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Interlaboratory evaluation of an off-line supercritical fluid extraction and gas chromatography with atomic emission detection method for the determination of organotin compounds in soil and sediments

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Abstract

A collaborative study was conducted, with eight laboratories participating, to determine the method accuracy and precision of an off-line supercritical fluid extraction (SFE) method for organotin compounds. This method involves extraction of organotin compounds from solid matrixes with supercritical carbon dioxide, modified with 5% methanol, at 450 atm and 60°C for 20 min in the static mode followed by 30 min in the dynamic mode. The extracted material was collected in either methylene chloride or on a C₁₈-bonded silica trap followed by a methylene chloride rinse. The extracted material was derivatized with pentyl magnesium bromide and analyzed by gas chromatography with atomic emission detection (GC–AED). The study design was based on the AOAC blind-replicate design with balanced replicates. The study samples consisted of three solid matrixes that were spiked with organotin compounds at 1000 ng/g (as Sn) and one unspiked matrix that contained dibutyltin and tributyltin compounds at independently determined levels. The results of this interlaboratory study indicate that the SFE method works satisfactorily for the tri- and tetra-substituted organotin compounds but that the di- and mono-substituted organotin compounds are quite difficult to extract under these conditions. Higher pressures and different modifiers may be required to enable extraction of the mono- and di-substituted organotin compounds from soils and sediments. © 1997 Elsevier Science B.V.

Keywords: Supercritical fluid extraction; Organotin compounds

1. Introduction

Organotin compounds (e.g., tributyltin and triphenyltin) are widely used as agricultural fungicides, biocides, stabilizing agents in polymers, and catalysts [1,2] and their subsequent release into the environment has contributed to environmental pollution

[2,3]. Trialkyltin compounds with short alkyl substituents, such as triethyltin, are more toxic to mammals than their corresponding monoalkyl analogs. To understand the biological effects of organotin compounds and to assess their environmental impact, precise analytical methods are needed for their determination and speciation. Over the past decade, continuous progress has been made in the development and improvement of analytical techniques for determination of organotin compounds at

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low parts-per-billion levels in marine sediments and biological samples [4–18].

Among the analytical techniques reported in the literature, a few will be briefly reviewed here. Zhang et al. [4] evaluated ten extraction techniques for butyltin species and reported that only four techniques were satisfactory for the extraction of dibutyl- and tributyltin species and that none of the techniques worked for the monobutyltin species. The extraction techniques evaluated included direct extraction with an organic solvent with or without a chelating agent (e.g., tropolone–hexane, tropolone–methylene chloride), acid leaching, alkali leaching or a combination of these techniques. Cai et al. [5–7] reported on a gas chromatographic–atomic absorption spectroscopy (GC–AAS) technique to analyze parts-per-billion levels of butyltin compounds after extraction from sediment with a solution of hydrochloric acid in methanol and derivatization with sodium tetrahydroborate [5] or sodium tetraethylborate [6,7]. Alkylation is preferred over hydride formation since the alkyl derivatives are more thermally stable than the hydride derivatives and the alkylation can be performed directly in aqueous solution [5]. Capillary GC coupled with flame photometric detection [8,9], microwave-induced helium plasma atomic emission detection or AED [10–18] or high-performance liquid chromatography coupled with mass spectrometry [19,20] have been successfully used for speciation of organotin compounds in environmental samples.

We have developed an off-line complexation–supercritical fluid extraction (SFE)–GC–AED method for the determination of organotin compounds in soil and sediment samples [10–12]. In this method, a soil or sediment sample is amended with diethylammonium diethyldithiocarbamate (DEA-DDC), which forms neutral complexes with ionic organotin species. The amended sample is then extracted with supercritical carbon dioxide, modified with 5% methanol, at 450 atm and 60°C for 20 min in the static mode, followed by 30 min in the dynamic mode. Organotin compounds in the SFE extract are then derivatized with *n*-pentylmagnesium bromide (C₅H₁₁MgBr) and determined by GC–AED. A single-laboratory evaluation of the off-line complexation–SFE and GC–AED method can be found elsewhere [12]. In addition, we conducted an inter-

laboratory study of the GC–AED technique and found that the intralaboratory precisions ranged from 1.3 to 22% relative standard deviation (R.S.D.), depending on the compound and the interlaboratory method precisions ranged from 11 to 40% R.S.D. [13].

