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Gas phase detection of tributyltin chloride arising from aqueous and solid matrices†

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The vapour phase above water spiked with tributyltin chloride (TBTCl) and PACS-2 sediment certified reference material was sampled with a solid phase microextraction fiber. The collected volatile compounds were analysed by GC-MS using a HBr–methanol-treated capillary column. Two ion sources were used for this study and their performance characteristics compared. These were electron impact (EI) and negative chemical ionisation (NCI), which allowed both detection of trace amounts of analytes (NCI source) and their identification. This approach provides structural information on the sampled species; at this stage no quantitation was attempted. TBTCl can be detected in the vapour phase above saline water or PACS 2 sediment after one night of passive sampling without any stirring or heating of the sample. This work indicates the need to consider evaporation of TBT as the chloride as a mechanism of loss of this analyte from water or sediment. This may take place from natural settings and contributes to the global biogeochemical cycle of tin; hydride or methyl forms of trace metals are not the only compounds capable of volatilising into the atmosphere.

Introduction

Butyltin compounds are assumed to be absent from the atmosphere because of their low volatility, and few investigations into their atmospheric abundance have been attempted. Results reported for volatile tin compounds mainly suggest the occurrence of volatile tin hydrides,[1] methyl species ($Me_nSn^{(4-n)+}$ with $n = 1$–4)[2,3] or methylbutyl species.[4,5]

Vella and Vassallo[4] have suggested that marine sediment contaminated with TBT can host methylbutyltins, presumably formed by environmental methylation of TBT. In their studies, emission of the polar TBT was not detected from the sediment. They argued that the TBT probably evaporated in the chloride form, although this could not be ascertained analytically by the protocol used.[4]

Model experiments conducted in our laboratory have pointed to the release of volatile organotin species that have been detected in the gas phase above sea-water[6] and sediment[7] mixtures. As the sediment was sterilized prior to the analytical study, any bio-assisted formation of volatile metal species was excluded. The most probable explanation of these observations is the naturally occurring formation of metal chlorides, fueled by the abundance of chloride ion (or other halides) present in sea-water and many other natural environments.[6] In a similar manner, detection of volatile metallic compounds in solid samples has been achieved by examining the headspace above the sample using solid phase microextraction (SPME) coupled with thermal desorption and ICP-TOF-MS detection.[7] Although this study demonstrated that TBT can volatilize and can be trapped and detected in the vapor phase above solid samples, no positive identification of the species was achieved. Detection of monomethylmercury[8] and arsenic trichloride ($AsCl_3$)[9] have also been reported using this technique.

Various techniques have been used for sampling gaseous TBT species, including cryogenic trapping,[5,10] adsorption onto a solid phase, followed by back-extraction and conversion into volatile butyl hydrides by ethanolic sodium tetrahydroborate[4] or ethylation with sodium tetraethylborate.[11] More recently, passive sampling using a sorbent-coated SPME fiber[6,7,12–16] has been used.

In the speciation analysis of organotin compounds, conversion of ionic polar species to their fully alkylated forms is required in order to take advantage of their separation by gas chromatography. Prior to injection into the analytical system, anhydrous butylation using a Grignard reagent,[17] conversion of the analyte to its hydride form by use of sodium tetrahydroborate ($NaBH_4$),[18] aqueous phase ethylation by means of sodium tetraethylborate ($NaBEt_4$)[18] or aqueous phase propylation with $NaBPr_4$ have all been employed.[19,20] In this study, TBT was collected from the headspace above aqueous and solid samples using a SPME fiber and thermally desorbed directly into a GC injector port without derivatization. Detection of tributyltin as the chloride was accomplished by MS and was facilitated by a simple treatment of the GC capillary column with a solution of dilute HBr, as reported earlier by Mizuishi for detection of methylmercury chloride[21] and TBTCl.[22,23] This approach allowed direct injection of the sampled species and was used in order to determine the chemical form of the TBT species without resorting to any subsequent chemical modifications.

