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Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection¹

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Abstract

A method using ultrasonication extraction and solid phase extraction (SPE) clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in soils by reversed-phase liquid chromatography (RP-LC) with ultraviolet (UV) absorption detection was studied. Separation and detection of the 16 PAHs were completed in 31 min by RP-LC with a C₁₈ column (Bakerbond PAH 6 PLUS 125×3.0 i.d. mm or Phenomenex ENVIROSEP-PP 125×3.2 i.d. mm), acetonitrile–water gradient elution and UV absorption detection. The detection limits, for a 10 µl of solution injection, determined at 254 nm were less than 1 µg/ml, except for acenaphthene, which was 1.05 µg/ml. Because individual PAHs are present in soils at the ng/g level or below and few sample matrices can be analyzed directly without serious interference, efficient extraction, preconcentration and clean-up of PAHs from the samples are indispensable prior to the determination of the PAHs. Several organic solvents were tested for extraction of the PAHs from soils, and ultrasonication extraction was used for the extraction in acetone of the 16 PAHs in soils. Several SPE procedures were tested and compared, and Supelco 6 ml LC-18 SPE cartridge and acetone:tetrahydrofuran (THF)=1:1 eluant were used for the preconcentration and clean-up of the 16 PAHs in the soil. The method was successfully applied to determine the 16 PAHs in the soil sampled from an industrial land in the UK. © 1998 Elsevier Science B.V.

Keywords: Extraction methods; Ultrasonic solvent extraction; Soil; US EPA PAHs; RP-LC; SPE

1. Introduction

Parent polycyclic aromatic hydrocarbons (PAHs) are the basic polycyclic aromatic compounds (PAC) and their carcinogenesis has mainly been observed for tri-, tetra-, penta-, and hexacyclic compounds. Although hundreds of PAHs exist in the environment,

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only 16 PAHs, i.e. naphthalene (Naph), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (BaAn), chrysene (Chr), benzo[b]fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo[a]pyrene (BaPy), dibenzo[a,h]anthracene (DiAn), benzo[g,h,i]perylene (BePe), and indeno[1,2,3-cd]pyrene (InPy), have been selected by the US Environmental Protection Agency (US EPA) as “Consent Decree” priority pollutants, which are monitored routinely for regulatory purposes [1].

The advantages of liquid chromatography (LC) in the fractionation of complex PAH mixtures and sample clean-up are undoubtful, and some useful methods have been validated. For example the US EPA recommended analytical procedures are documented in EPA Methods 550.1 (drinking water), 610 (waste water), 8310 (solid waste), and TO-13 (air). All these methods are based on LC with ultraviolet (UV) absorption and fluorescence detection. Reversed-phase liquid chromatography (RP-LC) is widely used for analysis of the main 16 PAHs because of its great efficiency of separation. Applications of RP-LC to the determination of PAHs in air particulate matter [2–4], used engine oils [5] and edible oils [6], coal tar pitch [7], marine samples [8], water and waste water [2,9–12], sediment [2,13,14] and soil [2,15–19] have been reported.

As individual PAHs are present in soils at the ng/g level or below [20] and few sample matrices can be analyzed directly without serious interference, efficient extraction, preconcentration and clean-up of PAHs from the samples are indispensable prior to the determination of the PAHs. Soxhlet extraction, which has high extraction efficiency, has for many years been the standard method for preparing a solvent extract of solid matrices containing PAHs [21]. However, it is tedious as the extraction time is long, with about 16 h or more needed [2,22]. Use of mechanic shaking has the same disadvantage. Use of a Polytron homogenizer for extraction of PAHs from soil was reported by Fowlie et al., and it was indicated that the recovery of PAHs was lower than that achieved by Soxhlet extraction [21]. Although supercritical fluid extraction (SFE) has many advantages over other methods for sample preparation [18,23], complicated equipment is required and sometimes it costs more.

Microwave-assisted solvent extraction of PAHs has been published [24,25]. Considering the safety, the temperature and the pressure inside the extraction vessel should be controlled, though this method is able to reduce the solid sample preparation time to less than 30 min. One of the rapid extraction techniques for extraction of PAH in solid environmental samples is ultrasonication [2,14,15,19,26]. Ultrasonication procedures have been compared with the Soxhlet method for extraction of PAHs in samples, with short time ultrasonic extractions produce equivalent or better extraction recoveries than 6–8 h of Soxhlet extraction [2,14,22]. In addition, the equipment for ultrasonication is very simple, and it is easy to operate.

SPE is a popular procedure that is used to preconcentrate components to be analyzed and clean-up matrices from sample for analysis. The prepacked cartridges provide users of SPE with a variety of stationary phases to selectively separate and concentrate analytes for detection. Since PAHs have low polarity SPE of pollutants from samples is usually carried out on a bonded octadecyl-silica stationary phase [6,10,27].

In this work a procedure has been devised for the determination of 16 PAHs in industrial soils. Ultrasonic solvent extraction and SPE are used to obtain an extract that is suitable for analysis by RP-LC with a C₁₈ column and UV absorption detection.

