SOXHLET-HRMS *vs* PFE-GC/MS/MS AND MAE-GC/MS/MS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

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Abstract

The extraction and determination of polychlorinated dibenzodioxins and polychlorinated dibenzofurans is still an ongoing subjet of study. Rapid extraction using Pressurized Fluid Extraction and Microwave-Assisted Extraction were considered for analysing fly ashes and sewage sludge contaminated at different levels. Final extracts were analysed by gas chromatography tandem mass spectrometry. The recoveries obtained were compared with those resulting from the reference analytical method: Soxhlet extraction and high-resolution gas chromatography coupled with high-resolution mass spectrometry.

Introduction

The standard analytical method for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) is USEPA 1613. This method uses conventional Soxhlet extraction and instrumental detection and quantification by high-resolution gas chromatography coupled with high-resolution mass spectrometry, HRGC-HRMS. But this analysis requires shorten and cheaper analytical procedures, besides minimazing waste solvents. Pressurized Fluid Extraction (PFE)[1,2] and Microwave-Assisted Extraction (MAE)[3,4] are two extraction techniques rather applied (used) for the analysis of PCDD/Fs in environmental samples. Both techniques need relatively short extraction time and small amount of solvent.

In the other hand, as HRGC-HRMS requires large investment and maintenance costs, alternative methods have been evaluated to replace the reference method or at least to alleviate analysis costs by their use in preliminary screening. This is the case of gas chromatography/tandem mass spectrometry (GC/MS/MS)[5,6].

In this study, PFE and MAE were used to determine PCDD/Fs in fly ash and sewage sludge samples. Conventional Soxhlet extraction with toluene was used to compare the extraction efficiency of both techniques. In all cases, quantification was realized by HRGC-HRMS and GC/MS/MS.

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).

Sample Extraction and Clean up
Two fly ashes from municipal waste incineration (MWI) and two sewage sludges were analysed. All samples were spiked with ^{13}C-labelled internal PCDD/F standards prior to the extraction. 1g (fly ash) and 5g (sewage sludge) were weighed in triplicate and Soxhlet extracted with toluene (300 ml) for 24 hours. 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 acetone:toluene (5:3) as solvent in PTFE vessels. Magnetic bars cover with Weflon were used during extraction for speeding up the heating of samples. The PFE and MAE extraction conditions were optimised elsewhere[7] and are listed in Table 1.

The clean up of the samples was carried out in an automated Power Prep™ System (FMS, Inc., USA) working with three chromatographic columns pre-packed with acid/basic silica gel, alumina and active carbon.

HRGC-HRMS and GC/MS/MS conditions

Final extracts were concentrated and further analysed by HRGC-HRMS and GC/MS/MS, according to method USEPA 1613.

- HRGC-HRMS analysis were performed in a MICROMASS AutoSpec Ultima NT system, at 10,000 resolving power, using a fused silica capillary column J&W DB-5ms (40 m, 0,18 mm of ID, 0,18 µm film thickness). The GC conditions were detailed in reference[8].
- GC/MS/MS analysis were realized in a VARIAN SATURN 2000 Ion Trap. Samples were splitless-injected in a fused silica capillary column J&W DB-5ms (40 m, 0,18 mm of ID, 0,18 µm film thickness). The GC and MS/MS conditions were detailed in reference[9].

PFE Conditions	Fly ash	Sewage sludge	MAE Conditions	Fly ash	Sewage sludge
Cell size (ml)	11	11	Solvent volume (ml)	30	30
Solvent	Toluene	Toluene	Solvent	Acetone/toluene (5:3)	Acetone/toluene (5:3)
Pressure (psi)	1500	1500	Power (%)	100	100
Temperature (ºC)	150	100	Ramp to Tª (min)	6	6
Nº Static Cycles	2	3	Extraction Tª (ºC)	120	125
Flush volume (%)	90	90	Extraction time (min)	30	15
Purge time (sec)	120	120	Stirring	Medium	Medium
Static time (min)	10	10			

Table 1. PFE and MAE conditions for PCDD/Fs extraction in fly ash and sewage sludge samples.

Results and Discussion

Results of the different extraction and analysis approaches are reported in Table 2. Comparing all the data versus those for the reference method (100 %), the recoveries varied between 84-107 % for fly ashes and 84-123 % for sewage sludge samples.

