Supercritical CO_2-assisted liquid extraction of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins and -furans from solid matrices[1]

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Abstract

In this work we present a supercritical fluid extraction method based on the technique of direct modifier addition. This supercritical CO_2-assisted liquid extraction method is shown to be superior to conventional liquid extraction methods such as e.g. Soxhlet extraction. Analytes of interest were polycyclic aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins and -furans in real-world soil samples. © 1997 Elsevier Science B.V.

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1. Introduction

The conventional methods for the extraction of organic substances are very time-consuming, labour intensive and difficult to automate. 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 limits of this technique became obvious. Even analytes of moderate polarity cannot be effectively extracted with typical supercritical fluids like CO_2. 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 [2,3].

Apart from supercritical fluid extraction (SFE) another extraction method using high pressures has been developed recently. This new technique called 'accelerated solvent extraction' (ASE) uses small amounts of pressurised organic solvents to perform the extraction under subcritical conditions [4].

Our approach is to combine these two techniques for the extraction of ecologically hazardous trace-level organics. The resulting 'supercritical CO_2-assisted liquid extraction' (SALE) profits from the advantages of ASE (high extraction efficiency, variety of solvents available, rapid desorption of analyte molecules) as well as from those of SFE (gas-like diffusion properties, high transport ratios, low solvent consumption, easy trapping of extracted compounds, integration of clean-up steps).

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According to previous studies we use organic solvents containing small amounts of polar additives for extraction. These binary mixtures are much more effective than the pure solvent [5].

2. Experimental

SALE extractions can be performed with any commercial SFE system which allows static extraction steps and which is equipped with variable restrictors. About 2–3 g solid sample are placed into a 5-ml extraction cell, and the void volume is completely filled with the extraction solvent.

The vessel is inserted into the oven chamber and heated to elevated temperatures (90–120°C) while both inlet and outlet valve are closed. Depending on the vapour pressure of the solvent the pressure inside the extraction cell raises and subcritical conditions are established.

After a static extraction period of about 15 min, CO_2 pressurised to 20 MPa is allowed to enter the cell. If necessary a secondary static step can be performed, but it turned out to be sufficient to flush the solvent and analytes out of the cell in the dynamic mode for most applications.

The best results are obtained if binary mixtures are used as extraction solvent. If small amounts (1–5%) of polar additives e.g. triflouroacetic acid (TFA) are added to a suitable organic solvent, the extraction efficiencies can be distinctly enhanced. Presumably the additives can interact more effectivly with the active sites of the matrix surface than the solvent molecules themselves and thus displace the analyte molecules and suppress their re-adsorption during the extraction process [5].

The extractions of the investigated analytes were performed using the ISCO SFX 200 system (ISCO, Lincoln, NE, USA). The following exact extraction conditions were employed:

Solvent: toluene containing 2% (v/v) TFA; solvent extraction step: 15 min static extraction at 90°C; secondary static step: none for polycyclic aromatic hydrocarbon samples (PAHs) and 15 min at 20 MPa for the analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) dynamic SFE step: 30 min at 20 MPa and 90°C (flow-rate: 1 ml/min); trapping system: silica

(10% water) and hexane for PAH extraction and silica (10% H_2SO_4) and hexane for extraction of PCDDs/PCDFs; elution of the solid phase: PAH: 10 ml toluene–hexane (1:3, v/v), PCDDs/PCDFs: 10 ml hexane–CH_2Cl_2 (1:1, v/v).

Due to the fact that major losses during high-pressure extractions are caused by insufficient trapping of the analytes after leaving the restrictor unit [6,7], we use a combined solid–liquid collection device as shown in Fig. 1. This construction allows quantitative trapping and reduces the requirements for the clean-up procedure. If e.g. silica is used as solid phase, highly polar organic compounds are already restrained and do not affect the sample preparation to follow. After extraction a glass pipe 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.