2. Experimental

2.1. Reagents and materials

16 mixed PAHs stock standard solutions: 2000 µg/ml of Ac; 1000 µg/ml of Ace and Naph; 200 µg/ml of BbFl, BePe, DiAn, Fluo and Flu; 100 µg/ml of Anth, BaAn, BaPy, BkFl, Chr, InPy, Phe, Pyr were obtained in 1:1 methanol:methylene chloride from Supelco, Bellefonte, PA, USA. Appropriate dilutions of the standard solution with acetonitrile were made to the working solutions.

Supelco 6 ml LC-18 SPE cartridge (Supelco, Bellefonte, PA, USA) was used for the preconcentration and clean-up of the 16 PAHs in the extraction solution from soils.

Water was distilled and further purified by a Mill-Q system (Millipore, Bedford, USA) to obtain nano-water.

Solvents: Acetonitrile, methanol, 2-propanol, dichloromethane, cyclohexane, acetone, and THF were of HPLC grade.

2.2. Apparatus

All chromatographic analyses were performed on a Philips LC instrument (Pye Unicam, Cambridge, UK), which consisted of a PU4003 solvent delivery system containing two parts, a precision dual-headed reciprocating pump and a microprocessor based controller, a PU4025 UV detector and a PU 4810 computing integrator. A Rheodyne Model 7125 sample injector (Rheodyne, CA, USA) equipped with a 10 μ l loop was used for injecting sample solution. A 125 \times 3.0 mm i.d. Bakerbond PAH 6 PLUS (J.T. Baker, NJ, USA) separation column packed with 5 μ m ODS (C₁₈) particle size and a Phenomenex ENVIROSEP-PP 125 \times 3.2 mm i.d. separation column (Hurdsfield, Cheshire, UK) packed with 4 μ m Polymeric ODS (C₁₈) particle size were tested for the separation of 16 PAHs. Chromatograms were recorded on the integrator. A Decon Model FS 200 ultrasonic cleaning bath (Decon Ultrasonic, Hove Sussex, UK), which has 200 W average power output and mean operating frequency of 40 KHz, was used for the ultrasonication extraction of PAHs from soil sample into the solvent. A vacuum manifold or a glass syringe was used to control the flow rate for the SPE.

2.3. Preparation of sample

Contaminated soil at an industrial area in the UK was taken from Dr. P. Anderson (University of Strathclyde, Glasgow, UK). The soil was dried for 10 days at room temperature. The stones, bricks, clinker, fibrous roots and so on were picked out, and the dried soil was fractionated using a nylon mesh sieve of 1 mm. The finer fraction, i.e. \leq 1 mm was thoroughly homogenized, and approximately 50 g were ground down to a fine granular material, and further sieved using copper mesh sieves of 500 and 250 μ m, respectively, and stored in a plastic bag.

2.4. Extraction of PAHs in soil

0.5 g of soil sample was placed in a 25 ml volumetric flask, and 10 ml of acetone was added. The

sample was ultrasonicated in the sonication bath for 30 min with occasional swirling to prevent sticking on the bottom of the flask. The extraction solution was filtrated into a 50 ml beaker using a 9.0 cm GF/C glass microfibre filter (Whatman International, Maidstone, UK). Water was added to the filtrates to make the extraction solution to be 40% acetone in water.

The sample was also treated by the Soxhlet extraction with 20 ml of acetone and 8 h reflux.

2.5. SPE for clean-up of extraction solution

The sorbents of 6 ml Supelco LC-18 SPE cartridge were conditioned by 5 ml of acetone and 40% acetone in water, respectively. The extraction solution was aspirated through the cartridge at \leq 2 ml/min flow rate. The cartridge was centrifuged for 15 min at 4500 rpm, and then eluted by 3 \times 1 ml of acetone:THF=1:1 at \leq 1 ml/min flow rate (each time the sorbents were soaked for 10 min with the elution solution before the elution). The eluates were collected into a 3 ml volumetric flask and exactly made to be 3 ml using the elution solution.

2.6. Selection of solvent for the extraction

Different solvents, cyclohexane, 2-propanol, methanol, acetonitrile, dichloromethane and acetone, were tested to select a solvent for the extraction of the 16 PAHs from the soil. The procedure of the extraction was almost the same as that described in Section 2.4, except that the extraction solution was evaporated to near dryness by a gentle stream of nitrogen gas, and the residues were dissolved by 10 ml of 40% methanol in water when cyclohexane was used as the extraction solvent; 1 ml of acetonitrile was added to the extraction solution, and the following steps were the same as that of cyclohexane when dichloromethane was used as the extraction solvent; water was added to the extraction solution to make the solution contain 40% 2-propanol, methanol, acetonitrile and acetone, respectively, when 2-propanol, methanol, acetonitrile and acetone were tested as the extraction solvent. After the extraction the SPE procedure was almost the same as that described in Section 2.5, except that the sorbents of the SPE cartridge were conditioned by 5 ml of the tested solvent and 40% of the tested solvent in water, respectively,

Table 1
Gradient elution program of mobile phase for the separation of 16 PAHs

Segment	Time (min)	A% (H ₂ O)	B% (acetonitrile)	Exponent
<i>Bakerbond column</i>				
0	0	55	45	
1	4	55	45	
2	16	30	70	1
3	21	20	80	9.9
4	31	0	100	9.9
<i>Phenomenex column</i>				
0	0	51	49	
1	4	51	49	
2	26	0	100	1
3	31	0	100	

3×2 ml of dichloromethane was used to elute the isolates, 1 ml of acetonitrile was added to the eluates, the eluates were dried to near dryness by the gentle stream of nitrogen gas and the residues were dissolved by 500 µl of acetonitrile:water=49:51.

