

## Analysis of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans by the Accelerated Solvent Extraction (ASE) and HPLC Cleanup

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### Introduction

In this study, an analytical method for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and co-planer PCBs using a combination of accelerated solvent extraction (ASE), high performance gel permeation chromatography (GPC) and porous graphite carbon chromatography (PGC) are studied for the application to the soil samples.

The main target of the proposed method is,

- (1) to establish fixed procedure without sample-dependent small adjustment of the method procedures,
- (2) to omit the unstable fractionation steps,
- (3) to establish possible automation with HPLC fractionation.

Many efforts for the automation of the dioxin analysis have been done, and some automated cleanup systems are already commercially produced. However, we consider that the fixed procedural steps without sample-dependent adjustment should be the key property for the full-automation and our aim of this research is to approach to this objective, for the soil and sediment samples. Method description and the feasibility study, the cross-check effort with soxhlet extraction are the main result of this study.

### Materials and Methods

#### *Accelerated solvent extraction*

Figure 1 shows the schematic diagram of the whole analytical procedure.

ASE extraction was performed by the ASE-200 from Dionex Corporation. Extraction temperature was 150 °C and the pressure was 2000 psi. Each sample was prepared in 33ml cell and extracted twice by acetone, then twice by toluene, under the condition of static time 10min. and flush volume 60%<sup>1,2</sup>. Carbon-13 labeled internal standards were added to the sample prior to the extraction. The acetone and toluene extracts were mixed and concentrated to about 0.5ml. The concentrate was made up to about 1.8ml by the cyclohexane/ethyl acetate (1:1).

#### *Gel permeation chromatography and sulfuric acid impregnated silica gel chromatography*

Gel permeation chromatography was performed by HPLC using the Environgel GPC column (19×150mm + 19×300mm, Waters) with 5ml/min. of cyclohexane/ethyl acetate (1:1) as the eluent. A fraction containing PCDD/Fs and mono ortho- to non ortho- coplaner PCBs was collected. The

majority of matrix component with higher molecular weight, sulfur and part of polyaromatic hydrocarbons (PAHs) could be removed by this process.

GPC fraction was concentrated and was followed by the sulfuric acid impregnated silica gel treatment. The 4.5 grams of 44% sulfuric acid impregnated silica gel was used in a normal manner. The n-hexane eluate was concentrated for the next step.

#### *Porous graphite carbon chromatography*

HPLC cleanup using HyperCarb PCB (4.6×50mm) column was performed under the conditions in Table 1<sup>3,4</sup>. Contamination from the carryover of former sample was found in this chromatography. The toluene wash by the backflush flow under raised temperature (80 °C) was effective to reduce the carryover blank. For the analysis of soil samples, the observed blank level was low enough, which was generally acceptable for the analysis.

#### *Other methods*

High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was operated under the selected ion monitoring (SIM) mode. The mass resolution was 10,000 and the GC columns were DB-5 and DB-17. The operating condition was essentially similar to the previously reported<sup>5</sup>.

Same sample set was extracted by the soxhlet extraction for the comparison, followed by the similar cleanup steps. Toluene was used for the extraction solvent.

## Results and Discussions

### *Comparison between ASE extraction and soxhlet extraction*

Table 2 shows the analytical results of three different soil samples, A, B and C, by ASE and soxhlet extraction, respectively. The TEQ results from ASE and soxhlet extraction for samples A and B are almost equal each other. For sample C, the TEQ result from ASE extraction is larger than that of soxhlet extraction. Congener data in Table 2 show that the results from both extraction procedures were nearly close each other for lower chlorinated congeners. However, results from ASE extraction are apparently higher than the results from soxhlet extraction, especially for OCDF, which show almost two-fold difference between two extraction procedures. Because the extraction condition used in the ASE process are 150 °C for 10

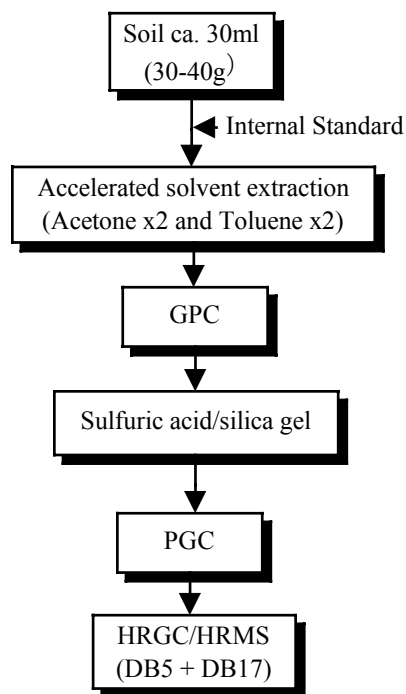


Figure 1 Schematic diagram of the method

Table 1 Condition of PGC fractionation

Solvent	Compounds
Hexane 3.5ml	other PCBs
1-2% Toluene/Hexane 8ml	mono-ortho PCBs
50% Toluene/Hexane 11.5ml	non-ortho PCBs
Toluene backflush at 60 °C	PCDD/Fs

minutes, which should be relatively mild condition compared to the soxhlet extraction with prolonged heating time, the results from ASE might be closer to the true sample levels than the results from soxhlet extraction. However, more study should be necessary to establish the precise relationship between the ASE extraction and the soxhlet extraction.

