

# Determination of Organotin Compounds in Sediments Using Accelerated Solvent Extraction (ASE<sup>®</sup>)

## **INTRODUCTION**

Organotin compounds (OTs) are a highly versatile group of organometallic chemicals used in industrial and agricultural applications. Tributyltin (TBT) is the most widely used of these compounds and has been under scrutiny due to its significant environmental effects. Organotin compounds with alkyl or phenyl substituents exhibit considerable toxicity toward both aquatic organisms and mammals<sup>1</sup>.

Aquatic contamination from these compounds is attributed mainly to leaching of anti-fouling marine paints; however, the growing use of organotins as agricultural pesticides can potentially contaminate the aquatic environment by leaching and runoff<sup>2</sup>. Annual worldwide production of organotin compounds was estimated to be 33,000 tons in 1983. Recent regulatory legislation in the European Community has increased the need for analytical methods for the determination of the tri-substituted organotin compounds and their two degradation products (mono- and dibutylphenyltin) in the aquatic environment. Analysis of sediments is of particular importance because they are the ultimate depository of these compounds. These accumulated materials then can be released into the environment, creating an environmental hazard long after initial deposition has ceased.

Trace-level determinations of organotin compounds in environmental samples are complicated by the fact that compounds with 1-3 substituents are non-volatile due to their polar and ionic character. Traditional methods for extracting and analyzing these compounds are not only time consuming but have been shown to have poor analyte recovery and poor reliability<sup>3</sup>.

Accelerated Solvent Extraction uses a combination of increased pressure and temperature to increase the efficiency of the extraction process. ASE is currently used in the environmental industry to replace traditional extraction methods such as sonication and Soxhlet. Using ASE, extracts can be generated in much less time and using significantly less solvent than these traditional methods. ASE also has been shown to provide better or equivalent recoveries compared to these techniques for compound classes covering a wide range of polarities and exhibiting both high and low levels of bonding to the matrix.

## **EQUIPMENT**

Dionex ASE 200 Accelerated Solvent Extractor equipped with 11-mL cells  
Dionex vials for collection of extracts (40 mL, P/N 49465)  
HP 5890 Gas Chromatograph and 5971A mass spectrometer (Hewlett-Packard)

## **REAGENTS AND STANDARDS**

Methanol (pesticide residue grade, Burdick & Jackson)  
Water (HPLC grade, Burdick & Jackson)  
Sodium tetraethylborate ( $\text{NaBEt}_4$ , >98%, Strem Chemicals)  
Sodium acetate (>99%, Merck)  
Acetic acid (>99.8%, Merck)  
Organotin standards (Fluka)  
PACS-1 Reference Sediment (National Research Council of Canada)  
RM 424 Reference Material (European Commission, Community Bureau of Reference)

## **SAMPLE PREPARATION**

Samples (2.5 g) of freeze-dried sediment were weighed into 25-mL beakers. The samples were spiked with 500  $\mu\text{L}$  of the OT standard solution, resulting in a concentration of 100 ng/g. The spiked sediments were then thoroughly mixed with 9 g of sand, transferred to 11-mL extraction cells, and set aside for 2 h prior to extraction.

## **EXTRACTION CONDITIONS**

Extraction Solvent: 1 M sodium acetate, 1 M acetic acid in methanol (1:1)  
Temperature: 100 °C  
Pressure: 1500 psi (10 MPa)  
Heat-up Time: 5 min  
Static Time: 5 min  
Flush Volume: 60%  
Purge Time: 100 s  
Static Cycles: 3–5  
Total Extraction Time: 25–35 min per sample  
Total Solvent Use: 16–20 mL per sample

