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Speciation of butyltin compounds in sediments using gas chromatography interfaced with quartz furnace atomic absorption spectrometry

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Abstract

A method is presented for the determination of tri- and dibutyltin in sediments by gas chromatography–quartz furnace atomic absorption spectrometry. The compounds are released from the matrix by the action of acetic acid and extracted into hexane after formation of an extractable complex with diethyldithiocarbamic acid (DDTC). Pentylmagnesium bromide is used to derivatize the non-volatile organotin–carbamate complexes. A detection limit of 2.5 ng/g (as Sn) can be achieved. The optimization of the different parameters is discussed and the accuracy of the method was validated by the analysis of two certified reference materials. A first approach was made to determine tri- and dimethyltin compounds forming extractable complexes with NaDDTC under pH controlled conditions.

1. Introduction

Organotin compounds comprise one of the most thoroughly studied groups of organometallic chemicals in terms of their uses and applications as insecticides, fungicides, bactericides, stabilizers of polyvinyl chloride (PVC) plastics and autifouling agents. The deletereous effects of tributyltin (TBT) leached from antifouling paints into the marine environment have been the subject of extensive studies in recent years. The recognition of the toxicity of these compounds has led to environmental legislation restricting their use in a number of countries [1,2].

Soils and sediments are the main source of trace elements that enter the food chain and the main receptor of contaminants from anthropogenic activities. In the particular case of organotin compounds, several researchers have shown that butyltin compounds readily sorb onto suspended particulate matter and sediments [3,4].

To evaluate environmental risks, and in order to measure and speciate low levels of butyltins in waters and sediments, practical, reproducible and sensitive analytical methods are essential. As organotin compounds are not involved in mineralogical processes and bind to the surface of the sediment, the complete dissolution of the sediment prior to the analysis is not considered necessary. The basic approach to release organotin compounds from sediments involves acid leaching (HCl, HBr, HOAc) in aqueous or methanolic medium by sonication, stirring, shaking or Soxhlet extraction with an organic solvent.

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The formation of volatile gas chromatographable species after liberation of the organotin compounds is done either by *in situ* hydridization using $NaBH_4$ [5–7] or by Grignard derivatization after complexation of the organotin compounds with tropolone [8–10] or sodium diethyldithiocarbamate (NaDDTC). More recently, sodium tetraethylborate ($NaBEt_4$) has gained popularity as a derivatizing reagent in organometallic speciation analysis [11–13].

Gas chromatography (GC) is the most widely used separation technique in organotin speciation analysis owing to its high resolution power and the availability of sensitive detection methods such as flame photometric detection (FPD), atomic absorption spectrometry (AAS), mass spectrometry (MS) and atomic emission spectrometry (AES) [14,15].

This paper presents an optimized procedure for the speciation of TBT and dibutyltin (DBT) in sediments. It is based on acid leaching followed by extraction of the liberated compounds in hexane, using DDTC as complexing agent. The complexes are derivatized using pentylmagnesium bromide (n-PeMGBr) leading to stable and species amenable to GC. The accuracy of the method was validated by the analysis of two certified reference materials. Further, it was successfully used in a number of exercises and a certification programme organized by the Community Bureau of Reference (BCR). An attempt was made to adapt the method to the determination of trimethyltin (TMT) and dimethyltin (DMT).

2. Experimental

2.1. Reagents

Bu_3SnCl (96%), Bu_2SnCl_2 (95%), $BuSnCl_3$ (95%), Me_3SnCl (99%), Me_2SnCl_2 (97%), $MeSnCl_3$ (97%), Pr_3SnCl (98%) and n-PeNgBr (2.0 mol/l in diethyl ether) were obtained from Aldrich (Milwaukee, WI, USA) Stock standard solutions were prepared following the method described in detail elsewhere [16]. Working standard solutions were prepared by a series of dilutions of the stock standard solutions with octane.

Diethyldithiocarbamic acid (DDTC) solution was prepared by dissolving 2.25 g of sodium diethyldithiocarbamate salt (NaDDTC) (Merck, Darmstadt, Germany) in 10 ml of water. The solution of DDTC in pentane, used for sediment analysis, was obtained by shaking the aqueous solution of NaDDTC with 20 ml of 0.5 mol/l H_2SO_4 and extracting with 10 ml of pentane for 5 min.

ICN Alumina B-Super I (ICN Biomedicals, Eschwege, Germany) was used in the clean-up step for sediment samples.

All other reagents were of analytical-reagent grade. Deionized water further purified in a Milli-Q system (Millipore, El Paso, TX, USA) was used throughout.

