Solid-Phase Microextraction and Gas Chromatography–Mass Spectrometry for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Solid Matrices

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Abstract

A solid-phase microextraction (SPME) and gas chromatography–mass spectrometry method for determining polycyclic aromatic hydrocarbons (PAHs) in environmental solid matrices is developed. Investigated matrices include seaweed (*Undaria pinnatifida* and *Himanthalia elongata*), humic substances (isolated from a wetland out-flow and purchased from Aldrich), and soil. Optimal conditions for a good SPME efficiency of 16 hydrocarbon compounds are obtained using a 100-µm polydimethylsiloxane fiber directly immersed in aqueous carrier medium. The method is remarkable for presenting short extraction times and considerably high sensitivities. The SPME results obtained by using internal calibration give the total analyte concentration based on the identical partitioning behavior of native and spiked pollutants. The detection limits range from 0.001 to 0.1 mg of PAH per kilogram of dry matrix. SPME external calibration provides information regarding freely dissolved analytes. The detection limits range from 0.001 to 0.05 µg of PAH per liter of carrier medium. The SPME with external calibration procedure can be applied to measure free concentrations of a target compound spiked into a carrier medium and onto a matrix. Based on a comparison of results obtained for the two samples, the partitioning of the target analyte between the matrix and the carrier medium is calculated.

Introduction

Determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples has drawn increasing concern because of their toxic, carcinogenic, and mutagenic effects. These compounds have been commonly carried into the environment in solvents such as coal tar or creosote. Depending on the characteristics of the site, contamination of the surface may be followed by subsurface contamination due to migration of liquid hydrocarbons and dissolution into rain/ground water. Regarding migration, these organic contaminants can meet a complex mixture of vegetation, mineral, organic material, and soil, which can be an effective sorbent. The overall sorption capacity is influenced by the nature of the vegetation, soil organic matter, mineral composition, soil moisture content, and presence of solvent. The main interactions are adsorption of organics on mineral surfaces and partitioning into vegetation and soil organic matter (1). A knowledge of these interactions is important in determining how much of the contaminant is really available to microorganism and human life (2). Several studies have demonstrated that the toxicity of chemicals is primarily governed by the freely dissolved fraction available for uptake by organisms (3). Recent studies demonstrated that a decrease in the freely dissolved aqueous concentration of organic pollutants has been found in the presence of dissolved organic carbon (DOC), so the presence of DOC can be responsible for a reduced bioaccumulation or toxicity of chemicals to organisms (4–7). Therefore, the development of effective extraction and enrichment techniques to selectively determine these pollutants in environmental samples is of great interest. The extraction of these compounds from a matrix can be achieved with conventional liquid extraction techniques such as Soxhlet extraction and sonication. These techniques are time consuming and require large amounts of organic solvents in addition to a highly tedious purification of the extracted solution before analysis. In recent years, new extraction techniques have been studied to reduce the consumption of organic solvent, improve the precision of analyte recoveries, and reduce extraction time and sample preparation cost. Among the new extraction techniques, solid-phase microextraction (SPME) presents a very promising method to determine concentrations of organic chemicals in solids, water, and air matrices. An SPME device consists of small fused-silica fiber coated with a polymeric stationary phase. The fiber is placed in a water sample and chemicals partition into the coating, which can subsequently be desorbed thermally in a gas chromatographic (GC) injector (8). SPME is a solventless extraction method, requires only a small amount of sample,

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and has a fast response time. When SPME is combined with GC and mass spectrometry (MS) in the selected-ion mass acquisition mode, the technique becomes extremely sensitive and appropriate for the determination of PAH in environmental matrices because this combination simultaneously takes into account the extraction, preconcentration, and purification steps.

In the present study, an SPME method is developed for the determination of 16 Environmental Protection Agency priority PAHs onto environmental matrices, which are green seaweed (SW) (*Undaria pinnatifida*), brown SW (*Himanthalia elongata*), dissolved humic subtances (isolated from a wetland out-flow), humic acid (HA) (Aldrich, St. Louis, MO), and soil (real contaminated soil). SPME is compared with traditionally liquid–solid extraction. SPME results obtained for spiked carrier medium and spiked matrices are compared, and pollutant partition coefficients can be calculated.

