

Accelerated Solvent Extraction (ASE) of Different Matrices in the Analysis of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans: Method Development and Comparison to Soxhlet Extraction

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Introduction

The most common extraction method in the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) is the Soxhlet extraction. But its disadvantages are the need of large solvent volumes (100-400 ml) and long extraction times (up to 24 h). Another lack is the limited possibility of automation in the analysis of large numbers of samples. Since three years a new extraction method becomes more significant, the accelerated solvent extraction (ASE). This technique uses conventional liquid solvents at elevated pressures (7-20 MPa) and temperatures (50-200°C) to extract solid samples quickly (< 30 minutes), and with much less solvent (< 60 ml). The Dionex company introduced a device (ASE 200) with fully automated extraction of up to 24 samples [1].

In this paper, we report some results of introducing ASE as a new extraction method in our analysis of PCDD/F. Different matrices are extracted with the focus on complete extraction and the results are compared to the Soxhlet method.

Materials and Methods

All samples (lake sediment, soil, sewage sludge) were freeze dried, grounded and spiked with ¹³C-labeled internal PCDD/F standards prior to extraction. For Soxhlet extraction 200 ml toluene was used and the extraction time was 24 h. The ASE extractions were carried out with a Dionex ASE 200 Accelerated Solvent Extractor and toluene as solvent. The extraction temperature was 175°C/200°C at a pressure of 14 MPa. The static extraction time was 10 minutes per cycle. At minima 2 cycles were performed for each sample.

The clean up of the samples and the following analysis with HRGC/HRMS are described elsewhere [2].

Results and Discussion

To determine the exact amount of the analytes in a sample, the extraction method must be evaluated for completeness [3]. In table 1 the spiked soil and sewage sludge sample were extracted by ASE, first performing 2 static cycles and then re-extracting them with another two cycles. The first two extracts were combined, while the next two were analysed separately. For the soil the extraction rates of the different PCDD/F congeners were greater than 99% after the first two cycles. Thus, for the matrix soil, a complete extraction is achieved after two static cycles. In the case of the sewage sludge, in the third extraction eluate up to 20.8 % of certain PCDD/F congeners

were remaining. Very interesting to see is the difference in extraction rates between the native compounds and the labeled standards. For the native congeners only at maximum 3.8 % were found in the third extraction, whereas the labeled standards remained in much higher amounts. If the extraction was finished after 2 cycles, it would be incomplete and due to the different extraction rates of the standards and the native compounds the amounts would be overestimated. Therefore, at least 3 static cycles were needed to extract this sewage sludge.

Table 1: Extraction rates (%) of a soil and a sewage sludge using ASE, each extraction represents a 10 min static cycle

	Soil				Sewage sludge					
	1.+2. extraction		3.+4. extraction		1.+2. extraction		3. extraction		4. extraction	
	labeled	native	labeled	native	labeled	native	labeled	native	labeled	native
2,3,7,8-TCDD	99.7	100	0.3	0	79.3	100	18.9	0	1.8	0
1,2,3,7,8-PCDD	100	100	0	0	81.3	100	17.4	0	1.3	0
1,2,3,4,7,8-HxCDD	100	100	0	0	80.8	100	18.1	0	1.1	0
1,2,3,6,7,8-HxCDD	99.9	100	0.1	0	80.3	97.8	18.5	2.2	1.2	0
1,2,3,7,8,9-HxCDD	100	100	0	0	80.5	99.2	18.3	0.8	1.2	0
1,2,3,4,6,7,8-HpCDD	99.9	100	0.1	0	78.4	97.0	19.7	2.7	1.9	0.3
OCDD	100	100	0	0	83.7	97.6	14.9	2.1	1.4	0.3
2,3,7,8-TCDF	98.7	100	1.3	0	80.4	96.2	17.7	2.1	1.9	1.7
1,2,3,7,8-PCDF	99.6	100	0.4	0	81.2	96.7	17.2	2.2	1.6	1.1
2,3,4,7,8-PCDF	99.7	100	0.3	0	81.3	97.6	17.4	1.7	1.3	0.7
1,2,3,4,7,8-HxCDF	99.9	100	0.1	0	81.3	97.6	17.4	2.2	1.3	0.2
1,2,3,6,7,8-HxCDF	99.9	100	0.1	0	80.4	98.1	18.1	1.4	1.5	0.5
1,2,3,7,8,9-HxCDF	99.9	100	0.1	0	78.7	-	19.4	-	1.9	-
2,3,4,6,7,8-HxCDF	99.9	100	0.1	0	77.3	95.9	20.8	3.8	1.9	0.3
1,2,3,4,6,7,8-HpCDF	99.4	100	0.6	0	79.1	98.7	19.3	1.2	1.6	0.1
1,2,3,4,7,8,9-HpCDF	99.8	100	0.2	0	80.6	100	17.4	0	2.0	0
OCDF	100	100	0	0	94.0	99.7	5.0	0.3	1.0	0

To investigate the reason of the different extraction rates between the labeled standard and the native congeners of the sewage sludge in table 1, a second experiment was performed, where the standard was spiked not on the top of the sample or rather the top of the extraction cell, but on the SiO₂ layer (figure 1).

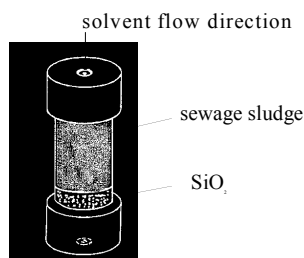


Figure 1: Extraction cell filled with sewage sludge and SiO₂

The result of this experiment showed an extraction rate of about 99% after the first two cycles. This suggests that there is nearly no homogenization of the solvent during the static extraction step. The compounds only seem to be solved and then rinsed out of the cell. If now the standard is spiked on the top of the extraction cell, it has to be forwarded through the whole sewage sludge layer. Here adsorption effects could occur which hold back the analytes. Especially in the case of the lipophilic PCDD/F which have to pass the hydrophobic sludge matrix.

To compare the ASE with Soxhlet extraction with regard to the amount of PCDD/F, we analysed different matrices with both extraction methods [4]. The results are shown in table 2. As could be seen, there are no obvious differences in the amounts. All are in the range of analytical variation.

Table 2: Comparison of ASE and Soxhlet extraction of different matrices, results are listed in ng I-TE/kg

	ASE	Soxhlet
sewage sludge	27.9	34.4
soil	151.5	133.2
lake sediment I	19.9	20.9
lake sediment II	93.3	100.2

But not in all cases we got corresponding results between Soxhlet and ASE. Due to the elevated temperature and pressure, the extraction efficiency of the ASE is higher when the analytes are strongly adsorbed to the matrix or even are enclosed. In 1997 the german federal environment office performed an interlaboratory comparison study in the analysis of PCDD/F of two soils. There, the results of the laboratories who used ASE were up to 100% higher than those of Soxhlet extraction [5].

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