COMPARISON OF DIFFERENT EXTRACTION TECHNIQUES FOR THE DETERMINATION OF PCDD/Fs IN SOIL AND SEDIMENT

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Introduction

The determination of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) requires complicated and time-consuming procedures in sample extraction and clean up. Conventional Soxhlet extraction is probably the most widely used extraction method for organics in different matrix. There are many alternative methods applied for reducing time and solvent consumption. Accelerated Solvent Extraction[1,2] (ASE) and Microwave-Assisted Extraction[3] (MAE) extract samples under relative high temperature and pressure. Soxtherm is a kind of automated soxhlet extraction using shorter extraction time[4]. Shake Solvent Extraction[5] (SSE), a sample pretreatment procedure of DR CALUX®, is a low cost technique available by only flasks and shakers. To compare performances of these extraction techniques, validation tests with these five methods were carried out by analysis of two kinds of certified reference materials EDF-2513 (soil) and DX-1 (sediment) in this investigation.

Materials and Methods

Sample extraction

0.5g EDF-2513 (Cambridge Isotope Laboratories) and 1g DX-1 (National Water Research Institute, Canada) were weighed in quadruplicate. All samples were spiked with ^{13}C-isotopes labeled PCDD/Fs internal standards prior to extraction. Conditions used to extract PCDD/Fs are list in Table 1.

Table 1. extraction conditions for Soxhlet, MAE, ASE, Soxtherm and SSE

Method	Solvent	Extraction conditions	Apparatus
Soxhlet	toluene 300 mL	24hr	
MAE	toluene/acetone (4:1 v/v) 50 mL	Extraction temperature 125℃; hold 20 min	CEM MARS
ASE	toluene	Pressure 2500 psi; temperature 195℃	DIONEX ASE 200
Soxterm	toluene 135 mL	Hot extraction 270℃ 1hr; rinsing time 1.5hr	Gerhardt
SSE	30 mL water/isopropanol (1:1 v/v); 30 mL n-hexane/diethyl ether (97:3 v/v) as extraction solution	Shake 200±20 strokes per minute for 1hr then transfer the organic layer; repeat adding again 30.0 mL extraction solution and shaking for 30 min and transfer twice.	

Clean-up

Extracts were concentrated to dryness and solvent exchanged to n-hexane for further clean-ups using sulfuric acid silica gel and activated carbon column kits[4] (CAPE).

HRGC/HRMS

The analysis of samples was performed on a HRGC (HP 6890)/ HRMS (JEOL JMS-700) using DB-5MS column. Compounds identification and quantitative analysis were done by isotope dilution following the USEPA Method 1613B.

Results and Discussion

Table 2 shows the mean concentrations (n=4) of PCDD/Fs obtained by each of the five extraction methods in comparison with the certified value. To compare the mean recoveries obtained by individual method, the ratios of the method value to the certified value for each PCDD/Fs congener are given in fig. 1. Data form all methods, excluding SSE, are within the Lower and Upper bounds for the reference material. Most of the values obtained from ASE and Soxtherm approaches have higher than those from classic Soxhlet extraction. The values obtained using MAE were comparable to the soxhlet results however they were consistently lower the certified reference value (73% to 93%). In comparison, shake solvent extraction was not very efficient since only four congeners were within the certified values acceptance criteria.

The reproducibility of all extraction methods is expressed by the relative standard deviation (RSD) showed in Table2. The RSD values ranged from 4.3 to 9.1% for Soxhlet and from 3.7 to 9.1% for MAE, from 2.3 to 11.1% for ASE, from 1.5 to 10.6% for Soxtherm and from 2.5 to 16.5% for SSE. The mean RSD of each method ranged from 4.6% (Soxtherm) to 8.3% (SSE).

