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WORKING METHODS PAPER

Effects of Complexing Agents and Acid Modifiers on the Supercritical Fluid Extraction of Native Phenyl- and Butyl-tins from Sediment

Y. Cai,[1] M. Abalos[2] and J. M. Bayona[2]*
[1]Department of Chemistry and Southeast Environmental Research Program, Florida International University, University Park, Miami, FL 33199, USA
[2]Environmental Chemistry Department, CID–CSIC, Jordi Girona Salgado 18–26, E-08034, Barcelona, Spain

The effects of: (1) the modifier type (methanol and formic, acetic and propionic acids), (2) complexing agents (diethylammonium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate) either with or without acidic modifiers, (3) the extraction temperature (50–80 °C) and pressure (30–50 MPa), (4) the extraction procedure (static–dynamic or dynamic), and (5) the volume of static modifier, on the extraction efficiency of native butyl- and phenyl-tin compounds from sediment, were evaluated comprehensively. The highest extraction efficiency for butyl- and phenyl-tin compounds was obtained at 30 MPa and 50 °C by using CO_2 modified with acetic acid (200 μl in the cell). Supercritical fluid extraction (SFE) extracts were hexylated and determined by GC–FPD using a 610 nm bandpass filter without any clean-up step. In summary, the developed analytical procedure is robust (no restrictor clogging; free from FPD interferences), it is low-cost (no complexing agents needed), it has a high sample throughput (<3 h), it is independent of the matrix for the determination of butyltin compounds in sediment, and it provides the highest precision among the SFE procedures reported for organotin determination. © **1998 John Wiley & Sons, Ltd.**

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* Correspondence to: J. M. Bayona, Environmental Chemistry Department, CID–CSIC, Jordi Girona Salgado 18–26, E-08034, Barcelona, Spain.
E-mail: jbtqam@cid.csic.es
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INTRODUCTION

During the 1990s, a great deal of attention has been devoted to the development of analytical procedures for organotin (OT) speciation from environmental samples aiming to reduce the usage of toxic solvents and expanding the range of analytes of interest.[1,2] In this regard, several analytical procedures based on aqueous-phase ethylation combined with solid-phase extraction (SPE) followed by supercritical fluid extraction (SFE) have been developed for the extraction of butyl-, phenyl- and cyclohexyl-tin compounds[3,4] from aqueous matrices. These methods make possible a substantial reduction in the solvent usage and analysis time in comparison with conventional liquid–liquid extraction methods.[2,5]

Until now attempts to apply SFE to OT extraction from sediment have been partially successful due to a stronger interaction of ionic species with the matrix, leading to moderate to poor recoveries of the more ionic species mono-alkyl and mono-aryl species). In one of the first SFE

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methods, supercritical carbon dioxide was modified with acidified (HCl) methanol; this is effective for tributyltin from spiked sediment and certified reference materials[6] (CRMs). Interest in the determination of a broad spectrum of OTs and their degradation products has led to the development of alternative approaches, including (1) use of complexing agents to increase the solubility of ionic species in supercritical carbon dioxide[7–9] and (2) hexylation *in situ* before the SFE extraction.[10] Although the latter approach is particularly attractive because it yields a clean extract ready for GC determination, its main limitations are the sample size (*ca* 100 mg) and the reactivity of sulfur species occurring in sediments with the derivatization agent (Grignard reagent), which might lead to alkyl sulfide formation that interferes with the determination of OTs by tin-selective FPD.[10] However, the former approach (complexing agent) appears to be particularly interesting, especially for mono- and di-substituted organotin compounds, because the use of complexing agents can improve the solubility of ionic organotin compounds in the supercritical fluid. The feasibility of acidic CO_2 modifiers[11,14] (formic and acetic acids) or polar fluids[12] ($CHClF_2$) for the extraction of OT compounds from sediment and biota has been assessed for a variety of environmental and food matrices, but these extraction procedures have not been validated.

