



ELSEVIER

Journal of Chromatography A, 816 (1998) 201–211

JOURNAL OF  
CHROMATOGRAPHY A

# Effects of various binary and ternary supercritical phases on the extraction of polycyclic aromatic hydrocarbons from contaminated soils<sup>1</sup>

Christoph Lutermann\*, Elke Willems, Wolfgang Dott, Juliane Hollender

*Institut für Hygiene und Umweltmedizin, RWTH Aachen, Pauwelsstrasse 30, D-52057 Aachen, Germany*

Received 29 December 1997; received in revised form 9 May 1998; accepted 20 May 1998

## Abstract

Polycyclic aromatic hydrocarbons (PAHs) were extracted from two real environmental soil samples using supercritical fluid extraction (SFE) with organic modifiers. The modifiers (*n*-pentane, acetone, toluene, dichloromethane, methanol) as well as modifier mixtures (methanol containing acetone, toluene, acetic acid; acetone containing toluene, ethanolamine; *n*-pentane containing acetic acid) were used in two different concentrations. In general, extraction efficiency increased with reduced polarity of the modifier used and at higher concentrations of co-solvent. Extraction of PAHs from the minor polluted soil with a high content of humic acids was enhanced greatly by the use of modifiers in comparison with pure CO<sub>2</sub> and Soxhlet extraction utilising dichloromethane or *n*-pentane. The highest PAH yields were received with CO<sub>2</sub> containing 10 or 2 mol% pentane followed by CO<sub>2</sub> with 10 mol% toluene. In contrast, for the soil highly contaminated with mineral oil products but with a low content of humic substances, the extraction efficiency was only increased a little by the addition of modifiers in comparison with pure CO<sub>2</sub> and decreased in comparison with Soxhlet extraction. The results lead to the conclusion that the use of modifiers during SFE is well appropriated to break strong matrix–analyte interactions, like humic acids–PAH interactions in the low contaminated soil. But for soils highly contaminated with aliphatic hydrocarbons, SFE is less suitable, because of the viscosity and solubility of the hydrocarbons for PAHs. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Supercritical fluid extraction; Extraction methods; Soil; Environmental analysis; Particle size; Polynuclear aromatic hydrocarbons

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) with carcinogenic and antiestrogenic effects [1] are ubiquitous detectable pollutants in soils. They are used to bind to the organic compounds in soils.

Therefore the extraction of PAHs from soils with a high concentration of humic substances is difficult. PAH–matrix bondings have to be broken or overcompensated by the extraction solvent. Apart from Soxhlet extraction, CO<sub>2</sub> as supercritical fluid is suitable for the extraction of PAHs. Pure CO<sub>2</sub> is not able to extract all PAHs from real environmental soils because of very strong interactions between the analytes and the matrix [2–9]. Variation of supercritical fluid extraction (SFE) parameters like the in-

\*Corresponding author.

<sup>1</sup> Presented at the 2nd SFE, SFC and XSE Symposium, Siegen, 8–9 October 1997.

crease of temperature [10–13] or fluid composition can vastly improve analyte yields from contaminated natural samples. The addition of modifiers to the nonpolar CO<sub>2</sub> enhances the extraction efficiency [14,15]. The co-solvents with different physical and chemical properties can break the analyte–matrix interactions like Van der Waals forces, electron–acceptor electron–donor interactions and hydrogen bondings. Further their dipole moment or their Brønsted acidity, or basicity respectively, are useful properties to disrupt the analyte–matrix interactions [13,15–17]. Additionally, modifiers can alter the matrix by swelling, facilitating the fluid to access interstitial pores and allow the transport of the analytes to the surface of the matrix [18,19]. A variety of different organic co-solvents has been employed in SFE in the last years, but methanol remains the most popular showing mostly good extraction results [9,18,20]. So far, for the extraction of PAHs, polar modifiers like acetic acid or ethanolamine [13,21,14–17] as well as nonpolar like toluene [14] have shown good extraction yields. The investigations show that the modifier identity generally has a larger effect on the extraction efficiency than the concentration of the modifier [15,16].

The aim of this study was to investigate the influence of modifiers on the extraction efficiency of PAHs from soils with different matrices. The modifier were selected so that they are able to interact with the soil matrices and the PAHs in different ways. Twelve co-solvents differing in their physical and chemical properties (Table 1) were used in a low and higher concentration. Apart from often used

modifiers like toluene [13,16], dichloromethane [9,10,13,16,20,22], methanol [9–11,13,16,18,20], we utilised also unusual solvents like *n*-pentane and solvent mixtures (methanol and acetone, methanol and toluene, acetone and toluene, ethanolamine and acetone, *n*-pentane and toluene, acetic acid and *n*-pentane, acetic acid and acetone, ethanolamine and acetone). The reasons for this selection and the use of an unusual solvent, was getting information about the kind of interactions which have to be suppressed if PAHs in soil are to be extracted. Two natural environmental samples having different matrix types and different levels of PAHs contaminants were selected to study the effect of PAH concentration and humic substances. All other important SFE parameters like pressure, temperature, flow-rate, etc. were kept constant. For comparison Soxhlet extraction and SFE using pure CO<sub>2</sub> were carried out on the soil samples.

