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Screening method for polycyclic aromatic hydrocarbons in soil using hollow fiber membrane solvent microextraction

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Abstract

A fast, inexpensive screening method for polycyclic aromatic hydrocarbons in soil has been developed. Using hollow fiber membrane solvent microextraction, 8 μl of octane extraction solvent was placed inside a porous, polypropylene fiber. Following an 8 min analyte preconcentration step, 4 μl of extract was injected into a gas chromatograph. Separation was achieved in less than 10 min with a detection limit of 0.13 mg/kg for 2-methylnaphthalene. Results of both spiked and real soil samples are presented.

Keywords: Hollow fiber membrane; Solvent microextraction; Extraction methods; Soil; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

A rising environmental concern is the contamination of soil with polynuclear aromatic hydrocarbons (PAHs). As regulatory agencies are faced with increasing workloads, the development of a fast, low cost, reduced waste method to screen samples is crucial. In 1995, PAHs were added to the hazardous substance list produced by the Agency for Toxic Substances and Disease Registry (ATSDR) and the Environmental Protection Agency (EPA). In 2001, these agencies ranked PAHs as the ninth most threatening compound to human health [1]. Over 100 different PAHs have been identified. They often enter the soil as complex mixtures by leakage from fuel storage containers or after the incomplete burning of a variety of substances such as coal, oil, gas, wood, garbage, or tobacco [1]. The Department of Health and Human Services has determined that several PAHs are known animal carcinogens following the inhalation, consumption, or skin absorption of the compounds. Long-term exposure of humans to PAHs has resulted in cataracts, kidney and liver damage, reproductive difficulties, and many types of cancer [1].

There are a variety of methods for the extraction of PAHs in soil, with sample preparation often the most time-consuming step. Pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), and extractions with superheated water use elevated temperatures to improve extraction [2,3]. Both PLE and SFE have extraction times of less than 10 min, but require more complex apparatus [4]. Superheated

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water extractions have reported extraction times of up to 30 min.

Traditional liquid–liquid extractions or solid-phase extractions have been utilized for the extraction of PAHs. These methods often require that the original solvent be evaporated and the sample reconstituted in a solvent more suitable for analysis [5]. This lengthens the overall process, utilizes large amounts of solvent, and risks loss of analyte by evaporation and adsorption. Another widely used extraction technique is solid-phase microextraction (SPME). Although it is a solvent free technique, it has reported PAH extraction times of 90 min, and a desorption step is necessary to avoid sample carry-over between runs [6].

Solvent microextraction (SME) is a technique that involves suspending a drop of organic solvent from a syringe tip into the sample, as described by Jeannot and Cantwell [7,8]. As the analytes move from the bulk sample to the drop, they are effectively pre-concentrated. The use of SME has been reported effective for numerable extractions including pesticides from river water, drugs from urine, and PAHs from soil [9–11]. Although SME has several advantages over the previously mentioned extraction methods, it is susceptible to drop instability both at high stir rates and in samples with significant particulate matter. To overcome these limitations, hollow fiber membrane solvent microextraction (HFMSME), a technique in which the organic extraction solvent is placed inside a porous fiber, has been employed. Previously reported for the extraction of drugs of abuse in urine and saliva [12–14], HFMSME allows for the sample to be stirred more vigorously, reducing the Nernst diffusion layer and therefore improving extraction efficiency. Additionally, a larger volume (up to 20 μl) of extraction solvent can be used as opposed to only 1–2 μl with the hanging drop. This improves the rate and efficiency of analyte transfer across the membrane. Similar fiber extraction techniques have been developed with different names. Liquid phase microextraction (LPME), has been used for drug extractions [15–17]. The main difference between HFMSME and LPME is the fiber set-up. LPME uses a U-shaped fiber in which extraction solvent is injected in one end and withdrawn from the other. HFMSME seals the fiber on one end and both injects and withdraws solvent from the top. Another membrane extraction techniques is microporous membrane liquid–liquid extraction (MMLLE) [18,19]. Instead of a hollow fiber, MMLLE clamps a porous membrane between two blocks and does not dispose of the membrane after each run. However, the MMLLE design can be combined on-line to analytical instruments.