Both capillary GC-electron impact (EI) MS and capillary GC-negative ion chemical ionization (NCI) MS were investigated for the direct identification of TBT as the chloride. The NCI-MS mode was used to obtain high sensitivity (250–400-fold better than EI mode)[23] whereas EI-MS was used to confirm the identify of the species generated and released from the samples. It should be stressed that no attempt was made in the study to undertake quantitative analysis.

Experimental

Reagents and samples

OmniSolv® methanol (glass-distilled) and sodium chloride were purchased from EM Science (Gibbstown, NJ, USA). High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis

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domestic feed water (Barnstead/Thermolyne Corp., Dubuque, IA, USA). Hydrobromic acid (33 wt% solution in glacial acetic acid) was from ACROS organics (New Jersey, USA). Methanolic HBr solutions were prepared by diluting the 33% HBr–acetic acid solution with methanol to 0.3 mM and stored at 4 °C.

Tributyltin chloride (96%) was purchased from Alfa Products (Danvers, MA, USA). A stock solution of 1000 mg L^{-1}, as tin, was prepared in methanol and kept refrigerated until used. Working standard solutions were prepared by dilution in isopropyl alcohol and, finally, in hexane.

National Research Council of Canada PACS-2 sediment reference material (CRM), certified for mono-, di- and tributyltin contents,[24] was selected as a model sediment for this study. The certified values for butyltin species in this sediment are: 0.45 ± 0.05 for monobutyltin (MBT), 1.09 ± 0.15 for dibutyltin (DBT) and 0.98 ± 0.13 μg g^{-1} for TBT, as tin.

Instrumentation

A Hewlett-Packard HP 6890 GC-MS (Agilent Technologies Canada Inc., Mississauga, Ontario, Canada) fitted with a DB-17 column 30 m × 0.25 mm id × 0.25 μm film thickness (J & W Scientific, Brockville, Ontario, Canada) was used. Typical GC-MS operating conditions are presented in Table 1 for EI and NCI detection modes.

A manual SPME device, equipped with a fused silica fiber coated with a 65 μm thick partially cross-linked poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) (Supelco, Bellefonte, USA) was used for sampling the TBT from the headspace above aqueous solutions and the sediment. The efficacy of the chosen extraction media for the targeted species has been demonstrated previously.[7,25]

SPME sampling procedure

Aqueous sampling

In order to detect volatilization of TBTCl from water, the following experiments were performed. A 25 mL volume of a 40 ng mL^{-1} (as tin) TBTCl solution was mixed with 1 g of NaCl in an amber glass vial fitted with a PTFE–silicone septum. The solution was stirred with a magnetic stir bar for predetermined times and sampled from the headspace by means of a PDMS/DVB fiber placed in the vortex of the solution. After sampling, the fiber was retracted into the needle of the holder. The SPME fiber was then inserted into the GC injector, where the compounds were thermally desorbed for 1.5 min, allowing for a complete desorption and transfer of all species to the head of the GC column.

Sediment sampling

One gram of PACS-2 sediment was placed in an amber glass vial, capped with a PTFE–silicone septum, and positioned on a hot plate. The SPME fiber was inserted into the headspace for a predetermined time and for various sample temperatures. After the sampling, the fiber was inserted into the GC injector where the analytes were thermally desorbed onto the GC column.

Results and discussion

Direct analysis of TBTCl

Few results have been reported concerning the release of organotin species into the atmosphere.[3–7,10] In such studies, the major components detected were methylated or hydrated (TBT-H) species arising as a result of biological/chemical methylation–hydride generation.[3–5,10] Moreover, in many cases, the evaporated forms cannot be clearly identified by the analytical protocol used.[4] Indeed, volatile analytes are usually collected by cryogenic trapping and interfaced with gas chromatography combined with an element selective detector. Species detected are usually identified by comparison of their retention time and order of elution with those from standard solutions, for which it is required to have pure standards for calibration. Use of "organic" mass spectrometry methods could provide direct structural information on the sampled species, but frequently the concentrations of these species are not high enough. Additionally, when cryo-trapping is employed, an initial cold trap for the removal of water vapour from the gas stream is usually located in line with the liquid nitrogen trap. The first non-analytical trap efficiently removes the water from the sampled gas and most probably everything else having a boiling point higher than the trap temperature, which is in the −20 °C range. Most metal/organometal halide species have a boiling point well over +150 °C, with the consequence that the analytical trap has to be heated to over +200 °C during the release stage.