According to the extraction method applied, recoveries ranged between 84-94 % for PFE and 84-123 % for MAE. In all cases, recoveries were higher than 100 % for sewage sludge analysed by GC/MS/MS, ranging between 101-107 % for Soxhlet extraction; 91-105 % for PFE extraction and 91-116 % for MAE extraction. Therefore, all results are comparable, expressed as pg I-TEQ/g, independently on extraction or quantification technique used.

References	Soxhlet-HRMS	Soxhlet-GC/MS/MS	PFE-HRMS	PFE-GC/MS/MS	MAE-HRMS	MAE-GC/MS/MS
Fly ash A	1045	1120 (107)	895 (86)	1044 (100)	877 (84)	1022 (98)
Fly ash B	696	715 (103)	655 (94)	631 (91)	601 (86)	631 (91)
Sludge C	28	30 (107)	25.1 (90)	28.8 (103)	30 (107)	33.4 (119)
Sludge D	7.7	7.8 (101)	6.5 (84)	8.1 (105)	9.5 (123)	8.9 (116)

Table 2. Results of PCDD/Fs analysis, expressed in pg I-TEQ/g. In parenthesis, the recovery obtained versus the standard analytical method: Soxhlet extraction and HRMS quantification.

Differences were observed between data obtained for each congener analysed by HRMS or GC/MS/MS. In this case, comparing quantification techniques, recoveries were always higher than 80%, varing between 88 and 129 % for Soxhlet extraction; 91-228 % for PFE and 90-163 % for MAE for ash A. In the case of Ash B, the results obtained were very similar: 93-135 % for Soxhlet extraction; 78-137 % for PFE and 81-156 % for MAE. Higher differences were observed for the most chlorinated congeners: hepta- and octa- dioxins and furans. Comparing the alternative techniques (PFE-GC/MS/MS and MAE-GC/MS/MS) versus the reference method (Soxhlet-HRMS) recoveries ranged between 84 and 132 % for PFE and 73 and 147 % for MAE in Ash A and between 76-115 % for PFE and 70-146 % for MAE in Ash B. Results from ash A were displayed in Figure 1.

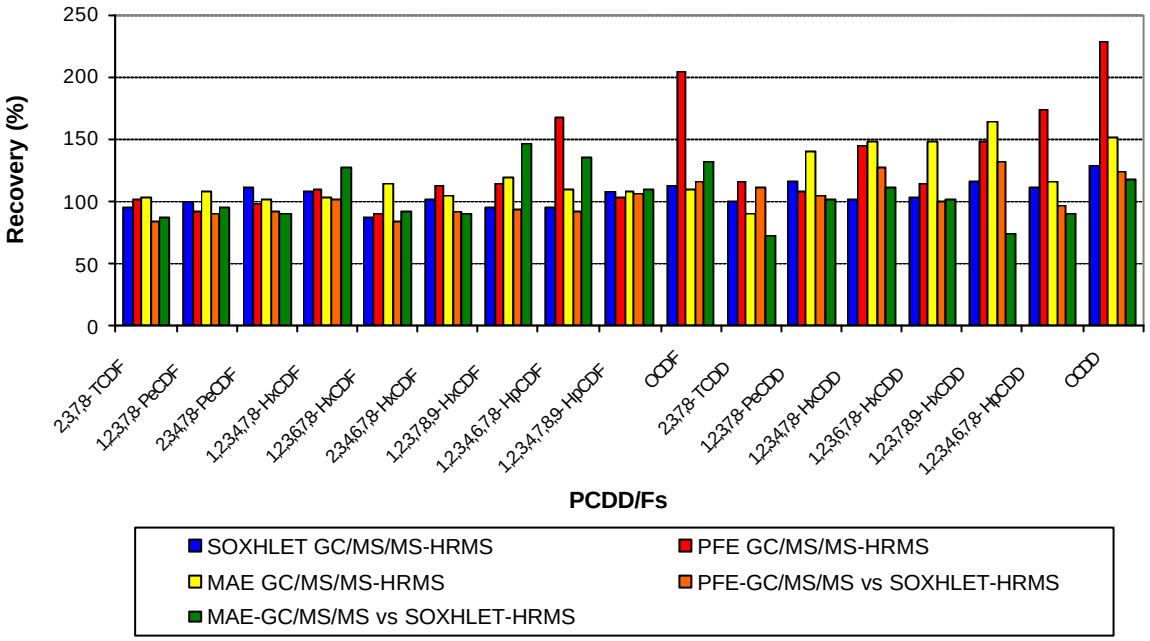

Figure 1. Recoveries obtained for each congener 2,3,7,8-PCDD/F analysed of ash A, comparing the three extraction techniques (Soxhlet, PFE and MAE) and the two quantification techniques (HRMS and GC/MS/MS) applied.

