

# Parallel Pressurized Solvent Extraction of PCDDs/Fs and PFCs from Soil and Sludge Samples



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## Abstract

The efficiency of pressurized solvent extraction (PSE) with Büchi's new SpeedExtractor E-916 was examined for the extraction of dioxins/furans (PCDDs/Fs) and perfluorinated compounds (PFCs) from soil and sewage sludge samples. For this, the samples were extracted with the SpeedExtractor E-916 and the ASE<sup>®</sup> 200 (Dionex) and the extracts were analyzed by gas and liquid chromatography, respectively. The results obtained with both instruments were comparable. Both instruments delivered high recoveries and high reproducibility and used small amounts of solvent. But in terms of speed the SpeedExtractor E-916 has more advantages than the ASE<sup>®</sup> 200, due to its parallel set-up.

## Introduction

PCDDs/Fs and PFOS of the PFC family are persistent organic pollutants (POPs) reported on the black list of the Stockholm Convention<sup>[1]</sup> and they are therefore monitored globally. Soxhlet is the classical method for the extraction of POPs. However, PSE has emerged as an alternative to Soxhlet and gained U.S. EPA approval (U.S. EPA method 3545)<sup>[2]</sup>. The Büchi's new SpeedExtractor E-916 is a parallel PSE system especially designed for environmental analysis. Its unique design enables extraction with high speed and prevents cross contamination. The purpose of this study was to determine the levels of PCDDs/Fs and PFCs in soil and sewage sludge samples and to compare the efficiency of the new Büchi's SpeedExtractor E-916 with the ASE<sup>®</sup> 200 (Dionex).



Fig. 1: SpeedExtractor E-916

## Materials and Methods

PCDDs/Fs were extracted from soil samples and PFCs were extracted from soil and sewage sludge samples using the SpeedExtractor E-916 and the ASE<sup>®</sup> 200.

Tab. 1: Extraction parameters for the PCDDs/Fs

PCDDs/Fs in soil		
	SpeedExtractor E-916	ASE <sup>®</sup>
Solvent	Toluene	Toluene
Temperature	130°C	130°C
Pressure	100 bar	100 bar
Cells	10 ml	10 ml
Cycles	4	3
Hold	2 min	15 min
Discharge	2 min	-
Flush with solvent	2 min	40%
Flush with gas	2 min	140 s

**Determination of PCDDs/Fs in soil:** Soil samples (approx. 1 g) were mixed with sand and filled into 10 ml extraction cells. <sup>13</sup>C-labeled PCDDs/Fs standards were added, and the extraction was performed according to the parameters given in Table 1. The extracts were cleaned on silica gel (basified and acidified silica), alumina (alumina B Super I for dioxin analysis), and the residue was slowly concentrated to 15 µl. The determination of PCDDs/Fs was performed by GC/HRMS. A HP 5890 high resolution gas chromatograph was coupled with a MAT-90 Finnigan mass spectrometer operated in multiple ion detection mode (MID). The samples were separated on a DB-5MS column from J&W Scientific (60 m x 0.25 mm x 0.25 µm). Concentrations of PCDDs/Fs were determined by the isotopic dilution method.

Tab. 2: Extraction parameters for the PFCs

PFCs in soil and sewage sludge		
	SpeedExtractor E-916	ASE <sup>®</sup>
Solvent	Methanol	Methanol
Temperature	80°C	100°C
Pressure	100 bar	100 bar
Cells	40 ml	33 ml
Cycles	4	3
Hold	5/20/20/20 min	15 min
Discharge	2 min	-
Flush with solvent	2 min	40%
Flush with gas	3 min	60 s

**Determination of PFCs in soil and sewage sludge:** Approx. 1 g of soil or sewage sludge samples were mixed with sand and filled into the extraction cells. After addition of <sup>13</sup>C-labeled (PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFOS) and <sup>18</sup>O-labeled (PFHxS) internal standards samples were extracted according to the conditions given in Table 2. Extracts were purified by SPE using Oasis WAX cartridges (Waters). Cleaned extracts were finally subjected to LC-ESI-MS/MS analysis using a Waters LCQuattro mass spectrometer. Chromatographic separation was performed on a Phenomenex LUNA (PFP). Quantification was done by the isotopic dilution method.