The goals of the present collaborative study were to validate the off-line complexation SFE–GC–AED method for organotin compounds in soil or sediment samples and to generate interlaboratory and intralaboratory precision and accuracy data of this method using currently available SFE instrumentation. To minimize errors associated with extract derivatization and analysis, all sample extracts were derivatized and analyzed in our laboratory.

2. Experimental

2.1. Study design

The study design was based on the AOAC blind-replicate design with balanced replicates for the collaborative evaluation of precision and accuracy of an analytical method [21]. The number of replicates was three, and the number of matrixes extracted by SFE was four (a description of the four matrixes is given below). The organotin compounds investigated in this study are identified in Table 1.

Each laboratory received three 5-g portions from matrixes 1 and 2 and three 1-g portions from matrixes 3 and 4. Matrixes 1, 2 and 4 were spiked with the target organotin compounds at 1000 ng/g (as Sn) per compound and matrix 3 was an unspiked marine sediment that contained dibutyltin and tributyltin compounds.

Test samples were sent to ten laboratories; however, only eight laboratories completed the round-robin study. Laboratories were to perform the extractions according to the instructions they received and to submit the extracts to Midwest Research Institute (MRI) for derivatization and analysis by GC–AED. To reduce any possible sources of contamination, we sent each laboratory the complexing agent to be used in the extractions, glass wool, aluminum dishes and empty vials for shipping the extracts back to MRI. In addition, we made arrangements with Scott Specialty Gases to provide each

Table 1
Organotin compounds used in this study

Compound no.	Compound name	Compound structure ^a	Concentration of individual stock solutions ($\mu\text{g/ml}$), as Sn	Solvent
1	Methyltin trichloride	CH_3SnCl_3	10 000	Methanol
2	Butyltin trichloride	$\text{C}_4\text{H}_9\text{SnCl}_3$	10 000	Methanol
3	Dimethyltin dichloride	$(\text{CH}_3)_2\text{SnCl}_2$	10 000	Methanol
4	Diethyltin dichloride	$(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	10 000	Methanol
5	Dibutyltin dichloride	$(\text{C}_4\text{H}_9)_2\text{SnCl}_2$	10 000	Methanol
6	Diphenyltin dichloride	$(\text{C}_6\text{H}_5)_2\text{SnCl}_2$	10 000	Methanol
7	Trimethyltin chloride	$(\text{CH}_3)_3\text{SnCl}$	10 000	Methanol
8	Triethyltin bromide	$(\text{C}_2\text{H}_5)_3\text{SnBr}$	10 000	Methanol
9	Tributyltin chloride	$(\text{C}_4\text{H}_9)_3\text{SnCl}$	10 000	Methanol
10	Triphenyltin chloride	$(\text{C}_6\text{H}_5)_3\text{SnCl}$	4000	Methanol
11	Tetraethyltin ^b	$(\text{C}_2\text{H}_5)_4\text{Sn}$	10 000	<i>n</i> -Hexane
12	Tetrabutyltin	$(\text{C}_4\text{H}_9)_4\text{Sn}$	10 000	<i>n</i> -Hexane
13	Tetracyclohexyltin	$(\text{C}_6\text{H}_{11})_4\text{Sn}$	2000	<i>n</i> -Octane
14	Tetraphenyltin	$(\text{C}_6\text{H}_5)_4\text{Sn}$	1000	Benzene
I.S.	Trimethylphenyltin	$(\text{CH}_3)_3\text{C}_6\text{H}_5\text{Sn}$	10 000	<i>n</i> -Octane

^a The butyl group in the butyltin compounds is *n*-butyl.

