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Optimization of a Solid-Phase Extraction Method Using Centrifugation for the Determination of 16 Polycyclic Aromatic Hydrocarbons in Water

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ABSTRACT: A fast and reliable method for the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples by solid-phase extraction (SPE) using centrifugation has been developed and optimized. A silica-based C18 cartridge was used; parameters affecting the extraction procedure such as type and volume of the elution solvent, breakthrough volume of the percolated water sample, drying of the sorbent, and evaporation of the elute have been studied. The innovation of this work was the examination of the use of a centrifugation technique in both the drying and elution steps. When combined with centrifugation, the volume of the elution solvent was reduced to 1 mL and the time for sorbent drying decreased also to 10 min under vacuum. Under optimal conditions, recoveries for the 16 U.S. EPA PAHs were between 70 and 85% and the relative standard deviation varied between 1 and 14%. Surrogate standard recoveries were similarly between 61 and 94% with a relative standard deviation between 2 and 15%. The simplicity of the described method, use of less of organic solvent, short procedure time, and good recoveries demonstrate the advantages of this environmentally friendly approach for routine analysis of numerous samples.

KEYWORDS: polycyclic aromatic hydrocarbons (PAHs), solid-phase extraction (SPE), centrifugation, organic contaminants, water, gas chromatographic−mass spectrometric analysis (GC-MS)

1. INTRODUCTION

Water pollution by organic compounds has caused considerable concern worldwide. The evaluation and monitoring of trace levels of the contaminants in environmental samples are important objectives. Among a wide variety of organic pollutants present in water, polycyclic aromatic hydrocarbons (PAHs) are of particular importance as widespread, persistent, and toxic contaminants.[1,2] Due to their mutagenic and carcinogenic characteristics,[3] PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) and the European Union (EU).[4,5] These organic compounds, which mainly contain two or more fused aromatic rings of carbon and hydrogen atoms, originate from a wide variety of natural and anthropogenic sources.[6] They are generally formed during incomplete combustion or pyrolysis of organic matter. Their sources in the aquatic environment include various routes, such as fossil fuel, oil spills, and domestic and industrial wastewater discharges, as well as atmospheric fallout deposition.

Due to their low water solubility and high hydrophobicity, PAHs are usually present in water samples at nanogram per liter levels and lower. As a result, selective and sensitive analytical procedures are required for their detection and control. One of the high-performance methods in sample preparation is solid-phase extraction (SPE), which has been increasingly used for extracting and concentrating different target components from liquid samples including PAHs.[7,8] For instance, two U.S. EPA methods, 525.2 and 3535, describe the use of a SPE method for the determination of the low microgram per liter levels of organic compounds such as PAHs from aqueous samples.[9,10] Other analytical protocols based on the SPE technique are proposed and described in the literature for PAH extraction at trace level from environmental water samples.[11−13]

Although SPE has been extensively used for the analysis of PAHs in aqueous media, relatively few studies were reported for its development and optimization.[14,15] Low recoveries of the low molecular weight (LMW) PAHs are obtained especially for the two-ring PAH naphthalene (Nap) (16% for Kicinski et al.[16] and 28% for Kabzinski et al.[17]). For these reasons, there is an interest in developing a more efficient SPE method that achieves higher recoveries for the extraction of these pollutants from water, decreasing the analysis time and reducing the excessive amounts of organic solvents used. Rather than using traditional vacuum flow-based SPE, centrifugation is an alternate format to overcome the inconveniences in the typical SPE techniques. Although investigation of the use of centrifugation with SPE has not been carried out widely, it has been reported that centrifugation in SPE was utilized

