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EVALUATION OF EXTRACTION PROCEDURES FOR THE ANALYSIS OF BUTYLTIN COMPOUNDS IN AIR

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Evaluation of Extraction Procedures for the Analysis of Butyltin Compounds in Air

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MANAGEMENT PERSPECTIVE

Although the toxicity of organotin compounds has raised great health concerns, there have been few investigations on the existence of butyltin compounds in air because of their low volatilities. An analytical method for determining butyltin chlorides in ambient atmosphere was developed. The NaDDC/toluene/pentylmagnesium bromide extraction and derivatization procedure, previously shown to be efficient for the analysis of organotin species in sediment, has been successfully modified for the recovery of butyltin compounds from spiked glass filters and XAD-2 resin used for air sampling. Dervatized butyltin species were determined by gas chromatography with plasma atomic emission detection (GC-AED). In the near future, this technique will be evaluated under field conditions.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Bien que la toxicité des composés organostanniques ait soulevé d'importantes inquiétudes en matière de santé, peu d'études ont été réalisées sur la présence des composés du butylétain dans l'air en raison de leurs faibles volatilités. On a mis au point une méthode analytique pour la détermination des chlorures de butylétain dans l'air ambiant. La méthode d'extraction et de dérivatisation à NaDCC/toluène/bromure de pentylmagnésium, qui a déjà fait ses preuves pour l'analyse des composés organostanniques dans les sédiments, a été modifiée avec succès pour la récupération des composés du butylétain au moyen de filtres de verre dopés et de résine XAD-2 utilisés dans l'échantillonnage atmosphérique. Les composés du butylétain dérivatisés ont été dosés par chromatographie gazeuse avec détection par émission atomique à plasma. Dans un avenir rapproché, cette technique sera évaluée dans des conditions de terrain.

ABSTRACT

Butyltin chlorides spiked onto glass fibre filters and XAD-2 resin were extracted in toluene using tow different chelating agents, either tropolone with acetic acid or sodium diethyldithiocarbomate (NaDDC), and derivatized with pentylmagnesium bromide. Derivatized butyltin species were determined by gas chromatography with plasma atomic emission detection (GC-AED). Higher extraction recoveries were obtained using NaDDC as the chelating agent. Glass fibre filters and XAD-2 resin were both determined to be suitable air sampling media for the analysis of butyltin compounds.

KEY WORDS

Butyltin, organotin, air analysis, gas chromatography, atomic emission detection, sodium diethyldithiocarbamate

RÉSUMÉ

Les chlorures de butylétain ajoutés sur des filtres de fibre de verre et sur une résine XAD-2 ont été extraits dans le toluène au moyen de deux chélateurs, soit la tropolone avec acide acétique ou le diéthyldithiocarbomate de sodium (NaDDC), puis dérivatisés avec du bromure de pentylmagnésium. Les composés du butylétain dérivatisés ont été dosés par chromatographie gazeuse avec détection par émission atomique à plasma. On a obtenu une meilleure extraction avec le NaDCC comme chélateur. On a établi que les filtres de fibre de verre et la résine XAD-2 étaient tous deux de bons médiums pour l'échantillonnage atmosphérique en vue de l'analyse des composés du butylétain.

MOTS CLÉS

Butylétain, organostannique, analyse de l'air, chromatographie gazeuse, détection par émission atomique, diéthyldithiocarbamate de sodium

INTRODUCTION

Organotin compounds are used in a wide range of products including stabilizers for polyvinyl chloride (PVC), catalysts in the production of polyurethane foam, industrial biocides, and as precursors for tin oxide films on glass. There has been concern about organotin compounds as environmental contaminants due to their toxicity to aquatic organisms and mammals. In humans, butyltin chlorides are known to be skin and eye irritants[1]. Butyltin compounds have low volatility, so the majority of studies have been focused on their presence in sediments and water, but recently there has been more interest in the analysis of butyltin compounds in air. Organotin compounds have been detected in air from heated PVC[2,3], wood preservatives[4] and paint[5].

