

**Optimisation of Selective Supercritical Fluid Extraction of PCDD/PCDFs and PCBs from Fly Ash.**

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Introduction

Supercritical Fluid Extraction (SFE) of environmental pollutants as PCDD/PCDFs, PCBs and pesticides from different matrices has recently been described as an efficient and convenient method<sup>1-5</sup>. The method uses less organic solvents than the conventional Soxhlet extraction and extracts are much cleaner so elaborate additional clean up of the extracts is not necessary. By using different supercritical fluids (CO<sub>2</sub>, N<sub>2</sub>O) and extraction conditions it is possible to selectively extract PCBs and PCDFs/PCDDs from different adsorbent materials<sup>6</sup>. Selective extraction of PCBs and PCDDs, PCDFs directly from the matrix has an even greater potency. In order to establish the extraction conditions for the different compounds the best approach is an experimental design<sup>7</sup> and not varying one condition at a time. By using an experimental design the parameters of interest can directly be established and even trends can be discussed outside the experimental design.

Experimental

1 g of fly ash obtained from a municipal incinerator, Alidhem, Umeå, Sweden was added to 20 ml of a 20% HCl solution and stirred for 30 minutes. The fly ash was then filtered and dried overnight. The remaining fly ash, about 0.3 g, was then placed to the SFE vessel, an 8-cm x 4-mm i.d. extraction cartridge. The <sup>13</sup>C labeled PCDD, PCDF and PCB sikes (in 100 µl toluene) were directly added to the extraction vessel as well as the different entrainers (200 µl methanol, propanol or toluene). The SCE system is shown in figure 1 and consisted of a Varian 8500 liquid chromatography pump, a Carlo Erba Fractovap Series 2150 gas chromatograph oven and a linear capillary restrictor (22-cm x 25-µm i.d. deactivated silica, SGE). The capillary restrictor was heated (175-190 °C) during the dynamic extraction mode to avoid blocking of the capillary restrictor during CO<sub>2</sub> expansion. The end of the capillary restrictor was immersed into 5 ml CH<sub>2</sub>Cl<sub>2</sub> in order to collect the compounds of interest. All extractions were carried out using SFC grade CO<sub>2</sub> (Scott Speciality Gases, Plumsteadville, PA, USA). Before the HRGC/HRMS analysis the extracts were evaporated to near dryness and eluted over a H<sub>2</sub>SO<sub>4</sub>-silica/silica/NaOH-silica column (1g, 0.5g, 1g) with 20 ml hexane.

30  $\mu$ l tetradecane was added as a keeper and after evaporation the recovery spike (1,2,3,7,8-PeCDF) was added to remaining tetradecane. HRGC/HRMS analysis was performed using a non-polar CP-SIL 8 column and operating the MS (VG 70 250) at a resolution of 5000 in the selected ion monitoring mode (SIM).

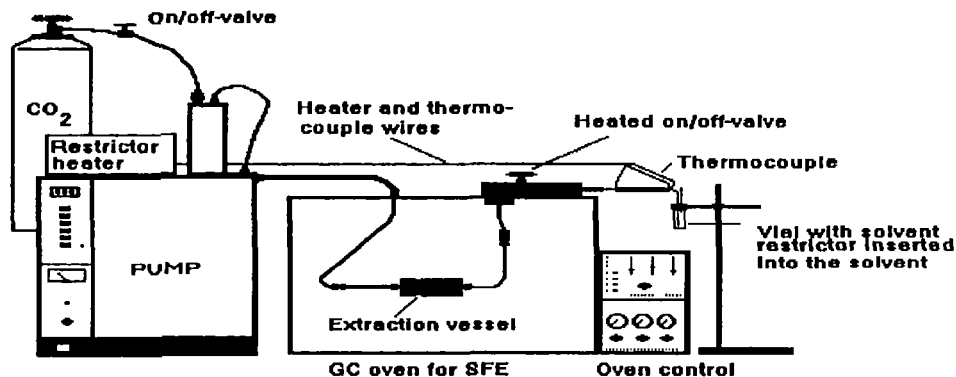


Figure 1 Off line SFE instrumentation

A fractional factorial design ( $2^{4-1}$ ) with 3 centerpoints was calculated for this study by the MODDE package, UMETRI AB, S 901 24 Umeå, Sweden. This design allows to vary four parameters at the same time and needs 11 experiments to establish which parameters are of any significance and if the model is indeed linear as assumed in the fractional factorial design. The experimental space of the design is given in figure 2, the following parameters were changed in the design: pressure (100, 300, 500 atm.), temperature (40, 70, 100 °C), time in static mode before dynamic mode (10, 30, 50 min.) and entrainer added (toluene, propanol, methanol, dielectric constant 2, 18, 33 resp.).

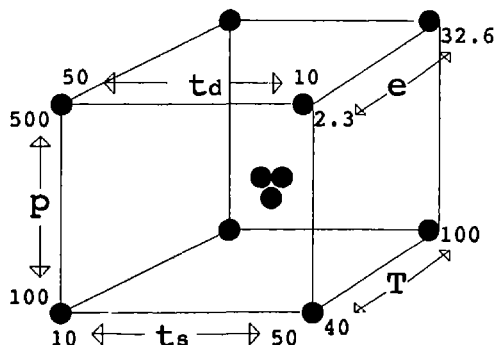


Figure 2 Fractional factorial experimental space ( $2^{4-1}$ ) with 3 centerpoints,  $t_s$  (static extraction time) and  $t_d$  (dynamic extraction time) in minutes,  $T$  n °C,  $P$  in atm. and  $e$  as the dielectric constant at 25 °C of the entrainer.