Consequently, it is of primary interest to intercompare the performance of different SFE procedures for native organotin compounds because most of the published method development has been carried out on spiked samples. Furthermore, because of the large number of variables involved in the development of SFE procedures, some of them are not considered. Therefore, a systematic evaluation of the effect of modifiers, temperature and complexing agents is particularly needed for the extraction of incurred phenyl and butyltin compounds. Moreover, the lack of reference materials with a certified phenyltin content makes it necessary to develop precise and accurate extraction procedures for their certification in environmental samples.

The objectives of this work were to intercompare the effect of different modifiers and complexing agents for the recovery of native phenyl- and butyltin compounds from a marina sediment using a stepwise optimization. In addition, temperature, pressure and the effect of static versus dynamic extraction were also evaluated. The developed analytical procedure was validated with a CRM (PACS-1) and a research material (CRM-424), either certified or with an indicative value of the butyltin content.

EXPERIMENTAL

Apparatus

Supercritical fluid extraction

Extractions were performed with an SFE 30 system (Fisons Instruments, Milan, Italy) using SFE-grade carbon dioxide (Praxair, Barcelona, Spain). The apparatus consisted of two 150 ml syringe pumps, a single extraction cell, linear flow restrictors, and a solvent trap to collect the extracts. The syringe pump which delivered CO_2 was refrigerated at 4 °C to keep the CO_2 liquid. An extraction cell with an internal volume of 3.5 ml (50 mm × 9.4 mm) (Dionex, Sunnyvale, CA, USA) was used. The SFE instrumental setup is described in detail elsewhere.[10] The SFE flow rate varied from 1.3 to 1.9 ml min^{-1} (measured as liquid fluid at the pump). All extracts were collected by inserting the low-pressure end of the restrictor through a septum into a 30 ml glass vial containing an inner glass liner for effective collection of extracts. The collection vial contained 15 ml of methylene chloride. The top part of the restrictor (about 10 cm) was maintained at 150 °C to prevent plugging. The collection solvent was held at 5 °C to minimize the losses of volatile OTs. A 1 mm i.d. × 10 cm length of steel tubing was used to vent the decompressed CO_2.

GC–FPD

Analyses of SFE extracts were performed in duplicate using a Fisons Mega 2 Series gas chromatograph (Milan, Italy) and an FPD detection system (FPD 700, Fisons, Milan, Italy) containing a 610 nm bandpass filter. The detector temperature was set at 225 °C. A 30 m × 0.25 mm i.d. fused-silica column coated with a DB-17 film 0.25 μm thick (J&W Scientific, Folsom, CA, USA) was used as the analytical column. The column temperature was held at 60 °C for 1 min. then programmed at 10 °C min^{-1} to the final temperature of 300 °C, which was held for 5 min. Helium at a linear velocity of 30 cm s^{-1} and nitrogen at 30 ml min^{-1} were used as carrier and detector makeup gases, respectively. Flow rates of fuel detector gases were 120 ml min^{-1} of hydrogen and 100 ml min^{-1} of air.

Data were acquired and processed by a Perkin-Elmer–Nelson interface connected to a PC.

Reagents and materials

Surficial sediments were collected in the Masnou marina (Barcelona, Spain), freeze-dried, and sieved through 120 μm. A reference material (harbor sediment, PACS-1) was obtained from the National Research Council of Canada, Ottawa, Canada, and a research material (estuarine sediment, CRM-424) was obtained from the Community Bureau of Reference (BCR), Commission of the European Communities, Brussels, Belgium.