Few analytical methods have been developed for the analysis of butyltin compounds in air. Often, these methods use hydride derivatization techniques and gas chromatography with flame photometric detection[2,6]. Poor butyltin recoveries have been observed with hydride generation due to matrix components inhibiting the reaction[7,8]. Many of these methods, developed for air analysis in the workplace, have high detection limits and are not suitable for the determination of butyltin compounds in the environment. In addition, many of these methods are not validated for monobutyltin. Monobutyltin compounds are significant because they are used in industry and they are degradation products of the more commonly used dibutyltin and tributyltin species. Difficulties reported with the extraction of monobutyltin indicate the importance of specific methods for monobutyltin compounds[9,10]. Speciation analysis is also necessary due to the difference in toxicity between the various butyltin compounds[11,12].

There is no agreement in the literature on the efficiency of various air-sampling media for organotin analysis. A variety of air sampling media have been evaluated based on their retention efficiencies including Chromosorb 102[5], glass fibre filters[2], quartz fibre filters with activated carbon fibre filters[4], and Poropak-N[6] for a variety of organotin compounds. This evaluation is based on the recovery of organotin compounds from a sorbent previously spiked with a liquid solution of the compounds. It is difficult to determine the collection efficiency for air sampling media due to the problems involved in preparing and delivering accurate gaseous standards, so evaluation is typically based on retention efficiency[2]. The collection efficiency of gas-phase dibutyltin and dioctyltin was investigated, however, on a sampling cartridge containing sodium

acetate, glass fibre filters, and XAD-2 resin[3]. The gas-phase organotin compounds were generated from heated PVC tubing. This study demonstrates that the compounds examined are completely retained on this combination of sampling media. Compounds extracted from the sorbent are derivatized by $NaBEt_4$ and analyzed using GC-AED. Although high recoveries were reported in the study, extraction recoveries were not determined for all butyltin species. Derivatization with ethylmagnesium bromide following tropolone extraction has been shown to give more consistent results than $NaBEt_4$ derivatization for all butyltin species extracted from mussels[13].

There is a need for a method for the analysis of organotin compounds in air, which offers high collection efficiency, high extraction recovery and low detection limits for all butyltin species. Two recent methods have been successful for the analysis of butyltin compounds in sediments[9,14]. Samples are extracted in toluene with tropolone or sodium diethyldithiocarbamate (NaDDC) as chelating agents, and derivatized with a Grignard reagent. High recoveries were obtained for all three butyltin compounds. In the present study, these two extraction methods will be evaluated for the recovery of butyltin species adsorbed on glass fibre filters and XAD-2 resin.

METHODS

Apparatus

The GC-AED system consists of a gas chromatograph (HP model 5890, Series II, Hewlett-Packard, PA, USA) equipped with a split/splitless injection port, a HP microwave plasma atomic emission detector (model 5921A) and a HP automatic sampler (model 7673A). Optimal operation parameters of the GC-AED system for tin are given in Table 1. An ultrasonicator, Branson 1210 (CT, USA) was used for sample extraction. An Airchek Sampler (model 224-43XR, SKC Inc., Eighty Four, PA) was used to draw air through the filters and XAD-2 tubes.

Materials

Glass fibre filters (37mm, Gelman Sciences Inc., Ann Arbor, MI) and XAD-2 resin tubes (ORBO™-43, 100/50 mg, Supelco Inc., Bellefonte, PA) were used as sampling devices for the spike and recovery experiments.

Solvents and common reagents were of analytical grade. Distilled water further purified by a Milli-Q (Millipore, Bedford, MA, USA) system was used throughout. The carrier gas for the GC-AED system was high-purity helium (99.999%). Reagent gases for the AED were oxygen (99.999%) and hydrogen (99.999%), all supplied by Canox Ltd. (Mississauga, Canada). The chlorides of monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT) were obtained from Alfa Chemicals (Ward Hill, MA). Tripentyltin (TPeT) chloride was obtained from Aldrich (Milwaukee, WI). Stock standard solutions of organotin (100 μg/mL as Sn) were prepared in toluene and diluted for subsequent use.

