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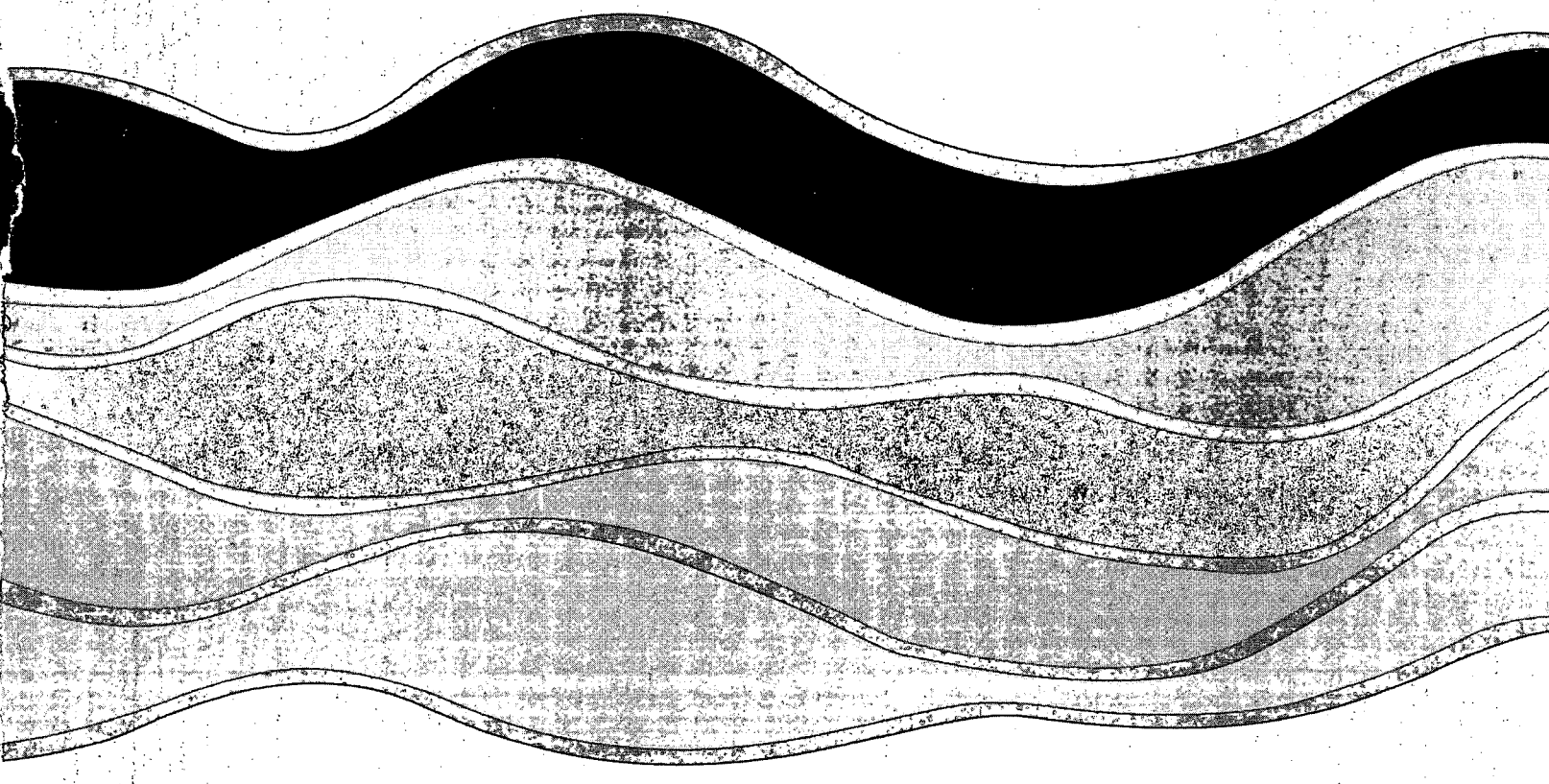

SOLID PHASE EXTRACTION OF BUTYLTIN COMPOUNDS IN AQUEOUS SAMPLES FOLLOWING DERIVATIZATION *IN SITU* WITH SODIUM TETRAETHYLBORATE

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NWRI Contribution No. 98-022

