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Analysis of Polychlorinated Dibenzo-p-dioxins and Polycholorinated Dibenzofurans by the ASE-HPLC method

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Introduction

Due to the widespread occurrence and toxicity, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) have been monitored in air, water, soil, fly ash, fish tissues etc. basing on the standard analytical methods, such as EPA 1613, EPA8290, JIS K0311 and JIS K0312. However, compared with analysis for other organic pollutants, PCDD/Fs analysis is more time-consuming, costly, manual, dangerous and sample-dependent.

In order to improve these properties, this paper studied an analytical method for PCDD/Fs in soils using a combination of accelerated solvent extraction (ASE) and high performance liquid chromatography (HPLC) with porous graphite carbon (PGC) column. The efficiency of the ASE and HPLC steps was studied, and a comparison of the ASE-HPLC method and the classical method for PCDD/Fs analysis was made using interlaboratory testing data.

Methods and Materials

HPLC fractionation

200μl ^{13}C labelled internal standards (20pg/μl) were fractionated by .HPLC (Shimadzu) with HyperCarb column (100×4.6mm, Thermoquest Hypersil) under the conditions in table 1[1,2,3].

Table 1 Conditions of HPLC fractionation

Conditions	Fractionations
Hexane, 8ml, 2ml/min, 25	
50% methylene chloride/toluene, 40ml, 2ml/min, 25	
30% toluene/hexane, 40ml, 2ml/min, 25	
Back-flush, toluene, 50ml, 2ml/min, 50 , collected each 5 ml.	, , , , , , , , , ,

Each fractionation was concentrated and analyzed by HRGC-HRMS (JMS-700D, JEOL), which is described elsewhere[4,5].

Accelerated Solvent Extraction and analyzed by ASE-HPLC method

ASE extraction was performed by the ASE-300 from Dionex Corporation. Extraction temperature was 185 °C and the pressure was 1500 psi. Common soil (G-97, provided by Hideaki MIYATA, Setsunan University, Japan) was prepared in 33ml cell and statically extracted three times by toluene, under the condition of static time 7min, flush volume 90%, and purge time 120 second[6,7]. ^{13}C labeled internal standards were added to the soil prior to the extraction. And in order to evaluate the completeness of PCDD/Fs extraction, this soil sample was extracted three times under the upper extraction conditions. The extracts were separately collected, treated by sulphuric acid[4,5],

cleaned-up by multilayer silica column[4,5], fractionated by HPLC (using evaluated conditions) and analyzed by HRGC-HRMS[4,5], as described in figure 1.

Interlaboratory testing for…

The soil used had previously been analyzed by twenty Japanese groups during an interlaboratory testing in 2002. Among them, six groups used classical method, Soxhlet extraction and Alumina fractionation, instead of ASE and HPLC fractionation.

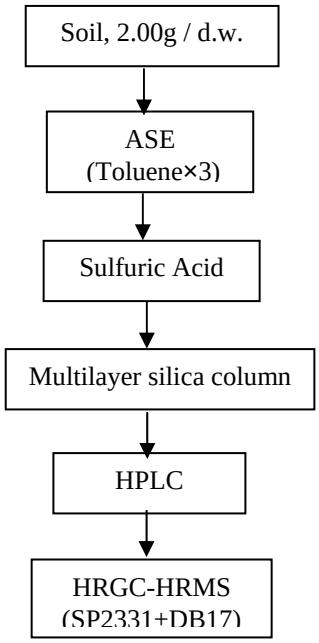

Figure 1 Schematic diagram of the new method

Results and Discussion

Efficiency of HPLC fractionation

The relative contents of each fractionation are summarized in Table 2. It shows that ^{13}C labelled isomers are only detected in back-flush fractionations, mostly in the fractionation , and . Moreover, more than 99.4% ^{13}C labelled isomers are in the former 40 ml toluene. Interestingly, ^{13}C-2378-TCDD/F and ^{13}C-123789-HxCDF are the easiest to elute, but are also the most difficult to recover completely.

