DEVELOPMENT OF A SOLID PHASE CARBON TRAP IN SUPERCRITICAL FLUID EXTRACTION FOR DETERMINATION OF PCDDs AND PCDFs IN SOIL SAMPLES

M. Mannila[1], J. Koistinen[1] and T. Vartiainen[1,2]

[1] National Public Health Institute, Division of Environmental Health
P.O. Box 95, FIN-70701 Kuopio, Finland
[2] Department of Environmental Sciences, University of Kuopio, P.O. Box 1627, FIN-70211 Kuopio, Finland

Introduction

Supercritical Fluid Extraction (SFE) is an efficient, selective and fast extraction method reported to be a comparative method to the traditional sample preparing methods. In off-line supercritical fluid extraction the efficient trapping system is important for developing a quantitative extraction method. There are three different types of trapping systems which are commonly used for dynamic SFE: a liquid trap, a cryogenically cooled solid surface and a solid phase adsorbent (1). The main advantage of solid trapping seems to be the possibility of using high flow rates while keeping good collection efficiency and the possibility to do fractionation from impurities by different solvents.

The aim of this study was to develop an effective solid phase adsorbent trap for determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in soil samples. Our main objectives were to optimize the consumption of eluent solvents and to obtain a clean extract for direct analysis after concentration. Because the levels of the toxic PCDDs and PCDFs are usually one to three orders of magnitudes lower than those of polychlorinated biphenyls (PCB) and pesticides, it is beneficial to separate PCDDs/PCDFs from other extractable compounds before quantitative analysis. Activated carbon has been reported to be an effective adsorption material to separate PCDDs/PCDFs from PCBs in SFE (2).

Materials and Methods

The SFE instrument used for this work was a Suprex AutoPrep 44™ combined with a fraction collector (AccuTrap) and a modifier pump. SFE grade carbon dioxide (99.9992 purity, Hamburg, Germany) was used as a fluid. In all experiments the SFE conditions were kept the same: extraction chamber temperature 100 °C, pressure 400 atm, flow rate of CO_2 3 ml/min, static extraction time 10 min and dynamic time 60 min. The temperatures of trap and restrictor were 40 °C and 45 °C, respectively. A modifier was not used in these experiments. These conditions were selected based on a preliminary study (3).

The solid phase adsorption material used in this study was an activated carbon (Carbopack C, 60/80 mesh, Supelco, Bellefonte, USA) mixed with Celite 545 (0,01-0,04 mm, E. Merck, Darmstad, Germany) as a support material. Three different configurations of carbon content were tested: the ratio of carbon/Celite was 1:25 (w/w) in trap A, 1:10 (w/w) in trap B and 1:5 (w/w) in

trap C. The solid phase trap was filled with 0.370 g of adsorbent. The aim was to find an adsorbent mixture that makes possible to separate PCBs from PCDDs/PCDFs with a minimal consumption of eluent solvents.

Tests were performed by using native and ^{13}C-labeled PCB and PCDD/PCDF standard solutions as a sample. Standard 10 ml steel extraction vessels were filled with layers of Na_2SO_4 (5 g Merck), standard solutions (150 µl) or soil spiked with ^{13}C-labeled solution (150 µl), basic Al_2O_3 (2.5 g; Merck 1097) and Na_2SO_4 (2.5 g). Na_2SO_4 and Al_2O_3 were used to fill a dead volume of the vessel. After extraction, the trap was flushed first with hexane (4 or 5 ml, Merck p.a.) to elute impurities and then with xylene (15 ml; Merck p.a.) to collect PCDDs and PCDFs. Trap and lines were flushed with hexane (5 ml) for reconditioning of the system for the next sample. Before analysis, recovery standards were added to sample: decachlorinated diphenylether for low resolution mass spectrometry (LRMS) and ^{13}C-1234-TCDD and ^{13}C-123789-HxCDD for high resolution mass spectrometry (HRMS).

