

OPTIMIZATION OF A PARALLEL PLE PROCEDURE FOR THE EXTRACTION OF PCDDs AND PCDFs IN SEPIOLITE

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Abstract

The paper describes the optimization of the PLE parameters for the extraction of PCDD/Fs in sepiolite using a Plackett-Burman experimental design. The major parameters are identified and a pre-set of optimum is proposed.

Introduction

Pressurized liquid extraction (PLE) has been used for few years in the dioxin analytical area because of its efficiency and ease of use. Most, if not all, PLE is carried out on the ASE instrument from Dionex. This instrument offers sequential extraction capability and can quite easily be incorporated in QA/QC procedures. As a new instrument is now available for parallel extraction (Fluid Management Systems Inc, Waltham, USA), one decided to perform an optimization study to find the best conditions to extract sepiolite samples for dioxins with the new tool. Sepiolite is one of the most delicate matrices that dioxin laboratories are confronted to as it consist in a clay mineral (magnesium silicate) presenting a fibrous crystalline structure acting as a strong adsorbant for various compounds. It is most often consist in a fine particulate powder of high surface area. It is used as an additive in animal feeding stuff preparation as a source of minerals for the animal. The description of the instrument is available in another paper at this conference (see Focant *et al.*).

Materials and Methods

Test Material

The test material consists of a sepiolite sample (EXAL, Tolsa Spain) used as mineral feed for animals. The particle size lies in the range between 38-250µm with <35% smaller than 38µm and <4% larger than 250µm.

Target compounds

The content in all the seventeen 2,3,7,8 toxic PCDD/Fs, the twelve dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) were measured by GC-HRMS.

Analytical procedure

Sepiolite material was dried overnight at 60°C. Extractions were carried out with a pressurized liquid extraction (PLE) instrument from FMS. Raw extract in toluene/ethanol (LGC promochem, France) was then filtrated through Na₂SO₄, concentrated to dryness and solvent exchange to hexane using nonane as keeper. The sample was purified through a multi-layer acid silica column (5 g Na₂SO₄, 20g of 22% silica gel and 20g of 44% silica gel). PCDD/Fs and DL-PCBs were eluted with 150 mL of hexane (LGC promochem, France). The extract was further cleaned and fractionated with a Power-Prep system using acid silica, alumina and carbon columns. PCDD/Fs fraction was injected into a gas chromatography - high resolution mass spectrometer (GC-HRMS, autospec ultima, Waters, UK). All details regarding the analytical procedure for Power-Prep and GC-HRMS can be found elsewhere¹.

Results and discussion

For the present optimization exercise, we did not perform acid digestion of the samples, following the Community Reference Laboratory recommendation regarding bioavailability².

In order to evaluate the PLE extraction efficiency of PCDD/Fs from sepiolite, seven parameters were selected. A Plackett-Burman experimental design was used as a screening test to study their influence within a pre-defined working range. The parameters studied were the following: a mixture of toluene/ethanol, temperature, pressure, extraction time, number of extraction cycles, sepiolite mixed (or not mixed) with sodium sulphate, ¹³C labelled compounds spiked below or above the sample in the extraction cell. The experimental set-up of the screening test is given in Table 1. It comprises twelve experiments. Table 1 gives an overview of the factors and levels examined. The modifications introduced were chosen in a range that can usually be expected. The experiments were performed during one week in repeatability conditions.

Table 1: Experimental design Plackett-Burman

	Solvent (Toluene/Ethanol)	Temperature (°C)	Pression psi	Extraction Time minute	Cycles	mix with sodium sulfate	spike
+----+--	50-50	100	2100	5	3	not mixed	below
+++-----	50-50	150	2100	5	1	not mixed	above
--+-----	90-10	100	1500	5	3	mixed	above
-----+	90-10	100	1500	5	1	mixed	below
-+-----	90-10	150	1500	15	3	mixed	below
+++++++	50-50	150	2100	15	3	mixed	above
-----+	90-10	100	1500	15	1	not mixed	above
-+-----	90-10	150	1500	5	3	not mixed	above
+-----+	50-50	100	2100	15	3	not mixed	below
+-----+	50-50	100	2100	15	1	mixed	above
-----+	90-10	150	1500	15	1	not mixed	below
+-----+	50-50	150	2100	5	1	mixed	below

The response measured is the concentration in pg/g. We selected 7 representative congeners and the sum of the 17 PCDD/Fs. The analyte concentration is directly related to the effect of the varying parameters. Figure 1 and 2 illustrate the influence of the tested parameters on PCDD/F responses.

