Determination of Polycyclic Aromatic Hydrocarbons in Sediment Using Solid-Phase Microextraction with Gas Chromatography–Mass Spectrometry

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Abstract

Manual solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) is applied for the determination of polycyclic aromatic hydrocarbons (PAHs) from natural matrix through a distilled water medium. Seven of the 16 PAH standards (naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene) are spiked on a marine muddy sediment. The samples, containing PAHs in the range of 10–20 ppm, are then aged at room temperature more than 10 days before analysis. The influence of the matrix, SPME adsorption time, pH, salt content, and SPME adsorption temperature are investigated. The reproducibility of the technique is less than 13% (RDS) for the first 6 considered PAHs and 28% (RDS) for benzo(a)anthracene with a fiber containing a 100-µm poly dimethylsiloxane coating. Linearity extended in the range of 5–50 picograms for PAHs direct injection, 5–70 picograms for PAHs in water, and 1–170 picograms for PAHs in sediment. The detection limit is estimated less than 1 µg/kg of dry sample for the first 6 considered PAHs in sediment and 1.5 µg/kg of dry sample for benzo(a)anthracene using the selected ion monitoring mode in GC–MS. The recoveries of the considered PAHs are evaluated.

Introduction

Sample preparation techniques based on adsorption have been widely used to preconcentrate the analytes from different matrices for quick analysis in situ or for trace analysis. Solid-phase microextraction (SPME) (1) is a new variation of these adsorption techniques that has been used mainly for the analysis of pollutants in environmental water samples. The principal component of SPME is a fused-silica fiber coated with an adsorbent such as polydimethylsiloxane. When the fiber is immersed in an aqueous solution, a partitioning of organic compounds between the aqueous phase and the hydrophobic fiber surface occurs. By removing the fiber and inserting it into a heated gas chromatography (GC) inlet, the adsorbed target compounds can then be thermally desorbed directly in the injection chamber of a GC–mass spectrometer (MS). SPME has been successively applied to the determination of substituted benzene compounds (2,3), fuel-PAHs (4–7), PCBs (4), phenols (8–10), organometallic compounds (11,12), pesticides (13), herbicides (14), and VOCs including chlorinated hydrocarbons (15–18).

Polycyclic aromatic hydrocarbons (PAHs) are the target of many environmental analytical methods. For soil analysis, SPME has been applied to the determination of chlorinated contaminants (19), TPH, and BTEX in gasoline and diesel contaminants (20).

In this study, the manual SPME technique was applied to determine PAHs spiked on muddy sediment using distilled water as a carrier medium. Although PAHs are known to be poorly soluble in water, their quantitation in environmental solid matrices is revealed to be very suitable by the SPME-water–GC–MS system. The recoveries of PAHs from sediment into water and from water onto the coated fiber have been evaluated in the optimal extraction conditions; the detection limits were estimated as well.

Experimental

Sample preparation

Muddy sediment was collected from a 0–15 cm depth in the Adriatic Sea east of Ravenna (Italy). The sediment was air dried at room temperature for 1 week until it reached a residue content of water of about 5% (w); the percentage of residue water

was measured by dividing the difference of starting weight and dried weight sample (at 105°C for 24 h) by the starting weight. Tests for impurities by extraction with SPME and a solvent have been carried out on this sediment blank.

Single pure standards of naphthalene (PAH 1), acenaphthene (PAH 2), fluorene (PAH 3), anthracene (PAH 4), fluoranthene (PAH 5), pyrene (PAH 6), and benzo[*a*]anthracene (PAH 7) were weighed and dissolved in acetone to prepare the spiking solution of approximately 1000–2000 ppm. The considered PAH standards were used as purchased from Fluka AG (Buchs, Switzerland) with purities from 97 to 99%.