2.7. Chromatographic conditions

10 µl of the eluates were injected onto the column, utilizing the sample injector. The two columns were used for the separation of 16 PAHs, and their programmes of gradient elution for the separation are listed in Table 1. The flow rates of the mobile phase were set at 1.3 ml/min. The UV detector, the attention of the integrator, the absorbance range and the chart speed were set at 254 nm, 32, 1.28 and 0.5 cm/min, respectively. A peak area was used for the preparation of 16 PAH standard curves.

3. Results and discussion

3.1. Chromatographic separation

The Bakerbond PAH 6 PLUS and Phenomenex ENVIROSEP-PP were studied for the separation of 16 PAHs under several conditions of gradient elution with acetonitrile and water, and they provided com-

plete separation of all the 16 PAHs (10 µl of 1/500 of the mixed PAHs stock standard solution) as shown by the chromatograms in Figs. 1 and 2, respectively. Although Naph, Ac and Ace were eluted faster in the first column than in the second column, the retention times for other PAHs were almost the same and the time for a chromatographic cycle of the complete separation for the 16 PAHs was 41 min including 10 min for the equilibration of the two columns. This time is suitable for economic and routine analysis of the 16 PAHs.

The following results were obtained by using the Phenomenex ENVIROSEP-PP column.

3.2. Linearity, sensitivity and precision

Peak areas were used to evaluate the linearity, sensitivity and precision of the method, and the results are presented in Table 2. They show good linearity because their values of the regression coefficient were in the range 0.9918–0.9988. The precisions represented as RSD from 10 replicate analyses were less than 10% except for Ace which was 17.6%. The detection limits calculated with a signal to noise ratio of three (IUPAC criterion), for a 10 l loop injection, were less than 1 µg/ml and 10 ng for the concentration and amount of the PAHs, respectively, except for those of Ace, where 1.05 µg/ml and 10.5 ng were found. However, the sensitivity was still not high enough to directly determine the PAHs in soil samples. Therefore, an extraction/preconcentration procedure for the analytes was studied.

3.3. Efficiency for extraction of PAHs from soil samples

3.3.1. Selection of extraction mode

We compared the ultrasonication extraction technique with the Soxhlet procedure, using the procedure in Section 2.4. The ratios of the ultrasonication mode to the Soxhlet mode for the extraction efficiency for the 16 PAHs from the soil are shown in Fig. 3. The extraction efficiencies for most of the 16 PAHs by the ultrasonication mode were higher than those by the Soxhlet mode because the ratios for the most of the PAHs were higher than 1 (from 1.02 to 1.60), except for those of BbFl, BkFl, BePe and InPy. Moreover, the ultrasonication extraction consumed much

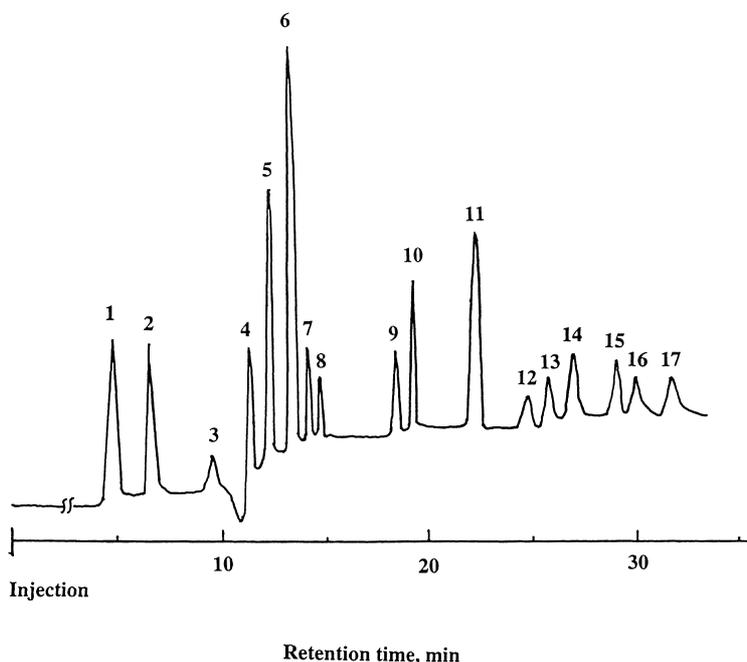


Fig. 1. Chromatogram for the separation of 16 PAHs using Bakerbond PAH 6 PLUS Column: 1=Naph, 5.06'; 2=Ac, 6.89'; 3=Ace, 9.99'; 4=Flu, 11.73'; 5=Phe, 12.64'; 6=Anth, 13.53'; 7=Fluo, 14.41'; 8=Pyr, 14.95'; 9=BaAn, 18.63'; 10=Chr, 19.57'; 11=BbFl, 22.57'; 12=BkFl, 25.00'; 13=BaPy, 26.02'; 14=impurity in water, 27.22'; 15=DiAn, 29.38'; 16=BePe, 30.25'; 17=InPy, 31.81'.