For PAH analysis further sample clean-up was unnecessary, the solvent had only to be removed under a gentle stream of nitrogen and changed to acetonitrile before injection into the HPLC system equipped with fluorescence detector. For analysis of the PCDDs and PCDFs the extract had to be cleaned-up by three liquid chromatographic steps [1, silica, loaded with 10% sulphuric acid; 2, multilayer column (silver nitrate, caesium hydroxide); 3, alumina Super B] [8]. Separation and quantification have been carried out by GC–MS, according to US Environmental Protection Agency (EPA) method 8280.
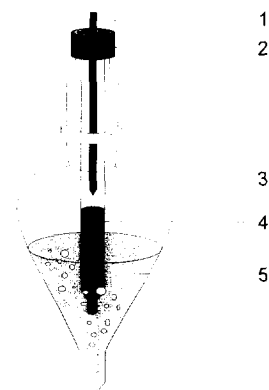
Due to the well-known fact that real-world sam-

Fig. 1. Collection device. 1=Restrictor; 2=quick-fit® connector; 3=flask; 4=solid-phase; 5=solvent trap.

ples cannot be simulated with spike experiments, only native samples were investigated [9]. Soxhlet extraction according to EPA method 3540B was chosen as reference. The samples were extracted for 24 h with toluene and the extracts were cleaned-up as described above.

3. Results and discussion

For the extraction studies two groups of environmentally hazardous substances were investigated, i.e. PAHs due to their ubiquitousness in most kinds of environmental samples and PCDDs/PCDFs, a group of highly toxic ultra trace-level contaminants, which require a comprehensive sample preparation.

For the extraction of PAHs different solid matrices (soil, sediment, ash) were examined. A comparison of the performances of the extraction techniques tested is given in Table 1 for a sediment sample.

As the table indicates, the extraction yields of the SALE method (extraction time 80 min) correlate well with those obtained from Soxhlet extraction (24 h). Furthermore it is obvious, that extraction with neat supercritical CO_2 is not suitable, because PAHs of higher molecular masses were recovered in low amounts. However, even SFE with modified CO_2 (premixed with 5 mol% toluene) it was not possible to enhance the extraction efficiencies significantly.

The relative yields of the different extraction methods compared to each other were almost the same for all other matrices investigated, therefore they are not shown here.

These results guided us to some conclusions concerning the mechanism of our extraction technique: The supercritical CO_2 itself has only a minor influence on the removal of analytes from a sample-surface. Its main function is to work as a medium for the interaction between the organic solvent (equivalent to modifier in SFE), the matrix surface and the analytes. On the other hand the supercritical CO_2 is an appropriate transport-medium, which, due to its high diffusion coefficient, can quickly transport the solvated analytes out of the extraction vessel. For the desorption of the analytes the organic solvent (modifier) is the decisive component. As our results indicate, the efficiency of modifiers can be enhanced if used with a small percentage of polar additives like e.g. TFA.

Pawliszyn suggested a model for the SFE process [9,10] which can be used to explain the effects of the binary solvents. In his kinetic model he divided the extraction process into a desorption and an elution step. The latter he compared with the chromatographic retention: Until the analyte molecules leave the extraction cell, they undergo several re-adsorptions and -desorptions at the matrix active sites. We investigated the influence of additive amount in SFE

Table 1
Extraction of PAHs from a sediment sample using Soxhlet, SFE and the new SALE technique