A suitable amount of the muddy sediment blank (approximately 500 g total) was placed layer by layer (approximately 100 g per layer), alternating with the spiking operation (drop by drop of approximately 1 mL of the standard solution per layer) in a 500-mL container with an open-top screw cap and Teflon-faced silicon septum. The container was capped immediately and hand shaken for at least 5–10 min after each layer spiking. The total amount of solid sample was chosen to leave a minimal necessary headspace in the container above the sediment for mixing. The prepared spiked samples containing 10–20 ppm of each of the studied PAHs were stored at room temperature for at least 10 days before extraction.

The same procedure was used to prepare spiked samples with different concentrations of PAHs.

General SPME procedures

The manual SPME device and various thicknesses of poly dimethylsiloxane fibers (7 and 100 µm) were purchased from Supelco (Bellefonte, PA). The SPME fibers were thoroughly activated according to the manufacturer's recommendations (heating it in the injector of the chromatograph under a helium flow at 250°C for 1 h for the 100-µm fiber and 320°C for 4 h for the 7-µm fiber). The activated fiber was than checked and thermally purified in the GC injection chamber until a clean baseline had been obtained. In this study, the 100-µm fiber was used during the whole experiment because it gave a better extraction yield of all considered PAHs than that of the 7-µm fiber.

Suitable amount of sample (0.5–3 grams) was weighed in a 20-mL vial, and 10 mL of distilled water was added together with a magnetic stirrer bar. The vial was immediately capped with a crimp-top septum silicon PTFE–aluminum combination. The dimensions of the septum-sealed cylindrical vial were approximately 2 cm in diameter by 7.5 cm in height. Once the solution or suspension was placed in the sealed vial, it was allowed to stand undisturbed for eventual pretreatment before sampling. When the extraction step occurred, the solution was stirred at a fixed rate, and the entire fiber, which was fresh from thermal desorption, was immersed in the stirring solution for a selected time. 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. Carry-over with SPME fiber was found to be absent in the considered injection conditions. The same SPME fiber was used for the duration of the study (if a new SPME fiber is necessary, it should be recalibrated).

GC–MS analysis

The analysis was performed on a Hewlett-Packard (Palo Alto, CA) model 5890 GC equipped with a model 5970 mass selective detector (MSD) with the energy of ionization of 70eV. A ZEBRON (Phenomenex, Torrance, CA) fused-silica column (95% methyl and 5% phenyl polysiloxane) with dimensions of 30 m × 0.25-mm i.d. (0.5-µm film thickness) was used. A 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 300°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 helium with a flow rate of 0.7 mL/min, a linear velocity of 30 cm/s, and a pressure of 3.5 psi at 50°C.

The column temperature was held initially at 80°C for 1 min, increased to 280°C at 15°C/min, and held for 15 min. For thermal desorption, the SPME fiber was left in the injector for 1 min.

For direct injection, 1 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 to 300°C at 3°C/min, and held for 5 min.

Retention times and three relevant ion masses with major spectral abundance used in this work for identifying and quantitating the studied PAHs are reported in Table I.

PAH calibration standards were prepared by diluting the same solution used for spiked samples. The calibration curves by direct injection were obtained using GC–MS in the selected ion mass (SIM) acquisition mode. The quantitation was based on the most abundant ion (denoted with asterisk) of the three relevant ion masses reported in Table I. All compounds demonstrated linearity in the range from 1 to 50 ppm with regression coefficient r^2 = 0.97–0.99 and a high value of slopes from 1.2–2.1 × 10^6.

Results and Discussion

SPME of seven PAHs from muddy sediment through a water medium was examined. The absolute amount of each PAH adsorbed by the 100-µm polydimethylsiloxane SPME fiber was in the range of 1–200 pg.

Table I. Identification File for PAH Compounds

PAH	Retention time (min)	Mass (amu)
Naphthalene	11.64	**127***, 128, 129
Acenaphthene	17.88	**152***, 153, 154
Fluorene	19.80	**163***, 165, 166
Anthracene	23.62	**176***, 178, 179
Fluoranthene	28.10	**200***, 201, 203
Pyrene	28.92	**200***, 201, 203
Benzo[a]anthracene	33.88	**226***, 228, 229

* Most abundant ion.

