# PARALLEL PRESSURIZED SOLVENT EXTRACTION OF PCDD/PCDF, PBDE, AND PFC FROM SOIL, SLUDGE, AND SEDIMENT SAMPLES

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#### Abstract

The efficacy of pressurized solvent extraction with Buchi's new SpeedExtractor was examined for the extraction of dioxins/furans (PCDDs/PCDFs), polybrominated diphenyl ethers (PBDEs), and perfluorinated compounds (PFCs) from different environmental matrices: PCDDs/PCDFs from soil samples, PFCs from soil and sewage sludge, and PBDEs from lake sediments.

The results of the extraction of PCDDs/PCDFs and PFCs were compared to the results obtained with the Dionex Accelerated Solvent Extractor (ASE<sup>®</sup>) and show very similar results. The isolation of PBDEs was performed with certified sediments from the Netherlands Institute for Fishery Research (RIVO). High recovery rates were found from the extraction of PBDEs of the certified sediment.

Based on these results, there is strong evidence for the equivalence of both PFE instruments with respect to the extraction of several POPs from environmental solid matrices.

## Introduction

The extraction process for the determination of different persistent organic pollutants (POPs) like PCDDs/PCDFs or PBDEs in solid samples is normally time and solvent consuming, especially if the classical Soxhlet method is applied. Therefore, pressurized fluid extraction (PFE) has established itself in environmental analysis during recent years and has gained U.S. EPA approval (EPA3545<sup>1</sup>). At elevated pressure and temperature conditions, analytes diffuse from the matrix to the extracting solvent more quickly due to higher analyte solubility and improved penetration of the sample matrix. The elevated pressure ensures that the solvent remains in a liquid state and that the extraction cell is quickly filled with fresh solvent.

The EPA3545 method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, PCBs, PCDDs/PCDFs, and diesel range organics from soils, clays, sediments, sludges, and waste solids, which can then be determined by different chromatographic procedures<sup>1</sup>. In contrast, the extraction of PFC from solid environmental samples is not harmonized yet and thus both, liquid-solid extractions (LSE) and PFE, were examined in recent reviews<sup>2,3</sup>. Pressurised liquid extraction of PFC has the advantage of automatic processing. However, special attention is necessary to ensure that Teflon<sup>®</sup> parts are removed from the PFE instrument prior to use in order to reduce PFOA blank values.

With Buchi's new SpeedExtractor, PFE can be applied to four or six samples in parallel (depending on the instrument layout), whereas with the  $ASE^{\circledast}$  samples are extracted consecutively one after another. As a result, a batch of six samples can be extracted in one sixth of the time. However, the application of this new PFE instrument for the extraction of persistent organic pollutants POP has not been examined yet.

The purpose of this study was to investigate the efficacy of parallel pressurized solvent extraction with the SpeedExtractor. For this, the isolation of various POPs was performed in different solid sample matrices: PCDDs/PCDFs were extracted from contaminated soil samples and the concentrations were compared to the results obtained with the ASE<sup>®</sup>. Extractions of PFCs from soil and sludge were performed with the SpeedExtractor and the ASE<sup>®</sup>. PBDEs were isolated from the Certified Reference Material BROC-02, a

sediment sample collected from a chemical factory in the Netherlands producing brominated flame retardants (BFR).

### Materials and Methods

*Instrumentation*: Parallel pressurized solvent extraction of PCDDs/PCDFs, and PFCs was performed with the SpeedExtractor E-916 equipped with 6 extraction cells. PBDEs were isolated with the SpeedExtractor E-914 containing 4 extraction cells. An illustration of the parallel extraction concept of the E-916 is shown in Figure 1. Sequential pressurized solvent extraction of PCDDs/PCDFs, and PFCs was conducted with the Dionex Accelerated Solvent Extractor, ASE 200.

