ELSEVIER

Journal of Chromatography A, 883 (2000) 151–162

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Pressurised liquid extraction of polycyclic aromatic hydrocarbons from contaminated soils

Staffan Lundstedt*, Bert van Bavel, Peter Haglund, Mats Tysklind, Lars Öberg

Environmental Chemistry, Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Received 28 December 1999; received in revised form 30 March 2000; accepted 31 March 2000

Abstract

The reliability and efficiency of the pressurised liquid extraction technique (PLE) for extracting polycyclic aromatic hydrocarbons (PAHs) from contaminated soil has been investigated. Experimental design was used to study the influence of seven extraction variables (sample load, solvents used, solvent ratios, pressure, temperature, extraction time, and rinse volume). The results show that large sample loads in combination with small solvent volumes may result in low extraction efficiency. They also indicate that the recovery of low-molecular-mass PAHs is reduced by low extraction temperatures. The exact settings of the other variables are, however, less significant for the extraction efficiency. Repeated extractions at optimised settings of the tested variables show that PLE is an exhaustive extraction technique that generally results in high yields. In addition, extraction of a certified reference material (CRM 103-100) revealed that the method is both accurate and precise. Another finding was that adding the internal standard on top of the soil in the extraction cell causes considerable over-estimation of the concentrations when large samples are extracted with small solvent volumes. This is because the PLE-cell resembles a chromatographic column, so compounds added to the top of the soil layer have a longer distance to travel through the soil compared to the average distance of the native compounds, which are distributed evenly throughout the column. We therefore recommend that the internal standard should be added to the extract immediately after the extraction or, alternatively, carefully mixed with the sample prior to extraction.

Keywords: Pressurized liquid extraction; Soil; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Extraction of organic pollutants from soil is a critical step during soil analysis, because hydrophobic compounds are strongly sorbed to the soil material. The sorption occurs through a combination of surface adsorption and partitioning (or dissolution) into organic phases, the latter being generally regarded as the major mechanism [1,2]. However, this partitioning process is slow, and the fraction of pollutants bound to the organic matter increases with time, a phenomenon referred to as ‘aging’. Consequently, the reverse process, i.e. desorption, is also slow, limiting the pollutants’ bioavailability and extractability [3–5]. Extraction methods developed using freshly spiked soil may therefore work less efficiently on real samples. On the other hand, when extraction methods are used on real soil samples it is

*Corresponding author.

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00419-2

impossible to know if the target compounds have been fully recovered. The best approach is to carefully optimise the method using real soil samples, and then to validate the optimised method with certified reference materials.

The traditional extraction methods for solid matrices are Soxhlet and ultrasonic extraction. Both of these methods are time- and labour- intensive, and require large amounts of organic solvents. Therefore, new extraction methods have been developed, e.g. microwave assisted extraction (MAE) [6–8], supercritical fluid extraction (SFE) [6,9–12] and pressurised liquid extraction (PLE) [6,13,14]. Several studies have shown that these methods can be equally or even more efficient than Soxhlet extraction [8,15–32], although, in some cases they have been reported to be less efficient [29–33]. Thus, it appears that the extraction efficiencies of these new methods are more dependent on analyte properties, sample quality and optimisation than Soxhlet extraction [27–31,34,35].

PLE, Soxhlet and SFE are all continuous extraction techniques, which result in higher mass transfer rates compared to batch extraction systems, such as ultrasonic extraction and MAE. During the dynamic phase of PLE fresh solvent is continuously introduced into the extraction cell, maintaining a high concentration gradient between the solvent and the surface of the sample matrix. The larger the concentration gradient, the faster the mass transfer rate or flux according to Fick's first law of diffusion [36].

PLE utilises organic solvents at temperatures above the normal boiling point and at high pressures. The elevated pressure maintains the solvent in the liquid state at these higher temperatures, and it also forces the solvent through the sample, and into areas of the matrix where the analytes have been trapped in pores. In addition, high pressure aids in the solubilisation of air bubbles, thereby exposing more of the sample to the extraction media. The elevated temperature during PLE increases the capacity of the solvent to dissolve both analytes and water. The latter process facilitates the extraction of analytes that are trapped in water-sealed pores. High temperature also helps to disrupt strong analyte–matrix interactions and increases diffusion rates, which shortens the equilibration time. In addition, elevated temperatures reduce both solvent viscosity and surface tension, thus improving the contact between the analytes and the solvent [14].

However, the highest possible pressures and temperatures do not necessarily result in the most efficient extraction [15]. The effects may be counteractive, and there are also practical limits for both temperature and pressure when using PLE on environmental samples. In addition, there are several other variables that affect the extraction efficiency, for instance, extraction time, solvent choice, solvent volume and sample load may all be important. The sample pre-treatment techniques, e.g. drying, grinding and addition of bulk material [18,19,27–29], as well as the composition of the original sample, (in terms of factors such as organic content, water content, particle size and heterogeneity) may also influence the result.

In this study the reliability and efficiency of the PLE technique for extracting PAHs from contaminated soil was investigated. Seven extraction variables were varied according to an experimental design and the effects of these variations were evaluated. The aim was both to find the optimal extraction conditions and to develop a robust, straightforward method that can be easily combined with a subsequent clean-up procedure.