2.2. Apparatus

A laboratory interfaced GC–AAS system described previously [16,17] consisting of a Varian Model 3700 gas chromatograph and a Perkin-Elmer Model 2380 atomic absorption spectrometer was used. The system was adapted to the use of an RSL 150 Megabore column. Chromatograms were recorded on a Spectra-Physics SP 4290 integrator in the peak-height mode. The optimum parameters used for GC and AAS are given in Table 1.

2.3. Procedure

A river scheldt sediment, sampled with a box corer mounted on the Research Vessel Belgica, was used to develop the leaching–extraction procedure. The Scheldt sediment was oven-dried on watch-glasses at 50°C, ground with an agate mortar and pestle and successively sieved with polyethylene sieves ranging from 600 to 45 μm, prior to organotin determination. Only the 63–180-μm fraction was selected for the optimization experiments.

A 1-g amount of sediment was accurately weighed and transferred into a 100-ml Pyrex erlenmeyer flask equipped with a ground-glass stopper, followed by 4 ml of deionized water, 1 ml of glacial acetic acid (96%), 1 ml of DDTC

Table 1
Optimum GC–AAS operating parameters

GC parameters	
Injection port	Wide-bore on-column liner
Injection port temperature	230°C
Injection volume	4 μl
Column	RSL 150 (15 m × 530 μm I.D., 1.2 μm film thickness)
Argon (carrier gas) flow-rate	6 ml/min
Oven program	
Initial temperature	100°C
Ramp rate	10°C/min
Final temperature	270°C
GC detector temperature	270°C
Block temperature	270°C
Interface parameters	
Transfer line	Deactivated fused silica, 530 μm I.D.
Transfer line temperature	270°C
AAS parameters	
Wavelength	286.4 nm
Light source	Sn electrodeless discharge lamp (8 W)
Slit	0.7 nm normal
Hydrogen flow-rate	350 ml/min
Air flow-rate	45 ml/min
MHS-20 furnace temperature	900°C

solution in pentane and 25 ml of hexane. The mixture was sonicated in an ultrasonic bath (Branson Model 1200) for 30 min. After phase separation, the organic phase was decanted into a 100-ml beaker. In the original erlenmeyer flask, the sediment was extracted again for 30 min with a fresh 25-ml portion of hexane with magnetic stirring. The sample was then centrifuged at 4000 *g* for 5 min (IEC Centra-CL centrifuge). The combined hexane extracts were dried over Na_2SO_4. The Na_2So_4 was rinsed twice with 10-ml portions of hexane.

The combined organic phase was then evaporated to dryness in a 50-ml erlenmeyer flask under reduced pressure at 40°C on a rotatory evaporator. Subsequently 250 μl of *n*-octane containing Pr_3SnPe as the internal standard were added, after which pentylation with 1 ml of 1 mol/l n-PeMgBr in diethyl ether was carried out; the mixture was gently agitated for 3 min. Excess Grignard reagent was destroyed by the addition of 10 ml of 0.5 mol/l H_2SO_4. The mixture was shaken for 1 min and then transferred into a capillary separating funnel. The octane layer was sampled for clean-up.

A Pasteur pipette was dry packed in successive order with glass-wool and 5 cm (±1.25 g) of Al_2O_3 B-Super I, which had been activated at 140°C for 24 h. After cooling, 5% (v/w) of water and 1 g of anhydrous sodium sulphate were added. The packing was first conditioned by passage of 5 ml of hexane–diethyl ether (9:1). The colourless eluate was evaporated to ca. 0.25 ml by means of a stream of nitrogen. This solution was then transferred into a small conical vial and was ready for analysis by GC–AAS. A scheme of the leaching–extraction procedure is shown in Fig. 1.

3. Results and discussion

3.1. Optimization of the extraction parameters

The parameters to be investigated were the extraction solvent, the influence of acetic acid

