

## **Rapid extraction of PCDD/Fs from soil and fly ash samples: Pressurized Fluid Extraction (PFE) and Microwave-Assisted Extraction (MAE)**

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### **Introduction**

The main reference extraction method in the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) is still the Soxhlet extraction<sup>1</sup>. But it requires long extraction times (up to 24 hs), large volumes of hazardous organic solvents (100-300 ml) and its automation is limited. Pressurized Fluid Extraction (PFE) and Microwave-Assisted Extraction (MAE) are two relatively new extraction techniques that reduce the time and the volume of solvent required for extraction. However, very different PFE extraction conditions are found for the same environmental matrices in the literature<sup>2,3,4</sup>. MAE is not a extraction technique very applied for the analysis of PCDD/Fs yet, although it is used for the determination of other organic compounds, such as PCBs<sup>5</sup> and PAHs<sup>6</sup>.

In this study, PFE and MAE extraction conditions were optimized to determine PCDDs y PCDFs in fly ash and soil/sediment samples. Conventional Soxhlet extraction with toluene was used to compare the extraction efficiency of both techniques.

### **Methods and Materials**

#### *Chemical and Reagents*

All chemicals employed were of high purity for pesticide residue analysis and were provided from Merck (Darmstadt, Germany). All PCDD/Fs standard solutions (EPA 1613 LCS; EPA 1613 ISS and EPA 1613 CVS) were obtained from Wellington Laboratories (Ontario, Canada). Packaged columns were provided by Fluid Management Systems Inc (Watertown, USA).

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### *Sample Extraction and Clean up*

Samples analysed were: Soil B (river clay sample) from 6<sup>th</sup> Round Intercalibration Study organized by Professor van Bavel, Örebro University, Sweden<sup>7</sup>, and the certified fly ash reference material CRM 490<sup>8</sup>. All samples were spiked with <sup>13</sup>C-labelled internal PCDD/F standards prior to the extraction. Amounts of 0.5 g (fly ash) and 20 g (soil B) were weighed in triplicate and Soxhlet extracted with toluene (300 ml) for 24 hours. Analysis of PCDD/Fs was done according to Method US EPA-1613.

The PFE extractions were carried out in an ASE 100 extractor (DIONEX, USA) with toluene as solvent. Closed-vessel MAE was performed in a MARS X apparatus (CEM, USA) with toluene and acetone/hexane (1:1) as solvents. Acetone/hexane (1:1) is one of the solvent mixtures more applied for microwave extraction of organic compounds<sup>9,10</sup>. Samples can be simultaneously extracted in up to fourteen 100 ml closed glass vessels. The PFE and MAE extraction conditions are listed in Table 1.

The clean up of the samples was carried out in an automated Power Prep<sup>TM</sup> System (FMS, Inc., USA) supplied with three chromatographic columns pre-packed with acid/basic silica gel, alumina and active carbon. Final extracts were concentrated and further analysed by GC/MS/MS.

### *GC/MS/MS conditions*

Analysis were made in a VARIAN SATURN 2000 GC/MS/MS (Ion Trap) equipped with gas chromatograph CP-3800 and programmable injector 1079 (Varian, Walnut Creek, CA, USA). Software version 5.51 was employed. Samples were splitless-injected by means of an autosampler CP-8200 in a fused silica capillary column VF-5ms (30 m, 0,25 mm of ID., 0,25 µm film thickness) (FactorFour, Varian Inc., USA). The GC and MS/MS conditions were detailed in reference<sup>11</sup>.

## **Results and Discussion**

### *a) Optimization of PFE extraction conditions*

Applying the PFE conditions displayed in Table 1, soil B and CRM 490 fly ash samples were extracted three times in toluene at different temperatures: 100, 125, 150 and 200 °C. The recovery for Soxhlet and ASE extractions of Soil B is shown in Figure 1, assuming as 100 % the average value reported for this sample in the 6<sup>th</sup> Round Intercalibration Study<sup>7</sup>.