^b This compound was not spiked into the soil samples because it could not be efficiently trapped in the collection solvent or by the trap column due to its high volatility ([12]), but it was included in the calibration standards

Table 2
Operating conditions used by Labs. 1, 9 and 10 (Dionex SFE systems)

	Lab. 1	Lab. 9	Lab. 10
SFE System Model No.	SFE-703M	SFE-703M	SFE-723
Pressure (atm)	450	340 and 400 ^a	450
Temperature ($^{\circ}\text{C}$)	60	60	60
Flow-rate (ml/min) ^b	400–1500	300–1600	900–1100
Direction of fluid flow	Horizontal	Horizontal	Horizontal
Static extraction time (min)	^c		
Dynamic extraction time (min)	30	40	30
Extraction vessel volume (ml)	10	7	^d
Extraction vessel dimensions	6 cm \times 14 mm I.D.	9 cm \times 10 mm I.D.	^d
Extraction vessel orientation	Horizontal	Horizontal	Horizontal
Restrictor type	Dionex restrictor		
(500 ml/min)	Dionex restrictor		
(500 ml/min or 1000 ml/min)	Dionex restrictor		
(500 ml/min)			
Restrictor temperature ($^{\circ}\text{C}$)	100	100	125
Collection solvent/volume (ml)	Methylene chloride (13 ml)	Methylene chloride (12–17 ml)	Methylene chloride (15 ml)
Temperature of collection vial ($^{\circ}\text{C}$)	–3	^d	^d

^a Lab. 9 used 340 atm for topsoil and clay soil samples and 400 atm for PACS-1 marine sediment samples

^b Measured as gaseous carbon dioxide.

^c No static step.

^d Not specified.

laboratory with SFE-grade carbon dioxide modified with 5% methanol.

2.2. Materials

Analytical reference standards of the compounds listed in Table 1 were obtained from Aldrich (Milwaukee, WI, USA) and Johnson Matthey (Ward Hill, MA, USA). Individual stock solutions were prepared in the solvents and at the concentrations listed in Table 1. Trimethylphenyltin was used as internal standard. The Grignard reagent pentylmagnesium bromide (PMB) at 2.0 mol/l in diethyl ether and diethylammonium diethyldithiocarbamate (DEA-DDC) were obtained from Aldrich. Standard solutions of each target organotin compound (Table 1) were prepared by accurately weighing appropriate amounts of the pure target organotin compounds (resulting in 0.100 g per compound, as Sn), dissolving the ionic organotin compounds in HPLC-grade methanol and the neutral organotin compounds in hexane, *n*-octane or benzene and diluting to volume in separate 10-ml volumetric flasks. Three compounds including triphenyltin chloride, tetracyclohexyltin and tetraphenyltin were not soluble at 10 000 µg/ml (as Sn) but they were soluble at 4000, 2000 and 1000 µg/ml, respectively (see Table 1). A

composite standard solution at 200 µg/ml per compound (as Sn) in methylene chloride was prepared from the individual stock solutions. Several working calibration solutions were prepared by serial dilution of the composite stock solution and were treated with PMB as described below. All other reagents and solvents used in this study were of analytical grade.

The topsoil (pH 7.5; cation exchange capacity 14.6 mequiv/100 g; organic carbon content 0.1%; water content 2.6%; sand, 57.6%; silt, 21.8%; and clay, 20.6%) and clay soil (pH 7.4; cation exchange capacity 21.3 mequiv/100 g; organic carbon content 1.8%; water content 10.6%; sand, 33.6%; silt, 35.4% and clay 31%) were obtained from Sandoz Crop Protection (Gilroy, CA, USA). The marine sediment reference material PACS-1 (cation exchange capacity, organic carbon and sand/silt/clay contents unknown; water content 0%) was obtained from the National Research Council of Canada (Ottawa, ON, Canada).