Experimental

Materials

The manual SPME device and various thickness of polydimethylsiloxane (PDMS) fibers (7, 30, and 100 µm) were purchased from Supelco (Bellefonte, CA). New fibers were thoroughly activated according to the manufacturer recommendations (by heating in the injector of the chromatograph under helium flow at 250°C for 1 h for the 30- and 100-µm fibers and at 320°C for 4 h for the 7-µm fiber). Additionally, the fibers were conditioned daily in the GC injection chamber until a clean base line had been obtained.

Single pure standards of naphthalene (PAH-1), acenaphthylene (PAH-2), acenaphthene (PAH-3), fluorene (PAH-4), phenanthrene (PAH-5), anthracene (PAH-6), fluoranthene (PAH-7), pyrene (PAH-8), benz(a)anthracene (PAH-9), chrysene (PAH-10), benzo(b)fluoranthene (PAH-11), benzo(k)fluoranthene (PAH-12), benz(a)pyrene (PAH-13), indenopyrene (PAH-14), dibenz(ah)anthracene (PAH-15), and benzo(ghi)perylene (PAH-16) were weighed and dissolved in acetone to prepare the spiking solution of 1000–2000 mg/L of each PAH. The PAH standards were used as purchased from Fluka AG (Buchs, Switzerland) of purities from 97% to 99%.

Spiked matrix preparation

The four environmental matrices used in this study were: (*i*) green SW (*Undaria pinnatifida*) (Algamar, Redondela, Pontevedra, Spain), (*ii*) brown SW (*Himanthalia elongata* and *Sacchoriza polyschides*) (Conservas and Ahumados Lou, Riveira, A Coruna, Spain), HA (Aldrich), and dissolved humic substances (DHS) collected from a wetland out-flow of Northern Germany. The last was aquatic and terrestrial humic substances isolated and concentrated by ultrafiltration with molecular weights ranging from 1 to 100 kD. DHS solution was first reduced to a small volume and then brought to dryness. SW was dried at 40°C in a ventilated oven to constant weight and cut into small pieces. All of the dried matrices were homogenized and subjected to elementary and thermogravimetric analyses. Elementary analysis gave the content of C, H, and N, and thermogravimetric analysis gave the content of matter burnt at 650°C in dry sample (corresponds approximately to the organic matter content) (Table I).

Tests for impurities were carried out by extraction of blank matrices. Spiked matrix samples were prepared as follows: 0.5 g of the matrix was placed in a 15-mL vial and a suitable volume of PAH standard acetone solution was added. The vial was hermetically closed with a Teflon-faced silicon top cap (Penicillin type) and aged overnight under stirring. Fifteen milliliters of water or water–acetone was introduced into the vial just before analysis. These spiked matrices were used for internal SPME calibration.

GC–MS analysis

The analysis was performed with a Hewlett-Packard model 5890 GC equipped with a mass selective detector (MSD), model 5970 in the energy of ionization of 70 eV (Hewlett-Packard, Palo Alto, CA). A Phenomenex fused-silica column with 30 m of length, 0.25 mm of internal diameter, 0.5 µm of film thickness, ZB5 (95% methyl–5% phenyl polysiloxane) was used. The splitless mode was used for both the SPME and direct injection with the purge valve closed for 3 min. The inlet temperature was set to 280°C and 310°C (for SPME and direct injection, respectively) and that of the MSD chamber was 300°C (for both SPME and direct injection). The carrier gas was

Table I. Content of Burnt Matter at 650°C in Dry Sample

Matrix	C (%)	H (%)	N (%)	Mass loss at 650°C (%)
Green SW	28.16	4.32	2.39	74
Brown SW	36.04	3.46	1.89	81
HAs	39.27	4.42	0.49	34
Dissolved humic substances	14.46	1.83	0.96	31