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MANAGEMENT PERSPECTIVE

The release of tributyltin biocides from antifouling paints has caused high toxicity towards aquatic organisms. During the last decade, many countries have regulated the use of butyltin compounds, and numerous analytical methods have been published for monitoring butyltin compounds in the aquatic environment. Liquid-liquid extraction techniques (LLE) are commonly applied to the extraction of these compounds from water. However, these methods are time consuming and usually require large amounts of organic solvents. This report describes the use of the solid phase extraction (SPE) technique to pre-concentrate the butyltin compounds from aqueous samples. The butyltin compounds in water were derivatized *in situ* with sodium tetraethylborate ($NaBEt_4$), and extracted by C_{18} Empore disks. After elution of the disks with a small amount of hexane, the various butyltin species were determined by gas chromatography-atomic emission detection. The highly sensitive and selective GC-AED system combined with efficient SPE extraction method provides a simple and high quality analytical procedure for the determination of butyltin compounds in aqueous samples. The recoveries of butyltin compounds and tripropyltin (as internal standard) in spiked water were tested under different experimental conditions. The relative detection limit of butyltin compounds in 0.5 L water sample is 1.0 ng Sn/L and recoveries ranged from 78.8 - 92.8%.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Les biocides à base de tributylétain libérés par les peintures antisalissure ont été très toxiques pour les organismes aquatiques. Depuis une dizaine d'années, bien des pays ont interdit l'utilisation des composés du butylétain, et de nombreuses méthodes d'analyse applicables à la surveillance de ces composés dans le milieu aquatique ont été décrites dans les publications. Pour extraire ce type de composés de l'eau, on utilise souvent des techniques d'extraction liquide-liquide. Avec ces méthodes, toutefois, l'extraction prend beaucoup de temps et nécessite habituellement d'importantes quantités de solvants organiques. Dans ce rapport, nous expliquons comment nous avons utilisé l'extraction sur phase solide pour pré-concentrer les composés du butylétain présents dans des échantillons d'eau. Nous avons d'abord préparé *in situ* des dérivés des composés du butylétain de l'eau avec du tétraéthylborate de sodium ($NaBEt_4$), puis nous les avons extraits au moyen de disques C_{18} Empore. Après élution avec une petite quantité d'hexane, nous avons caractérisé les divers composés du butylétain obtenus en les soumettant à une chromatographie en phase gazeuse avec détection par spectrométrie d'émission atomique. En conjuguant ce système de chromatographie très sensible et très sélectif à une méthode d'extraction sur phase solide efficace, nous obtenons une procédure d'analyse à la fois simple et supérieure pour la caractérisation des composés du butylétain présents dans l'eau. Nous avons évalué dans diverses conditions expérimentales la récupération de composés du butylétain et du tripropylétain (étalon interne) dans un échantillon d'eau enrichi. La limite de détection relative des composés du butylétain dans un échantillon de 0,5 L d'eau est de 1,0 ng de Sn/L, et le taux de récupération est compris entre 78,8 et 92,8 %.

ABSTRACT

The application of the solid phase extraction (SPE) technique for the pre-concentration of butyltin compounds from aqueous samples is described. The butyltin compounds in water were derivatized *in situ* with sodium tetraethylborate ($NaBEt_4$), and extracted by C_{18} Empore disks. After elution of the disks with a small amount of hexane, the various butyltin species were determined by gas chromatography-atomic emission detection. The high sensitivity and selectivity of the GC-AED system combined with efficient SPE method provided a simple and high quality analytical procedure for the determination of butyltin compounds in aqueous samples. The recoveries of butyltin compounds and tripropyltin (as internal standard) in spiked water were tested under different experimental conditions. The relative detection limit of butyltin compounds in 0.5 L water sample is 1.0 ng Sn/L and recoveries ranged from 78.8 - 92.8%.

Keywords: Solid phase extraction, butyltin compounds, water, gas chromatography, atomic emission detection, sodium tetraethylborate.

RÉSUMÉ

On décrit l'application de l'extraction sur phase solide pour pré-concentrer les composés du butylétain présents dans des échantillons d'eau. On prépare *in situ* des dérivés des composés du butylétain de l'eau avec du tétraéthylborate de sodium ($NaBEt_4$), puis on les extrait au moyen de disques C_{18} Empore. Après élution avec une petite quantité d'hexane, on caractérise les divers composés du butylétain obtenus en les soumettant à une chromatographie en phase gazeuse avec détection par spectrométrie d'émission atomique. En conjuguant ce système de chromatographie très sensible et très sélectif à une méthode d'extraction sur phase solide efficace, on obtient une procédure d'analyse à la fois simple et supérieure pour la caractérisation des composés du butylétain présents dans l'eau. La récupération des composés du butylétain et du tripropylétain (étalon interne) d'un échantillon d'eau enrichi a été évaluée dans diverses conditions expérimentales. La limite de détection relative des composés du butylétain dans un échantillon de 0,5 L d'eau est de 1,0 ng de Sn/L, et le taux de récupération est compris entre 78,8 et 92,8 %.