The screening test highlighted the following important parameters: the extraction time, the number of extraction cycles, and the fact of mixing or not the sepiolite with sodium sulphate inside the cell. Therefore, a set of preliminary promising parameters is: toluene/ethanol 90:10, temperature 150°C, pressure 1500 psi, extraction time 15 min, minimum 2 cycles, mixed matrix to sorbant, and spiking at the entrance of the extraction cell. Those conditions are currently under further refinement to get the optimum efficiency.

References

1. J.-F. Focant, G. Eppe, C. Pirard, E. DePauw, J. Chromatogr.A 925 (2001) 207.
2. CRL Workshop Freiburg, Germany October 12/2006

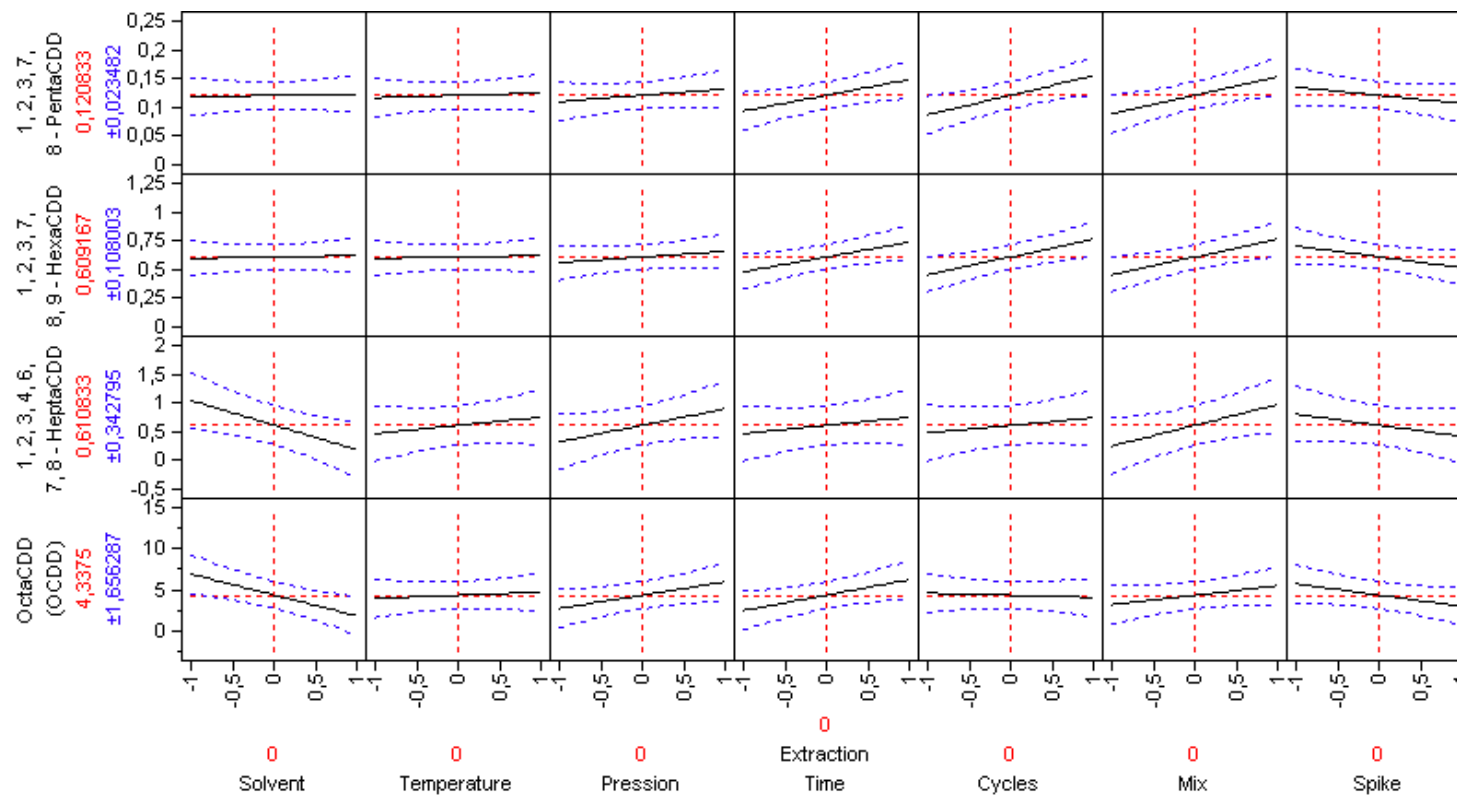


Figure 1: Response of the selected representative congeners to the varying parameters within the investigated ranges (Level +1 and -1 correspond to the signs of the first column of Table 1).