Table II. Analytical Parameters for the Identification of PAH Compounds

Analyte	t_R (min)	Mass (amu)
Naphthalene (PAH-1)	11.32	102,128
Acenaphthylene (PAH-2)	16.87	151,152,153
Acenaphthene (PAH-3)	17.55	151,152,153
Fluorene (PAH-4)	19.53	163,165,166
Phenanthrene (PAH-5)	23.20	152,178,179
Anthracene (PAH-6)	23.40	152,178,179
Fluoranthene (PAH-7)	27.86	200,201,202
Pyrene (PAH-8)	28.70	200,201,202
Benzanthracene (PAH-9)	33.65	113,226,228
Chrysene (PAH-10)	33.80	113 226,228
Benzo(b)fluoranthene (PAH-11)	38.79	126,252,253
Benzo(k)fluoranthene (PAH-12)	38.93	126,252,253
Benz(a)pyrene (PAH-13)	40.35	126,252,253
Indeno(cd)pyrene (PAH-14)	45.91	138,276,278
Dibenz(ah)anthracene (PAH-15)	46.11	138,276,278
Benzo(ghi)perylene (PAH-16)	47.10	138,276,278

helium with a flow rate of 0.7 mL/min, linear velocity of 30 cm/s, and pressure of 3.5 psi at 50°C. The thermal desorption of SPME fiber lasted for 3 min in the GC injector. For direct injection, 2 µL of standard solution was injected manually. The column temperature was held initially at 50°C for 1 min, increased to 100°C at 10°C/min, then to 250°C at 6°C/min, then 300°C at 3°C/min, and then held for 5 min.

For the determination of PAH, GC–MS analysis was used in the selected ion monitoring (SIM) acquisition mode. The retention times (t_R) and the most abundant selected ion masses used for identifying and quantitating the 16 PAH standards are reported in Table II. A constant dwell time of 100 ms was used for each ion, and the scan rate was 2.86 cycles/s for each analyte except naphthalene, which was 4.26 cycles/s.

SPME procedures

SPME extraction was performed by introducing 15 mL of water or water–acetone solution (16% by weight of acetone) into a 15-mL vial sealed by crimping with an open centered aluminium cap and a Teflon-faced silicon septum. An appropriate volume of standard solution was injected by syringe through the septum. The SPME fiber was immersed into the solution, and the system was then introduced in a sonication bath (or a magnetic stirring bath) for a selected time (15 min) at a desired temperature (60°C). Fresh samples were used for each measurement. Upon completion of exposure, the compound laden fiber was rapidly transferred to the GC, and a manual injection was effectuated. Carryover with the SPME fiber was checked to be absent in the considered injection conditions. The same SPME fiber was used for the whole duration of the study. If new SPME fiber was necessary, it was recalibrated. SPME extraction of spiked matrices was performed on the same vial used for the preparation of spiked samples described previously.

Results and Discussion

Optimization of SPME conditions

The sequence of optimization studies was the extraction time, temperature, carrier medium and agitation. The choice of the most appropriate polymethylsiloxane fiber of various thickness (7, 30, and 100 µm) was determined by extraction of a standard mixture of 16 PAH. The most suitable SPME fiber was revealed to be the 100-µm PDMS coating because it gave the highest responses for all of the 16 studied compounds. A compromise range of extraction temperature was selected between 40°C and 60°C, which allowed reasonable extraction efficiencies for all 16 PAHs. Sonication at 40°C was demonstrated to be the most effective agitation mode for SPME of PAH from water medium.

Effect of extraction time on the SPME efficiency

SPME is an equilibrium extraction mode; the equilibrium time determines the maximum amount of analyte that can be extracted by the fiber, which controls the sensitivity of the method. Knowledge of the adsorption kinetics provides information for determining optimum sampling times. For this purpose, adsorption profiles were determined for each of 16 PAHs from water. The effect of time on extraction efficiency was studied in the range of 5–90 min by direct immer-