Table 2. concentration (ng/g) of PCDD/Fs in the EDF-2513 obtained by different extraction techniques

Compound	Soxhlet(n=4)		MAE(n=4)		ASE(n=4)		Soxtherm(N=4)		SSE(n=4)		EDF-2513		
	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	Target value	Lower Bound	Upper Bound
2,3,7,8-TeCDF	0.462	9.1	0.402	3.7	0.507	6.4	0.531	4.9	0.135	9.4	0.5	0.26	0.64
1,2,3,7,8-PeCDF	0.952	6.3	0.873	7.1	1.06	3.8	1.13	1.5	0.313	7.2	1.0	0.59	1.15
2,3,4,7,8-PeCDF	0.940	6.7	0.847	5.6	1.02	5.1	1.10	3.6	0.355	7.2	1.0	0.41	1.31
1,2,3,4,7,8-HxCDF	0.927	8.1	0.820	6.6	1.04	4.4	1.07	3.4	0.395	7.3	1.0	0.53	1.23
1,2,3,6,7,8-HxCDF	0.957	7.1	0.93	5.8	1.09	2.3	1.11	3.5	0.403	8.1	1.0	0.34	1.56
2,3,4,6,7,8-HxCDF	0.940	6.2	0.897	8.1	1.03	3.9	1.13	5.2	0.453	7.7	1.0	0.48	1.35
1,2,3,7,8,9-HxCDF	0.924	8.4	0.845	3.7	0.980	7.6	1.05	4.2	0.316	11.2	1.0	0.39	1.26
1,2,3,4,6,7,8-HpCDF	1.55	8.3	1.31	3.7	1.54	4.7	1.62	2.5	0.679	7.7	1.5	0.52	2.01
1,2,3,4,7,8,9-HpCDF	1.38	8.9	1.20	9.1	1.56	4.5	1.55	4.4	0.564	10.9	1.5	0.25	1.98
OCDF	2.28	6.7	2.17	6.4	2.35	4.9	2.58	5.6	1.03	16.5	2.5	1.17	3.33
2,3,7,8-TeCDD	0.421	7.4	0.375	7.1	0.553	11.1	0.514	5.7	0.112	8.5	0.5	0.26	0.67
1,2,3,7,8-PeCDD	0.944	7.4	0.852	5.7	1.03	4.2	1.00	5.2	0.308	9.2	1.0	0.56	1.37
1,2,3,4,7,8-HxCDD	0.821	9.1	0.726	7.8	0.953	4.1	0.928	5.8	0.372	7.2	1.0	0.50	1.29
1,2,3,6,7,8-HxCDD	0.836	8.6	0.790	8.1	0.852	3.2	0.933	10.6	0.382	8.3	1.0	0.52	1.21
1,2,3,7,8,9-HxCDD	0.883	7.7	0.766	6.4	0.921	2.7	0.874	4.6	0.384	2.5	1.0	0.46	1.33
1,2,3,4,6,7,8-HpCDD	1.38	6.2	1.28	3.7	1.47	4.4	1.56	3.4	0.726	6.3	1.5	0.71	2.07
OCDD	3.73	4.3	2.96	4.9	3.52	8.9	3.40	3.8	1.89	6.1	3.5	1.98	5.03
Average RSD(%)		7.5		6.1		5.1		4.6		8.3			

Concentrations and the reproducibility of PCDD/Fs from reference sediment DX-1 are summarized in Table 3

for the different extraction methods. The ratios of the method value to the certified value for each PCDD/Fs congener are shown in fig. 2. Excepting 2,3,7,8-TeCDF, recoveries were higher than 85%, varying between 91 to 175% for soxhlet extraction; 86 to 185% for MAE and 85 to 185% for ASE. Soxtherm is comparable to these three methods with slightly lower recovery ranges. Similarly to EDF-2513 case, lower recovery were observed for solvent shake extraction. However, only two congeners, namely 2,3,7,8-TeCDF and 2,3,7,8-TeCDD, were outside the acceptance criteria. For the other congeners, recoveries ranged from 76 to 151% using SSE.