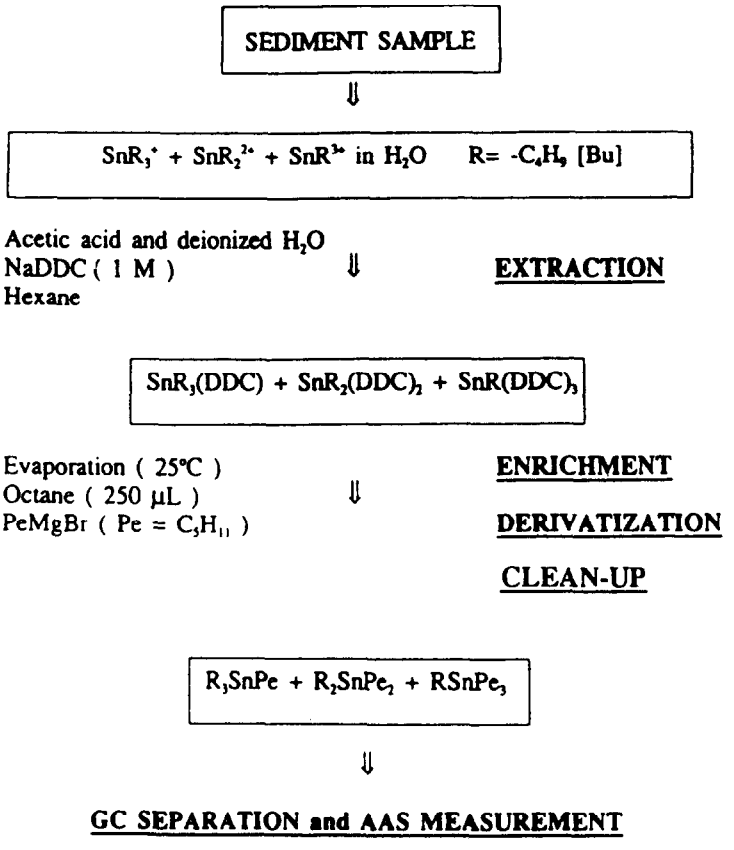

Fig. 1. Scheme of the speciation procedure for TBT and DBT determination in sediments.

and DDTC concentrations on the extraction recovery of butyltin compounds, spiking equilibrium time, the extraction time and the effect of the sediment itself.

Choice of extraction solvent

Hexane was chosen instead of other non-polar solvents such as pentane for the extraction because the latter (b.p. 36°C) was partially evaporated especially during the 30-min ultrasonic leaching–extraction step.

Organotin compounds have different properties in terms of polarity. Non-polar solvents, such as hexane, are optimum for the extraction of TBT and/or DBT, but more polar solvents seem to be necessary for the extraction of other species such as tri-, di- and monomethyltin and monobutyltin.

Chloroform and hexane–isopropyl acetate (80:20) were used as organic solvents to evaluate the possibility of increasing the extraction efficiency of the more polar organotin compounds. The use of both solvents was rejected because a certain amount of water and acetic acid were dissolved in them, remaining in the erlenmeyer flask after the evaporation of the organic solvent with the rotavapor. Under these conditions derivatization of the organotin compounds with Grignard reagents could not be carried out as these derivatizating agents decompose in the presence of small amounts of water.

Selection of the optimum amount of acetic acid

Most of the existing procedures use acids (HCl, HBr or acetic acid) to release the organotin compounds from the matrix. In this work, the best results were obtained with glacial acetic acid (96%). The variation in extraction recovery with changing acetic acid concentration

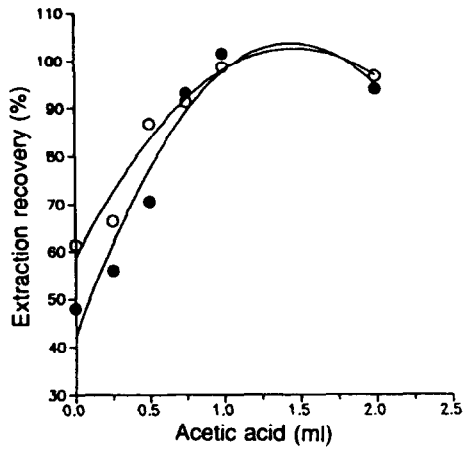

Fig. 2. Effect of the amount of acetic acid (96%) on the recovery of TBT and DBT. ○ = Bu_3Sn^+; ● = Bu_2Sn^{2+}.

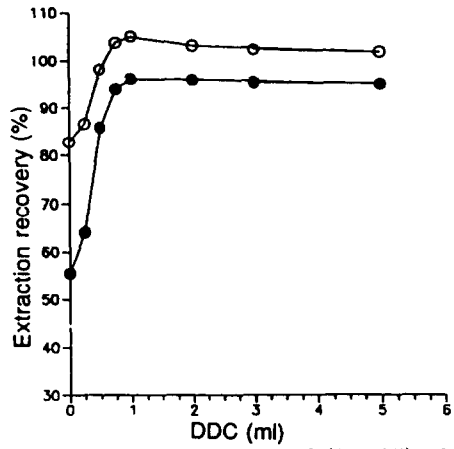

Fig. 3. Effect of the amount of DDTC (1 mol/l) solution on the extraction of TBT and DBT from sediments. ○ = Bu_3Sn^+; ● = Bu_2Sn^{2+}.

is illustrated in Fig. 2. The experiments were performed with spiked concentrations of the six ionic alkyltin species of the order of 1 $\mu g\ g^{-1}$ (as Sn). Apart from the variable amount of acetic acid, the normal analytical procedure was used. From Fig. 2 it can be seen that 1 ml of the concentrated acetic acid per gram of sediment is sufficient to liberate all DBT and TBT from the sediment surface within 60 min.