Procedure for Spiking Sampling Media

To determine the recovery of butyltin compounds from a glass fiber filter, the filter was spiked with 100 ng (as Sn) each of MBT, DBT and TBT chlorides in 10 μL of hexane. The solvent was allowed to evaporate before the filter was placed in a plastic cartridge with openings at the front and back to allow air to flow through the cartridge. The front end of an XAD-2 tube was connected to the back of the filter cartridge using a minimum length of Tygon tubing. The back end of the XAD-2 tube was connected to the sampling pump with another piece of Tygon tubing. Air was drawn through the spiked sampling media at a rate of 1.2 L/min for 5 hours. A schematic diagram of the sampling apparatus is shown in Figure 1.

To determine the recovery of butyltin compounds from XAD-2 resin, 100 ng of each butyltin species was spiked directly onto the front section of the XAD-2 resin in the tube. Air was then pumped through the tube as described above except that no filter was attached to the front of the XAD-2 tube. For experiments comparing the two extraction methods, the XAD-2 resin and glass fiber filter were combined for extraction and analysis. For subsequent experiments using Method II, the filter and XAD-2 resin were extracted and analyzed separately.

Method I: Tropolone Extraction

The filter was removed from the cartridge and placed in a small Erlenmeyer flask with the XAD-2 resin from the tube. After additions of 4 mL acetic acid, 4 mL water, 1.6 g NaCl, 3 mL 0.5% tropolone in toluene and 100 ng tripentyltin chloride as the internal standard, the mixture was magnetically stirred for 1 h. The extract was transferred to a vortex tube and evaporated to almost dryness using a nitrogen stream. One mL of hexane was added and again evaporated to almost dryness. The volume of the extract was adjusted to 1 mL with hexane and the extract was allowed to react with 0.5 mL of pentylmagnesium bromide (2 M) for 10 min. Excess pentylmagnesium bromide was destroyed by shaking the mixture with 2 mL of 1 M H_2SO_4. The organic phase was transferred to a vortex tube and evaporated to 1 mL with nitrogen. A 1 µL aliquot was injected into the GC-AED system for analysis.

Method II: NaDDC Extraction

The filter or XAD-2 resin was transferred from the cartridge to a vortex tube. The sample was extracted in 3 mL of toluene saturated with NaDDC. After addition of 10 uL of a 10 µg/mL solution of tripentyltin chloride as internal standard, the mixture was sonicated for 5 min in the ultrasonic processor. The extract was then placed on a vibrator while 0.5 mL of 2 M pentylmagnesium bromide was added dropwise to the solution. The extract was allowed to stand for 10 min, then 2 mL of 2 M H_2SO_4 was added to destroy the excess pentylmagnesium bromide. After centrifugation at 4000 rpm for 3 min, the organic layer was quantitatively transferred to a glass tube and washed with 2 mL of 1 M NaOH. The organic layer was then transferred to another glass tube and evaporated to almost dryness under a stream of nitrogen. The extracts were diluted to 1 mL with hexane and cleaned up with a silica column (1 cm Na_2SO_4 was placed on top of 5 cm silica in a 1.5-cm diameter column) to remove excess reagent and impurities from the sampling media. The column was pre-washed with 25 mL hexane prior to the application of the sample. The sample was then applied to the column and eluted with another 25 mL of hexane. The eluate was reduced to 1-2 mL under vacuum, transferred to a test tube and evaporated to 1 mL with nitrogen. A 1 µL aliquot was injected into the GC-AED system for analysis.

