

## COMPARISON OF SFE WITH SOXHLET AND SONICATION FOR THE DETERMINATION OF PCDD/PCDF IN SOIL SAMPLES

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### Introduction

Liquid-based extraction techniques such as Soxhlet and ultra sonication have been used to isolate target analytes from sample matrix for over 90 years (1). Because these extraction methods take a lot of time and consume hazardous organic solvents, the need for a more ecological technique is evident. Supercritical fluid extraction (SFE) is one new promising technique, which not only reduces the consumption of solvents but also offers effective and fast extraction.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are toxic compounds which are formed as by-products of several different combustion and industrial processes. The background levels of PCDD/PCDFs are found all over the world and there is also some certain areas that are highly contaminated. SFE offers a good alternative for a fast and more economical analysis of these sites.

The objective of this study was to investigate, whether the previously developed SFE method (2) is capable to replace the conventional extraction methods, Soxhlet and ultra sonication, in common laboratory use.

### Materials and Methods

*Samples.* Three soil samples that contain different levels of PCDD/PCDFs (A, B and C as low, medium and high level samples, respectively) were selected in this study. The samples were oven-dried (50 °C) over night before the extractions. The dried samples were grinded by hands and large particles were removed before taking the subsamples. In all experiments sample size was 1 g, and all samples were extracted as 5 replicates by SFE and as triplicates by Soxhlet and sonication. After extraction, the extract of soil A was concentrated as a whole, whereas extracts B and C were diluted to 1/10 and 1/20, respectively.

*Standards.* An internal standard solution that contained <sup>13</sup>C-labelled PCDD/PCDFs (115 pg/congener) was added to the soil A before extraction and to the dilutions of extracts B and C after extraction. The recovery standards, <sup>13</sup>C-labelled 1234-TCDD and 123789-HxCDD (40 pg/congener), were added to the samples before the analysis.

*SFE.* An extraction cell (10 ml) was packed with a layer of activated Na<sub>2</sub>SO<sub>4</sub> (5 g; Merck), the soil sample (1 g), Al<sub>2</sub>O<sub>3</sub> (2 g; Merck 101078) and finally a layer of activated Na<sub>2</sub>SO<sub>4</sub> (2 g; Merck). Samples were extracted with a Suprex Autoprep 44<sup>TM</sup> instrument, which contains an automated extraction module, a solid phase adsorption trap and a modifier pump. Extractions were carried out with a SFE grade (5.2) carbon dioxide (AGA gases). SFE conditions were the following: chamber temperature 100 °C, pressure 400 atm, static extraction time 10 min, dynamic time 60 min and the flow rate of CO<sub>2</sub> 3 ml/min. The temperatures of restrictor and trap were 45 °C and 40 °C, respectively, and the flow rate of eluent solvents 2 ml/min. The solid phase trap was filled with a mixture (1:5 w/w) of activated carbon (Carboback C, 60/80 mesh, Supelco, Bellefonte, USA) and Celite 545 (0.01-0.04 mm, E. Merck, Darmstadt, Germany). The total amount of adsorb-

ent in the trap was 0.38 g. After extraction, the trap was flushed first with hexane (4 ml) to elute impurities and then with toluene (10 ml) to collect PCDD/PCDFs. To clean and recondition the system for the next sample, the trap and lines were flushed with additional fractions of xylene (5 ml) and hexane (5 ml). The recovery standard solution was added to the toluene fraction which was concentrated and analysed.

*Soxhlet and sonication.* Soxhlet extraction was carried out with 300 ml of toluene for at least 18 hours. Sonication was performed by extracting each sample three times with 10 ml toluene for 30 min at a room temperature. Following sonication extraction, the solvent was decanted and the extracts were combined. Both Soxhlet and sonication extracts were cleaned up by column chromatography using silica gel, basic alumina and activated carbon columns before analyses. The clean-up procedure has been presented in details previously (3).

*Analysis.* The samples were analysed with a high resolution gas chromatograph (Hewlett Packard 5890, column DB-Dioxin: 60 m, 0.25 mm, 0.15  $\mu$ m) which was coupled to a high resolution mass spectrometer (magnetic sector instrument VG 70-250SE). Samples were splitlessly injected at 270 °C, and helium (4.6 AGA Gas) at a flow rate of 1 ml/min was used as a carrier gas.