The analysis of PBDE in sediments was carried out at the CNR Water Research Institute, Via della Mornera, 25, 20047 Brugherio, Italy. The PCDD/PCDF and PFT analysis in soil and sewage sludge was done at the Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Str. 35, 85354 Freising, Germany.



Fig. 1: Illustration of the parallel extraction system E-916

Determination of PCDDs/PCDFs in soil: Soil samples (about 1 g) were mixed with sand and filled into 10 ml extraction cells. <sup>13</sup>C labelled PCDD/PCDF standards (LGC-Promochem, Germany) were added, and the extraction was performed according to the parameters given in Table 1. The extracts were cleaned by flash chromatography on silica gel (basified and acidified silica) and alumina (alumina B Super I for dioxin analysis). After elution, the residue was slowly concentrated to 15  $\mu$ l under a gentle stream of nitrogen. The determination of PCDDs and PCDFs 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  $\mu$ m). Concentrations of PCDDs and PCDFs were determined by the isotopic dilution method.

*Determination of PBDEs in sediment*: The extraction cells were filled with sediment samples (about 2 g), mixed with sand. BB-209 (AccuStandards) was used as internal standard and the extraction process was performed according to the parameters presented in Table 1.

The extract was concentrated and transferred onto a solid-phase extraction cartridge filled (from the top) with 0.5 g acidified silica (30% concentrated sulfuric acid, w/w), 0.5 g potassium silicate, 1 g acidified silica (30% concentrated sulfuric acid, w/w), and 0.5 g activated Florisil. The elution was done with 10 ml of

hexane/dichloromethane (1:1, v/v). The eluate was concentrated to near dryness and resolubilized in 1 ml of isooctane. The final extract was concentrated to 0.10 ml via a gentle nitrogen stream.

The determination of tri- to hepta-BDEs was performed by GC/MS. A Trace GC 2000 gas chromatograph was equipped with a PTV injector and coupled with a PolarisQ Ion-Trap mass spectrometer (Thermo Electron, Austin, Texas). 2 µl aliquots were injected into the GC/MS under the following conditions: Column 18 m, 0.18 mm ID (Rxi-5MS, Restek, Bellefonte, PA, USA); injection port: 60 °C for 6 s, 5 °C/s to 320 °C, hold 2 min; oven: 125 °C for 0.5 min; 20 °C/min to 320 °C, hold 0.5 min; carrier gas helium at 0.6 ml/min; injection flow 0.6 ml/min; transfer flow 1.2 ml/min. Samples were analyzed using MS/MS acquisition mode: transfer line: 300 °C, damping gas at 1 ml/min, ion source: 260 °C.

PCDD/PCDF in soil	
SpeedExtractor	ASE®
Toluene	Toluene
130 °C	130 °C
100 bar	100 bar
10 ml	10 ml
4	3 (40% flush)
5/10/10/10 min (hold time)	15 min
2 min	
2 min solvent / 2 min $N_2$	140 s N <sub>2</sub>
<b>PBDE</b> in sediments	
SpeedExtractor	ASE®
<i>n</i> -hexane/acetone $(3/1)$	-
100 °C	-
100 bar	-
40 ml	-
1	-
10 min (hold time)	-
2 min	-
1 min solvent / 2 min $N_2$	-
PFC in soil and sewage sludge	
SpeedExtractor	ASE®
Methanol	Methanol
80°C	100°C
100 bar	100 bar
40 ml	33 ml
4	3 (40% flush)
5/20/20/20 min	15 min
(hold time)	
2 min	
2 min solvent/ 3 min gas	1 min N <sub>2</sub>
	PCDD/PCDF in soilSpeedExtractorToluene130 °C100 bar10 ml4 $5/10/10/10$ min (hold time)2 min2 min solvent / 2 min N2PBDE in sedimentsSpeedExtractor <i>n</i> -hexane/acetone (3/1)100 °C100 bar40 ml110 min (hold time)2 min1 min solvent / 2 min N2PFC in soil and sewage sludgeSpeedExtractorMethanol80°C100 bar40 ml45/20/20/20 min(hold time)2 min2 min solvent/ 3 min gas