*Feasibility of the ASE-HPLC method for soil samples*

For the dioxin analysis of soil, this method is working well for many samples. Generally only negligible interference could be found on the chromatograms, which are generally lower than the samples from normal cleanup processes.

Sulfuric acid impregnated silica gel chromatography and concentration procedures between cleanup steps are still remaining in manual procedures. However, the use of disposable sulfuric acid impregnated silica column and the automated concentration apparatus could be the solution for those manual steps.

*Analytical results of soil samples*

Table 3 shows the analytical results for the soil samples from paddy field, urban park, residential area and forest using the proposed method. Paddy field soil shows characteristic very high concentration of TCDDs, mainly 1368- and 1379-TCDD, which should come from the impurities in the herbicide CNP (Chlornitrofen). However, the concentration of other congeners is also relatively high, that may reflect the impurities in PCP (Pentachlorophenol) and CNP<sup>6</sup>.

(pg/g dry wt.)	A		B		C	
	ASE	Soxhlet	ASE	Soxhlet	ASE	Soxhlet
2378-TCDD	ND	0.00	0.13	0.11	0.14	0.10
12378-PeCDD	0.30	0.28	0.64	0.60	1.05	0.79
123478-HxCDD	0.40	ND	0.83	0.77	2.00	1.48
123678-HxCDD	0.79	0.60	1.64	1.39	4.20	3.08
123789-HxCDD	0.58	0.31	1.36	0.96	2.68	2.56
1234678-HpCDD	4.94	3.74	17.69	15.54	45.09	31.80
OCDD	70.57	53.07	140.91	113.71	353.45	266.99
Total PCDD TEQ	0.446	0.320	1.146	0.989	2.357	1.796
2378-TCDF	0.34	0.28	0.70	0.65	0.62	0.40
12378-PeCDF	0.47	0.46	0.99	0.94	1.17	0.86
23478-PeCDF	0.65	0.75	1.35	1.54	2.00	1.36
123478-HxCDF	1.00	1.06	2.11	2.22	4.13	2.87
123678-HxCDF	1.07	1.08	2.60	2.43	4.18	3.26
123789-HxCDF	0.07	ND	0.18	0.16	0.23	0.24
234678-HxCDF	1.31	1.41	4.11	3.77	8.98	7.13
1234678-HpCDF	4.12	3.93	13.93	13.28	36.79	28.45
1234789-HpCDF	0.41	0.44	1.46	1.36	4.04	3.38
OCDF	6.53	3.80	11.54	6.59	41.19	19.23
Total PCDF TEQ	0.781	0.825	1.858	1.893	3.323	2.453
Total TEQ (pg/g)	1.23	1.15	3.00	2.88	5.68	4.25

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Table 3 Analytical results for soil samples (pg/g dw)

(pg/g dw)	P.F.(1)	P.F.(2)	P.F.(3)	P.(1)	P.(2)	R.(1)	R.(2)	F.
2,3,7,8-TCDF	1.3	3.5	0.8	0.8	0.2	0.3	0.0	0.3
TCDFs	2201	2291	134	32	5.5	12	2.6	19
1,2,3,7,8-PeCDF	4.3	4.8	1.7	1.0	0.5	0.3	0.1	0.5
2,3,4,7,8-PeCDF	5.0	7.1	1.1	1.3	0.6	0.4	0.1	0.7
PeCDFs	62	364	28	21	9.0	6.7	1.2	9.0
1,2,3,4,7,8-HxCDF	12	32	9.0	1.8	1.1	0.8	0.2	1.1
1,2,3,6,7,8-HxCDF	4.5	19	5.0	2.2	1.2	0.8	0.2	1.0
2,3,4,6,7,8-HxCDF	34	44	7.7	3.4	2.1	1.3	0.3	1.4
1,2,3,7,8,9-HxCDF	0.4	nd	nd	0.1	0.1	nd	nd	0.1
HxCDFs	202	495	105	27	15	9.4	2.2	13
1,2,3,4,6,7,8-HpCDF	69	320	76	10	7.4	4.2	1.3	6.5
1,2,3,4,7,8,9-HpCDF	11	28	7.6	1.3	1.0	0.6	0.2	0.7
HpCDFs	227	955	241	16	13	7.3	2.9	13
OCDFs	333	1836	535	10	12	6.5	3.8	20
2,3,7,8-TCDD	nd	nd	nd	nd	nd	nd	nd	Nd
TCDDs	154880	121735	5710	559	73	448	111	341
1,2,3,7,8-PeCDD	23	27	4.1	0.7	0.3	0.2	0.1	0.3
PeCDDs	11662	8053	400	48	10	34	7.8	28
1,2,3,4,7,8-HxCDD	15	35	8.7	0.7	0.6	0.3	0.1	0.5
1,2,3,6,7,8-HxCDD	63	108	15	1.3	1.0	0.5	0.2	0.8
1,2,3,7,8,9-HxCDD	48	50	10	1.1	1.7	0.4	0.1	0.6
HxCDDs	586	734	104	19	33	7.1	1.5	8.3
1,2,3,4,6,7,8-HpCDD	987	2780	333	12	19	5.5	2.7	11
HpCDDs	1616	4541	540	21	51	8.9	4.6	21
OCDD	24774	37511	5998	99	219	49	37	184
TEQ	68	117	19	2.6	1.8	0.9	0.3	1.5

P.F. : Paddy field soil, P.: Park, R.: Residential area, F.: Forest