Table 2

Linearity, detection limit (DL) and precision for the determination of 16 PAHs by RP-LC

Name	Concentration ($\mu\text{g/ml}$)	DL ($\mu\text{g/ml}$)	DL (ng)	RSD (%)	Range ($\mu\text{g/ml}$)	Regression coefficient
Naphthalene	2	0.337	3.37	5.63	1–20	0.9936
Acenaphthylene	4	0.911	9.11	7.59	2–40	0.9926
Acenaphthene	2	1.05	10.5	17.6	1–20	0.9939
Fluorene	0.4	0.113	1.13	9.38	0.2–4	0.9939
Phenanthrene	0.2	0.034	0.34	5.66	0.1–1	0.9958
Anthracene	0.2	0.025	0.25	4.18	0.1–0.5	0.9930
Fluoranthene	0.4	0.020	0.20	6.75	0.4–4	0.9988
Pyrene	0.2	0.024	0.24	7.90	0.2–2	0.9988
Benzo[a]anthracene	0.2	0.050	0.50	8.30	0.1–1	0.9982
Chrysene	0.2	0.036	0.36	6.00	0.1–1	0.9953
Benzo[b]fluoranthene	0.4	0.067	0.67	5.55	0.2–2	0.9972
Benzo[k]fluoranthene	0.2	0.044	0.44	7.40	0.15–1	0.9971
Benzo[a]pyrene	0.2	0.050	0.50	8.39	0.2–2	0.9918
Dibenzo[a,h]anthracene	0.4	0.103	1.03	8.57	0.2–1	0.9972
Benzo[g,h,i]perylene	0.4	0.067	0.67	5.54	0.3–2	0.9973
Indeno[1,2,3-c,d]pyrene	0.2	0.040	0.40	6.60	0.1–0.5	0.9927

less time (30 min) and solvent (10 ml) than that the Soxhlet extraction did (8 h and 20 ml). Therefore, the ultrasonication extraction was used in this work.

3.3.2. Selection of solvent for extraction

Large differences at the extraction step and the solvent used for the extraction of PAHs from soil samples were reported. Acetone, cyclohexane, hex-

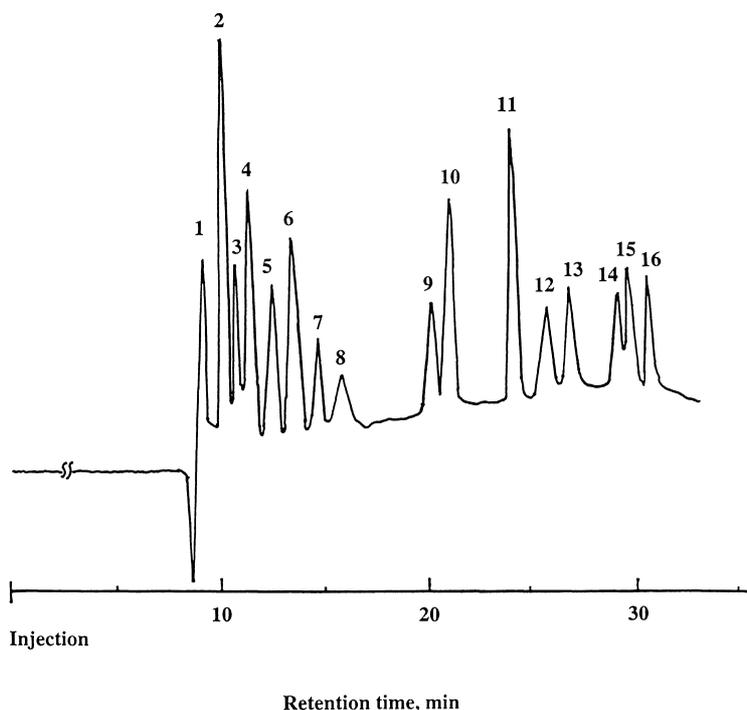


Fig. 2. Chromatogram for the separation of 16 PAHs using Phenomenex ENVIROSEP-PP Column: 1=Naph, 9.50'; 2=Ac, 10.40'; 3=Ace, 11.13'; 4=Flu, 11.86'; 5=Phe, 12.82'; 6=Ant, 13.94'; 7=Fluo, 15.18'; 8=Pyr, 16.13'; 9=BaAn, 20.27'; 10=Chr, 21.22'; 11=BbFl, 24.32'; 12=BkFl, 25.99'; 13=BaPy, 27.00'; 14=DiAn, 29.32'; 15=BePe, 29.81'; 16=InPy, 30.88'.

