

Rapid ple extraction and clean-up for the analysis of PCDD/Fs in environmental samples

Jordi Sauló¹, Karell Martinez¹, Esteban Abad¹, Miguel Angel Adrados¹, Josep Caixach¹, Josep Rivera¹

¹Mass Spectrometry Lab., Dept. of Ecotechnologies, IIQAB-CSIC

Introduction.

Different extraction procedures have been developed in the last years with the aim of reducing the solvent consumption, the sample preparation time and to allow the automation of the process. Microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) are the most utilized methods for extracting organic pollutants from food samples or environmental matrices such as soils, sediments and sludges¹.

PLE, just like the other aforementioned techniques, improves the efficiency of the extraction process by means of using high temperatures and pressures. In this case the most important factor is the temperature since the elevated pressures are used only to keep the solvent from boiling^{2,3,4}. However, the elevated temperatures reduce the viscosity and the surface tension of the solvent. These parameters are key factors in increasing the solubilization of the target analytes in the solvent, the diffusion rates, and the capacity of the solvent to disrupt the interactions of the analytes and the matrix.

The analysis of PCDD/Fs in environmental samples include a 24h Soxhlet extraction step and an indispensable and complex clean-up before introducing the extract in the HRGC/HRMS system. In this paper, preliminary results of the coupling of a PLE module to the automated clean-up system (Power-Prep/PLE, Fluid Management System, MA, USA) used in our laboratory for routine PCDD/F analysis are presented⁵. The Power-Prep/PLE system is capable of carrying out the on-line extraction and clean-up of 3 to 6 samples in 3 hours.

Materials and methods

Power-prep/PLE was tested using different certified reference materials (CRM) obtained from the Community Bureau of Reference of the European Commission (BCR). CRM 529 (sandy soil), CRM 677 (sludge) as well as a known soil sample previously analyzed by Soxhlet, were used to prove the efficiency of the system and its suitability for such matrices.

PLE extraction and Clean-up

PLE extraction and clean-up were performed with the automated Power-prep/PLE extraction and clean-up system (FMS, Fluid Management Systems, inc., Waltham, MA, USA). A diagram of the system is shown in figure 1. The extraction cell is made of stainless-steel, and supplied with quick connect stainless steel end caps and filters. The on-line extraction and clean-up is controlled by a PC. With the addition of FMS' data management system (DMS6000) hardware to the PC. Temperature, pressure, HPLC pump, flow rate, volume, cooling system, types of solvent, and different states of valves can be programmed, controlled, monitored and recorded in real time.

About 10 g of soil or sludge samples were analyzed. The samples were spiked with 10 µL of the EPA1613LCS (Wellington Labs. Guelph, Ontario, Canada) two hours before the beginning of the PLE process. The extraction cells were filled in the direction of the solvent flow. First, sodium sulphate was put in the extraction cell, next the sample mixed with copper and lastly sodium sulphate, to ensure the removal of the water from the sample. Once the PLE cell is loaded and connected to the PowerPrep/PLE, the extraction solvent (hexane) is added and the cell is pressurized and heated until 180°C and 1800 psi. In this way three static extractions of 10 min were performed. After which, the extracts were pushed out of the cell with an additional amount of n-hexane and were introduced into the multilayer silica column on the clean-up module of the Power-Prep/PLE⁵. In the case of sludge samples, high capacity disposable silica columns were used in order to substitute the necessary acid digestion of the Soxhlet extracts.

Instrumental analysis

The analysis of the cleaned-up extracts were based on the isotopic dilution quantification method and the high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS). All analyses were performed on an Agilent gas chromatograph fitted with a high resolution 40m x 0.18 mm i.d. x 0.18µm film thickness DB-5ms fused silica column (J&W Scientific, CA, USA) connected through a heated transfer line kept at 280°C to a AutoSpecUltima NT (Waters, UK) high resolution mass spectrometer (EBE geometry) controlled by a Masslynx data system.

