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Comparative Evaluation of "Soxhlet-" and "Accelerated Solvent-" Extraction in the Determination of PCDD/F in Sediment

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Introduction

Modern GC/MS systems are now capable of routinely measuring PCDD/F congeners in the low femtogram range. The main analytical interest of PCDD/F shifted towards optimization and an acceleration of extraction and clean-up¹. The extraction efficiencies strongly depend on: (1) the partition coefficient between the solvent and the sample matrix; (2) the contact between the solvent and the particles². The conventional and robust extraction methods of PCDD/F are Soxhlet extraction for solid samples and separatory funnel extraction for liquid samples. However the traditional extraction methods need more solvent (normally 100-400 ml) and are time consuming. Supercritical fluid extraction with carbon dioxide (SFE) has the advantage to reduce solvent, waste and cost. While the major disadvantage of SFE is the extraction efficiency, especially for the complex matrices³.

Recently, a new technology of accelerated solvent extraction (ASE) which applies temperature and pressure to accelerate the extraction process and to improve the efficiency of solvent extraction was developed by Dionex company^{3, 4}. ASE significantly reduces solvent consumption and analytical time and is easy to automate⁴. This study shows comparative results of soxhlet and ASE in the determination of PCDD/F in different sediments. The extraction results from the raw and milled sediment samples are also compared.

Experimental Methods

Extraction method

Sediment samples were collected from Ya-Er lake, Hubei, China by a kajak sampler. The samples were freeze-dried in the laboratory. Soxhlet extraction was carried out for 1-5 g sediment using 180 ml toluene for 24 hours. ASE extraction was performed at pressure of 2000 psi and temperature of 175°C with toluene as solvent. 1-5g sediment samples were transferred into stainless steel extraction cells. The remaining dead volume was filled with purified seasand. After being filled with solvent, the cell was heated up and pressurized, followed by a static extraction for 10 min. This cycle was done twice. Then the sample was purged with nitrogen during 150s. The total volume of the extraction solvent was about 40 ml. Prior to all extraction, the samples were spiked with 17 ¹³C₁₂-2,3,7,8 substituted labeled PCDD/F internal standards.

Clean-up

Following the extraction, in order to remove interference, a clean up based on several liquid chromatography steps was applied according to the method by Schramm⁵⁾. The multiple column chromatography included basic and super active alumina, sulphuric acid coated and active silica, deactivated florisilTM and small basic super and active alumina. All columns were covered with Na₂SO₄. Prior to analysis, the sample was reconstituted with a recovery standard (1,2,3,4-¹³C₁₂ Cl₄DD, 100 pg/μl)

Instrumental analysis

The identification and quantification were accomplished with capillary GC/MS system where a high resolution gas chromatography (HRGC) is obligatory. After splitless injection, the sample was separated on a Rt_x 2330 polar capillary GC column (60 m x 0.25 mm ID x 0.25 μm) and quantified by Finnigan MAT 95 mass spectrometer at resolution 10000.

Results and discussion

The comparative extraction results of PCDD/F of Soxhlet and accelerated solvent extraction are presented in table 1. Higher concentration of TCDD, PeCDD, 1,2,3,4,6,7,8-HpCDD were obtained by ASE method than by traditional "Soxhlet-" extraction in sample 1A. These congeners showed no difference in sample 2B and 3C. This accounts for the different amount of sediments used in 1A. 1 g 1A sediment was used for "Soxhlet-" extraction, and 2 g for accelerated solvent extraction. Thus some congeners in Soxhlet extraction were at the concentration of the determination limits. For sample 3C, higher concentration OCDF was found in ASE but lower concentration of 1,2,3,7,8-PeCDD. In sample 1A and 2B, there was a little lower OCDF concentration in ASE compared to "Soxhlet-" extraction. Wagenaar showed that ASE at high temperature did not cause more degradation of the concentration of OCDF⁴⁾. This difference of some PCDD/F congeners was caused by the inhomogeneity of samples. Some 2,3,7,8-substituted congeners were too low to compare the results. The other congener results showed excellent agreement, especially in sample 2B, and for PCDF. The comparative results of sum of PCDD/F and I-TEQ were very favorable. The more difference in sample 1A was due to the complex matrix in this sample that was co-contaminated with high PCB- and PAH-content. Its total carbon was up to 10%. No difference was found between the result of the raw and milled sample by ASE. The results also showed good agreement with Soxhlet method.

