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# Solid-phase extraction of polycyclic aromatic hydrocarbons from soil samples

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**Abstract**

A new solid-phase extraction (SPE) method was developed for the analysis of 16 polyaromatic hydrocarbons (PAHs) on the US Environmental Protection Agency priority list, in soil samples. Different types of SPE columns were tested and conditioning and elution steps were optimised. In the final procedure, soil samples are extracted with acetone and, after dilution with HPLC-grade water, loaded on a $C_8$ SPE column. After washing, all PAHs are eluted with tetrahydrofuran (THF). The final THF extract is analysed on an HPLC system for PAHs.

Recoveries of the volatile PAHs, naphthalene, acenaphthylene and acenaphthene were 80–90%. All other recoveries are comparable with standard liquid–liquid extraction (LLE) and range from 75 to 90%.

The method is compared with the conventional LLE method for different types of real soil samples of a Dutch monitoring programme. Results indicate that SPE is a good method for the sample preparation for the analysis of PAHs in soil samples. Compared with LLE, correlation coefficients are better than 0.9 with relative standard deviations for SPE between 0.8 and 9.1%. LLE standard deviations ranged from 1.1 to 15.1%.

## 1. Introduction

Polyaromatic hydrocarbons (PAHs) are wide-spread environmental contaminants and suspected to be carcinogenic [1,2]. The determination of PAHs in soil samples requires a good clean-up while aqueous samples need concentration because of low concentration levels. Today, sample preparation of soil is routinely done by liquid–liquid extraction (LLE) or Soxhlet extraction [3] in combination with column chromatography or solid-phase extraction (SPE) clean-up, as described by Kicinski [4]. In that paper a double-phase SPE method is described with an amino and a $C_{18}$ SPE column. Unfortunately, this method also involves an evaporation step so only 11 of the 16 US Environmental Protection Agency (EPA) priority PAHs can be analysed. Supercritical fluid extraction (SFE) is also used for sample pretreatment [5–7]. SPE for the analysis of PAHs is mainly used for water samples, as described by the EPA (see [8]). In combination with an automated SPE system [9,10], good results can be obtained for both water or soil samples, but high investments are needed. Several laboratories in the Netherlands involved in environmental control and monitoring are routinely using this automated SPE

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method. Summarised, column chromatography and evaporation steps in the clean-up procedures of the sample pretreatment might cause low recoveries for all PAHs and this will result in a loss of the volatile PAHs like naphthalene. In this paper, the development of a simple and cost-effective SPE method is described to replace the laborious and time-consuming LLE method used in our laboratory.

## 2. Experimental

### 2.1. Reagents and samples

Bakerbond SPE columns $C_8$ [200 mg 3 ml-LD (low displacement) 200 or 500 mg, 40 $\mu$m] and $C_{18}$ (3 ml LD, 500 mg, 40 $\mu$m), HPLC-grade methanol, HPLC-grade acetonitrile and "Baker analysed" HPLC-grade water, Baker analysed tetrahydrofuran (THF), Baker analysed 2-propanol and a Bakerbond PAH 16 plus HPLC column (250 × 3 mm I.D.) were purchased from J.T. Baker (Deventer, Netherlands). LC-grade water was obtained by purifying demineralised water with a Milli-Q system (Millipore, Bedford, MA, USA). The EPA PAH standard reference material SRM 1647C of the National Institute of Standards and Technology (USA) was used (range 1–20 $\mu$g/ml for the different PAHs). All other reagents were of analytical grade and purchased from several local distributors.

Soil samples were collected for a Dutch monitoring programme on soil, to determine background levels of PAHs in the Netherlands. A selection was made of different types of soil (grass land, agriculture and orchard soil, including sand, peat and clay) and covered a wide concentration range of PAHs. For optimisation experiments, blank OECD soil [11,12] was used.