The present study examines the use of HFMSME as an extraction method for the screening of PAHs in soil. This technique uses small amounts of solvent, minimal extraction equipment, and requires less than 10 min for extraction. Studies on spiked soil samples were conducted to optimize the process and determine detection limits. The developed method was validated using a certified reference material.

2. Experimental

2.1. Reagents and materials

A standard mixture of 17 PAHs in methylene chloride was obtained from NSI Environmental Solutions (Research Triangle Park, NC, USA) at concentrations of approximately 1000 μg/ml. Non-polluted sandy loam soil was also obtained from NSI as well as contaminated soil collected from the Southern Branch of the Elizabeth River (Chesapeake Bay area) that contained 18 PAHs ranging from 0.51 to 24.6 mg/kg. One gram of soil was used in all extraction experiments. High-purity (99.5%) perylene was purchased from Aldrich (Milwaukee, WI, USA). HPLC-grade solvents used were octane (Fluka, Milwaukee, WI, USA), acetonitrile (EM Science, Gibbstown, NJ, USA), acetone (EM Science), methylene chloride, (Fisher Scientific, Fairlawn, NJ, USA), and methanol (Fisher Scientific). Water used was ultrapure, distilled, deionized (18.2 MΩ) obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA). All gases were supplied by Air Products (Parkersburg, WV, USA). The 22-ml extraction vials were bought pre-silanized from Supelco (Bellefonte, PA, USA). An octagonal 7×2×2-mm stirring bar (Fisher, Pittsburgh, PA, USA) and a stir plate were used. Stir rate was measured with a 631-BL Strobotac strobe light (General Radio, Cambridge, MA, USA). Q 3/2 Accurel KM polypropylene hollow fiber tubing (200

μm wall thickness, 0.64 μm pore size, 600 μm inner diameter) was obtained from Akzo Nobel (Wuppertal, Germany). A 10-μl syringe (model 701N, Hamilton, Reno, NV, USA) was used to fill the fiber, and the same model syringe fitted with a Chaney adaptor was used for injections. Six compounds were chosen to represent the class of PAHs based on their range of molecular mass values: 2-methylnaphthalene (M_r=142.2 g/mol), fluorene (M_r=162.2 g/mol), fluoranthene (M_r=202.3 g/mol), benzo[*b*]fluoranthene (M_r=252.3 g/mol), benzo[*a*]pyrene (M_r=252.3 g/mol), and benzo[*ghi*]perylene (M_r=276.3 g/mol).

2.2. Instrumentation

A Hewlett-Packard (HP) 6890 GC system with split–splitless injection port (Wilmington, DE, USA) was used in all experiments. The GC system was equipped with an HP flame ionization detector and connected to a desktop computer with HP Chemstation (Version A.06.03) software. Ultrapure helium (99.999%) was used as the carrier gas at a flow-rate of 2 ml/min, and was passed through hydrocarbon traps, oxygen traps, and moisture traps (Alltech Associates, State College, PA, USA). Separation was performed using a HP-5 phenylmethylsiloxane column (30.0 m×250 μm, 0.25 μm; Restek, Bellefonte, PA, USA). The oven temperature program began with an initial temperature of 150 °C held for 1 min. The temperature was then ramped at a rate of 40 °C/min to a final temperature of 300 °C and held for 5.2 min, making the total run time 9.95 min. All samples were injected in the split mode (25:1) and the needle was held in the injection port for 5 s before removal. Inlet temperature was 275 °C and detector temperature was 300 °C.

2.3. Extraction procedure

Hollow fiber tubing was cut into approximately 6.5 cm pieces, and sealed on one end after being singed with a flame. Octane was the extraction solvent used in all procedures [11]. Before being placed in the vial for extraction, the fiber was first dipped briefly in octane. By first saturating the pores, the octane extraction solvent added to the fiber was not be adsorbed by the fiber, hindering extraction and solvent withdrawal. After being dipped in octane, the fiber was threaded through a polypropylene septum, with approximately 1 cm of the unsealed end protruding through the opening. The septum then rested on top of the open 22 ml pre-silanized vial. A schematic diagram of the extraction apparatus is shown in Fig. 1. A 10-μl syringe was inserted completely into the fiber to fill the fiber with octane extraction solvent. The octane used to fill the fiber contained 30.0 μg/ml of perylene, the selected internal standard. By placing the internal standard inside the tubing instead of the vial, the reproducibility of the injection could be monitored by using the ratio between the area of the analyte peak and the internal standard peak. The solution was stirred throughout the extraction time, and a 10-μl syringe fitted with a Chaney adaptor was used to withdraw the solvent from the fiber. The recovered extract was immediately injected into the GC system for analysis. PAH peaks were identified by retention time and all peak areas measured were divided by the peak area of the internal standard for that particular injection.

