Supercritical Fluid Extraction of PCDD´s and PCDF´s from Polyurethane Foam and Soil

N. Hüsers[1], W. Kleiböhmer[1], K. Cammann[1], I. Schulz[2], P. Schwerdt[2], H. Stoffers[2]
[1]Institut für Chemo- und Biosensorik
Lehrstuhl für Analytische Chemie der Westfälische Wilhelms-Universität Münster
Wilhelm Klemm-Str. 8, 4400 Münster, Germany
[2]Institut für Umwelt und Gefahrstoffanalytik, Raumlufthygiene,
TÜV Hannover/Sachsen-Anhalt e. V.
3000 Hannover, Germany

Introduction

Supercritical Fluid Extraction (SFE) is a modern method in sample preparation. Several studies have shown that SFE yield quantitative recoveries of PAH´s and PCB´s from soil [1] and sorbent materials [2]. Liquid extractions often are time consuming and require relatively high quantities of organic solvents. Here supercritical fluid extraction with non-toxic carbon dioxide may be a promising alternative, because extraction times and the amount of organic solvents are reduced.
In this paper the extraction of PCDD´s and PCDF´s with supercritical CO_2 is investigated. The extraction of PCDD´s and PCDF´s from fly ash and soil already is described by other authors [3].
The aim of our present work is to analyze polyclorinated dioxines and furanes in air samples and soil. In the former case it is necessary to collect the analytes on an appropiate adsorbent material, which has to be extracted afterwards. For this purpose polyurethane foam (PUF) was used, because its ability to trap organic pollutants is known [4].

Experimental

For our first investigations the precleaned PUF plugs were spiked with an extract of incinerator fly ash. The sorbents were analyzed using soxhlet extraction (24 h, toluene) and SFE. The supercritical fluid extraction was performed by a Lee Scientific model SFE 703 extraction system with SFE 703M modifier modul (DIONEX, Idstein, Germany). The extraction conditions were 40 MPa, 90°C, 3h. CO_2 modified with 5% toluene was used as supercritical fluid. The collection vials contained 12 ml of hexane.
In the soil analysis 2.36 g of dry material was extracted with supercritical carbon dioxide with 5 % toluene under the same conditions.

After the extraction the collection solvent was evaporated and a conventional clean up was performed. The separation and quantitative determination of the PCDD's and PCDF's was performed by GC-HRMS (GC: HP 5890 II, MS: Finnigan MAT 95) [4].

Results and Discussion

a. Supercritical fluid extraction of polyurethane foam

In the first studies two spiked PUF plugs were extracted with supercritical fluids and one with a soxhlet extractor, as described above. The results are summarized in **table 1**. The first column gives the spike level for each compound and the second one the recovery rates of the soxhlet extraction.

Table 1: Polyurethane foam extraction

		percent recovery		
	Probe 1 pg	Soxhlet	SFE 1	SFE 2
2,3,7,8-Tetra CDD	16,3	83,44	97,55	108,59
1,2,3,7,8-Penta CDD	48,6	92,80	77,37	66,26
1,2,3,4,7,8-Hexa CDD	33,8	88,46	82,25	60,95
1,2,3,6,7,8-Hexa CDD	38,1	91,86	77,69	73,23
1,2,3,7,8,9-Hexa CDD	67,1	90,16	79,73	67,06
1,2,3,4,6,7,8-Hepta CDD	277	94,58	88,81	74,37
Octa CDD	452	94,25	92,92	75,44
2,3,7,8-Tetra CDF	344	84,59	80,52	71,51
1,2,3,7,8/1,2,3,4,8-Penta CDF	208	84,13	84,13	64,42
2,3,4,7,8-Penta CDF	188	97,87	96,28	72,34
1,2,3,4,7,8/1,2,3,4,7,9-Hexa CDF	326	90,49	89,57	73,31
1,2,3,6,7,8-Hexa CDF	159	95,60	95,60	81,76
1,2,3,7,8,9-Hexa CDF	14,5	80,69	99,31	80,69
2,3,4,6,7,8-Hexa CDF	126	90,48	88,89	80,95
1,2,3,4,6,7,8-Hepta CDF	351	92,31	93,16	82,62
1,2,3,4,7,8,9-Hepta CDF	52,4	79,39	75,38	65,46
Octa CDF	114	92,11	86,67	83,86
Σ Tetra CDD	165	118,18	118,18	111,52
Σ Penta CDD	274	106,57	100,73	83,21
Σ Hexa CDD	434	94,47	85,71	68,66
Σ Hepta CDD	534	88,39	89,33	73,60
Σ Tetra CDF	2730	86,45	82,42	68,17
Σ Penta CDF	2810	86,48	87,19	67,62
Σ Hexa CDF	1154	122,18	122,18	103,99
Σ Hepta CDF	585	94,02	92,65	80,00

