

Microwave Assisted Extraction of Solid Samples for PCDD/PCDF-Analysis

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1. Introduction

Standard soxhlet extraction is a well tested and accepted method in PCDD/PCDF analysis¹. However, this method has several drawbacks. The solvent consumption is considerable. Furthermore, soxhlet extraction is time consuming, with up to 24 h extraction time and the need for evaporation of extensive amount of solvent before further clean-up.

Different approaches are tested to reduce solvent consumption and to speed up extraction time compared to standard soxhlet extraction procedures. Supercritical fluid extraction (SFE) is tested and used by some groups². However, the possible sample size is still very small. This limits SFE to highly contaminated samples. Furthermore, CO₂, the supercritical fluid normally used in SFE, has a very low dielectric constant ($\epsilon \approx 1 - 1,6$), which makes the extraction of the slightly polar PCDD/PCDF difficult.

Recently, microwave assisted extraction (MAE) has been tested for the extraction of PAH, chlorinated pesticides, and other semivolatile contaminants^{3,4}. In this method a mixture of sample and solvent are sealed in a Teflon-lined reaction vessel and treated with microwaves for about 15 to 30 min. Pressure and temperature in a control vessel are measured and used to control the microwave energy. We have adapted this approach for the extraction of solid samples for the analysis of PCDD/PCDF. For the control of the new method the same samples were extracted by standard soxhlet extraction.

2. Experimental

A CEM MES-1000 microwave extraction system was used (CEM Corporation, Matthews, NC). The system is equipped with 12 microwave transparent extraction vessels with inner liners made from PFA. One control vessel is connected to a pressure control unit and is equipped with a fibre-optic temperature probe. All vessels are supplied with a safety rupture membrane and have vent tubes in case of excess internal pressure. The measured pressure and temperature are used to regulate the microwave power according to a stored program.

10 g to 25 g of the sample was spiked with ¹³C-labeled internal standard mixture, homogenised with 2,5 % ultra pure water and poured into the extraction vessel. 30 ml of toluene (pesticide grade) was added, before the vessel was sealed with the cover. The control vessel was filled with an identical sample with same water and solvent content. As much as 12 samples can be treated at the same time. It is essential that the samples have similar microwave absorbance as the control sample otherwise temperature and pressure

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will exceed the limits. All vessels were placed on the turntable. Exhaust tubes, pressure control tube, and the fibre-optic temperature probe were connected and it was checked that the rotation of the turntable was not disturbed by the tubing. The following temperature program was used: with 100 % microwave power to 125°C (30 sec - 3 min, depending on sample matrix) then 20 or 40 min at 125°C. Before opening, the vessels were allowed to cool down to room temperature. The supernatant extract was filtered through a glass fibre filter (Gelman, type AE) and combined with two washes of the sample with 20 - 25 ml toluene. Water was removed with a Pasteur pipette and the extract was dried with Na₂SO₄.

Soxhlet extraction of 10 g to 25 g of an identical sample was performed with 300 ml warm toluene. The sample was spiked with a ¹³C-labeled internal standard mixture.

The extracts from microwave assisted extraction and from soxhlet extraction were either rinsed by a multicolumn cleanup with different types of silica columns and an activated charcoal column or by a combination of gel permeation chromatography (GPC) and activated charcoal. Both methods are described in detail earlier^{1,5)}.

3. Results

The following sample types were included in our experiments: a dried and homogenised sewage sludge sample from an intercalibration exercise, a fly ash sample, a wet sediment sample and two soil samples from a remote area.

Table 1. Comparison of microwave assisted (MAE) and soxhlet extraction for sewage sludge, fly ash and sediment samples.

Compound	Sewage sludge		Fly ash		Sediment	
	MAE pg/g	Soxhlet pg/g	MAE pg/g	Soxhlet pg/g	MAE pg/g	Soxhlet pg/g
2378-TCDD	0,83	0,67	21,0	18,3	1,99	0,69
12378-PeCDD	1,97	1,62	60,0	51,5	4,94	4,42
123478-HxCDD	2,38	2,46	65,1	56,9	12,8	6,59
123678-HxCDD	8,32	9,57	89,8	74,9	11,9	11,5
123789-HxCDD	5,45	6,06	70,8	32,8	9,14	12,8
1234678-HpCDD	311	323	834	453	121	145
OCDD	2398	2453	2134	1675	565	542
2378-TCDF	4,9	4,25	95,9	87,5	23,5	12,0
12378/12348-PeCDF	2,67	1,78	191	170	22,8	10,5
23478-PeCDF	5,07	3,32	227	182	20,8	16,1
123478/123479-HxCDF	6,50	3,30	298	255	22,3	20,8
123678-HxCDF	5,52	2,29	264	211	20,9	12,8
123789-HxCDF	<0,70	<0,60	109	26,2	<10,0	0,98
234678-HxCDF	9,70	3,54	379	231	12,8	18,0
1234678-HpCDF	36,4	25,4	787	581	54,5	60,5
1234789-HpCDF	3,10	2,51	220	168	13,1	8,76
OCDF	102	72,3	1165	916	168	126
i-TE	14,8	12,5	333	256	31,0	23,8
Recovery %	35 - 50	65 - 85	46 - 78	5 - 78	56 - 65	61 - 98
Extraction time	20 min	24 h	20 min	24 h	20 min	24 h

Table 2. Comparison of microwave assisted (MAE) and soxhlet extraction for soil samples and typical results of method blanks.