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PFE Conditions	Sediment	Fly ash	MAE Conditions	Sediment	Fly ash
Sample size (g)	20	0.5	Sample size (g)	15	0.5
SO <sub>4</sub> Na <sub>2</sub> anhydrous (g)	10	8	SO <sub>4</sub> Na <sub>2</sub> anhydrous (g)	---	3.5
Cell size	33 ml	11 ml	Solvent volume (ml)	50	20 50*
Solvent	Toluene	Toluene	Solvent	Acetone/hexane (1:1)	Acetone/hexane (1:1) Toluene*
Pressure (psi)	1500	1500	Power (%)	100	100
Temperature (° C)	100-200	100-200	Ramp to Temperature (min)	15	10 20*
Flush Volume (%)	90	90	Extraction Temperature (° C)	115	115 140*
Purge Time (sec)	120	120	Extraction time (min)	10-45	45
Number of Static Cycles	3	3	Stirring	Medium	Medium
Static Time (min)	10	10			

**Table 1.** PFE and MAE conditions applied for PCDD/Fs extraction in soil/sediment and fly ash samples.

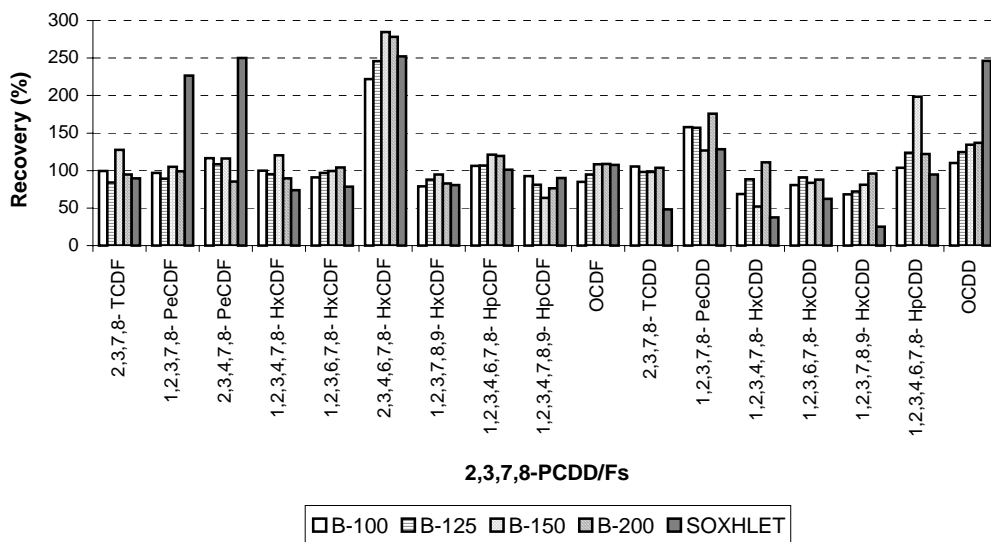
The recoveries obtained with Soxhlet method varied from 25 to 252 %. The highest results were obtained for 1,2,3,7,8-PeCDF (227 %), 2,3,4,7,8-PeCDF (250 %), 2,3,4,6,7,8-HxCDF (252 %), 1,2,3,7,8-PeCDD (129 %) and OCDD (246 %), although, in the case of 2,3,4,6,7,8-HxCDF and 1,2,3,7,8-PeCDD congeners it could be a problem of coelution with interfering compounds that the chromatographic column (VF-5ms) does not resolve, because similar results were achieved in PFE and MAE extractions. In the other way, the recoveries for 2,3,7,8-TCDD (50 %), 1,2,3,4,7,8-HxCDD (38 %), 1,2,3,6,7,8-HxCDD (63 %) and 1,2,3,4,7,8-HxCDD (25 %) were the lowest.

For PFE extractions, the recovery of all congeners was above 80 % for any of the extraction temperatures tested, except for 1,2,3,4,7,8-HxCDD (69-101 %) and 1,2,3,7,8,9-HxCDD (68-96 %), but in all cases the results were better than those obtained by Soxhlet extraction.