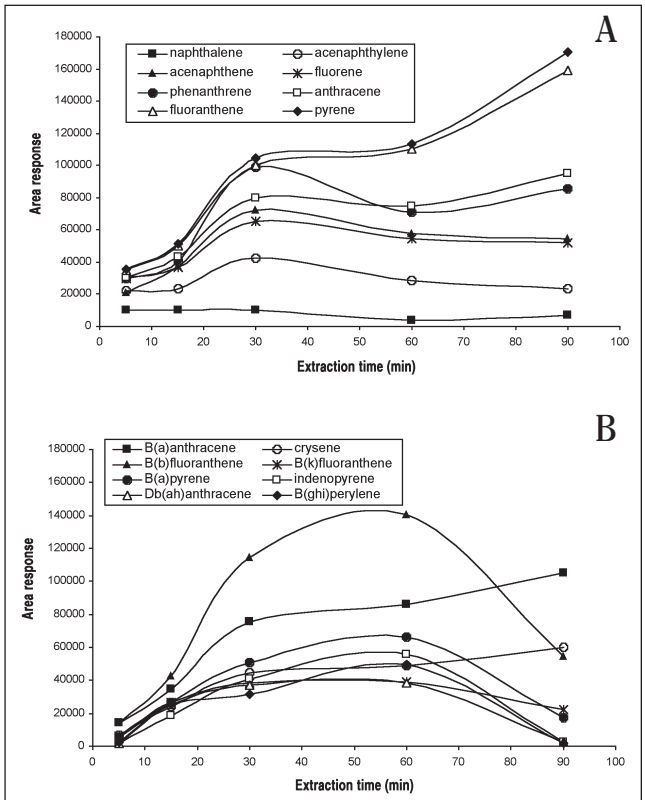

Figure 1. Extraction of 16 PAHs by SPME vs. extraction time.

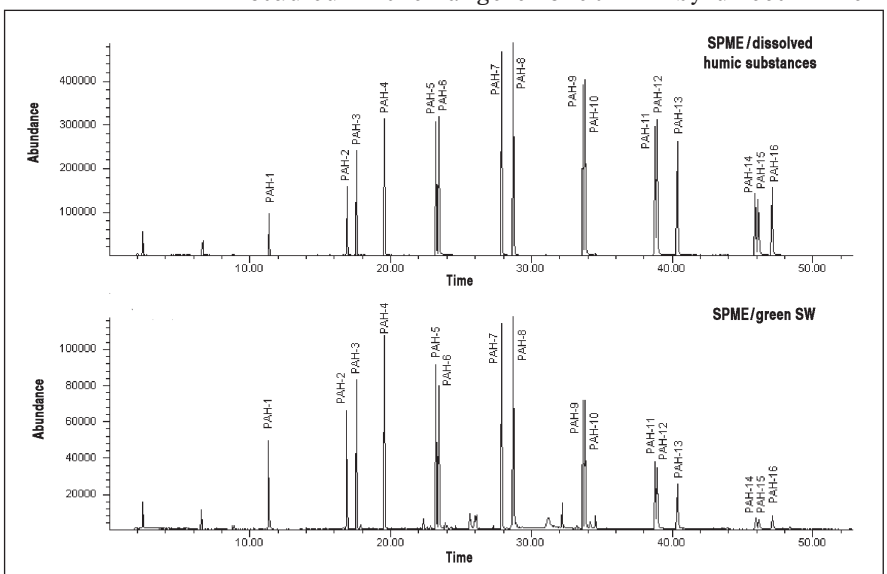

Figure 2. Chromatograms of 16 PAHs by SPME from dissolved humic substances and green SW. GC–MS in SIM acquisition mode. Spiked concentration, 1 mg/kg.

sion/sonication at 40°C. The adsorption profiles of the 16 PAHs are reported in Figures 1A and 1B. Each time point was measured in triplicate, the standard deviations were 15%. As can be seen from Figures 1A and 1B, and the maximum sorption onto the fiber for each PAH occurred at different extraction times. The lighter compounds (naphthalene, acenaphthene, phenanthrene, acenaphthylene, and fluorene) were rapidly sorbed after 30 min, and a decrease in area response thereafter reflected competition from the heavier molecular fractions [benzo(b)fluoranthene, benz(a)pyrene, dibenz(ah)anthracene, benzo(k)fluoranthene, indenopyrene, benzo(ghi)perylene], which showed an adverse trend at 90 min. No equilibrium was obtained for fluoranthene, anthracene, pyrene, benzanthracene, and chrysene, even after 90 min. However, for the aim of this study, which was the determination of 16 PAHs onto solid environmental matrices, it was not necessary for the analytes to reach equilibrium.