In our previous studies, although volatile tin and mercury species have been detected above spiked solutions and solid samples, the employed detection system (ICP-MS) was not able to provide structural confirmation. The exact nature of the species released from samples polluted and/or spiked with TBT or methylmercury was unknown. The abundant halide, especially chloride, content of the samples suggested the formation of TBT-Cl and MMHg-Cl species. In this study, an analytical system capable of providing structural confirmation of these semivolatile organometallic species was devised. Organotin halides have often been derivatized because they interact with the materials in a GC system. As a consequence, polar/ionic species have to be converted to more volatile forms before attempting separation. With the intention of identifying the TBT form, direct determination of organotin halides by GC without derivatization was used. Pretreatment with HBr serves to deactivate any active sites in the GC column, including silanol groups and metal oxides. When TBTCl is injected, a halogen exchange reaction from chloride to bromide readily occurs during the GC separation. In order to pretreat the column, 10 successive injections of a 1 μL volume of a 0.3 mM methanolic solution of HBr were performed. Standard

Table 1 Operating conditions for GC-MS

Oven temperature program	40 to 220 °C at 15 °C min^{-1} (temperature hold 2 min)
Carrier gas; flow rate	Helium; 0.7 mL min^{-1}
Transfer line temperature	200 °C
MS	HP Model 5973 mass selective detector
EI mode—	
MS quad. temperature	150 °C
MS source temperature	200 °C
NCI mode—	
CI reagent gas	Methane
MS quad. temperature	106 °C
MS source temperature	200 °C
SIM parameters	Measured ions: m/z = 309, 311, 312, 313, 315 Dwell times: 50 ms for each m/z

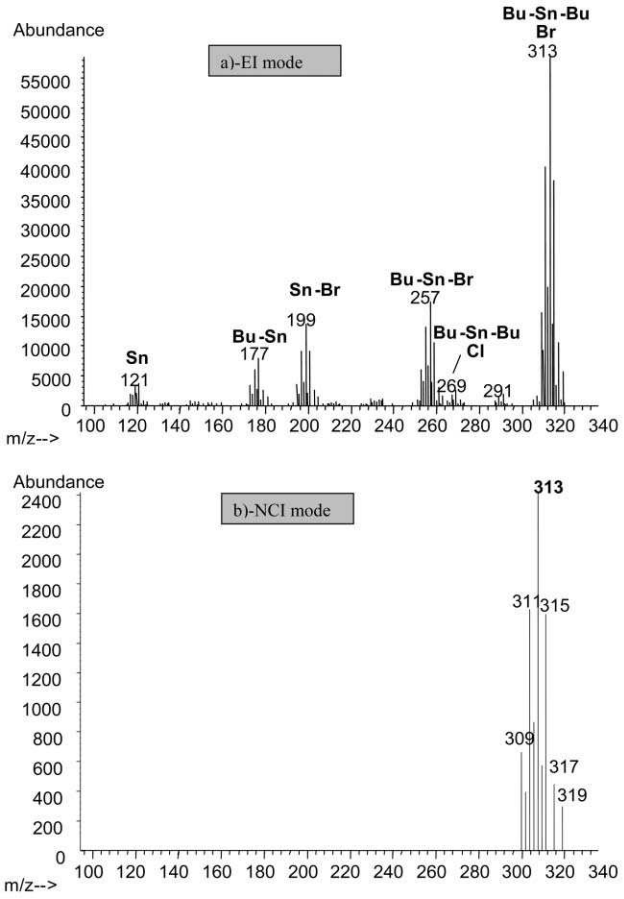

Fig. 1 Isotope pattern of TBTCl (a) GC-EI MS and (b) GC-NCI MS scan mode.

solutions of TBTCl in hexane were then injected for EI and NCI detection.