ane, dichloromethane, toluene or mixtures of these solvents were used for the extraction [15,17,19,22,24]. In most published papers the easy volatile PAHs with 2 or 3 aromatic rings, such as Naph, Ac and etc., were lost more because the solvent used for the extraction and the eluate in the SPE step was evaporated to almost dryness using a vacuum rotary evaporator or a gentle stream of nitrogen gas [28]. In order to avoid loss of the easy volatile PAHs and to increase the extraction efficiency, a suitable selection of solvents to optimize the procedure of extraction and clean-up/preconcentration of the 16 PAHs without the step for the evaporation of solvent is indispensable. In this work six different solvents, acetone, cyclohexane, 2-propanol, methanol, acetonitrile and dichloromethane, were tested. All of the used solvents are not/or little toxic. The results, using the procedure in Section 2.6, are shown in Fig. 4. The extraction efficiencies for the 16 PAHs from the soil by acetone were defined as 1, and others were represented by a ratio of the signals

obtained by the other solvents to the signals obtained by acetone. Fig. 4 shows that the highest extraction efficiencies for most of the 16 PAHs were obtained by using acetone in all the six solvents, except for those of BkFl and BePe. The orders of the extraction efficiencies for most of the 16 PAHs from the soil by the solvents were as follows: Acetone>methanol>dichloromethane \approx acetonitrile>2-propanol>cyclohexane. Because acetonitrile–water were used as the mobile phase, the solvent which can be miscible with the mobile phase is the best for the final injection solution. Therefore, acetone was selected as the extraction solvent because it could mix well with the mobile phase, which resulted in hardly any loss of the easily volatile PAHs because the step for the evaporation of the solvent to almost dryness could be omitted if the sensitivity was enough for the determination of the PAHs by the method. Besides it had the highest extraction efficiency for most of the 16 PAHs from soil in all the tested solvents.

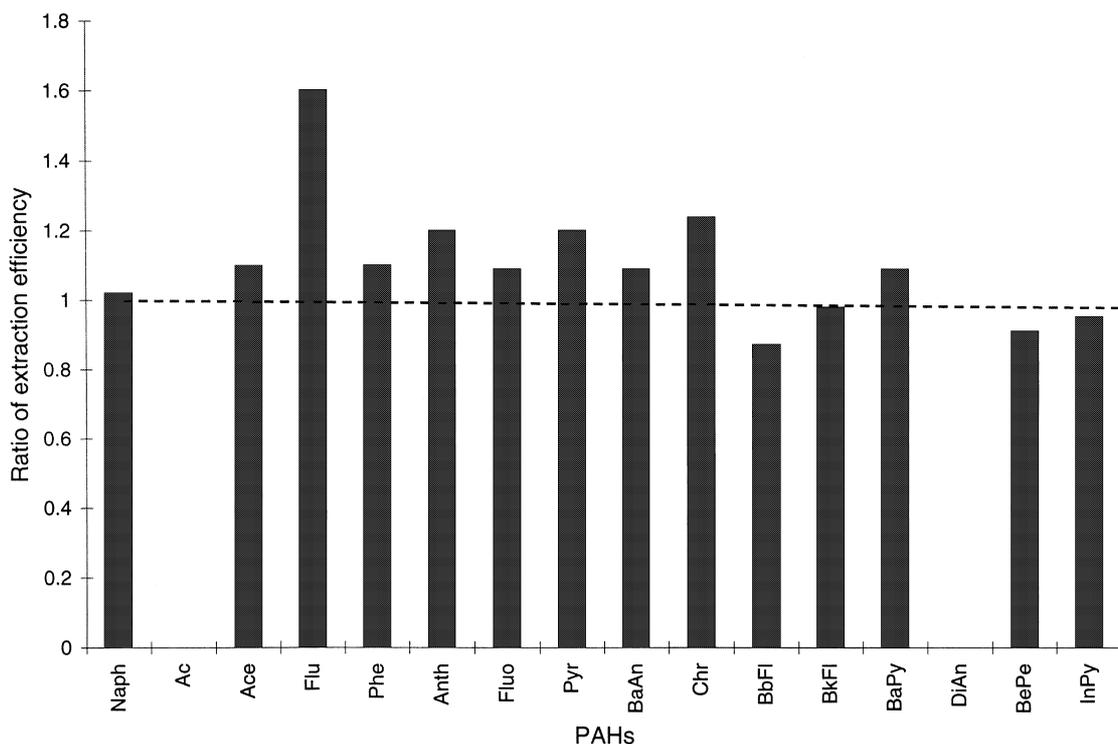


Fig. 3. Selection of extraction mode for 16 PAHs. The vertical axis is the ratio of the signals for the PAHs extracted from the soil by the ultrasonication mode to those obtained by the Soxhlet mode.

3.4. Optimization of SPE procedure

In contaminated soils, besides the 16 PAHs which will be analyzed, other components may interfere with the determination of the 16 PAHs. In addition, the 16 PAHs in the extraction solution from the soil cannot be determined directly because of their lower concentrations. As SPE offers a faster, more cost-effective sample preparation method with dramatic time savings over many traditional liquid/liquid extraction techniques, 6 ml Supelco C₁₈ SPE cartridge was used for the clean-up/preconcentration of the extracted 16 PAHs.