### 2.2. Apparatus

SPE columns were manually eluted on a Baker SPE-12 vacuum system. The high-pressure gradient LC system consisted of a Gynkotec (Germening, Germany) dual-piston low-pressure gradient LC pump. All LC solvents were degassed with a Separations GT-103 degasser (Separations, H.I. Ambacht, Netherlands). For detection of PAHs a Perkin-Elmer LS-4 fluorescence spectrometer was used in combination with an ABI 757 UV detector (Applied Biosystems, Foster City, CA, USA). Both detectors were wavelength programmed (described later). Data acquisition was performed on an HP 3365 Series II ChemStation equipped with an HP35900 A/D converter, running on an HP Vectra QS/20 personal computer (Hewlett-Packard, Rockville, USA).

### 2.3. Sample pretreatment SPE method

A 10-g amount of soil is placed into a 150-ml tube with 20 ml of acetone and the mixture is shaken for 30 min. After centrifugation at 1000 *g* for 5 min, exactly 10 ml of the acetone are pipetted in a 100-ml volumetric flask together with 5 ml of 2-propanol. The sample is brought to 100 ml with HPLC-grade water.

$C_8$ cartridges are conditioned with 1 × 3 ml of methanol, followed by two times 3 ml of water–2-propanol (9:1, v/v). The 100 ml sample solution are loaded onto the SPE column under vacuum. Then the column is washed with 3 ml of methanol–water (50:50, v/v). The PAHs are eluted with two times 1.5 ml of THF. The first 1.5 ml have to soak the cartridge for some minutes before eluting. After elution, the final THF extract is ready for injection. All flows through the cartridge are about 2 ml/min. For samples with fines in solution, after centrifugation, a filtration step is necessary.

### 2.4. Liquid–liquid extraction

A soil sample of 20 g is shaken with 25 ml of acetone for 10 min, 50 ml of light petroleum (b.p. 30–60°C) are added and the resulting solution is shaken for 20 min. After centrifugation (10 min at 1000 *g*), the extract is put into a separation funnel. The soil is extracted for a second time with 75 ml of acetone–light petroleum (1:3, v/v) and shaken for 30 min. The two extracts are combined and washed twice with 500 ml of Milli-Q water. The organic layer is sepa-

rated and dried over anhydrous sodium sulphate. The extract is reduced to 10 ml by evaporation (Kuderna Danish) and to 1 ml with a stream of nitrogen. The extract is purified over a 30-cm chromatography column, packed with 10 g of alumina. Light petroleum is used as eluent. The volume of this extract is reduced to 10 ml by evaporation (Kuderna Danish). This extract, with 50 μl 1-butanol as holder, is reduced at 50°C to dryness with a stream of nitrogen. The residue is dissolved in 1 ml of acetonitrile and the sample is ready for injection.

### *2.5. HPLC analysis*

Mobile phase A consists of water and mobile phase B consists of acetonitrile. All flows are 0.5 ml/min. After equilibration, 5 min at acetonitrile–water (50:50, v/v), a linear gradient from 50 to 100% acetonitrile in 30 min is used for the elution of the PAHs. Both fluorescence and UV detection were used for all analyses. Fluorescence was wavelength programmed as indicated on the chromatogram. Details of the analytical conditions are described by Hesselink et al. [13].

## 3. Results and discussion

### *3.1. SPE method development*

SPE method development was based on the selection of a SPE column type, followed by the optimisation of the conditioning and elution parameters. During method development the EPA mixture was in all cases 1:20 diluted in acetone–water. Primarily, the double phase SPE method according to Kicinski [4] was followed, although this method involves evaporation of organic solvent. The PAHs could not be eluted from the cartridge with only 6 ml of methanol or acetonitrile. Only a small percentage ($< 15\%$) of the three most polar compounds (naphthalene, acenaphthylene and acenaphthene) was recovered.

Secondly, Bakerbond $C_8$ cartridges (200 and 500 mg) were selected because of the good results with $C_8$ materials on automated SPE systems. Recoveries, with 3 ml of acetonitrile as eluent, were improved (20–40% for 200 mg $C_8$ and 30–50% for a 500-mg $C_8$ cartridge), but not sufficient. With 3 ml THF as eluent, recoveries increased to 60–70%. These partial recoveries can be explained by losses due to volatility, losses due to differences of binding capacity or losses due to interactions of PAHs with the wall of the cartridge.

According to Kicinski [4] and others, PAHs may interact with the wall. To prevent this kind of interaction, 2-propanol (10%, v/v) is frequently used in conditioning of the cartridge. With this modification, elution with 3 ml of THF lead to recoveries up to 90%.

