COMPARATIVE PCDD/Fs ANALYSIS IN DIFFERENT MATRICES (FISH, HARBOUR SEDIMENT, INDUSTRIAL SLUDGE, MSWI ASH) EXTRACTED BY PRESSURIZED FLUID EXTRACTION AND BY TRADITIONAL SOXHLET. PRELIMINARY RESULTS.

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Introduction

Many official analytical methodologies do not provide for the use of Pressurized Fluid Extraction (PFE) system in the PCDD/F extraction from solid sample, in spite of being much less time and solvent consuming than the traditional soxhlet extraction. The US-EPA method 3545A/98 do not contemplate the PFE procedure for extracting fish. In order to compare extraction yields and reproducibility, four different matrices (fish, harbour sediment, industrial sludge and mswi boiler ash) have been extracted using Accelerated Solvent Extraction (ASETM) and soxhlet methods. Preliminary results of a large project on the way are presented in advance.

Materials and Methods

Chemicals. All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate, benzene) were pesticide free reagent grade (Carlo Erba). Native and ¹³C₁₂-labeled PCDD and PCDF standards were purchased from Cambridge Isotope Laboratories, Woburn, MA. The fish Certificate Reference Material CARP-1 was purchased from National Research Council Canada Halifax, Nova Scotia, and the hygroscopic Sample Dispersing Agent (Spe-ed Matrix) from Applied Separation, Inc Allenton, PA.

Procedure. All glassware was washed with basic detergent, rinsed with distilled water, treated with a solution of ammonium persulphate 350 g/L in sulphuric acid (98%) and rinsed twice with distilled water and acetone. Subsequently, the cleaned glassware was treated with dimethyldichlorosilane 5% in toluene, rinsed twice with distilled water and acetone, heated to 300°C for 3h, and covered with aluminium foil.

Sample preparation. For each sample, four different aliquots were prepared, two for each kind of extraction method. The wet harbour sediment and the industrial sludge samples were obtained from the 4° round robin of Umeå University, 1999, and were treated as received. The ampoule of fish sample (CARP-1 Cyprinu carpio) was sonicated in an ultrasonic bath for 15 minutes. The boiler ash was obtained from a modern Italian MSWI boiler; it was manually ground until a fine powder was obtained. All samples were then spiked with a series of 15 $^{13}C_{12}$ -labeled 2,3,7,8 PCDD/F substituted isomers as internal standards. Before the extraction, the sample aliquots for ASE were mixed with Spe-ed Matrix, the boiler ash aliquots for soxhlet were treated with 1M HCl for 2h, filtered and rinsed thoroughly with distilled water.

Sample extraction. Two sample aliquots were extracted by soxhlet/Dean-Stark and two ones by ASE 200 (DIONEX Sunnyvale, CA). The aliquots for the soxhlet extraction were loaded into a Pyrex thimble and extracted with 300 mL toluene for 36 h. The ASE extractions were performed with 50 mL toluene at 175 °C, 13.8 MPa (2000 psi), 8 min. heat-up and 2 cycles of 10 min. static time (50 mL toluene 5% in glacial acetic acid (v/v) at 185 °C, 13.8 MPa, 9 min. heat-up and 2

ORGANOHALOGEN COMPOUNDS 239 Vol.40 (1999) cycles of 15 min. static time, in the case of the boiler ash sample). The extracts were transferred to hexane before the clean up treatment.

Clean up. The sample extracts were treated with sulphuric acid (98%) and potassium hydroxide (20%) in a 100 mL separatory funnel and then cleaned up using the automatic three column system, Dioxin Prep (Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica, alumina and carbon were used.

Analysis. The HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Sample injections were performed in the splitless mode on a 60 m Rtx 5 ms column (Restek 0.25 mm ID, 0.25 μ m film) and on a 30 m Rtx 200 one (Restek 0.25 mm ID, 0.25 μ m film) for verification.

The quantitative determination of PCDDs/PCDFs was performed by an isotope dilution method using relative response factors previously obtained from five standard solutions injections (EDF 9999 Cambridge Isotope Laboratories, Woburn, MA.), as recommended by the US-EPA [1].

Results and Discussion

Fish tissue. Comparative results are reported in table 1. The comparison between ASE data, soxhlet data and certified values demonstrate the reliability of the two extraction methods and their excellent agreement. The only exception is represented by the OCDD soxhlet value $(12.4 \pm 5.6 \text{ ng/kg})$, to be compared with ASE 6.4 ± 1.7 and certified value 6.3 ± 1.9 , probably because of typical cross-contamination effects of the octachlorinated PCDD/F congeners in one of the two samples. In the same extraction, clean up and HRGC/HRMS analysis (US-EPA 1668), some comparative PCB data were also obtained; they are reported in table 2, together with the certified values. The same conclusions seen for PDCC/Fs can be drawn also for PCBs.

