

Determination of PCDDs/PCDFs and PCBs in Sediments Using Microwave-Assisted Solvent Extraction

Chung Chiu, Gary Poole, Mylaine Tardif, Walter Miles and Richard Turle, Analysis and Air Quality Division, Environment Technology Centre, Environment Canada, 3439 River Road, Ottawa, Ontario, Canada K1A 0H3

Abstract

Solvent extraction of PCDDs/PCDFs and PCBs from two lake sediments (EC-2 and DX-1) and one marine sediment (SRM-1944) using microwave energy was investigated. Results of triplicate analyses were very comparable to Soxhlet extraction with respect to recovery and precision.

Introduction

Applications of a conventional microwave oven or a laboratory microwave oven to extract PAH, pesticides and PCBs from aqueous, soil and ambient air samples have been reported in recent years.⁽¹⁻⁶⁾ Benefits in using microwave energy to assist solvent extraction as opposed to conventional techniques (e.g., liquid-liquid, ultrasonic and Soxhlet extractions) are faster extraction, consumption of less energy and solvents, and cost effectiveness.

The Environmental Technology Centre (ETC) of Environment Canada has been investigating the application of microwave energy to enhance the solvent extraction of organic pollutants from a variety of environmental samples.⁽⁷⁻⁹⁾ As part of a series of studies, this paper describes the comparison results between microwave and Soxhlet extraction for the determination of PCDDs/PCDFs and PCBs in sediment reference materials.

Experimental Methods

Sample Materials

A total of three reference materials was used for the study. The Lake Ontario sediment EC-2 and the Great Lake sediment DX-1 were supplied by National Water Research Institute (NWRI) of Environment Canada. Sediment EC-2 was certified for total PCBs while sediment DX-1 was certified for PCDDs/PCDFs.⁽¹⁰⁾ The third reference material SRM-1944, provided by National Institute of Standards and Technology (NIST), is a marine sediment from New York harbour.

Sample Extraction

The microwave-assisted solvent extraction was conducted using the CEM model MES-1000 microwave equipped with temperature and pressure control systems and a carousel for 12 vessels.

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This microwave has an operator selectable output of up to 950 watts. Each pre-weighed sample (2.0 g) was quantitatively transferred into a 100-ml vessel and spiked with a mixture of $^{13}\text{C}_{12}$ -labelled PCB and PCDD/PCDF surrogates. After adding 20 ml of hexane/acetone mixture (1:1), vessels were placed evenly in the carousel and extracted for 20 minutes at 100 °C using 500 watts microwave energy. After extraction, vessels were cooled to room temperature in a running water bath. Each sample extract was then passed through a filtration apparatus consisting of anhydrous sodium sulphate on a filter paper inside a glass funnel. Extracts were concentrated by rotary evaporation to a small volume before the cleanup.

In order to assess the extraction efficiency using microwave, sediment samples were also extracted with the conventional method - 20 hr Soxhlet extraction with 350 ml toluene.

Sample Analysis

All sample extracts were subjected to a cleanup followed by fractionation before GC-MS analysis. PCB fractions were analyzed using the HP GC-MSD in electron impact (EI) and Selected Ion Monitoring (SIM) mode. The GC column used was a 30 m x 0.25 mm ID x 0.25 μm , bonded methyl 5% phenyl silica. PCDDs/PCDFs were measured using the VG AutoSpec GC-HRMS in the EI and SIR mode with a resolution of 10,000. A similar GC column but with a length of 60 meters was used for dioxin analysis. Detailed analytical procedures and performance criteria are described elsewhere.^(11, 12)

Results and Discussion

PCB Analysis

PCBs were quantified as homologue groups with a substitution of 3 to 10 chlorine atoms. Octa-, nona- and deca-chlorobiphenyls were not detected in these sediments. Comparison results of microwave and Soxhlet extraction of PCBs in lake sediment EC-2 and marine sediment SRM-1944 are shown in Table 1 and Table 2 respectively. Results showed that 20 to 30% more trichlorobiphenyls were reported using microwaves as opposed to Soxhlet. On the other hand, the standard deviation values of microwave extraction were higher than the Soxhlet extraction for trichlorobiphenyls in both materials. These discrepancies are probably due to the variability in measuring the relatively volatile trichlorobiphenyls. Recoveries of tetra- penta- and hexa-homologue and total PCBs were very close for both methods. The concentration ratios (microwave/Soxhlet) were between 1.0 and 1.09. A low ratio of 0.74 for heptachlorobiphenyls was observed at levels near the detection limit. The precision of both methods was comparable for the two sediments. Reported PCBs for both extraction methods were slightly lower than the certified value of sediment EC-2.

