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ORIGINAL PAPER

Off-line solid-phase extraction procedure for the determination of polycyclic aromatic hydrocarbons from aqueous matrices

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Abstract An off-line solid-phase extraction procedure followed by high-performance liquid chromatography with ultraviolet detection for the determination of 16 priority polycyclic aromatic hydrocarbon pollutants in aqueous matrices was described. Diverse aspects determining extraction efficiency such as packing type (disk or cartridge), elution solvents and addition of organic modifiers to the sample were evaluated. Elution with acetonitrile yields the highest recoveries. Rinsing the sample bottle with acetonitrile and combining the rinse with the sample extract avoids the adsorption of polycyclic aromatic hydrocarbons on the walls of the water containers. The use of isopropanol or methanol 10 % (V/V) was the most appropriate amount for the enrichment of 2- to 6-ring aromatic compounds only on C18 cartridge. The recoveries for all studied polycyclic aromatic hydrocarbons are ranged from 71.4 to 95.2 % for a treated water samples of 500 mL. The proposed method gives very low detection limits (subnanograms per liter) and it has been applied to drinking water, surface water and industrial effluent (oil refinery) samples with good results.

Keywords Polycyclic aromatic hydrocarbons · Off-line solid-phase extraction · Water · HPLC

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds coming mainly from petroleum and the incomplete combustion of organic substance. They are introduced into surface waters via atmospheric fallout, municipal effluents leaching or by oil spills. They are a source of concern for the environment since some of them are mutagenic or carcinogenic (Coluci et al. 2002; UNEP 2002; Arulazhagan et al. 2010; Mahadevan et al. 2005; Abrajano Jr et al. 2007). Due to the extensive amount of data suggesting the hazards of these compounds, many PAHs are included in the US Environmental Protection Agency (EPA) and in the European Union priority lists of pollutants. In Europe, the reference concentration in groundwater for one of the most dangerous PAHs, benzo[a]pyrene, is 0.01 ppb, while that for fluoranthene and pyrene is 0.02 ppb. Moreover, the concentration values for the six target PAHs (fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) cannot exceed 0.2 ppb in groundwater whereas in surface water, maximum levels can go up to 1 ppb depending on the surface water treatment process (European Communities 1998).

The PAHs of 2 and 3 rings are both volatile and hydrophobic. The logarithmic water–octanol partition coefficient values (log K_{ow}) are between 3.3 and 5.2. The 4–6 rings are very hydrophobic (log $K_{ow} \geq 5$) (de Maagd et al. 1998), they tend to stick everywhere, causing losses during sampling and storage. Thus, to carry out a reliable analysis powerful analytical methods ought to be set up.

Due to the usual low levels of PAHs in water samples a pre-concentration step prior to analysis is required and owing to the trend for decreasing the use of organic solvents in laboratory, solid-phase extraction (SPE) is preferred over liquid–liquid extraction (LLE).

Classical extraction sorbents used for the extraction of PAHs from water are C8, C18 or polymers of styrene-divinyl benzene (Marcé and Borrull 2000; Martinez et al. 2004). In most cases, the sorbent is packed in cartridges or disks. However, to avoid the adsorption of PAHs on sample containers or connection tubing, an organic solvent (Tfouni et al. 2007) or a surfactant should be added before extraction (Ballesteros-Gomez and Rubio 2009; Pino et al. 2002; Hung et al. 2007). More recently, solid-phase microextraction (SPME) coupled to liquid chromatography (LC) has been used for determination of PAHs in water (Chen 2004). This process is significantly simpler than conventional techniques, thereby reducing analyte loss during extraction. SPME sensitivity and precision are generally as good as or better than standard methods. Nevertheless, the SPME fiber is usually damaged when analyzing complex matrices.

A new promising extraction technique which is known as stir bar sorptive extraction (SBSE) was applied for the assessment of eight PAHs in water samples (Garcia-Falcon et al. 2004). This technique was followed by high-performance liquid chromatography (HPLC) with a fluorescence detector.

The analysis of the concentrated extract can be carried out using gas chromatography (Stroher et al. 2007; Yusa et al. 2006; Mzoughi et al. 2002; Fagbote and Olanipekun 2010; Olajire Abbas and Brack 2005) and liquid chromatography (LC) (Simon et al. 2007; Pojana and Marcomini 2007; Garcia-Falcon et al. 2004). Different detection devices are used to achieve simultaneously high resolution, sensitivity and selectivity. HPLC has been the selected technique for PAHs determination with several detectors: ulraviolet (UV)–visible (Windal et al. 2008; Busetti et al. 2006), fluorometric (Okuda et al. 2006; Serpe et al. 2010; Windal et al. 2008; Busetti et al. 2006; Williamson et al. 2002; Garcia-Falcon et al. 2004) and mass spectrometer (Viguri et al. 2002; Lien et al. 2007). However, UV detection yields a sensitivity and selectivity lower than that of fluorometric detection. Nevertheless, its performances can be widely improved by selecting the wavelength of maximum absorbance for each compound to be determined (Kuppithayanant et al. 2003).