Results and discussion

The added  $^{13}\text{C}$  PCDD and PCDF spikes were not recovered during the 11 extractions of the fly ash matrix, but only from a system blank sample (no fly ash, only the spikes in  $100\ \mu\text{l}$  toluene,  $70\ ^\circ\text{C}$ , 300 atm., 30 min. static mode, 30 min. dynamic mode, no entrainer). Selective extraction of PCB  $^{13}\text{C}$  was discovered in the experimental space used in this experiment. The planar PCBs IUPAC no. 77, 126, 169 and the non-ortho PCBs IUPAC no. 101, 153, 202 were recovered from the fly ash in different amounts for different extraction conditions. For the planar isomers the two significant factors were temperature and time of the static extraction mode. From figure 3, where the response surface diagram for PCB isomer #77 is shown, can be seen that better recoveries occur at low temperature and with a short static extraction mode (long dynamic mode), this also applies for PCB isomer #153 and #202. For the non-planar isomers again the temperature is significant but not the time in the static extraction mode, of more influence for these compounds is the pressure. Better recoveries are obtained at low temperature and high pressure (i.e. at high density), as an example for this PCB group the response surface diagram for isomer #101 is shown in figure 4. For both groups of PCBs the polarity of the entrainer was of no influence, this is in accordance with ref. 6. However for the extraction of PCDD/PCDFs and for the extraction of different matrixes the polarity of the entrainer is shown to be of importance<sup>1-4</sup>. The selective extraction of PCBs was earlier reported but a difference in optimum extraction conditions for planar and non-planar was not earlier reported.

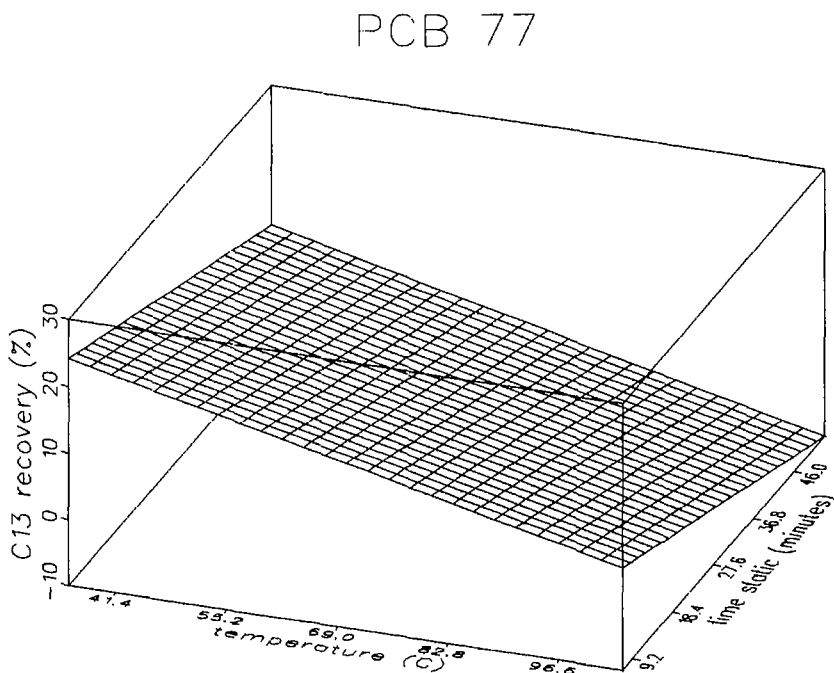


Figure 3 Response surface plot PCB isomer 77.

### Conclusions

There is a difference in optimum extraction conditions between PCDD/PCDFs, planar PCBs and non-planar PCBs. This offers the possibility for selective extraction of these compound directly from the matrix.

Optimums occur just above the critical temperature of the supercritical fluid. Other significant parametres are the time in the different extraction modes (static, dynamic) and the pressure. For the extraction of PCBs the polarity of the entrainer was not found to be significant.

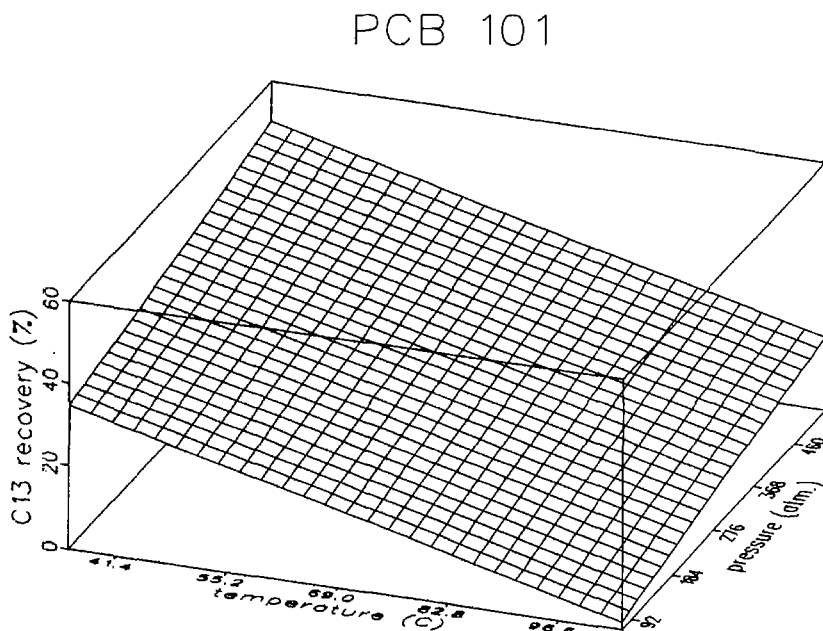


Figure 4 Resonse surface plot PCB isomer 101.

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