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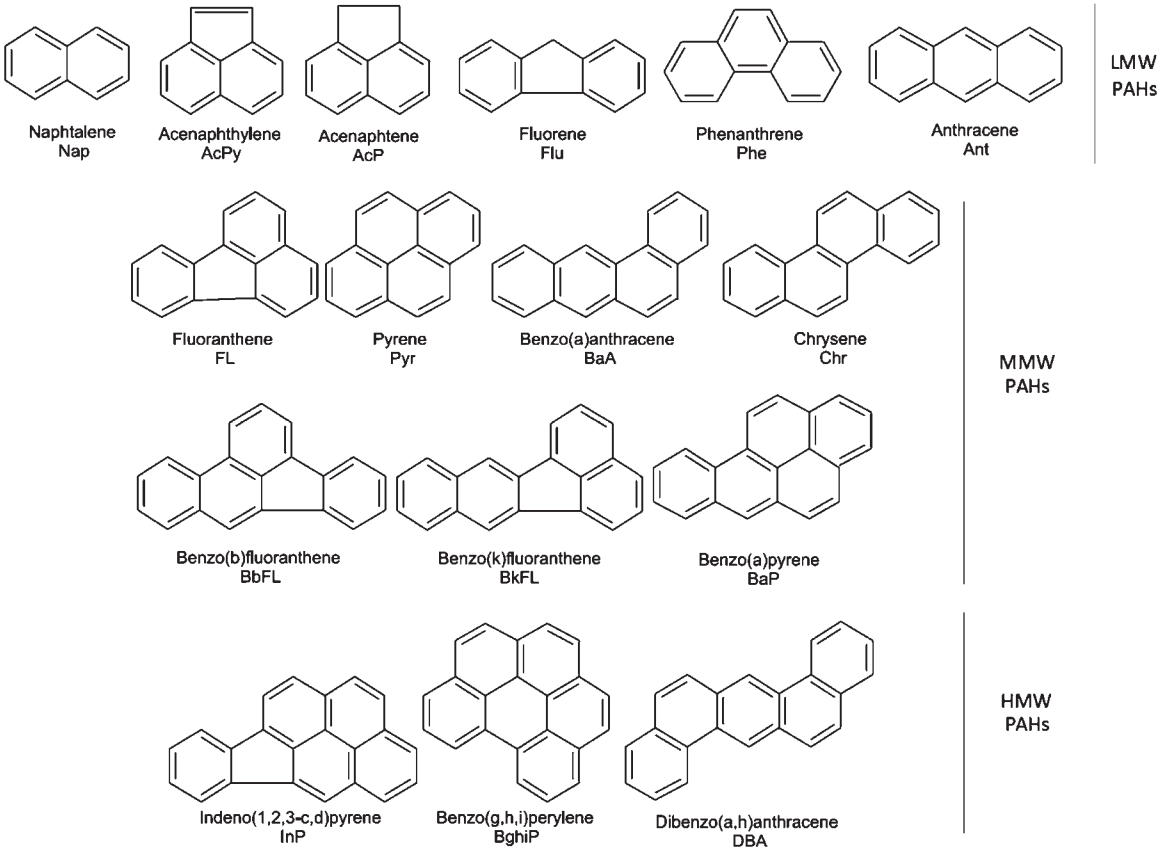

Figure 1. Structures of the 16 U.S. EPA PAHs studied in our work. LMW, low molecular weight; MMW, medium molecular weight; HWW, high molecular weight HMW.

to force the sample through the cartridge for the analysis of peptides, proteins, and DNA.[18]

In the present work, a new approach for an economical, fast, and efficient SPE method using centrifugation was proposed and developed for the analysis of the 16 U.S. EPA PAHs in aqueous samples. Parameters affecting the recovery, extraction tim, and solvent consumption were studied and optimized: Selection of the Cartridge Type (section 3.1), Breakthrough Volume (section 3.2), Drying after Sample Loading (section 3.3), Elution Solvent (section 3.4), and Evaporation Step (section 3.5).