PAH	Soxhlet toluene (mg/kg)	SFE CO_2 (mg/kg)	SFE CO_2–toluene (mg/kg)	SALE CO_2–toluene–TFA (mg/kg)
Acenaphtene	2.7±0.1	2.6±0.1	2.5±0.1	2.7±0.1
Fluorene	6.3±0.4	6.9±0.1	6.7±0.2	6.6±0.1
Phenanthrene	48.8±2.3	60.9±0.6	60.2±2.0	65.9±0.3
Anthracene	4.4±0.2	5.7±0.1	4.8±0.2	5.2±0.2
Fluorathene	52.9±3.9	50.9±0.6	51.0±1.5	53.9±0.5
Pyrene	36.9±2.0	20.4±0.2	21.1±0.8	34.3±0.1
Benzo[a]anthracene	14.7±0.9	9.9±0.1	10.1±0.2	14.9±0.1
Chrysene	11.6±0.6	6.8±0.1	7.2±0.2	11.1±0.1
Benzo[b]fluoranthene	7.9±0.4	5.1±0.1	6.2±0.2	7.6±0.1
Benzo[k]fluoranthene	4.2±0.3	3.2±0.1	3.7±0.1	4.1±0.1
Benzo[a]pyrene	8.9±0.6	3.9±0.1	5.7±0.2	6.5±0.1
Dibenzo[ah]anthracene	1.4±0.2	0.7±0.1	0.9±0.1	1.4±0.1
Benzo[ghi]perylene	8.9±0.9	1.4±0.1	2.8±0.2	8.5±0.1
Indeno[123-cd]pyrene	2.1±0.1	2.2±0.1	4.0±0.1	4.4±0.1

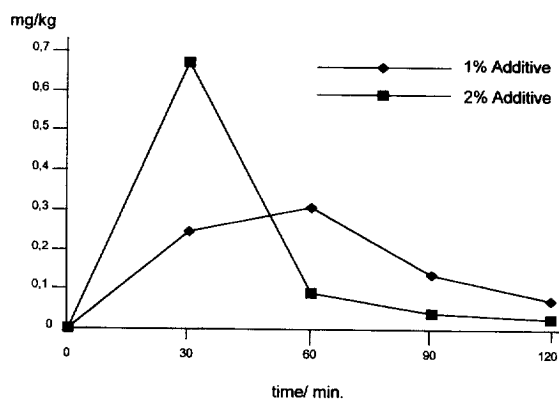Uncertainty represents standard deviation for $n=3$.

Fig. 2. Amount of extracted PAHs vs. extraction time for different additive-percentages in SFE of a soil sample. (Solvent: toluene, additive: TFA)

modifiers and obtained a change in the extraction profile (see Fig. 2). According to the Pawliszyn model this effect can be compared to peak sharpening in chromatography. The total amount of extracted PAHs remained almost the same after 120 min extraction time, but the extraction kinetic was significantly accelerated with a higher additive percentage.

In summary three effects of the polar additives can be postulated: (1) deactivation of the matrix-surface,

(2) displacement of analyte-molecules and (3) suppression of re-adsorption during the elution.

To evolve whether supercritical conditions are in general necessary for extraction or if pressurised solvents are sufficient, several SALE extractions were performed at different pressures. Table 2 shows that above 10 MPa there is only a little effect of pressure on extraction efficiency, but an extraction at 6.5 MPa results in a significant decrease of the yields.

To estimate the exact pressure for the transition of our CO_2–toluene mixture from subcritical to supercritical conditions by theoretical means is almost impossible. All theoretical or empirical approaches take closed systems as a basis, where the phases have enough time to equilibrate [11,12]. However, during the dynamic step of the SALE-method, the ratio between CO_2 and the solvent decreases permanently. Furthermore the CO_2 does not necessarily mix with the remaining solvent spontaneously, but may push a liquid solvent plug towards the cell outlet. Therefore we only can assert with certainty that, at pressures above $P_c(CO_2)$, the SALE system becomes supercritical after almost all solvent has been flushed out of the extraction vessel (We observed, that it takes about 7–8 min to remove toluene completely from the extraction cell).