2. Experimental

2.1. Sample

PAH-contaminated soil was collected from the site of a former gasworks in Stockholm, Sweden, on two different sampling occasions. The amount of water and organic matter (loss-on-ignition; LOI) in the soil was determined by heating the soil to 130°C for two h and then to 550°C for 5 h. The soil from the first and second samplings contained 12% and 9% water and 8.7% and 3.6% organic matter, respectively. A certified reference soil ''PAH Contaminated Soil'' CRM 103-100 [US Environmental Protection Agency, RTC Laramie, WY, USA, (EPA)] was obtained from Promochem (Ulricehamn, Sweden), containing 7% water and 15% organic matter. Prior to extraction the gasworks soil samples were air-dried at room temperature, and ground to a fine

powder in a ball mill. The certified reference soil was ground with anhydrous sodium sulphate in a mortar prior to extraction.

2.2. Materials and chemicals

Bulk Isolute Sorbent was purchased from International Sorbent Technology (IST, Mid Glamorgan, UK). Silica gel (Merck, Darmstadt, Germany) was rinsed with methanol and dichloromethane and then activated at 130°C prior to use. Sodium sulphate (Merck) was activated at 550°C before use. All solvents were of glass-distilled grade (Burdick & Jackson). The internal standards ([$^2H_8$]naphthalene, [$^2H_8$]acenaphthylene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]fluorene, [$^2H_{10}$]anthracene, [$^2H_{10}$]pyrene, [$^2H_{12}$]benzo[*a*]anthracene, [$^2H_{12}$]benzo[*k*]fluoranthene, [$^2H_{12}$]benzo[*ghi*]perylene, 30–40 μg/g in toluene) were obtained from Cambridge Isotope Lab. (Andover, MA, USA). Two reference standard mixtures (QTM PAH Mix and NIST SRM 2260) containing PAHs, as listed in Table 4 (7–10 μg/g) were obtained from Supelco (Bellefonte, PA, USA) and Promochem (Ulricehamn, Sweden), respectively.

2.3. Pressurised liquid extraction

The soil samples were extracted using a Dionex ASE 200 Accelerated Solvent Extractor, equipped with 11 ml stainless steel extraction cells. The extraction procedure starts with a dynamic extraction step, during which the cell is heated and solvent is continuously pumped through the sample. The extraction continues under static conditions i.e. with the same volume of solvent and at constant temperature and pressure, for a specified time. This static extraction step can be repeated once or twice with fresh solvent (giving 1–3 cycles in all). After the last static step the sample is rinsed with another portion of fresh solvent (1–100% of the cell volume) under low pressure. Each full extraction sequence consumes 20–40 ml of solvent.

A cellulose filter was placed at the bottom of the extraction cell before the sample was added. The soil from the first sampling occasion, used during the screening study, was added to the cell between two layers of bulk material (Isolute), without mixing. 50 μl of internal standard (IS) solution was added on top of the soil layer. The samples were extracted according to Table 1. The extracts were then evaporated to a volume of approximately 1 ml. The soil from the second sampling occasion, used during the optimisation study, and the reference soil, were carefully mixed with anhydrous sodium sulphate prior to extraction. The samples were extracted as described in Table 2. Immediately after extraction, one tenth of each extract was taken for analysis and spiked with 50 μl IS. These portions were evaporated to a final volume of approximately 1 ml.

2.4. Open column liquid chromatography

The evaporated extracts were fractionated on 15 mm (internal diameter) columns packed with 10 g silica gel, deactivated with 10% water, and 1 g anhydrous sodium sulphate. The packed columns were rinsed with 40 ml hexane before the samples were applied. The compounds were then eluted with 10 ml hexane, 30 ml hexane and 30 ml hexane–dichloromethane (3:1, v/v). The first fraction was discarded and the next two were collected and combined. The combined fractions were gently evaporated and reconstituted in 1 ml toluene.

2.4.1. Gas chromatography–low resolution mass spectrometry analysis

All samples were analysed using a Fisons GC 8000 (60 m×0.32 mm DB-5 capillary column, 0.25 μm film thickness, J&W Scientific, CA, USA) gas chromatograph coupled to a Fisons MD 800 mass-selective detector. The GC was operated in splitless mode and 1-μl portions of the extracts were injected using an autosampler. The MS system was operated in single ion monitoring (SIM) mode. The PAHs were identified by matching retention times and ion ratios of the compounds in the calibration standard with those detected in the samples. The PAH concentrations were calculated by comparing peak areas using either the external or internal standard technique. Use of the IS technique compensates for analyte losses during the clean-up procedure, provided the IS compounds and the analytes have

Table 1
Experimental design for pressurised liquid extraction (PLE) of PAH-contaminated soil. Screening of the most important extraction variables (V_n). Each sample was extracted with one static extraction cycle.

Sample No.	V_1: sample load (g)	V_2 and V_3: solvent mixtures (v/v)	V_4: pressure (MPa)	V_5: temperature (°C)	V_6: static extraction time (min)	V_7: rinse volume (ml)
1	1.0	Toluene–hexane (80:20)	6.9	60	2	4.4
2	5.0	Toluene–hexane (80:20)	19	60	10	11
3	1.0	Toluene–hexane (80:20)	6.9	200	2	4.4
4	5.0	Toluene–hexane (80:20)	19	200	10	11
5	5.0	Toluene–hexane (20:80)	6.9	60	2	11
6	1.0	Toluene–hexane (20:80)	19	60	10	4.4
7	5.0	Toluene–hexane (20:80)	6.9	200	2	11
8	1.0	Toluene–hexane (20:80)	19	200	10	4.4
9	5.0	Acetone–hexane (80:20)	6.9	60	10	4.4
10	1.0	Acetone–hexane (80:20)	19	60	2	11
11	5.0	Acetone–hexane (80:20)	6.9	200	10	4.4
12	1.0	Acetone–hexane (80:20)	19	200	2	11
13	1.0	Acetone–hexane (20:80)	6.9	60	10	11
14	5.0	Acetone–hexane (20:80)	19	60	2	4.4
15	1.0	Acetone–hexane (20:80)	6.9	200	10	11
16	5.0	Acetone–hexane (20:80)	19	200	2	4.4
17	3.0	Toluene–hexane (50:50)	13	130	6	7.7
18	3.0	Toluene–hexane (50:50)	13	130	6	7.7
19	3.0	Toluene–hexane (50:50)	13	130	6	7.7
20	3.0	Acetone–hexane (50:50)	13	130	6	7.7
21	3.0	Acetone–hexane (50:50)	13	130	6	7.7
22	3.0	Acetone–hexane (50:50)	13	130	6	7.7