Optimization of SPME adsorption

The initial step was to optimize the SPME extraction conditions. The parameters investigated were matrix effect, extraction time, pH, ionic strength, and extraction temperature.

Sample matrix effect

The sample matrix has been shown to give dramatic effect on the SPME of phenols from aqueous solution (8). To obtain an impression of the magnitude of the muddy sediment influence on the SPME of PAHs, a series of experiments was conducted using a fixed amount of water (10 mL) with increasing amounts of blank matrix: experiments having a sample weight of 0.523, 0.524, 1.593, and 2.690 g extracted with SPME for 15 min at room temperature; an experiment with 1.592 g extracted with SPME for 30 min at room temperature; an experiment with 1.472 g (previously sonicated for 30 min) extracted with SPME for 30 min at room temperature; and an experiment with 1.583 g (aged for 20 h at room temperature) extracted with SPME for 30 min at room temperature.

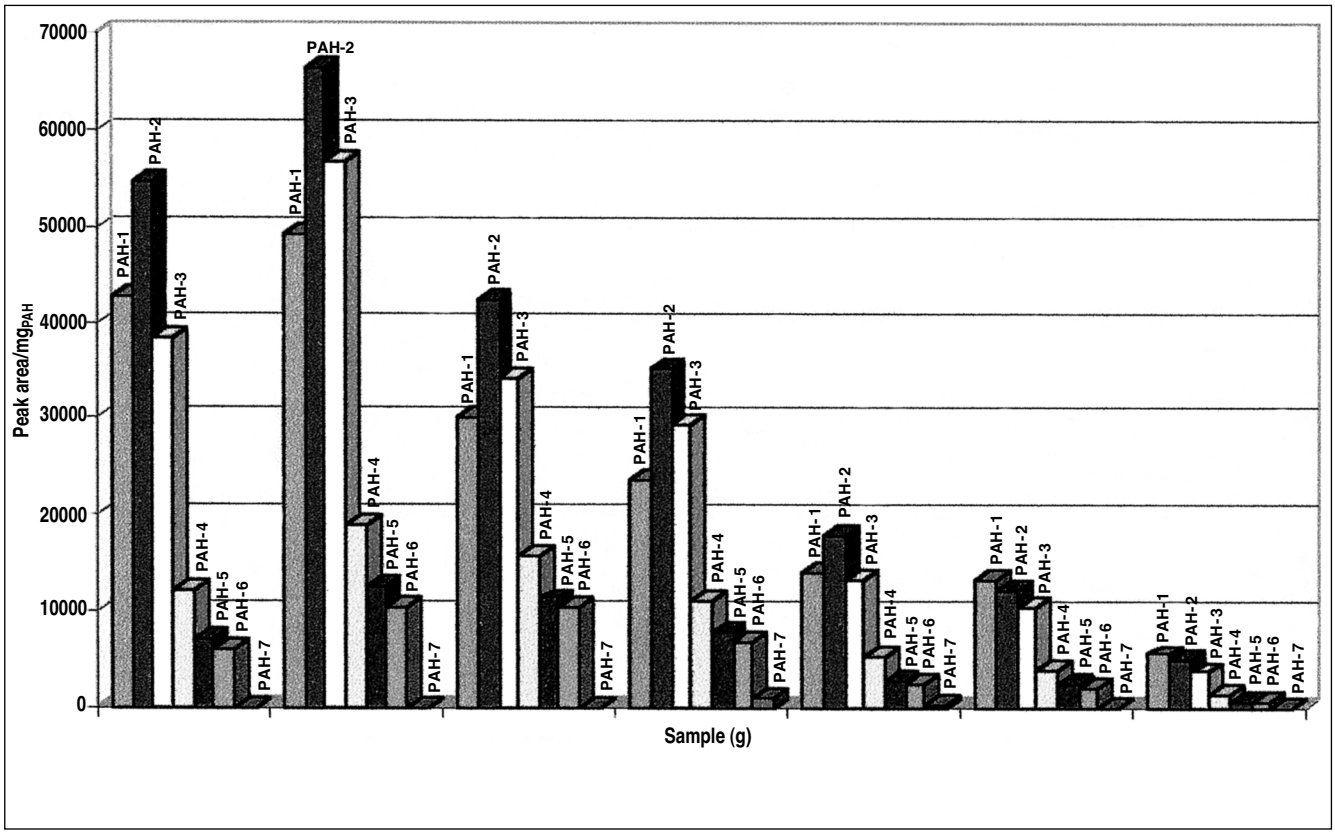
It is readily apparent that decreases in the peak areas of PAHs with increasing amounts of matrix can be noticed, irrespective of the pretreatment operation (Figure 1). Thus, it seemed that the presence of multiple components, inorganic and organic, in the aqueous extract of natural muddy sediment might result in significant competition between each component for adsorption onto the SPME fiber. An impact on quantities of the analytes adsorbed in SPME studies employing poly dimethyl siloxane-coated fibers with natural product has been already examined by other authors (10,21).