Efficiency of ASE

Table 3 shows the relative contents of each ASE extract. It shows that the first extraction efficiency of unlabelled isomers is above 87.7%, and the former two extraction efficiency is above 94.6%, so PCDD/Fs in soils can be effectively extracted by twice extraction using ASE.

Interestingly, the extraction efficiency of ^{13}C labeled isomers and unlabelled isomers is different, which is also reported by B. Henkelmann[8]. The first extraction efficiency of all ^{13}C labeled isomers is 100%, and no ^{13}C labeled isomers are detected in the second or third extract. This phenomenon may be attributed to the different superficial and interior interactions of soils. So another conclusion can also be achieved that it is the same to add ^{13}C labeled isomers before or after extraction for the analysis of PCDD/Fs in soils.

In addition, it is important to note that it is not known how much of the PCDD/Fs that are not extracted by three ASE extractions in Table 3. But almost as much TCDD was recovered in the third extract (5.0%) as in the second (7.3%). The same is true for the PeCDFs. That indicate a slow release of TCDD from the PGC of these potent (high TEF) PCDD/F congeners.

Comparison of two different analysis method

Table 4 shows the analytical results of this ASE-HPLC method and the classical method. It reveals that total PCDD/Fs concentration of this ASE-HPLC method (4000pg/g) is slightly higher than the result of, but between the maximum and minimum of, the classical method (3600 (3200,4200) pg/g). The similar conclusion can also be achieved by comparing each isomer or homologue concentration of both methods in table 4. So this ASE-HPLC method is comparable with the classical method for the analysis of PCDD/Fs in soils.

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Table 2 Relative contents of ^{13}C labelled isomers in each HPLC fractionation (%)

Isomer	Fractionations												
^{13}C-2378-TCDD	0.0	0.0	0.0	0.0	10.9	71.9	8.4	2.4	2.8	2.0	1.5	0.2	0.0
^{13}C-12378-PeCDD	0.0	0.0	0.0	0.0	4.3	86.5	5.3	1.3	0.9	0.6	0.3	0.0	0.4
^{13}C-123478-TxCDD	0.0	0.0	0.0	0.0	1.6	85.6	11.1	0.8	0.4	0.2	0.2	0.0	0.1
^{13}C-123678-TxCDD	0.0	0.0	0.0	0.0	1.7	76.6	19.5	0.9	0.5	0.3	0.2	0.0	0.2
^{13}C-123789-TxCDD	0.0	0.0	0.0	0.0	4.5	88.0	3.4	1.4	1.1	0.6	0.3	0.0	0.3
^{13}C-1234678-HpCDD	0.0	0.0	0.0	0.0	1.6	85.6	9.9	1.1	0.7	0.4	0.3	0.4	0.0
^{13}C-OCDD	0.0	0.0	0.0	0.0	1.8	85.6	10.9	0.8	0.5	0.0	0.2	0.2	0.0
^{13}C-2378-TCDF	0.0	0.0	0.0	0.0	6.5	83.4	4.8	1.3	1.5	1.0	0.7	0.0	0.4
^{13}C-12378-PeCDF	0.0	0.0	0.0	0.0	5.4	86.5	4.0	1.3	1.0	0.7	0.5	0.0	0.3
^{13}C-23478-PeCDF	0.0	0.0	0.0	0.0	3.8	80.5	11.6	1.4	0.9	0.6	0.4	0.0	0.4
^{13}C-123478-HxCDF	0.0	0.0	0.0	0.0	2.3	73.0	22.4	1.0	0.5	0.3	0.2	0.0	0.1
^{13}C-123678-HxCDF	0.0	0.0	0.0	0.0	1.8	60.0	35.5	1.1	0.5	0.3	0.4	0.0	0.2
^{13}C-234678-HxCDF	0.0	0.0	0.0	0.0	1.7	66.0	29.7	0.9	0.7	0.4	0.3	0.0	0.1
^{13}C-123789-HxCDF	0.0	0.0	0.0	0.0	11.2	80.3	3.5	1.6	1.2	0.8	0.6	0.0	0.4
^{13}C-1234678-HpCDF	0.0	0.0	0.0	0.0	0.8	64.0	32.4	1.0	0.5	0.3	0.2	0.2	0.5
^{13}C-1234789-HpCDF	0.0	0.0	0.0	0.0	3.1	90.8	3.0	1.1	0.6	0.6	0.4	0.2	0.3