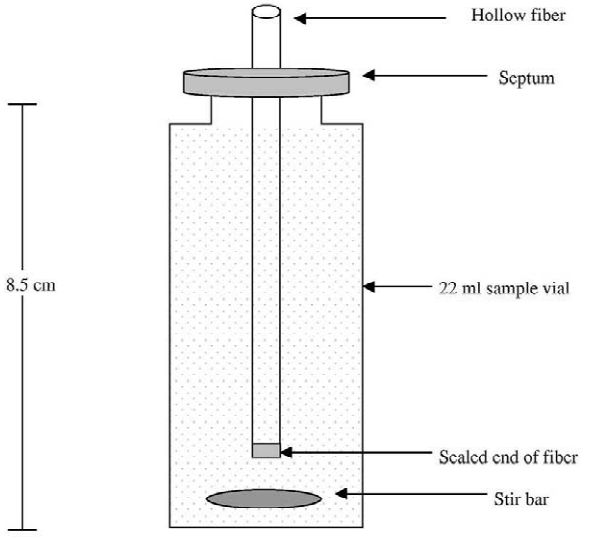

Fig. 1. Hollow fiber membrane solvent microextraction apparatus. A 10-μl syringe fitted with a Chaney adaptor is inserted into the hollow fiber to withdraw 4 μl of solution after an 8-min extraction.

3. Results and discussion

3.1. Method development

In a previous study in our laboratory, solvent microextraction (SME) was used for PAH analysis in contaminated soil [11]. The results indicated that octane extraction solvent and 22-ml sample volumes provided the highest peak areas, and were kept for the HFMSME study. It was also determined in this study that the addition of acetone to the sample vial aided the extraction process by promoting the release of the analytes from the soil matrix. However when over 7 ml of acetone was added, the solvent drop became soluble in the sample solution and dislodged from the syringe tip. Using the fiber, increased acetone volumes could be investigated without drop concern. This parameter, along with extraction time, stir speed, solvent fill volume and injection volume were analyzed in water first to obtain a general extraction procedure. Acetone volumes of 7, 10, 12, and 15 ml were tested with the water volume varying so that the total volume in the vial remained 22 ml. All experiments involving method development were performed using a PAH concentration of 0.10 μg/ml, and were carried out in three replicate trials. The designated volume of PAHs was added to the vial immediately following the addition of water and acetone. The vial was then shaken by hand for approximately 30 s. The fill volume of octane–perylene extraction solvent in the fiber was 10 μl, and stir rate was 800 rpm. The Chaney adaptor was set to withdraw 4 μl from the fiber after extraction to be injected into the GC system, but it was estimated that a certain amount of air was drawn up so that the actual GC injection volume was less. As seen with SME [11], the largest peak areas were observed with 7 ml acetone and 15 ml water, therefore all remaining experiments were performed with these volumes. The addition of acetone above 7 ml further hindered the extraction of the PAHs into the octane–perylene extraction solvent.

To determine the most effective extraction time, the stir speed, fill volume, and injection volume remained the same as above. Extractions were carried out at 4, 6, 8, 10, and 20 min, and the mean relative peak area was plotted vs. extraction time. All PAHs gave similar trends. An approximate 45% gain in peak area was observed at 4 and 20 min compared to the other times, but the standard deviations associated with these values averaged approximately 50%. Extraction times of 6, 8 and 10 min all provided similar peak areas with lower relative standard deviations, and 8 min was used for further experiments because it maximized sample throughput with the GC run time. Extractions were then performed at stir speeds of 0, 400, 800, and 1225 rpm, as these speeds corresponded to manufacturer settings on the stir plate and could be easily reproduced. As expected, increasing the stir speed enhanced extraction, but past the 800 rpm setting the stirring became too violent, resulting in a loss of extraction solvent out of the fiber. 800 rpm was selected for all further extractions.

