Organohalogen Compounds, Volume 60, Pages 37-40 (2003)

SIMULTANEOUS EXTRACTION OF PCDD/PCDF AND PCBS USING ACCELERATED SOLVENT EXTRACTION FOR SEDIMENT, TISSUE AND SLUDGE MATRICES

Mark Misita, Mary Schrock, Karen Tracy, Joe Tabor

Battelle Memorial Institute, 505 King Avenue, Columbus Ohio, 43201, USA

Introduction

PCDD/PCDF and PCBs conventionally have been extracted separately using Soxhlet extraction techniques.[1,2,3] Soxhlet extraction methods are very dependable, but are very time consuming and use large volumes of solvent. To meet increasing demands for the determination of PCDD/PCDF and PCB in environmental samples, accelerated solvent extraction (ASE) methods have been used for tissues, sediment and sludge samples;[4] however, still as separate extractions. The benefits in using ASE as opposed to Soxhlet extractions are decreased extraction time, decreased solvent consumption and decreased cost. The methods described in this paper build upon the improvements gained with ASE extraction by using ASE to simultaneously extract samples for both PCDD/PCDF and PCBs. This paper describes the results obtained using ASE methods to simultaneously extract PCDD/PCDF and PCBs from tissue, sediment and sludge samples.

Methods and Materials

Tissue Samples

Ten-gram aliquots of various homogenized marine tissue (e.g., fish, lobster meat, lobster hepatopancreas, clams and worms) were weighed into jars and spiked with a mixture of $^{13}C_{12}$-labeled PCDD/PCDF and PCB (Cambridge Isotope Laboratories (CIL) catalog numbers, EDF-8999 and EC-4977, repectively). Matrix spike samples were also spiked with a mixture of native PCDD/PCDF and PCB (CIL catalog numbers, EC-4989 and EDF-7999). After spiking, the samples were dried with 6 to 8 grams of hidromatrix (Varian 0019-8003). Once dry the samples were packed into individual 33-mL extraction cells containing a Dionex ASE 200 filter. Any remaining space in the extraction cell was filled with hidromatrix and the samples were capped. The samples were extracted using a Dionex ASE 200 at the conditions for tissues listed in Table 1.

Sediment and Sludge Samples

Ten-gram aliquots of various homogenized sediment and one- to ten-gram aliquots of homogenized sludge were weighed into jars and spiked with $^{13}C_{12}$-labeled PCDD/PCDF and PCB and native PCDD/PCDF and PCB, dried with hidromatrix, and packed into ASE cells in the same fashion as described for tissue samples above. The samples were extracted using a Dionex ASE 200 using the conditions for sediment/sludge listed in Table 1.

Extract Clean Up

After extraction the tissue, sediment, and sludge extracts were dried with sodium sulfate and partitioned against sulfuric acid. The sediment and sludge extracts were also partitioned against potassium hydroxide. Each extract was then split equally into two aliquots. One aliquot (PCDD/PCDF) was processed thru general EPA Method 1613B[2] clean up procedures and the other aliquot (PCB) was processed thru general EPA Method 1668A[3] clean up procedures. The PCDD/PCDF extract fractions were concentrated to a final volume of 20 µL and spiked with

PCDD/PCDF recovery standard (CIL EDF-5999). The PCB extract fractions were concentrated to a final volume of 50 uL and spiked with PCB recovery standard (CIL EC-4979.).

Table 1. ASE Conditions for Tissues, Sediments and Sludge

ASE Conditions	Tissue	Sediment/Sludge
Pressure (psi)	2000	2000
Temperature (ºC)	125	150
Static Time (min)	10	5
Flush Volume (%)	60	60
Purge Time (sec)	120	120
Number of Static Cycles	3	2
Solvent	1:1 DCM / Hexane	Toluene

Sample Analysis

PCDD/PCDF and PCB extracts were analyzed at a resolution of 10,000 using a VG AutoSpec high resolution mass spectrometer (Micromass) following general procedures of EPA Method 1613B for PCDD/PCDF and EPA Method 1668A for PCB. A J&W DB5 (60M x 0.32mm x 0.25µm) GC column was used for PCDD/PCDF analysis and a Supelco SPB-Octyl (30M x 0.25mm x 0.25µm) column was used for PCB analysis.

Results and Discussion

Table 2 presents the average internal standard percent recoveries and recovery ranges for 44 tissue, 36 sediment and 3 sludge samples prepared using the ASE extraction procedures described above. The average percent recovery for all analytes regardless of matrix type ranged from 44% to 98% indicating good extraction efficiency. Tissues had the greatest range of recoveries most likely because of the variety of tissue types with differing lipid contents which made up this matrix set. Lobster meat had the lowest recoveries of all tissue types. Table 3 presents matrix spike recoveries for 7 tissues and 4 sediments. The matrix spike recoveries are similar between tissues and sediments indicating good extraction efficiency and the ability to generate accurate results using this method. The internal standard recoveries and matrix spike recoveries using the sediment and tissue ASE method for simultaneous extraction of PCDD/PCDF and PCBs indicate that these procedures provide accurate results for these matrices.