Selection of the optimum amount of DDTC

When 4 ml of Milli-Q-purified water and 1 ml of glacial acetic acid were added to the sediment sample, the measured pH in the mixture was ca. 2.0. Under these acidic conditions the aqueous NaDDTC solution cannot be used because of its known instability in acidic media. To overcome this problem, the acid form of NaDDTC, which is soluble in the organic solvent, needs to be used. Therefore, the daily prepared aqueous solution of NaDDTC (1 mol/l) was shaken with 10 ml of pentane and 20 ml of a 0.5 mol/l H_2SO_4 solution to obtain a solution of the carbamic acid (DDTC) in pentane, to be used in the leaching extraction procedure.

Fig. 3 shows the recovery of TBT and DBT from sediment as a function of the DDTC concentration. Both species showed optimum recoveries with 1 ml of 1 mol/l DDTC solution. When larger volumes (5–10 ml) of DDTC solution were added, the recoveries obtained for dimethyltin and monobutyltin increased up to 70 and 20%, respectively. However, simultaneously a decrease in the recoveries of TBT and DBT was observed. The extraction recoveries for TMT and MMT did not increase. Therefore, 1 ml of a 1 mol/l DDTC solution in pentane was used in subsequent work.

Effect of extraction time

An extraction time of 10 min provided a recovery of 75% for the butyltin species. To obtain higher recoveries the extraction time should be increased, and a maximum was reached at about 60 min (2×30 min), which kept the overall leaching–extraction procedure time reasonably short for practical use.

Spiking equilibrium time

Spiking experiments may present many problems that are not always faced in an appropriate way. One of the major problems is that the compounds naturally present and the spiked compounds are usually not in the same chemical form and are not bound to the sample (especially in solid samples) in the same way. Therefore, the results obtained from spiking experiments may not completely reflect the amount of organotin extracted from real sediment samples.

For this study, two series of spiked sediment samples were prepared, one series with an

Table 2
Extraction recoveries (%) of TBT and DBT in a spiked sediment after different equilibrium times ($n = 4$)

Species	15 min	24 h
Bu_3Sn^+	93 ± 5	87 ± 5
Bu_2Sn^{2+}	93 ± 5	80 ± 6

equilibrium time of 15 min and the other series with an equilibrium time of 24 h in the dark. The extraction recoveries obtained are shown in Table 2. For tributyltin only a different of 6% could be noted, whereas for dibutyltin the difference was twice as large. Despite this small difference, an equilibrium time of 15 min after spiking was used in further application studies.

Influence of sediment composition

After optimization of the above-mentioned parameters, different kinds of sediments were spiked with organotins and the effect of the kind of sediment on the extraction efficiency was studied. The sediments used were sediment sampled in Lake Maggiore, Italy, and certified reference materials estuarine sediment (CRM 277), lake sediment (CRM 280) and river sediment (CRM 320). Blank determinations showed that all sediments were free from butyltin except that sampled in Lake Maggiore, which contained both DBT and TBT. Some differences, up to 15%, were found in the recovery of TBT and DBT for the different sediments. Therefore, it is wise to control and/or to re-optimize all parameters when analysing an unknown sediment matrix.

3.2. Analytical characteristics of the leaching extraction procedure

Precision and recovery efficiency

Recovery and/or speciation of analytes from a complex matrix such as sediment are often difficult to assess and interpret. A common approach consists in the addition of a known amount of the analyte to the matrix of interest, allowing time for equilibration and then subjecting the spiked material to the analytical procedure.

An aqueous working standard solution (containing all six butyl- and methyltin species) was added to the river Scheldt sediment (63–189 μm) leading to concentrations of about 5 $\mu g/g^{-1}$ as Sn for each species. Analyses were conducted as mentioned above.

An estimate of the reproducibility of the optimized method for TBT and DBT speciation in sediments was obtained by analysing six replicates. The reproducibility of the entire procedure was estimated as ca. 5 % (relative standard deviation). The extraction recoveries were 95% and 103% for TBT and DBT, respectively.