## 2. Experimental

### 2.1. Characterisation of the samples

In this study two real environmental soil samples were used, which were extremely different in their composition. Sample FR was obtained from a contaminated site, sample LUT1 was a unpolluted soil of a private garden with a high concentration of humic acids. The samples were homogenised for uniformity in a mill till, the particle size was less 600 µm. Water content was determined according to DIN

Table 1  
Modifiers and mixtures of modifiers used

Modifier (mol%)	Interactions	Contents in the CO <sub>2</sub> fluid (mol%)
Methanol	Polar/hydrogen-bonding	2 and 10
Acetone	Polar/aprotic	2 and 10
Dichloromethane	Polar/aprotic	2 and 10
<i>n</i> -Pentane	Apolar	2 and 10
Toluene	Apolar/ $\pi$ – $\pi$ interactions	2 and 10
Methanol–acetone (64:36)	Protic-polar	4 and 10
Methanol–toluene (74:24)	Protic-polar/ $\pi$ – $\pi$	4 and 10
Acetone–toluene (61:39)	Polar/ $\pi$ – $\pi$ -interactions	4 and 8
Ethanolamine–acetone (29:71)	Polar-basic/polar	4 and 10
<i>n</i> -Pentane–toluene (19:81)	Apolar/ $\pi$ – $\pi$ interactions	10
Acetic acid–acetone (29:71)	Protic-polar/polar	4 and 10
Acetic acid–pentane (40:60)	Protic-polar/apolar	4

51718 (1978). To prevent freezing of water in the SFE process in the outlet of the fluid-line, the samples were air-dried. Total organic carbon (TOC) analysis of the samples was performed using a LECO CR-12 carbon determinator. The content of humic acids was determined by gravimetric analyses after extraction with alkaline solution, reprecipitation of the soluted humic acids with hydrochloric acid and filtration. Sieve analysis of the soil samples were prepared with a Retsch sieve and shake machine (Retsch, Haan Germany) using sieves with widths of 32, 45, 63, 90, 125, 180, 250, 355, 500 and 710  $\mu\text{m}$ .

## 2.2. Soxhlet extraction

A mass of 30 g of the soils were Soxhlet-extracted for 8 h with dichloromethane and *n*-pentane. The extracts were concentrated to 100 ml by rotary evaporation and subsequently concentrated using an evaporator (Buchler Vortex-Evaporator, NJ, USA) with a gentle vacuum (30 mbar). A volume of 5 ml of acetonitrile was added, respectively, and the extracts were further evaporated to 5 ml.

This procedure was performed to avoid the loss of highly volatile PAHs like naphthalene.

## 2.3. Supercritical fluid extraction

The SFE experiments were performed using a Dionex SFE Model 703 consisting of an extractor and a co-solvent addition module (Dionex, Sunnyvale, CA, USA). The fluids used were SFE grade carbon dioxide (Air products, Hattingen, Germany) or mixtures of it and co-solvents (analytical-reagent grade; Merck, Darmstadt, Germany and Fluka, Neu-Ulm, Germany), which were mixed dynamically during the extraction. Each of the single co-solvents used in the SFE experiments was mixed with carbon dioxide containing 2 and 10 mol% (Table 1). The binary co-solvent mixtures were added to a content of 4 and 10 (8) mol%. For all experiments, 10-ml extraction cells and restrictors with a flow-rate of 500 ml/min  $\text{CO}_2$  at 34 MPa were used. The cells were filled consecutively with, clean sea-sand (Aldrich, Steinheim, Germany), approximately 1 g of copper granulate to remove elemental sulphur, the soil sample mixed with 0.5 g hydromatrix (ICT-ASS-Chem Handels GmbH, Germany) to remove

traces of water and at last, clean sand again. A sample size of 5.0 g was used from the soils and empty space was filled with clean sand.

The extractions were started with a pressure of 10 MPa, which in the following was raised 5-MPa steps at a time, at 3-min intervals up to 40 MPa. The final pressure was kept for a further 22 min. The restrictor temperature was regulated at 180°C. The temperature at which samples were extracted, was kept constant at 90°C. All extracts were collected in 12 ml of acetone in 30-ml vials which were cooled to 5°C. 1,1-Binaphthyl (10 mg/ml) was added as internal standard after SFE prior to HPLC analysis. The extracts were filled up to a volume of 10 ml and filtrated through PTFE filters.

Three extractions were performed at each condition and the data received was averaged.