## **POST-EXTRACTION PROCEDURE**

Extracts were transferred to 250-mL volumetric flasks containing 7.3 g of NaCl, diluted with HPLC-grade water, and then pH-adjusted to  $5.0 \pm 0.1$  with 1 M NaOH. One milliliter of a 5% w/v sodium tetrabutylborate aqueous solution (derivatizing agent) was added to each flask and the volume was adjusted to 250 mL with water. Finally, 2 mL of hexane was added and the samples were shaken for 12 h. A 500- $\mu\text{L}$  aliquot of the hexane layer was transferred to a 2-mL GC vial and spiked with 10  $\mu\text{L}$  of surrogate standard (tetrabutyltin, 50 ng/10  $\mu\text{L}$ ). Prior to analysis, sewage sludge hexane extracts were transferred to 10-mL centrifuge tubes containing 0.9 g of deactivated silica gel and 2 mL water. The tubes were shaken vigorously and centrifuged. Minor losses were associated with this clean-up procedure; recoveries averaged 99%. (Losses were evaluated by putting standard solutions through the clean-up procedure.)

## **EXTRACT ANALYSIS**

Sediment extracts were analyzed with a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5971A mass spectrometer. Extracts (1  $\mu\text{L}$ ) were injected on-column except for sewage sludge extracts, which were injected in the splitless mode (injector temperature 200 °C). The GC was equipped with a 2-m x 0.53-mm deactivated fused silica precolumn and a 30-m x 0.32-mm DB-5 capillary column (film thickness 0.25  $\mu\text{m}$ ). The helium flow velocity was regulated at 50 cm/s. Temperature programming was performed as follows: 1 min at 60 °C, to 250 °C at 10 °C/min, and 4 min at 250 °C. The GC-MSD interface temperature was set to 300 °C. Detection was performed in the electron impact ionization mode and single-ion monitoring (SIM). Correct identification and quantification of a given analyte was assured by using two compound-specific ions and a mass ratio similar to the one determined with calibration (variation <10%).

## **RESULTS AND DISCUSSION**

Initial recovery studies were performed using spiked sediments to optimize method conditions and because no reference material is available containing known amounts of the phenyltin compounds, which bond tightly to the matrix and can be the most difficult to extract. Extractions were performed with varied concentrations of acetic acid and sodium acetate in methanol and varied extraction temperatures. Additives were used to enhance the extraction of the OTs, particularly the polar mono- and diorganotin compounds. Optimal conditions were determined to be 100 °C with a solvent mixture of 1 M sodium acetate and 1 M acetic acid in methanol (1:1). The number of extraction cycles was varied from 3 to 5 to ensure quantitative extraction from difficult matrices. Table 1 shows absolute and relative extraction recoveries, relative standard deviations (RSDs), and method detection limits (MDLs) of organotins from spiked lake sediment. At the high spike level (1000 ng/g), absolute recoveries for all butyltin and phenyltin compounds varied between 80 and 100%; at the high and low (10 ng/g) levels, relative recoveries for these compounds ranged from 87–105%. Satisfactory recoveries of 72 and 54% were obtained for TCyT. Even at the low concentration level, excellent precision ( $\leq 7\%$ ) was achieved for all compounds.

**Table 1 Absolute and Relative Recoveries, RSDs, and MDLs Determined from Lake Sediments**

Compound <sup>a</sup>	1000 ng/g spike (n=3)				10 ng/g spike (n=5)			
	Absolute Recovery <sup>b</sup>		Relative Recovery <sup>c</sup>		Relative Recovery <sup>c</sup>		MDL <sup>d</sup> (ng/g)	
	%	RSD	%	RSD	%	RSD		
MBT	97	4	100	1	105	3	0.9	
DBT	100	2	102	3	101	2	0.5	
TBT	98	6	102	2	100	4	1.1	
MPT	80	7	87	3	104	7	2.0	
DPT	95	6	97	2	98	1	0.4	
TPT	94	(5)	100	(2)	101	(2)	0.5	
TCyT	73	(4)	72	(2)	51	(4)	1.0	

<sup>a</sup> Compound abbreviations: monobutyltin (MBT), tributyltin (TBT), dibutyltin (DBT), monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT), tricyclohexyltin (TCyT)