Table 2
Experimental design for pressurised liquid extraction (PLE) of PAH-contaminated soil. Optimisation of the extraction variables (V_n). Each sample consisted of 1 g soil and was extracted at 14 MPa, with two static extraction cycles and an 11 ml rinse volume

Sample No.	V_1 and V_2: solvent mixtures (v/v)	V_3: temperature (°C)	V_4: static extraction time (min)
S1	Toluene–methanol (95:5)	200	2
S2	Toluene–methanol (50:50)	100	11
S3	Toluene–methanol (5:95)	150	20
S4	Hexane–ethyl acetate (95:5)	200	11
S5	Hexane–ethyl acetate (50:50)	150	2
S6	Hexane–ethyl acetate (5:95)	100	20
S7	Hexane–acetone (95:5)	150	11
S8	Hexane–acetone (50:50)	200	20
S9	Hexane–acetone (5:95)	100	2
S10	Hexane–acetone (50:50)	150	11
S11	Hexane–acetone (50:50)	150	11
S12	Hexane–acetone (50:50)	150	11
S13	Dichloromethane–acetone (95:5)	100	5
S14	Dichloromethane–acetone (50:50)	100	5
S15	Dichloromethane–acetone (5:95)	100	5

similar properties, and the IS has been added prior to the clean-up procedure.

2.4.1.1. Statistical evaluation

The experimental results were statistically evaluated by multiple linear regression (MLR) (Modde 4.0, Umetrics AB, Umeå, Sweden). In brief, a regression coefficient (x_1, x_2, x_3 . . .) is calculated, for each design variable (V_1, V_2, V_3 . . .), which is connected to a first or second order polynomial representing the relationship between the variable and the experimental result (C_{PAH}). However, during this study only first order models were used (Eq. (1)). Variables with large coefficients have more influence on the response than those with smaller coefficients. Experimental design and data evaluation has been described in detail by Box et al. [37].

$$C_{PAH} = C_0 + x_1V_1 + x_2V_2 + x_3V_3 \ldots + e \quad (1)$$

(C_0 = average concentration, e = model error)

3. Results and discussion

3.1. Screening study

Seven extraction variables were varied according to an experimental design (Table 1): sample load, solvents used, solvent ratios, pressure, temperature, extraction time and rinse volume. The results from the experiments are presented in Fig. 1. PAH concentrations were calculated using both the internal and external standard technique, giving IS-compensated and non-compensated values respectively. However, during this part of the study the non-compensated values were found to describe the extraction process better than the IS-compensated values and were therefore used to select variables in further optimisation experiments.

MLR evaluation of the non-compensated values for the total PAH recovery resulted in a model with a correlation coefficient (R^2) of 0.82 and a prediction coefficient (Q^2) of 0.73 (Table 3). The model

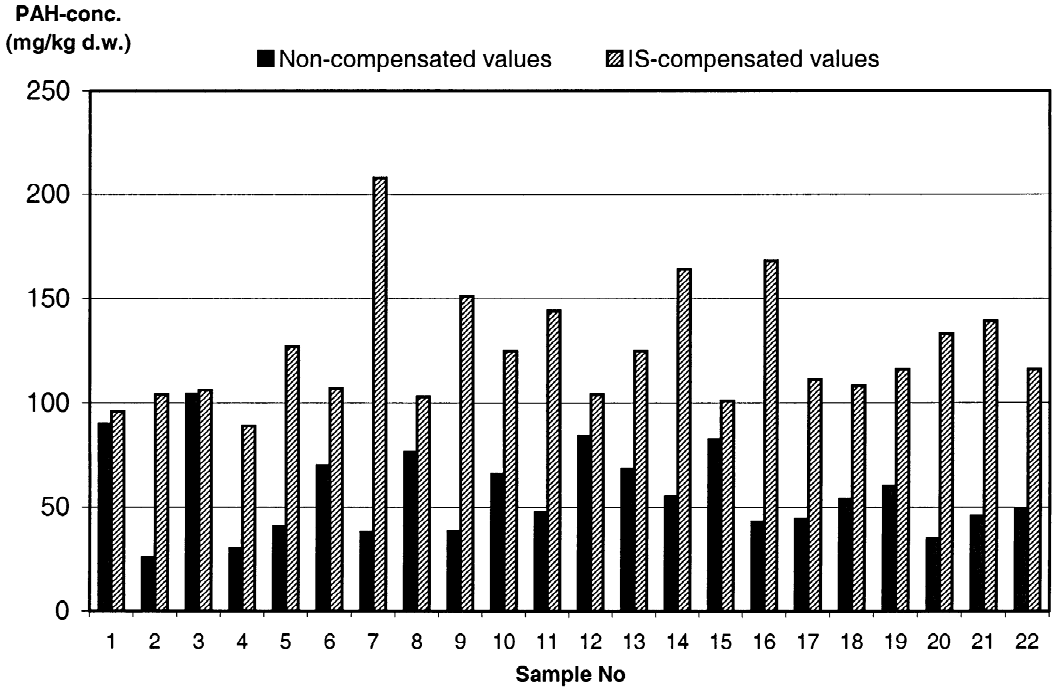

Fig. 1. Extraction results from screening the PLE variables. The PAH concentrations are calculated using either external or internal standard technique, giving non-compensated and IS-compensated values, respectively. Extraction conditions for each sample can be found in Table 1. d.w. = Dry mass.