2. MATERIALS AND METHODS

2.1. Chemicals, Standards, Solvents, and Small Apparatus. All chemicals were of analytical reagent grade and were used without further purification. The 16 U.S. EPA PAHs (Figure 1) were purchased from ChemService as mix Standard Reference Solution of 100 mg/L in methanol (PPH-10 rpm), Chem Service, West Chester, PA): naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benzo[*a*]anthracene (B[*a*]A), chrysene (Chr), benzo[*b*]fluoranthene (B[*b*]FL), benzo[*k*]fluoranthene (B[*k*]FL), benzo[*a*]pyrene (B[*a*]P), indeno[1,2,3-*cd*]pyrene (InP), dibenzo[*a*,*h*]anthracene (DBA), and benzo[*ghi*]perylene (B[*ghi*]P). Intermediary solutions (containing 10 mg/L of each analyte) were prepared by diluting the standard reference solution of PAHs with an appropriate solvent (ethanol, acetone, or isooctane). From the intermediary solutions, PAH working solutions at a level of 1 mg/L were prepared. The pure solid surrogate standards, naphthalene-d_8 (Nap-d_8), phenanthrene-d_{10} (Phe-d_{10}), anthracene-d_{10} (Ant-d_{10}), fluoranthene-d_{10} (FL-d_{10}), chrysene-d_{12} (Chr-d_{12}), benzo[*e*]pyrene-d_{12} (B[e]P-d_{12}), benzo[*a*]pyrene-d_{12} (B[a]P-d_{12}), and benzo[*ghi*]perylene-d_{12} (B[ghi]P-d_{12}), were purchased from Supelco (Bellefonte, PA) with two additional deuterated PAHs, pyrene-d_{10} (Pyr-d_{10}) and benzo[*b*]fluoranthene-d_{12} (B[b]FL-d_{12}), used as internal standard at the end of the protocol. Separate 1000 mg/L stock solutions of each deuterated standard were prepared by dissolving about 0.01000 g of the corresponding compound in isooctane or ethanol. Intermediary 50 mg/L deuterated mix solutions of surrogate and internal standards were prepared in different solvents (ethanol, acetone, or isooctane), and working solutions at a level of 2 mg/L were prepared by appropriate dilution. All standard solutions were stored at −20 °C.

Solvents (methanol (MeOH), ethanol (EtOH), acetone, dichloromethane (DCM), hexane (Hex), and isooctane) of HPLC grade were obtained from Merck (Darmstadt, Germany), BDH (VWR, USA), LabScan (POCH, Gliwice), Sigma-Aldrich (St. Louis, MO), and Romil (Waterbeach, Cambridge). Two salts (NaCl and Na_2SO_4) were purchased from Sigma-Aldrich. SPE Chromabond C18 ec polypropylene 3 mL cartridges packed with 200 mg of adsorbent were purchased from Machery-Nagel (Duren, Germany). A Vac Elut SPE vacuum manifold from Varian (Santa Clara, CA) with a Visiprep large-volume sampler from Supelco (Sigma-Aldrich, St. Louis, MO) was used to simultaneously process up to 20 cartridges. An analytical balance from Sartorius (±0.01 mg; Goettingen, Germany) was used. A Boeco centrifuge (model U-320R, Boeco, Germany) was employed in different steps of the preparation method. A sample concentrator from Techne (Staffordshire, U.K.) was used for sample concentration under nitrogen. Other small apparatus such as an ultrasonic bath and a vortex shaker were used.

2.2. SPE Experimental Procedure. During a regular SPE process a sequence of operations must be reproduced carefully to avoid additional changes; this was taken into account in the optimization carried in our

Table 1. Ions Monitored for Each Analyte Studied, Surrogate Standard, and Corresponding Internal Standard

compound	*m/z*	surrogate standard	*m/z*	internal standard	*m/z*
Nap	128, 129	Nap-d_8	136, 137, 135	Pyr-d_{10}	212, 211, 213
AcPy	152, 151, 153	Phe-d_{10}	188, 189, 184		
AcP	154, 153, 152				
Flu	166, 165, 167				
Phe	178, 176, 179				
Ant	178, 176, 179	Ant-d_{10}	188, 189, 184		
FL	202, 200, 203	FL-d_{10}	212, 213		
Pyr	202, 200, 203				
B[*a*]A	228, 226, 229	Chr-d_{12}	240, 236		
Chr	228, 226, 229				
B[*b*]FL	252, 250	B[e]P-d_{12}	264, 263	B[b]FL-d_{12}	264, 263
B[*k*]FL	252, 250				
B[*a*]P	252, 250	B[a]P-d_{12}	264, 263		
InP	276, 277, 274	B[ghi]P-d_{12}	288		
DBA	278, 276				
B[*ghi*]P	276, 277, 274				