## 2.4. HPLC analysis

Finally PAH analysis was performed using a Hewlett-Packard 1050 HPLC-system with Beckmann pumps (model 126, Beckmann, Munich, Germany). Separation was achieved on a 250 $\times$ 3 mm I.D. MZ-PAH RP-C<sub>18</sub> column (particle size 5  $\mu\text{m}$ ) with a 20 $\times$ 3 mm I.D. precolumn (MZ-Analytik, Germany). The columns temperature was stabilised at 35°C with the peltier thermostat BFO-04 (Optilab, Berlin, Germany). An acetonitrile–water gradient (0 min: 60% acetonitrile in 35 min up to 100% acetonitrile, 35–45 min: 100% acetonitrile, 45–55 min down to 60% acetonitrile) was used as mobile phase with a total flow-rate set to 0.6 ml/min. For detection fluorescence and dioden array detectors were used in series. A time program was used to detect the different PAHs at optimal absorption and emission wavelengths. Quantitative analysis of the 16 US Environmental Protection Agency (EPA) PAHs was performed using external standard calibration with a reference standard solution (Promochem, Wesel, Germany) diluted appropriately.

## 2.5. Gas chromatography

Analysis of unknown compounds in the extracts were performed using a Hewlett–Packard 5890 GC system equipped with a HP-5-MS-capillary column (30 m $\times$ 0.25 mm I.D.) coated with chemical bonded

SE-54 ( $d_F=0.25 \mu\text{m}$ ; Hewlett–Packard, Germany). Helium (1.6 ml/min) was utilised as carrier gas. The analyses were performed using the following temperature program: 40°C held 1 min isothermal, heating rate 4°C/min up to 310°C, final temperature held for 1.5 min. Injector and detector temperatures were 250°C, respectively 300°C, detection was achieved using a mass detector (5872, Hewlett–Packard).

### 3. Results and discussion

#### 3.1. Sample characterisation

The sample LUT1 contained 63.4 g/kg of humic acids; sample FR only 0.04 g/kg. The TOC yield of sample LUT1 was 50 g/kg and the soil FR contained 55 g/kg TOC. The GC analysis showed a concentration of toluene and xylene lower than 0.2 g/kg in the soil sample LUT1. The sample contained aliphatic hydrocarbons in minor concentration. In contrast soil FR contained a high concentration of aliphatic hydrocarbons (about 35 g/kg), but the BTX concentration was lower than 1 g/kg.

The yields of the sieve-analysis after grinding of the samples are shown in Table 2. The main part of sample LUT1 (80%) contained particles with a size of 63  $\mu\text{m}$ –250  $\mu\text{m}$ . The distribution of the particle size of sample FR was very regular between 90  $\mu\text{m}$  and 710  $\mu\text{m}$ .

Table 2  
Sieve analysis

Size of the sieve ( $\mu\text{m}$ )	Sieve residue (%)	
	LUT1	FR
710	0.76	15.95
500	0.58	12.67
355	3.98	20.48
250	9.14	10.30
180	18.28	13.36
125	28.92	14.98
90	28.12	10.84
63	8.86	0.18
45	1.20	0.01
32	0.00	0.00

#### 3.2. Effect of extraction temperature and particle size on the SFE

For sample LUT1 the influence of the extraction temperature on the extraction efficiency was tested in preliminary experiments (data not shown). Starting at a temperature of 35°C, the temperature was raised performing 30°C steps up to 150°C. For each temperature, three extractions with CO<sub>2</sub>/10 mol% pentane were conducted and the temperature optimum was determined to be 90–110°C. Therefore the further experiments were performed at an extraction temperature of 90°C. Hawthorne et al. [12] found increasing extraction yields depending on increasing temperature. But they tested only three different temperatures. Other groups achieved comparable results with our investigations [21].

The influence of the particle size on the extraction efficiency was investigated with the soil sample LUT1. Therefore the sample was fractionated in three different parts with a particle size greater 355  $\mu\text{m}$ , particles size between 355  $\mu\text{m}$  and 188  $\mu\text{m}$ , and particles between 188 and 45  $\mu\text{m}$ . The extraction yield of the last named fraction increased up to 150% in comparison with the yield of the fraction with the largest particles (Table 3), obviously because of a

Table 3  
Influence of the particle size on the extraction yields

	Extraction yields from soil LUT1 using SFE modified with 10 mol% <i>n</i> -pentane ( $\mu\text{g/ml}$ )	
	355–600 $\mu\text{m}$	45–180 $\mu\text{m}$
Acenaphthylene	0.17	0.09
Naphthalene	0.0	0.16
Acenaphthene	0.01	0.02
Fluorene	0.01	0.03
Phenanthrene	0.08	0.23
Anthracene	0.03	0.05
Fluoranthene	0.31	0.50
Pyrene	0.30	0.72
Benzoanthracene	0.17	0.22
Chrysene	0.18	0.24
Benzo[ <i>b</i> ]fluoranthene	0.08	0.23
Benzo[ <i>k</i> ]fluoranthene	0.06	0.06
Benz[ <i>a</i> ]pyrene	0.02	0.12
Dibenzo[ <i>a,h</i> ]anthracene	0.02	0.03
Benzo[ <i>ghi</i> ]perylene	0.03	0.09
Indeno[1,2,3- <i>cd</i> ]pyrene	0.03	0.11

larger surface. Without grinding the samples, we had a less amount of small particles.

