Microwave vs. Soxhlet for the Extraction of Dioxins and Furans from Solid Samples

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1. Introduction

Using microwave energy to assist solvent extraction of toxic organics from solids and aqueous solutions has been investigated by several laboratories in recent years.[1-8] The drastic saving in extraction time, solvent consumption, waste and energy have made this technique a very attractive alternative to the conventional method - Soxhlet extraction.

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.[9-11] As part of a series of studies, this paper describes the comparison results between microwave and Soxhlet extraction for the determination of PCDDs/PCDFs in solid reference materials.

2. Experimental

Sample Materials
Solid materials used for this study were: a Lake Ontario sediment (DX-2) from NWRI, Environment Canada; sediment (SRM-X) from NIST, USA; and Urban Dust (SRM-1649) from NIST, USA. Of the three reference materials, DX-2 is the only material certified for PCDDs and PCDFs. SRM-X is a new material provided by NIST for the characterization for organics. Sample size used for DX-2, SRM-X and SRM-1649 were 1.0-2.5, 1.0 and 0.1-0.5 g respectively.

Microwave Extraction
The microwave apparatus (MES-1000 of CEM Corporation) used was equipped with a temperature control device and safety features including a solvent sensing alarm, pressure relief device and explosion protective shield. After spiking the sample inside a 100-ml Teflon vessel with the surrogate solution, 20 ml of hexane/acetone mixture (1:1 ratio) was added. Vessels containing sample materials were placed evenly in the carousel and extracted for 10 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 passed through a filtration apparatus consisting of anhydrous sodium sulphate on a filter paper inside a glass funnel. The apparatus was washed with 10 ml of hexane/acetone and the extract was concentrated to a few ml by rotary evaporation. These concentrated extracts were subjected to cleanup following the Environment Canada's method EPS 1/RM/19.[12)]

Soxhlet Extraction
Each pre-weighed sample was quantitatively transferred into a pre-extracted glass fibre thimble and spiked with the surrogated solution. The thimble was placed into a Soxhlet apparatus that contained 350 ml of toluene. Samples were extracted for 20 hours at a reflux rate of three to four cycles per hour. After extraction, the extract and the toluene rinses of the Soxhlet were combined and concentrated to a few ml by rotary evaporation. Sample extracts were subjected to the same cleanup procedure applied for microwave extraction.

Sample Analysis
Analyses were done on a HP-5890 gas chromatograph interfaced to a VG 70s mass spectrometer. A 1-ul sample was injected through a CTC A2000s autosampler into a 60 m length x 0.25 mm ID x 0.25 um film thickness, bonded methyl 5% phenyl silicone column (Quadrex). PCDDs/PCDFs were measured at 10,000 resolution using the electron impact (EI) and selected ion recording (SIR) modes. Detailed operating procedures and performance criteria were described eleswhere.[12)]

3. Results and Discussion

Sediment DX-2
Results of microwave and Soxhlet extraction of PCDDs/PCDFs in sediment DX-2 are compared for the 17 2,3,7,8-substituted congeners, eight homologues and total dioxins and furans as in Table 1. Both methods have similar precision with an average relative standard deviation (RSD) of 8%. Congeners with lower concentrations show relatively higher RSD values. The concentration ratios of the two methods are in a range of 0.68 to 1.31 with an average of 0.88. It appears that the Soxhlet method produced slightly higher dioxin/furan values for this material. However, the mean values of both methods are in good agreement with the certified values [13)] with the exception of 1,2,3,7,8-P5CDF. This congener was reported at a higher value under microwave extraction.

Sediment SRM-X
Comparison results of microwave and Soxhlet extraction of PCDDs/PCDFs in sediment SRM-1944 are shown in Table 2. The average RSD are 12.8 and 16.8% for microwave and Soxhlet methods respectively. Higher RSD values for penta and hexa-CDD congeners are expected because of the near-detection limit concentrations. Mean concentrations are comparable between the two methods with ratios of 0.63 to 1.18 and an average value of 0.95.

Urban Dust SRM-1694
Comparison results of microwave and Soxhlet extraction for PCDDs/PCDFs in urban dust SRM-

1649 are presented in Table 3. The precision of microwave extraction (3.9%) appears to be significantly better than the Soxhlet extraction (15.2%). It should be noted that the triplicate microwave extraction and subsequent analysis were performed as one batch while Soxhlet extraction and analysis (n=7) were carried out in three batches over a period of six months. As a result, the higher RSD values of the Soxhlet method may have been contributed partially from the analytical variation between batches. The lowest and the highest ratios are 0.39 for 1,2,3,7,8,9-H6CDF (0.07 ng/g) and 1.37 for Total TCDD (0.1 ng/g). The average concentration ratio for this material is 0.98.