Note that the amount of compound adsorbed on the fiber decreased with PAH molecular weight even though the concentration of all compounds spiked was the same (10–20 ppm). The difference in PAH recovery is due mostly to the decreasing solubility of PAHs in water with the increasing of their molecular weight; (for example, the solubility of naphthalene with a molecular weight of 128 in water is 31 mg/kg, whereas anthracene with a molecular weight of 178 is 0.075 mg/L and benzo(a)anthracene with a molecular weight of 229 is 0.009 mg/L. The low recovery is also caused by the affinity of the specific PAH for the relatively polar solid matrix.

However, the maximum peak area/mg_{PAH} for all seven studied PAHs was obtained when using a sample water ratio of 1:20 (w/w).

Adsorption rate studies

In order to demonstrate the time required for all PAHs to equilibrate with the fiber, fibers were exposed to fresh spiked sample–water solutions for selected times. The selected time should be long enough for a constant amount of analyte to be removed from the solution. For this system of extraction, a fixed rate of magnetic stirring was used, and the equilibrium time was established by the diffusion of analytes from sediment to water and from water to SPME thin-layer fiber. Figure 2 shows that the three lower molecular weight PAHs (from PAH 1 to PAH 3) reach their maximum recovery value after 30 min of extraction at room temperature, whereas the remaining higher molecular weight PAHs (from PAH 4 to PAH 6) need more than 120 min to reach their equilibrium, probably because of the low solubility of the latter in water (the solubility of PAH 3, fluorene, in water at 15°C is 1.7 ppm versus 0.075 ppm of that of PAH 4, anthracene). Note that PAH 7 was hardly extracted after 120 min of extraction with SPME at room tem-



perature. The decrease in PAH 1/PAH 2 recovery at more than 60 min of extraction with SPME may be due to the loss of these volatile PAHs from the fiber; when the time of extraction is prolonged, any antagonistic phenomenon may occur between the low molecular weight PAHs and the higher ones to be adsorbed onto the fiber. Because their distribution constants are very different, the absorption onto a fiber is kinetically favored for low-molecular-weight PAHs but thermodynamically favored for high-molecular-weight PAHs.

pH, ionic strength, and temperature

The "salting out" effect is widely used to increase the effectiveness of an organic solvent to extract organic compounds dissolved in water. It has been demonstrated that NaCl enhances the performance of SPME fibers in the extraction of phenol compounds (8–10). An opposite trend was found in the examination of considered PAHs onto muddy sediment. Figure 3 reports the influence of different ionic strengths on the recovery of PAHs from sediment through water by SPME using a constant extraction time of 15 min at room temperature. The presence of NaCl probably decreases the dissolution of PAHs into water, hence their absorption onto the SPME fiber; KOH (pH 10) shows no significant effect.

The extraction at 60°C shows the highest recovery value for all examined PAHs (Figure 3).