Nevertheless, the results presented in Table 2

Table 2
Effect of pressure in the SALE extraction of PAHs from a fly ash sample

PAH	Soxhlet (toluene)	SALE (CO_2–toluene–TFA)			
		40 MPa	20 MPa	10 MPa	6.5 MPa
	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)
Fluorene	8.2±0.6	12.8±1.7	12.3±0.0	13.3±0.5	10.4±0.3
Phenanthrene	1108.7±32.9	1240.2±218.9	1122.7±107.2	1150.7±16.2	898.0±19.3
Anthracene	15.0±16.9	88.1±20.8	77.9±9.7	83.4±1.9	61.2±1.3
Fluorathene	857.1±37.6	848.9±214.8	780.3±100.6	812.3±18.5	634.5±19.0
Pyrene	583.0±173.5	751.1±191.6	689.3±86.0	719.1±14.6	584.6±8.7
Benzo[a]anthracene	78.2±63.0	131.3±39.1	121.6±21.6	127.4±5.2	101.3±3.3
Chrysene	184.8±13.2	159.7±46.1	147.2±24.3	153.1±4.4	122.1±4.3
Benzo[b]fluoranthene	220.3±12.0	228.8±53.6	216.5±30.6	230.8±10.7	188.1±1.4
Benzo[k]fluoranthene	88.2±12.4	85.7±19.0	82.2±10.8	84.5±2.1	67.8±0.7
Benzo[a]pyrene	27.1±22.8	98.2±20.5	97.6±15.4	106.6±6.3	88.9±1.4
Dibenzo[ah]anthracene	12.7±2.0	12.5±1.5	12.3±1.0	12.7±0.2	11.9±0.2
Benzo[ghi]perylene	158.3±88.4	138.4±22.4	135.8±18.0	141.2±2.9	118.9±0.3
Indeno[123-cd]pyrene	171.6±24.4	146.6±25.3	145.5±23.4	152.3±2.0	118.3±1.3

Uncertainty represents standard deviation for $n=3$.

allow the conclusion, that conditions above the critical parameters of CO_2 are to be applied following 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 were found to be about 10–20 MPa pressure in the supercritical step.

Then this optimised method was applied to the extraction of PCDDs/PCDFs from solid matrices. As there was no certified reference material available for our investigations, a 24-h Soxhlet extraction according to EPA method 3540B was used as a reference. A comparison of the extraction efficiencies of these two techniques is given in Table 3 exemplarily for a soil sample. The SALE extraction appeared to be superior to the reference method. The extraction efficiencies of SALE were comparable or higher than those of the Soxhlet extraction for all investigated compounds. Furthermore two additional congeners could be found using the new technique. Besides, as already mentioned above, 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 hardware with other equipment, but the combination of SFE and pressurised solvent extraction is a possible way to fulfil the demand of a simple, rapid and reliable extraction method.

4. Conclusion

The new SALE technique has shown to be as quantitative as the Soxhlet extraction for both PAHs and PCDDs/PCDFs. The main advantages of this method are: (1) SALE is rapid (overall extraction time: 60–80 min), (2) SALE uses only 10–15 ml of organic solvents per extraction, (3) SALE combines the advantages of SFE and ASE, (4) SALE does not need high-tech equipment (standard SFE-system will be sufficient), (5) SALE is less matrix-influenced than conventional supercritical extraction techniques and (6) SALE can be used for different types of analytes.

Acknowledgments

Table 3
Extraction of PCDD/PCDF using SALE

PCDD/PCDF	Soxhlet toluene		SALE CO_2–toluene–TFA	
	Conc. (ng/kg)	Int.-TE (ng/kg)	Conc. (ng/kg)	Int.-TE (ng/kg)
2378-TCDF	211.6	21.2	299.8	30.0
2378-TCDD	171.1	171.1	216.1	216.1
12378-PCDF	164.5	8.2	177.0	8.9
23478-PCDF	73.9	36.9	155.8	77.9
123478-HxCDF	169.9	17.0	305.8	30.6
123678-HxCDF	82.8	8.3	246.0	24.6
234678-HxCDF	n.d	n.d	109.8	11.0
1234678-HpCDF	178.1	1.8	184.1	1.8
1234678-HpCDD	128.0	1.3	132.1	1.3
1234789-HpCDF	n.d	n.d.	164.9	1.6
OCDD	300.5	0.3	351.0	0.4
OCDF	222.0	0.2	364.5	0.4
Sum PCDD	599.5	172.6	699.1	217.8
Sum PCDF	1102.9	93.6	2007.7	186.7
Sum PCDD/PCDF	1702.4	266.2	2706.9	404.5

T=tetra; P=penta; Hx=hexa; Hp=hepta; O=octa.

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