### Results and Discussion

The results obtained in this study are mainly considered as TCDD equivalents (TEQ), which are derived using the WHO toxic equivalent factors (TEFs) for human (4). TEQ-value can be used as a measure to predict the needed remedial action of a certain soil site. A proposed threshold value for clean soil is 20 pg/g TEQ dry weight (dw) and a limit value for contaminated soil, which needs to be cleaned, is 500 pg/g TEQ (dw) in Finland (5).

The results of SFE compared to Soxhlet and sonication were at the same level for all samples. Soxhlet gave the highest results for low level sample A (Figure 1A), whereas the SFE results for medium and high level samples (B and C, respectively) were highest (Figures 1B and 2).

The standard deviation (SD) of sample C was comparatively high (Table 1). This is most likely due to the inhomogeneity of the sample. The high SD of 1234678-HpCDD and OCDD in the results of Soxhlet and sonication extractions is probably due to laboratory contamination. The concentrations and the TEF-values for these congeners, however, are so small that this does not effect significantly to the TEQ values.

Overall, the results and reproducibility of SFE corresponded well with the Soxhlet and sonication results. Furthermore, the standard deviations were lower in all extracted SFE samples than those of the conventional extractions.

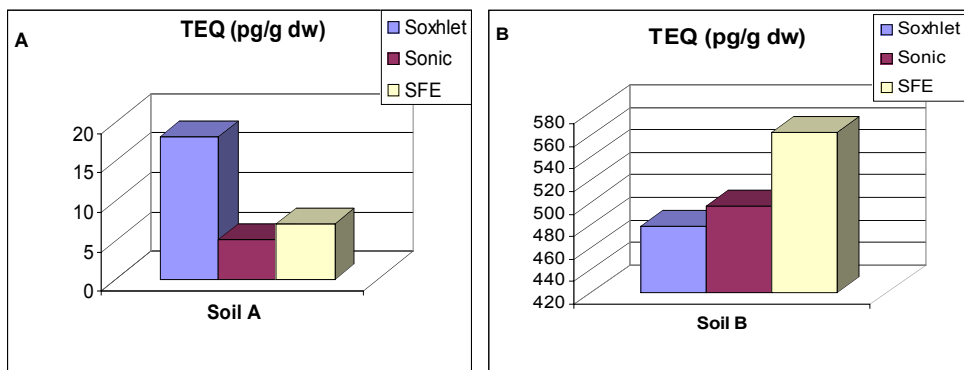


Figure 1. TEQ values (pg/g dw) of soil samples A (low level) and B (medium level) from Soxhlet, sonication and SFE.

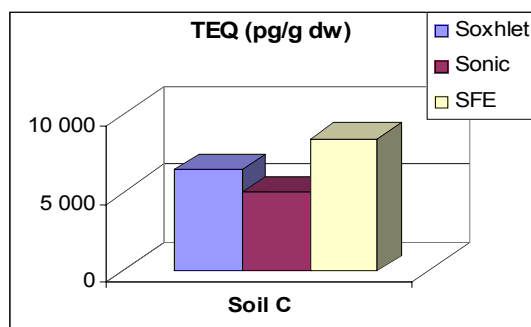


Figure 2. TEQ values (pg/g dw) of soil sample C (high level) from Soxhlet, sonication and SFE.

Table 1. The Soxhlet, sonication and SFE results of toxic PCDDs/PCDFs (pg/g) from sample C (SD= standard deviation)\*.

	Soxhlet (n=3)		Sonication (n=3)		SFE (n=5)	
	Mean	SD	Mean	SD	Mean	SD
12378-PeCDF	51	19	33	11	35	7
23478-PeCDF	140	17	120	47	139	11
234678-HxCDF	701	229	379	111	590	112
123678-HxCDD	191	80	153	83	171	38
123789-HxCDD	37	17	50	26	51	14
1234678-HpCDF	608 000	215 669	479 333	95 845	813 400	178 005
1234789-HpCDF	1 194	240	1 402	402	1 500	242
1234678-HpCDD	545	472	1 467	543	701	134
OCDF	742 000	156 758	643 667	172 732	864 000	173 924
OCDD	1 880	3 256	8 460	5 341	1 227	263
Total	1 356 667	376 475	1 138 746	264 421	1 686 838	349 634
TEQ	7 173	2 132	5 007	1 020	8 395	1 819

\* Levels of 2378-TCDD, 2378-TCDF, 12378-PeCDD, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF and 123478-HxCDD were <20 pg/g.

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