Carbon dioxide (SFC grade) modified with 5% methanol was obtained from Scott Specialty Gases (Plumsteadville, PA, USA).

2.3. Apparatus

To perform this method a supercritical fluid

Table 3
Operating conditions used by Labs 2, 5, and 7 (ISCO SFE systems)

	Lab. 2	Lab. 5	Lab. 7
Pressure (atm)	450	450	450
Temperature (°C)	60	60	60
Density (g/ml) ^a	0.92	0.92	0.92
Flow-rate (ml/min)	1.0	2.0	1.0–2.5
Direction of fluid flow	Downward	Downward	Downward
Static extraction time (min)	20	20	20
Dynamic extraction time (min)	30	30	30
Extraction vessel volume (ml)	10	10	10
Extraction vessel dimensions	5.5 cm×15 mm I.D. (disposable high-temperature polymer)	5.5 cm×15 mm I.D. (stainless steel)	5.5 cm×15 mm I.D. (stainless steel)
Extraction vessel orientation	Vertical	Vertical	Vertical
Restrictor type	Coaxial heated stainless steel capillary	Stainless steel capillary (50 cm×50 µm I.D.)	Stainless steel capillary (45 cm×50 µm I.D.)
Restrictor temperature (°C)	60–80	35	Room temperature
Collection solvent	Methylene chloride	Methylene chloride	Methylene chloride
Volume of collection (ml)	15	15	15
Temperature of collection vial (°C)	Room temperature	Room temperature	Room temperature

^a Calculated using the Isco SF Solver software package.

extraction system capable of performing extractions at 450 atm and 60°C, equipped with fixed or variable restrictor and an extract collection system (solvent or C₁₈-bonded silica trap) is required. All extractions were performed with supercritical carbon dioxide modified with 5% methanol. The critical temperature and pressure of the modified carbon dioxide, calculated with the Isco SF Solver software, are 41.3°C and 73.8 atm, respectively. The operating conditions for each SFE system used in this study are identified in Tables 2–4. Laboratories 4 and 6 operated at 45°C and 355 atm to achieve the same fluid density as the laboratories that operated at 60°C and 450 atm. Laboratory 9 extracted the spiked topsoil and clay soil samples at 340 atm and 60°C but used 400 atm and 60°C for the PACS-1 sediment samples.

A gas chromatograph equipped with a microwave-induced helium plasma atomic emission detector Model HP 5921A AED (Hewlett–Packard, Wilmington, DE, USA) was used for analysis of all extracts from the participating laboratories. The GC–AED system was equipped with an automatic sample injector and electronic pressure controller and linked to a computerized data-acquisition and processing system (HP 330 computer with the HP 35920B

GC–AED software). A deactivated retention gap (1.5 m×0.53 mm I.D., uncoated) was used as the interface between the cool on-column injection inlet and the 25 m×0.32 mm I.D.×0.52 μm film thickness capillary column coated with phenyl–methyl (5:95) silicone. The GC oven temperature was programmed from 55 (hold 5 min) to 260°C (hold 15 min) at a rate of 15°C/min (Table 5). Other details of the GC–AED analysis can be found in [12].