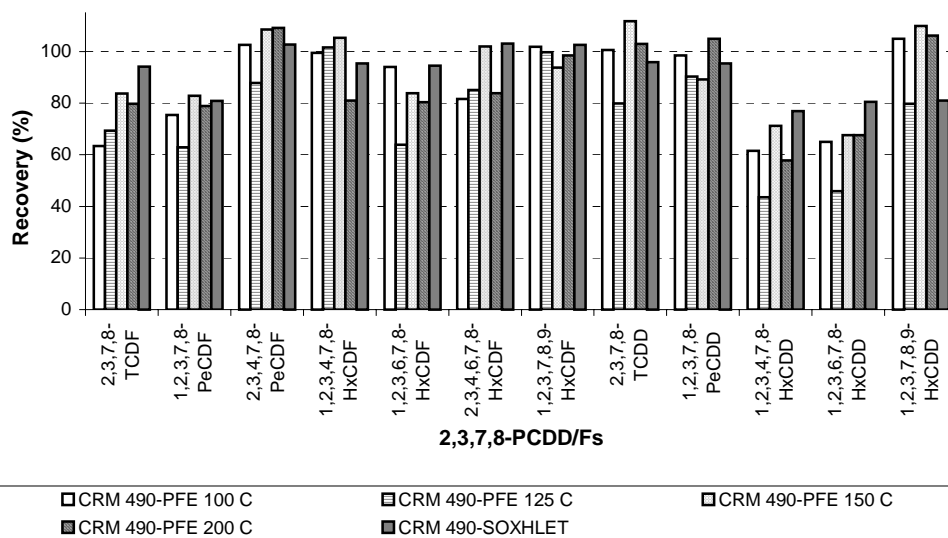
Similar results were observed for CRM-490 extracted by PFE technique according to the conditions listed in Table 1 (Figure 3). In this case, the recovery of all congeners was above 80 % when the sample was extracted at 150 °C, except for 1,2,3,4,7,8-HxCDD (71 %) and 1,2,3,6,7,8-HxCDD (68 %).

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In the light of the results, the temperature is a factor that does not have a great influence on the PFE extraction of soil samples and 100 °C provides enough efficient extraction yields for the PCDD/Fs analysis in this matrix. However, CRM 490 fly ash should be extracted at 150 °C to obtain a recovery near to the 80 % for all 2,3,7,8-PCDD/Fs congeners.



**Figure 1.** Recovery of PCDD/Fs of Soxhlet and PFE extractions at different temperatures (100, 125, 150 and 200 °C) versus the average value reported in the 6<sup>th</sup> Intercalibration Study for soil B<sup>7</sup>.

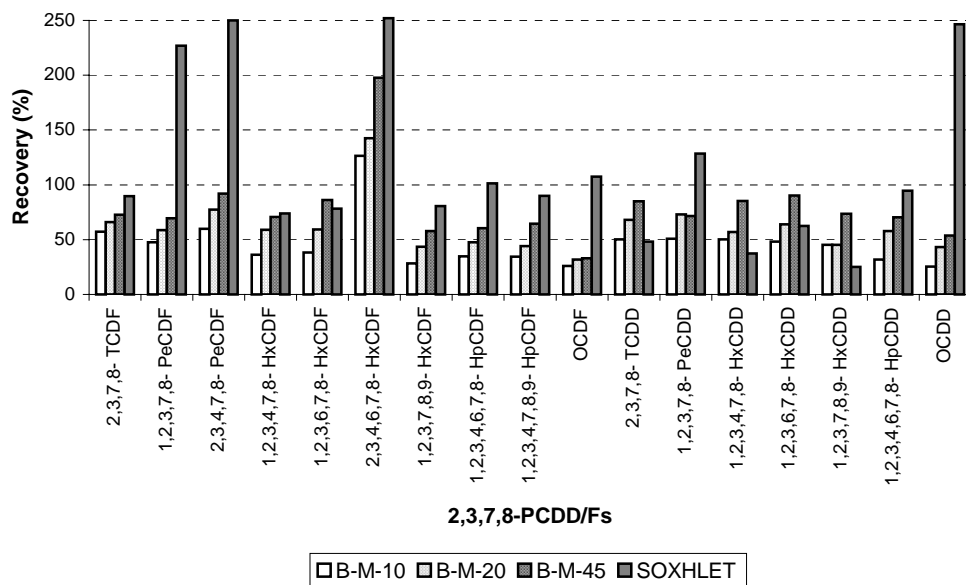


**Figure 2.** Recovery of PCDD/Fs for CRM 490 extracted by PFE at different temperatures (100, 125, 150 and 200 °C) versus the certified value<sup>8</sup>.