Table 3
MLR models obtained from the screening study. The last model is calculated from the IS-compensated values, while the others are calculated from the non-compensated values. The models are linear in the form: $C_{PAH} = C_0 + x_1V_1 + x_2V_2 + x_3V_3 \ldots + r$. C_{PAH} = PAH concentration, C_0 = average concentration, V_n = variables (Table 1), x_n = coefficients. The quality of the fit for the models is described by the correlation coefficient (R^2) and the prediction coefficient (Q^2).

	C_0	Significant coefficients (95% confidence interval)	R^2	Q^2
Total PAH	57	$x_1 = -20$	0.82	0.73
Naphthalene	0.67	$x_5 = 0.26$	0.89	0.79
Acenaphthylene	0.79	$x_5 = 0.06$	0.94	0.90
Acenaphthene	0.44	$x_5 = 0.02$	0.53	0.17
Fluorene	0.45	$x_5 = 0.07$	0.95	0.92
Phenanthrene	7.7	$x_1 = -0.39$, $x_5 = 1.1$, $x_6 = -0.39$, $x_7 = -0.65$	0.83	0.63
Anthracene	1.7	$x_2 = \pm 0.19$, $x_3 = 0.16$, $x_5 = 0.29$,	0.82	0.59
Fluoranthene	11	$x_1 = -2.8$, $x_7 = -1.4$	0.72	0.55
Pyrene	9.5	$x_1 = -2.4$, $x_7 = 1.2$	0.75	0.60
Benzo[*a*]anthracene	4.2	$x_1 = -1.9$	0.85	0.68
Chrysene	4.8	$x_1 = -2.3$	0.85	0.75
Benzo[*b*]fluoranthene	3.9	$x_1 = -2.3$	0.85	0.79
Benzo[*k*]fluoranthene	3.1	$x_1 = -1.9$	0.83	0.71
Benzo[*a*]pyrene	3.4	$x_1 = -2.1$	0.84	0.70
Dibenz[*a,c*]anthracene	0.65	$x_1 = -0.44$	0.81	0.67
Indeno[*cd*]pyrene	2.3	$x_1 = -1.6$, $x_3 = -0.59$	0.83	0.73
Benzo[*ghi*]perylene	2.9	$x_1 = -2.0$, $x_3 = -0.89$	0.88	0.81
Total PAH (IS comp.)	121	$x_1 = 12$, $x_2 = \pm 13$, $x_3 = 5.8$, $x_6 = -5.3$, $x_7 = -9.2$	0.90	0.77

showed that small sample loads were favourable for high total PAH recovery, while changes in the other variables had no significant influence on the total PAH recovery. However, direct comparison of the non-compensated values in Fig. 1 indicates that the choice of extraction solvent also influences recovery. For instance, the highest PAH-recoveries were obtained when the soil was extracted with solvents containing a large proportion of toluene (samples 1 and 3).

When separate models were established for each PAH (Table 3) further information was obtained. The high-molecular-mass PAHs showed similar behaviour to the total PAHs, i.e. their recovery increased as sample load decreased. The low-molecular-mass PAHs, on the other hand, behaved differently. These compounds were extracted to a similar extent across the range of sample loads, but they were more efficiently extracted at high temperatures. For some of the medium sized compounds it was more difficult to explain the extraction results with these variables, resulting in less reliable models (with lower R^2 and Q^2 values).

The model obtained when the IS-compensated values were statistically evaluated (Table 3) suggested that large sample loads and small rinse volumes favour PAH recovery. In addition, this model suggested that the acetone–hexane mixture extracts PAHs more efficiently than the toluene–hexane mixture, and that mixtures with a large proportion of hexane favour PAH recovery. The lowest recovery was obtained when the extraction solvent contained a large proportion of toluene (Fig. 1). However, since this result was in disagreement with the result obtained from the non-compensated values, it was concluded that the IS-compensated values did not accurately describe the extraction process.

During this part of the study the IS was added on top of the soil sample in the extraction cell, and was thus eluted through the soil layer before reaching the collection vial. The recovery of the internal standard may therefore be regarded as a chromatographic process rather than an extraction process. Consequently, large, strongly retained molecules would be more difficult to recover from a thick soil layer. In Fig. 2 the GC–MS peak areas obtained for [$^2H_{12}$]chrysene and [$^2H_{10}$]acenaphthene in the 22