2.4. Sample preparation

The topsoil and clay soil samples were passed through a 1-mm mesh-size sieve; the reference marine sediment was used as received. Portions (1–5 g) of topsoil, clay soil and the marine sediment were accurately weighed into 15-ml glass vials and were spiked with a composite stock solution (50–250 μl) containing the organotin compounds at 20 μg/ml (as Sn) per compound. After the solvent had evaporated completely (~10 min), the contents of the vial were thoroughly mixed with a spatula. The laboratories received individual spiked portions of the four matrixes for extraction and were asked to keep all samples refrigerated until immediately prior to ex-

Table 4
Operating conditions used by Labs 4 and 6 (HP systems)

	Lab. 4	Lab. 6
Pressure (atm)	355 ^a	355 ^a
Temperature (°C)	45	45
Density (g/ml)	0.92	0.92
Flow-rate (ml/min)	2.0	2.0
Direction of fluid flow	Upward	Upward
Static extraction time (min)	20	20
Dynamic extraction time (min)	30	30
Extraction vessel volume (ml)	7	7
Volumes swept	8.6	8.6
Extraction vessel dimensions	9 cm×10 mm I.D. (stainless steel)	9 cm×10 mm I.D. (stainless steel)
Extraction vessel orientation	Vertical	Vertical
Restrictor type	Variable nozzle	Variable nozzle
Nozzle temperature (°C)	80 (during extraction), 30 (during rinse)	80 (during extraction), 30 (during rinse)
Trap packing material	Octadecyl-bonded silica	Octadecyl-bonded silica
Rinse solvent (ml)	1.8 ml (methylene chloride), three rinses	1.7 ml (methylene chloride), three rinses
Trap temperature (°C)	70 (during extraction) 30 (during rinse)	70 (during extraction) 30 (during rinse)

^a The operating conditions were adjusted to achieve a fluid density of 0.92 g/ml.

Table 5
GC–AED operating conditions used in this study

Instrument	Hewlett Packard HP 5890 Series II gas chromatograph interfaced to an HP 5921A atomic emission detector, equipped with an electronic pressure controller and a 7673A automatic sample injector
Data system	HP Chemstation
<i>GC column and carrier gas conditions</i>	
Stationary phase	HP-5
Column length (m)	25
Column inner diameter (mm)	0.32
Column film thickness (μm)	0.52
Helium flow (ml/min)	4 (using electronic pressure controller)
Helium linear velocity (cm/s)	59
<i>GC injector conditions</i>	
Type	Cool on-column injection
Temperature ($^{\circ}\text{C}$)	Oven track on ($+3^{\circ}\text{C}$)
Volume injected (μl)	1.0
<i>GC temperature program</i>	55 $^{\circ}\text{C}$ (hold 5 min) to 260 $^{\circ}\text{C}$ (hold 5 min) at 15 $^{\circ}\text{C}/\text{min}$
<i>Detector operating conditions</i>	
Transfer line	HP-5 column
Transfer line temperature ($^{\circ}\text{C}$)	280
Cavity temperature ($^{\circ}\text{C}$)	280
Solvent vent begin (min)	0.0
Solvent vent end (min)	7.9
Spectrometer window purge (l/min)	2 (nitrogen)
Helium make-up gas flow (ml/min)	220
Make-up and reagent gas pressures	65 p.s.i. helium, 65 p.s.i. hydrogen and 30 p.s.i. oxygen
Determinative wavelengths	Sn: 270.651 nm, C: 248.857 nm

traction. Each laboratory extracted samples as instructed; they first weighed out 1–5-g portions of the sample matrixes in the aluminum dishes supplied by MRI and then amended each sample with 1 ml of 0.3 M DEA-DDC solution in methylene chloride (this solution was also supplied by MRI). The solvent was allowed to evaporate for about 10 min and then the amended sample was transferred to the extraction vessel for extraction with carbon dioxide modified with 5% methanol at 450 atm and 60 $^{\circ}\text{C}$ for 20 min static and 30 min dynamic.

All extractions were completed within 30 days of the date when the samples were spiked in our laboratory. Another set of samples was kept in our laboratory in a refrigerator at 4 $^{\circ}\text{C}$ and was analyzed at defined time intervals (0, 3, 8 and 24 days) to establish whether any compound degradation had occurred during storage of the spiked materials at

4 $^{\circ}\text{C}$. Details on extract derivatization can be found elsewhere [12].

