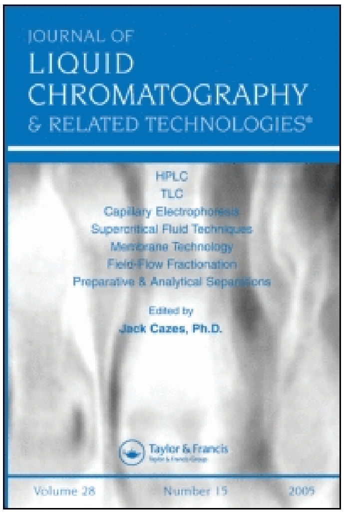

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Monofluorinated Polycyclic Aromatic Hydrocarbons: Surrogate Standards for HPLC Analysis of Surface Water and Sediment Samples

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Abstract: A study was conducted to demonstrate the potential use of selected F-PAHs, 1-fluoronaphthalene (F-Np), 1-fluoropyrene (F-Py), and 9-fluorobenzo(k)fluoranthene (F-BkF1), as surrogate standards (SSs) in the analysis of PAHs in surface and sediment samples from the Danube River, Hungary. An accelerated solvent extraction (ASE) process followed by a high performance liquid chromatography (HPLC) technique was applied. Recoveries of selected F-PAHs and corresponding PAHs were generally good and similar within experimental errors. However, recovery of F-Np in surface water was poor (29.2%), and F-Py could not be extracted from sediment samples. The results indicate that only F-Py and F-BkFl were suitable SSs for surface water samples while F-Np and F-BkFl showed potential as SSs for sediments.

Keywords: PAH, Surrogate, Sample preparation, HPLC, ASE, Danube river

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) consist of two or more aromatic (benzene) rings and have mutagenic, carcinogenic, and teratogenic

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properties.[1] Although PAHs enter the environment via natural and anthropogenic combustion processes, emissions from human activities are the main source. Volcanic eruptions and biomass burning are the major natural sources of PAHs. Anthropogenic sources of PAHs include automobile exhaust emissions, industrial emissions from catalytic cracking and air blowing of asphalt, domestic heating, refuse incineration, power generation, and biomass burning.[2–5]

Because of widespread concerns about the effects of PAHs on the environment, they are included in the United States Environmental Protection Agency (USEPA) and the European Union (EU) priority pollutants lists and have to be determined regularly in environmental studies.

Solid phase extraction (SPE) is commonly used to extract PAHs from surface waters.[6,7] Several extraction techniques, such as Soxhlet extraction, microwave assisted extraction, sonication extraction, micro focused ultrasonic solid liquid extraction, supercritical fluid extraction (SFE), and accelerated solvent extraction (ASE), are applied for PAH analysis in sediments.[8–12] The extraction techniques are complexed and are associated with many problems, which may adversely affect the recoveries of PAHs from samples. It is, however, possible to determine the extent of such losses and, if necessary, to correct the concentration of PAHs by using one or more properly selected internal (surrogate) standards. It is an established practice to use several surrogate standards (SSs) to analyze low to high molecular weight PAHs.

Deuterated PAHs are generally recommended SSs, but their limitations include high price, limited availability, and inapplicability to all kinds of measurements.[13,14] Alternatively, monofluorinated PAHs (F-PAHs) have a strong potential as SSs in PAH analysis. F-PAHs, which are very similar to PAHs in terms of chemical and physical properties, have not been found naturally.[13–15] Andersson and Weiss[13] have, therefore, suggested F-PAHs as internal standards in gas chromatography using flame ionization detection (GC-FID). Recently, Luthe et al.[14] have proposed the use of F-PAHs as SSs for liquid chromatography (LC). Antizar-Ladislao et al.[16–19] have used 1-fluoronaphthalene and 2-fluorobiphenyl as SSs to determine PAHs in soil, using ASE for sample preparation and a GC-MS technique for analyses.

In this paper, 1-fluoronaphthalene (F-Np), 1-fluoropyrene (F-Py), and 9-fluorobenzo(k)fluoranthene (F-BkFl) were tested as SSs for PAH analysis in sediment and surface water samples of the Danube and the Ipoly Rivers, Hungary, respectively. SPE and ASE methods were applied for extraction of PAHs from surface water and sediment samples, respectively. This is the first report on the potential use of F-PAHs as SSs in the ASE process for PAHs from sediments, followed by quantitative determination by high performance liquid chromatography (HPLC).