Monobutyltin (MBT), monophenyltin (MPhT), diphenyltin (DPhT), triphenyltin (TPhT) and tripentyltin chloride (TPeT) (Aldrich Chem. Co., Milwaukee, WI, USA), dibutyltin (DBT), tributyltin chloride (TBT) and tripropyltin chloride (TPrT) (Merck–Schuchardt, Hohenbrunn, Germany), and tetrabutyltin (TeBT) (Fluka AG, Buchs, Switzerland) were used as received. Diethylammonium diethyldithiocarbamate (DEA-DDC), ammonium pyrrolidinedithiocarbamate (APDC) and hexylmagnesium bromide (HexMgBr, 2.0 mol l^{-1}) in diethyl ether were obtained from Aldrich. Nanograde dichloromethane and methanol (MeOH) were obtained from Merck and 99.7% acetic acid (HOAc) from Aldrich. All other chemicals were of analytical-reagent grade or better.

Organotin chlorides and TeBT stock standards were prepared at a concentration of *ca* 1000 mg l^{-1} (as Sn) in hexane (for MBT, DBT and TBT) or acetone (for MPhT, DPhT, TPhT, TPrT and TPeT). The hexylated organotin standards were prepared by hexylation of the appropriate organotin salts with an excess of HexMgBr, following a similar procedure reported by Unger *et al.*[13]

Procedure

Sample preparation

The extraction cell was filled first with pre-extracted glass wool, then with about 1 g of elemental copper and 1 g of sediment. The remaining void volume was filled with pre-extracted glass wool. When DEA-DDC was used as the complexing agent, a sample preparation procedure reported by Liu *et al.* was employed.[8] Briefly, 1 g sediment was weighed into an aluminum dish and then amended with 0.5 ml of 0.3 mol l^{-1} DEA-DDC in methylene chloride directly in an aluminum dish. The treated sample was allowed to stand for 20 min to allow the solvent to evapore, then it was mixed with a spatula, and loaded into the extraction cell. When APDC was used as the complexing agent, 25 mg of APDC was added directly to the sediment, thoroughly mixed with a spatula and then loaded into the extraction cell. The HOAc was either added directly (200 μl) into the extraction cell containing 1 g of sediment or delivered by the modifier pump as a methanolic solution.

SFE extraction

Following sediment loading (*ca* 1 g), the extraction cell was placed in the SFE oven. For each extraction, 30 ml of CO_2 was passed through the cell (measured as liquid at the pump) at an average flow rate of 1 ml min^{-1}. The flow rate ranged from approx. 1.3 to 1.9 ml min^{-1}. The dynamic addition of modifiers (neat MeOH or a methanolic solution of HOAc) was carried out by the slave pump. When an additional static extraction step was included the extraction cell was held in the oven at 50 or 80 °C for 10 min, then subjected to a 20 min dynamic extraction. For PACS-1 and CRM-424 analyses, 294 ng of TPrT was added as a surrogate to the collection solvent before the extraction.

Derivatization

Following the SFE extraction, 226–564 ng of TeBT and 103–309 ng of TPeT were added to the extract. Then the solvent contained in the collection vessel was carefully evaporated to about 0.5 ml by a gentle stream of dry nitrogen. Organotin derivatization was performed using hexylmagnesium bromide (HexMgBr) 2 ml of which was added dropwise to the extract; the reaction vessel was kept on an ice bath during this derivatization reaction. **Caution: occasional presence of small amounts of HOAc in some extracts can cause a violent reaction with HexMgBr.** The mixture was allowed to stand for 30 min and was shaken a few times during this period. To stop the reaction and to destroy the excess HexMgBr, the reaction vessel was placed in an ice bath, 5 ml of water was added dropwise into the mixture followed by 5 ml of HCl (25%). The mixture was transferred into a 60 ml separating funnel and the vessel was washed twice with 2 ml portions of hexane which were also transferred to the same separating funnel. The mixture was shaken manually for 5 min and allowed to stand for a few minutes more until phase separation had occurred. The aqueous phase was discarded, and the organic phase was dried over anhydrous sodium sulfate. The excess of solvent was evaporated under a gentle stream of nitrogen to 1 ml (0.5 ml for CRM-424), and 1 μl was injected, in duplicate, into the (GC–FPD apparatus.