2.5. Outlier testing

The outlier testing was done using both Cochran test and Grubbs test [21]. Cochran test was used first to remove any laboratory with results showing significantly greater variability among replicate analyses (within-laboratory variability) than the other laboratories for a given test sample. Grubbs tests were performed to remove laboratories with extreme averages when compared with those of the other laboratories for a given test sample. All tests were performed at the 1% significance level. When a laboratory was rejected on the basis of these tests, its results were removed from the set of data for the

particular compound and the test was then repeated one more time using the remaining data in the subset.

2.6. Statistical analysis

The statistical analysis was performed using the AOAC Lotus spreadsheet developed for the analysis of data from interlaboratory studies [22]. The spreadsheet program calculates method performance parameters according to the Harmonization Guidelines in [21]. Summary statistics (s_r , s_R , R.S.D._r, R.S.D._R) were calculated for the average concentrations and the overall method precisions for each of the three test samples. The single-analyst standard deviation (s_r , repeatability) is the precision associated with the performance of an individual laboratory and the overall standard deviation (s_R , reproducibility) is the precision associated with measurements generated by a group of laboratories. The repeatability R.S.D._r, which was determined from the repeatability standard deviation (s_r) and the average concentration for a particular test sample, is an indication of the intralaboratory precision. The reproducibility R.S.D._R, which was determined from the reproducibility standard deviation (s_R) and the average concentration for a particular test sample, is an indication of the interlaboratory method precision. The interlaboratory method accuracy was calculated as the average recovery from the interlaboratory average concentration and the concentrations listed in Table 2 for each organotin compound in the three test samples.

2.7. Quality assurance

The extractions of the study samples were performed according to the instructions provided by MRI to all collaborators. To minimize errors due to reagent contamination, we provided each laboratory with the extractant (carbon dioxide modified with 5% methanol), the complexing agent (10 ml of 0.3 M DEA-DDC), glass wool, aluminum dishes and 15-ml glass vials. Each laboratory was also instructed to report the SFE operating conditions on special forms (provided by us) and to record the exact weight of the study sample extracted by SFE.

The GC–AED analyses of the derivatized extracts were performed by MRI. MRI also derivatized all extracts submitted by the participating laboratories. To ensure the quality of the data generated, the following control procedures were implemented: (1) a five-level calibration (31, 63, 125, 250 and 500 $\mu\text{g/l}$) was performed with every batch of extracts submitted for analysis. The multilevel calibration was verified every ten analyses by analyzing a standard at 125 $\mu\text{g/l}$; (2) trimethylphenyltin was used as internal standard to monitor GC–AED performance and (3) method blanks and blank soil sample extracts (topsoil and clay soil) were analyzed to monitor that no organotin compounds were detected in the unspiked soils and method blanks.

3. Results and discussion

Tables 6–8 present the average recoveries for the four matrixes by compound. As the data indicate, the tetra-substituted organotin compounds were the easiest to extract by SFE and their recoveries (with the exception of tetracyclohexyltin in two of the spiked matrixes) were above 75%. The average recoveries of the tri-substituted organotin compounds ranged from 22.6 to 85.6% with most of the values above 60% and their recoveries did not appear to be a function of matrix. The disubstituted organotin compounds were not only the most difficult to extract but they degraded quite quickly following spiking. The fastest degradation rate was exhibited by diphenyltin (recovery after 30 min following spiking was 10.8%). Dibutyltin exhibited a 79.1% recovery in the topsoil samples stored for 30 min and the recovery dropped to 47.3% after 8 days of storage at 4°C. Data for the mono-substituted organotin compounds are not included since these compounds could not be recovered by SFE. The extraction of the monobutyltin from sediment has been difficult; however, Chau et al. have reported recoveries in excess of 60% by using carbon dioxide modified with 10% methanol and extracting at 500 atm and 70°C [Y.K. Chau, personal communication (1995)].