Table III. SPME Calibration of 16 PAHs from Water–Acetone* Using a 100-µm PDMS Fiber, Direct Immersion for 15 min at 60°C†

Analytes	Slope	Intercept	R	DL (µg/L)	%RSD
Naphthalene	79027	–22001	0.9935	0.005	11.6
Acenaphthylene	112755	–41804	0.9934	0.01	10.9
Acenaphthene	210951	–36313	0.9956	0.01	13.5
Fluorene	287122	–45547	0.9957	0.005	11.6
Phenanthrene	302702	15462	0.9972	0.005	7.0
Anthracene	324504	–112811	0.9952	0.005	6.2
Fluoranthene	514855	136910	0.9979	0.001	5.8
Pyrene	563852	110082	0.9983	0.001	5.6
Benz[a]Anthracene	598895	204547	0.9996	0.005	5.8
Chrysene	629433	418093	0.9984	0.001	7.2
Benzo(b)Fluoranthene	671311	302036	0.9990	0.002	7.1
Benzo(k)Fluoranthene	699085	383056	0.9975	0.003	8.1
Benz(a)Pyrene	594162	210347	0.9983	0.05	6.6
Indenopyrene	407624	29388	0.9966	0.05	8.6
Dibenz(ah)anthracene	292661	224379	0.9895	0.05	13.2
Benzo(ghi)perylene	437368	242616	0.9944	0.05	7.6

* In the amount of 13:2 mL.
† The calibration range is 0.01–30 µg/L.

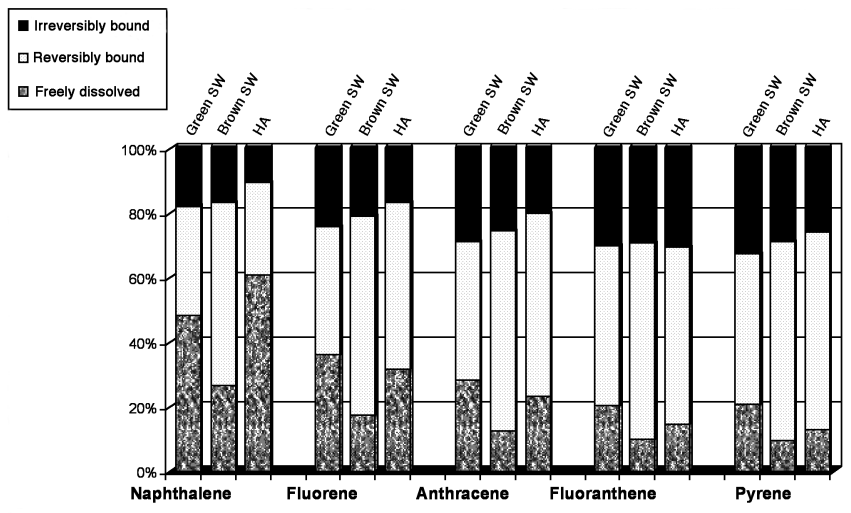

Figure 3. Recovery of PAH from different matrices by different extraction modes.

Effect of organic solvents on the SPME efficiency

Several authors have indicated that hydrocarbons compounds were lost to glass walls when water was the only solvent used. It is well known that several surfactants or organic solvents can enhance the apparent water solubility of many hydrophobic compounds. The influence of surfactants and organic solvents on the enhancement of the SPME extraction efficiency of linear aliphatic hydrocarbons and PAH from a soil matrix has been demonstrated (9–12). The same behavior has been verified with SW matrices when extracting PAH in the presence of acetone in the water carrier medium.