PCDD/PCDF Analysis

Comparison results of microwave-assisted extraction vs. Soxhlet extraction of PCDD/PCDF in lake sediment DX-1 and marine sediment SRM-1944 are illustrated in Table 3 and Table 4 respectively. Concentration ratios of microwave to Soxhlet for sediments were within a narrow range of 0.94 to 1.17 for the 17 2,3,7,8-substituted congeners and homologues of PCDDs/PCDFs. The standard deviation of triplicate analyses for both methods were also similar. In addition, reported PCDD/PCDF concentrations of both methods agreed very well with the

certified values. Results clearly suggest that microwave-assisted extraction is comparable to Soxhlet with respect to extraction efficiency and variability for the determination of PCDDs and PCDFs in sediments. Comparing to a previous study,⁽⁹⁾ these analytical data have been improved significantly. One of the reasons is that the efficiency of microwave-assisted extraction was improved by extending the extraction time from 10 to 20 minutes. Secondly, sample extracts of both methods were analyzed as one batch to minimize the analytical variation between batches.

Conclusions

In view of extraction efficiency and variability of the two methods studied, solvent extraction of PCDDs/PCDFs and PCBs from sediments using microwave energy is comparable to Soxhlet. The microwave-assisted solvent extraction, however, is the preferable method because it reduces extraction time from 20 hours to 20 minutes and solvent quantity from 350 ml of toluene to only 20 ml of hexane/acetone.

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Table 1 Comparison of Extraction Results of PCBs in Lake Sediment EC-2

PCB Homologue	Microwave Extraction		Soxhlet Extraction		Mic./Sox. Ratio	Certified Value
	ug/g, Mean (n=3)	%RSD	ug/g, Mean (n=3)	%RSD		
Trichloro	0.133 (4)	21.8	0.103 (4)	14.6	1.29	
Tetrachloro	0.400 (10)	13.2	0.393 (10)	10.2	1.02	
Pentachloro	0.307 (9)	1.9	0.300 (9)	8.7	1.02	
Hexachloro	0.120 (3)	0.0	0.110 (3)	9.1	1.09	
Total PCBs (Cl ₃ to Cl ₁₀)	0.963	3.6	0.903	4.7	1.07	1.16 ± 0.15

Number in bracket represents no. of PCB peaks detected.

Table 2 Comparison of Extraction Results of PCBs in Harbour Sediment SRM-1944

PCB Homologue	Microwave Extraction		Soxhlet Extraction		Mic./Sox. Ratio
	ug/g, Mean (n=3)	%RSD	ug/g, Mean (n=3)	%RSD	
Trichloro	0.447 (8)	10.1	0.363 (6)	5.8	1.23
Tetrachloro	0.583 (12)	3.9	0.577 (11)	6.0	1.01
Pentachloro	0.330 (9)	6.1	0.330 (9)	7.9	1.00
Hexachloro	0.257 (3)	12.4	0.237 (3)	5.1	1.08
Heptachloro	0.057 (2)	43.8	0.077 (2)	27.3	0.74
Total PCBs (Cl ₃ to Cl ₁₀)	1.676	3.6	1.583	5.8	1.06

Number in bracket represents no. of PCB peaks detected.