The average recovery for Soxhlet procedure method is 80%, and 90% for ASE. Though the recovery did not really represent the extraction efficiency, the results indicated that ASE is also a very good extraction method.

Conclusion

The comparative results and good recoveries show that ASE method can be a substitute extraction method for sediment in the laboratory. There is no difference between the raw and the milled samples after freeze-drying.

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Table 1 Comparative evaluation of PCDD/F between Soxhlet and ASE in Ya-Er lake sediment (ng/kg)

Extraction methods	Soxhlet	ASE	Soxhlet	ASE	ASE	Soxhlet	ASE
Samples	3C	3C	2B raw	2B raw	2B mill	1A	1A
sum TCDD	33.80	44.84	121.93	116.12	131.72	173.63	272.79
sum PeCDD	85.16	71.01	116.55	83.98	87.70	16.93	84.97
sum HxCDD	297.78	294.43	215.13	182.93	178.66	111.39	122.48
sum HpCDD	711.31	771.71	321.01	342.87	350.50	201.87	251.48
OCDD	6730.30	6467.40	3039.27	3073.48	3076.17	2271.9	2341.76
sum TCDD to OCDD	7858.36	7649.39	3813.64	3799.393	3824.74	2775.71	3073.47
2,3,7,8-TCDD	0.26	n.d.	n.d.	n.d.	n.d.	nd	n.d.
1,2,3,7,8-PeCDD	3.07	0.50	n.d.	n.d.	n.d.	nd	n.d.
1,2,3,4,7,8-HxCDD	35.55	36.87	23.60	20.76	21.27	1.04	3.09
1,2,3,6,7,8-HxCDD	7.31	n.d.	n.d.	n.d.	n.d.	nd	n.d.
1,2,3,7,8,9-HxCDD	1.93	n.d.	n.d.	n.d.	n.d.	nd	n.d.
1,2,3,4,6,7,8-HpCDD	172.32	198.61	107.07	115.66	118.76	57.85	103.91
sum TCDF	384.50	407.88	503.55	491.40	501.38	2411.35	2314.08
sum PeCDF	52.89	57.58	102.85	83.10	82.47	483.39	539.20
sum HxCDF	65.85	57.65	84.24	65.61	65.42	430.19	465.25
sum HpCDF	29.99	47.67	34.01	46.61	46.99	292.17	312.31
OCDF	39.84	123.21	162.46	140.88	141.96	931.2	750.11
sum TCDF to OCDF	573.07	693.98	887.12	827.60	838.21	4548.31	4380.96
2,3,7,8-TCDF	9.44	14.32	15.76	20.44	19.32	99.71	102.45
1,2,3,7,8/1,2,3,4,8-PeCDF	13.62	15.64	15.30	15.25	15.31	67.23	61.55
2,3,4,7,8-PeCDF	4.89	6.09	15.94	15.08	15.69	114.28	102.31
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	12.78	13.22	21.62	20.09	21.04	138.94	133.28
1,2,3,6,7,8-HxCDF	4.55	4.85	8.86	6.41	4.88	80.04	59.65
1,2,3,7,8,9-HxCDF	0.06	n.d.	n.d.	n.d.	0.04	nd	n.d.
2,3,4,6,7,8-HxCDF	1.97	1.26	2.59	1.97	1.66	16.47	28.47
1,2,3,4,6,7,8-HpCDF	13.23	20.58	18.65	25.03	24.02	195.44	156.88
1,2,3,4,7,8,9-HpCDF	0.81	0.60	1.84	0.67	0.71	37.81	63.23
sum PCDD/F (tetra to octa)	8431.4	8343.4	4700.7	4626.9	4663.0	7324.0	7454.4
I-TEQ	20.91	19.92	20.46	19.90	20.08	100.23	93.26

3C, Pond 3 sediment core (24-36 cm); 2B, Pond 2 sediment core (12-24 cm); 1A, Pond 1 sediment core (0-12 cm). n.d., not detected.

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Fig. 1 PCDD/F in Ya-Er lake sediment (0-12 cm)