study. The sum of the 16 PAHs analyzed in this study was evaluated in a high-quality Lebanese drinking water (mineral spring water), and its low value was considered to be negligible, so it was used as a blank during the experiments. Samples were prepared by spiking blank water with target analytes at a known concentration (0.05 μg/L). The eight deuterated PAHs used as surrogate standards were added at this stage at the same concentration. For the preconcentration step, the Chromabond C18 cartridges were preconditioned and activated at the beginning with 3 mL of methanol and then 3 mL of water. Each water sample was percolated using a regulated vacuum through the SPE cartridge with a flow rate of 5−10 mL/min, and then the cartridge was dried. The analytes were eluted by percolating the elution solvent on the SPE cartridge at atmospheric pressure. When the centrifugation was used for sample elution, the solvent was added to the cartridge with the valve closed, then the cartridge was centrifuged, and finally the elute was recovered. The extract, if necessary, was stored at about −20 °C until analysis or was evaporated directly to about 100 μL with a weak nitrogen stream. The obtained extract was reconstituted in 200 μL of isooctane, and the solution of recovery internal standards (Pyr-d_{10} and B[b]FL-d_{12}) was added. Samples were stored in the dark at about −20 °C until measurement.

2.3. Gas Chromatographic−Mass Spectrometric (GC-MS) Analysis. The analysis of PAHs was carried out on an Agilent 6890N gas chromatograph coupled to an Agilent 5975 mass spectrometer system (GC-MS) with an Agilent 7683B autosampler (Agilent Technologies, Santa Clara, CA). Chromatographic separation was performed on a HP-5MS fused silica capillary column (30 m, 0.25 mm, 0.25 μm, Agilent J&W GC columns). Helium (purity > 99.999%) was used as the carrier gas at a flow rate of 1.5 mL/min. The split−splitless injector temperature was set at 240 °C. The GC oven was initially held at 50 °C for 2 min and then programmed to 155 °C at a rate of 5 °C/min. After being kept at 155 °C for 2 min, the oven was programmed to 280 °C at a rate of 3 °C/min. Finally, it was held for 2 min to achieve a running time of 69 min. The mass spectrometer was operated in the electron ionization mode (EI, 70 eV). Transfer line, ion source, and quadrupole analyzer temperatures were maintained at 280, 230, and 150 °C, respectively, and a solvent delay of 10 min was selected. The injection volume was 1 μL, and all injections were in splitless mode. Selective ion monitoring (SIM) mode was adopted for quantitative determination of the analytes using two or three ions for each compound. The ions monitored for each analyte, the surrogate standards, and the corresponding internal standards are summarized in Table 1. The first ion, which in all cases corresponded to the molecular mass, was used as quantifier, and the second and the third ions were used as qualifiers.

3. RESULTS AND DISCUSSION

The purpose of this study was to develop and optimize a new SPE method using centrifugation for the analysis and ultratrace quantification of the 16 PAHs identified by the U.S. EPA as priority pollutants in water samples. Experiments were performed to evaluate the different SPE parameters and carried out in triplicates. The purpose was to determine the recoveries of the compounds in each individual step to evaluate the optimal conditions.

3.1. Selection of Cartridge Type. PAHs belong to the class of weak polarity organic compounds. According to the rule of like dissolves like, a SPE sorbent with similar polarity will facilitate enrichment. At present, the preferred SPE sorbent for the extraction of PAHs from water is reversed-phase carbon 18 bonded-silica (C18) as it gives the best performance among the different SPE polymeric and carbon-based sorbents.[19,20] On the basis of the theoretical principle as well as literature account, SiO_2-C18 was selected as the SPE sorbent in this study.

3.2. Breakthrough Volume. Breakthrough of the analyte occurs either when the analyte is no longer retained by the sorbent

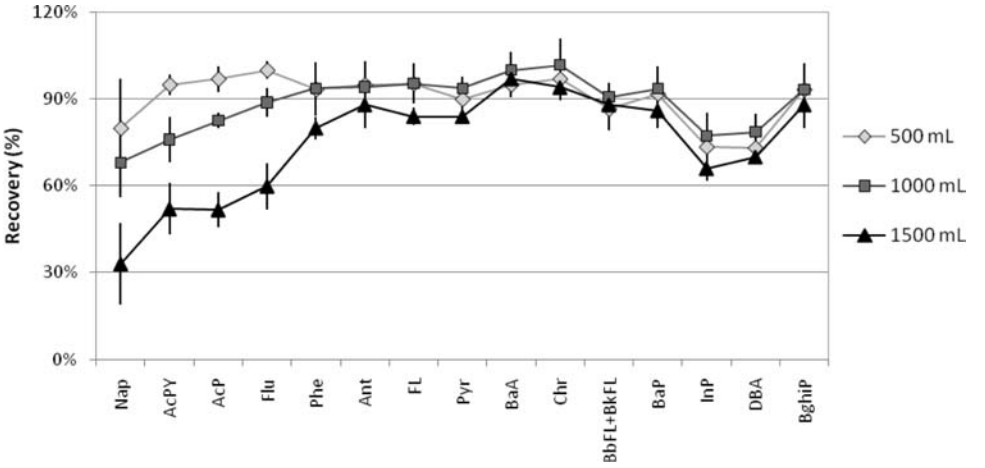

Figure 2. Extraction recovery (%) of the 16 PAHs obtained for a loaded sample volume between 500 and 1500 mL with 0.05 μg/L of analyte.