3.4.1. Optimization for the condition of sorbents

The recoveries of 1/250 of the mixed 16 PAHs stock standard solutions using 5 ml of different percentages of acetone in water (10%, 30%, 40%, 50% and 70%) for the conditioning the sorbents are shown in Fig. 5. The procedure for the conditioning of the cartridge sorbents was almost the same as that described in

Section 2.5, except that after the sorbents were conditioned by 5 ml of acetone, the sorbents were then conditioned by 5 ml of 10%, 30%, 40%, 50% and 70% acetone in water, respectively; and after the cartridge was centrifuged, others were the same as that described in Section 2.6. From Fig. 5 it is clear that the recoveries of the 16 PAHs were very low when 10% and 70% acetone in water were used; and the recoveries were almost satisfied, except for those of Naph, Ac, Ace and Flu, when 30%, 40% and 50% acetone in water were used, respectively. Among the three different percentages of acetone 40% of acetone was the best, so 40% of acetone in water was selected for the conditioning.

3.4.2. Selection of elution solution

In order to omit the step, in which the easily volatile PAHs can be lost because of the evaporation of eluates to near dryness by the gentle stream of nitrogen gas, and make the operation easy and reproducible, 3×1 ml of acetone and acetone:THF=1:1 were tested

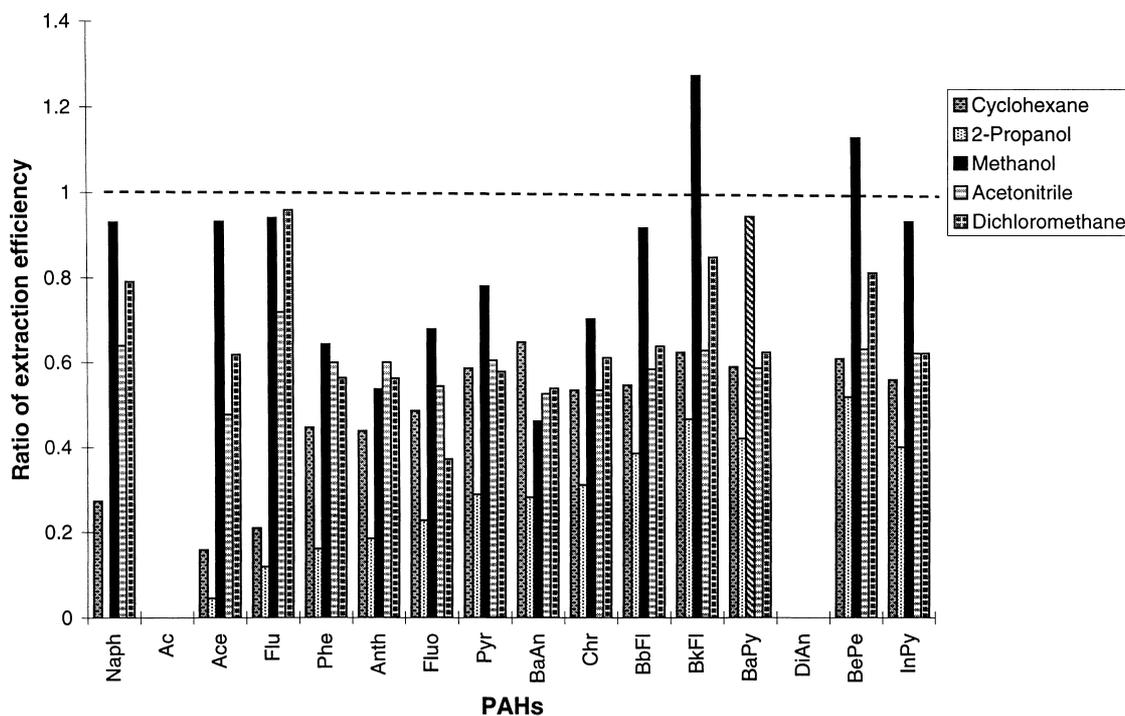


Fig. 4. Selection of solvent for extraction of 16 PAHs. The vertical axis is the ratio of the signals for the PAHs extracted from the soil by the other solvents to that obtained by acetone.

for the elution, respectively, and the recoveries of 1/250 of the mixed 16 PAHs standard solution, comparing with that obtained by 3×2 ml of dichloromethane, are shown in Fig. 6. The recoveries of the easily volatile PAHs, such as Naph, Ace, Ac and Flu, were lower when dichloromethane was used for the elution solution because of the evaporation of the eluates. This was also reported by some other authors [28]. The recoveries for most of the PAHs with 4–6 aromatic rings, such as BaAn, Chr, BaFl, BaPy, DiAn, BaPe, InPy, etc., were lower than those obtained by dichloromethane when acetone was used for the elution solution. This may be caused by the following reasons: The polarity of acetone is higher than the polarity of dichloromethane, but the polarities of the PAHs with 4–6 rings are very low, or almost equal to zero. Considering this, the mixed elution solution, i.e. acetone:THF=1:1 was tested because the polarity of THF is more lower than that of acetone, and it can also be easily miscible with the mobile phase (acetonitrile–water), omitting the step of the evaporation of eluates to near dryness. The recoveries of all the 16 PAHs

were satisfactory, they were between 90.0% and 108%. Therefore, acetone:THF=1:1 was selected as the elution solution in this work.