The fill volume of the fiber with octane–perylene extraction solvent was examined at volumes of 6, 8, 10, 12, and 15 μl. Using the 6-μl volume, it was difficult to consistently inject 4 μl because some of the extraction solvent evaporated out of the fiber during the extraction time. Extraction solvents with lower volatility were not examined because they would mask early eluting PAH peaks. A less than 20% increase in peak area was observed from 8 to 15 μl, and relative standard deviations improved an average of 60% using the 8-μl fill volume. Thus, all remaining extractions were performed using a fill volume of 8 μl octane with perylene internal standard.

Finally, the GC injection volume was investigated at 2, 4, 6, or 8 μl. Volumes of 6 and 8 μl withdrew excess air from the fiber, resulting in low peak area ratios. The 4 μl volume was selected for use in all subsequent extractions because it maximized peak area and provided the greatest reproducibility compared to 2 μl.

3.2. Method development in soil

All of the previously described parameters were selected using a water sample matrix and were retained for the soil experiments. For the soil analyses, one gram of soil was added to an empty vial and the specific volume of PAH standard was added. The sample was then vortexed, left to dry overnight with the cap on, and vortexed again immediately prior to addition of the 7 ml acetone and 15 ml water. The

vials were hand shaken for approximately 30 s, until the contents were visibly well mixed.

In the previous PAH study in our laboratory using SME, a metal screen was used to filter the solution so that the soil particulates would not dislodge the solvent drop [11]. Using HFMSME, the solvent within the fiber was not disrupted by the soil. However, some of the fiber pores were becoming clogged by the end of the extraction time. This resulted in slightly higher relative standard deviations for the soil extractions because it was impossible to have a completely homogenous soil sample from one run to the next. Still, the time-consuming, cumbersome filtration step was eliminated because the detection limits necessary for a screening analysis could be obtained without it.

The amount of time the soil was soaked in the water–acetone before extraction was investigated to determine if longer exposure to the liquids significantly increased extraction. The vials were filled with 7 ml of acetone and 15 ml of water at 0, 1, 3, 6, 9, and 24 h prior to extraction. Peak area increased by approximately 30% for 2-methylnaphthalene and fluorene when soak time increased from 0 to 3 h and then no significant change was observed between 3 and 24 h. The amount of soak time had no effect on peak area for fluoranthene. However, with the later eluting compounds, benzo[*b*]fluoranthene, benzo[*a*]pyrene, and benzo[*ghi*]perylene, increasing the soak time from 0 to 3 h caused a 26% average decrease in peak area, and again no significant change was observed from 3 to 24 h. In an effort to keep sample preparation to a minimum and because detection limits required for a screening analysis could be met without soaking the soil, all remaining samples were analyzed immediately following the addition of water and acetone.

In the water samples, speeds above 800 rpm were too violent and resulted in a loss of extraction solvent. With the addition of soil, the viscosity of the solution increased, allowing the fiber to withstand more rapid stirring. Stir speeds of 800, 1100, and 1350 rpm were tested in the soil matrix, and peak area increased with higher stir speeds. Again, at settings above 1350 rpm, the fiber shook violently and no results could be obtained, so 1350 rpm was used for all remaining extraction experiments.

3.3. Calibration

Plots of calibration data were created for the standard mixture of PAHs diluted in acetonitrile, at concentrations ranging from 1 to 30 μg/ml. Then, 4 μl of standard was injected and each peak area was divided by the area of a 4-μl injection of perylene at a concentration of 30 μg/ml. This area ratio represented the concentration of analyte in the fiber after the 8-min extraction. Calibration and regression data were also obtained for water and soil extractions, and the values for the six PAHs chosen to represent the class of PAHs are given in Table 1. Average relative standard deviation (RSD) values for the PAH standard, water extractions and soil extractions were 12.6, 15.6, and 23.3%, respectively.