The same study was realised for sludge C and D. The main differences lied in the lower PCDD/Fs content and the matrix complexity. For quantification techniques, recoveries were always higher than 80 % for sludge C, varing between 90 and 187 % for Soxhlet extraction; 84-168 % for PFE and 93-167 % for MAE. In this case, the variability of the results was higher than for ashes case. For sludge D, the intervals were greater, owing to the lower content in PCDD/Fs: 82-186 % for Soxhlet extraction; 96-192 % for PFE and 53-202 % for MAE. Similarly to ash case, higher differences were observed for the most chlorinated congeners: hepta- and octa-dioxins and furans, apart from 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD for sludge C, and only for the congeners 2,3,7,8-TCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; OCDF and 1,2,3,7,8,9-HxCDD for sludge D. Comparing the alternative techniques versus the reference method ,recoveries ranged between 86 and 139 % for PFE and 88 and 205 % for MAE in Sludge C, and 65-159 % for PFE and 70-264 % for MAE in Sludge D. Results from sludge C are displayed in Figure 2.

From the present investigation it can be concluded that MAE is an important and potential extraction technique to apply in this kind of analysis, especially for its prize, since commercial equipments allow to extract up to 14 samples simultaneously. Solvent blanks of TFE vessels were analysed after each MAE extraction to detect possible memory effects, but no problem was detected.

Regarding to quantification technique, GC/MS/MS is a reliable technique for samples with high PCDD/F content and it could be used for analysing environmental samples as sludge, whenever an enough amount of sample is extracted, (10-15 g for sludge).

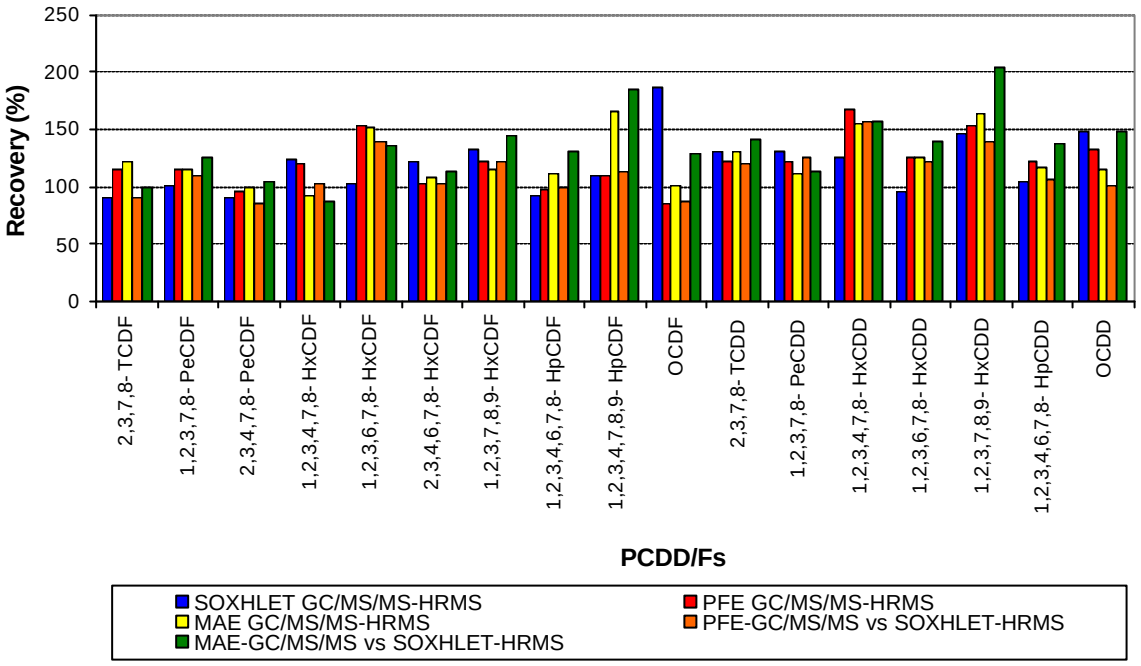

Figure 2. Recoveries obtained for sludge C, analysed by different extraction and quantification techniques.

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