The recoveries vary between 80 and 120 percent. In the next two columns the results of the supercritical fluid extractions are listed. In most cases the amount of extracted PCDD's and PCDF's is lower than that obtained by soxhlet extraction, but cover the same range. However, the reproducibility of the SF extractions is still unsatisfying and further work has to be done. In a sescend step the same experiment was carried out using PUF which was spiked with twice the amount of fly ash extract. In this case the recovery rates of soxhlet extraction and SFE vary from 88 to 120 % and 76 to 120 %, respectively.

b. Supercritical fluid extraction of soil

In a further step a real soil sample was extracted with soxhlet and supercritical fluids. **Table 2** shows the results. Compared to the results obtained by soxhlet extraction, the supercritical fluid extraction gives lower amounts. The aim of our future investigations will be to enhance the extraction efficiency.

Table 2: Soxhlet and SFE results of a soil sample

	Soxhlet in pg	SFE in pg	SFE in %
2,3,7,8-Tetra CDD	0,68	n. b.	
1,2,3,7,8-Penta CDD	2,56	< 3	
1,2,3,4,7,8-Hexa CDD	2,89	4,57	158,13
1,2,3,6,7,8-Hexa CDD	6,62	6,54	98,79
1,2,3,7,8,9-Hexa CDD	8,01	7,83	97,75
1,2,3,4,6,7,8-Hepta CDD	78,1	58,8	75,29
Octa CDD	270	210	77,78
2,3,7,8-Tetra CDF	26,9	16,1	59,85
1,2,3,7,8/1,2,3,4,8-Penta CDF	22,4	8,76	39,11
2,3,4,7,8-Penta CDF	12,6	6,54	51,90
1,2,3,4,7,8/1,2,3,4,7,9-Hexa CDF	80,3	64,4	80,20
1,2,3,6,7,8-Hexa CDF	28,8	18	62,50
1,2,3,7,8,9-Hexa CDF	< 2	< 2	
2,3,4,6,7,8-Hexa CDF	31	23,5	75,81
1,2,3,4,6,7,8-Hepta CDF	322	221	68,63
1,2,3,4,7,8,9-Hepta CDF	56	37,1	66,25
Octa CDF	726	431	59,37
Σ Tetra CDD	52,8	n. b.	
Σ Penta CDD	64,7	< 30	
Σ Hexa CDD	85,1	57,5	67,57
Σ Hepta CDD	141	110	78,01
Σ Tetra CDF	104	61,7	59,33
Σ Penta CDF	193	88,7	45,96
Σ Hexa CDF	291	205	70,45
Σ Hepta CDF	538	369	68,59

Summary

The supercritical fluid extraction of PCDD's and PCDF's from PUF plugs gave results with high variations. Further, it is necessary to optimize the extraction conditions in order to shorten the extraction time and to improve the reproducibility of the supercritical fluid extraction. This may be accomplished by increasing the density and therefore the solvent strenght of the supercritical fluid. Another possibility is the use of more polar modifiers, e. g. methanol [3].

References

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