Optimal conditions of PAH extraction via SPME from muddy sediment and reproducibility of their recovery

Because the time for reaching equilibrium between phases takes several hours for high-molecular-weight PAHs, depending on the experimental conditions, it was necessary to work under nonequilibrium conditions to settle the sample analysis to a reasonable time. Reproducibility was controlled with the following SPME experimental conditions: fiber immersion for 30 min at 60°C on 0.5 g of spiked sample in 10 mL of distilled water. Figure 4 reports the recovery of PAH 1 to PAH 7 and their relative standard deviation (RSD) calculated on four replicates; the RSD values are 13, 2, 9, 13, 12, 8, and 28%, respectively, for PAH 1 to PAH 7. Naphthalene may be lost by thermal desorption when hot extraction with SPME is adopted.

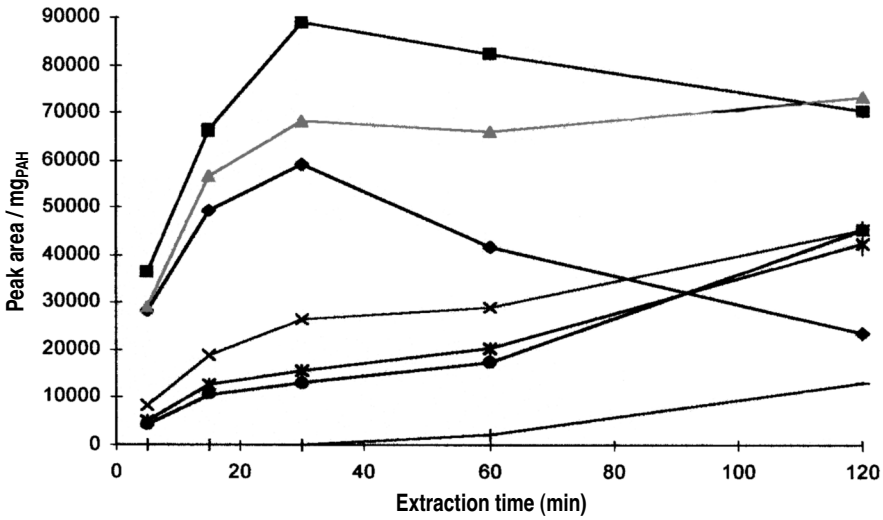


Figure 2. Extraction time effect on SPME of PAHs. ◆ = PAH 1, ■ = PAH 2, ▲ = PAH 3, ✕ = PAH 4, ✕ = PAH 5, ● = PAH 6, | = PAH 7.

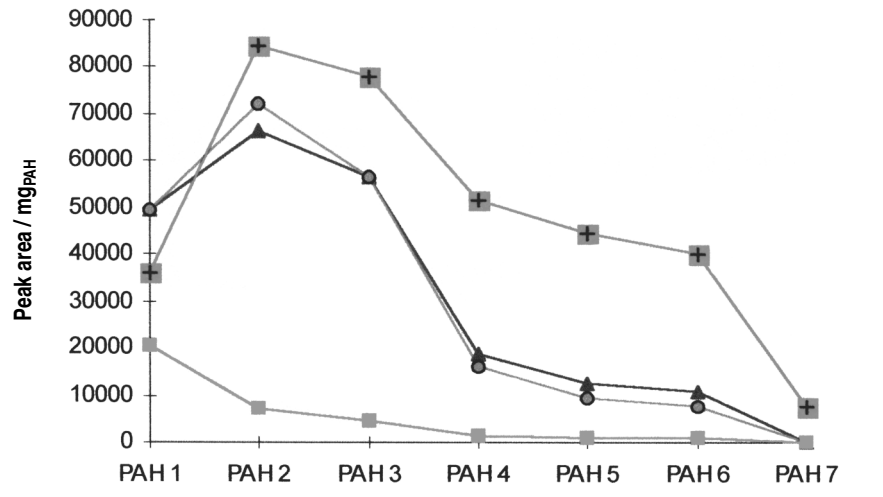


Figure 3. Temperature, pH, and ionic strength effect on SPME of PAHs. ▲ = no treatment, ● = +KOH, ■ = +NaCl, ✚ = extr. T. 60°C.