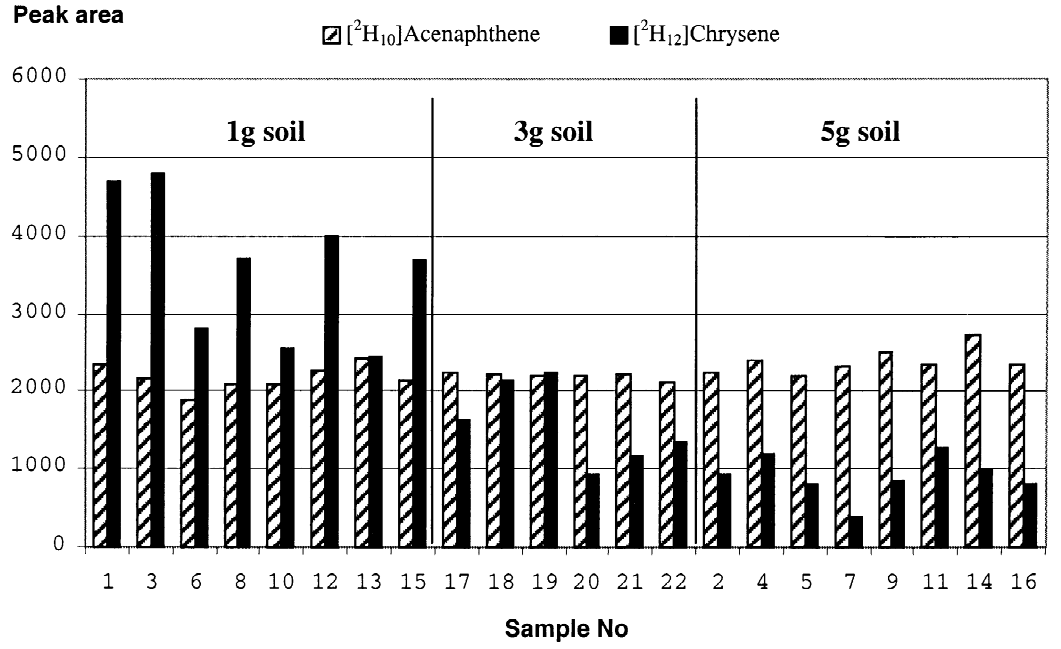

Fig. 2. Peak areas of [^{2}H$_{10}$]acenaphthene and [^{2}H$_{12}$]chrysene in the GC–MS chromatograms from the screening study. Samples 1, 3, 6, 8, 10, 12, 13, 15 are extracts of 1 g soil. Samples 17–22 are extracts of 3 g soil. Samples 2, 4, 5, 7, 9, 11, 14, 16 are extracts of 5 g soil. Extraction conditions for each sample can be found in Table 1.

samples are compared. Clearly, the peak-area of [^{2}H$_{12}$]chrysene decreases relative to that of [^{2}H$_{10}$]acenaphthene when the sample load increases. In addition, the heavier IS-compounds seem to be relatively more abundant when the sample has been extracted with a large amount of toluene (experiments 1 and 3). Similar relationships could be seen when comparing the peak areas of other high- and low-molecular-mass IS compounds. The native analytes were, however, not affected to the same extent, presumably since they were distributed evenly in the soil bed, and therefore had a shorter average distance to travel through the sample bed. Consequently, when large samples were extracted with weak solvents, such as hexane, smaller amounts of the IS compounds were recovered than of the corresponding native compounds, especially for large, strongly retained PAHs. The concentrations of the native compounds were then overestimated by calculations using the IS technique. In contrast, smaller samples extracted with a strong solvent gave similar recovery of both native PAHs and IS, with apparently lower PAH concentrations as a result.

3.2. Optimisation study

During the subsequent optimisation experiments the IS was added to the extracts immediately after the extraction, since adding it on top of the sample in the extraction cell so strongly influenced the result. The sample load was fixed at 1 g of dry soil since the screening study had indicated that large sample loads reduce the extraction efficiency. The soil was carefully mixed with anhydrous sodium sulphate prior to extraction, to increase the solvent penetration of the sample and to prevent channelling. In addition, the extractions were performed with two extraction cycles, instead of one, and with a large rinse volume (11 ml) to prevent recoveries being low because of insufficient elution. It has also been shown that two short static extraction cycles are more effective than one longer cycle [29]. The extraction pressure was fixed at 14 MPa (2000 p.s.i.), since this variable, in the studied interval, had limited influence on the extraction efficiency. The extraction solvent, temperature and time were then further optimised.

Four binary solvent mixtures (toluene–methanol,

hexane–ethyl acetate, hexane–acetone and dichloromethane–acetone) were tested, each in three different mixing ratios. The extraction temperature was investigated at three levels and the extraction time at four levels. The extraction conditions are compiled in Table 2, and the results are shown in Fig. 3. No significant differences were found in total PAH recovery. When studying the recovery of each PAH separately (Table 4) the differences between the treatments were also found to be relatively small. The MLR models for naphthalene ($C_0=15$, $x_3=2.3$, $R^2=0.96$ and $Q^2=0.64$, cf. Table 3) and acenaphthylene ($C_0=22$, $x_3=6.4$, $R^2=0.82$ and $Q^2=0.64$) indicate, however, that the recovery of the low-molecular-mass PAHs is influenced by the extraction temperature. This effect, although small, indicates that the extraction temperature should not be too low.

Re-extraction of one of the samples resulted in low PAH yields. Only 0.2% and 0.1% of the total PAHs recovered during the first extraction were found after a second and a third extraction, respectively. In conclusion, the optimisation study reveals that the PLE technique is both reliable and exhaustive. The choice of extraction solvent is not very important if a slightly larger volume is used (two static cycles and 11 ml flush volume). However, it has previously been shown [38] that use of non-polar solvents, such as hexane, may result in lower extraction recoveries. Hexane–acetone (50:50, v/v) was chosen as the preferred extraction solvent since it contains no chlorinated components, and it is more easily combined with the subsequent clean-up procedure compared to toluene–methanol. An extraction temperature of 150°C is recommended since higher temperatures are known to shorten the lifetime of the equipment