Compound	Soil 1		Soil 2		Method blank	
	MAE pg/g	Soxhlet pg/g	MAE pg/g	Soxhlet pg/g	MAE pg/g	Soxhlet pg/g
2378-TCDD	0,05	0,05	0,12	0,09	<0,03	<0,03
12378-PeCDD	0,14	0,13	0,37	0,34	<0,05	<0,05
123478-HxCDD	0,55	0,14	0,27	0,31	<0,08	<0,08
123678-HxCDD	0,56	0,57	0,79	0,92	<0,08	<0,08
123789-HxCDD	0,39	0,35	0,24	0,55	<0,08	<0,09
1234678-HpCDD	3,89	2,94	7,74	6,83	<0,10	<0,12
OCDD	40,5	15,1	43,2	37,3	<0,15	0,52
2378-TCDF	0,40	0,37	1,75	1,30	<0,03	<0,03
12378/12348-PeCDF	0,30	0,52	0,67	1,07	0,07	<0,05
23478-PeCDF	0,50	0,49	1,17	0,83	<0,06	<0,05
123478/123479-HxCDF	0,47	0,50	1,06	0,84	<0,08	<0,09
123678-HxCDF	0,32	0,39	0,76	0,61	<0,09	<0,09
123789-HxCDF	0,13	0,14	0,17	0,17	<0,09	<0,09
234678-HxCDF	0,47	0,38	0,64	0,50	<0,09	<0,09
1234678-HpCDF	1,69	1,74	3,51	2,22	<0,10	<0,10
1234789-HpCDF	0,17	0,22	0,42	0,30	<0,10	<0,10
OCDF	2,47	3,12	7,75	4,62	<0,20	<0,18
i-TE	0,84	0,74	1,66	1,38		
Recovery %	22 - 42	63 - 94	23 - 38	55 - 94	40 - 75	79 - 88
Extraction time	20 min	24 h	20 min	24 h	20 min	

4. Discussion

In the beginning we tested the cleanliness of the vessels and the risk for cross contamination by analysing an extract on GC/MS without any further clean-up. No PCDD/PCDF was found but the cyanopropyl GC column was destroyed by unknown compounds dissolved from the vessel. On inquiry the supplier recommended to bake out the Teflon liner at a 200°C for about 6 h. The method blanks determined with sample vessels baked out and used for extraction of real samples, are below the detection limit.

The concentrations of PCDD/PCDF extracted by MAE are in good agreement with the results from standard soxhlet extraction. For the sediment sample the agreement is reduced due to problems with homogenisation of the wet sample. Except for the very low recovery of higher chlorinated PCDD/PCDF in the soxhlet-extracted fly ash sample (5 - 8 %), the recovery of the 13C-labeled internal standards is generally lower with MAE. Since the "native" compounds are in good agreement, we ascribe the low recovery to the fact that the treatment of the samples after extraction is not optimised for a mixture of wet particles and toluene.

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In general, microwave assisted extraction allows the extraction of PCDD/PCDF from solid samples with same efficiency as with standard soxhlet extraction. Solvent consumption is decreased from 300 ml to about 70 ml of toluene. This will reduce the costs for supply and destruction of solvents, will probably lead to lower method blank and will at least have a lesser environmental impact. Extraction time is reduced from 24 h to about 30 min. Furthermore, it is not necessary to dry samples before extraction. This will give a further reduction of the total time for analysis.

5. References:

- 1) Oehme, M., J. Klungsøyr, A. Biseth and M. Schlabach (1993): Quantitative determination of ppq-ppt levels of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments from the Arctic (Barents sea) and the North sea. *Anal. Meth. & Instr.* 1, 153-163.
- 2) Larsen, B. and s. Facchetti (1994): Use of supercritical fluid extraction in the analysis of polychlorinated dibenzodioxins and dibenzofurans. *Fresenius J. Anal. Chem.* 348, 159-162.
- 3) Lopez-Avila, V., R. Young and W.F. Beckert (1994): Microwave-Assisted Extraction of Organic Comounds from Standard Reference soils and Sediments. *Anal. Chem.* 66, 1097-1106.
- 4) Onuska, F.I., K.A. Terry (1993): Extraction of Pesticides from Sediments Using a Microwave Technique. *Chromatographia* 36, 191-194.
- 5) Schlabach, M., A. Biseth, H. Gundersen, M. Oehme (1993): On-line GPC/carbon clean-up method for determination of PCDD/F in sediment and sewage sludge samples. H. Fiedler et.al. (red.) *DIOXIN '93. Organohalogen compounds Vol. 11 Federal Environmental Agency, Wien, 71-74.*