Table 1: Extraction parameters chosen for parallel and sequential pressurized fluid extraction

The determination of BDE-209 was performed by GC/ECD equipped with a cold on-column injector. 1  $\mu$ l aliquots was injected into the GC/ECD under the following conditions: Column 7 m, 0.32 mm ID (Rtx-5MS, Restek, Bellefonte, PA, USA) coupled to a retention gap 0.5 m, 0.53 mm ID (DB-1MS, J&W Scientific, Palo Alto, CA, USA); oven: 80 °C for 1 min; 40 °C/min to 285 °C, hold 12 min; carrier gas helium at 2.5 ml/min. Concentrations of BDE-28/33, 47, 49, 66, 85, 99, 100, 153, 154, and 183 were determined by external calibration using standard mixtures EO-5099 (Cambridge Isotope Laboratories, Andover, MS, USA) and BDE-

CM (AccuStandards, New Haven, CT, USA). Decabromobiphenyl (BB-209, AccuStandards) was used as internal standard for BDE-209.

*Determination of PFC in soil and sewage sludge*: About 1 g of soil or sewage samples were mixed with silica and filled into extractions cells. After addition of <sup>13</sup>C-labelled (PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFOS) an <sup>18</sup>O-labelled (PFHxS) internal standards (Wellington) samples were extracted according to conditions given in Table 1. It should be noted that in both instruments Teflon<sup>®</sup> tubes were replaced by equivalent items made from stainless steel.

Extracts were purified by SPE using Waters OASIS Wax cartridges. Details of this procedure have been reported elsewhere [4]. 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) using a mixture of aqueous ammonium acetate and methanol. Quantification was done by the isotope dilution method using the above mentioned mass labelled internal standards.

#### **Results and Discussion**

*Extraction of PCDD/F from soil samples:* Extracts both from the SpeedExtractor and the ASE<sup>®</sup> are characterized by good recoveries of internal standards in the range from 80-110 %. Figure 2 shows absolute concentrations measured in both extracts in a highly contaminated soil sample. Values are closely comparable and indicate an equivalence of both PFE instruments with respect to PCDD/F extraction from soil samples. Relative standard deviations of three SpeedExtractor analyses were calculated for all 17 2,3,7,8-substituted PCDD/F and range from 3-25%. The relative standard deviation of the WHO-TEQ was 7%.

Additionally, no cross contamination was recognized in the SpeedExtractor extraction cells filled with prewashed silica and extracted in parallel with a highly contaminated soil sample.



Figure 2: Comparison of PCDD/F concentrations (arithmetic means) in a contaminated soil sample obtained in extracts of both PFE instruments,  $ASE^{\text{\ensuremath{\mathbb{R}}}}$  and SpeedExtractor.  $ASE^{\text{\ensuremath{\mathbb{R}}}}$  extractions were performed twice, analyses with the SpeedExtractor were performed three times

*Extraction of PBDEs from sediment samples:* The concentrations obtained by extraction with the SpeedExtractor are comparable to the certified values (Figure 3). All congeners show similar values. The results also show good reproducibility; the relative standard deviations (RSD) are below 15% for all congeners except BD-28/33 with a RSD of 23%. The concentration of the congener BDE-209 is 1207 mg/kg with a relative RSD of 8%, comparable to the certified value of 1197 mg/kg. The recoveries of the <sup>13</sup>C labelled internal standards are good for the analyzed congeners, ranging from 69-97%, therefore meeting the acceptance criteria of the US EPA method 1614 which describes the analysis of PBDE in water, soil, sediment, and tissue.