3.5. Determination of PAHs in soil

The developed method presented in this paper was applied to determine the 16 EPA PAHs in real world soil samples taken from an industrial area in the UK. As the background of the absorption band for some of the 16 PAHs in the chromatogram of the extraction solution was still high, different percentages of methanol in water were tested as washing solution for SPE to try to remove or decrease the band. The test was almost not effective except for 60% methanol. Although the band was reduced much more when 60% methanol was used, some of the PAHs were also washed away. So the washing step was not a good idea for reducing the band. Therefore, a standard addition method was used to determine the 16 PAHs in the soil sample. The regression coefficients of the standard addition curves for the PAHs are presented in Table 3,

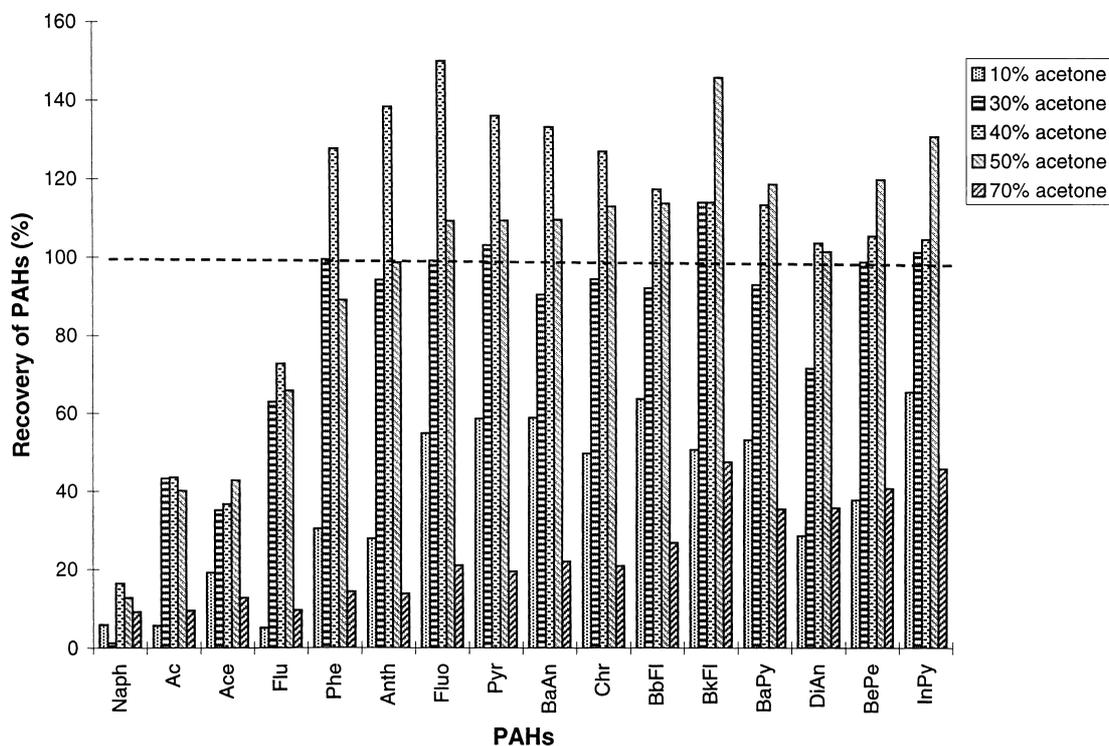


Fig. 5. Optimization for conditioning of the SPE cartridge sorbents.

they were between 0.9268 and 0.9999. An example of the standard addition curve for Anth is expressed by the following equation:

$$Y = 1480X + 140,$$

where Y is the emission signal; and X is the concentration of Anth ($\mu\text{g}/\text{ml}$) and others were similar to it. The results of the PAHs in the soil, determined by this method, are also listed in Table 3. The qualitative results of the PAHs in this soil, determined by gas chromatography mass spectroscopy (GC-MS) in the Macaulay Land Research Institute, Aberdeen, UK and supplied by Dr. P. Anderson, showed that 10 of the 16 PAHs, i.e. Naph, Phe, Fluo, Pyr, BaAn, Chr, BbFl, BaPy, BePe, and InPy were detected in the sample. Besides the 10 PAHs, in our experiments Ace, Flu, Anth, and BkFl were also found. The contents of the 16 PAHs in the soil were less than $3 \mu\text{g}/\text{g}$, except for those of Naph and Ace, which were 9.65 ± 1.08 and $5.65 \pm 0.57 \mu\text{g}/\text{g}$, respectively.