The objective of this study was to evaluate an off-line SPE method for pre-concentration and determination of PAHs in water using SPE cartridges and LC with a variable wavelength UV detection. This required study of different factors can influence the recovery of PAHs in many ways: (1) nature of the cartridge packing, (2) the concentration of PAHs in the sample, (3) the necessary addition of organic solvents in water samples before extraction. The performance of this method was finally checked with surface and drinking waters as well as industrial effluents collected from the region of Bizerte (North of Tunisia), in December 2010.

Materials and methods

Chemical and reagents

High-purity crystalline and liquid reference substances (purity > 99 %) were used to prepare (PAHs) calibration and spiking solutions by gravimetry. The following compounds were purchased from Sigma-Aldrich (Saint Quentin Falavier, France) : a Mix in methylene chloride:benzene (1:1) of naphthalene (Naph), acenaphthylene (Act), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Ft), pyrene (Py), benzo[a]anthracene (B(a)An), chrysene (Ch), benzo[a]pyrene (B(a)Py), benzo[b] fluoranthene (B(b)Ft), benzo[k]fluoranthene (B(k)Ft), dibenzo [a,h]anthracene (D(a,h)An), benzo[ghi]perylene (B(ghi)Pe) and indeno[1,2,3-cd]pyrene (Ind(1,2,3-cd)Py), The prepared solutions were protected from light and stored in the cold (4 °C).

Various reagents were purchased from Sigma-Aldrich: dichloromethane, methanol, acetonitrile, acetone (all of them pestanal grade), isopropanol (chromasolv plus grade), anhydrous sodium sulfate (purity > 99 %). The water used in all experiments was purified by a milli-Q system (Millipore, Saint-Quentin-en-Yvelines, France).

Extraction procedure

SPE C18 cartridges

The off-line SPE was performed with Supelclean-Envi-C18 cartridges (0.5 g) and Bond-Elut-C18 cartridges (1 g) purchased respectively from Supelco and Varian. The cartridge was connected to a 1 L separating funnel with appropriate fittings. Prior to the extraction procedure, the solid phase was sequentially prewashed with 6 mL of methanol and Milli-Q water (10 mL) at a flow of 1–2 mL min^{-1}. After this step, samples were allowed to flow through the cartridge at 10–12 mL min^{-1} under water aspirator vacuum. The analytes were eluted with the appropriate organic solvent (6 mL). When the methylene chloride was used as elution solvent, the solid-phase cartridge was duly dried by flowing air for 5 min before the desorption of analytes. The separatory funnel was washed with 2 mL of acetonitrile and this volume was added to the cartridge extract (this step of washing the separatory funnel was discussed in this work). The obtained extract was reduced to 1 mL, before chromatographic analysis, under a gentle stream of nitrogen in a Kuderna Danish evaporator (at a temperature of 30–35 °C on water bath).

SPE C18 disks

The ENVI-18DSK, C_{18} membrane extraction disks were manufactured by Supelco and purchased from Sigma-Aldrich. They have the following characteristics: a diameter of 47 mm, a thickness of 0.5 mm and each disk contains 500 mg of C_{18} sorbent. Before use, Disks were washed with two sequential 5-mL volumes of methylene chloride to remove impurities. They were then conditioned with two sequential 10-mL volumes of methanol followed immediately by 10 mL of ultra-pure water. During the conditioning step and the following extraction step, the SPE material was not allowed to run dry. The sample solutions (from 500 to 1,000 mL), containing 0.5 and 10 % of methanol, were aspirated through the disk by vacuum pump, at a flow-rate of 5–8 mL min^{-1}. After the passage of sample solution, the disk was dried by vacuum suction for 10 min and the analytes were then eluted with successively 2 mL of acetone and 10 mL acetonitrile. This step was performed simultaneously with the rinsing of the glass container of the ENVI disk Holder. The combined aliquots (extract and rinsing volumes) were dried over anhydrous sodium sulfate to remove water and then reduced with a gentle stream of Nitrogen gas to a volume of 500 μL.

Apparatus and operating conditions

Apparatus

The chromatographic system consisted of a Thermo Finnigan system formed by a Spectra SYSTEM Model MP1000XR solvent degasser, a Spectra SYSTEM Model MP1000XR solvent delivery system, a Spectra SYSTEM Model UV2000 UV–Vis detector, a Rheodyne (Cotati) 7125 sample injector with 20 μL loop, a C18 Hypersil column (Supelco), 250 × 4.6 mm I.D., 5 μm particulate size and a Supelco LC-18 guard column. The whole chromatographic system is piloted by a HP computer with an AZUR program.

