

Analytical Extraction of PCBs and OCPs from Water by Direct Supercritical Fluid Extraction

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SUMMARY

A laboratory-scale extractor for direct supercritical fluid extraction (SFE) of liquid samples was used for removing organic pollutants from water. The extractor operates in a continuous mode, and it allows extraction of a theoretically unlimited volume of the sample. In the present study, polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were chosen as target analytes. The method was optimized for extraction of model samples that were prepared by spiking distilled water. The method was tested by extracting real samples of river water where we have found 24 – 162 ng.L⁻¹ of the target analytes. Reference data on the same samples were obtained by solid phase extraction (SPE).

INTRODUCTION

Analytical SFE has mostly been used for sample pretreatment of solid samples. However, the properties of supercritical carbon dioxide can also be exploited in analytical extraction of aqueous (liquid) media although there are fewer papers on this topic. This situation probably results from the need for a more sophisticated apparatus when a direct and continuous extraction of a liquid medium is desired. Different instrument designs for direct SFE of water samples in discontinuous mode were used for extraction of various organic compounds [1,2,3] from water. However, the sample volume is limited by using these apparatuses and therefore, they are insufficient when there is a need to determine trace amounts of analytes. A prospective approach seems to be in the use of a continuous arrangement, as reviewed [4]. In this paper we describe the use of a direct continuous SFE analytical device for removal of PCBs and OCPs from aqueous samples.

EXPERIMENTAL SECTION

SFE. The design and theoretical background of the SFE apparatus used were already described before [5]. However, the main features will be explained. The method is based on the low mutual solubility of water and supercritical carbon dioxide [6,7]. The principal parts of the extraction apparatus are a vertically mounted extraction column packed with an inert material, and a phase separator attached to the bottom. In the cocurrent mode, two high-pressure pumps deliver separately the aqueous sample and liquid CO₂ to the top of the column. There, both phases are brought into mutual contact and flow down the extraction column to the phase separator while reaching a steady state in the water–supercritical carbon dioxide–solute system. In the phase separator, both phases get separated because of their different densities, and leave the extractor through fused-silica capillary restrictors that are attached at appropriate vertical positions. The end of the CO₂ restrictor is connected to a trapping device (in this work it was a U-tube with ethanol as solvent) where analytes are collected. A control unit connected with a PC to enter and display extraction parameters (flow rate of the liquid phase, pressure and temperature) controls the extraction apparatus.

SPE. Extraction cartridges from J&W had a volume of 6 mL and they were filled with 500 mg of C18 reverse phase packing each. The SPE cartridge was attached to the vacuum cell manifold and the sorbent was initiated conditioned by consecutive rinsing with 2 mL of acetone, 2 x 2 mL of CHCl₃, 2 mL of acetone and 2 mL of distilled water, respectively.

GC. The ethanolic extract was analyzed by gas chromatograph (GC) HP5890 series II equipped with electron capture detector (ECD). The column used was DB5 (30 m x 320 μ m x 0.1 μ m) from J&W, and nitrogen was the carrier gas as well as the make up gas for ECD. Pressure and temperature gradient programs were used so that the analysis time was 33 min. Injection was done in splitless mode at 300 °C. The usual volume of injection was 1.8 μ l.

Reagents. The standard mixture of PCB–Mix3 was provided by Dr. Ehrenstorfer, and the standard mixture of OCP by AccuStandard. Ethanol of UV-VIS purity and methanol for trace analysis were purchased from Lachema, a.s., Czech Republic. Water was twice distilled in our laboratory.

Procedure. Samples were extracted by SFE, and the analytes were collected from the CO₂ stream in the U-tube filled with ethanol. Then the volume of the ethanol extract was then lowered down to 0.5 mL by nitrogen blowing. The concentrated extract was directly injected to the GC.

RESULTS AND DISCUSSION

There were done several extraction runs with standard water samples to optimize the extraction process.