## Results

**Extraction of PCDDs/Fs from soil samples:** Extracts both from the SpeedExtractor E-916 and the ASE<sup>®</sup> 200 were characterized by good recoveries of internal standards in the range from 80-110 %. Values were closely comparable (Figure 2). Relative standard deviations of three SpeedExtractor extractions were calculated for all 17 2,3,7,8-substituted PCDDs/Fs and ranged from 2 to 29%. The relative standard deviation of the WHO-TEQ<sup>[3]</sup> was calculated to be 6%. Additionally, no cross contamination was recognized in the SpeedExtractor E-916 extraction cells filled with pre-washed silica and extracted in parallel with a highly contaminated soil sample. In terms of solvent consumption both instruments are equivalent. But in terms of processing time, the SpeedExtractor E-916 has more advantages than the ASE<sup>®</sup> 200, due to the parallel extraction of 6 samples.

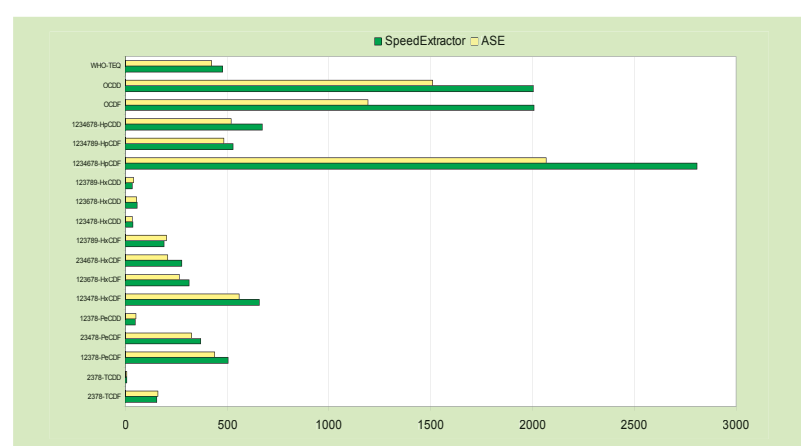


Fig. 2: Concentration of PCDDs/Fs in pg/g in a contaminated soil sample (mean values: E-916: n=3; ASE: n=2)

**Extraction of PFCs from soil and sewage sludge:** Analytical results of three samples are displayed on Table 3 and are based on two extractions with the SpeedExtractor E-916 and one extraction with the ASE<sup>®</sup> 200. The results were very similar. The amounts of solvent used by both instruments were also equivalent but, again, the SpeedExtractor E-916 proved to be much faster than the ASE<sup>®</sup> 200, due to the parallel extraction technique.

Tab. 3: Concentration of PFCs in ppm

		ppm					
		PFTeA	PFPeA	PFHxA	PFHpA	PFOA	PFNA
Soil 1	PSE	< 0.5	< 0.5	< 0.5	< 0.5	2.8	0.2
	ASE <sup>®</sup>	< 0.5	< 0.5	< 0.5	< 0.5	1.7	0.2
Soil 2	PSE	< 0.5	< 0.5	< 0.5	< 0.5	2.1	< 0.5
	ASE <sup>®</sup>	< 0.5	< 0.5	< 0.5	< 0.5	1.5	< 0.5
Sludge	PSE	< 0.5	< 0.5	2.2	1.7	17.7	0.6
	ASE <sup>®</sup>	< 0.5	< 0.5	2.5	1.0	15.5	0.9

		ppm					
		PFDA	PFUnA	PFDoA	PFHxS	PFOS	PFDS
Soil 1	PSE	0.2	1.2	< 0.5	< 0.5	0.4	0.5
	ASE <sup>®</sup>	0.2	< 0.5	2.3	< 0.5	0.4	< 0.5
Soil 2	PSE	0.2	1.4	< 0.5	< 0.5	0.5	< 0.5
	ASE <sup>®</sup>	0.2	< 0.5	0.7	< 0.5	0.6	< 0.5
Sludge	PSE	8.0	3.2	9.5	< 0.5	1065	29.3
	ASE <sup>®</sup>	7.4	2.6	4.8	< 0.5	1043	24.8

## Conclusion

The concentration values obtained with the SpeedExtractor E-916 and the ASE<sup>®</sup> 200 were comparable. Both instruments delivered high recoveries and reproducibility and used little amounts of solvent. However this study shows that the SpeedExtractor E-916 is better than the ASE<sup>®</sup> 200 in terms of sample processing time, due to its parallel extraction set-up.

## References

- [1] Stockholm Convention on POPs, COP4, 4-9 May 2009
- [2] U.S. EPA method 3545: Pressurized Fluid Extraction (PFE)
- [3] World Health Organization-Toxic Equivalent:  
The WHO-TEQ weighs the toxicity of the less toxic compounds as fractions of the toxicity of the most toxic TCDD. Each compound is attributed a specific Toxicity Equivalency Factor (TEF), which indicates the degree of toxicity compared to 2,3,7,8-TCDD

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