<sup>b</sup> Absolute recoveries determined by addition of internal standard to sediment extracts

<sup>c</sup> Relative extraction recoveries determined by addition of internal standard to sediments prior to extraction

<sup>d</sup> MDL = three times the standard deviation of the low spike concentration

The levels of OT compounds were then determined in standard reference materials PACS-1 and RM 424 sediments. Data shown in Table 2 indicate that DBT and TBT concentrations were in excellent agreement with the certified values for the PACS-1 sediment, whereas the concentration of MBT exceeded the certified value by a factor of 2.4. This is in agreement with other published evaluations of this material.<sup>4</sup> Because no degradation of DBT or TBT was observed, it is assumed that quantitative recovery of MBT was not achieved with the analytical methods used in the validation process of the PACS-1 material. Concentrations of MPT, DPT, and TPT were also detected in the PACS-1 sediment, although the material is not certified for these compounds. The RM 424 sediment is a difficult matrix due to its high organic content and low OT concentrations. Recoveries shown in Table 3 are in excellent agreement with the certified values for the three OT compounds.

## CONCLUSION

The data presented here indicate that ASE provides excellent recovery and precision for the extraction of organotin compounds from spiked and natural sediment samples. Using ASE, extraction times can be reduced and the sample preparation process automated to make more efficient use of laboratory resources.

**Table 2 Recoveries and Certified Values of Organotin Compounds from PACS-1 Reference Sediment**

Compound	Recovery (ng/g, n=5)	Certified Value
MBT	672 ± 11	280 ± 170
DBT	990 ± 44	1160 ± 180
TBT	1133 ± 15	1270 ± 220
MPT	62 ± 5	na
DPT	8 ± 2	na
TPT	70 ± 8	na

**Table 3 Recoveries and Certified Values of Organotin Compounds from RM 424 Reference Sediment**

Compound	Recovery (ng/g, n=9)	Certified Value
MBT	165 ± 5	174 ± 36
DBT	22 ± 1	27 ± 10
TBT	6.5 ± 0.2	8 ± 2

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## LIST OF SUPPLIERS

Hewlett-Packard, 2850 Centerville Rd., Wilmington, DE 19808, USA, Tel: 800-227-9770

Merck, Frankfurter Str. 250, D-64293 Darmstadt, Germany, Tel: +49 61 51 72 0

Fluka Chemika-BioChemika, Industriestrasse 25, Buchs CH-9471, Switzerland, Tel: +081 755 25 11

Burdick & Jackson, 1953 South Harvey Street, Muskegon, MI 49442, USA, Tel: 1-800-368-0050

Strem Chemicals Inc., 7 Mulliken Way, Newburyport, MA 01950, USA, Tel: 1-508-462-3191



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**Dionex Corporation**  
1228 Titan Way  
P.O. Box 3603  
Sunnyvale, CA  
94088-3603  
(408) 737-0700

**Dionex Corporation**  
Salt Lake City Technical Center  
1515 West 2200 South, Suite A  
Salt Lake City, UT  
84119-1484  
(801) 972-9292

**Dionex U.S. Regional Offices**  
Sunnyvale, CA (408) 737-8522  
Westmont, IL (630) 789-3660  
Houston, TX (281) 847-5652  
Atlanta, GA (770) 432-8100  
Marlton, NJ (856) 596-0600

**Dionex International Subsidiaries**  
*Austria* (01) 616 51 25 *Belgium* (015) 203800 *Canada* (905) 844-9650 *China* (852) 2428 3282 *Denmark* (45) 36 36 90 90  
*France* 01 39 30 01 10 *Germany* (06126) 991-0 *Italy* (06) 66 51 50 52 *Japan* (06) 6885-1213 *The Netherlands* (0161) 43 43 03  
*Switzerland* (062) 205 99 66 *United Kingdom* (01276) 691722  
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