For the CI mode, in addition to the sample and carrier gas, large amounts of reagent gas (methane in this work) are introduced into the ionization chamber. Since there is so much more reagent gas than sample, most of the emitted source electrons collide with reagent gas molecules, forming reagent ions. CI results in much less fragmentation, with the result that CI spectra usually show a high abundance of the molecular ion.

Fig. 1 shows the mass spectra of TBT chloride in both EI and CI mode. In EI mode, one peak was observed with a retention time of 12.62 min, resulting from four different fragments {Sn}, {Bu–Sn}, {Sn–Br} and {Br–Sn–Bu_n} with $n = 1$–2 (Fig. 1 (a)). In CI mode, the spectrum of TBTCl is relatively simple, with only the cluster peak from 309 to 320 appearing, corresponding to the fragment {Br–Sn–Bu_2} (Fig. 1 (b)). As high concentrations of sample were not injected, conversion of TBTCl to the bromide adduct was complete. For high concentrations, a fragment ion corresponding to {$(C_4H_9)_2$Sn–Cl} at $m/z = 269$ was observed.

The effectiveness of the treatment of the column was checked by examining the repeatability of consecutive runs ($n = 10$) of 20 mg L^{-1} and 100 μg L^{-1} (as tin) standard solutions in EI and NCI modes, respectively. The relative standard deviation of the TBTCl peak area was 4% in both cases.

Standard solutions of $MBTCl_3$ and $DBTCl_2$ were also directly injected using the GC-MS in EI mode. No peak was observed for $MBTCl_3$. For $DBTCl_2$, a peak was obtained at a retention time of 8.30 min, corresponding to four different fragments {Sn–Cl}, {Bu–Sn}, {Bu–Sn–Cl} and {Cl–Sn–Bu_2}, as shown in Fig. 2. The column pretreatment does not result in conversion of $DBTCl_2$ to the bromide adduct but the compound can be detected and identified.

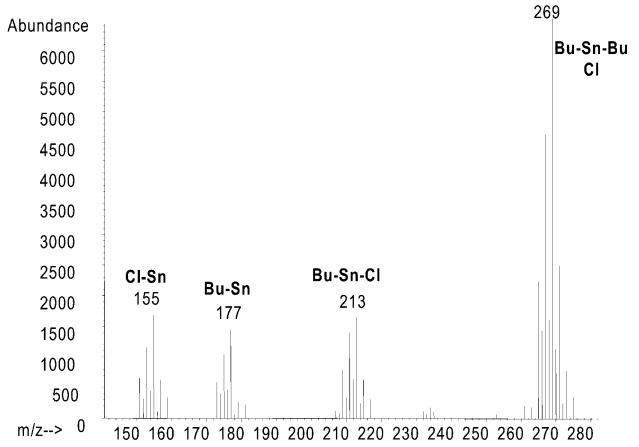

Fig. 2 Isotope pattern of $DBTCl_2$ in GC-EI MS.

Volatilization of TBTCl

Aqueous solutions

Blank runs were first performed, wherein 25 mL of DIW and 1 g of NaCl were placed in an amber glass vial and capped with a PTFE–silicone septum. After stirring and sampling by SPME above the liquid phase for 20 min, the fiber was then inserted into the GC injector. No organotin compounds were detected in either EI or NCI mode. When high concentrations of TBTCl were sampled, it was particularly important to verify that no organotin compounds remained on the GC column or SPME fiber, as verified by running a blank. No residual contamination was detected in either the sampling (SPME) or detection (GC) systems at any time.

The initial hypothesis for the model experiments was that, in the presence of sufficiently high chloride concentration, organotin halide is formed and, given a sufficiently high vapor pressure, can escape from the liquid phase into the headspace above the sample solution.[6] To verify this hypothesis, samples containing 25 mL volumes of a 40 ng mL^{-1} TBTCl solution and 1 g of NaCl were placed in an amber glass vial and capped with a PTFE–silicone septum.