Extraction Efficiency
The extraction efficiency was further assessed by extracting the sediment SRM-X in sequence using both extraction techniques. Table 4 suggests that up to 8% of total dioxins/furans can be recovered in the 2nd microwave extraction and 1 to 2% in the 3rd microwave extraction. Only 1% of total dioxins/furans are found in the 2nd Soxhlet extraction. This finding implies that recovery can be enhanced for microwave extraction if the 2nd extraction is included as part of the extraction procedures. On the other hand, there is no significant gain by doing the 2nd Soxhlet extraction.

4. Conclusions

Both microwave and Soxhlet methods give comparable extraction efficiencies and precision for the determination of PCDDs/PCDFs in sediments and urban dust. Of the three materials studied, sediment DX-2 is the only material of which Soxhlet extraction appears to gain higher concentration. The extraction efficiency using microwaves could be enhanced for some samples when materials are extracted twice instead of once. The real benefits in replacing the Soxhlet with the microwave method are that we can reduce the extraction time from 20 hours to 10-20 minutes (excluding the time required to evaporate solvents before a cleanup) and solvent quantity from 350 ml to 20-40 ml per sample. Moreover, the solvents (hexane/acetone) used for microwave extraction are less hazardous than toluene required for Soxhlet extraction. In view of these advantages, development of methodologies in applying microwave energy to assist solvent extraction of pollutants from environmental samples of various matrices is warranted.

5. Acknowledgment
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Table 1 Comparison Results of Microwave and Soxhlet Extraction of Sediment DX-2

	Microwave Extraction		Soxhlet Extraction			Certified
	Mean ng/g(n=4)	%RSD	Mean ng/g(n=16)	%RSD	Ratio	DX-2 Values
2378-TCDD	0.240	2.0	0.282	4.6	0.85	0.262 ± 0.051
12378-P_5CDD*	0.025	8.2	0.034	19.4	0.75	0.028 ± 0.014
123478-H_6CDD*	0.022	13.4	0.033	8.9	0.66	0.025 ± 0.008
123678-H_6CDD*	0.077	1.3	0.108	7.3	0.71	0.085 ± 0.033
123789-H_6CDD*	0.052	10.5	0.065	9.3	0.80	0.058 ± 0.019
1234678-H_7CDD	0.759	2.4	0.901	4.4	0.84	0.757 ± 0.320
OCDD	4.347	2.9	4.898	4.9	0.89	4.402 ± 1.257
2378-TCDF*	0.130	10.6	0.131	8.3	0.99	0.134 ± 0.061
12378-P_5CDF*	0.062	45.2	0.048	9.6	1.31	0.046 ± 0.010
23478-P_5CDF*	0.085	6.3	0.103	14.4	0.82	0.088 ± 0.028
123478-H_6CDF*	0.823	12.2	0.861	3.9	0.96	0.825 ± 0.348
123678-H_6CDF*	0.128	8.7	0.181	9.6	0.71	0.153 ± 0.061
234678-H_6CDF*	0.072	10.7	0.074	14.0	0.97	0.070 ± 0.047
123789-H_6CDF*	<0.01	-	0.058	12.5	-	0.036 ± 0.045
1234678-H_7CDF	3.231	12.4	3.165	6.5	1.02	3.064 ± 0.745
1234789-H_7CDF	0.140	10.4	0.193	12.7	0.72	0.152 ± 0.084
OCDF	7.923	8.5	8.645	8.3	0.92	7.830 ± 3.087
TOTAL TCDD	0.374	1.6	0.460	5.6	0.81	0.418 ± 0.125
TOTAL P_5CDD	0.254	4.3	0.313	7.5	0.81	0.253 ± 0.150
TOTAL H_6CDD	0.713	3.2	0.871	4.8	0.82	0.739 ± 0.218
TOTAL H_7CDD	1.461	1.1	1.703	4.5	0.86	1.486 ± 0.476
TOTAL TCDF	0.982	5.5	1.453	7.4	0.68	0.975 ± 0.588
TOTAL P_5CDF	1.293	7.5	1.029	6.0	1.26	0.916 ± 0.351
TOTAL H_6CDF	2.195	11.3	2.419	4.8	0.91	2.111 ± 0.662
TOTAL H_7CDF	4.506	12.4	4.308	5.7	1.05	4.068 ± 1.306
TOTAL DIOXINS	7.123	1.4	8.258	4.0	0.86	7.294 ± 1.733
TOTAL FURANS	16.51	12.9	17.85	5.9	0.92	15.98 ± 4.177
Average		8.7		8.0	0.88	