Table 1 SFE experimental conditions

Expt no.[a]	MeOH in CO_2 (%, v/v)	HOAc in MeOH	Complexing agent	Temperature (°C)	Extraction mode[b]
1	2	0	None	50	D
2	2	20%	None	50	D
3	2	20%	DEA-DDC	50	D
4	2	0	DEA-DDC	50	D
5	5	20%	None	50	D
6	10	20%	None	50	D
7	5	200 µl	None	50	S + D
8	0	200 µl	None	50	S + D
9	2	20%	APDC	50	D
10	2	0	APDC	50	D

[a] Experiments were carried out in duplicate or triplicate.
[b] S, static; D, dynamic.

RESULTS AND DISCUSSION

Polluted harbor sediments from the Masnou marina (Barcelona, Spain) were used throughout the extraction-variable optimization, as well as two CRMs for method validation. Because the large number of extraction variables considered in this study (modifiers, complexing agents, temperature, pressure and mode of modifier addition), preliminary experiments were carried out at 50 °C and 30 MPa to evaluate the effect of the modifier on the extraction efficiency of OTs. Once the extraction agent was selected, temperature and pressure were optimized (Table 1).

Effect of acid modifiers

Formic, acetic and propionic acids were selected for the extraction of butyl- and phenyl-tin compounds and were evaluated in the combined static (10 min) and dynamic extraction (20 min) (Fig. 1). Some of these carboxylic acids are effective for the extraction of OTs under atmospheric conditions, because of the combined effect of matrix displacement and complexing capability. It has been found that formic acid can displace the different counterions of OTs (e.g. chlorides, acetates) when they are analyzed by SFC using CO_2 modified with formic acid.[11] Furthermore, acetic acid was also found effective for the extraction of triphenyl and tributyltin from biotic matrices[15] but it has not been evaluated in the case of sediments. Among the three carboxylic acids evaluated, acetic acid was the most efficient modifier for the extraction of di- and tributyltin compounds, and propionic acid for the monosubstituted OT compounds. The higher ex-

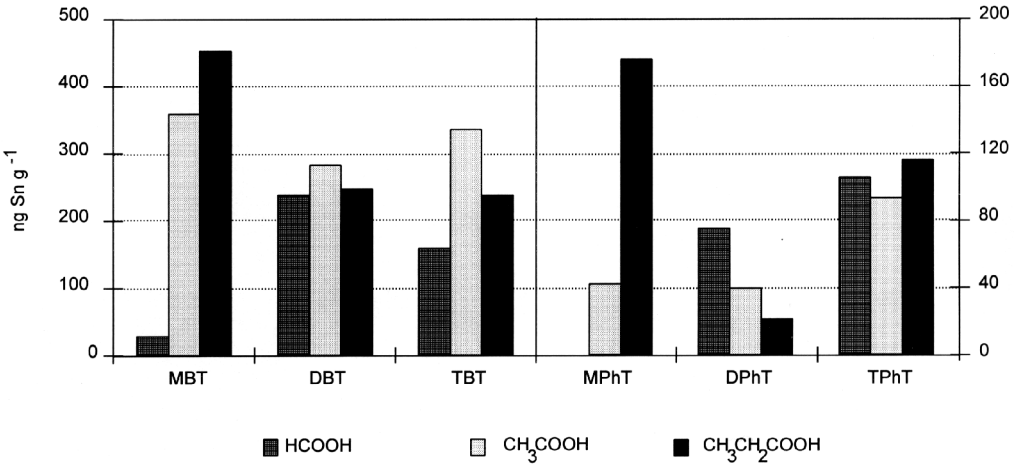

Figure 1 Effect of the different acid modifiers (200 µl) added to the extraction cell for the extraction of butyl- and phenyl-tim from a marina sediment. Extraction was carried out at 50 °C and 30 MPa in a combination of static (10 min) and dynamic (20 min) modes. Abbreviations are identified in the text.