Operating conditions

The mobile-phase (acetonitrile–water) gradient: 60 % acetonitrile 40 % water for $t = 0$ min, increasing linearly up to 90 % acetonitrile in 17 min; then increasing linearly up to 100 % acetonitrile at $t = 30$ min. The flow rate was 1 mL min^{-1} and the temperature was 25 °C. During chromatographic separation the mobile phase was degassed. UV detection was performed using programmable wavelength during the analysis: (time, λ); 0.01 min, 226 nm; 11.8 min, 254 nm; 15 min, 237 nm; 16.5 min, 265 nm; 19 min, 300 nm.

Water sampling

Drinking water samples were obtained from the public water Supply system. Surface water and industrial effluent (oil refinery) samples were collected from the region of Bizerte.

All water samples were collected in 2,500-mL amber glass bottles, which were rigorously cleaned, rinsed with methanol and dried prior to use. Samples were extracted as soon as possible to avoid adsorption of PAHs in the glass of bottles.

Results and discussion

Chromatographic analysis

The 16 studied PAHs contain from two to six rings, these PAHs correspond to the US-EPA priority list. Figure 1 shows the chromatographic separation on a C18 column of the studied hydrocarbons when using the conditions already detailed above. It is noted that among the studied compounds only B(a)An and Ch peaks overlap (Fig. 1). Nevertheless, despite many changes in the chromatographic conditions such as the mobile-phase flow rate and the elution gradient rate, it was not possible to improve the resolution.

The UV absorption spectra of the studied PAHs obtained in the range 200–400 nm show that these compounds have no maximum absorbency at the same wavelength (λ). It is worth noting that PAH λ increases when its aromaticity increases. Thus, using a single detection wavelength, such as $\lambda = 254$ nm which is often called upon for PAH analysis does not allow for the best sensitivities. However, the variation during the chromatographic elution improves both sensitivity and selectivity. Concerning, the former quality, it is best to select for each compound the detection wavelength which corresponds to its maximum absorbency through the detector programming in terms of retention times. There were no problems getting the LC operational by this method. The only precaution that needed to be taken was to ensure that the wavelength changes on the UV detector occurred after the appropriate peaks.

When the analysis of samples extracted from complex matrices is carried out, it is only possible to change the detector parameters a few times during the chromatographic separation. Various PAHs are therefore detected at the same wavelength. Table 1 gives the λ_{det} chosen for this work. The accuracy and the linearity of the detector response were checked for each solute at the corresponding λ_{det}. The repeatability evaluated by the relative standard deviations of five consecutive injections originating from a

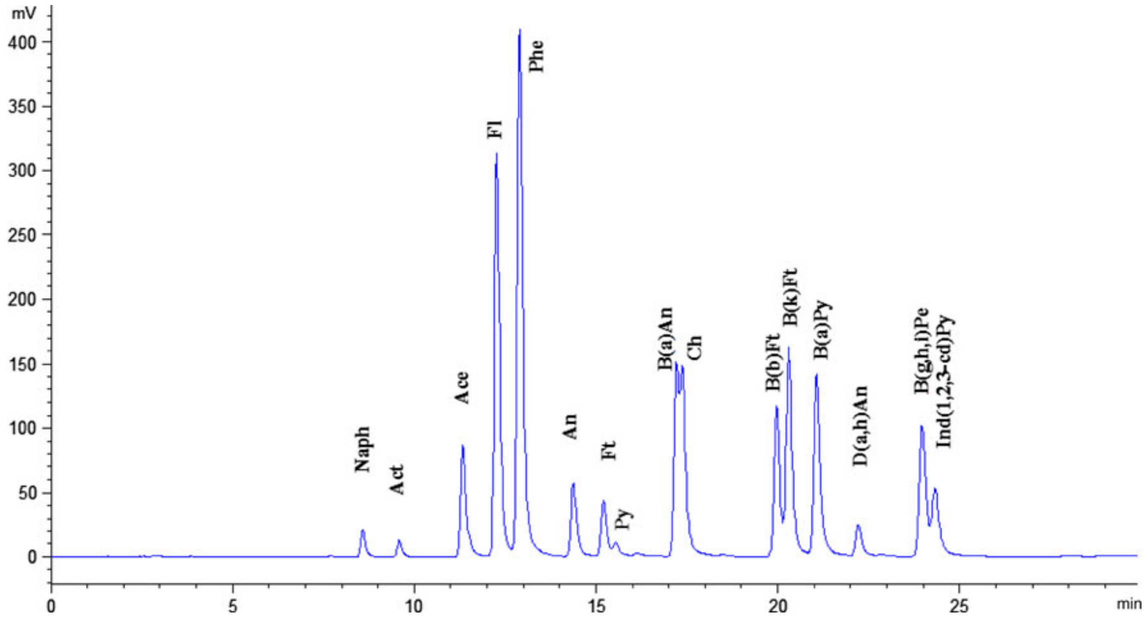


Fig. 1 Chromatogram obtained for the 16 PAH solutions. Mobile phase: eau/acetonitrile, first linear gradient from 60 to 90 % of acetonitrile between 0 and 17 min then a second linear gradient from 90 to 100 % of acetonitrile between 17 and 30 min; Column (LC18, 250 × 4.6 ID mm). Flow 1 mL min^{-1}