References

1. SW-846 Method 8290: Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography / High-Resolution Mass Spectrometry, Revision 0 (1994)
2. U.S. EPA Method 1613, Revision B: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, (1994), EPA 821-B94-0059 Office of Water, Engineering and Analysis Division.
3. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, (1999), EPA-821-R-00-002 Office of Water.
4. SW-846 Method 3545, Pressurized Fluid Extraction (PFE), Revision 0, (1996)

Table 2. Internal Standard Recovery

Analyte	Tissue n = 44		Sediment n = 36		Sludge n = 3	
	Average	Range	Average	Range	Average	Range
^{13C}-PCB-81	60	31-94	70	42-98	51	47-55
^{13C}-PCB-77	61	35-92	73	41-110	52	49-54
^{13C}-PCB-123	56	25-88	51	27-74	51	44-62
^{13C}-PCB-118	58	26-88	50	27-72	52	44-64
^{13C}-PCB-114	58	27-90	47	25-66	53	44-67
^{13C}-PCB-105	61	30-93	53	34-75	54	48-62
^{13C}-PCB-126	62	33-98	56	35-87	58	53-67
^{13C}-PCB-167	61	29-97	69	34-87	58	48-70
^{13C}-PCB-156	62	31-100	67	46-84	57	47-72
^{13C}-PCB-157	62	31-100	67	46-84	57	47-72
^{13C}-PCB-169	64	22-108	75	49-102	66	54-80
^{13C}-PCB-189	78	29-142	70	33-104	63	53-79
^{13C}-2,3,7,8-TCDD	63	44-94	70	54-90	48	38-56
^{13C}-1,2,3,7,8-PeCDD	72	51-121	88	61-116	59	38-73
^{13C}-1,2,3,4,7,8-HxCDD	72	41-102	86	68-114	63	48-75
^{13C}-1,2,3,6,7,8-HxCDD	74	43-116	92	72-113	64	48-75
^{13C}-1,2,3,4,6,7,8-HpCDD	76	37-118	97	76-132	60	57-65
^{13C}-OCDD	71	30-112	95	68-128	55	47-63
^{13C}-2,3,7,8-TCDF	63	35-97	68	50-87	44	26-64
^{13C}-1,2,3,7,8-PeCDF	69	48-95	77	59-107	59	38-73
^{13C}-2,3,4,7,8-PeCDF	74	34-124	98	49-141	55	23-83
^{13C}-1,2,3,4,7,8-HxCDF	74	39-106	87	65-105	67	48-86
^{13C}-1,2,3,6,7,8-HxCDF	73	40-105	86	65-101	66	46-82
^{13C}-1,2,3,7,8,9-HxCDF	79	47-113	90	68-110	70	65-73
^{13C}-2,3,4,6,7,8-HxCDF	76	44-107	88	67-107	67	48-84
^{13C}-1,2,3,4,6,7,8-HpCDF	77	33-115	97	75-116	56	51-62
^{13C}-1,2,3,4,7,8,9-HpCDF	73	32-122	95	73-123	54	46-61

Table 3. Matrix Spike Recovery

Analyte	Tissue n = 7		Sediment n = 4	
	Average	Range	Average	Range
PCB-81	98	79-112	101	99-104
PCB-77	97	83-110	96	90-99
PCB-123	114	98-147	102	99-105
PCB-118	102	67-126	93	89-98
PCB-114	103	93-112	100	97-103
PCB-105	119	79-170	96	92-99
PCB-126	104	90-113	95	91-99
PCB-167	98	77-113	100	94-102
PCB-156	100	77-116	104	101-107
PCB-157	100	77-116	104	101-107
PCB-169	100	80-118	96	93-100
PCB-189	109	98-118	104	101-108
2378-TCDD	101	93-112	92	86-108
12378-PeCDD	99	96-104	103	100-108
123478-HxCDD	93	91-97	99	96-108
123678-HxCDD	104	99-106	107	105-110
123789-HxCDD	99	94-109	102	96-110
1234678-HpCDD	93	89-101	99	94-110
OCDD	94	88-106	105	103-110
2378-TCDF	100	93-111	100	96-110
12378-PeCDF	108	98-112	100	97-110
23478-PeCDF	103	101-110	96	90-110
123478-HxCDF	100	93-104	101	98-110
123678-HxCDF	101	97-106	99	96-110
123789-HxCDF	99	92-114	95	91-110
234678-HxCDF	104	98-110	102	99-110
1234678-HpCDF	98	93-105	100	98-110
1234789-HpCDF	99	94-109	103	100-110
OCDF	102	91-111	107	104-113