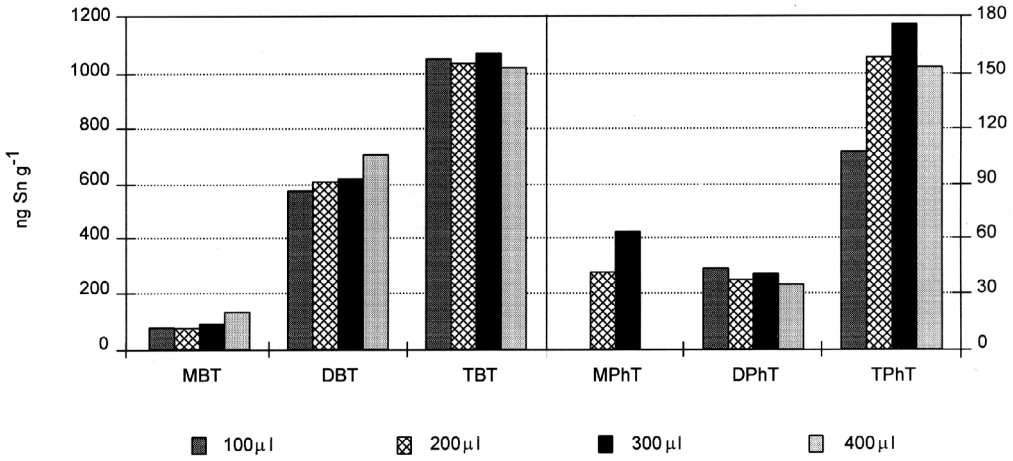

Figure 2 Effect of the volume of HOAc used as a static modifier in the extraction efficiency of OTs from sediment. Compound identification and other extraction conditions are identical to those in Fig. 1, but the sediment is different.

traction efficiency for monosubstituted OTs in the presence of propionic acid can be attributed to the dealkylation of the di- or tri-substituted species since the extraction efficiency of di- and tri-alkyltin and phenyltin species is usually lower in comparison with acetic acid. Therefore, acetic acid was selected as the more suitable modifier for the extraction of both butyl- and phenyl-tin compounds.

The extraction procedure (e.g. 20 min static combined with 10 min dynamic, versus 30 min dynamic) was also evaluated for the 2% mixture of HOAc and MeOH (1:4, v/v) but in both cases the extraction efficiency was 20–30% poorer in comparison with that when the HOAc was to added the extraction cell. These results are consistent with the formation of OT acetates in the SFE conditions, and the addition of a polar modifier such as methanol does not improve the extraction because the solubility parameter of the extractant is too high compared with the OT acetates.

The volume of acetic acid added to the extraction cell as a static modifier was also evaluated (Fig. 2). The best results were obtained with 200–300 µl of HOAc. At higher volumes, a slight degradation of phenyltins was observed. In addition, occasional restrictor plugging was found when large volumes (>300 µl) of HOAc were used.

Effect of complexing agent

Since some complexing agents, such as DEA-DDC, have been reported to be effective in the extraction of di- and tri-organotins from soil and sediment,[7–9] they have been considered in this study. In addition, the effect of the combination of the complexing agent with acidic conditions was also considered. However, because it is reported that DEA-DDC is less stable in acidic conditions than APDC,[15] we have considered both complexing agents in this study. Therefore, APDC and DEA-DDC were evaluated both in neat MeOH and in MeOH acidified with HOAc. The effect of complexing agents compared with neat MeOH was to increase the extraction efficiency of dibutyltin and tributyltin compounds which was more apparent in the case of APDC (Fig. 3). The less soluble OTs in CO_2–MeOH exhibited a greater improvement in extraction in the presence of complexing agents. These results indicate that the rise in the extraction efficiency when complexing agents are used can be attributed primarily to an enhancement of solubility in the fluid. However, MBT was not extracted as reported elsewhere,[8] probably because it is strongly bound to the matrix. In order to improve the extraction of the monosubstituted OTs, 20% HOAc was added to the MeOH; this led to an improvement in the extraction efficiency for all analytes (Fig. 4), but it was still poorer than that with neat HOAc, particularly in the case of monosubstituted OTs (Fig. 5).