A multiday calibration study was performed with soil extractions to test the inter-day reproducibility of the extraction procedure. One trial at each concentration was run on three consecutive days. The results of this study can be seen in Table 2. The concentration ranges varied for the different PAHs to

Table 1
Equations and r^2 values for five point calibration lines produced in this study

	2-Methyl naphthalene	Fluorene	Fluoranthene	Benzo[*b*]fluoranthene	Benzo[*a*]pyrene	Benzo[*ghi*]perylene
Standards	$0.017x + 0.0008$ $r^2 = 0.9990$	$0.023x - 0.007$ $r^2 = 0.9977$	$0.028x - 0.010$ $r^2 = 0.9978$	$0.029x - 0.014$ $r^2 = 0.9971$	$0.029x - 0.002$ $r^2 = 0.9959$	$0.031x - 0.0006$ $r^2 = 0.9974$
Water	$3.55x + 0.009$ $r^2 = 0.9860$	$3.90x + 0.002$ $r^2 = 0.9922$	$4.48x + 0.004$ $r^2 = 0.9914$	$4.49x + 0.006$ $r^2 = 0.9969$	$4.76x - 0.002$ $r^2 = 0.9962$	$4.37x + 0.779$ $r^2 = 0.9985$
Soil	$2.491x + 0.0125$ $r^2 = 0.9818$	$2.80x + 0.0047$ $r^2 = 0.9953$	$2.783x + 0.021$ $r^2 = 0.9954$	$1.865x + 0.020$ $r^2 = 0.9889$	$1.434x + 0.022$ $r^2 = 0.9497$	$1.291x + 0.034$ $r^2 = 0.9787$

All injections and extractions were performed in triplicate and the ratio of the peak area of each analyte to the peak area of the internal standard was used for all calculations.

Table 2
Equations and r^2 values from the multiday calibration study of soil extractions

Day	2-Methylnaphthalene	Fluoranthene	Fluorene	Benzo[*b*]fluoranthene	Benzo[*a*]pyrene	Benzo[*ghi*]perylene
1	$2.40x + 0.0046$ $r^2 = 0.9963$	$2.34x + 0.002$ $r^2 = 0.9992$	$3.25x + 0.0078$ $r^2 = 0.9785$	$1.28x + 0.0209$ $r^2 = 0.9330$	$1.22x + 0.0076$ $r^2 = 0.9566$	$0.985x + 0.003$ $r^2 = 0.9830$
2	$2.59x + 0.012$ $r^2 = 0.9714$	$2.77x + 0.0055$ $r^2 = 0.9666$	$3.42x + 0.0104$ $r^2 = 0.9980$	$1.42x + 0.0382$ $r^2 = 0.9675$	$1.57x - 0.0084$ $r^2 = 0.9977$	$1.41x - 0.0053$ $r^2 = 0.9796$
3	$1.764x + 0.028$ $r^2 = 0.9298$	$2.01x + 0.0193$ $r^2 = 0.9511$	$1.618x + 0.063$ $r^2 = 0.9087$	$1.23x + 0.0152$ $r^2 = 0.9818$	$0.99x + 0.0073$ $r^2 = 0.9442$	$0.817x + 0.017$ $r^2 = 0.9846$
Pooled data	$2.25x + 0.0149$ $r^2 = 0.9867$	$2.37x + 0.009$ $r^2 = 0.9831$	$2.89x + 0.009$ $r^2 = 0.9831$	$1.38x + 0.0193$ $r^2 = 0.9965$	$1.24x + 0.0038$ $r^2 = 0.9944$	$1.07x + 0.0049$ $r^2 = 0.9921$

All injections and extractions were performed in triplicate and the ratio of the peak area of each analyte to the peak area of the internal standard was used for all calculations.

include the lowest detection limit obtainable for that compound. Concentrations from 0.006 to 0.10 μg/ml were used for 2-methylnaphthalene and fluorene, 0.0085–0.10 μg/ml for fluoranthene, and 0.01–0.10 μg/ml for benzo[*b*]fluoranthene, benzo[*a*]pyrene, and benzo[*ghi*]perylene.