EXPERIMENTAL

Sample Collection

Seven samples from the upper 0.3 m layer of the waters of the Ipoly River were collected in 500 mL in dark brown glass bottles. The Ipoly River is a tributary of the Danube River, one of the largest rivers in Europe. To each sample, 50 mL acetonitrile and 3 mL orthophosphoric acid ($pH < 3$) was added to prevent bacterial growth. The samples were placed on ice after sampling and were immediately transferred to the laboratory to keep at −4°C before the analysis. For sediments, forty surface samples along the middle part of the Danube river from Klosterneuburg (48°19′53.3″north latitude and 16°19′49.6″ east longitude) to Calafat (44°00′25.6″north latitude and 22°56′10.8″ east longitude) were collected using a grab sampler. The sediment samples were placed on ice and immediately transferred to the laboratory. Samples were freeze dried and were kept in the refrigerators at −18°C before the analysis.

Materials

The three surrogate standards of F-PAHs (F-Np, F-Py, and F-B[k]Fl) were obtained from Chiron (Trondheim, Norway). A US-EPA 610 PAH mix was used as the PAH standard material and was obtained from Supelco Inc. (Bellefonte, Pennsylvania, USA). Acetonitrile and dichloromethane of ultra gradient grade quality were obtained from Merck (Darmstadt, Germany). LC grade water was obtained by passing distilled water through a Millipore ion exchanger. Waters (Milford, Massaschusetts, USA) Sep-Pak® Plus C18 Cartridges were used for SPE of PAHs in the water samples. Waters Sep-Pak® Plus Silica Cartridges were used for the cleanup process. The filler silica gel (2–5 mm) was obtained from Merck.

Solid Phase Extraction (SPE) Procedure

A mixture of three F-PAH (surrogate standards) (0.5 mL) was added to surface water samples. The final concentration in samples were 50 ng/L of 1-fluoronaphthalene, 20 ng/L of 1-fluoropyrene, and 20 ng/L of 1-fluorobenzo (k)fluoranthene. The samples were filtered through a Schleicher & Schüll 100 filter to remove the solid particles greater than 10 μm. Before the SPE procedure, the SPE cartridges were washed with 10 mL of dichloromethane and conditioned with 10 mL of acetonitrile, followed by another washing with 10 mL deionized water. A flow rate of 5 mL min^{-1} under vacuum was used for samples to pass through the cartridges. Columns were then dried under vacuum for 15 minutes. PAHs were finally eluted with 4 mL of acetonitrile and 5 mL of dichloromethane. The samples were concentrated to 0.5 mL under a nitrogen stream at room temperature.

Accelerated Solvent Extraction (ASE) Procedure

Initially, a 2.2 mL mixture of the 3 F-PAHs was added into 6.6 g dried sediment. The concentrations of surrogate standards in the mix were 50 ng/mL, 20 ng/mL, and 20 ng/mL for F-Np, F-Py, and F-B[k]Fl, respectively. After homogenization and drying, 3.3 g of each sample was weighed in duplicate into the pressure tubes used for ASE (Dionex ASE 200). Pure silica gel was added to the tubes as filler. The ASE procedure was similar to that described by Mielke et al.[20] A process was performed with dichloromethane at 10.35 MPa and 100°C. The heating phase was 5 min, and the static extraction time was 10 min. Elution was performed with 60% of the total cell volume. The extracted analytes were purged from the sample cell using pressurized nitrogen (125–150 psi) for 60 s. After the ASE extraction procedure, a stream of nitrogen gas was used to evaporate the extracts to a volume of 5–7 mL, and they were then filtered and cleaned on a Waters Sep-Pak® Plus silica cartridge column. The Sep-Pak silica column was washed with 10 mL of dichloromethane to remove any residue sample extract. The samples were then evaporated with a stream of nitrogen gas to a volume of 2 mL, to which 4 mL acetonitrile was added. Finally, the extract was evaporated in a stream of nitrogen to a volume of 3 mL at room temperature.