Table 3
Determination of 16 PAHs in soil sample

Name	Regression coefficient	$\mu\text{g}/\text{g}$	RSD (%)
Naphthalene	0.9883	9.65 ± 1.08	11.2
Acenaphthylene	0.9877	<DL	—
Acenaphthene	0.9999	5.65 ± 0.57	10.1
Fluorene	0.9991	0.743 ± 0.069	9.29
Phenanthrene	0.9974	1.64 ± 0.089	5.43
Anthracene	0.9987	0.557 ± 0.019	3.41
Fluoranthene	0.9813	0.776 ± 0.021	2.71
Pyrene	0.9930	1.55 ± 0.04	2.58
Benzo[a]anthracene	0.9636	1.31 ± 0.09	6.87
Chrysene	0.9647	1.42 ± 0.06	4.23
Benzo[b]fluoranthene	0.9832	1.91 ± 0.10	5.24
Benzo[k]fluoranthene	0.9722	1.40 ± 0.09	6.43
Benzo[a]pyrene	0.9268	2.89 ± 0.23	7.96
Dibenzo[a,h]anthracene	0.9907	<DL	—
benzo[g,h,i]perylene	0.9869	2.60 ± 0.20	7.69
Indeno[1,2,3-cd]pyrene	0.9462	2.73 ± 0.13	4.76

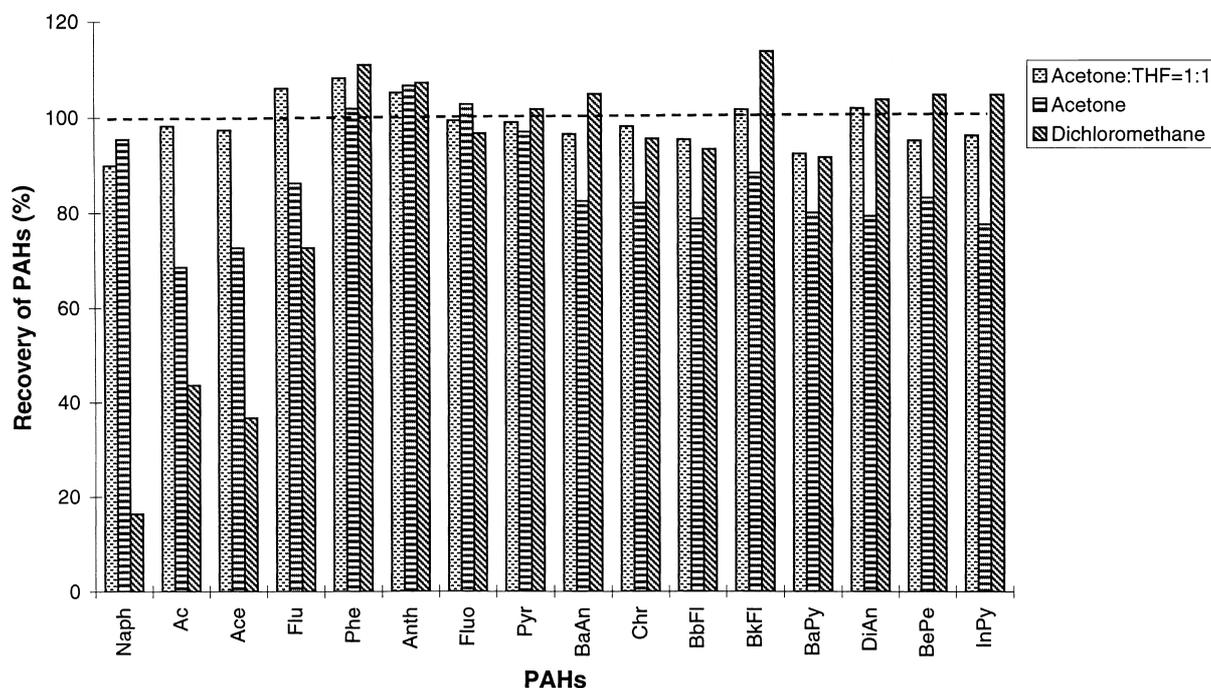


Fig. 6. Selection of elution solution for 16 PAHs from SPE cartridge sorbents.

4. Conclusions

The US EPA 16 PAHs can be separated and determined well by RP-LC with UV absorption detection using C₁₈ Bakerbond PAH 6 PLUS column or Phenomenex ENVIROSEP-PP column and acetonitrile–water gradient elution. The time for the chromatographic cycle is 41 min including 10 min for the equilibration, and it is suitable for economic and routine analysis of the 16 PAHs. The ultrasonication extraction was better than the Soxhlet extraction for the extraction of the 16 PAHs from soils because it was not only higher in the extraction efficiency, but also economic and easily operated. Acetone was the best solvent among the six solvents tested for the extraction of the 16 PAHs from the soil, and the orders of the extraction efficiencies for most of the 16 PAHs from the soil by the six solvents were as follows: acetone > methanol > dichloromethane ≈ acetonitrile > 2-propanol > cyclohexane. 6 ml Supelco LC-18 SPE cartridge was suitable for the preconcentration/clean-up of the soil extraction solution, and acetone:THF=1:1 was the best elution solution among the solutions tested for the elution of the 16 PAHs from

the cartridge because the recoveries for most of the 16 PAHs were higher than those obtained by the other SPE procedures, and this procedure was simple and not time-consuming. The developed analytical method was successfully applied to determine the 16 PAHs in a real soil sample using the standard addition procedure.

Finally it should be mentioned that the proposed methodology could be applied to the 16 PAHs control in other environmental solid samples, such as air particles, sediment, and the methodology may also be useful for the determination of the 16 PAHs in other environmental samples, such as river, lake and sea waters, with slight modifications.

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