or when the capacity of the sorbent has been overloaded.[21] In practical environmental analysis, the need to determine trace amounts of organic compounds has led to an increase of the sample volume from a few milliliters to hundreds of milliliters and even liters,[18,22] and consequently breakthrough becomes more of a concern. Some authors have shown experimentally that the retention and recovery of analytes depend on the sample volume that flows through the SPE cartridge.[23] For PAH analysis, the sample volume ranged between 50 mL[17] and 2 L[24] depending on the concentration of analytes in water, the quantity of adsorbent in the SPE cartridge, and the detector sensitivity in the analytical method.

Predicting the breakthrough volume based on the analogy between liquid chromatography (LC) and SPE has largely been described by Hennion et al.[25] Among the various tools for predicting recoveries according to the percolated sample volume, the most important factor is the retention factor of the analyte in water, K_w. Another mathematical approach was developed by Ferrer et al.[26] and successfully applied to calculate the breakthrough volume of 15 PAHs. The calculated values of the breakthrough volume were compared to those obtained experimentally with no significant differences.

In our study, we varied the loaded volume on the cartridge between 500 and 1500 mL to determine the possible loss of PAHs. The chosen volumes took into consideration the concentration factor of analytes needed and the period required for the percolation of the whole volume on cartridge. As seen in Figure 2, there was no apparent decrease in recoveries with water volume between 500 and 1000 mL except for the four LMW PAHs (Nap, AcPy, AcP, and Flu), for which the recovery fell by only 10−20%. For a volume of 1500 mL, the recoveries of the LMW PAHs decreased significantly to about 40%. The medium molecular weight (MMW) and high molecular weight (HMW) PAHs did not show any recovery change with volume up to 1500 mL. The relative standard deviations varied between 1 and 9% for all of the compounds and by up to 17% for Nap. Consequently, a volume between 500 and 1000 mL can be safely selected as the sample volume.

3.3. Drying after Sample Loading. After sample loading, the concentrated analytes should be removed from the cartridge with an appropriate organic solvent. It must be kept in mind that the SPE column will usually be filled with water at this point. Thus, immediate elution will produce an effluent containing some water, which is not compatible with the analytical instrument

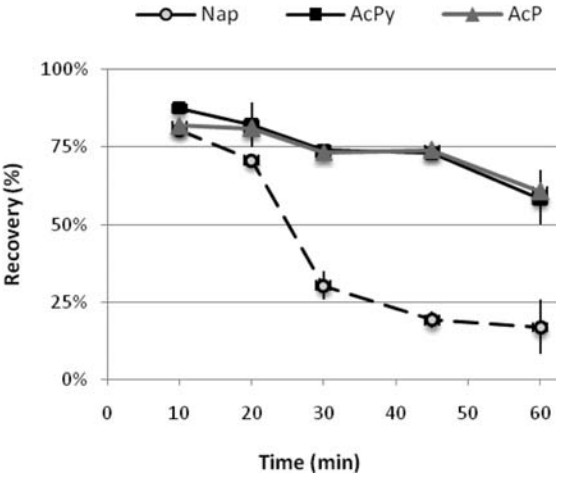

Figure 3. Recoveries (%) of Nap, AcP, and AcPy for a drying time between 10 and 60 min under vacuum. Sample volume was 500 mL with 0.05 μg/L of analyte.

to be used (GC-MS). On the other hand, the drying step is an important aspect to be taken into account when an apolar solvent is used to elute the PAHs. If the drying process is ignored and the pores are still filled with water, the eluting solvent cannot penetrate the pores or can penetrate them only slowly because of immiscibility and/or reasons of viscosity. As a result, lower recovery and lower repeatability may be obtained.[13]