Method precision (Tables 6–8) is reported for each compound as the relative standard deviation (R.S.D.) for each laboratory (R.S.D._r) and also as the

Table 6
Interlaboratory method accuracy and precision for the spiked topsoil samples^a

Compound no.	Compound name	Before outlier removal				After outlier removal				Laboratory removed		
		Average concentration (ng/g)	s_r (ng/g)	s_R (ng/g)	R.S.D. _r (%)	Average concentration (ng/g)	Average recovery (%)	s_r (ng/g)	s_R (ng/g)		R.S.D. _r (%)	R.S.D. _R (%)
3	Dimethyltin	54.8	62.4	62.4	114	54.8	5.5	62.5	62.4	114	114	—
4	Diethyltin	78.0	38.0	52.8	48.8	78.0	7.8	38.0	52.8	48.8	68.0	—
5	Dibutyltin	341	84.8	150	24.8	341	34.1	84.8	150	24.8	43.9	—
6	Diphenyltin	^b	—	—	—	—	—	—	—	—	—	—
7	Trimethyltin	664	82.4	336	12.4	664	66.4	82.4	336	12.4	50.6	—
8	Triethyltin	260	51.2	141	19.7	226	22.6	33.2	103	14.8	45.6	No. 7
9	Tributyltin	632	133	177	21.1	632	63.2	133	177	21.1	28.0	—
10	Triphenyltin	448	105	165	23.6	448	44.8	105	165	23.6	37.0	—
12	Tetabutyltin	868	165	232	19.0	880	88.0	102	218	11.6	24.7	No. 4
13	Tetracyclohexyltin	804	138	172	17.1	804	80.4	138	172	17.1	21.4	—
14	Tetraphenyltin	880	132	172	15.0	880	88.0	132	172	15.0	19.5	—

^a Average concentrations are in ng/g (as Sn); s_r and s_R are the standard deviations for repeatability and reproducibility, respectively, and R.S.D._r and R.S.D._R are the corresponding relative standard deviations for repeatability and reproducibility, respectively. The number of replicates was three for each lab. Compounds 1 and 2 could not be recovered by SFE and therefore are not listed.

^b None of the laboratories recovered this compound which degrades within 30 min when spiked into unsterilized soil.

Table 7

Interlaboratory method accuracy and precision for the spiked clay soil samples^a

Compound no.	Compound name	Before outlier removal				After outlier removal				Laboratory removed		
		Average concentration (ng/g)	s_r (ng/g)	s_R (ng/g)	R.S.D. _r (%)	Average concentration (ng/g)	Average recovery (%)	s_r (ng/g)	s_R (ng/g)		R.S.D. _r (%)	R.S.D. _R (%)
3	Dimethyltin	^b	—	—	—	—	—	—	—	—	—	—
4	Diethyltin	78.0	29.2	78.4	37.4	78.0	7.8	29.2	78.4	37.4	100	—
5	Dibutyltin	325	72.8	162	22.4	325	32.5	72.8	162	22.4	50.0	—
6	Diphenyltin	^c	—	—	—	—	—	—	—	—	—	—
7	Trimethyltin	596	65.2	304	11.0	596	59.6	65.2	304	11.0	51.1	—
8	Triethyltin	552	53.6	282	9.7	552	55.2	53.6	282	9.7	51.0	—
9	Tributyltin	856	77.2	172	9.0	856	85.6	77.2	172	9.0	20.1	—
10	Triphenyltin	428	106	274	24.7	428	42.8	106	274	24.7	64.1	—
12	Tetabutyltin	896	62.8	235	7.0	896	89.6	62.8	235	7.0	26.3	—
13	Tetracyclohexyltin	226	278	278	12.3	226	22.6	278	278	12.3	123	—
14	Tetraphenyltin	796	111	246	14.0	796	79.6	111	246	14.0	31.0	—

^a Average concentrations are in ng/g (as Sn); s_r and s_R are the standard deviations for repeatability and reproducibility, respectively, and R.S.D._r and R.S.D._R are the corresponding relative standard deviations for repeatability and reproducibility, respectively. The number of replicates was three for each laboratory. Compounds 1 and 2 could not be recovered by SFE and therefore are not listed.