### 3.3. Soxhlet extraction versus SFE with pure carbon dioxide

Looking on the Soxhlet extraction yields, soil LUT1 was contaminated with EPA PAHs to a minor extent, meanwhile the soil FR is heavily polluted as shown in Table 4. Naphthalene is the main component in the soil LUT1, while the sample was minor contaminated with acenaphthene and fluorene. In contrast, in the soil FR naphthalene was a minor component whereas pyrene, fluoranthene, benzoanthracene and benzo[*a*]pyrene were the main components.

Comparing the Soxhlet extractions of both samples with dichloromethane and *n*-pentane, the extraction with *n*-pentane supplied higher concentrations of PAHs (Table 4). Especially the extraction yields from soil FR of benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*a*]pyrene increased up to 40% and chrysene up to 100%. The average of the PAHs from soil LUT1 was enhanced to 50%.

Comparing Soxhlet extraction with pentane versus SFE with pure carbon dioxide (Tables 5 and 6)

Soxhlet extraction seems to be the better method for the extraction of PAHs from highly contaminated soils like FR. The sample yielded on average only 40–80% of the PAHs using pure CO<sub>2</sub> than performing Soxhlet extraction, except fluoranthene which was found in equal concentrations. The high content of aliphatic hydrocarbons in the soil FR, which dissolve PAHs in a better way than CO<sub>2</sub>, could be the reason for the bad extraction yields by SFE for this soil. Soxhlet extraction of the PAHs with *n*-pentane from the soil LUT1 yielded, on average, 50% higher results than SFE with pure CO<sub>2</sub>, apart from fluoranthene whose yield decreased down to 40%. The situation changes with the use of modifiers which are suitable to break the PAH–matrix interactions (see below).

### 3.4. SFE using binary mixtures

The addition of nonpolar co-solvents like *n*-pentane and toluene, or minor polar modifiers like dichloromethane to carbon dioxide improved the ability of the supercritical CO<sub>2</sub> to displace PAHs from matrix active sites. SFE of sample LUT1 with several modifiers and modifier mixtures (Table 7) reached the extraction efficiency of Soxhlet extrac-

Table 4  
Soxhlet results with different solvents

PAH	Soil LUT1				Soil FR			
	Pentane		CH <sub>2</sub> Cl <sub>2</sub>		Pentane		CH <sub>2</sub> Cl <sub>2</sub>	
	mg/kg	R.S.D. (%)	mg/kg	R.S.D. (%)	mg/kg	R.S.D. (%)	mg/kg	R.S.D. (%)
Naphthalene	3.23	(±) 1	2.25	(±) 2	0.59	(±) 2	7.13	(±) 1
Acenaphthene	0.08	(±) 5	0.03	(±) 4	1.11	(±) 1	0.33	(±) 2
Fluorene	0.04	(±) 5	0.03	(±) 4	16.09	(±) 1	10.45	(±) 1
Phenanthrene	0.40	(±) 10	0.27	(±) 3	59.49	(±) 1	48.63	(±) 1
Anthracene	0.12	(±) 3	0.09	(±) 5	64.09	(±) 1	49.96	(±) 1
Fluoranthene	0.93	(±) 1	0.70	(±) 1	82.06	(±) 1	132.81	(±) 1
Pyrene	1.40	(±) 1	0.54	(±) 1	233.18	(±) 1	225.88	(±) 1
Benzoanthracene	0.31	(±) 2	0.32	(±) 2	106.66	(±) 1	74.10	(±) 1
Chrysene	0.41	(±) 1	0.35	(±) 1	85.74	(±) 1	39.96	(±) 1
Benzo[ <i>b</i> ]fluoranthene	0.48	(±) 1	0.43	(±) 1	84.3	(±) 1	59.71	(±) 1
Benzo[ <i>k</i> ]fluoranthene	0.23	(±) 2	0.21	(±) 1	39.81	(±) 1	33.56	(±) 1
Benzo[ <i>a</i> ]pyrene	0.36	(±) 2	0.31	(±) 1	113.4	(±) 1	81.63	(±) 1
Dibenz[ <i>a,h</i> ]anthracene	0.07	(±) 5	0.05	(±) 4	8.44	(±) 1	11.90	(±) 1
Benzo[ <i>ghi</i> ]perylene	0.35	(±) 2	0.2	(±) 2	77.21	(±) 1	58.36	(±) 1
Indeno[1,2,3- <i>cd</i> ]pyrene	0.33	(±) 1	0.20	(±) 3	66.58	(±) 1	53.68	(±) 1

Table 5  
SFE-extraction yields with various modifiers in comparison to the *n*-pentane Soxhlet extraction yields of soil LUT1 (Soxhlet yields=100%)