Figure 3: Comparison of PBDE concentrations (arithmetic means) in a certified reference material obtained by PSE with the corresponding certified values

Table 2: Comparison of PFC concentrations in two soil samples and one sewage sludge sample obtained with	1
two different PFE instruments (SpeedExtractor and ASE <sup>®</sup> )	

		mg/kg					
		PFTeA	PFPeA	PFHxA	PFHpA	PFOA	PFNA
Soil 1	SpeedExtractor	< 0.5	< 0.5	< 0.5	< 0.5	2.8	0.2
	ASE®	< 0.5	< 0.5	< 0.5	< 0.5	1.7	0.2
Soil 2	SpeedExtractor	< 0.5	< 0.5	< 0.5	< 0.5	2.1	< 0.5
	ASE®	< 0.5	< 0.5	< 0.5	< 0.5	1.5	< 0.5
Sewage sludge	SpeedExtractor	< 0.5	< 0.5	2.2	1.7	17.7	0.6
	ASE®	< 0.5	< 0.5	2.5	1.0	15.5	0.9
		mg/kg					
				mg	/kg		
		PFDA	PFUnA	mg/ PFDoA	/kg PFHxS	PFOS	PFDS
Soil 1	SpeedExtractor	PFDA 0.2	PFUnA 1.2	mg/ PFDoA < 0.5	/kg PFHxS < 0.5	PFOS 0.4	PFDS 0.5
Soil 1	SpeedExtractor ASE <sup>®</sup>	PFDA 0.2 0.2	PFUnA 1.2 < 0.5	mg/ PFDoA < 0.5 2.3	/kg PFHxS < 0.5 < 0.5	PFOS 0.4 0.4	PFDS 0.5 < 0.5
Soil 1 Soil 2	SpeedExtractor ASE <sup>®</sup> SpeedExtractor	PFDA 0.2 0.2 0.2	PFUnA 1.2 < 0.5 1.4	mg, PFDoA < 0.5 2.3 < 0.5	/kg PFHxS < 0.5 < 0.5 < 0.5	PFOS 0.4 0.4 0.5	PFDS 0.5 < 0.5 < 0.5
Soil 1 Soil 2	SpeedExtractor ASE <sup>®</sup> SpeedExtractor ASE <sup>®</sup>	PFDA 0.2 0.2 0.2 0.2 0.2	PFUnA 1.2 < 0.5 1.4 < 0.5	mg/ PFDoA < 0.5 2.3 < 0.5 0.7	/kg PFHxS < 0.5 < 0.5 < 0.5 < 0.5 < 0.5	PFOS 0.4 0.4 0.5 0.6	PFDS 0.5 < 0.5 < 0.5 < 0.5 < 0.5
Soil 1 Soil 2 Sewage sludge	SpeedExtractor ASE <sup>®</sup> SpeedExtractor ASE <sup>®</sup> SpeedExtractor	PFDA 0.2 0.2 0.2 0.2 0.2 8.0	PFUnA 1.2 < 0.5 1.4 < 0.5 3.2	mg, PFDoA < 0.5 2.3 < 0.5 0.7 9.5	/kg PFHxS < 0.5 < 0.5 < 0.5 < 0.5 < 0.5 < 0.5	PFOS 0.4 0.4 0.5 0.6 1065.4	PFDS 0.5 < 0.5 < 0.5 < 0.5 < 0.5 29.3

*Extraction of PFCs from soil and sewage sludge:* Analytical results of three samples are displayed in Table 2 and are based on two analyses by SpeedExtractor and one analysis by  $ASE^{\text{(B)}}$ . It is apparent that the results obtained by the 2 different PFE instruments are very similar. Based on this data, it is safe to say that both PFE instruments perform similarly well in the extraction of PFC from solid environmental matrices.

# Acknowledgements

We greatly thank the analytical team of the Fraunhofer Institute for Process Engineering and Packaging IVV in Germany for helping us determine the different POPs. We would also like to thank C. Roscioli and L. Guzelle from the CNR Water Research Institute in Italy for their substantial effort to test the efficacy of the SpeedExtractor.

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