RESULTS AND DISCUSSION

Comparison of Extraction Procedures

Extraction efficiencies were determined for two different procedures, Method I and Method II, for the recovery of butyltin compounds from air sampling devices. Results from the two methods for the recovery of three butyltin species are listed in Table 2. In this experiment the XAD-2 resin and spiked glass fibre filter were combined for extraction. Unsatisfactory results were obtained using Method I. This method was inefficient for recovering TBT from the spiked sorbent. In contrast, recoveries of well over 100% were determined for MBT and TPeT. The exceptionally high recovery for the latter two species suggests that TBT may have decomposed in the acidic extraction solution, by the loss of alkyl substituents, to monobutyltin or Sn(IV). Degradation of TBT and DBT has previously been observed in the presence of acid at concentrations greater than 0.5 M[15]. Dealkylation of triphenyltin to diphenyltin and monophenyltin in acid has also been reported[13,16,17].

The samples are not acidified during the extraction or derivatization procedures of Method II. Recovery of TBT was much higher using Method II than was observed using Method I. Extraction efficiencies for DBT and MBT using Method II were lower than values previously reported in sediment extracts[14], but higher than the efficiencies reported using Method I. Method II also provided more consistent results and thus was chosen for the remainder of the experiments.

Evaluation of Air Sampling Media

Previous studies using glass fibre filters have shown that breakthrough can occur for some butyltin compounds, indicating that a back-up sorbent such as XAD-2 resin is required[2,3]. Retention efficiencies of the glass fibre filter and XAD-2 resin were determined separately using Method II for extraction and derivatization.

A typical GC-AED chromatogram of the butyltin derivatives extracted from a spiked glass fibre filter using Method II is shown in Figure 2. Peak identifications are listed in the figure legend. A blank glass fibre filter and a blank XAD-2 cartridge were each processed in the same manner as the spiked sampling media. The chromatograms of the blank media extracts did not contain any interfering peaks. The detection limit of the method is 0.5 pg as Sn.

Recoveries of butyltin compounds extracted from spiked glass fibre filters are listed in Table 3 (column A). All three butyltin compounds were quantitatively recovered from the filters. Air drawn through the spiked filters was passed through an XAD-2 cartridge to trap any butyltin compounds that may be released from the filter. Butyltin species were not detected in the XAD-2 extract indicating that no significant breakthrough occurred from the glass fibre filter under these sampling conditions. These recoveries are higher than the values listed in Table 2 for the same method in the extraction procedure comparison study. In this experiment, the filters were analyzed separately from the XAD-2 resin, and the extracts were cleaned up on a silica column. It may be possible that the XAD-2 resin interferes with the complete extraction of butyltin species, causing the low recoveries observed when XAD-2 and filter are extracted together. Low recoveries of butyltin compounds extracted from XAD-2 resin using HCl in methylene chloride have been reported previously[6].

To test the retention and extraction efficiency of the XAD-2 resin using Method II, in a separate experiment, the front section of an XAD-2 cartridge was spiked with the butyltin mixture and air was drawn through the cartridge in the absence of a glass fibre filter. The back section of XAD-2 resin is separated from the front by a foam plug. The recoveries of butyltin compounds from spiked XAD-2 resin are included in Table 3 (column B). High recoveries were obtained for all three butyltin compounds. These results indicate that XAD-2 resin and glass fibre filters are both suitable media for the efficient extraction of butyltin compounds using toluene with NaDDC. Butyltin species were not detected on the back section of XAD-2 resin, indicating that the front section retained the butyltin species while air was drawn through the cartridge. This technique will be useful for monitoring concentrations of butyltin compounds in ambient air in locations where these compounds are used.

CONCLUSION

The NaDDC/toluene/pentylmagnesium bromide extraction and derivatization procedure (Method II), previously shown to be efficient for the analysis of organotin species in sediments, has been successful for the recovery of butyltin species from spiked glass fibre filters and XAD-2 resin used for air sampling. High retention of the butyltin species was observed for both sorbents when air was drawn through the spiked media. Low detection limits obtained using this method would allow the method to be used for either ambient or indoor air measurements. Further studies are necessary to investigate the lower recovery of DBT and MBT when the XAD-2 resin and glass fibre filter are extracted together.