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

Table 2 Comparison Results of Microwave and Soxhlet Extraction of Sediment SRM-X

	Microwave Extraction		Soxhlet Extraction			
	Mean ng/g(n=7)	%RSD	Mean ng/g(n=8)	%RSD	Ratio	% Difference
2378-TCDD	0.142	15.6	0.120	9.9	1.18	16.8
12378-P_5CDD*	0.018	21.2	0.017	29.6	1.11	10.3
123478-H_6CDD*	0.021	14.4	0.023	44.6	0.91	-9.1
123678-H_6CDD*	0.048	8.5	0.059	36.4	0.81	-21.1
123789-H_6CDD*	0.052	11.7	0.068	23.8	0.77	-26.2
1234678-H_7CDD	0.820	13.1	0.829	7.5	0.99	-1.0
OCDD	5.055	22.1	5.212	9.1	0.97	-3.1
2378-TCDF*	0.140	8.2	0.157	17.1	0.89	-11.2
12378-P_5CDF*	0.044	12.7	0.048	14.6	0.93	-6.7
23478-P_5CDF*	0.040	9.7	0.046	13.0	0.88	-13.3
123478-H_6CDF*	0.229	5.2	0.237	15.4	0.97	-3.2
123678-H_6CDF*	0.077	10.5	0.079	13.5	0.98	-2.2
234678-H_6CDF*	0.050	10.6	0.059	8.0	0.86	-15.1
123789-H_6CDF*	<0.006	-	<0.008	-	-	-
1234678-H_7CDF	1.010	14.0	0.896	9.0	1.13	12.0
1234789-H_7CDF	0.029	15.5	0.041	14.8	0.70	-35.6
OCDF	0.982	12.8	1.081	25.4	0.91	-9.6
TOTAL TCDD	0.223	12.2	0.236	12.9	0.95	-5.4
TOTAL P_5CDD	0.132	22.2	0.209	30.1	0.63	-45.1
TOTAL H_6CDD	0.578	9.2	0.725	20.1	0.80	-22.5
TOTAL H_7CDD	1.913	9.6	1.893	6.5	1.01	1.0
TOTAL TCDF	0.712	16.6	0.751	25.7	0.95	-5.4
TOTAL P_5CDF	1.029	12.7	0.870	13.8	1.18	16.7
TOTAL H_6CDF	1.013	4.3	1.027	10.5	0.99	-1.4
TOTAL H_7CDF	1.508	11.3	1.385	6.1	1.09	8.5
TOTAL DIOXINS	7.901	16.4	8.260	8.0	0.96	-4.4
TOTAL FURANS	5.314	11.3	5.114	10.8	1.04	3.8
Average		12.8		16.8	0.95	-6.6

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

Table 3 Comparison Results of Microwave and Soxhlet Extraction of Urban Dust SRM-1649

	Microwave Extraction		Soxhlet Extraction			
	Mean ng/g(n=3)	%RSD	Mean ng/g(n=7)	%RSD	Ratio	% Difference
2378-TCDD	<0.005	-	<0.08	-	-	-
12378-P_5CDD*	0.071	3.5	<0.1	-	-	-
123478-H_6CDD*	0.238	2.2	0.243	28.4	0.98	-2.1
123678-H_6CDD*	0.576	3.9	0.676	8.9	0.85	-16.0
123789-H_6CDD*	0.749	13.0	0.723	9.8	1.04	3.5
1234678-H_7CDD	19.63	4.1	18.40	6.7	1.07	6.5
OCDD	153.7	2.1	189.0	7.2	0.81	-20.6
2378-TCDF*	0.091	1.1	0.144	18.1	0.63	-45.1
12378-P_5CDF*	0.087	3.4	0.154	18.2	0.56	-55.6
23478-P_5CDF*	0.257	2.9	0.283	13.4	0.91	-9.6
123478-H_6CDF*	1.027	2.5	1.058	8.9	0.97	-3.0
123678-H_6CDF*	0.334	2.7	0.393	9.7	0.85	-16.1
234678-H_6CDF*	0.662	2.6	0.583	8.4	1.14	12.7
123789-H_6CDF*	0.027	10.0	0.070	42.2	0.39	-88.7
1234678-H_7CDF	3.733	2.2	3.380	10.9	1.10	9.9
1234789-H_7CDF	0.404	5.2	0.354	17.8	1.14	13.3
OCDF	6.983	4.5	6.790	5.3	1.03	2.8
TOTAL TCDD	0.141	6.7	0.103	53.4	1.37	31.4
TOTAL P_5CDD	0.754	3.1	0.667	16.9	1.13	12.2
TOTAL H_6CDD	5.833	2.8	5.950	10.1	0.98	-2.0
TOTAL H_7CDD	39.13	4.3	35.20	7.4	1.11	10.6
TOTAL TCDF	0.496	6.4	0.541	33.3	0.92	-8.6
TOTAL P_5CDF	2.197	3.4	1.710	11.1	1.28	24.9
TOTAL H_6CDF	4.513	1.6	4.380	11.4	1.03	3.0
TOTAL H_7CDF	9.970	2.2	8.090	9.4	1.23	20.8
TOTAL DIOXINS	199.7	2.5	230.9	7.2	0.86	-14 5
TOTAL FURANS	24.17	2.9	21.50	3.1	1.12	11.7
Average		3.9		15.2	0.98	-4.7