Mots-clés: Extraction sur phase solide, composés du butylétain, eau, chromatographie en phase gazeuse, détection par spectrométrie d'émission atomique, tétraéthylborate de sodium.

INTRODUCTION

The release of tributyltin biocides from antifouling paints has caused high toxicity towards aquatic organisms. During the last decade, many countries have regulated the use of butyltin compounds, and numerous analytical methods have been published for monitoring butyltin compounds in the aquatic environment.[1-5]

Because concentrations of butyltin compounds are usually found at sub-ppt levels in natural waters, a pre-concentration step is normally required before their final determination. Liquid-liquid extraction techniques (LLE) are commonly used for extraction of the butyltin compounds from water.[2-4] However, these methods are time consuming and usually require large amounts of organic solvents.

The pre-concentration of butyltin compounds in water by SPE combined with using tropolone has been reported.[6-8] After elution of the analytes from the absorbent, the extract has to be further derivatized by Grignard reagents for GC determination. $NaBEt_4$ was introduced into the on-line sample preparation with a C_{18} microcolumn for the determination of butyltin and phenyltin compounds in water.[9] The application of SPE can greatly reduce the use of organic solvent, extraction time and risk of contamination. In the SPE procedure, butyltin compounds are first derivatized or complexed with special agents in water, then sorbed on a sorbent surface by passing through the Empore disk or cartridge, and finally eluted by small amounts of organic solvents.

In this paper, a modified analytical procedure for the determination of butyltin compounds in aqueous samples is presented. The C_{18} Empore disk was used to extract the butyltin compounds derivatized *in situ* with sodium tetraethylborate ($NaBEt_4$). The concentrated butyltin species were eluted with a small amount of organic solvent, and then determined by Gas chromatography-atomic emission detection (GC-AED). The high sensitivity and selectivity of the GC-AED combined with efficient SPE provide a simple, cost-effective, and high quality analytical method for the determination of butyltin compounds in water.

EXPERIMENTAL

Apparatus. The GC-AED system consists of a HP gas chromatograph model 5890, Series II (Hewlett-Packard, PA) equipped with a split/splitless injection port, a HP microwave plasma atomic emission detector model 5921A, and a HP automatic sampler model 7673A. A 6-station Empore extraction manifold (VWR Canlab) was used for solid phase extraction.

The ethyl-derivatized organotin compounds in hexane (1 μL) were injected into the GC-AED system and the operation parameters of the GC-AED system are listed in Table 1.[4]

Reagents. Butyltin compounds, Bu_3SnCl (96%), and Bu_2SnCl_2 (95%) were obtained from Johnson Matthey (Ward Hill, MA), and $BuSnCl_3$ and sodium tetraethylborate ($NaBEt_4$) were purchased from Alfa Chemicals (Danvers, MA). All solvents and acids were of

analytical grade. Distilled water was further deionized in a Milli-Q (Millipore) system and used throughout the experiment. A 1.0 % (w/v) $NaBEt_4$ reagent solution was prepared daily by dissolving 1 g of sodium tetraethylborate in 100 mL of water. Buffer solution (pH=5) was prepared by mixing equal volumes of 1.0 M sodium acetate and 1.0 M acetic acid water solutions.

Procedure

***In-situ* derivatization of organotin in water.** Experiments were carried out using 500 mL of water spiked with 100 µL 0.1µg Sn/mL tripropyltin (TPrT in hexane) as an internal standard. After additions of 50 mL of 0.5M buffer solution and 1 mL of 1% $NaBEt_4$ solution, the mixture was shaken for one minute. Another 1 mL $NaBEt_4$ was added before the solution was well mixed for the solid phase disk extraction.