3.3. Reference soil

In order to estimate the accuracy and precision of the procedure developed, a reference soil (CRM 103-100) was extracted in triplicate using PLE at the identified optimal conditions. The extraction conditions and the results are presented in Table 5. All but three values fell within the 95% confidence interval established during the certification process (2-methylnaphthalene, phenanthrene and anthracene were found in concentrations slightly above the upper confidence limit). In Fig. 4, the PAH concentrations found are presented as percentages of the certified values. The results show that PLE is an

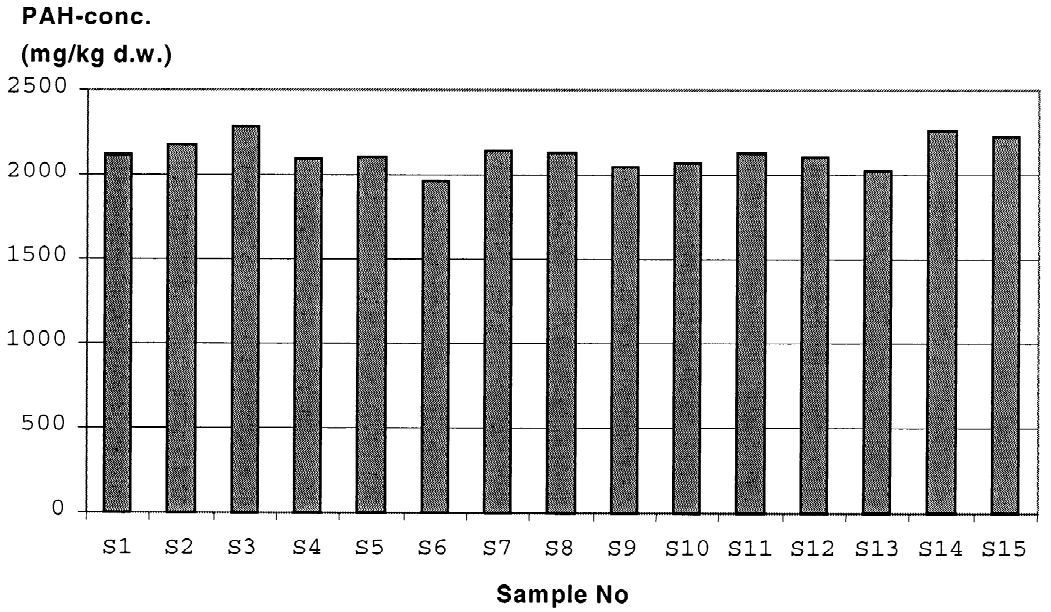

Fig. 3. Extraction results obtained during the PLE optimisation. Extraction conditions for each sample can be found in Table 2.

Table 4
Extraction results for 24 individual PAHs obtained during the PLE optimisation. All values are expressed in mg/kg dry mass. Extraction conditions for each sample can be found in Table 2

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Naphthalene	17	15	48	16	13	12	14	19	12	15	15	15	11	13	14
2-Methylnaphthalene	15	14	76	14	15	13	13	15	12	13	13	13	10	20	22
1-Methylnaphthalene	12	12	68	11	13	11	11	11	9.9	11	10	10	8.7	18	21
Biphenyl	4.0	4.5	3.7	3.6	3.5	3.9	4.6	4.4	4.4	4.3	4.4	3.9	3.2	3.1	3.0
2,6-Dimethylnaphthalene	7.6	7.8	6.0	7.4	7.2	7.0	8.0	8.4	7.6	7.9	8.1	8.0	6.9	7.0	6.1
Acenaphthylene	25	19	26	34	19	16	23	31	16	20	19	18	15	14	17
Acenaphthene	2.9	3.3	3.0	3.0	3.0	2.9	2.9	3.2	2.8	3.0	3.0	2.9	2.7	2.8	2.7
2,3,5-Trimethylnaphthalene	2.3	2.4	2.2	2.2	2.2	2.1	2.3	2.7	2.3	2.3	2.4	2.3	2.1	2.3	2.0
Fluorene	43	46	44	42	43	40	43	44	42	42	43	43	37	41	38
Phenanthrene	260	275	267	253	263	236	258	261	253	251	250	251	284	338	431
Anthracene	63	63	63	63	61	55	62	65	59	58	61	61	54	60	60
1-Methylphenanthrene	13	13	12	12	12	12	12	12	12	12	11	11	14	17	21
Fluoranthene	371	382	378	372	369	351	377	370	366	363	380	378	349	391	363
Pyrene	265	271	269	267	267	251	267	265	260	257	269	269	247	275	256
Benzo[*a*]anthracene	157	170	166	156	163	142	168	156	153	158	154	158	154	167	152
Chrysene	158	173	160	161	157	142	173	159	149	162	159	161	155	166	168
Benzo[*b*]fluoranthene	145	148	137	139	143	131	143	142	130	136	143	142	120	135	126
Benzo[*k*]fluoranthene	119	120	126	117	119	115	122	123	120	122	124	119	126	133	123
Benzo[*e*]pyrene	100	103	100	99	99	97	102	102	100	100	105	101	95	103	95
Benzo[*a*]pyrene	111	119	115	110	110	112	115	113	115	117	120	113	103	110	97
Perylene	33	35	35	33	33	35	35	34	37	35	36	34	32	35	30
Dibenz[*a,c*]anthracene	25	24	25	24	25	23	25	25	24	24	25	25	25	27	25
Indeno[*cd*]pyrene	94	88	87	86	88	84	88	89	90	86	94	89	88	99	85
Benzo[*ghi*]perylene	77	76	76	74	77	72	76	77	74	75	77	77	79	85	77
Total	2120	2180	2290	2100	2110	1970	2140	2130	2050	2070	2130	2110	2020	2260	2230

Table 5
PAH-concentrations found in the reference soil CRM 103-100 (USEPA, RTC Laramie, WY USA), using PLE [1 g soil, hexane–acetone (50:50, v/v), 150°C, 14 MPa, 2×5 min static extraction, 11 ml rinse volume]. Average of three separate samples. All values are expressed in mg/kg dry mass. Reference values in parentheses are not certified and are listed for information only. The confidence interval (CI) is the 95% CI for the reference values.