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

Table 4 Microwave and Soxhlet Extraction Efficiency for PCDDs/PCDFs in Sediment SRM-X

	1st Mic. Ext.	2nd Mic. Ext.		3rd Mic. Ext.		1st Sox. Ext.	2nd Sox. Ext.	
	Mean ng/g n=4	Mean ng/g n=4	Rec. %	Mean ng/g n=2	Rec. %	Mean ng/g n=3	Mean ng/g n=3	Rec. %
2378-TCDD	0.131	.008	6.3	<0.006	-	0.119	0.001	0.8
12378-P_5CDD*	0.018	<0.003	-	<0.006	-	0.020	<0.001	-
123478-H_6CDD*	0.021	<0.004	-	<0.006	-	0.031	0.002	4.8
123678-H_6CDD*	0.050	0.005	10.0	<0.006	-	0.078	0.005	6.8
123789-H_6CDD*	0.054	<0.004	-	<0.006	-	0.082	0.005	6.5
1234678-H_7CDD	0.876	0.078	8.9	0.046	5.2	0.880	0.013	1.4
OCDD	5.911	0.475	8.0	0.124	2.1	5.380	0.036	0.7
2378-TCDF*	0.143	0.013	8.8	0.007	4.9	0.180	0.003	1.7
12378-P_5CDF*	0.046	<0.004	-	<0.004	-	0.052	<0.001	-
23478-P_5CDF*	0.043	0.004	-	<0.004	-	0.047	<0.001	-
123478-H_6CDF*	0.233	0.021	9.1	<0.004	-	0.268	0.003	0.9
123678-H_6CDF*	0.080	0.007	8.8	<0.004	-	0.089	0.002	2.3
234678-H_6CDF*	0.054	<0.004	-	<0.004	-	0.060	0.003	5
123789-H_6CDF*	<0.006	<0.004	-	<0.004	-	<0.003	<0.001	-
1234678-H_7CDF	1.058	0.074	7.0	0.023	2.2	0.960	0.011	1.2
1234789-H_7CDF	0.029	<0.004	-	<0.007	-	0.041	<0.005	-
OCDF	1.035	0.101	9.7	0.021	2.0	1.128	0.007	0.6
TOTAL TCDD	0.206	0.011	5.2	<0.006	-	0.261	0.003	1.1
TOTAL P_5CDD	0.149	<0.004	<2.7	<0.006	-	0.259	0.008	3
TOTAL H_6CDD	0.492	0.038	7.7	<0.008	-	0.855	0.042	4.9
TOTAL H_7CDD	2.008	0.159	7.9	0.086	4.3	1.954	0.024	1.2
TOTAL TCDF	0.704	0.043	6.1	0.008	1.1	0.916	0.003	0.3
TOTAL P_5CDF	0.932	0.044	4.8	<0.006	-	0.878	0.005	0.5
TOTAL H_6CDF	1.020	0.056	5.5	<0.004	-	1.123	0.014	1.2
TOTAL H_7CDF	1.552	0.109	7.0	0.026	1.7	1.458	0.015	1
TOTAL DIOXINS	8.866	0.692	7.8	0.226	2.5	8.679	0.112	1.3
TOTAL FURANS	5.368	0.353	6.6	0.070	1.3	5.504	0.043	0.8

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