HPLC-UV-FL Analyses

PAHs were determined by HPLC with programmable UV and fluorescence detectors (HPLC-UV-FL). The HPLC system consisted of a Merck-Hitachi LaChrom L-7100 pump, a Merck-Hitachi LaChrom L-7250 programmable autosampler L-7250, a Merck-Hitachi LaChrom L-7400 UV detector, a Merck-Hitachi LaChrom L-7480 fluorescence detector, a Merck-Hitachi LaChrom L-7350 column oven, a Merck-Hitachi LaChrom D-7000 interface model D-7000, and Merck HPLC System Manager Ver. 4.1 chromatography data station software. A 250 × 4.6 mm, 5 μm particle size Supelco Supelcosil LC-PAH column was used with an acetonitrile/water gradient. The

Table 1. HPLC solvent gradient program for analysis of PAHs

Time (min)	Solvent composition 50/50 acetonitrile/water (% A)	Solvent composition 100% acetonitrile (% B)
0	100	0
2	100	0
30	7	93
42	7	93
45	100	0
60	100	0

Table 2. Time program of the fluorescence detector for analyzing PAH compounds

Time (min)	Excitation wavelength (nm)	Emission wavelength (nm)
0.0	280	330
17.2	249	362
18.7	246	370
20.2	285	450
21.8	330	390
23.5	270	405
28.5	296	425
30.5	290	430
35.5	300	500
60.0	300	500

solvent gradient program given in Table 1 was used to separate PAH compounds. The mobile phase flow rate was 1 mL $\min^{-1}$ and the injection volume was 25 μL. The time program of the fluorescence detector for determining PAHs is presented in Table 2. Fluorescence detection has been found very suitable for the quantification of PAHs in samples because of the high fuorescence quantum yields of PAHs.

RESULTS AND DISCUSSION

F-PAHs and PAHs Analysis

Figure 1 shows the HPLC-FL chromatogram of three F-PAHs and their corresponding parent PAHs. The chromatogram shows the reasonable separation of F-PAHs and the fifteen parent molecules. The resolutions (USP) between F-PAHs and the nearest PAH compounds were 2.38, 4.76, and 1.21 for naphthalene (Np), pyrene(Py), and benzo(k)fluoranthene (B[k]Fl), respectively. Slightly higher retentions of the fluorinated analogues than in their parent compounds were found (Figure 1). F-PAHs have more lipophilic character than their corresponding PAHs molecules, which causes fluorinated analogues to be retained a little longer at the column than in their parent molecules. Overall, reasonable separations of F-PAHs and their parent PAH in chromatograms suggest the potential of using F-PAHs as SSs.

Surface Water Samples

The represented HPLC-FL chromatogram for F-PAHs and PAHs of the surface water sample after the SPE procedure is shown in Figure 2. The chromatogram shows the reasonable separation of F-PAHs and their parent molecules from the Ipoly River's surface water. The comparison of the recovery results of F-PAHs

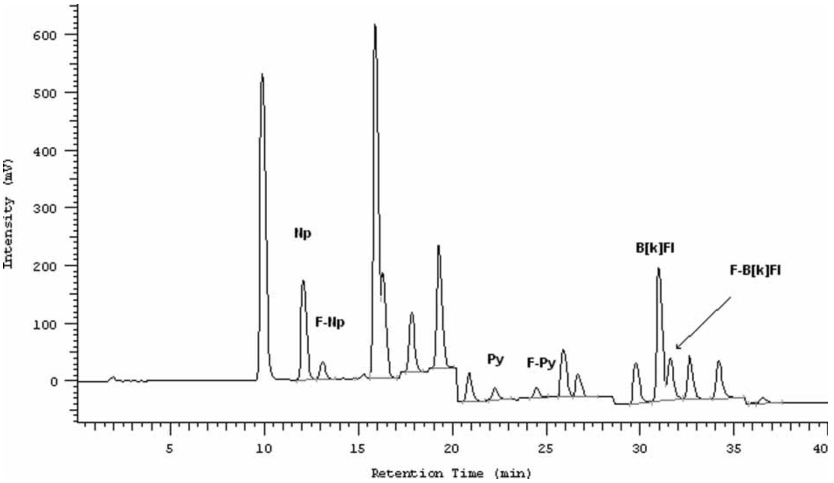

Figure 1. Gradient fluorescence chromatogram of F-PAHs and their parent PAHs.