Calibration for the optimal conditions of SPME analysis

Linearity has been evidenced for the SPME of PAHs from water and from sediment. The data of calibration for SPME concerning PAHs from distilled water are reported in Table II. The range of calibration is from 0.01 to 0.1 ppm using 30 min of exposure time at 60°C. It can be noticed that the response factor (slope) increased from PAH 1 to PAH 7, because the distribution constant (K_{fs}) of these compounds from the coated fiber into water is 1300 for naphthalene, 3200 for acenaphthene, 3200 for fluorene, 2800 for anthracene, 5500 for fluoranthene, 4300 for pyrene, and 4800 for benzo[*a*]anthracene. The partition between the stationary phase on the fiber and the aqueous phase is particularly favored for the last PAHs. The aforementioned K_{fs} for the direct extraction of considered PAHs from water (10 mL of volume) with a 100-µm thick PDMS fiber has been calculated from the following equation (1):

$$K_{fs} = nV_s/V_f(C_0V_s - n) \quad \text{Eq. 1}$$

where n is the amount of analyte partitioned into the coating phase, V_s is the sample volume, V_f is the fiber coating volume (6.1×10^{-4} mL), and C_0 is the initial concentration of the analyte.

The data of calibration for SPME concerning PAHs absorbed in sediment using distilled water as carrier medium are reported in Table III. The range of calibration is from 0.1 to 10 ppm using 30 min of exposure time at 60°C. It can be noted that the response factor (slope) decreased from PAH 1 to PAH 7, because their solubility into water decreases according the high molecular weight of the last PAHs.

With these conditions of SPME, the detection limits were estimated (22) as 0.5, 0.2, 0.6, 0.9, 0.5, 0.4, and 1.5 ppb for PAH 1 to PAH 7, respectively, on sediment.

Table II. Calibration of PAHs from Water by SPME

PAH	Slope (10^{-6})	Intercept (10^{-6})	r^2
Naphthalene	1161.4	–3.2681	0.9252
Acenaphthene	1868.4	5.0328	0.9847
Fluorene	1943.4	10.046	0.9886
Anthracene	2466.4	23.095	0.9693
Fluoranthene	4374.9	33.682	0.9809
Pyrene	3937.8	27.449	0.9843
Benzo[*a*]anthracene	4241.2	–3.2467	0.9938

Table III. Calibration of PAHs from sediment by SPME

PAH	Slope (10^{-6})	Intercept (10^{-6})	r^2
Naphthalene	25.61	4.272	0.9991
Acenaphthene	34.845	10.777	0.9957
Fluorene	33.768	11.119	0.9948
Anthracene	22.187	14.949	0.9713
Fluoranthene	32.818	21.992	0.9889
Pyrene	30.06	10.046	0.9972
Benzo[*a*]anthracene	10.294	4.0108	0.9795

Recovery of PAHs by SPME

The process which releases analytes from solid matrices is difficult to optimize, because the interaction between analytes and matrices is poorly understood and it usually varies according to the complexity of analyte/matrix types. In Table IV, the two steps of recovery of the seven studied PAHs from a muddy sediment using the optimum extraction conditions are reported.

Heating at 60°C was demonstrated to be adequate for the extraction of high-molecular-weight PAH 7, which has not been extracted in other mild conditions probably due to its low solubility into water at room temperature or to the fact that analytes are bound too strongly to the matrix. It is noted that thin fibers are more suitable for the SPME of high-molecular-weight PAHs.