Table 1 Detection wavelengths and regression coefficients of the studied compounds

Compounds	λ_{det} (nm)	R^2	Compounds	λ_{det} (nm)	R^2
Naph	226	0.9960	B(a)An	265	0.9997
Act	226	0.9982	Ch	265	0.9964
Ace	226	0.9947	B(a)Py	300	0.9987
Fl	226	0.9985	B(b)Ft	300	0.9979
Phe	254	0.9981	B(k)Ft	300	0.9989
An	254	0.9996	D(a,h)An	300	0.9943
Ft	237	0.9978	B(ghi)Pe	300	0.9971
Py	237	0.9991	Ind(1,2,3-Cd)Py	300	0.9975

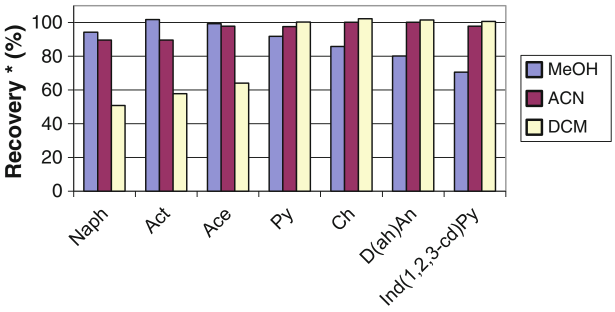


Fig. 2 Variation in the recovery of selected PAHs extracted by the Bond Elute cartridge according to elution solvent. (*Asterisk*) Mean value of three determinations

standard solution, at 20 µg mL^{-1} concentration level, lay between 1.48 % for naphthalene and 3.82 % for acenaphthene. A good linearity is observed for all the solutes. The regression coefficients obtained vary between 0.9943 and 0.9997 (Table 1). Detection limits obtained by direct injection of the PAHs standard mixture and calculated with a signal-to-noise of three are between 0.05 and 4 ng. These findings are similar with other research (Chen 2004).

SPE procedure optimization

Influence of elution solvent on analyte recovery

There are a number of factors that can influence the recovery of PAHs during SPE. The first step is to select an appropriate eluent to desorb PAHs from the cartridge. For this study, 1 mL of seven selected PAHs mixed at 1 µg L^{-1} concentration level in methanol was injected directly onto the SPE cartridge instead of loading a standard aqueous solution of PAHs onto the SPE cartridge. Three solvents were evaluated (methanol, acetonitrile and methylene chloride). These solvents were selected to provide a range of different polarities. Elution of PAHs from previously loaded cartridge was performed with 6 mL of the selected organic solvent. Then the eluate was concentrated to 1 mL, except for methylene chloride eluate. In this last case, the evaporation has been led to dry because methylene chloride disturbs analysis in reversed phase LC.

Figure 2 shows the obtained recoveries of selected PAHs. Among the three chosen solvents, acetonitrile provides the highest overall recoveries. Using methanol as the

Table 2 Evaluation of the PAHs lost by adsorption on the glass container and no retention on the Bond Elut C18 cartridge

Compounds	Recovery* (%)				
	Cartridge C18	Rinsing bottle	Total (1)**	LLE of sample eluate	Total (2)***
Naph	88.08	0.32	88.40	5.68	94.08
Ace	87.95	0.53	88.48	6.91	95.39
Act	82.68	1.42	84.10	8.14	92.24
Py	48.58	5.38	53.96	16.20	70.16
Chy	26.38	13.64	40.01	30.50	70.51
D(a,h)An	9.37	11.22	20.60	44.94	65.54
Ind(1,2,3-cd)Py	12.44	22.41	34.85	40.57	75.42