From the above experiments (Figs 3–5), we can conclude that HOAc is the best modifier for the extraction of native butyl- and phenyl-tin compounds from the harbor sediment analyzed, because it provides a higher extraction efficiency and less

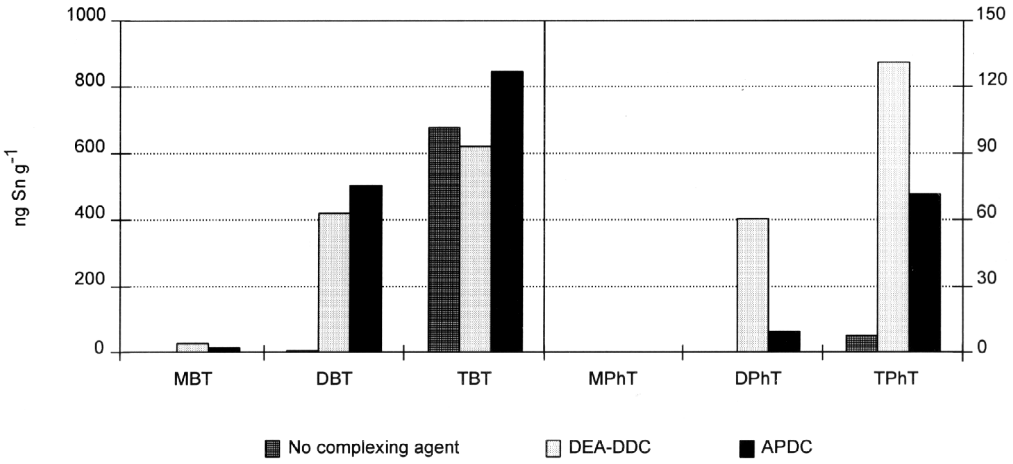

Figure 3 Effects of different complexing agents (diethylammonium diethylcarbamate, DEA-DDC; ammonium pyrrolydenedithiocarbamate, APDC) on the extraction efficiency of OTs from a sediment (the same sample as in Fig. 2). Compound identification and extraction conditions are identical to those in Fig. 1 but 2% MeOH was used as a CO_2 modifier.

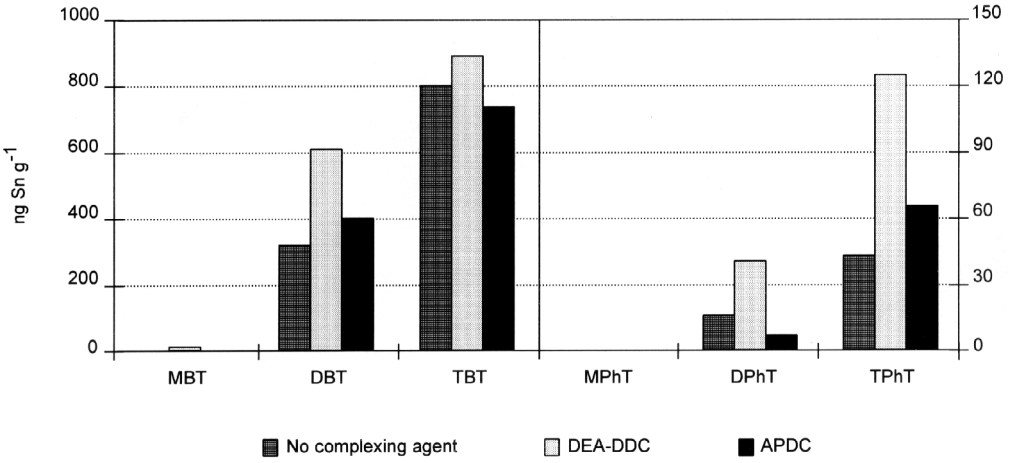

Figure 4 Effects of different complexing agents (diethylammonium diethylcarbamate, DEA-DDC; ammonium pyrrolydenedithiocarbamate, APDC) on the extraction efficiency of OTs from sediment (the same sample as in Figs 2 and 3). Compound identification and extraction conditions are identical to those in Fig. 1 but 2% MeOH containing 20% HOAc was used as a CO_2 modifier.

chance of interferences in the CGC–FPD determination than in the presence of complexing agents. Furthermore, the SFE extracts are amenable to derivatization with Grignard reagents since HOAc added to the extraction cell is not displaced during the SFE extraction.