3.4. Calculations

The amount of PAHs present in the fiber following extraction was calculated using the peak area ratio measurements and the calibration curves of the standards only (no extraction). From that data, the preconcentration factor and extraction efficiency for each compound were determined and are presented in Table 3. Preconcentration factor is defined as the ratio of the final analyte concentration in the extraction solvent to the analyte concentration in the original sample, and is calculated using the average of the three trials obtained for each concentration from the water and soil extractions. The preconcentration factors ranged from 165.8 to 233.5 for water extractions and from 80.1 to 170.7 for soil extractions. Extraction efficiency was calculated by determining the percent of the total analyte present in the original sample that was extracted into the fiber. The extraction efficiencies were calculated for water and soil extractions from the average peak area ratio of three replicate trials at each concentration, with the average values and relative standard deviations being 7±1% for the water and 5±1% for the soil. Extraction efficiencies remained higher with HFMSME compared to the less than 0.05% extraction efficiency values obtained using SME [11]. This is explained by the larger surface area of octane exposed using the hollow fiber membrane than the hanging drop, and the ability to use faster stir speeds

Table 3
Preconcentration factors and extraction efficiencies for water and soil (*italics*) extractions

	Preconcentration factor[a]	Extraction efficiency (%)[b]
2-Methylnaphthalene	223.4	8.1
	170.7	*6.2*
Fluorene	182.0	7.7
	140.1	*5.1*
Fluoranthene	185.4	6.7
	155.0	*5.6*
Benzo[*b*]fluoranthene	182.6	6.6
	123.8	*4.5*
Benzo[*a*]pyrene	165.8	6.0
	80.1	*2.9*
Benzo[*ghi*]perylene	233.5	8.5
	88.3	*3.2*

Results are reported as the average value of three replicate extractions from the calibration lines.

[a] Calculated as the ratio of the final analyte concentration in the extraction solvent to the analyte concentration in the original sample.

[b] Calculated as the percent of the total analyte present in the original sample that was extracted into the fiber.

Table 4
Observed limits of detection in soil from the multiday calibration study based on a signal-to-noise ratio of 3

	Molecular mass (g/mol)	Concentration (mg/kg)
2-Methylnaphthalene	142.2	0.13
Fluorene	166.2	0.13
Fluoranthene	202.3	0.18
Benzo[*b*]fluoranthene	252.3	0.22
Benzo[*a*]pyrene	252.3	0.22
Benzo[*ghi*]perylene	276.3	0.22

Table 5
Results of certified soil analysis

Compound	Determined concentration (mg/kg)	Reference value (mg/kg)
2-Methylnaphthalene	0.0	Trace
Fluorene	0.34	0.65
Fluoranthene	23.4	24.6
Benzo[*b*]fluoranthene	10.27	9.69
Benzo[*a*]pyrene	4.63	5.09
Benzo[*ghi*]perylene	2.05	3.58

Determined concentrations were based on the average of triplicate 8-min extractions with 1 g of certified soil.

which is assumed to cause a reduction in the Nernst diffusion layer, and allows an increase in the mass transfer coefficient. The result is more analyte preconcentrating within the fiber during the 8-min extraction time [7,8].

The observed limit of detection for each of the six analyzed compounds was determined based on a signal-to-noise ratio of 3, and the results are shown in Table 4. The limit of detection was lower for the low-molecular-mass PAHs (2-methylnaphthalene, fluorene, and fluoranthene) than for the high-molecular-mass compounds (benzo[*b*]fluoranthene, ben-