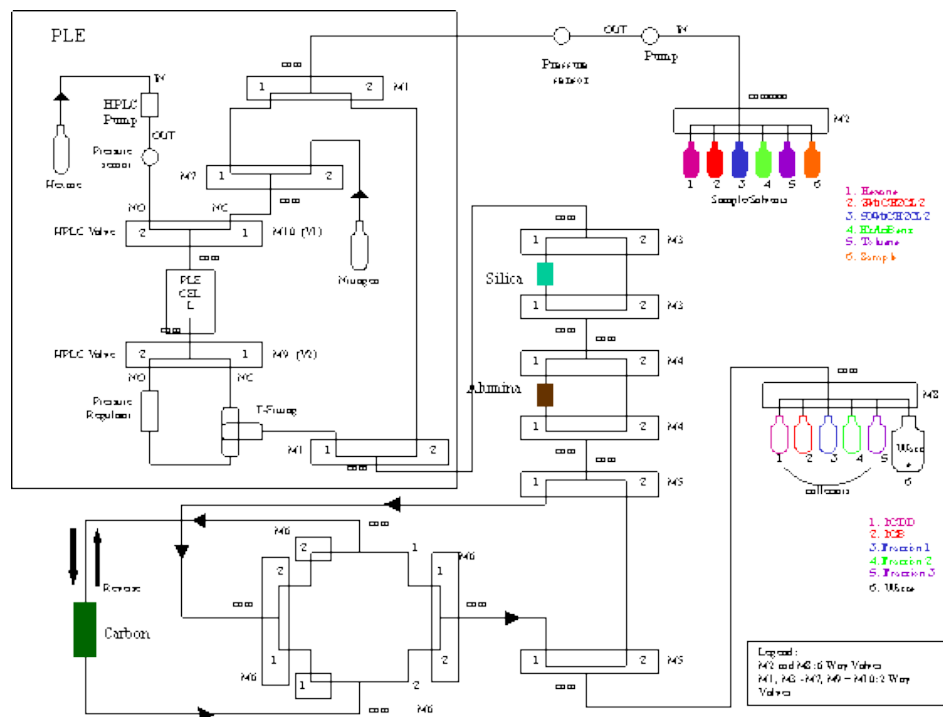


Figure 1. Scheme of the Power-Prep/PLE system, extraction and clean-up.

Results and discussion

Table 1 shows the results of the analysis of a quality control sample (QC soil 1212) which had been previously analyzed in our laboratory using the conventional method: Soxhlet extraction and clean-up in the Power-Prep system. The results obtained with the PLE match quite well with the Soxhlet ones. Regarding the recovery values the of the PLE are even better than the ones obtained with Soxhlet.

The preliminary validation of the PLE was performed with CRMs. For this purpose, two environmental matrices were used: CRM-529 (soil) and CRM-677 (sludge). Table 2 summarizes the results of the analysis of these materials. Comparing our results with the certified ones for each congener, it can be observed that both are similar considering the uncertainty of the CRM. In general, the recovery values of the soil sample are better than the sludge ones. This is logical since the sludge is a matrix more complex than the sludge and it was necessary to include an additional Silica column to clean-up the extract. However, the PCDD/F recovery in the sludge sample were between 60 and 78 %.

Table 1. Comparison results of PLE vs. Soxhlet in quality control soil sample.

Congener	QC Soil 1212			
	PLE Analyzed Conc. pg/g	Rec. C ¹³ (%)	Soxhlet Value Conc. pg/g	Rec. C ¹³ (%)

Dioxins/Furans		(n=3)			
2,3,7,8-TCDF	0.36		104	0.39	96
1,2,3,7,8-PeCDF	0.33		101	0.34	102
2,3,4,7,8-PeCDF	0.30		103	0.31	104
1,2,3,4,7,8-HxCDF	0.26		100	0.25	79
1,2,3,6,7,8-HxCDF	0.32		96	0.31	78
2,3,4,6,7,8-HxCDF	0.25		96	0.24	79
1,2,3,7,8,9-HxCDF	0.72		104	0.73	88
1,2,3,4,6,7,8-HpCDF	1.12		101	1.04	77
1,2,3,4,7,8,9-HpCDF	0.19		99	0.09	75
OCDF	1.56		-	1.14	-
2,3,7,8-TCDD	0.08		104	0.09	90
1,2,3,7,8-PeCDD	0.63		105	0.96	98
1,2,3,4,7,8-HxCDD	0.19		102	0.13	77
1,2,3,6,7,8-HxCDD	1.71		93	1.62	76
1,2,3,7,8,9-HxCDD	3.05		-	3.14	-
1,2,3,4,6,7,8-HpCDD	3.87		100	3.75	79
OCDD	24.69		93	25.35	65
I-TEQ (pg/g)		1.34		1.47	

Table 2. Results of PLE analysis compared with CRM in soil and sludge samples.