Table 3 Relative contents of ^{13}C labelled isomers in each ASE extract (%)

Isomers	First Extraction		Second Extraction		Third Extraction	
	PCDD/Fs	^{13}C-PCDD/Fs	PCDD/Fs	^{13}C-PCDD/Fs	PCDD/Fs	^{13}C-PCDD/Fs
2378-TCDD	87.7	100.0	7.3	0.0	5.0	0.0
12378-PeCDD	91.0	100.0	5.9	0.0	3.1	0.0
123478-HxCDD	95.7	100.0	4.3	0.0	0.0	0.0

123678-HxCDD	95.9	100.0	4.1	0.0	0.0	0.0
123789-HxCDD	90.6	100.0	7.1	0.0	2.4	0.0
1234678-HpCDD	93.5	100.0	4.3	0.0	2.2	0.0
OCDD	95.7	100.0	3.0	0.0	1.3	0.0
2378-TCDF	91.0	100.0	7.3	0.0	1.8	0.0
12378-PeCDF	90.8	100.0	5.8	0.0	3.4	0.0
23478-PeCDF	91.7	100.0	5.2	0.0	3.1	0.0
123478-HxCDF	93.7	100.0	3.9	0.0	2.4	0.0
123678-HxCDF	92.2	100.0	6.3	0.0	1.6	0.0
123789-HxCDF	92.9	100.0	7.1	0.0	0.0	0.0
234678-HxCDF	95.0	100.0	3.4	0.0	1.7	0.0
1234678-HpCDF	96.2	100.0	2.7	0.0	1.1	0.0
1234789-HpCDF	96.5	100.0	3.5	0.0	0.0	0.0

Table 4 Results of ASE-HPLC method and Classical Method* (pg/g)

Isomer	ASE-HPLC Method	Classical Method (Max, Min)	Isomer	ASE-HPLC Method	Classical Method (Max, Min)
2378-TCDD	1.8	1.5 (N.D., 2.1)	1234789-HpCDF	19	20 (17, 31)
12378-PeCDD	14	14 (11, 17)	OCDF	92	101 (87, 120)
123478-HxCDD	11	12 (8.2, 19)	TCDDs	640	610 (480, 800)
123678-HxCDD	13	18 (11, 26)	PeCDDs	340	280 (220, 360)
123789-HxCDD	20	17 (11, 21)	HxCDDs	320	300 (240, 380)
1234678-HpCDD	150	134 (120, 150)	HpCDDs	310	270 (230, 300)
OCDD	530	586 (510, 650)	OCDD	530	590 (510, 650)
2378-TCDF	12	10 (7.9, 12)	Total PCDDs	2100	2000 (1800, 2500)
12378-PeCDF	26	25 (21, 31)	TCDFs	390	320 (210, 400)
23478-PeCDF	29	26 (20, 34)	PeCDFs	480	420 (370, 500)
123478-HxCDF	40	31 (25, 38)	HxCDFs	450	410 (350, 450)
123678-HxCDF	40	34 (29, 37)	HpCDFs	290	260 (240, 290)
123789-HxCDF	5.7	5.1 (N.D,. 7.8)	OCDF	92	100 (87, 120)
234678-HxCDF	58	51 (40, 58)	Total PCDFs	1700	1500 (1400, 1700)
1234678-HpCDF	150	140 (120, 160)	Total PCDD/Fs	3800	3600 (3200, 4200)

* the results of ASE-HPLC method is the addition of the analytical results of the former two ASE extracts; and the results of classical method is the average results of the six Japanese groups mentioned before.