* Mean value of three determinations

** Total 1: the addition of cartridge recovery and the fraction of adsorbed PAHs on glass bottle

*** Total 2: total 1 + the fraction corresponding to LLE of sample eluate by methylene chloride

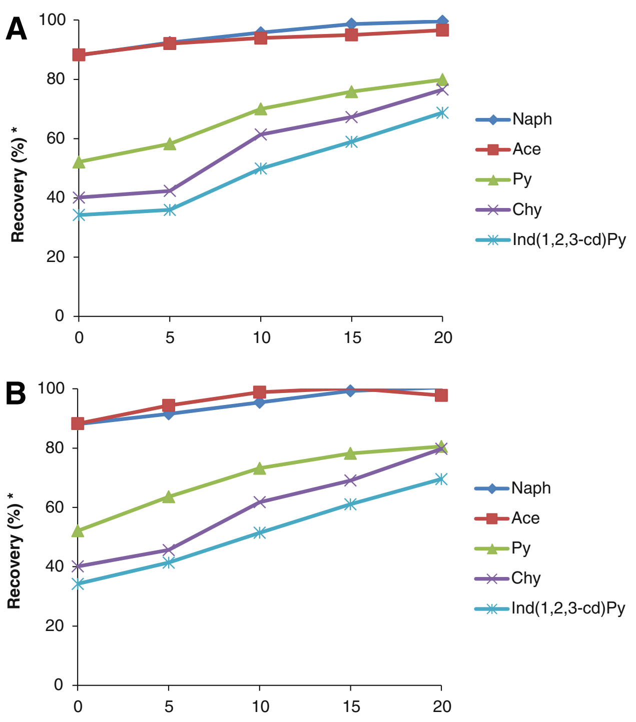


Fig. 3 Variation of PAHs recovery according to the percentage of organic modifiers. **a** Methanol, **b** Isopropanol. Water volume (200 mL) spiked with 5 PAHs at 25 μg L^{-1}; Bond Elut C18 SPE cartridge

eluting solvent, a lower efficient desorption of 5- and 6-ring PAHs was achieved. Finally in the case of methylene chloride, the recovery of the more volatile 2- to 3-ring PAHs (acenaphthylene, acenaphthene and naphthalene) ranged between 50 and 60 %. These results show that the complete evaporation of the eluate leads to significant losses. Hence, acetonitrile was chosen in further optimization experiments.

PAHs recovery

The PAHs recoveries from studied samples for the overall process were determined from spiked Milli-Q water samples that were processed according to the test procedures. The initial handling of the sample in this manner did not have yield acceptable analytes recoveries. To determine where the analytes were lost in the sample preparation process, two experiments were performed. These experiments included rinsing the sample bottle with acetonitrile for concentration and analysis. Furthermore, re-extracting collected eluate sample with methylene chloride using LLE and analysis. Table 2, indicates that much of the error in the SPE extraction process comes from making and loading the aqueous PAHs standard. In fact, rinsing the sample container with acetonitrile and adding the rinse solvent to

Table 3 Variation in the recovery of the studied PAHs using Envi-Disk-C18 according to the percentage of organic modifier (MeOH)

Compounds	Recovery (%)* when adding methanol		Relative variation** (%)
	(*a*) 0.5 %	(*b*) 10 %	
Naph	95.67 (3.0)	26.04 (4.4)	−72.6
Ace	101.48 (4.5)	53.41 (3.7)	−47.4
Act	97.19 (3.1)	50.51 (4.5)	−48.4
Py	79.13 (9.9)	84.60 (10.1)	6.9
Chy	71.83 (8.3)	80.40 (4.3)	11.9
D(a,h)An	50.72 (11.8)	62.04 (10.4)	18.3
Ind(1,2,3-cd)Py	61.17 (12.1)	67.48 (12.8)	10.3

* Mean value of three determinations, the values between brackets are the relative standard deviation (%)

** $[(b - a)/b] \times 100$

the solvent extract improves the recoveries for the 4- to 6-ring compounds. Moreover, for all PAHs and especially for high molecular weight PAHs (4–6 rings), their recoveries were improved significantly by adding the amount of PAHs obtained by LLE of the sample eluate. This latter result can be correlated to the octadecyl chains in the SPE cartridge which must be kept in an activated form during application of the water sample. Otherwise, a large amount of water will remove the activating organic solvent from the hydrocarbons layer of the packing, and the alkyl chains will collapse to a tight film due to their hydrophobic character. As a consequence, the penetration of the solute molecules between the bonded octadecyl chains is hampered. Hence, a weak retention is observed and therefore low recoveries of PAHs, essentially those having higher molecular weight, may be obtained.

Table 4 Recovery variation of the studied PAHs using Supelclean C18 Cartridge according to PAHs concentrations