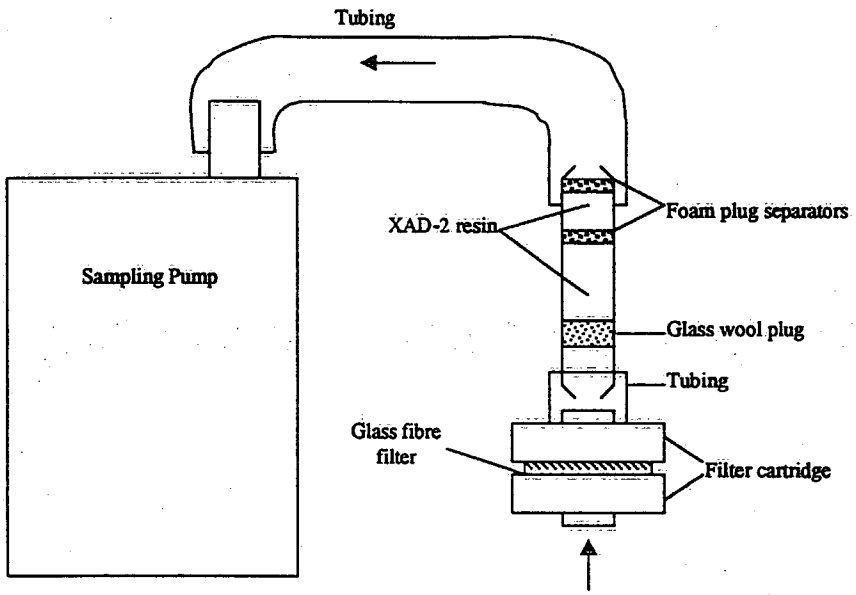

Figure 1. Schematic diagram of the apparatus for sampling butyltin compounds in air.

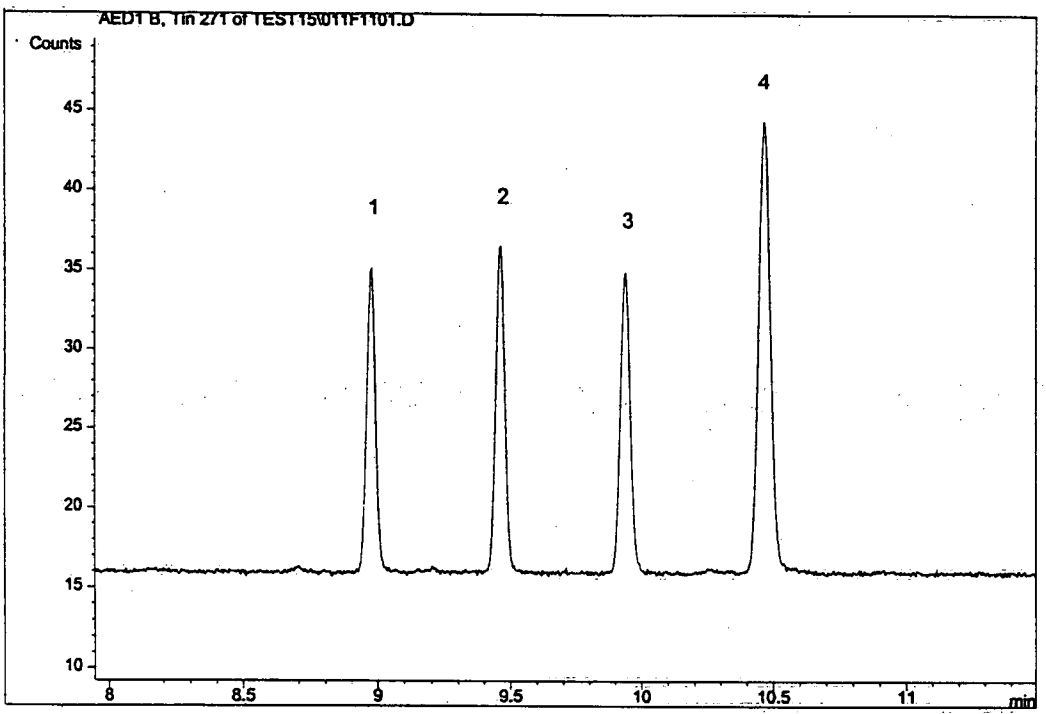

Figure 2. Gas chromatogram of derivatized organotin species extracted from a glass fibre filter. 1 = Tributyltin (TBT); 2 = Dibutyltin (DBT); 3 = Monobutyltin (MBT); 4 = Tripentyltin (TPeT), internal standard.