Optimized SPME conditions and PAH calibration

Although sonication was demonstrated to be the most effective and reproducible agitation mode, it caused noticeable deterioration of the coating after just a small number of extractions. That was why from hereafter in this work, sonication has been substituted by magnetic stirring. The following SPME extraction conditions were found to be favorable: T = 60°C, t = 15 min, and direct immersion into a carrier medium composed of acetone–water (16% wt). With these sampling conditions, all 16 PAHs did not reach the extraction equilibrium, but they could be determined with sufficient sensitivity. Figure 2 shows chromatograms obtained for DHS and green SW spiked with 1 mg/kg of each PAH. GC–MS was performed following sampling by SPME in the optimized conditions.

Table III summarizes all parameters of the external calibration using SPME. Linearity was obtained in the range of concentration from 0.01 to 30 µg/L; the R values from 0.993 to 0.999; and the detection limits (DL) ranged from 0.001 µg/L for fluoranthene, pyrene, and chrysene to 0.05 µg/L for the last four PAHs [benz(a)pyrene, indeno(1,2,3)pyrene, dibenz(ah)anthracene, and benzo(ghi)perilene]. The precision of the method was determined by performing three SPME methods from 20 µg/L PAH solutions. The relative standard deviation (RSD) values obtained ranged from 6% to 13%. SPME internal calibration was car-

ried out on the four considered matrices: green and brown SW and on two different kinds of humic substances, which covered a wide range of hydrophobicity. One of the humic matrices had low molecular weights (from 1 to 100 kDa), and it was isolated from a wetland out-flow and had the following elementary composition: C = 14.5%, H = 2%, and N = 1%. The other was a sodium salt of HA with the following elementary composition: C = 39%, H = 4%, and N = 0.5%. The spiked matrices were prepared as mentioned in the experimental section and PAH extraction was carried out under optimized SPME conditions. Linearity was obtained in the range of concentration from 1 to 10 mg/kg, and the DL ranged from 0.001 mg/kg for the most sensitive PAHs (fluoranthene and pyrene) to 0.1 mg/kg for others.

Distribution of PAH in environmental matrices

The aim of applying solvent-free SPME to the analysis of spiked or contaminated samples was to obtain more information about the binding state of pollutants on environmental matrices. External SPME calibration was obtained with solutions of known concentration of analyte, hence the results gave analyte concentration that was freely dissolved in the medium. Internal SPME calibration was obtained with spiked matrices of known concentration of analyte, therefore the results gave total analyte concentration, composed of freely a dissolved portion and portion that was reversibly and irreversibly bound onto the matrix. Figure 3 shows the percentage of the three binding states of the lighter 5 PAHs spiked onto different matrices: (*i*) the irreversibly bound concentration of analyte was obtained by SPME internal calibration, in this case, it coincided with the spiking concentration of each analyte; (*ii*) the reversibly bound concentration of PAH was obtained by traditional organic solvent extraction (13); and (*iii*) the freely dissolved concentration of PAH was obtained by SPME external calibration. Note that the concentration of reversibly bound PAH was lower than the spiked concentration because it is known that PAHs interact with environmental matrices (14,15). Figure 3 also demonstrates the very low presence of pollutants in the free state, except for naphthalene, which is highly soluble in water (31.7 mg/L). These results suggest that hydrocarbon pollutants that had been spread into the environment were mainly bound (reversibly and irreversibly) onto solid matrices, and only small amounts can be released in the free state and extended through the water medium.

In order to compare the absorption capacity of different environmental matrices, the partition coefficients for PAH between green SW, brown SW, HA, DHS, soil, and water have been calculated according to the following equation (16):