Method	SPE		SFE	
	recovery	RSD	recovery	RSD
α -HCH	35%	12%	100%	35%
β -HCH	48%	13%	99%	39%
γ -HCH	36%	9%	117%	29%
δ -HCH	41%	10%	91%	46%
Heptachlor	19%	19%	84%	9%
heptachlor epoxide	31%	16%	100%	18%
Aldrin	5%	13%	55%	14%
Dieldrin	27%	15%	93%	8%
Endrin	29%	18%	121%	28%
endrin aldehyde	28%	15%	64%	29%
p,p-DDE	14%	16%	80%	9%
p,p-DDD	23%	13%	100%	8%
p,p-DDT	34%	21%	46%	39%
endosulphan I	27%	11%	75%	15%
endosulphan II, PCB 118	17%	20%	83%	7%
PCB 28	10%	10%	58%	17%
PCB 101	13%	23%	73%	17%
PCB 153	12%	13%	67%	16%
PCB 138	15%	19%	67%	15%
PCB 180	15%	11%	75%	26%

Table 1: Comparison of SFE and SPE. Endosulphan II and PCB 118 eluted together and we have calculated it in once.

The operating pressure and temperature can influence the mass transfer and solubility in both phases of not only the target analytes but also of water or the organic modifier. These factors are hard to predict, and it is necessary to acquire the data experimentally. 100 mL of distilled water was fortified with $0.6 \mu\text{g}\cdot\text{L}^{-1}$ of each analyte, and this sample was extracted at different temperatures of 40, 60 and 80 °C at a pressure of 20 MPa. The highest extraction recovery was achieved at 80 °C.

The presence of organic modifier in the water–supercritical CO_2 –solute system can influence the equilibrium in both directions. Addition of ethanol or methanol to the water sample was tried to increase the extraction efficiency. The standard water sample was fortified with 5, 10 and 20 % of each organic modifier. The highest increase of extraction efficiency was observed when 20 % of methanol was added. But in this case the RSD value became unacceptably high. It was decided to work on with modification by 15 % of methanol.

The salting-out effect was tested to increase the extraction yield. The result was a little bit surprising – the increase of ion strength by NaCl (5 g to 100 mL of water sample) had no effect. This phenomenon was also observed in another work [8] by the author. Salty water samples, such as mineral water or seawater, can therefore be extracted without a change in extraction recovery.

The optimized extraction conditions were: 20 MPa, 80 °C, modification by 15 % of methanol, flow rates of liquid CO_2 and water were $2.6 \text{ mL}\cdot\text{min}^{-1}$ and $2.1 \text{ mL}\cdot\text{min}^{-1}$ respectively. Table 1 shows the extraction efficiencies that were compared with SPE extraction. The sample concentration was $60 \text{ ng}\cdot\text{L}^{-1}$ of each analyte and the extracted volume was 500 mL. The experiment was repeated three times. The SFE reached higher extraction recoveries for all target compounds than SPE. However, this benefit is weakened by a higher value of RSD.

The project was concluded with analysis of real samples that were taken from the river Morava. The results were compared with SPE (Table 2). The amounts of analytes found in the Morava river water by SFE and SPE were not identical in all items. This could be caused by an error that was brought to the results by calculating the final amount using the extraction recovery, and also by the higher RSD of the SFE step.

CONCLUSION

The method described shows the possibility to use direct SFE for extraction of water samples containing PCBs and OCPs with reasonable results. Compared to SPE the direct SFE is marked by higher extraction recovery but also by higher inaccuracy. This drawback is balanced by automation of the SFE step where only a minimum care of operator is required.

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Method	SFE	SPE
	c [ng.l-1]	
α -HCH	11	14
β -HCH	28	48
γ -HCH	14	119
δ -HCH	14	13
Heptachlor	22	90
heptachlor epoxide	13	22
Aldrin	45	44
Dieldrin	17	15
Endrin	23	157
endrin aldehyde	111	48
p,p-DDE	53	25
p,p-DDD	38	7
p,p-DDT	76	28
endosulphan I	13	6
endosulphan II, PCB 118	33	2
PCB 28	46	128
PCB 101	40	27
PCB 153	9	50
PCB 138	53	18
PCB 180	30	48

Table 2: Analysis of the Morava river water by SFE and SPE. The RSD values vary from 7 – 35 %.