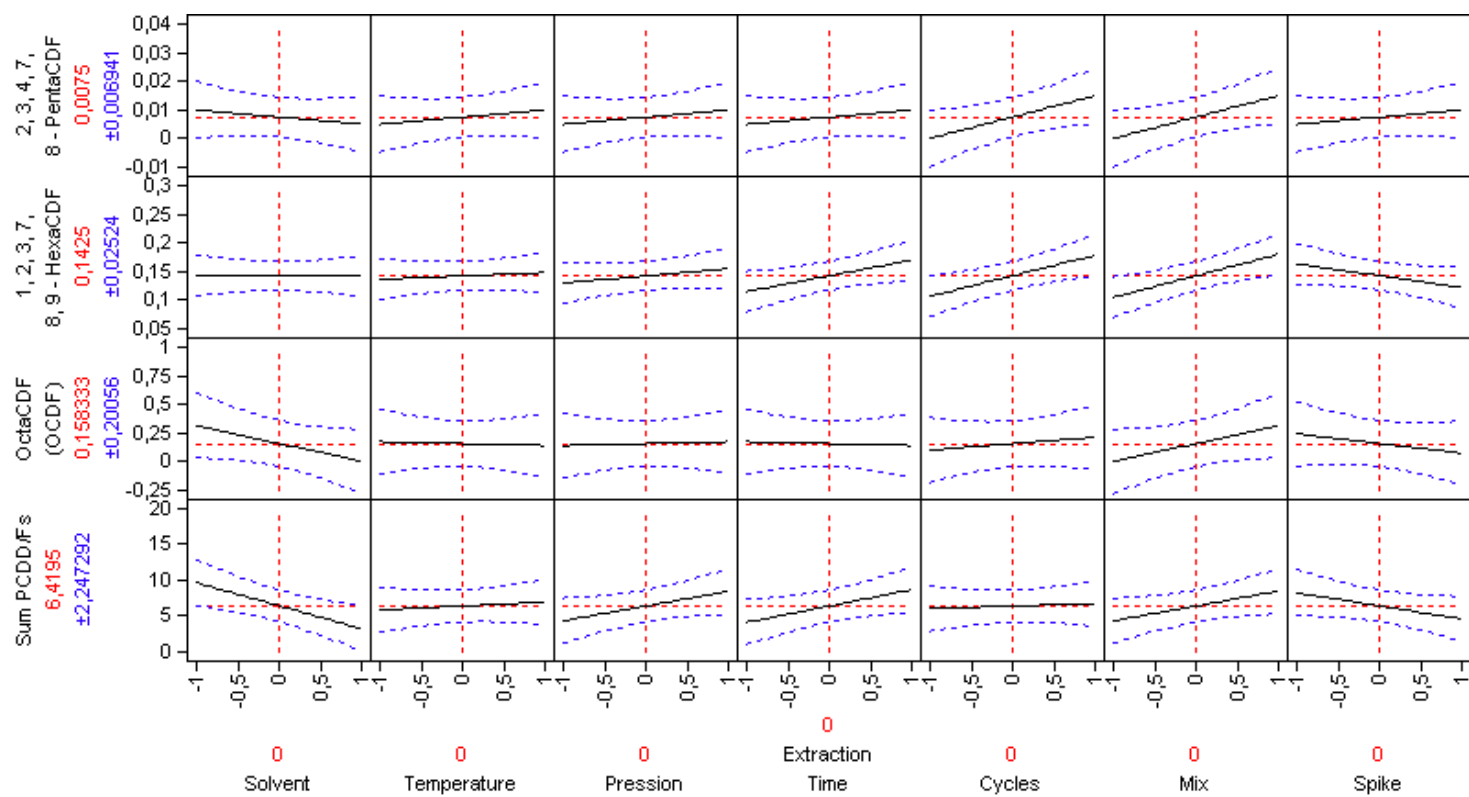


Figure 2: Response of the selected representative congeners to the varying parameters within the investigated ranges (Level +1 and -1 correspond to the signs of the first column of Table 1).