The recoveries of PAHs in water and onto the fiber were calculated by comparing the response factors of each PAH obtained from the three calibration curves by PAH direct injection, PAHs dissolved in water, and PAHs spiked on sediment, respectively. It can be noticed that the phenomenon of releasing analytes from the matrix into water is adverse with respect to that of partitioning them onto the coated fiber. In fact, the recovery of PAH 1 to PAH 7 from sediment into water gradually decreases, whereas that from water onto SPME fiber increases. It is worthwhile to notice that the recovery of PAH 1 (naphthalene) from water onto an SPME fiber is 3.1 times less than that of PAH 7 (benzo[*a*]anthracene), quite consistent with the ratio of the distribution constant of the corresponding compounds (3.5).

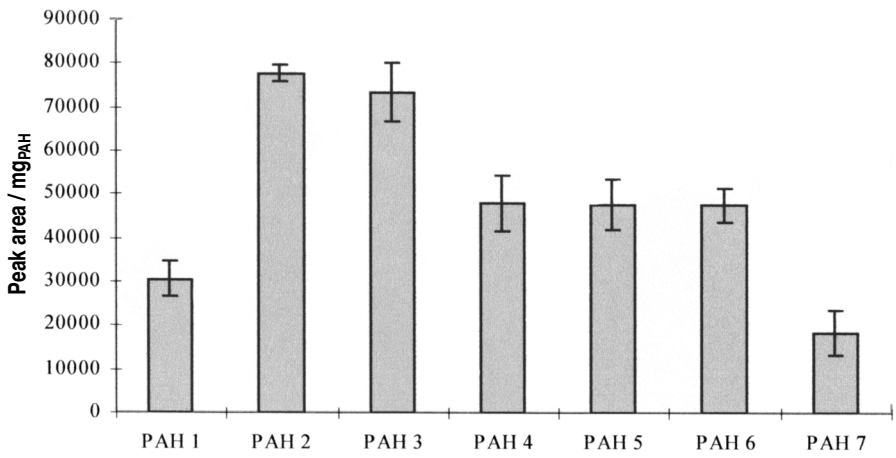


Figure 4. Recovery and reproducibility of PAHs by SPME under the optimal conditions of extraction.

Table IV. Recovery of PAHs

	% Recovery (sediment → water)	% Recovery (water → SPME)	% Recovery (sediment → SPME)	µg$_{PAH}$ adsorbed on SPME
PAH 1	46.1	7.3	3.4	0.1–0.2
PAH 2	37.4	16.3	6.1	0.3–0.6
PAH 3	34.1	16.5	5.6	0.2–0.4
PAH 4	17.6	14.6	2.6	0.1–0.2
PAH 5	14.9	25.1	3.7	0.1–0.2
PAH 6	14.7	20.9	3.1	0.1–0.2
PAH 7	5.1	22.6	1.1	0.05–0.1

Conclusion

The use of SPME–GC in SIM mode has been shown to be a very suitable method for the determination of PAHs in sediment through water. The 100-µm thick PDMS fiber has a proven viable affinity for naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, and benzo[*a*] anthracene with a 60°C working temperature and 30 min of sampling time. The extraction method has good linearity extended in the considered concentration range (5–50 pg for PAH direct injection, 5–70 pg for PAHs in water, and 1–170 pg for PAHs in sediment). The detection limits of the considered PAHs on muddy sediment were predicted to be less than 1 ppb for naphtalene, acenaphthene, fluorene, anthracene, fluoranthene, and pyrene and 1.5 ppb for benzo[*a*]anthracene.

The recovery of the first six considered PAHs from sediment onto the 100-µm thick PDMS fiber ranges from 3 to 6%, except for benzo(a)anthracene, which shows almost a low recovery value (1%). A thinner PDMS fiber coating should be more suitable for determining high-molecular-weight PAHs.

This analytical technique is inexpensive and has the advantage of minimal sample preparation; it allows a direct sampling operation from the source and has very good selectivity. Water content in solid environmental matrices will create no more problems as it used to when adopting traditional technique of extraction. Future applications of this solvent-free methodology of extraction are encouraging for the monitoring of organic contamination in the environment.

Acknowledgments

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