Effect of temperature and pressure

Two temperatures were evaluated in this study: 50 and 80 °C (Fig. 6). Although no significant differences were found, we considered the lowest temperature more suitable to prevent possible degradation processes during the extraction. In this respect, thermal degradation of organotin halides has been reported in supercritical fluid chromatography (SFC) with CO_2 at temperatures above 100 °C.[16]

Two pressures (30 and 50 MPa) were evaluated at 50 °C. The results show that pressure does not

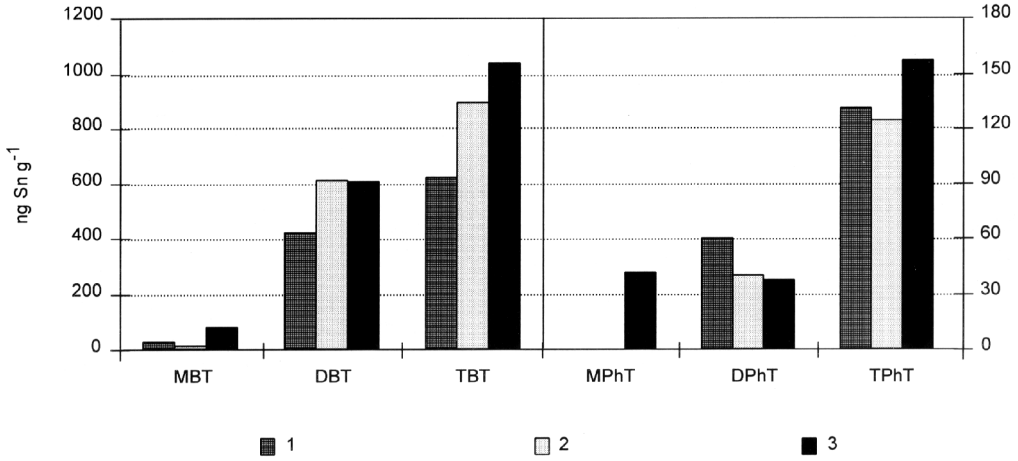

Figure 5 Intercomparison between the different CO_2 modifiers for OTs from a sediment (the same sample as in Figs 2–4). 1, DEA-DDC dissolved in MeOH; 2, DEA-DDC dissolved in MeOH containing 20% HOAc; 3, 300 µl HOAc in the extraction cell. Extraction was carried out at 50 °C and 30 MPa. Abbreviations are identified in the text.

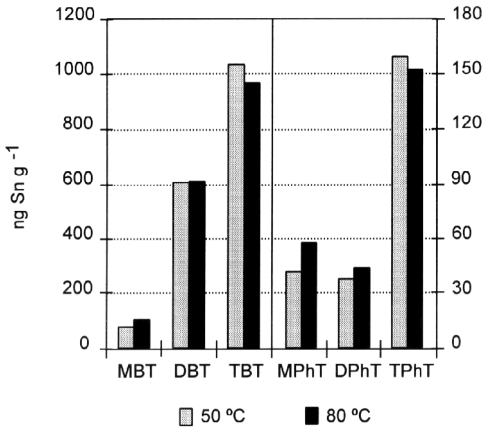

Figure 6 Effect of temperature on the extraction efficiency of OTs from sediment (the same sample as in Figs 2–5). Extraction was performed at 30 MPa. Abbreviations are identified in the text.

affect the extraction efficiency of butyl- and phenyl-tin compounds. These results are consistent with those reported above for the extraction of organotin compounds from sediment.[9] This could be attributed to the limited change in fluid density with any pressure increase above 30 MPa.