Solutions were stirred and the species were sampled from the headspace for 15 min. The fiber was then inserted into the GC injector. With the NCI source, a chromatographic peak was obtained corresponding to the retention time and isotope pattern of TBTCl. In order to confirm the identification of this compound, experiments were repeated with the EI source. The isotopic pattern of the analyte sampled above the solution was the same as that obtained with the TBTCl standard solution. It may be concluded that TBT can evaporate from the aqueous phase and that it does so as the chloride form.

Different extraction times and concentrations of TBTCl in the aqueous phase were studied. The results obtained are presented in Figs. 3 and 4, respectively. As expected, the amount of TBTCl detected increased with the extraction time and concentration added in solution.

Finally, headspace sampling of the saline solution containing 40 μg L^{-1} of the TBTCl standard solution was performed overnight in the dark without stirring. The fiber was then inserted into the GC injector and a small peak corresponding to TBTCl was detected in the NCI mode. Thus, even without stirring, a detectable amount of TBT (as chloride) evaporates from the aqueous phase.

Solid samples

Volatile species present in PACS-2 sediment were sampled directly from the headspace above the solid using SPME. After 20 min of sampling, the fiber was inserted into the GC injector.

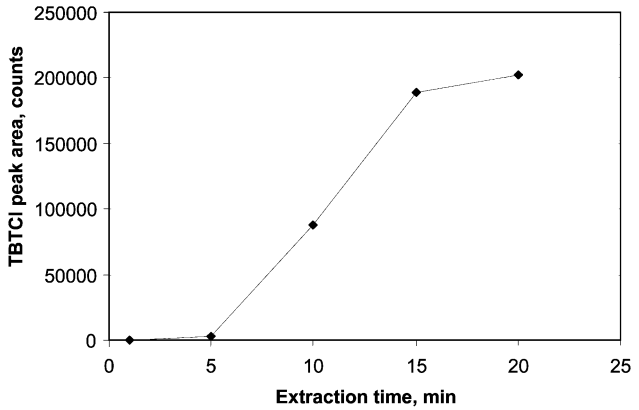

Fig. 3 Effect of extraction time on chromatographic peak area response above aqueous solutions containing 40 ng mL^{-1} of TBTCl.

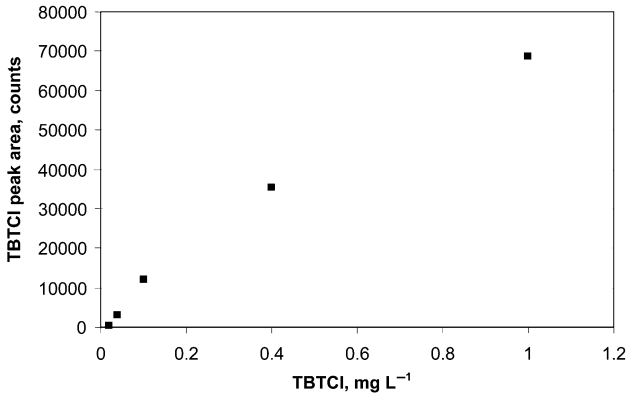

Fig. 4 Variation of chromatographic peak area response with concentration using 15 min stirring and sampling with SPME fiber of a TBTCl solution.

No peak was detected. If sampling was extended to overnight (at 25 °C), a small peak corresponding to TBT was detected.

Additional experiments were performed with heating the sample at 55 °C and sampling for different lengths of time. After 5, 10, 15 and 20 min of sampling, a TBT signal was detected with GC-NCI MS, which increased with the extraction time.

As in the case of the aqueous sample, all experiments were repeated in EI mode in order to confirm the TBT form. A lower signal intensity was obtained because of the inferior sensitivity achieved with electron impact ionization mode, but TBT as chloride can undoubtedly be identified as the compound volatilized from the PACS-2 sediment. As is shown in Fig. 5, for a 20 min sampling period, a fragment ion corresponding to $\{(C_4H_9)_2Sn\text{-}Cl\}$, at $m/z = 269$, was observed. In this case, the conversion of TBT as chloride to bromide was not completely achieved in the pretreated column, but the compound released from PACS 2 sediment is unquestionably TBTCl.