#### **b) Optimization of MAE extraction conditions**

A 15 g sample of soil B was MAE extracted with 50 ml of hexane:acetone (1:1) at 115 °C and different extraction times (10, 20 and 45 min), applying magnetic stirring. Results are represented in Figure 3.

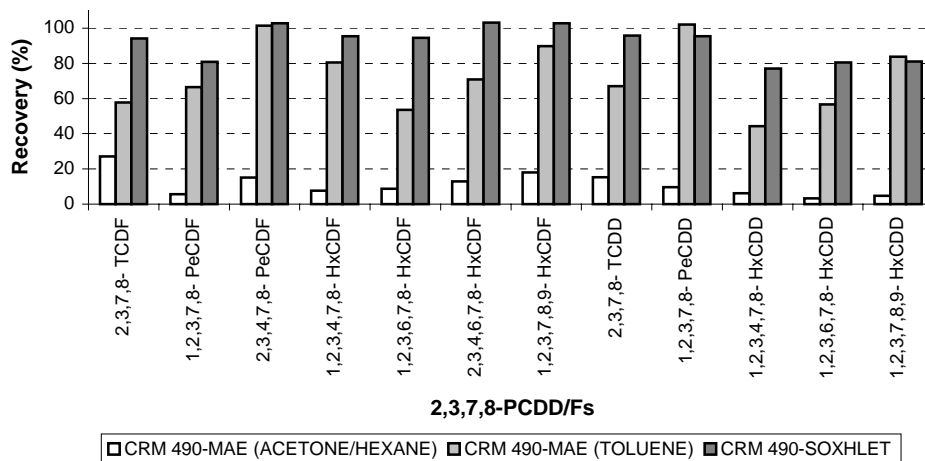
An extraction time of 45 min led to better results than Soxhlet extraction for: 1,2,3,7,8-PeCDF (70 %), 2,3,4,7,8-PeCDF (92 %), 1,2,3,6,7,8-HxCDF (86 %), 2,3,7,8-TCDD (85 %), 1,2,3,7,8-PeCDD (72 %), 1,2,3,4,7,8-HxCDD (85 %), 1,2,3,6,7,8-HxCDD (90 %) and 1,2,3,7,8,9-HxCDD (74 %) congeners; whereas better results were obtained for 2,3,7,8-TCDF (90 %), 1,2,3,7,8,9-HxCDF (80 %), 1,2,3,4,6,7,8-HpCDF (101 %), 1,2,3,4,7,8,9-HpCDF (90 %), OCDF (107 %) and 1,2,3,4,6,7,8-HpCDD (95 %) by Soxhlet extraction. Similar results was managed to 1,2,3,4,7,8-HxCDF for both extraction techniques. However, a recovery of 54 % was only achieved for OCDD.



**Figure 3.** Recovery of Soxhlet and MAE extractions of soil B versus the average value obtained for this sample in the 6<sup>th</sup> Intercalibration Study<sup>7</sup>.

A 0.5 g sample of CRM 490 was MAE extracted with 20 ml of hexane:acetone (1:1) at 115 °C and 45 min, applying magnetic stirring. As the recoveries obtained were very low, a new sample was extracted with 50 ml of toluene at 140 °C. A 1 ml of pure water was added to the toluene before extraction, in order to improve its polarity. Results are represented in Figure 4. In this case, the results were closer to the certified values and they were above the 60 % for all 2,3,7,8-PCDD/Fs congeners, except for 1,2,3,4,7,8-HxCDD (44 %) and 1,2,3,6,7,8-HxCDF (54 %).

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**Figure 4.** Recovery of MAE and Soxhlet extractions of CRM-490 versus the certified value<sup>8</sup>.

### Conclusions

The efficiency of PCDD/Fs extraction based on MAE and PFE techniques was shown for a soil and a fly ash samples. It was demonstrated that, by careful consideration of the experimental parameters such as temperature and solvent extraction, PFE and MAE techniques are capable of replacing the classical Soxhlet extraction.

Compared to Soxhlet extraction, the PFE and MAE methods decreased extractions times from 24 h to 1 h, and reduced the amount of solvent by 50-70 ml per sample. Further optimization of the ASE and PFE methods for each kind of matrix may improve the recoveries of all 2,3,7,8-PCDD/Fs congeners.

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