PAH	CO <sub>2</sub>		2% CH <sub>2</sub> Cl <sub>2</sub>		10% CH <sub>2</sub> Cl <sub>2</sub>		2% Toluene		10% Toluene		2% Pentane		10% Pentane		2% MeOH		10% MeOH		2% Acetone		10% Acetone	
	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)
Naphthalene	197	9	257	13	301.2	0.3	285	13	51	2	324	2	373.2	16	100.8	3	350.4	3	23.2	17	68.8	17
Acenaphthene	106	12	338	9	292	10	125	39	83	2	73.2	16	97.3	9	48.9	14	84.3	11	0.0	0.0	0.0	0.0
Fluorene	50	6	0	0	0	0	0	0	0	0	139.9	11	212.4	18	64.8	21	100.9	17	0.0	0.0	0.0	0.0
Phenanthrene	46	7	74	14	57	17	93	16	97	7	125.9	13	44.4	9	62.9	22	103.8	22	24.9	12	54.2	7
Anthracene	54	8	113	14	49	9	19	5	66	6	254.8	7	127.5	4	65.2	5	139.3	11	52.4	14	58	29
Fluoranthene	55	7	147	2	58	10	53	6	103	2	166.8	4	151.4	15	84.2	15	104.9	16	39.3	27	36.6	9
Pyrene	46	4	138	4	63	8	54	1	138	13	159	13	124.5	5	771.6	12	101.9	14	50.2	9	76.2	8
Benzoanthracene	51	6	265	10	105	7	79	4	186	5	186.1	12	219.7	8	0.0	11	170.1	8	94.9	12	136.6	10
Chrysene	38	5	160	13	85	12	74	1	161	10	159	13	233	15	51.3	15	126.6	11	60.5	9	96.4	11
Benzo[b]fluoranthene	45	6	131	14	62	6	67	5	137	9	136.8	4	167.6	10	73.5	16	103.3	10	57.8	12	102	11
Benzo[k]fluoranthene	60	4	108	7	55	2	53	3	74	6	67.2	3	79.8	10	146.6	15	60.7	3	47.5	10	59.5	3
Benzo[a]pyrene	41	4	113	18	50	3	34	5	97	9	109.5	5	135	8	27.5	12	87.1	7	59.4	15	72.8	5
Dibenzo[a,h]anthracene	43	8	0	0	0	0	171	9	107	15	71.9	26	152.1	15	139.3	15	55.5	10	48.4	11	61.5	6
Benzo[ghi]perylene	11	8	48	4	25	18	16	28	67	10	166.3	21	134.5	18	5.1	9	64	10	36.8	16	34.5	11
Indeno[1,2,3-cd]pyrene	24	8	69	7	38	6	38	12	96	12	93.5	12	105	13	14.5	8	60.2	6	33.8	19	55	10

Table 6  
SFE yields with various modifiers in comparison to the *n*-pentane Soxhlet extraction yields of soil FR (Soxhlet yields=100%)

PAH	CO <sub>2</sub>		2% CH <sub>2</sub> Cl <sub>2</sub>		10% CH <sub>2</sub> Cl <sub>2</sub>		2% Toluene		10% Toluene		2% Pentane		10% Pentane		2% MeOH		10% MeOH		2% Acetone		10% Acetone	
	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)
Naphthalene	0	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Acenaphthene	36	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fluorene	40	16	0	0	6	3	31	4	35	12	31	8	32	2	27	20	32	5	32	14	30	9
Phenanthrene	64	4	48	5	35	8	64	5	51	15	63	7	65	5	52	16	61	3	77	5	53	8
Anthracene	48	5	31	1	26	7	41	1	27	6	39	6	43	9	36	13	46	4	45	3	38	5
Fluoranthene	133	3	116	1	99	4	139	1	117	1	102	9	131	8	124	8	125	3	150	1	120	8
Pyrene	49	2	176	1	103	2	53	4	40	4	36	15	61	7	45	9	50	4	54	4	43	12
Benzoanthracene	47	5	56	1	53	4	54	3	47	4	38	8	52	5	0	4	51	5	52	3	42	6
Chrysene	35	6	40	1	4	8	48	4	41	7	33	9	51	8	56	5	48	8	38	3	36	9
Benzo[b]fluoranthene	33	5	33	1	15	6	44	6	36	7	27	8	45	13	40	7	46	11	39	3	41	14
Benzo[k]fluoranthene	31	3	13	2	13	1	34	3	31	4	26	5	34	6	74	20	33	3	33	3	32	6
Benzo[a]pyrene	22	6	23	1	3	8	23	7	18	9	18	8	33	9	22	4	29	8	20	3	22	14
Dibenzo[a,h]anthracene	30	25	2	23	6	14	64	6	0	0	0	0	77	11	0	0	61	11	39	12	51	18
Benzo[ghi]perylene	7	4	12	4	7	25	17	3	7	7	77	13	20	19	11	2	21	5	11	11	16	8
Indeno[1,2,3-cd]pyrene	11	13	12	1	14	10	19	9	13	6	11	11	22	17	15	5	28	17	17	5	20	9

Table 7  
SFE yields with various modifiers in comparison to the *n*-pentane Soxhlet extraction yields of soil LUT1 (Soxhlet yields=100%)