^b None of the participating laboratories recovered dimethyltin.

^c Only two laboratories (4 and 10) recovered diphenyltin and the average recoveries were 16.1% for Lab. 4 and 20.7% for Lab. 10.

Table 8
Interlaboratory method accuracy and precision for the PACS-1 marine sediment^a (unspiked and spiked samples)^b

Compound no.	Compound name	Before outlier removal				After outlier removal				Laboratory removed		
		Average conc. (ng/g)	s_r (ng/g)	s_R (ng/g)	R.S.D. _r (%)	R.S.D. _R (%)	Average concentration (ng/g)	Average recovery (%)	s_r (ng/g)		s_R (ng/g)	R.S.D. _r (%)
3	Dimethyltin											
4	Diethyltin											
5	Dibutyltin	536	108	302	20.4	56.6	536	24.8	108	302	20.4	56.6
6	Diphenyltin											
7	Trimethyltin	618	90	276	14.7	44.5	618	61.8	90	276	14.7	44.5
8	Triethyltin	658	96	314	14.5	47.8	658	65.8	96	314	14.5	47.8
9	Tributyltin	1650	156	508	9.4	30.7	1650	72.8	156	508	9.4	30.7
10	Triphenyltin	606	104	222	17.1	36.6	606	60.6	104	222	17.1	36.6
12	Tetraethyltin	1020	102	334	10.0	32.9	1020	102	102	334	10.0	32.9
13	Tetracyclohexyltin	646	86	200	13.3	30.9	646	64.6	86	200	13.3	30.9
14	Tetraphenyltin	746	166	270	22.4	36.2	746	74.6	166	270	22.4	36.2
Unspiked PACS-1 marine sediment ^c												
5	Dibutyltin	484	50	702	10.3	145	244	21.0	42	152	17.0	61.6
9	Tributyltin	936	194	538	20.8	68.2	936	73.7	194	638	20.8	68.2

^a Average concentrations are in ng/g (as Sn); s_r and s_R are the standard deviations for repeatability and reproducibility, respectively and R.S.D._r and R.S.D._R are the corresponding relative standard deviations for repeatability and reproducibility. The number of replicates was three for each lab. Compounds 1 and 2 could not be recovered by SFE and therefore are not listed.

^b Dimethyltin was recovered only by Lab. 1; diethyltin by Labs. 1, 2 and 6 but the average recoveries were below 10%. Diphenyltin was not recovered by any laboratory.

^c Certified values for PACS-1 marine sediment are 1160±180 ng/g for dibutyltin and 1270±220 ng/g for tributyltin.

interlaboratory R.S.D. ($R.S.D._R$). In general, as expected the $R.S.D._r$ values were lower than the $R.S.D._R$ values and the lower the concentration of the organotin compound was in the matrix, the higher was the R.S.D. Most of the $R.S.D._r$ values were below 25% (with the exception of dimethyltin, diethyltin and tetracyclohexyltin). Most of the $R.S.D._R$ values were in the 20–68% range (except diethyltin at 100% and tetracyclohexyltin at 123%).

The results of this interlaboratory study indicate that the SFE method works satisfactorily for the tri- and tetra-substituted organotin compounds but that the di- and mono-substituted organotin compounds are quite difficult to extract under these conditions. Since three of the participating laboratories did not use the static extraction step (i.e., the Dionex SFE system could not perform a static extraction because the system does not have any isolation valves), it appears that the static step of 20 min is not necessary. Higher pressures and different modifiers may be required to enable extraction of the mono- and di-substituted organotin compounds from soils and sediments.

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