Solid-phase extraction procedure. The Empore C_{18} disk was placed in the 6-station Empore extraction manifold attached to a vacuum source. Ten milliliters of hexane was added into the reservoir to soak the disk for 3 minutes. After the solvent was drawn through the disk by vacuum, 10 mL of methanol was added to soak the disk for another 3 minutes with the vacuum off. Without letting the disk become dry at low vacuum, 10 mL of water was added to displace the methanol, and then the water sample was continuously fed to the filtration reservoir. The water was drawn through the disk at a vacuum of about 15-20 inches of mercury. The vacuum was maintained for 10 seconds after all the sample had passed through the disk. After turning off the vacuum, a 15 mL centrifuge tube was placed in the manifold to collect the eluate, and 4 mL of hexane, which was previously used to rinse the sample container, was added to the reservoir and allowed to soak through the disk for 2 minutes. The solvent was sucked through the disk by turning on the vacuum slowly. The disk was eluted twice with 4 mL aliquot of hexane. The combined eluate was passed through anhydrous sodium sulfate and evaporated to 1 mL with a gentle stream of nitrogen. One µL of final solution was injected into the GC-AED system for the determination of organotin compounds.

RESULTS AND DISCUSSION

Recoveries of butyltin compounds from water

Known amounts of butyltin and tripropyltin standard solutions were spiked into distilled water samples, and determined by GC-AED following solid phase extraction. The recoveries were evaluated by comparing the peak areas to those of the corresponding butyltin compounds of a mixed standard solution directly derivatized with ethylmagnesium bromide.[4] The recoveries of organotin compounds from various water volumes and different spiked concentrations were reported in Table 2. The recoveries of butyltin compounds from 500 mL water were generally higher than those from 1000 mL aqueous sample. Lower recoveries observed with 1L water samples may be caused by break through problems. The recoveries were also quantitative in the range of 100 ppb to 10 ppb, which was close to the concentration level of butyltin compounds in natural water.

Sample preparation with SPE following *in situ* derivatization with $NaBEt_4$ in water

In the study, $NaBEt_4$ was used for the derivatization of butyltin compounds in water before the SPE with C_{18} Empore disk, which simplified the extraction procedure and obtained satisfactory recoveries of butyltin species from 1L or 0.5L of water samples.

Hexane was chosen as the eluting agent because it ensured rapid and quantitative elution. Moreover, it was easier to concentrate by evaporation after extraction and did not cause interference in the subsequent GC-AED determination. Dichloromethane, and methanol were also investigated as eluting solvents, but they did not improve the recoveries of organotin compounds from water.

Determination of Butyltin compounds with GC-AED

GC-AED is a very sensitive and selective technique for the determination of organotin compounds.[2,4] The optimal GC-AED conditions are summarized in Table 1. The absolute detection limit (as Sn) of the system is down to the 0.5 pg level. Therefore, the use of GC-AED ensures good sensitivity for determination of butyltin species in this work.

Conclusion

The combination of solid phase extraction and derivatization with sodium tetraethylborate provides an efficient pre-concentration method for butyltin compounds in aqueous samples. The C_{18} Empore disk could satisfactorily handle 0.5 to 1L water sample. The extraction manifold is able to process six samples automatically and simultaneously. The whole procedure is simple and offers a good alternative to liquid-liquid extraction, especially in large scale surveys of butyltin compounds in water.

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Table 1. Operational conditions for GC-AED

GC parameters

Injection port	Splitless
Injection port temperature	250^{0}C
Injection volume	1μL
Column	SPB-1, 30m x 0.53mm i.d., film thickness 1.5μm
Column head pressure	He, 100kPa (14.5 p.s.i.)
Temperature program	60^{0}C for 2 min, then 20^{0}C/min to 250^{0}C, with 3.5 min final hold