The step of drying is critical due to the high volatility of the LMW PAHs. Oleszczuk and Baran[20] found that the complete drying of the SPE column resulted in losses of volatile PAHs of 10−20%. In the work of Delhomme et al.,[17] recoveries of 0 and 10% were observed for Nap and AcPy when the cartridge was dried under vacuum for approximately 20 min. For these reasons, we decided to evaluate the losses of volatile PAHs during the drying step of the cartridge under vacuum at different specific durations (10, 20, 30, 45, and 60 min) for a 3 mL SPE tube with 200 mg of sorbent. Results of recoveries obtained for the three more volatiles PAHs (Nap, AcPy, and AcP) are presented in Figure 3.

Some previous observations were confirmed in our experiments. Drying for more than 20 min under vacuum decreased significantly the recovery of volatile PAHs, especially Nap, for

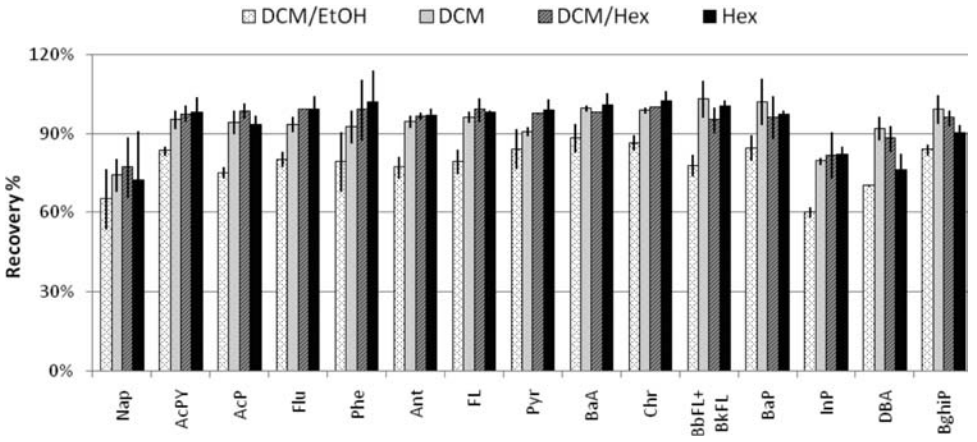

Figure 4. Influence of elution solvent polarity (DCM/EtOH, DCM, DCM/Hex, and Hex) on the recoveries of the 16 PAHs extracted from 500 mL of sample with 0.05 μg/L of analyte. Cartridges were dried with 2 min of centrifugation followed by 10 min under vacuum.

which a loss of 70% was observed (Figure 3). Lower decreases were noted for the less volatile PAHs (approximately 25% for AcPy and AcP). Besides, the Nap contamination from laboratory atmosphere increased with drying time as a blank cartridge showed. However, a duration of 30 min was necessary to achieve the complete drying of 200 mg of sorbent after the percolation of the water volume (1000 mL) in the 3 mL SPE cartridge. That is why we tested the centrifugation technique (2500 rpm for 2 min) immediately after sample application to eliminate the residual water from the cartridge and try to accelerate the vacuum drying. A successful decrease in the time required to dry the SPE sorbent to about 10 min was reached with recoveries between 77 and 82% for the three volatile PAHs. The relative standard deviations of the three triplicates were between 0.12 and 9%.

As a result, decreasing the drying time by centrifugation to about 10 min presented many benefits. It restricted the losses of the volatile PAHs, especially the Nap, reduced the time needed for the analysis, and limited the possible contamination.

3.4. Elution Conditions. The next step after drying the cartridge was to evaluate the elution parameters. Three elution conditions were studied, and recoveries were evaluated: the nature of the elution phase, the elution phase volume, and the investigation of the centrifugation.

3.4.1. Nature of the Elution Phase. The ideal elution solvent should be strong enough to elute all of the target compounds. The elution strength of the organic solvent depends on the type of sorbent used. For the reversed phase sorbent, an organic solvent with lower polarity will exhibit stronger elution. In the surveyed scientific literature, a considerable number of single organic solvents and mixtures with low polarities have been used for the elution of PAHs from a C18 cartridge. DCM,[27] Hex,[28] and their mixture (50:50 (v/v))[29] have been used extensively for this purpose with acceptable recoveries. These elution phases with a sufficient volume of 9 mL were tested in our study for the elution of the 16 analyzed PAHs. A more polar mixture of DCM/EtOH (50:50, (v/v)) was also tested to study the influence of the polarity.