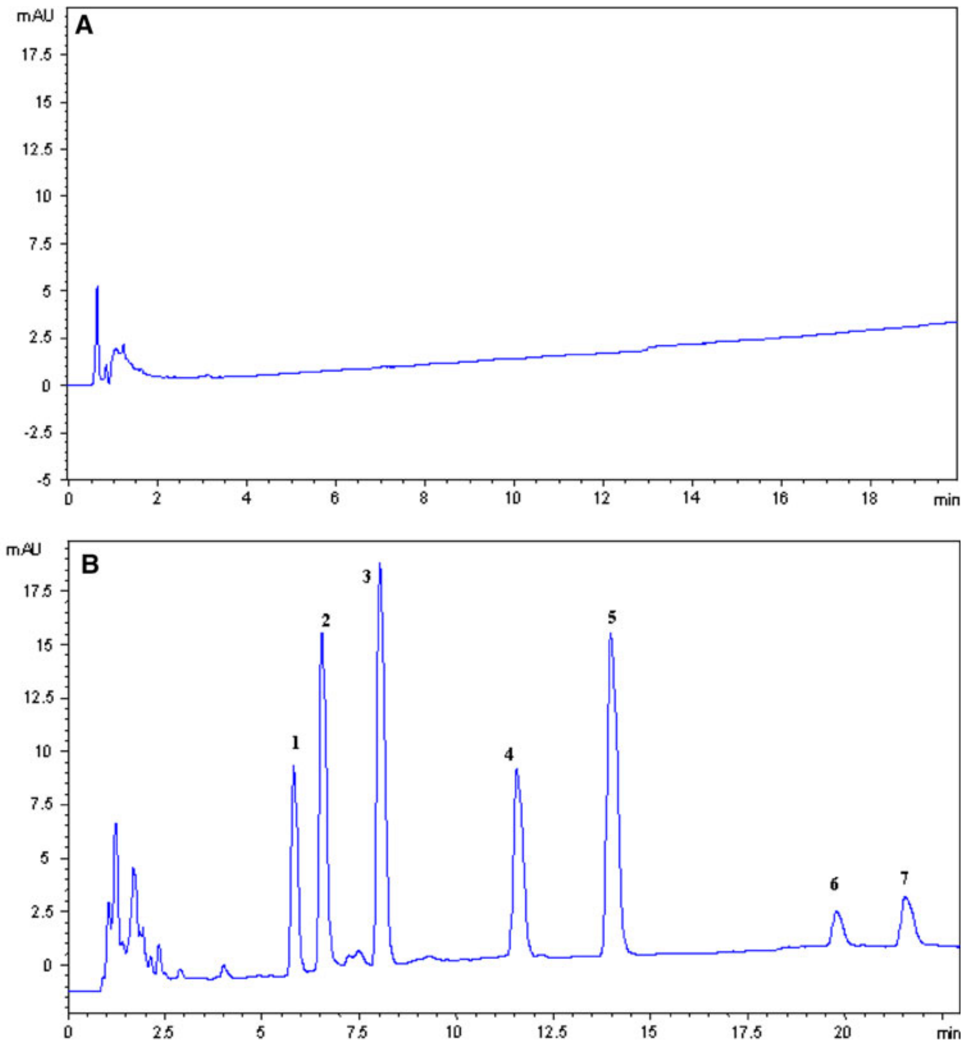
Compounds	Recovery* (%)		
	0.5 μg L^{-1}	2.5 μg L^{-1}	5 μg L^{-1}
Naph	92.14 (7.1)	99.59 (3.4)	106.75 (4.3)
Act	90.10 (10.6)	98.51 (6.0)	95.99 (5.2)
Ace	88.77 (11.7)	99.44 (2.5)	89.44 (6.1)
Py	70.28 (7.0)	72.74 (7.6)	74.18 (8.8)
Ch	70.38 (10.4)	70.04 (2.9)	79.03 (10.0)
D(a,h)An	55.61 (9.2)	58.53 (5.1)	60.94 (7.6)
Ind(1,2,3-cd)Py	63.37 (11.8)	64.69 (8.7)	72.28 (8.2)

* Values are mean of three determinations; the value between brackets is the relative standard deviation (%). Treated water sample = 500 mL

Addition of an organic modifier

Cartridge case In order to minimize the deactivation of the cartridge provoked by the flow of a relatively large amount of water, a certain percentage of organic solvent is often added to the water sample. However, the eluotropic strength of the sample increases when increasing organic

Fig. 4 Chromatograms of non-spiked (**a**) and spiked (**b**) tap water samples with selected PAHs (*1* Naph; *2* Act; *3* Ace; *4* Py; *5* Ch; *6* D(a,h)An; *7* Ind); *SPE* Supelclean cartridge