	Concentration found (mg/kg)	RSD (%)	Reference value (mg/kg)	Confidence interval (mg/kg)
Naphthalene	38	5.0	35	31–39
2-Methylnaphthalene	68	4.3	60	54–67
1-Methylnaphthalene	93	4.2		
Biphenyl	25	3.7		
2,6-Dimethylnaphthalene	329	4.6		
Acenaphthylene	20	2.7	(17)	
Acenaphthene	695	2.9	627	540–715
2,3,5-Trimethylnaphthalene	257	2.2		
Fluorene	481	4.0	443	398–488
Phenanthrene	2307	2.7	1925	1716–2134
Anthracene	517	2.7	431	389–473
1-Methylphenanthrene	244	6.1		
Fluoranthene	1540	5.7	1426	1259–1593
Pyrene	988	8.0	1075	934–1216
Benzo[*a*]anthracene	277	1.4	264	241–288
Chrysene	316	2.0	316	287–346
Benzo[*b*]fluoranthene	113	3.7	(115)	
Benzo[*k*]fluoranthene	101	3.7	(64)	
Benzo[*b*]fluoranthene + Benzo[*k*]fluoranthene	214	3.7	189	159–219
Benzo[*e*]pyrene	82	3.5		
Benzo[*a*]pyrene	107	1.8	97	85–108
Perylene	30	2.1		
Dibenz[*a,c*]anthracene	14	3.7	(14)	
Indeno[*cd*]pyrene	32	0.6	32	24–40
Benzo[*ghi*]perylene	35	2.2	(26)	

efficient technique for extracting PAHs from contaminated soil. The PAHs are extracted at least as efficiently as by Soxhlet extraction, which was used to certify the CRM-soil. The relative standard deviations (RSDs) for the three replicates were mostly below 5%. The concentrations of pyrene showed the largest variation, with an RSD of 8%.

4. Conclusion

This study shows that the sample load and the volume of extraction solvent significantly affect the extraction efficiency during PLE of PAHs from aged, contaminated soil. The best results are obtained if the amount of soil is kept small and is carefully mixed with a bulk material prior to extraction, and if the extraction includes two static cycles followed by rinsing with 100% of the extraction cell volume. In addition, the extraction temperature should exceed 100°C (we recommend 150°C). Under these conditions the exact settings of other variables are not critical for the PAH-extraction efficiency. Another important finding is that the internal standard should not be added on top of the sample in the extraction cell. This may cause overestimation of compounds that are strongly retained when the IS passes through the sample column, since the PLE cell resembles a chromatographic column. The IS should instead be thoroughly mixed with the sample matrix prior to extraction, or alternatively, added to the extract immediately after extraction.

Various binary solvents give similar extraction results. However, acetone–hexane (50:50, v/v) is the preferred mixture of those tested, since it contains no chlorinated solvents and is easily combined with subsequent clean-up steps.

Repeated extractions of the same sample showed

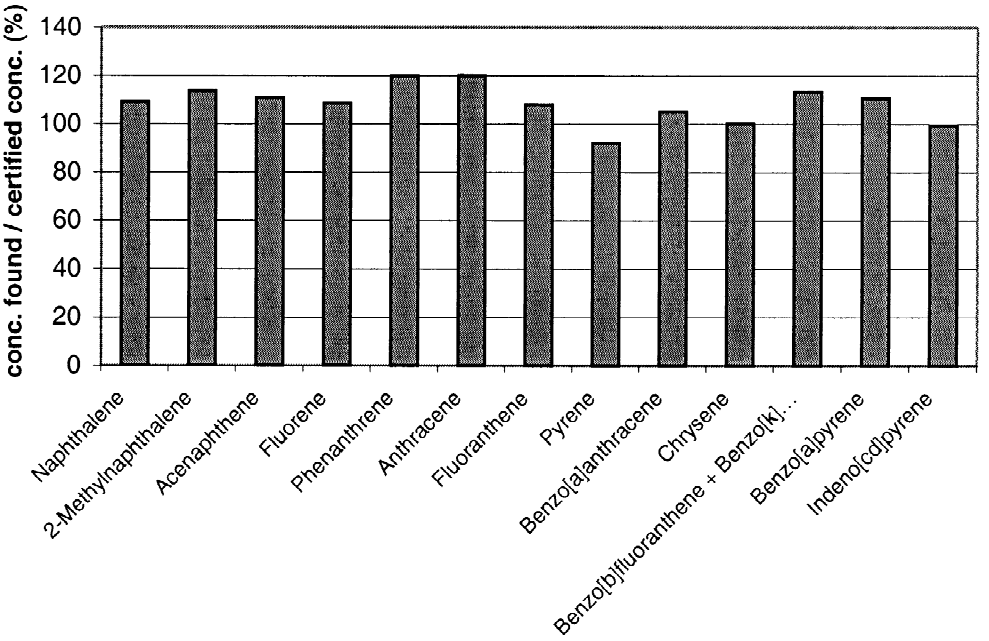

Fig. 4. PAH concentrations found in the certified soil sample CRM 103-100 (EPA, RTC Laramie, WY, USA), presented as percentages of the certified concentrations. Average of three separate samples extracted by PLE. Extraction conditions according to the legend in Table 5.

that PLE is an exhaustive extraction technique for PAHs in contaminated soil. In addition, analysis of a certified reference material showed that PLE produces results with good precision and accuracy.

