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Supercritical assisted liquid extraction (SALE) of polychlorinated dibenzo-p-dioxines (PCDD) and -furanes (PCDF) from solid matrices

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1. Introduction

The conventional methods for the extraction of organic substances are very time-consuming and expensive. Since the end of the last decade there has been an increase of interest in extractions using supercritical fluids (e.g. carbon-dioxide) instead of organic solvents ¹⁾. The first results were promising, but soon the limitations of this technique became obvious. Even analytes of moderate polarity can't be effectively extracted with typical supercritical fluids like CO₂. Therefore organic modifiers have to be added to enhance the polarity of the fluid and its ability to interact with analyte molecules and matrix-surfaces ²⁾. The relatively new technique called "accelerated solvent extraction" (ASE) uses small amounts of pressurized organic solvents to perform the extraction under subcritical conditions ³⁾.

Our approach is to combine these two techniques for the extraction of polychlorinated dibenzo-p-dioxines (PCDD) and -furanes (PCDF) and other ecological hazardous organics. This "supercritical assisted liquid extraction" (SALE) profits of the advantages of ASE (high extraction efficiency, variety of solvents available, rapid desorption of analyte molecules) as well as of those of SFE (gas-like diffusivity, high transport ratios, low solvent-consumption, easy trapping of extracted compounds).

2. Experimental

The SALE-extractions can be performed with commercial SFE-systems which allow static extraction steps and are equipped with variable restrictors. About 1-5 g solid sample is placed into a 5 mL extraction cell and the void-volume is filled with the extraction solvent. The vessel is placed into the oven chamber and heated to elevated temperatures while the valves before and behind the cell are

closed. Depending on the nature of the solvent the pressure inside the extraction cell raises and ASE-conditions are established. After an ASE-period of about 15 min. supercritical CO₂ is allowed to enter the cell. If necessary a static SFE-step can be performed, but mostly it is sufficient to flush the solvent and analytes out of the cell in the dynamic mode. Best results are obtained by using binary mixtures as extraction solvent. If small amounts (1-5%) of polar additives (e.g. trifluoroacetic acid (TFA)) are added to a suitable organic solvent the extraction efficiencies can be distinctly enhanced. Presumably the additives can interact much better with the active sites of the matrix surface than the solvent molecules themselves and so displace the analyte molecules and suppress their reabsorption during the extraction process⁴⁾.

Due to the fact that the major losses during high-pressure extractions are caused by insufficient trapping of the analytes after leaving the restrictor unit⁵⁾, we use a combined solid-liquid collection device as shown in figure 1.

This construction allows quantitative trapping and reduces the requirements for the clean-up procedure. If silica (with 10% sulfuric acid) is used as solid phase, oxidationable organic compounds are already restrained and don't affect the further sample preparation.

After extraction a distance ring is inserted between the flask and the glass-tube cover, so that elution of the solid-phase is possible without transferring the volume into other vessels.

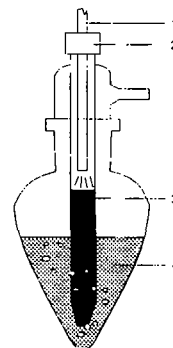


Figure 1: Collection device. (1: Restrictor, 2: Quick-Fit Connector, 3: solid-phase 4: solvent trap)

3. Results:

Because of the high toxicity of the PCDD /-F and the expensiveness of their standard-solutions the preliminary studies have been performed with polycyclic aromatic hydrocarbons (PAH) instead. These substances are suitable as model-compounds for method development and present in the same matrices as PCDD /-F.

The efficiencies of extractions of PAH from soil samples with the SALE-Method (extraction time 80 min.) correlated well with those obtained from soxhlet-extractions (24 h), which were chosen as reference. Compared to supercritical fluid-extractions with pure and continuously modified carbon-dioxide the yields could be distinctly enhanced for all investigated compounds.

These studies guided us to some conclusions concerning the extraction mechanism in SFE: The supercritical carbon dioxide is only insignificantly involved in the extraction process itself. Its main function is to work as medium for the reaction between the organic solvent (modifier), the matrix surface and the analytes. On the other hand the supercritical CO₂ is a appropriate transport-medium, which can, due to its high diffusion coefficient, quickly transport the solvated analytes out of the

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extraction vessel. For the desorption of the analytes the modifier is the decisive component. As our results indicate, the efficiency of modifiers can be seriously enhanced if used with small percentage of polar additives like TFA.