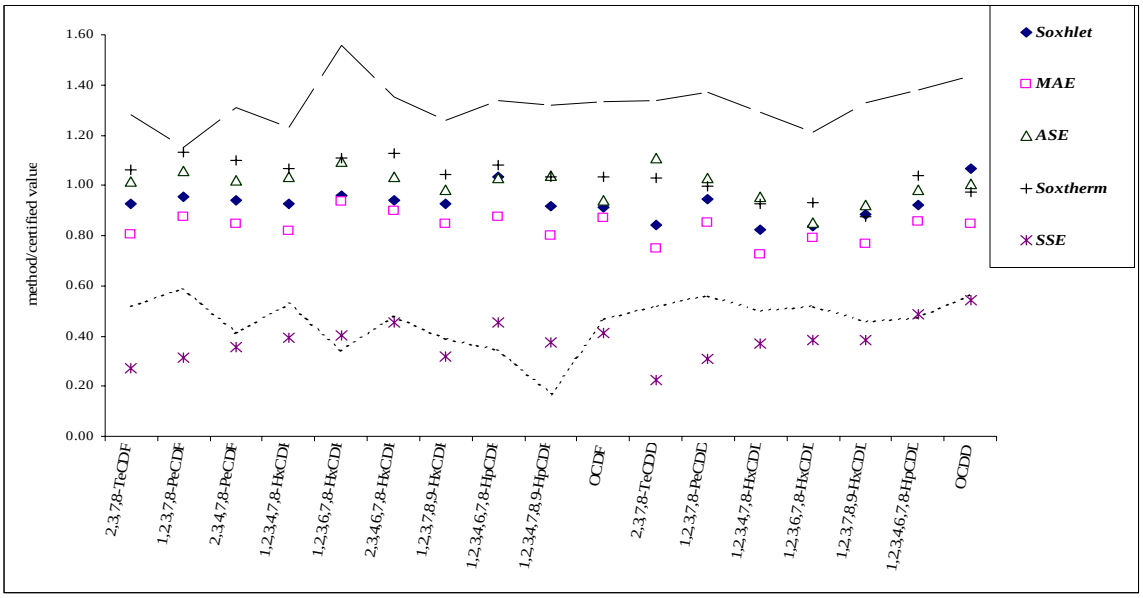

Fig. 1. Ratio of method value to certified value for PCDD/Fs extracted from EDF-2513

The reproducibility of all extraction methods is better than that in the extractions of EDF-2513. The RSD values ranged from 2.1 to 7.1% for Soxhlet and from 1.3 to 11.5% for MAE, from 1.9 to 6.6% for ASE, from 0.7 to 4.3% for Soxtherm and from 0.9 to 27.4% for SSE. The mean RSD of each method ranged from2.4% (Soxtherm) to 5.4% (SSE) showed good precision for most of extraction methods.

There was a high RSD value (OCDD, 27.4%) in SSE that came from a notable high value in one of the four experiment data (5797, 3594, 3534, and 3510 pg/g, respectively). If this data was excluded, SSE showed better yield and reproducibility in extracting DX-1 than EDF-2513. This is probably because DX-1 (sediment) is smaller and lighter than EDF-2513 (soil). Such fine particles suspend readily and contact with solvent more frequently.

MAE, ASE, and Soxtherm have been proved to be comparable with traditional Soxhlet method for extracting PCDD/Fs from soil and sediment reference material in this investigation. All of them can reduce extraction time

and solvent consumption. Solvent shake extraction is an alternative technique, but the operating parameters must be optimized to obtain good performance.

References

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Table 3. concentration (pg/g) of PCDD/Fs in the DX-1 obtained by different extraction techniques