Congener	Soil CRM. BCR 529				Sludge CRM. BCR 677			
	PLE		Certified Value		PLE Analyzed		Certified Value	
	Analyzed Conc.	R. C ¹³ (%)	Conc. ng/g	Uncertainty ng/g	Conc. pg/g	R. C ¹³ (%)	Conc. pg/g	Uncertainty pg/g
Dioxins/Furans (n=3)					(n=2)			
2,3,7,8-TCDF	0.073	80	0.078	0.013	42.64	69	45.00	4
1,2,3,7,8-PeCDF	0.130	79	0.140	0.03	24.186	78	24.80	1.6
2,3,4,7,8-PeCDF	0.320	77	0.360	0.07	16.77	66	16.90	1.5
1,2,3,4,7,8-HxCDF	3.682	76	3.400	0.5	15.72	72	14.50	1.6
1,2,3,6,7,8-HxCDF	1.157	72	1.090	0.15	6.19	72	6.10	0.8
2,3,4,6,7,8-HxCDF	0.382	71	0.370	0.04	5.97	60	5.60	0.6
1,2,3,7,8,9-HxCDF	0.031	77	0.022	0.01	0.93	66	0.84	0.29
1,2,3,4,6,7,8-HpCDF	12.385	52	-	-	62.37	68	62.00	3
1,2,3,4,7,8,9-HpCDF	2.046	69	-	-	5.55	69	6.30	0.8
OCDF	31.765	-	-	-	156.80	-	177.00	7
2,3,7,8-TCDD	4.197	86	4.500	0.6	1.47	75	1.51	0.16
1,2,3,7,8-PeCDD	0.498	77	0.440	0.05	4.39	74	4.10	0.9
1,2,3,4,7,8-HxCDD	1.164	79	1.200	0.3	2.90	70	-	-
1,2,3,6,7,8-HxCDD	5.161	68	5.400	0.9	230.11	69	235.00	16
1,2,3,7,8,9-HxCDD	2.846	-	3.000	0.4	74.49	-	79.00	7
1,2,3,4,6,7,8-HpCDD	39.040	70	-	-	3287.85	77	3500.00	400
OCDD	172.494	58	-	-	12645.42	67	12700.00	800

One of the key points of the PLE method was the use of hexane as extractant. It is well known that the hexane extraction power is lower than the toluene, which is the solvent commonly used for PCDD/F Soxhlet extraction. In fact, few analytical methods dealing with environmental matrices use hexane in the extraction step. Nevertheless, it seems that the nature of the PLE (high pressures and temperatures) can overcome the limitations of this low polarity solvent.

The preliminary results of the PLE/Power-Prep method for the analysis of soils and sludges prove that this device is a very important alternative to the Soxhlet extraction. The concentrations and the recoveries of the analytes determined with the PLE are similar to the Soxhlet ones but saving a lot of time and solvents, which are basic resources in POP analysis laboratories.

References

1. Bautz, H., Polzer, J., Stieglitz, L. (1998). *J. Chromatogr. A* 815, 231-241.
2. Björklund, E., Bowadt, S., Nilsson, T., Mathiasson, L. (1999). *J. Chromatogr. A* 836, 285-293.
3. Müller, A., Björklund, E., von Holst, C. (2001). *J. Chromatogr. A* 925, 197-205
4. Popp, P., Keil, P., Möder, M., Paschke, A., Thuss, U. (1997). *J. Chromatogr. A* 774, 203-211.
5. Abad E., Sauló J., Caixach J. and Rivera J. (2000). *Journal of Chromatography A*, 893, 383-391.