Table IV. Partition Coefficients between Matrices and Carrier Medium

Analytes	Log $K_{(A)}$*	Log $K_{(B)}$†	Log $K_{(C)}$‡	Log $K_{(D)}$§	Log $K_{(E)}$**	Log $K_{(DOM)}$††
Naphthalene	3.92	3.51	3.29	3.29	2.69	2.79(4)
Acenaphthylene	3.85	3.39	3.70	3.56	2.15	3.71(13)
Acenaphthene	4.13	3.71	3.94	3.74	3.10	3.67(13)
Fluorene	4.16	3.73	3.95	3.81	3.12	3.28(5); 3.58(4)
Phenanthrene	4.25	3.84	4.00	4.00	3.27	3.98(4); 4.29(13)
Anthracene	4.33	3.89	4.10	4.03	3.31	3.94(5); 4.11(4)
Fluoranthene	4.44	4.07	4.20	4.24	3.42	4.4(4); 4.86(13)
Pyrene	4.47	4.06	4.26	4.31	3.44	4.34(5); 4.53(4)
Benz[a]anthracene	4.62	4.29	4.59	4.51	3.51	5.49(13)
Chrysene	4.66	4.30	4.50	4.47	3.54	
Benzo[b]fluoranthene	4.76	4.52	4.82	4.76	3.59	
Benzo[k]fluoranthene	4.79	4.52	4.78	4.67	3.64	
Benz[a]pyrene	4.75	4.52	4.81	4.79	3.56	
Indeno[1,2,3-cd]pyrene	4.85	4.70	5.02	4.98	3.54	
Dibenz[a,h]anthracene	4.76	4.65	4.96	4.81	3.36	
Benzo[ghi]perylene	4.86	4.72	4.94	5.04	3.52	

* $K_{(A)}$: partition coefficient between brown SW and carrier medium obtained by calculation.
† $K_{(B)}$: partition coefficient between green SW and carrier medium obtained by calculation.
‡ $K_{(C)}$: partition coefficient between soil and carrier medium obtained by calculation.
§ $K_{(D)}$: partition coefficient between humic acid and carrier medium obtained by calculation.
** $K_{(E)}$: partition coefficient between dissolved humic substances and carrier medium obtained by calculation.
†† $K_{(DOM)}$: partition coefficient between dissolved organic matter and water from references (4,5,13).

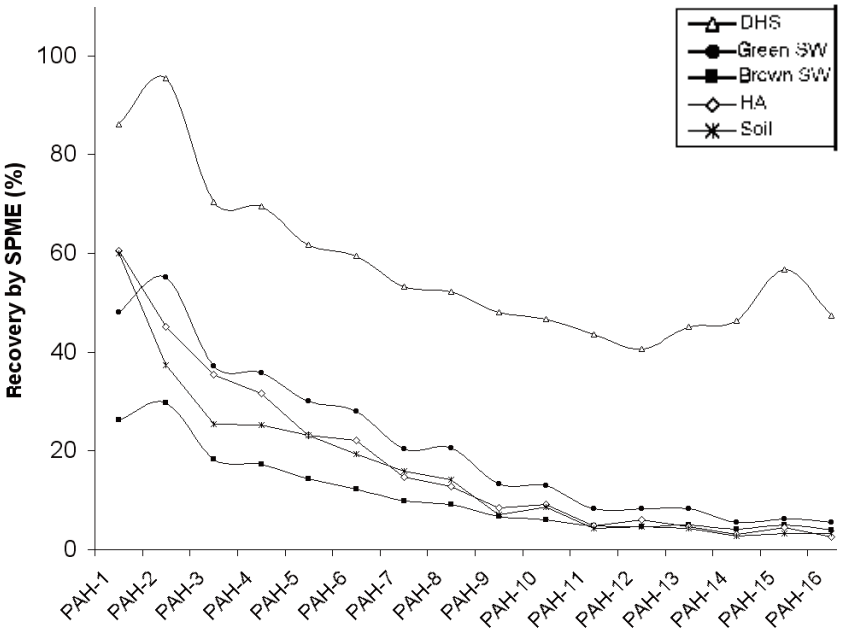

Figure 4. Recovery of 16 PAHs from different matrices by SPME with a spiked concentration of 10 mg/kg dry matrix.

$$K = (C_{tot}/C_{free} - 1)*1/C_{matrix} \quad \text{Eq. 1}$$

where C_{tot} is the concentration of PAH obtained by internal calibration (spiked concentration), C_{free} is the concentration of PAH obtained by external SPME calibration, and C_{matrix} is the concentration of the solid matrix suspended in the carrier medium.