Compound	Soxhlet(n=4)		MAE(n=4)		ASE(n=4)		Soxtherm(N=4)		Shake(n=4)		DX-1		
	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	mean	RSD(%)	Certified value	Lower Bound	Upper Bound
2,3,7,8-TeCDF	52	6.4	48	4.1	48	3.2	49	4.5	38	4.1	89	45	133
1,2,3,7,8-PeCDF	47	6.7	45	3.2	46	2.0	43	1.6	36	1.9	39	25	53
2,3,4,7,8-PeCDF	91	2.1	93	1.3	91	2.8	92	0.7	83	4.4	62	30	94
1,2,3,4,7,8-HxCDF	681	2.4	629	4.8	671	3.4	600	2.4	544	2.3	714	438	990
1,2,3,6,7,8-HxCDF	138	7.1	137	5.5	137	2.6	132	3.0	123	1.3	116	79	153
2,3,4,6,7,8-HxCDF	66	5.9	64	2.1	67	2.9	62	1.9	56	4.9	57	21	93
1,2,3,7,8,9-HxCDF	49	6.1	52	1.8	52	4.0	49	2.6	42	2.9	28	0	70
1,2,3,4,6,7,8-HpCDF	2723	5.9	2608	1.5	2620	3.8	2458	1.4	2288	2.9	2397	1601	3193
1,2,3,4,7,8,9-HpCDF	157	4.4	155	2.2	164	4.3	151	2.9	133	0.9	137	75	199
OCDF	7733	5.0	7208	3.1	7286	3.0	6666	4.3	6060	5.4	7122	4716	9528
2,3,7,8-TeCDD	278	4.2	250	2.5	260	1.9	258	0.9	197	2.7	263	210	316
1,2,3,7,8-PeCDD	26	7.0	24	3.8	24	3.2	22	1.3	20	4.0	22	14	30
1,2,3,4,7,8-HxCDD	22	4.1	23	11.5	24	6.4	21	4.2	20	4.4	23	16	30
1,2,3,6,7,8-HxCDD	87	5.9	73	5.3	79	6.6	74	3.1	67	3.5	77	50	104
1,2,3,7,8,9-HxCDD	48	4.3	46	2.6	45	3.0	44	2.9	44	10.2	53	29	77
1,2,3,4,6,7,8-HpCDD	709	4.7	680	3.0	709	2.2	638	2.4	611	7.9	634	452	816
OCDD	4372	5.7	4163	2.4	4201	2.3	3779	1.7	4109	27.4	3932	2999	4865
Average RSD(%)		5.1		3.6		3.4		2.4		5.4			

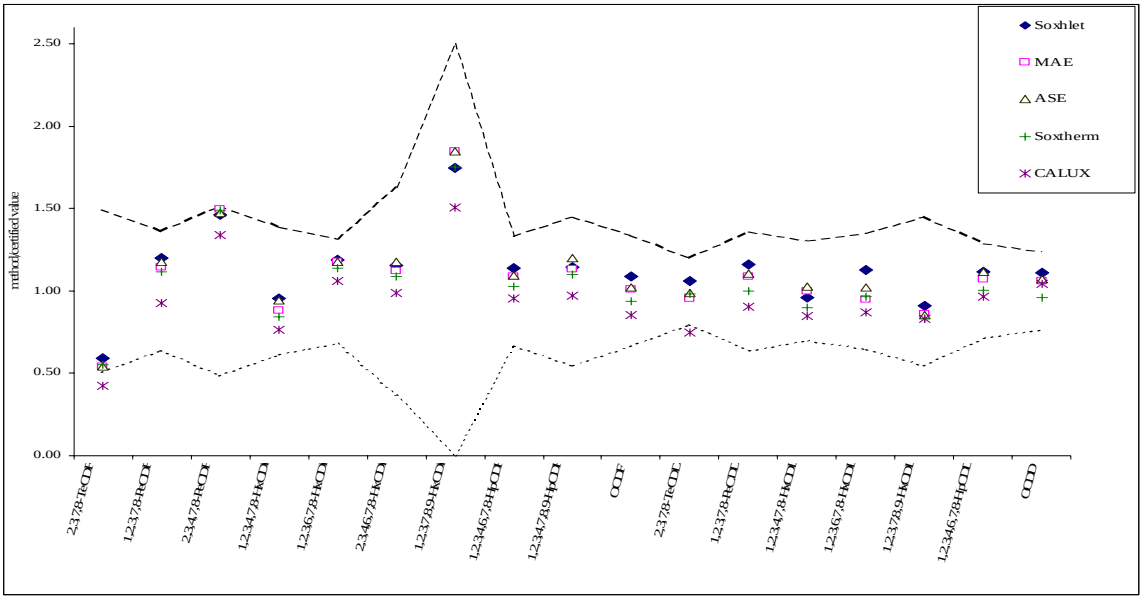

Fig. 2. Ratio of method value to certified value for PCDD/Fs extracted from DX-1