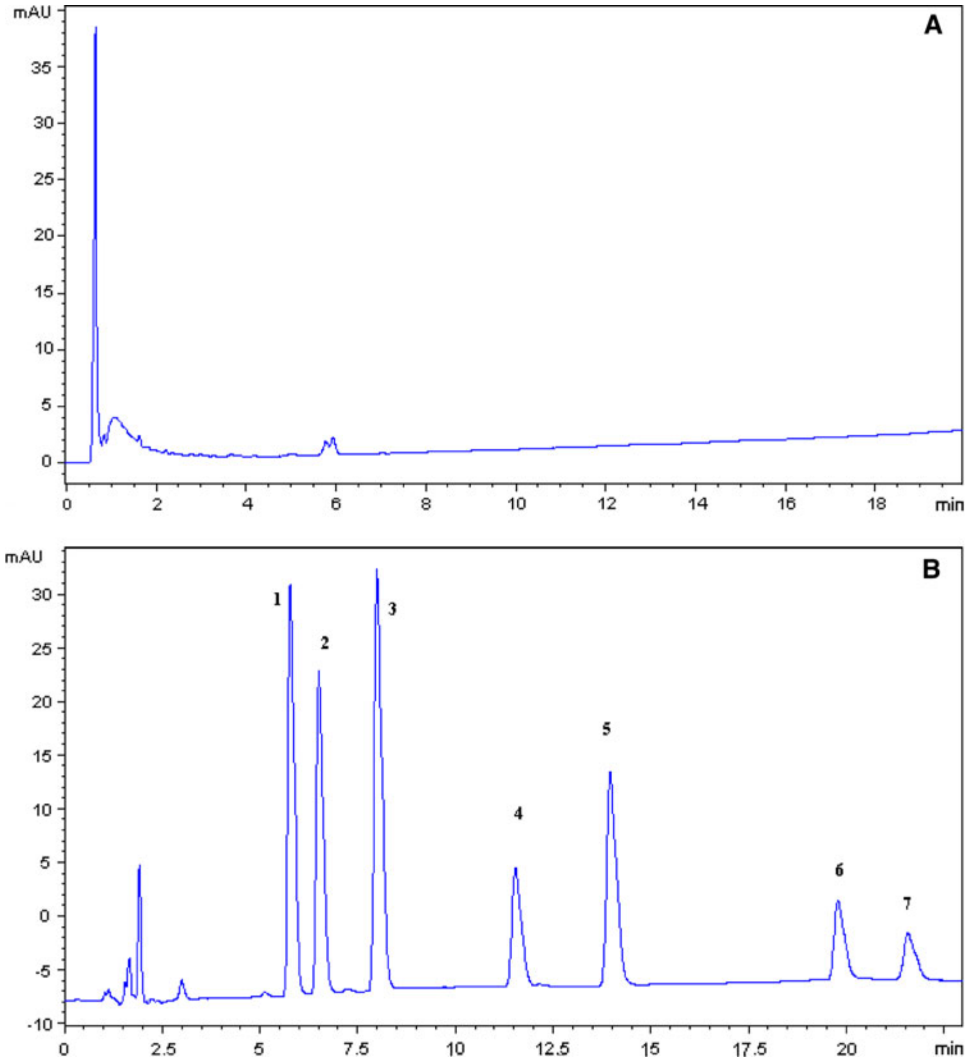


Fig. 5 Chromatograms of non-spiked (**a**) and spiked (0.05 μg L^{-1}) (**b**) surface water samples (500 mL) with selected PAHs (*1* Naph; *2* Act; *3* Ace; *4* Py; *5* Ch; *6* D(a,h)An; *7* Ind); SPE supelclean cartridge

modifier content. This results in a smaller breakthrough volume of PAHs which is conducive to lower recoveries especially in the case of the 2- and 3-ring compounds. Therefore, the main problem of the SPE of analytes in aqueous samples lies in the breakthrough volume effect. In fact, an SPE cartridge behaves like a chromatographic column: the analytes are displaced along them under the influence of the flow of sample solution, with a speed that depends on their physical and chemical characteristics and they are eluted in due time. This means that significant amounts of the analytes can be lost. This difficulty is further increased by adding an organic solvent to the treated samples. Hence, these contradictory effects must be considered when choosing the nature and amount of the organic modifier.

In the present work, the variation of PAHs recoveries was studied in function of the nature and percentage of two organic solvents (methanol and isopropanol) which have been selected among the various solvents found in the literature (Xie et al. 2003; Mao et al. 2003). This paper discusses the results obtained with the two types of SPE used: Bond-Elut-C18 cartridges and the Supelclean Envi-Disk-C18. On that account, 200 mL of an aqueous solution spiked with 1 mL of standard mixture at a 25 μg L^{-1} concentration level in methanol was used to examine the effect of these modifiers. The isopropanol as well as the methanol content of the sample was increased in each experiment from 5 to 20 % (V/V) and PAHs recoveries were determined accordingly. Results are presented in Fig. 3. It can be observed that the recoveries of naphthalene and acenaphthene are greater than 95 % at an isopropanol content of 20 %. Those of pyrene, chrysene and indeno(1,2,3-cd)pyrene are greater than 70 % at an isopropanol content of 20 % (Fig. 3a). Based on these results, 20 % isopropanol is suggested as an organic modifier, when the entire 2- to 6-ring PAHs have to be concentrated on a C18 SPE cartridge with a recovery for all studied compounds higher than 70 %. In the case of methanol, the

Table 5 Recovery of the studied PAHs using Supelclean C18 cartridge in spiked tap and surface waters

Compounds	Tap water	Surface water
Naph	95.2	92.2
Act	91.3	90.6
Ace	92.5	91.4
Py	83.8	82.4
Ch	82.7	80.4
D(a,h)An	74.8	73.4
Ind(1,2,3-cd)Py	72.1	71.4

Table 6 Concentration (mg L^{-1}) of the studied PAHs using Supelclean C18 cartridge in tap water, surface water and industrial effluent