To select the best SPE column type, $C_8$ or $C_{18}$, experiments were carried out to compare these two materials. In Table 1, results are summarised. From these results, it is clear that $C_8$ material (recoveries 73–90%) is better than $C_{18}$ (recoveries 51–88%). Probably, the binding of the PAHs to the $C_{18}$ material is too strong for complete elution with a small amount of solvent. Also the standard deviations on the $C_8$ cartridges are better. A typical HPLC chromatogram of a standard mixture using clean-up with SPE is shown in Fig. 1. With these conditions, the SPE method has been tested on real samples and the influence of the matrix has been investigated. No differences were found with four different batches of $C_8$ cartridges.

### *3.2. Comparison of the SPE method with LLE*

First, a blank soil sample was shaken with acetone for 30 min. The extract was spiked with 200 μl EPA standard, resulting in PAH concentrations between 10–200 ng/ml, and treated as described in the Experimental section.

Table 2 shows the results of the experiments with the spiked extracts. It is clear that volatile PAHs like naphthalene, acenaphthylene and acenaphthene, fluorene and phenanthrene, have better recoveries using the SPE method. This is due to the evaporation steps in the LLE procedure. There is also a slight improvement in the recoveries of dibenz[*a*,*h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene. For

Table 1
Comparison of $C_8$ (500 mg) and $C_{18}$ (500 mg) SPE columns ($n$ = 3)

| Compound | $C_8$ | | $C_{18}$ | |
|---|---|---|---|---|
| | Recovery (%) | R.S.D. (%) | Recovery (%) | R.S.D. (%) |
| Naphthalene[a] | 82 | 3.5 | 88 | 4.2 |
| Acenaphthylene[a] | 81 | 4.2 | 82 | 6.1 |
| Acenaphthene | 88 | 2.1 | 81 | 3.5 |
| Fluorene | 84 | 6.1 | 84 | 4.6 |
| Phenanthrene | 90 | 4.2 | 83 | 6.4 |
| Anthracene | 86 | 3.4 | 77 | 10.1 |
| Fluoranthene | 83 | 5.1 | 71 | 1.6 |
| Pyrene | 79 | 3.8 | 69 | 4.2 |
| Benz[*a*]anthracene | 80 | 2.1 | 68 | 3.8 |
| Chrysene | 80 | 4.2 | 75 | 4.9 |
| Benzo[*b*]fluoranthene | 82 | 5.0 | 64 | 3.8 |
| Benzo[*k*]fluoranthene | 77 | 4.9 | 66 | 6.0 |
| Benzo[*a*]pyrene | 73 | 4.2 | 51 | 5.8 |
| Dibenz[*a,h*]anthracene | 84 | 2.8 | 64 | 2.4 |
| Benzo[*ghi*]perylene | 87 | 6.9 | 65 | 5.2 |
| Indeno[1,2,3-*cd*]pyrene | 90 | 1.6 | 58 | 8.2 |

[a] UV detection.