Harbour sediment. Comparative results are reported in table 3. Also for this matrix, the precision and the reliability of the two extraction methods seem to be closely equivalent (their accuracy will be tested as soon as the 4° round robin data are available). This result was not surprising, because sediments are usually easy-extractable matrices, and the difficulty in their analysis lie in its clean up treatment.

Industrial sludge. Comparative results are reported in table 3. Some non-systematic differences (regarding congeners) between ASE and soxhlet data were observed for this matrix. We believe that these discordances should be ascribed to the very high PCDD/F concentrations in the samples rather than to different extraction efficiencies of the two methods. Anyway, ASE method showed a higher extraction capability, which is also evident from the TEQ value (6.5% higher).

Boiler ash. Comparative results are reported in table 4. These preliminary data show a reducted ASE extraction efficiency with respect to soxhlet one, due (in our opinion) to the toluene-acetic acid extraction without the HCl pretreatment. This alternative procedure has been proposed by DIONEX [2]for the fly-ash extraction and is extremely promising, because it bypasses the time consuming HCl treatment; however, an improvement of the operative conditions seems to be necessary, and therefore further investigations are needed.

Conclusions. Preliminary results of ASE/soxhlet comparison are very good, especially regarding time and solvent saving and the automation possibility of ASE. For a complete validation of the ASE extraction method for PCDD/F, a larger number of samples and matrices is needed; furthermore, the method shall be validated also for the hard-extractable matrices, like boiler ash, possibly without the preliminary HCl treatment changing the solvent and operation condition. CRM analysis showed that PCDD/F and PCB ASE extraction can be executed simultaneously.

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	Soxhlet (n=2)	ASE (n=2)	CARP-1
2,3,7,8 – TCDD	7.6 ±1.2	7.6 ± 1.1	6.6 ± 0.6
1,2,3,7,8-PCDD	4.3 ± 1.1	4.3 ±1.2	4.4 ± 1.1
1,2,3,4,7,8-HCDD	1.4 ± 0.5	1.4 ± 0.6	1.9 ± 0.7
1,2,3,6,7,8-HCDD	6.3 ± 1.5	6.4 ± 1.2	5.6 ±1.3
1,2,3,7,8,9-HCDD	0.5 ± 0.5	0.5 ± 0.4	0.7 ± 0.4
1,2,3,4,6,7,8-HpCDD	8.2 ± 2.1	7.0 ± 1.9	6.5 ± 1.8
OCDD	12.4 ± 5.6	6.4 ± 1.7	6.3 ±1.9
2,3,7,8-TCDF	13.4 ± 2.9	12.6 ± 3.1	11.9 ± 2.7
1,2,3,7,8-PCDF	5.4 ± 2.1	5.1 ±1.9	5.0 ± 2.0
2,3,4,7,8-PCDF	12.5 ± 2.5	12.2 ±2.3	
1,2,3,4,7,8-HCDF	3.7 ± 1.2	3.5 ± 1.3	
1,2,3,6,7,8-HCDF	2.4 ± 0.8	2.1 ±0.9	
2,3,4,6,7,8-HCDF	1.0 ± 0.5	0.9 ± 0.7	
1,2,3,7,8,9-HCDF	< 0.5	< 0.5	
1,2,3,4,6,7,8-HpCDF	4.7 ± 1.1	4.2 ± 1.4	
1,2,3,4,7,8,9-HpCDF	< 0.5	< 0.5	
OCDF	0.5 ± 0.5	< 0.5	

Table 1: Average Values (ng/kg) from CRM CARP-1 comparison of soxhlet versus ASE

Total I-TEQ 21.4 21.1

Table 2: Average Values (µg/kg) from CRM CARP-1 comparison of soxhlet versus ASE

		Soxhlet (n=2)	ASE (n=2)	CARP-1
3,3',4,4' TETRACB	77-CB	2.2 ±0.5	2.2 ±0.4	
2',3,4,4',5 PENTACB	123-CB	5.8 ± 1.1	6.4 ±0.9	
2,3',4,4',5 PENTACB	118-CB	92.6 ±11.4	99.9 ±10.1	132 ± 60
2,3,4,4',5 PENTACB	114-CB	7.3 ± 1.2	7.8 ± 1.3	
2,3,3',4,4' PENTACB	105-CB	44.4 ±13.5	49.2 ±11.1	54 ±24
3,3',4,4',5 PENTACB	126-CB	2.1 ± 0.8	1.7 ± 0.5	
2,3',4,4',5,5' ESACB	167-CB	13.7 ± 1.7	14.5 ± 1.5	
2,3,3',4,4',5 ESACB	156-CB	8.6 ± 1.2	8.9 ± 1.3	
2,3,3',4,4',5' ESACB	157-CB	1.6 ± 0.6	1.6 ± 0.5	
2,2',3,4,4',5,5' EPTACB	180-CB	44.4 ±8.1	46.2 ± 7.6	46 ±14
2,2',3,3',4,4',5 EPTACB	170-CB	23.4 ± 3.9	26.3 ± 3.6	22 ± 8
2,3,3',4,4',5,5' EPTACB	189-CB	0.8 ±0.6	0.8 ± 0.5	
Total I-TEQ		2.33	2.02	