Recoveries of ^{13}C-labelled PCDDs and PCDFs from trap C were monitored by spiking soil with these standards. Ten different soil were spiked. A ^{13}C-labelled PCDD/PCDF standard mixture (150 pg/congener) was added on the top of 100 mg soil layer in the extraction cell. The soil samples used in this study were contaminated with a chlorophenol formulation (KY-5) which has been used as a wood preservative. After extraction the recovery standards were added. The solid phase carbon trap (C) was eluted first with 4 ml hexane and PCDDs/PCDFs were collected in 15 ml xylene.

Analyses were performed with HRGC/LRMS and HRGC/HRMS. The LRMS instrument included a HP 5890 Series II gas chromatograph coupled to a HP 5978 mass selective detector (column HP-5: 60 m, 0.25 mm, 0.25 µm). The HRMS analyses were done with a magnetic sector instrument VG-70-250 coupled with a Hewlet Packard 5890 GC (column DB-Dioxin: 60 m, 0.25 mm, 0.15 µm). Helium (99.996 AGA Gas) at a flow rate of 1 ml/min was used as a carrier gas in both instruments. With HRMS and LRMS instruments the samples were splitlessly injected at 270 °C and 250 °C, respectively.

Results and Discussion

The recoveries of PCDDs and PCDFs observed in hexane fraction of different traps are shown in Table 1. The results of higher chlorinated PCDDs and PCDFs are not shown in this table, because these congeners were not eluted in this fraction. Because the aim was to collect impurities and PCDDs/PCDFs in different fractions, PCDDs/PCDFs should not be eluted at all in this fraction. As can be seen in Table 1, the separation power of the trap A was not good: tetra and penta chlorinated PCDDs/PCDFs were eluted in first hexane fraction. Adsorption material B worked better, but still some PCDDs/PCDFs were eluted in hexane. To overcome this problem, the activated carbon content was duplicated in the trap. Now PCDDs and PCDFs did not elute at all in hexane fraction (trap C).

When increasing the carbon content, the need to use more eluting solvent may also increase. Next step was to make sure that PCBs eluted in 4 ml hexane from trap C. In Figure 1 are shown the HRGC/LRMS chromatograms for PCBs eluted in two 2 ml hexane fractions after SFE (trap C). All PCB congeners were already eluted in first 2 ml fraction: the next 2 ml hexane fraction was clean.

Table 1. SFE analyte recovery in hexane from three different traps. The ratio of carbon/Celite was 1:25 (w/w), 1:10 (w/w) and 1:5 (w/w) in trap A, B and C, respectively. Traps A and B were eluted with 5 ml hexane and trap C with 4 ml hexane.

Analyte	Recovery % Trap A	Trap B	Trap C
2378-TCDF	89	30	-
12378-PCDF	94	3	-
23478-PCDF	68	-	-
2378-TCDD	81	15	-
12378-PCDD	96	-	-