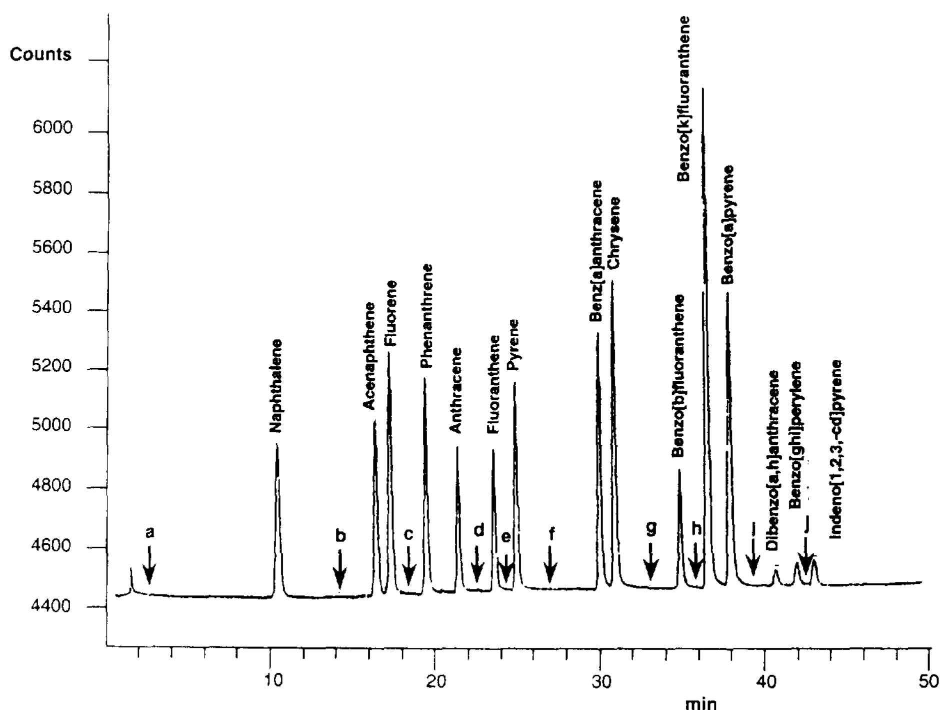


Fig. 1. Typical chromatogram of standard mixture with solid-phase extraction. Fluorescence detection with the following wavelength program (excitation/emission): a = 275 nm/325 nm; b = 253 nm/333 nm; c = 253 nm/373 nm; d = 285 nm/470 nm; e = 340 nm/395 nm; f = 270 nm/382 nm; g = 300 nm/440 nm; h = 300 nm/400 nm; i = 345 nm/420 nm; j = 300 nm/500 nm. Conditions: acetonitrile–water (50:50, v/v) to 100% acetonitrile in 30 min; Bakerbond PAH 16 plus column, 250 × 3 mm.

Table 2
Comparison between LLE and SPE of a spiked extract

| Compound | LLE | | SPE | |
|---|---|---|---|---|
| | Recovery (%) | R.S.D. (%) | Recovery (%) | R.S.D. (%) |
| Naphthalene[a] | 70 | – | 102 | 0.9 |
| Acenaphthylene[a] | – | – | 89 | 3.1 |
| Acenaphthene | 76 | – | 89 | 2.1 |
| Fluorene | 81 | 1.1 | 91 | 0.8 |
| Phenanthrene | 86 | 3.0 | 96 | 2.0 |
| Anthracene | 88 | 3.6 | 92 | 4.0 |
| Fluoranthene | 95 | 3.2 | 97 | 2.6 |
| Pyrene | 99 | 12.2 | 87 | 2.4 |
| Benz[*a*]anthracene | 104 | 8.0 | 85 | 3.1 |
| Chrysene | 105 | 8.3 | 90 | 2.6 |
| Benzo[*b*]fluoranthene | 105 | 4.7 | 91 | 4.5 |
| Benzo[*k*]fluoranthene | 106 | 1.7 | 86 | 3.2 |
| Benzo[*a*]pyrene | 106 | 6.5 | 93 | 6.0 |
| Dibenz[*a*.*h*]anthracene | 77 | 6.6 | 89 | 5.7 |
| Benzo[*ghi*]perylene | 81 | 15.1 | 105 | 3.1 |
| Indeno[1,2,3-*cd*]pyrene | 93 | 1.4 | 91 | 9.1 |

For details see text ($n = 3$).
[a] UV detection.

all the other components, recoveries are comparable.

Secondly the method was compared with the LLE of different types of real soil samples of a Dutch monitoring programme on soil. A total of 12 samples was analysed with both methods. In Fig. 2, the correlation between SPE and LLE is shown for 12 soil samples. A good correlation ($r^2 = 0.935$) exists between the two methods. However, above concentrations of 200 $\mu$g/kg, some deviation is possible. This may be due to a binding capacity of the $C_8$ material or due to the matrix. During the extraction procedure, some soil samples will clog the SPE column. Prefiltering over an empty SPE column or purified sand may be required. A typical HPLC chromatogram of a real soil sample using clean-up with SPE is shown in Fig. 3. Table 3 gives a summary of the characteristic differences between LLE and SPE as sample preparation method.