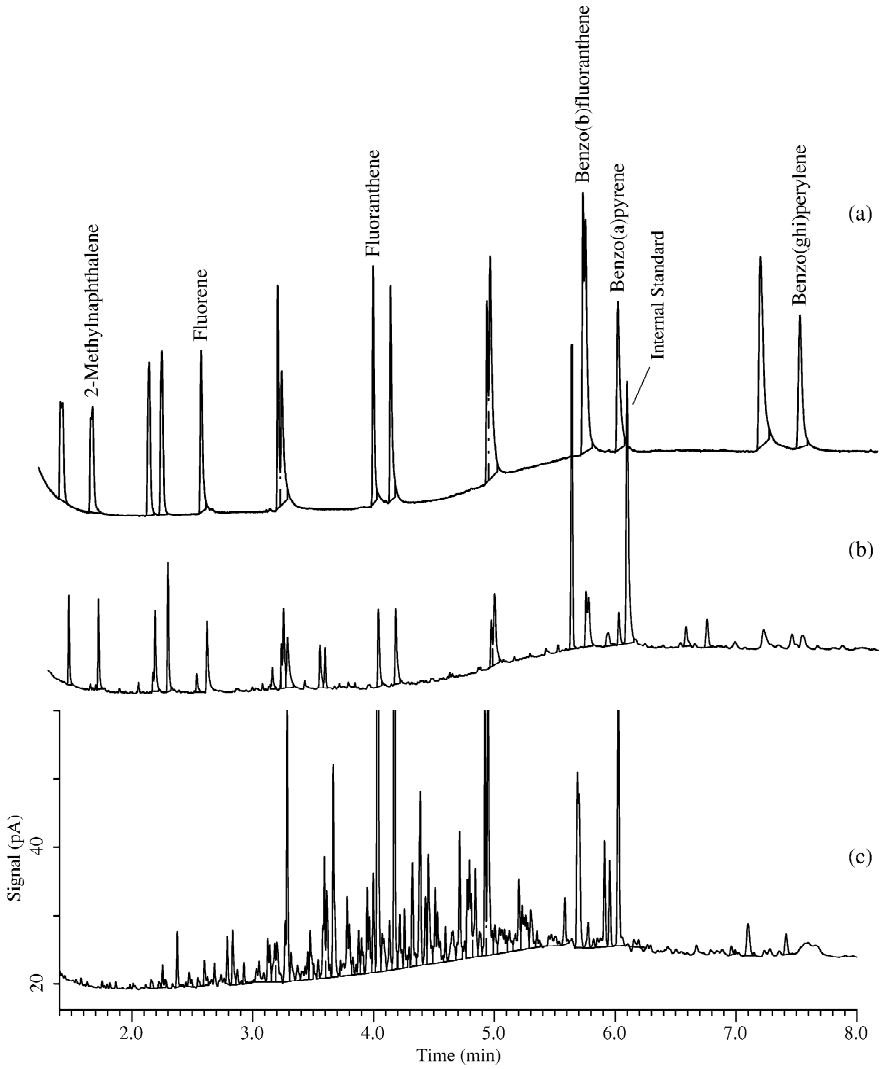

Fig. 2. Chromatogram of (a) standard PAH mixture in acetonitrile at 5.0 μg/ml, (b) extraction from soil spiked at a PAH concentration of 2.2 mg/kg, (c) extraction from certified soil reference material.

zo[*a*]pyrene, and benzo[*ghi*]perylene). This is explained by the increased water solubility of the lower-molecular-mass PAHs and the tendency for the higher-molecular-mass PAHs to somewhat partition back into the soil and not be extracted as efficiently [20].

To evaluate the success of this method in a real environment, contaminated soil collected from the Southern Branch of the Elizabeth River (Chesapeake Bay area) was analyzed in triplicate using HFMSME. These values were compared to the certified concentrations, and the results are summarized in Table 5. Good correlation was observed with certified standards, although low concentrations of PAHs were more difficult to extract and gave higher relative errors. Fig. 2 illustrates the complexity of the real soil sample compared to the PAH standards and the spiked soil.

4. Conclusion

A quick, inexpensive screening method for polycyclic aromatic hydrocarbons in soil has been developed using HFMSME. Octane extraction solvent and perylene internal standard were placed inside a hollow fiber membrane, and the analytes were preconcentrated after moving through the membrane into the solvent. Unlike the hanging drop method utilized in SME, use of the hollow fiber allows the sample to be stirred rapidly and eliminates the need for filtering. This provides lower limits of detection without the need for an additional time consuming step. Each extraction fiber costs less than one cent and is disposed of following each run, reducing the chance of sample carry-over between trials.

With HFMSME, extensive filtering or pretreatment of the sample is unnecessary. The only equipment required before separation is a stir plate and microsyringe. These features, along with the small amount of organic solvent needed, would allow HFMSME to be coupled with portable GC instrumentation for an effective, on-site, screening analysis for PAHs.

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