Accuracy

The accuracy of the procedure was validated by the analysis of certified PACS-1 sediment (National Research Council of Canada). The results obtained for TBT and DBT in PACS-1 are given in Table 3. MBT cannot be determined

Table 3
TBT and DBT determinations in CRM 462 and PACS-1

Sample	Butyltin species	Result	Certified value
BCR CRM 462	Bu_3Sn^+	64.8 ± 7.7[a]	70.5 ± 13.2[a]
	Bu_2Sn^{2+}	127.6 ± 7.2[a]	128.0 ± 16.0[a]
PACS-1	Bu_3Sn^+	1.24 ± 0.09[b]	1.21 ± 0.24[b]
	Bu_2Sn^{2+}	1.53 ± 0.17[b]	1.14 ± 0.20[b]
	$BuSn^{3+}$	–	0.28 ± 0.17[b]

[a] Concentrations in ng/g as compound (±95% confidence interval).
[b] Concentrations in μg/g as Sn (±95% confidence interval).

using this method. The results for TBT are in good agreement with the certified value, whereas for DBT the amount found in PACS-1 is higher but not significantly different from the certified DBT value. The method was also applied in a certification campaign organized by the BCR on coastal sediment CRM 462; the results obtained applying the described procedure for TBT and DBT agree well with the certified value within the 95% confidence interval, as can be seen from Table 3. Fig. 4 shows a chromatogram for a sample of CRM 462 sediment.

Detection limit

The detection limit of the method depends on the amount of sediment used for extraction and the final volume injected into the GC–QFAAS system. Starting from the analysis of 1 g of sediment, and assuming an injection of 4 μl of extract into the GC–QFAAS system, ionic butyltin compounds in the sediment can be detected at levels down to ca. 2.5 ng/g as Sn.

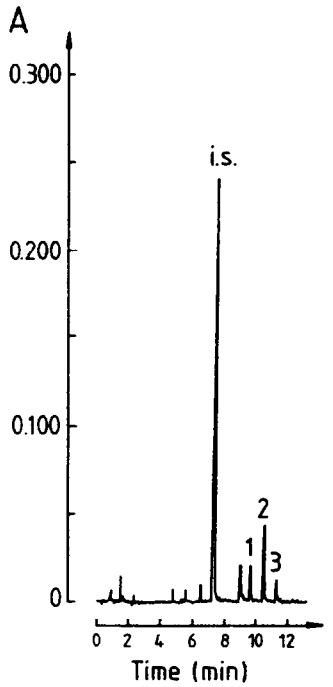

Fig. 4. GC–AAS of a sample of CRM 462 sediment. Peaks: 1 = Bu_3Sn^+; 2 = Bu_2Sn^{2+}; 3 = $BuSn^{3+}$; i.s. = internal standard (Pr_3SnPe). *A* = Detector response.

3.3. Determination of trimethyltin and dimethyltin

Different studies were carried out in order to test the possibility of extracting not only TBT and DBT, but also methylated compounds such as TMT and DMT.

The extraction of organotin compounds in hexane by complexation with NaDDTC has been successfully applied by Dirkx et al. [16] to the determination of these compounds in water. The simultaneous extraction of methyl- and butyltin species was possible by adjusting the pH of the sample to pH 5.

Adjusting the pH of the sediment slurry to pH 4.5–5.0 by adding appropriate amounts of powdered sodium acetate, after the leaching step and before the addition of NaDDTC, resulted in increases in the extraction efficiency for TMT (90%) and DMT (60%). NaDDTC solution in water could be used in these experiments because it is stable enough at this pH. However, under these conditions the recovery of TBT and DBT decreased considerably. Such a decrease in the recovery of the butylated species is not attributable to the non-desorption of the compounds from the matrix, because the leaching conditions were not modified with respect to the procedure proposed for DBT and TBT determination.

When TBT and DBT were first extracted following the previously described optimized procedure and after separation of the organic phase the pH of the remaining sediment was adjusted to pH 4.5–5, the recovery of DMT was 70% but only 40% of the spiked TMT was recovered.

On the basis of these promising results, further experiments will be carried out with different complexing agents and organic solvents in order to determine the four species simultaneously.

4. Conclusions

A reproducible method has been developed for the determination of di- and tributyltin present in sediments. The low detection limit

achieved, 2.5 ng/g, makes it suitable for the determination of these species in the environment, where butylated organotin compounds are released by anthropogenic activities. The feasiblity of DDTC as a complexing agent for the determination of both TBT and DBT without pH control and of NaDDTC for TMT and DMT at pH 4.5–5 has been demonstrated. The accuracy of the method has been tested through the analysis of certified materials, CRM 462 and PACS-1, with good agreement between the certified value and the results obtained with the proposed method. Method development for the determination of the methyltin compounds is of great interest for the clarification of biological processes, so far not completely understood.

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