ANALYSIS

Table 3 Comparison of Extraction Results of PCDDs/PCDFs in Lake Sediment DX-1

	Microwave Extraction		Soxhlet Extraction		Mic./Sox. Ratio	Certified DX-1 Values
	ng/g, Mean (n=3)	%RSD	ng/g, Mean (n=3)	%RSD		
2378-TCDD	0.249	0.4	0.251	3.6	0.99	0.263 ± 0.053
12378-P ₅ CDD*	0.024	4.2	0.023	4.3	1.04	0.022 ± 0.008
123478-H ₆ CDD*	0.024	12.5	0.024	8.3	1.00	0.023 ± 0.007
123678-H ₆ CDD*	0.089	5.6	0.076	5.3	1.17	0.077 ± 0.027
123789-H ₆ CDD*	0.059	6.8	0.054	5.6	1.09	0.053 ± 0.024
1234678-H ₇ CDD	0.694	2.7	0.634	0.3	1.09	0.634 ± 0.182
OCDD	4.054	7.4	3.788	3.7	1.07	3.932 ± 0.933
2378-TCDF*	0.084	2.4	0.089	4.5	0.94	0.089 ± 0.044
12378-P ₅ CDF*	0.029	10.3	0.028	10.7	1.04	0.039 ± 0.014
23478-P ₅ CDF*	0.057	7.0	0.058	6.9	0.98	0.062 ± 0.032
123478-H ₆ CDF*	0.643	0.2	0.604	1.7	1.06	0.714 ± 0.276
123678-H ₆ CDF*	0.105	2.9	0.108	1.9	0.97	0.116 ± 0.037
234678-H ₆ CDF*	0.051	2.0	0.055	1.8	0.93	0.057 ± 0.036
123789-H ₆ CDF*	<0.01	-	<0.01	-	-	0.028 ± 0.042
1234678-H ₇ CDF	2.210	1.4	2.191	2.1	1.01	2.397 ± 0.796
1234789-H ₇ CDF	0.122	2.5	0.122	3.3	1.00	0.137 ± 0.062
OCDF	7.264	1.0	6.699	1.7	1.08	7.122 ± 2.406
TOTAL TCDD	0.424	2.8	0.430	3.3	0.99	0.416 ± 0.121
TOTAL P ₅ CDD	0.288	1.0	0.292	3.1	0.99	0.226 ± 0.143
TOTAL H ₆ CDD	0.788	5.3	0.733	1.9	1.08	0.669 ± 0.185
TOTAL H ₇ CDD	1.289	2.6	1.176	1.2	1.10	1.251 ± 0.361
TOTAL TCDF	0.693	11.1	0.740	3.4	0.94	0.659 ± 0.259
TOTAL P ₅ CDF	1.060	5.8	0.946	5.8	1.12	0.790 ± 0.489
TOTAL H ₆ CDF	1.755	0.9	1.713	2.3	1.02	1.800 ± 0.809
TOTAL H ₇ CDF	3.291	0.6	3.197	1.5	1.03	3.567 ± 1.165
TOTAL DIOXINS	6.844	5.2	6.273	2.9	1.09	6.490 ± 1.309
TOTAL FURANS	14.060	1.1	13.30	1.3	1.06	13.68 ± 3.777

* Value represents maximum possible amount as this isomer could coelute with other isomer(s).

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Table 4 Comparison of Extraction Results of PCDDs/PCDFs in Harbour Sediment SRM-1944

	Microwave Extraction		Soxhlet Extraction		Mic./Sox. Ratio
	ng/g, Mean (n=3)	%RSD	ng/g, Mean (n=3)	%RSD	
2378-TCDD	0.122	8.2	0.120	5.0	1.02
12378-P ₅ CDD*	0.018	16.7	0.017	11.8	1.06
123478-H ₆ CDD*	0.025	4.0	0.024	16.7	1.04
123678-H ₆ CDD*	0.056	10.7	0.050	12.0	1.12
123789-H ₆ CDD*	0.060	6.7	0.056	10.7	1.07
1234678-H ₇ CDD	0.792	5.8	0.727	5.0	1.09
OCDD	5.986	9.7	5.626	6.3	1.06
2378-TCDF*	0.154	3.2	0.156	5.8	0.99
12378-P ₅ CDF*	0.038	2.6	0.040	2.5	0.95
23478-P ₅ CDF*	0.042	0.0	0.041	2.4	1.02
123478-H ₆ CDF*	0.241	2.5	0.230	4.3	1.05
123678-H ₆ CDF*	0.085	5.9	0.088	10.2	0.97
234678-H ₆ CDF*	0.053	3.8	0.055	9.1	0.96
123789-H ₆ CDF*	<0.005	-	<0.005	-	-
1234678-H ₇ CDF	0.966	9.5	0.900	5.7	1.07
1234789-H ₇ CDF	ndr (46)	-	ndr (48)	-	-
OCDF	1.107	11.7	0.973	15.2	1.14
TOTAL TCDD	0.269	5.2	0.253	2.8	1.06
TOTAL P ₅ CDD	0.183	2.7	0.197	9.1	0.93
TOTAL H ₆ CDD	0.672	6.5	0.617	5.8	1.09
TOTAL H ₇ CDD	1.866	6.0	1.676	4.7	1.11
TOTAL TCDF	0.831	3.7	0.840	3.7	0.99
TOTAL P ₅ CDF	0.929	2.7	0.850	4.8	1.09
TOTAL H ₆ CDF	1.050	2.0	1.021	5.0	1.03
TOTAL H ₇ CDF	1.435	5.2	1.515	1.1	0.95
TOTAL DIOXINS	8.676	6.7	8.369	4.9	1.04
TOTAL FURANS	5.352	4.3	4.995	3.6	1.07

* Value represents maximum possible amount as this isomer could coelute with other isomer(s).

ndr = not detected due to incorrect isotope ratio