with recoveries of PAHs is shown in Table 3. A mixture of PAHs was spiked into fifteen surface water samples of the Ráckevei-Soroksári Danube branch, and the same SPE procedure was carried out to extract PAHs. The recoveries were poor for both F-Np and Np while other analyzed compounds gave good recoveries. Interestingly, though F-PAH spiked concentrations were lower than in the parent PAH molecules, recoveries were similar within experimental error. This indicates the suitability of selected F-PAHs as SSs over a wide concentration range in surface water of rivers.

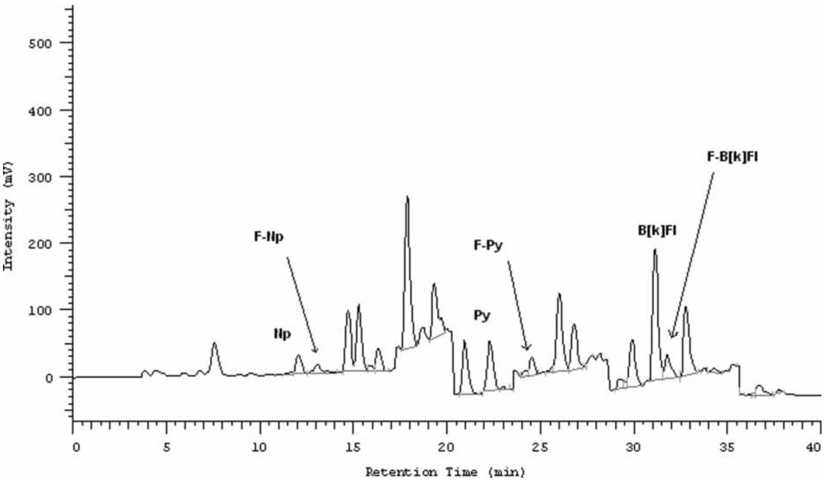

Figure 2. HPLC-FL chromatogram of a spiked surface water after SPE procedure.

Table 3. Limit of detection (LOD) and recovery of measured F-PAH and PAH compounds in water samples

Compound	LOD (ng/L)	Spiked conc. (ng/L)	Recovery (%)	SD (%)	RSD (%)	No. of samples
F-PAH						
1-fluoronaphthalene	0.7	50	29.9	28.8	96.6	7
1-fluoropyrene	0.9	20	98.2	4.4	4.5	7
9-fluorobenzo(k)fluoranthene	0.9	20	94.0	5.5	5.8	7
PAHs [5]						
Naphthalene	0.5	500	40.8	10.1	24.7	15
Acenaphthene	0.5	500	58.1	6.4	11.0	15
Fluorene	0.6	100	63.5	8.1	12.8	15
Phenanthrene	0.6	50	71.5	19.2	26.9	15
Anthracene	0.5	50	56.1	6.3	11.2	15
Fluoranthene	0.5	100	59.5	6.2	10.5	15
Pyrene	0.8	50	71.5	18.9	26.5	15
Benzo[á]antracene	0.5	50	61.9	7.4	11.9	15
Chrysene	0.8	46.5	63.7	5.9	9.3	15
Benzo[b]fluoranthene	0.6	100	64.1	5.9	9.3	15
Benzo[k]fluoranthene	0.5	50	67.1	8.6	12.8	15
Benzo[á]pyrene	0.6	50	55.1	6.9	12.5	15
Dibenz[á,h]anthracene	1	100	62.6	7.3	11.7	15
Benzo[ghi]perylene	1	100	62.0	7.2	11.6	15
Indeno[1,2,3-cd]pyrene	1	50	66.5	16.3	24.5	15