PAH	4% Acetone–toluene		8% Acetone–toluene		4% MeOH–toluene		10% MeOH–toluene		4% Acetic acid–pentane		4% Ethanolamine–acetone		10% Ethanolamine–acetone		4% Acetic acid–acetone		10% Acetic acid–acetone	
	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)
Naphthalene	106	2	58	14	103	2	87	12	78	3	75	6	50	21	59	19	0	0
Acenaphthene	78	5	41	1	59	8	37	10	62	7	58	8	30	7	40	19	52	5
Fluorene	81	4	774	8	0	0	0	0	94	11	77	12	46	4	53	10	77	13
Phenanthrene	102	11	61	8	76	10	48	17	24	20	55	10	47	3	48	15	68	13
Anthracene	73	4	59	9	57	12	39	7	78	5	45	13	53	10	36	15	58	12
Fluoranthene	82	1	58	7	80	12	45	11	76	1	57	8	69	7	50	10	80	4
Pyrene	76	5	59	9	67	12	55	13	91	1	62	6	63	11	49	6	83	2
Benzoanthracene	129	1	68	8	116	8	117	10	92	0	74	3	0	10	65	7	127	3
Chrysene	88	2	56	9	63	9	98	9	75	5	67	4	78	13	52	7	98	2
Benzo[ <i>b</i> ]fluoranthene	87	14	70	14	62	3	85	10	65	2	59	3	61	15	40	7	80	4
Benzo[ <i>k</i> ]fluoranthene	56	6	44	6	44	3	58	5	55	3	54	4	125	13	39	7	68	1
Benzo[ <i>a</i> ]pyrene	79	111	46	8	38	8	71	12	67	1	55	2	33	6	42	10	85	5
Dibenzo[ <i>a,h</i> ]anthracene	41	11	39	15	40	19	77	12	63	5	40	4	421	10	29	8	60	6
Benzo[ <i>ghi</i> ]perylene	37	9	27	8	28	18	57	9	3	4	37	7	13	12	21	7	37	14
Indeno[1,2,3- <i>cd</i> ]pyrene	45	10	34	7	48	14	51	15	37	4	36	13	28	6	22	6	44	11

tion and SFE with some co-solvents like *n*-pentane, 10 mol% toluene or 2 mol% dichloromethane exceeded the Soxhlet results. The best results were obtained using 10 mol% *n*-pentane (160% in comparison with the *n*-pentane Soxhlet-extraction), followed by 2 mol% *n*-pentane and 10 mol% toluene (100–120% in comparison with the *n*-pentane Soxhlet-extraction). The use of polar modifiers had minor influence on the recoveries in contrast to other investigations [15,16]. Looking at the highly volatile PAHs like naphthalene and acenaphthene, good recoveries from soil LUT1 were received using modifier-assisted SFE. In most cases these compounds were extracted in higher yields using these binary fluid phases compared to the studied *n*-pentane Soxhlet method (see Tables 5 and 6).

For high molecular weight PAHs, which interact strongly with the active sites of the matrix, nonpolar modifiers like *n*-pentane or toluene proved to be the best modifiers. For example, the recovery of dibenzo[*a,h*]anthracene with *n*-pentane was 160%, while the use of acetone (2 mol%) showed only 50% recovery in comparison to the *n*-pentane Soxhlet extraction.

Modifier-assisted SFE of soil FR improved the extraction yields by about 110–120% from soil FR in comparison with SFE using pure CO<sub>2</sub>. Because of the high content of aliphatic paraffins, the modifiers probably simply are capable of increasing the extraction of the aliphatics, thus better exposing the PAHs to the modified supercritical fluid. In comparison with the Soxhlet method modified-assisted SFE from soil FR showed irrespective of the modifier identity only 40–80% of the Soxhlet results, with the exception of fluoranthene. Obviously the high amount of paraffins in soil FR solutes the PAHs because of their lipophilic characters and viscosity so that the supercritical fluids with their high diffusivity are not able to detach the PAHs sufficiently from such a matrix. Maybe by using stronger SFE conditions like higher extraction temperature and longer extraction time, such samples could be extracted with similar results like an 8-h Soxhlet method is able to do. We suggest that the short extraction time (40 min), which is used in the SFE experiments, is the reason for the minor release of highly volatile PAHs by SFE of soil FR.

### 3.5. SFE using ternary mixtures

For studying the effect of Lewis bases or acid, modifiers like ethanolamine and acetic acid were added in minor quantities to acetone and *n*-pentane (Table 1). These solutions were utilized as modifiers (4 and 10 mol%) in the SFE experiments with the exception of the mixture acetic acid and *n*-pentane. The addition of acetic acid to the modifiers produced only in the mixture with *n*-pentane better results (Table 7, 150%) than the *n*-pentane Soxhlet extraction of soil LUT1 which is set as 100%. This combination of the best single co-solvent in the binary mixture *n*-pentane with acetic acid supplied good results because of the *n*-pentane part. Using SFE modified with 10 mol% *n*-pentane, we achieved an increase of up to 160%. The Lewis-base modifier mixture acetone with ethanolamine (4 mol%) increased the extraction yields in comparison with the Soxhlet method for 5–50%. Increasing the base modifier concentrations to 10 mol% ethanolamine–acetone did not improve the extraction yields further. Probably the humic acids of the sample LUT1 bind the PAHs in such a way that polar modifiers like Lewis bases or acids cannot break all these bondings. In other investigations, the disruption of PAH–matrix interactions in soils with high concentrations of silicates could be strongly improved with Lewis bases or acids [13,15,16]. In the sample FR mainly nonpolar interactions between the PAHs and the high concentration of aliphatic hydrocarbons exist. Therefore, no polar interactions have to be overcompensated in soil FR by polar modifiers. According to this, the use of polar modifiers had no significant influence on the extraction of soil FR.