According to the results shown in Figure 4, recoveries of all PAHs increased when the polarity of the elution phase was decreased, especially for the HMW PAHs. Recoveries of 61, 70, and 83% were obtained for InP, DBA, and BghiP with DCM/EtOH; 79, 92, and 99% with DCM, 82, 88, and 96% with DCM/Hex; and 82, 76, and 90% with Hex. The relative standard deviations were below 10% for the HMW compounds. Therefore, to ensure higher recoveries of PAHs, DCM, DCM/Hex, or Hex is recommended as elution solvent. In addition to the elution strength, DCM presents another advantage, which is the high vapor pressure necessary to achieve quick and effective solvent evaporation. Therefore, remaining experiments were conducted with DCM.

3.4.2. Elution Phase Volume. After the nature of the elution phase has been chosen, it is important to find the appropriate volume needed for a complete elution of the 16 analyzed PAHs. Different volumes of DCM, 3, 5, 7, and 9 mL, were evaluated, and recoveries are presented in Figure 5.

Using only 3 mL of DCM, the less hydrophobic PAHs or LMW PAHs were completely eluted (77% for Nap, 72% for AcPy, 69% for AcP, 81% for Flu, and 86% for Phe), but the volume of 3 mL was not sufficient for the elution of the HMW PAHs (48% for BghiP as for DBA and 51% for InP). When the amount of DCM was increased from 3 to 5 mL, recoveries increased slightly (11% for BghiP, 5% for DBA, and no significant difference for InP). Further increases to 7 and 9 mL resulted in remarkable additional increases in the recoveries of HMW PAHs (by as much as 17% for BghiP, 23% for DBA, and 35% for InP). As a result, 9 mL of DCM was required to ensure a maximum elution of the 16 PAHs, especially the HMW PAHs. The relative standard deviations of the three repetitions at each elution volume were between 0.23 and 16.19%.

3.4.3. Effect of Centrifugation. Previous experiments proved that 9 mL of DCM per sample is required for the quantitative elution of all 16 PAHs from the SPE cartridge. The 9 mL per sample is not an enormous quantity of solvent when only a few samples are being analyzed, but during monitoring programs and routine analyses of PAHs, thousands of samples are analyzed annually, which greatly increases the consumption of DCM and the costs of the analysis. Moreover, the evaporation of 9 mL of DCM under a weak stream of nitrogen may take up to an hour, which is a waste of time. Therefore, reducing the elution volume is a necessity to decrease the need for a long evaporation step and consequently the risk of loss of high vapor pressure compounds.

For this purpose, centrifugation was investigated as an alternate technique for elution. In the first experiment, we applied a centrifugation technique for 1 min at 2300 rpm using 1 mL of DCM three times. The total volume of elution solvent of 3 mL was analyzed and compared to the regular elution directly on cartridge using 3 and 9 mL of DCM. It is clear in the results