Although $DBTCl_2$ can also be detected using the present technique, even if it is present in the same range of concentrations as TBT in the PACS 2 sediment, it was never detected in this study. The poor sensitivity of the technique regarding $DBTCl_2$ may account for this result.

These results highlight the need to consider that evaporation of TBT as a chloride species from natural waters or sediment may occur in the natural environment and contribute to the global bio-geochemical cycle of tin. Hydride or methyl forms of trace metals are thus not the only compounds capable of volatilising into the atmosphere.

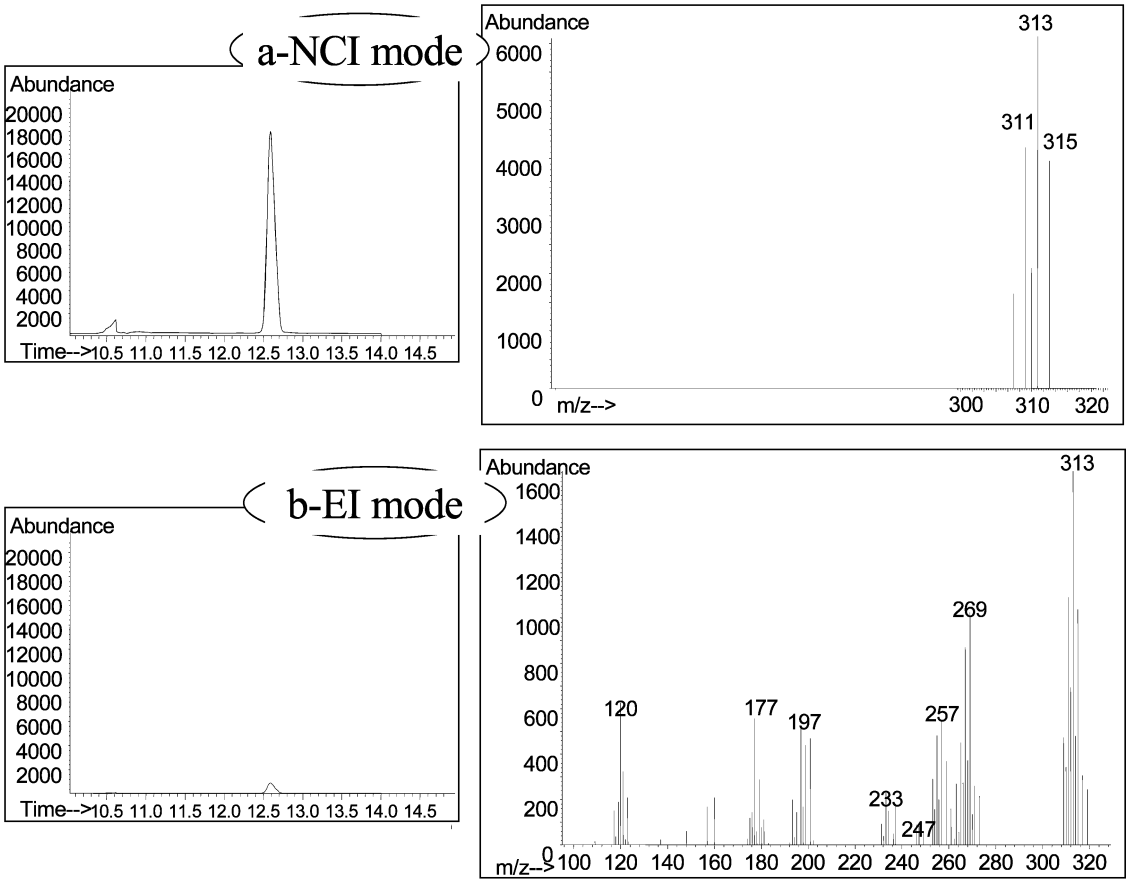

Fig. 5 Total ion chromatograms and mass spectrum obtained from 20 min headspace sampling with SPME fiber above heated (55 °C) PACS-2 using GC-MS: a, NCI source; and b, EI source.

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