AED parameters

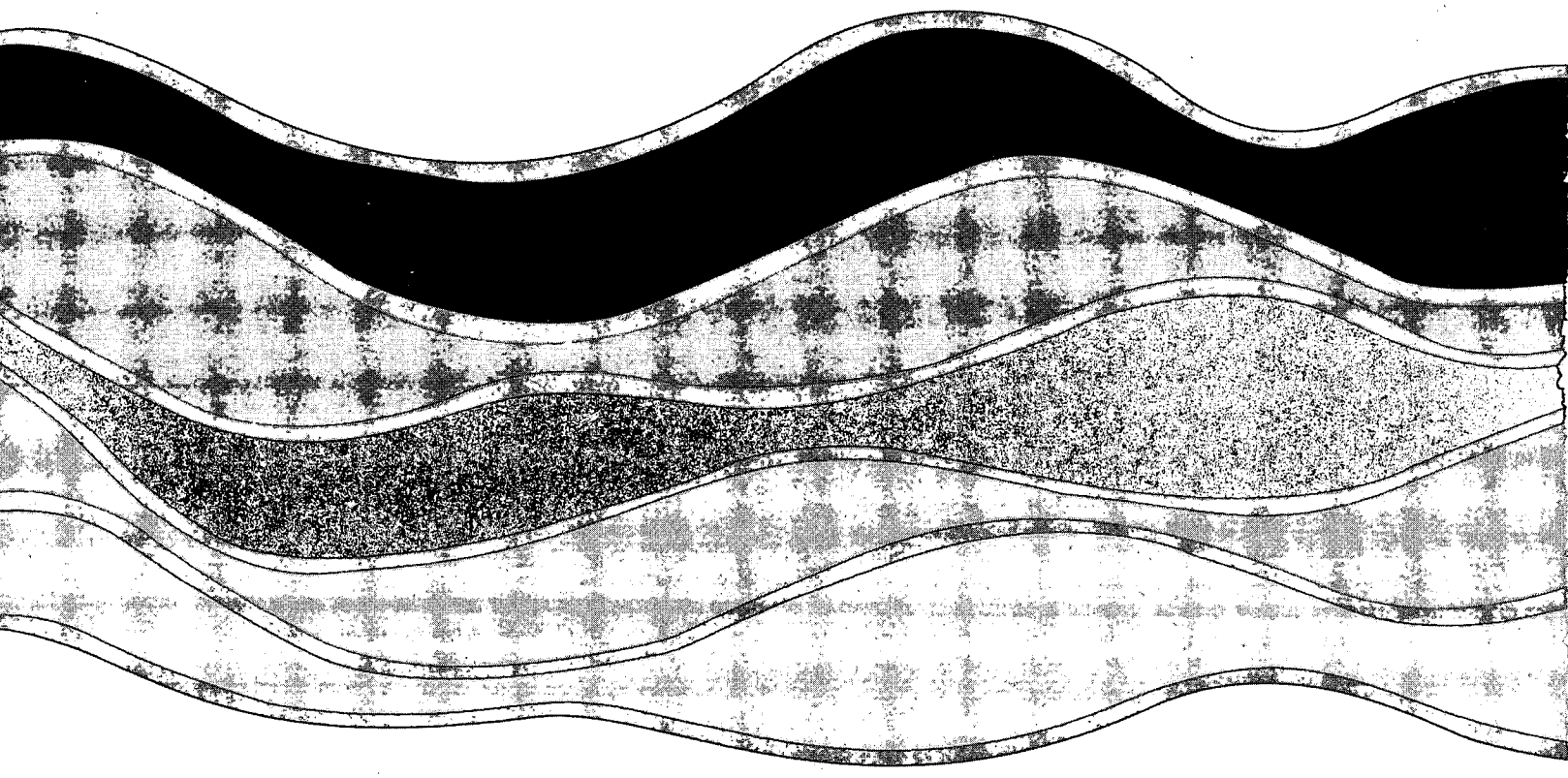
Transfer line	SPB-1
Transfer line temperature	270^{0}C
Cavity temperature	270^{0}C
Solvent vent time	2 min
Spectrometer purge gas	N_2 at 2 L/min
Make-up gas	He at 240 mL/min
Sn wavelength	271 nm
H_2 pressure	414 kPa (60 p.s.i.)
O_2 pressure	138 kPa (20 p.s.i.)

Table 2. Recoveries of butyltin and tripropyltin compounds from water

Compounds	water volume	Spiking level	Recovery(%)
	1 L	100 ng Sn/L	
MBT			77.5±4.9*
TPrT			76.1±5.3
DBT			72.1±5.5
TBT			67.0±7.3
	1 L	10 ng Sn/L	
MBT			88.5±13.8
TPrT			70.2±8.5
DBT			79.2±8.8
TBT			70.1±6.4
	0.5 L	20 ng Sn/L	
MBT			92.8±11.9
TPrT			81.9±7.0
DBT			85.4±7.7
TBT			78.8±7.2

* Standard Deviation (%); n = 4.

MBT - $C_4H_9SnCl_3$; DBT - $(C_4H_9)_2SnCl_2$; TBT - $(C_4H_9)_3SnCl$; TPrT - $(C_3H_7)_3SnCl$



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