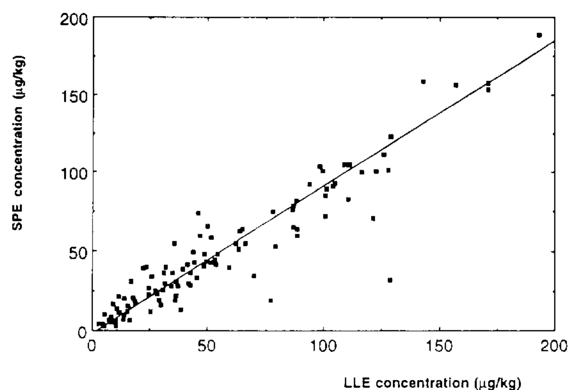


Fig. 2. Comparison of liquid–liquid extraction with solid-phase extraction of PAHs from 12 different type of soil samples.

Preliminary results indicate that the method can be adapted to water samples. Further experiments are in progress.

## 4. Conclusions

A method for SPE of PAHs in field samples has been developed using a general stepwise approach for SPE. Starting with a standard mixture and several types of solid phases a suitable adsorbent was selected. Then the conditioning and elution parameters were optimised

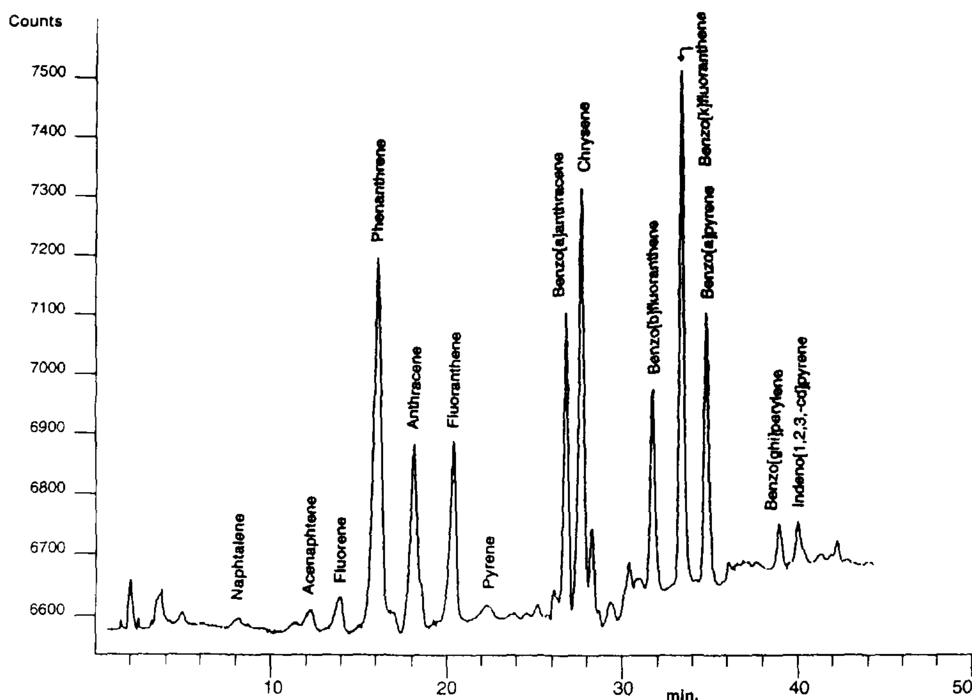


Fig. 3. Typical HPLC (fluorescence) chromatogram of peaty soil. SPE sample preparation as described in text. Conditions as in Fig. 1.

and finally these conditions were used to analyse real soil samples. Comparable results were found for PAH concentrations using SPE or LLE as sample preparation method. The SPE method showed improved recoveries for the volatile PAHs as expected, due to the omission of an evaporation step.

Table 3
Comparison between the characteristics of LLE and SPE

| Characteristic | LLE | SPE |
|---|---|---|
| Sample preparation time | 8 h | 2.5 h |
| Amount of organic solvent | 220 ml | 35 ml |
| Recovery (all PAHs) | Good | Good |
| Recovery (volatile PAHs) | Poor | Good |
| Automation potential | No | Yes |
| Purity of extract | Good | Very good |

The method is easy to use and has a good reproducibility.

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