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	Harbour Sediment		Industrial Sludge	
	Soxhlet (n=2)	ASE (n=2)	Soxhlet (n=2)	ASE (n=2)
2,3,7,8 – TCDD	<1.0	<1.0	8.5 ±2.8	10.2 ±2.2
1,2,3,7,8-PCDD	0.9 ± 0.5	1.5 ±0.6	26.1 ±8.3	37.9 ±9.4
1,2,3,4,7,8-HCDD	1.3 ± 0.5	1.3 ±0.7	86.4 ±13.5	121.7 ±16.7
1,2,3,6,7,8-HCDD	8.0 ± 1.3	7.3 ±1.5	83.4 ±14.3	167.9 ±15.4
1,2,3,7,8,9-HCDD	4.1 ±1.2	3.3 ±1.1	117.8 ±21.1	203.8 ± 18.2
1,2,3,4,6,7,8-HpCDD	94.4 ±22.1	91.5 ±12.9	2062 ± 230	2642 ± 219
OCDD	644.5 ± 56.5	649.5 ±41.7	12693 ±856	12426 ±941
2,3,7,8-TCDF	34.1 ±5.2	35.8 ± 6.3	7913 ±129	8808 ± 130
1,2,3,7,8-PCDF	42.4 ±4.8	36.4 ±4.9	11340 ±945	11756 ±844
2,3,4,7,8-PCDF	20.4 ±2.7	20.6 ±2.3	5009 ±127	5324 ± 256
1,2,3,4,7,8-HCDF	43.5 ±8.2	41.9 ±9.1	21557 ±1850	23755 ± 1900
1,2,3,6,7,8-HCDF	11.1 ± 2.8	11.4 ±2.7	5875 ± 789	7144 ±805
2,3,4,6,7,8-HCDF	4.7 ±1.2	6.7 ±1.7	830 ±94	1355 ±112
1,2,3,7,8,9-HCDF	1.1 ±0.6	1.4 ±0.5	730 ±87	658 ±93
1,2,3,4,6,7,8-HpCDF	55.5 ±9.2	54.6 ±8.7	17240 ±998	19276 ±1120
1,2,3,4,7,8,9-HpCDF	5.4 ± 1.4	6.0 ± 1.3	7708 ±112	8690 ± 107
OCDF	137.9 ± 15.4	124.3 ± 13.9	40806 ± 525	36069 ± 497
Total I-TEQ	26.7	26.1	7347	7830

Table 3: Average Values (ng/kg) from and Harbour sedimet and Industrial Sludge comparison of soxhlet versus ASE

Table 4: Average Values (ng/kg) from MSWI Boiler-Ash comparison of soxhlet versus ASE

	Soxhlet (n=2)	ASE (n=2)
2,3,7,8 – TCDD	20.8 ±3.7	13.7 ±1.4
1,2,3,7,8-PCDD	49.1 ±10.1	33.3 ±4.2
1,2,3,4,7,8-HCDD	30.9 ± 5.8	20.0 ± 1.7
1,2,3,6,7,8-HCDD	108.7 ±25.4	70.0 ± 6.5
1,2,3,7,8,9-HCDD	102.6 ±29.8	62.2 ± 5.4
1,2,3,4,6,7,8-HpCDD	1043.4 ± 221	638.2 ±54.2
OCDD	4010.9 ±527	2178.9 ±318
1,2,3,7,8-PCDF	97.9 ±22.4	72.6 ±6.6
2,3,4,7,8-PCDF	97.0 ±25.4	79.2 ±6.8
1,2,3,4,7,8-HCDF	263.3 ± 31.2	193.3 ±18.9
1,2,3,6,7,8-HCDF	163.0 ±19.5	109.5 ±9.9
2,3,4,6,7,8-HCDF	168.9 ± 18.7	119.1 ±8.7
1,2,3,7,8,9-HCDF	14.5 ± 1.9	11.4 ± 1.9
1,2,3,4,6,7,8-HpCDF	748.1 ±95.3	511.8 ±52.6
1,2,3,4,7,8,9-HpCDF	93.5 ±10.2	62.4 ±6.1
OCDF	484.4 ±54.7	322.6 ±35.1
Total I-TEQ	232.6	160.2

Reference

1 US EPA Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, **1994**, Revison B, EPA 821-B-94-005

2 Extraction of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Environmental samples using Accelerated Solvent Extraction. **1996** Application note 323 Dionex

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