Table 1. GC-AED operational parameters

GC parameters	
Injection port	splitless
Injection port temp.	250°C
Injection volume	1 μL
Column	SPB-1, 30 m × 0.53 mm i.d.
Column head pressure	Helium, 100 kPa (14.5 psi)
Temperature program	60°C (2 min) - 250°C (3.5 min) at 20°C/min
AED parameters	
Transfer line	SPB-1
Transfer line temp.	270°C
Cavity temperature	270°C
Solvent vent off time	1.2 min
Spectrometer purge gas	N_2 at 2 L/min
Helium make-up gas	240 mL/min
Sn wavelength	271 nm
H_2 pressure	414 kPa (60 psi)
O_2 pressure	138 kPa (20 psi)

Table 2. Recovery (%) of butyltin compounds from spiked glass fibre filters[a]

Compound[b]	Method I[c]	Method II[d]
TBT	37 ± 1	83 ± 6
DBT	70 ± 14	66 ± 5
MBT	126 ± 17	55 ± 10
TPT	150 ± 25	138 ± 2

[a] Filters spiked with 100 ng (as Sn) of each component; value is mean ± standard deviation; $n = 2$

[b] Abbreviations: TBT, tributyltin; DBT, dibutyltin; MBT, monobutyltin; TPT, tripentyltin (internal std.)

[c] Extracted with tropolone in toluene after the addition of acetic acid, water and sodium chloride

[d] Extracted with NaDDC in toluene

Table 3. Recovery (%) of butyltin compounds from spiked air sampling media using Method II[a]

Sampling Media	TBT		DBT		MBT		TPT[b]	
	A[c]	B[d]	A	B	A	B	A	B
Glass Fibre Filter	99 ± 6	na	106 ± 7	na	93 ± 9	na	86 ± 3	na
XAD-2 Resin (front)	nd	96 ± 6	nd	88 ± 8	nd	133 ± 19	79 ± 2	99 ± 5
XAD-2 Resin (back)	na	3 ± 5	na	nd	na	nd	na	80 ± 5

[a] $n = 5$, values is mean ± standard deviation
[b] internal standard added to each section analyzed
[c] glass fibre filter spiked, XAD-2 resin used as backup
[d] XAD-2 resin spiked, filter not used
na = not applicable
nd = not detected

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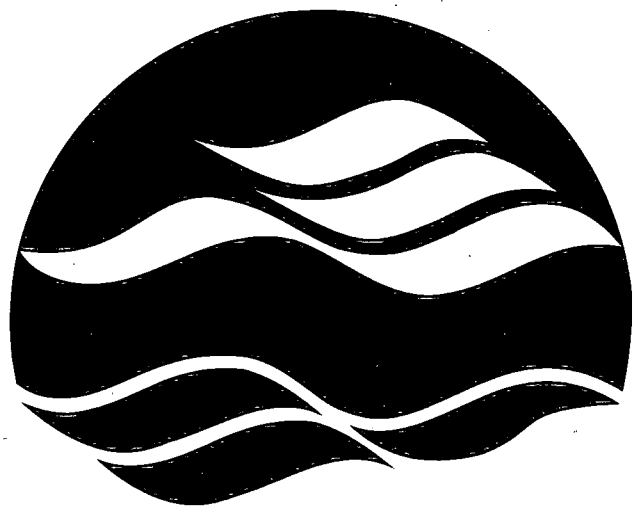

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