It is worth noticing that sorption coefficients reported in Table IV are very comparable with those obtained in the references (4,5,16), although the aqueous carrier medium used in this work was slightly different and the SPME sampling mode was under nonequilibrium conditions. However, they permitted a reliable measurement of the relative sorption coefficients of 16 PAHs on 5 different environmental matrices. Figure 4 shows very clearly the percentage of free analyte (obtained by SPME external calibration) released into the carrier medium from 5 different solid matrices that was spiked with 10 mg of each PAH per kilogram of dry matrix. It can be observed that, for the same matrix, the sorption capacity of PAH increases with the increasing of PAH molecular weight, hence the PAH's hydrophobicity. Regarding the same PAH, the sorption capacity decreases from brown SW > HA > soil > green SW > DHS. The higher absorption capacity of brown SW with respect to that of green SW could be attributable to its higher C content (36% vs. 28%, respectively), as is its dietetic fiber content (53% vs. 24%, respectively) (17). For HA and soil matrices, the sorption capacity depends upon a complex number of parameters, which is still the object of numerous studies. However, the results of this study indicate that the adsorption capacity of HA and soil can be considered equivalent to that of SW, yet DHS moderately absorbs PAH.

Table V. Determination of 16 PAHs in Real Soil Sample

	Soil (mg/kg dry soil)		
Analytes	**(1)***	**(2)†**	**(3)‡**
Naphthalene	0.46	0.21	0.006
Acenaphthylene	nd§	nd	nd
Acenaphthene	nd	0.01	0.0001
Fluorene	0.07	0.02	0.0001
Phenanthrene	0.66	0.08	0.0006
Anthracene	0.65	0.02	0.0001
Fluoranthene	0.44	0.11	0.0006
Pyrene	nd	0.08	0.005
Benz[a]anthracene	0.54	0.77	0.003
Chrysene	2.52	2.10	0.005
Benzo[b]fluoranthene	1.94	1.75	0.002
Benzo[k]fluoranthene	1.36	1.03	0.0009
Benz[a]pyrene	0.83	0.93	0.001
Indeno[1,2,3-cd]pyrene	0.14	1.42	0.001
Dibenz[a,h]anthracene	nd	0.29	0.0003
Benzo[ghi]perylene	1.17	0.60	0.0006

* Traditional extraction mode, analyte concentration expressed as mg/kg dry soil.
† SPME internal calibration, analyte concentration expressed as mg/kg dry soil.
‡ SPME external calibration, analyte concentration expressed as mg/L.
§ nd, not determined.

Determination of PAH in real soil sample

The optimized SPME conditions for the determination of PAH in a solid environmental matrices has been applied to a real soil sample. Internal calibration has been carried out using spiked samples by the addition of a known amount of PAH on the same soil sample to be analyzed. Table V compares results obtained by SPME with internal calibration and traditional extraction mode. It can be observed that data consistency has been obtained for naphthalene, benz(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benz(a)pyrene and benzo(ghi)perylene. Although the results for the remaining PAHs are significantly different for the two extraction methods, this is probably due to the interaction of analyte and matrix as a function of the weathering (aging) time, a factor that can be difficult to reproduce in the laboratory with spiked standards. However, SPME with external calibration allows for the measurement of PAH freely released in the aqueous surrounding medium. It reveals that approximately 10^{-3} of the concentration in a solid matrix is released into water.

Conclusion

Optimized SPME conditions have been identified for the extraction of 16 promulgated PAHs from environmental solid matrices. SPME calibrations have been carried out successfully, and external calibration allows the determination of freely dissolved analyte and SPME internal calibration allows the determination total PAH present in the matrices. SPME combined with GC–MS in the SIM acquisition mode was revealed to be an extremely comfortable and sensitive technique for the determination of PAH in environmental matrices. No organic solvent was needed and no purification operation was required. The optimized SPME conditions have been applied to determined 16 PAHs on a real soil sample, and results were compared with those obtained traditionally. Using the external SPME calibration, it was found that spiked PAHs are mostly bound to environmental solid matrices (SW matrices, HA, and soil), and only a very small portion of pollutants is released in the free state and spread over into the environment through the water medium. The absorption capacity of SW matrices is proportional to their fibrous content.

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