Acknowledgements

This study was carried out as part of the Swedish national research program COLDREM (Soil Remediation in a Cold Climate). The authors wish to acknowledge MISTRA (Foundation for Strategic Environmental Research) for its financial support.

References

[1] M. Alexander, Environ. Sci. Technol. 29 (1995) 2713.
[2] J.J. Pignatello, B. Xing, Environ. Sci. Technol. 30 (1996) 1.
[3] P.B. Hatzinger, M. Alexander, Environ. Sci. Technnol. 29 (1995) 537.
[4] J.J. Kilbane, Water. Air. Soil. Pollut. 104 (1998) 285.
[5] R.C. Loehr, M.T. Webster, J. Soil. Contam. 5 (1996) 361.
[6] J.R. Dean, Extraction Methods For Environmental Analysis, Wiley, Chichester, 1998, Ch. 6–10, 99.
[7] V. Lopez-Avila, R. Young, W.F. Beckert, Anal. Chem. 66 (1994) 1097.
[8] V. Lopez-Avila, R. Young, J. Benedicto, P. Ho, R. Kim, W.F. Beckert, Anal. Chem. 67 (1995) 2096.
[9] EPA Method 3560, 3561, Supercritical Fluid Extraction, Test Methods for Evaluating Solid Waste, EPA SW-846, US GPO Washington, DC, 3rd ed., Update III, July 1995.
[10] S. Bøwadt, S.B. Hawthorne, J. Chromatogr. A 703 (1995) 549.
[11] J.W. King, J.AOAC Int. 81 (1998) 9.
[12] J.R. Dean, Analyst 121 (1996) 85R.
[13] EPA Method 3545, Accelerated Solvent Extraction, Test Methods for Evaluating Solid Waste, EPA SW-846, US GPO Washington, DC, 3rd ed., Update III, July 1995.
[14] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter, N. Avdalovic, C. Pohl, Anal. Chem. 68 (1996) 1033.
[15] M.D. David, J.N. Seiber, Anal. Chem. 68 (1996) 3038.
[16] W.C. Brumley, E. Latorre, V. Kelliher, A. Marcus, D.E. Knowles, J. Liq. Chromatogr. Rel. Technol. 21 (1998) 1199.
[17] O.P. Heemken, N. Theobald, B.W. Wenclawiak, Anal. Chem. 69 (1997) 2171.
[18] J.A. Fisher, M.J. Scarlett, A.D. Stott, Environ. Sci. Technol. 31 (1997) 1120.
[19] J.D. Berset, M. Ejem, R. Holzer, P. Lischer, Anal. Chim. Acta 383 (1999) 263.
[20] M. Letellier, H. Budzinski, Analyst 124 (1999) 5.

[21] S. Bøwadt, B. Johansson, S. Wunderli, M. Zennegg, L.F. de Alencastro, D. Grandjean, Anal. Chem. 67 (1995) 2424.
[22] B.E. Richter, J.L. Ezzell, D.E. Knowles, F. Hoefler, A.K.R. Mattulat, M. Scheutwinkel, D.S. Waddell, T. Gobran, V. Khurana, Chemosphere 34 (1997) 975.
[23] G.S. Chen, K.W. Schramm, B. Henkelmann, Y. Xu, Y.Y. Zhang, T. Wottgen, A. Kettrup, Organohalogen Compd. 31 (1997) 114.
[24] C. Bandh, E. Björklund, L. Mathiasson, C. Näf, Y. Zebühr, Organohalogen Compd. 35 (1998) 17.
[25] Application Note 313, Dionex, Sunnyvale, CA, USA.
[26] M.M. Schantz, J.J. Nichols, S.A. Wise, Anal. Chem. 69 (1997) 4210.
[27] H. Bautz, J. Polzer, L. Stieglitz, J. Chromatogr. A 815 (1998) 231.
[28] E. Björklund, S. Bøwadt, T. Nilsson, L. Mathiasson, J. Chromatogr. A 836 (1999) 285.
[29] P. Popp, P. Keil, M. Möder, A. Paschke, U. Thuss, J. Chromatogr. A 774 (1997) 203.
[30] D.V. Kenny, S.V. Olesik, J. Chromatogr. Sci. 36 (1998) 59.
[31] D.V. Kenny, S.V. Olesik, J. Chromatogr. Sci. 36 (1998) 66.
[32] S. P Frost, J.R. Dean, K.P. Evans, K. Harradine, C. Cary, M.H.I. Comber, Analyst 122 (1997) 895.
[33] N. Saim, J.R. Dean, Md.P. Abdullah, Z. Zakaria, J. Chromatogr. A 791 (1997) 361.
[34] H. Budzinski, M. Letellier, P. Garrigues, K. Le Menach, J. Chromatogr. A. 837 (1999) 187.
[35] S.B. Hawthorne, D.J. Miller, Anal. Chem. 66 (1994) 4005.
[36] A. Fick, Ann. Phys.(Leipzig) 170 (1855) 59.
[37] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics For Experimenters, Wiley, New York, 1978, Ch. 9–15, 291.
[38] N. Saim, J.R. Dean, Md.P. Abdullah, Z. Zakaria, Anal. Chem. 70 (1998) 420.