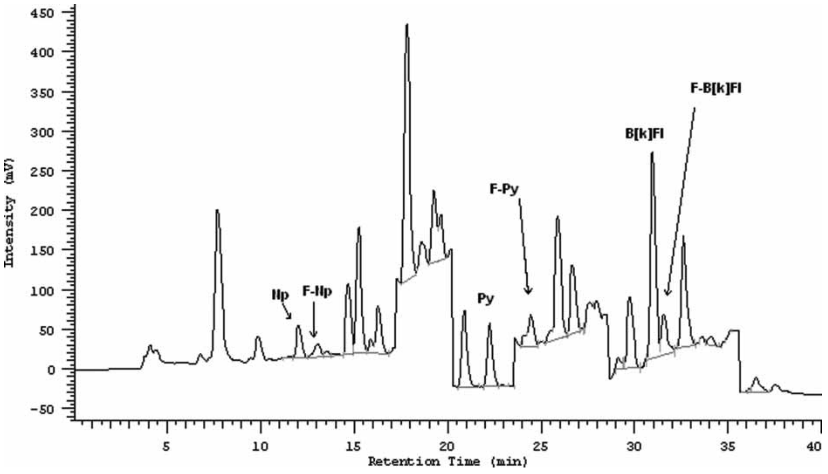

Figure 3. HPLC-FL chromatogram of a spiked sediment sample after ASE and cleanup procedures.

Sediment Samples

Figure 3 shows the separation of PAHs and their fluorinated analogues as surrogate standards for sediment samples after the ASE and cleanup procedures. Similar to surface water samples, F-PAH in sediments could be separated and quantified by using the HPLC-FL technique. The recoveries of F-PAH from the forty sediment samples are given in Table 4. To compare the recovery results of F-PAHs with recoveries of PAHs, a mixture of PAHs was spiked to two sediment samples. The same ASE and cleanup procedures as used previously were carried out on these samples. Recoveries of PAH in these samples are reported in Table 4. F-Py in sediments could not be extracted, possibly due to interference from the matrix of the sample. However, recoveries of other fluorinated PAHs, F-Naph, and F-B[k]Fl were good (Table 4). Moreover, recovery results agreed reasonably well with recoveries obtained in spiking of parent molecules to sediments (Table 4). Additionally, the spiked concentrations of F-PAHs were much lower than the corresponding PAHs concentrations, but similar recoveries of hydrocarbons were found.

Table 4. Limit of detection (LOD) and recovery of measured F-PAH and PAH compounds in sediment samples

Compound	LOD (ng/g dry weight)	Spiked conc. (ng/g)	Recovery (%)	SD (%)	RSD (%)	No. of samples
F-PAHs						
1-fluoronaphthalene	0.7	16.7	68.8	11.6	16.8	40
1-fluoropyrene	0.9	6.7	no data	no data	no data	40
9-fluorobenzo(k) fluoranthene	0.9	6.7	75.9	9.5	12.5	40
PAHs						
Naphthalene	0.5	330	59.4	—	—	2
Acenaphthene	0.5	330	64.2	—	—	2
Fluorene	0.6	66	101.0	—	—	2
Phenanthrene	0.6	33	94.4	—	—	2
Anthracene	0.5	33	95.1	—	—	2
Fluoranthene	0.5	66	87.8	—	—	2
Pyrene	0.8	33	79.3	—	—	2
Benzo[á]antracene	0.5	33	73.8	—	—	2
Chrysene	0.8	30.7	77.1	—	—	2
Benzo [b]fluoranthene	0.6	66	90.0	—	—	2
Benzo [k]fluoranthene	0.5	33	90.7	—	—	2
Benzo[á]pyrene	0.6	33	93.5	—	—	2
Dibenz[á,h]anthracene	1.0	66	85.9	—	—	2
Benzo[ghi]perylene	1.0	66	34.7	—	—	2
Indeno[1,2,3-cd]pyrene	1.0	33	48.5	—	—	2

This indicates the applicability of F-PAHs as SSs over a wide range of concentrations of PAHs in sediments.

CONCLUSIONS

In the HPLC technique, separation and intensity of peaks of hydrocarbons were very reasonable, and low levels of spiked concentrations were measurable. The SPE and ASE procedures for extractions of F-PAHs and PAHs in water and sediment samples, respectively, were mostly successful in recovering hydrocarbons. The good recovery and acceptable standard deviations for F-Py and F-B[k]Fl demonstrate the possibility of using these F-PAHs as SSs for surface water samples. However, the F-Py must be excluded as an SS in the analysis of PAHs in sediments.

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