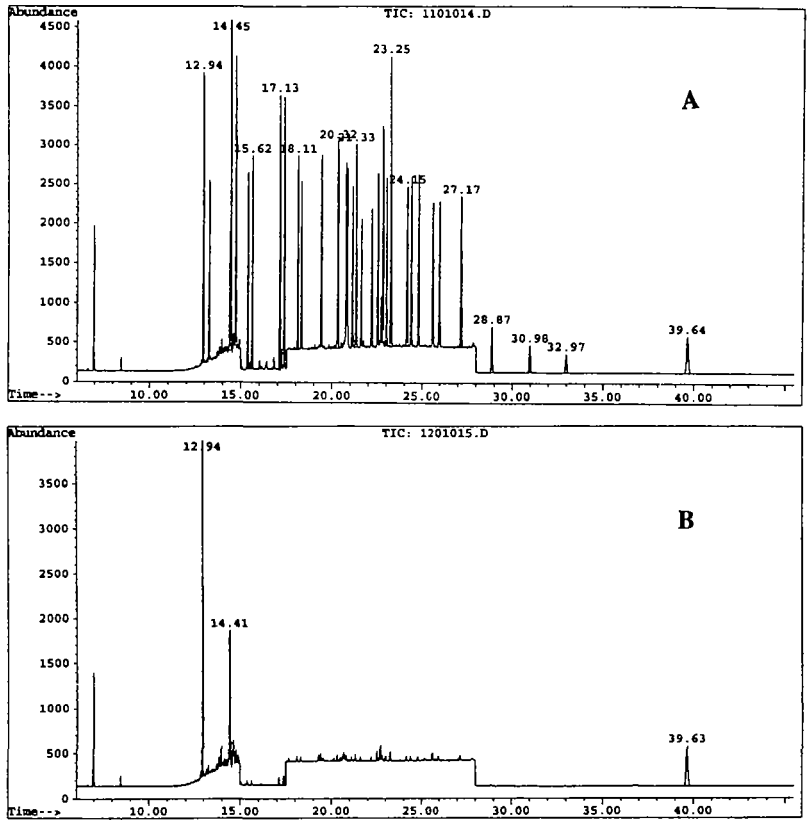

Figure 1. HRGC/LRSM chromatograms for the PCBs eluted in hexane fractions consecutively. A is the first 2 ml hexane and B is the second 2 ml hexane.

The recoveries of PCDDs/PCDFs from trap C were examined by extracting ten soil samples spiked with a ^{13}C-PCDD/PCDF standard solution. 4 ml hexane was used as a cleaning fraction and the labeled PCDDs/PCDFs were collected in xylene fraction (15 ml). As the Table 2 shows, recoveries for all except one congener were between 81-118 % in xylene. From the standard deviation values can be seen that reproducibility of this method was good, except for 1234678-HpCDF congener. The high recoveries of ^{13}C-1234678-HpCDF are most likely due to the extremelly high level of native 1234678-HpCDF in soil samples. This congener is one of the main impurities in soil contaminated with KY-5.

Comparison of the SFE and Soxhlet extractions were promising: concentrations of the toxic 2378- substituted congeners were at the same level. HRMS analyses showed that SFE extracts were clean and mass fragmentograms of PCDDs/PCDFs were similar to those of Soxhlet extracts purified by column chromatography. Only the concentrations of total penta and tetra PCDDs/PCDFs were higher in SFE extracts: other than tetra- or penta-CDDs/CDFs were also observed in their chromatograms.

Overall, the solid phase trap with high activated carbon content tested in this study worked well. Good separation power, high recoveries and reproducibility were achieved. However, the situation is more complicated when analyzing native analytes from real soil samples. Different types of soils may bind the same analyte to different extents. Most of the soil samples tested in this method were enough clean for direct analysis of toxic congeners after extraction and concentration.

Table 2. The recoveries of ^{13}C-labelled PCDDs/PCDFs from trap C (SD is a standard deviation).

Analyte	Recovery %	SD (n=10)
2378-TCDF	84	18
12378-PCDF	81	8
23478-PCDF	93	12
123478-HxCDF	114	3
123678-HxCDF	102	4
123789-HxCDF	119	5
1234678-HpCDF	187	49
1234789-HpCDF	111	7
2378-TCDD	104	13
12378-PCDD	104	6
123478-HxCDD	112	6
123678-HxCDD	90	7
OCDD	107	16

References

1. Taylor L.T. Chapter 5, p. 62-99, in Supercritical Fluid Extraction, John Wiley & Sons, New York, USA, **1996**; ISBN0-471-11990-3
2. Van Bavel B, Järemo M, Kalsson L, Lindstöm G; *Anal. Chem.* **1996**, 68, 1279.
3. Koistinen J, Mannila M, Mehtonen E,Vartiainen T, Dioxin **1998**, Stocholm, Sweden.