Method validation

Method validation was carried out only for butyltins because they are the only OTs certified in sediment. Therefore, PACS-1 was used for this purpose, and an additional research material (CRM-424) was selected to evaluate the matrix effects using the optimized extraction conditions (30 MPa, 50 °C, 200 µl HOAc, static–dynamic). Results are listed in Table 2. Extraction efficiency calculated from the certified values for DBT and TBT in PACS-1 is over 80% and the precision of the

Table 2 Validation of the SFE analytical procedure developed[a]

	PACS 1			CRM-424		
Compound	Certified concn. (ng/g as Sn)	Av. rec.[b] (%)	RSD ($n = 4$) (%)	Indicative value (ng/g as Sn)	Av rec. (%)	RSD ($n = 4$) (%)
MBT	280 ± 170	130	5.5	174 ± 36	59.5	5.02
DBT	1160 ± 180	72.0	2.1	27.2 ± 9.7	60.8	13.2
TBT	1270 ± 220	79.1	3.4	8.2 ± 2	140	12.9

[a] Extraction conditions used: 50 °C, 200 µl HOAc, 10 min static and 20 min dynamic.
[b] Av. rec. Average recovery.

method is high (RSD < 3.5%, $n = 5$). The precision of the developed method is consistently high, due to its simplicity (modifier is added directly to the extraction cell and no complexing agents are needed). The value found for MBT by the developed method exceeds the average certified value but it falls within its range. For other SFE methods recoveries were reported that were above the certified value for this CRM.[9]

The MBT and DBT recoveries calculated according to the given value (not certified) obtained for CRM-424 were slightly lower than those found for PACS-1; this could be attributed to the high complexity of the matrix and the low OT levels found in this matrix. The precision for this CRM was also lower than for PACS-1, but if it is taken into account that the concentrations of the OTs are from two to three orders of magnitude lower than in PACS-1, the precision of the developed SFE procedure is still reasonable (RSD < 13%). In the case of TBT, a higher value was found in this study in comparison with the indicative value for this compound. The very low TBT content and the complexity of the matrix could be responsible for the differences found between the two values.

CONCLUSIONS

A comprehensive evaluation of a number of variables that could affect the SFE extraction of native butyl- and phenyl-tin compounds from a marina sediment demonstrated that the best extraction conditions for butyl- and phenyltin compounds were the addition of HOAc to the extraction cell followed by a static period combined with a dynamic extraction with CO_2 (50 °C and 30 MPa). Use of MeOH combined with HOAc led to lower recoveries, probably because of a high solubility parameter for the extraction of the OT acetates that presumably were formed under the SFE conditions. The two complexing agents evaluated, DEA-DDC and APDC in either CO_2–MeOH or CO_2–HOAc–MeOH, enhanced the extraction efficiency only of the less soluble disubstituted phenyl- and butyl-tin, and triphenyltin, in comparison with CO_2–MeOH. Furthermore, the extraction efficiency of the procedures involving complexing agents for both butyl- and phenyl-tin compounds was lower than the HOAc method developed in this study.

The effectiveness of HOAc as a CO_2 modifier for the SFE of OTs from sediment is reported here for the first time. The improvement of the extraction efficiency by the addition of HOAc could be attributed to the ability of HOAc to interact with an analyte–matrix complex, and the subsequent formation during the extraction of OT acetates which are readily soluble. No polar modifiers are needed with the CO_2. By using a moderate amount of HOAc, restrictor clogging is obviated and the extracts are amenable to CGC–FPD determination following a Grignard derivatization without any clean-up step.

The application of this developed SFE method to the determination of CRMs demonstrates that the use of HOAc as a modifier is effective for the SFE extraction of organotins from sediment even in the case of low OT contents and complex matrices.

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