study, various published sediment extraction methods[1,5] were tried and found unquantitative for MESS-1 and PACS-1. The extraction methods reported here, whose emphases are on extraction efficiency, speed and simplicity, were subsequently developed for these two sediments. The toluene–isobutyl acetate–tropolone procedure is preferred as it extracts all three butyltin species efficiently —di- and tributyltin quantitatively while monobutyltin almost quantitatively (Table I). The efficiencies were determined by spiking micrograms per gram amounts of butyltin chlorides to MESS-1, which contains negligible amounts of butyltin species. The hexane–isobutyl acetate combination extracts 60–70% of the more nonpolar dibutyltin dichloride and tributyltin chloride, but only a small fraction of butyltin trichloride.

Sonication of the sediment with methanolic HCl releases butyltin most probably as chlorides. However, a significant fraction of tributyltin appears to sorb on the sediment —removal of the sediment phase prior to extraction resulted in low tributyltin recovery. Inclusion of the methanolic HCl digestion step is imperative, without which very low recovery of butyltin ensues. Maximum extraction of butyltin chlorides occurs under relatively high hydrochloric acid concentration for hexane–isobutyl ace-

TABLE I

EXTRACTION EFFICIENCIES FOR THE TOLUENE–ISOBUTYL ACETATE–TROPOLONE PROCEDURE

Species	*Recovery*[a]
Tributyltin	94.4 ± 4.7[b]
Dibutyltin	94.9 ± 2.2
Monobutyltin	86.3 ± 4.2

[a] $n = 4$.

[b] Standard deviation.

tate while under relatively low concentration for toluene–isobutyl acetate–tropolone. For the former extractant, hydrochloric acid is required to shift the equilibria to favour undissociated butyltin chlorides which are extracted; for the latter, relatively low acidity favours formation of the tropolone complexes of butyltin which dissolve preferentially in toluene. Of the two extractants, hexane–isobutyl acetate is the more efficient getter of tributyltin. Maximum transfer of tributyltin requires only about 10 min of vigorous shaking for hexane–isobutyl acetate while about 1 h for toluene–isobutyl acetate–tropolone. On the contrary, transfer of butyltin to toluene–isobutyl acetate–tropolone as well as dibutyltin to both extractants is rapid.

Determination of butyltin species in sediments

A 1-μl volume of the extractant was injected into the chromatograph for analysis. Aside from causing the build-up of a black deposit on the injector lining which required periodic cleaning, introduction of the crude extracts did not appear to degrade chromatography or column performance. Owing to the selectivity of the dual-flame photometric detector, very few non-tin peaks were seen: MESS-1 had none,

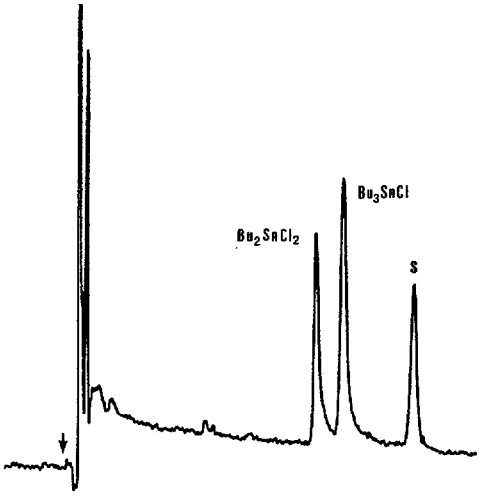

Fig. 2. Typical chromatogram of a toluene–isobutyl acetate–tropolone extract of PACS-1 showing the presence of di- and tributyltin. S = Concomitant sulphur compound.

TABLE II

DETERMINATION OF DIBUTYLTIN AND TRIBUTYLTIN IN PACS-1

Values are ± standard deviations. Number of replicate analyses is given in parentheses.

Technique	*μg tin per g dry weight*	
	Dibutyltin	*Tributyltin*
GC–FPD		
hexane–isobutyl acetate	1.07 ± 0.31 (8)	1.14 ± 0.27 (8)
toluene–isobutyl acetate–tropolone	1.08 ± 0.31 (6)	1.11 ± 0.33 (7)
HPLC–ICPMS	1.18 ± 0.15 (9)	1.61 ± 0.27 (8)
ISMS–MS		1.29 ± 0.07 (5)
Certified value	1.16 ± 0.18[a]	1.27 ± 0.22[a]

[a] 95% confidence interval.

while PACS-1 exhibited three sulphur-containing peaks all eluting later than the butyltin chlorides and causing no interference. There is little doubt that the butyltin species are injected as either chlorides or tropolone complexes into the chromatograph. The exact form matters little as any non-chloride butyltin species are rapidly derivatized by HCl *in situ* to butyltin chlorides[12,13].

MESS-1 contains no detectable butyltin species (less than 30 ng tin per g) and was studied here only for use as a sediment matrix for assessing butyltin extraction efficiencies. On the contrary, PACS-1 contains significant amounts of dibutyltin and tributyltin (Fig. 2). Quantitation of these two species was carried out by using standard additions employing both sediment extraction methods, whose results are comparable. These and results obtained by using HPLC–ICPMS and ion spray mass spectrometry–mass spectrometry (ISMS–MS) are listed in Table II. Agreement amongst the different methods is good.

Improving relative detection limits

The relative detection limits for dibutyltin and tributyltin in this method are about 30 ng tin per g sediment, sufficiently sensitive for PACS-1. For the analysis of

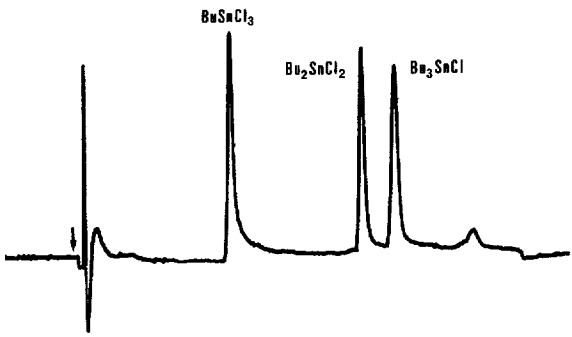

Fig. 3. Chromatogram of a toluene–isobutyl acetate–tropolone extract of MESS-1 spiked with 0.1 μg tin per g of butyltin chlorides.

sediments containing lower butyltin concentrations, the relative detection limits may be lowered by inserting a concentration step. This is demonstrated as follows. A 4-g sample of MESS-1 spiked with butyltin species at levels of 0.1 μg tin per g sediment was extracted in the usual fashion with 4 ml of toluene–isobutyl acetate–tropolone. The extract was evaporated to dryness with a stream of nitrogen and dissolved in 40 μl of methanol. A 1-μl volume of this solution was injected for analysis. Fig. 3 shows a typical chromatogram. The relative detection limits have been lowered to 3 ng tin per g sediment.

CONCLUSION

The open tubular columns tested work well for GC of butyltin chlorides. A method for determining butyltin species in sediment has been developed. The butyltin species are extracted in an efficient procedure as either chlorides or tropolone complexes, which are derivatized on column to chlorides. The accuracy of this method is assured by two other independent techniques.

ACKNOWLEDGEMENTS

We thank B. Kinsella, Curtin University of Technology, Bentley, Australia, for initiating extraction studies on sediments, and W. A. Aue, Dalhousie University, Halifax, Canada, as well as J. H. Weber, University of New Hampshire, Durham, NH, U.S.A., for helpful discussions on various aspects of butyltin species determination.

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