Using the ternary mixture of 4 mol% acetone–toluene–CO<sub>2</sub>, the extraction yields from soil LUT1 were improved for 50%–150% in comparison with the Soxhlet extraction using *n*-pentane. But they did not reach the results of SFE with 10 mol% *n*-pentane.

The mixture of a protic-polar and nonpolar modifier, 4 mol% methanol–toluene, increased the extraction yield of the di-, tri- and tetracyclic PAHs compared to the Soxhlet extraction of soil LUT1. Maybe special kinds of physisorption were overcompensated by the use of this modifier.



Table 8  
SFE yields with various modifiers in comparison to the *n*-pentane Soxhlet extraction yields of soil FR (Soxhlet yields=100%)

PAH	4% Acetone–toluene		8% Acetone–toluene		4% MeOH–toluene		10% MeOH–toluene		4% Acetic acid–pentane		4% Ethanolamine–acetone		10% Ethanolamine–acetone		4% Acetic acid–acetone		10% Acetic acid–acetone	
	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)	%	R.S.D. (%)
Naphthalene	0	0	0	0	0	0	0	0.0	0	0	0	6	0	0	0	0	0	0
Acenaphthene	0	0	95	12	0	0	0	0.0	63	14	54	8	21	4	0	0	13	4
Fluorene	32	7	45	11	26	16	36	5	35	12	37	12	34	6	26	5	32	6
Phenanthrene	67	2	65	1	55	12	69	3	62	5	62	10	65	5	45	5	50	5
Anthracene	42	2	50	1	39	9	44	3	49	2	50	13	45	3	36	7	41	3
Fluoranthene	125	2	119	6	122	5	132	5	141	2	131	8	127	1	107	3	103	1
Pyrene	44	5	50	13	55	3	49	6	58	4	60	6	52	1	48	7	44	1
Benzoanthracene	46	3	51	5	51	6	50	3	47	2	48	4	44	1	37	9	36	1
Chrysene	29	1	43	12	39	8	49	4	39	6	38	3	35	7	33	8	30	7
Benzo[ <i>b</i> ]fluoranthene	35	2	43	15	49	1	39	5	40	6	38	4	33	2	27	9	30	2
Benzo[ <i>k</i> ]fluoranthene	27	4	37	6	31	7	32	3	34	2	38	2	35	1	29	8	34	1
Benzo[ <i>a</i> ]pyrene	18	6	35	10	21	11	27	2	26	17	33	4	29	6	23	10	26	6
Dibenzo[ <i>a,h</i> ]anthracene	27	4	37	13	118	6	48	9	39	17	20	7	38	3	38	11	37	3
Benzo[ <i>ghi</i> ]perylene	14	7	17	17	19	41	18	4	10	7	17	13	10	1	9	12	11	1
Indeno[1,2,3- <i>cd</i> ]pyrene	16	5	28	13	15	12	20	4	20	8	23	5	15	3	13	14	18	3

The results of soil FR are not significantly improved using tenary mixtures at the SFE-extraction in comparison with pure CO<sub>2</sub> (Tables 6 and 8). We achieved on average an increase of 20% using modifiers, but the Soxhlet yields could not be obtained. The recoveries from soil FR are always similarly independent of the identity of the modifiers. Nevertheless the results indicate that the use of polar/nonpolar mixtures of modifiers are more profitable than polar/polar mixtures.

### 3.6. Effect of modifier concentration

Increasing modifier concentrations from 4 to 10 mol% in the supercritical fluid improved the extraction yields of PAHs for most co-solvents used. The organic solvent molecules compete with the active sites of the matrix to interact with the PAHs. The more solvent molecules that are available, the more analyte–matrix interactions can be broken and analytes can be extracted. The increase of acid concentration in the fluid leads to higher analyte yields likewise. The results of increasing concentration using the modifier mixture ethanolamine/acetone were different for soil LUT1 and FR. Meanwhile the higher modifier concentration of ethanolamine/acetone used in the SFE-extraction of soil LUT1 decreased the yield, the yields from soil FR were increased. For the highly contaminated sample FR, the increase of the polar modifiers dichloromethane and acetone were negatively correlated to the extraction yields. Probably the fluid becomes too polar using such modifiers which limits the solubility of the PAHs in the fluid. All these results indicate a total difference in the matrix–PAHs interactions in both soils.

In general, the modifier identity had a larger effect on the extraction efficiencies of the PAHs than the modifier concentration as also described by Langenfeld et al. [17]. The kind of matrix–analyte interactions like Van der Waals interactions, hydrogen bondings and electron–donor–acceptor complexes and the physical and chemical parameters of the co-solvent seems to have the largest impact on the extraction efficiency.