Compounds	Tap water	Surface water	Industrial effluent
Naph	nd	nd	7.5
Act	nd	nd	5.6
Ace	nd	0.1	nd
Fl	nd	nd	0.5
Phe	nd	nd	1.2
An	nd	nd	nd
Ft	nd	nd	0.9
Py	nd	nd	0.4
B(a)An	nd	nd	nd
Ch	nd	nd	nd
B(b)Ft	nd	nd	0.6
B(k)Ft	nd	nd	nd
B(a)Py	nd	nd	nd
D(a,h)An	nd	nd	nd
B(g,h,i)Pe	nd	nd	nd
Ind(1,2,3-cd)Py	nd	nd	nd

same outcome is observed (Fig. 3b). Nevertheless, we have chosen a proportion of organic modifier of 10 % as a compromise. This proportion increases of about 25 % the recovery of high molecular weight PAHs.

Disk case With C18 extraction disks, only the effect of the addition of MeOH as an organic modifier was evaluated. The volume of water used is 1,000 mL spiked by a mixture of 7 PAHs at a concentration of 1 μg L^{-1}. Two percentage of MeOH is tested in the extraction procedure of water samples.

The recoveries, illustrated in Table 3, show that the addition of 10 % of MeOH significantly reduces the recovery of the light PAHs (the losses reach the 50 %) and slightly increases the recovery of the heavy PAHs. Moreover, the addition of 0.5 % of methanol gives acceptable recoveries. Thus, this latter proportion is chosen.

The effect of PAH concentrations in the sample recovery

In order to assess the effect of the concentrations of treated water solutes on the yielded recovery, Milli-Q water samples (500 mL), spiked with the studied PAHs with final concentrations of 0.5; 2.5 and 5 μg L^{-1}, were extracted by a Supelclean SPE cartridge. The obtained results were reported in Table 4. It is to be noted that the PAH recoveries achieved in these PAH concentration levels show no significant discrepancy. Therefore, when analyzing water sample it is possible to use external calibration since it allows for acceptable linearity in tested concentration levels.

Method performance

All retained SPE conditions were assessed on real-spiked water samples (surface and drinking waters) to observe the effect of the matrices in the recoveries and the chromatographic separation. Chromatograms of tap water samples (Fig. 4a) do not show any interfering peaks, essentially from the Supelclean SPE cartridge. On the other hand, Fig. 4b shows the chromatogram of a spiked tap water sample at 0.05 μg L^{-1} level of concentration. In the extracts obtained from the collected surface water sample, a broad band was observed in the beginning of both chromatograms before PAHs elution, Fig. 5a, b. This band corresponds to humic substances which are present in natural waters. These humic substances can affect the repeatability of the extraction when analyzing such complex matrices with SPME fiber (Chen 2004) or SBSE (Garcia-Falcon et al. 2004). Because in these cases the sorbent is used many times (contrary to SPE sorbent). Thus, as the extraction proceeds, the repeatability of the extraction decreases. Therefore, it is the main advantage of our method using SPE sorbent. Nevertheless, when the quantity of samples is limited (few milliliters) we need to use SPME fiber.

The chromatogram of non-spiked surface water sample contains many peaks that do not interfere with those of studied PAHs as shown by the chromatogram of the spiked surface water sample. An exception was observed for Act. The chromatographic peak of this compound was partially overlapped with those of interferences.

Treated surface and tap waters were spiked at the same level of concentrations (0.05 μg L^{-1}). Obtained results (Table 5) showed similar recoveries of PAHs. These results were also similar to the ones obtained with Milli-Q water. Nevertheless, the average recovery values of 2- and 3-ring PAHs are slightly higher than the remaining PAHs.

Application

The validated analytical method was used to investigate the occurrence of PAHs in different environmental water samples. To get a first impression on the occurrence of this class of contaminants, several samples were analyzed (industrial effluents, surface water and tap water) (Table 6). We noted the presence of high molecular weight PAHs only in the industrial effluent.

Conclusion

Polycyclic aromatic hydrocarbons are considered as top priority pollutants due to their carcinogenic, hepatoxic and mutagenic effects. Because of their low concentrations in the environment, methods for selective enrichment and sensitive determination are indispensable. Current techniques for the extraction and preconcentration of PAHs from water are LLE or SPE.

This work describes simple and robust analytical protocols to determine the 16 PAHs of the US EPA priority list in drinking water, surface water and industrial effluent. Two kinds of cartridge (Supelclean Envi-18 and Bond Elut-18) containing C18 sorbent are compared. Also, the disk (Envi-18 DSK) with C18 sorbent is investigated. The C18 sorbent in cartridge or disks provided high recoveries with enrichment factors superior to 2,000.

This study shows that HPLC with reversed phases allows good separation of the 16 priority PAHs in reasonable time. Moreover, the use of wavelength programming permits limits of detection of the order of ppb. Besides, adding an organic modifier as methanol or isopropanol, in a proportion of 10 %, increases the recovery of high molecular weight PAHs of about 25 % on C18 cartridges.

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