Pawliszyn suggested a model for the SFE-process, consisting of a desorption- and an elution step ⁶⁾. The latter he compared with the chromatographic retention: Until the analyte molecules leave the extraction cell, they undergo several readsorptions and -desorptions at the matrix active sites. We investigated the influence of additive-amount in SFE-modifiers and obtained a change in the extraction profile (see figure 2). According to the Pawliszyn-model the effect can be compared to peak-sharpening in chromatography. Therefore the polar additives have 3 effects: 1. deactivation of the matrix-surface, 2. displacement of analyte-molecules and 3. suppression of readsorption during the elution (see figure 3).

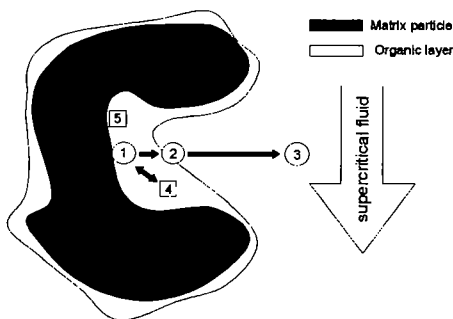


Figure 3: Schematic picture of the additive effects in SFE.

1: adsorbed analyte molecules, 2: analyte at the matrix-fluid interface, 3: analyte in the bulk fluid, 4: additive molecule competing for active sites at the matrix surface, 5: additive molecule blocking active site at the matrix surface.

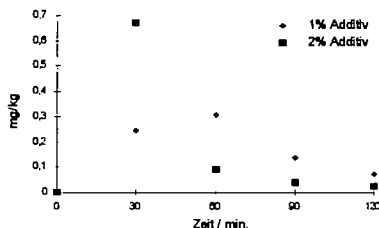


Figure 2: Amount of extracted PAH vs. extraction time for different additive-percentages in SFE of a soil sample. (solvent: toluene, additiv: TFA)

Finally there is the question left, if supercritical conditions are in general necessary for the extraction. We performed several SALE extractions under the same conditions except the pressure for the supercritical step. Figure 4 shows that above the critical point there is only a little effect of pressure, but extracting at subcritical conditions results in a significant decrease of the yields. Therefore it is necessary to apply supercritical conditions after the liquid extraction step in order to achieve quantitative yields.

Besides it is obvious that the standard deviations increase with the pressure.

Therefore the most effective conditions for the SALE extractions we found to be about 100 bar pressure in the supercritical step.

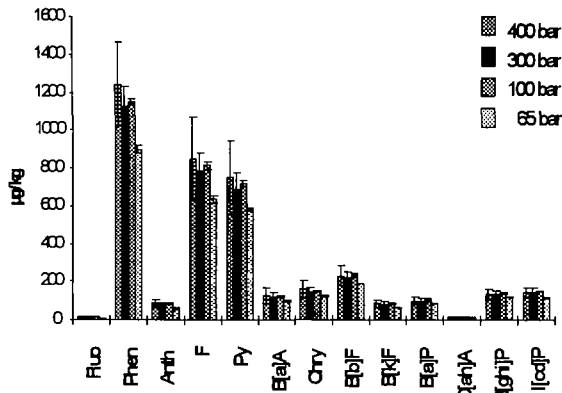


Figure 4: Effect of pressure in the SALE-extraction of PAH from a fly ash sample. (Error bars: standard deviation for N=2)

This optimized method was then applied to the extraction of PCDD /-F from solid matrices. As there were no certified reference materials available for our investigations, a 24 h soxhlet extraction according to EPA-Method 3540B was used as reference. The results of the SALE extraction correlated very good with those of the reference method, while extraction time and demand for organic solvents could be reduced by factor 20.

However, this new method shows that there is no need to replace SFE with other techniques, but the combination of SFE and pressurized solvent extraction is a possible way to fulfil the demand of a cheap, rapid and reliable extraction method.

4. References:

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