## 4. Conclusions

In general, the use of modifiers in SFE improves the extraction yields of PAHs from real contaminated soils. Comparing the extraction of the low- and high-molecular-mass PAHs for both the investigated soils, the influence of the modifiers on the extraction results is significantly higher for the latter. High-molecular-mass PAHs are able to interact with more bonding sites of the soil matrix. But with the use of the SFE these interactions can be suppressed. The effect of the different modifiers on the extraction efficiencies of the PAHs depends on the soil matrix. Humic substances, clay minerals or high concentrations of viscose aliphatics are responsible for different matrix–PAH interactions. Strong bondings between PAHs and humic substances like in soil LUT1 can be broken best with nonpolar modifiers. The presence of accompanying pollutants like aliphatics in the soil sample FR which solute PAHs excellent, hampers the extraction of PAHs. The addition of modifiers to CO<sub>2</sub> is not sufficient to overcome the strong PAH–aliphatic interactions in soil FR. In this case, for a complete extraction, a longer extraction time as performed in Soxhlet extraction seems to be necessary. Generally, for both tested soils which have very different soil matrices, the use of nonpolar modifiers like *n*-pentane achieved better results than the use of polar co-solvents like acetone, methanol, acids or bases. The nonpolar modifiers, *n*-pentane and toluene were almost similarly useful for obtaining good extraction results. The use of *n*-pentane instead of the often used *n*-hexane has the advantage of a lower toxicity. Furthermore *n*-pentane is more compatible with the following analysis of the PAHs by HPLC than toluene. The modifier character has a larger effect on the extraction efficiency of the PAHs than the modifier concentration. The effect of the modifier concentration is not quite clear. Most of the tested modifiers achieved better extraction results in higher concentrations, whereas some modifier archived poor results. In our investigation about extraction efficiency depending on the particle size, we proved better extraction yields by using smaller soil particles with a higher surface area.

## Acknowledgements

We thank M. Möller for providing the GC analysis and G. Götz for providing the mill for crushing the soils.

## References

- [1] G. Shaw, D. Connel, W. Barron, *Chemosphere* 30 (1995) 1957–1968.
- [2] S.B. Hawthorne, *Anal. Chem.* 62 (1990) 633A.
- [3] N. Alexandrou, J. Pawlisyzy, *Anal. Chem.* 61 (1989) 2770.
- [4] N. Alexandrou, J. Pawlisyzy, *Anal. Chem.* 64 (1992) 301.
- [5] R.W. Vannoort, J.-P. Chervet, H. Lingeman, G.J. DeJong, U.A.Th. Brinkman, *J. Chromatogr.* 505 (1990) 45.
- [6] S.B. Hawthorne, D.J. Miller, J.J. Langenfeld, *Proceedings of the International Symposium on Supercritical Fluid Chromatography and Extraction*, Park City, UT, January 1991, p. 91.
- [7] V. Seidel, W. Lindner, *Int. J. Environ. Anal. Chem.* 59 (1995) 15.
- [8] T.L. Chester, J.D. Pinkston, D.E. Raynie, *Anal. Chem.* 64 (1992) 153R.
- [9] S.T. Tena, M.D. Luque de Castro, M.J. Varcacel, *J. Chromatogr.* 38 (1994) 431.
- [10] H.-B. Lee, T.E. Peart, R.L. Hong-You, D.R. Gere, *J. Chromatographia* A 653 (1993) 83.
- [11] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawlisyzy, *Anal. Chem.* 65 (1993) 338.
- [12] S.B. Hawthorne, D.J. Miller, *Anal. Chem.* 66 (1994) 4005.
- [13] Y. Yang, A. Gharaibeh, S.B. Hawthorne, D.J. Miller, *Anal. Chem.* 67 (1995) 641.
- [14] V. Camel, A. Tambute, M. Caude, *J. Chromatogr.* 642 (1993) 263–281.
- [15] J. Hollender, J. Shneine, W. Dott, M. Heinzl, H.W. Hagemann, G.K.E. Götz, *J. Chromatogr. A* 776 (1997) 233.
- [16] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawlisyzy, *Anal. Chem.* 66 (1994) 909.
- [17] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawlisyzy, *Anal. Chem.* 67 (1994) 1727.
- [18] T.M. Fahmy, M.E. Paulaitis, D.M. Johnson, M.E.P. McNally, *Anal. Chem.* 65 (1993) 1462.
- [19] G.K.E. Götz, W. Pickel, M. Wolf, in: J.A. Pajares, J.M.D. Tascon (Eds.), *Coal Science and Technology*, Vol. 24, *Coal Science*, Vol. I, Elsevier, Amsterdam, 1995, p. 295.
- [20] X. Yu, X. Wang, R. Bartha, J.D. Rosen, *Environ. Sci. Technol.* 24 (1990) 1732.
- [21] S. Reindl, F. Höfler, *Anal. Chem.* 66 (1994) 1808.
- [22] J. Dankers, M. Groenenboom, L.H.A. Scholtis, C. van der Heiden, *J. Chromatogr.* 641 (1993) 357.