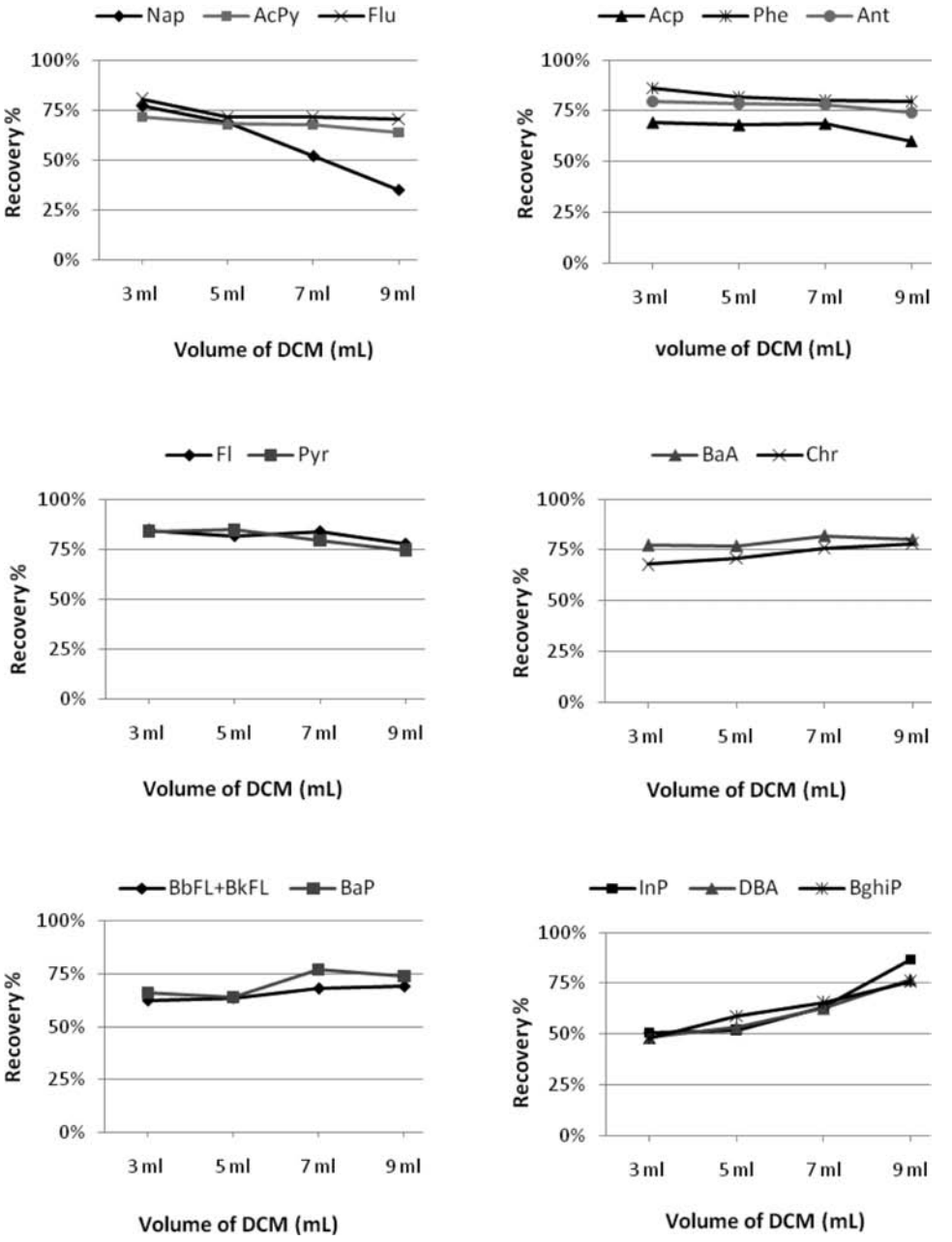

Figure 5. Effect of the elution volume of DCM (3, 5, 7, and 9 mL) on the recoveries of the 16 PAHs extracted from 500 mL of sample with 0.05 μg/L of analyte. Cartridges were dried with 2 min of centrifugation followed by 10 min under vacuum.

illustrated in Figure 6 that the recoveries obtained using only 3 mL of DCM with centrifugation were comparable to those with 9 mL of DCM for the HMW PAHs and better for the LMW PAHs. In fact, the rapid rotation of the centrifuge with the valve closed ensures that the adsorbent is well impregnated with the elution solvent, enabling a complete desorption of the analytes into the solvent; thus, when the valve was open, a complete elution of analytes, even the strongly adsorbed HMW PAHs, was done using a small volume of solvent. The relative standard deviations of the 16 PAHs were all below 5%.

During elution using centrifugation, each 1 mL of DCM was recovered and analyzed separately by GC-MS (Figure 7). For all 16 PAHs analyzed, a recovery of >70% was achieved with only 1 mL of DCM, and the relative standard deviations were below 10%. In the second and third elution volumes, an insignificant amount of analytes was found. Centrifugation speed and time are not critical factors in the elution as long as they are sufficient to ensure that the stationary phase is well impregnated with the elution solvent.

3.5. Evaporation Step. Evaporation is an important step in sample preparation to be considered and discussed, because it affects directly the recoveries and the time needed for sample analysis. The 16 PAHs selected in our study are a group of compounds with different physicochemical properties; the LMW PAHs present a high vapor pressure that could lead to loss during the evaporation, contrary to the HMW PAHs. Several factors influence the evaporation rate and losses of compounds: type of solvent, initial solvent volume, applied temperature, and nitrogen flow.

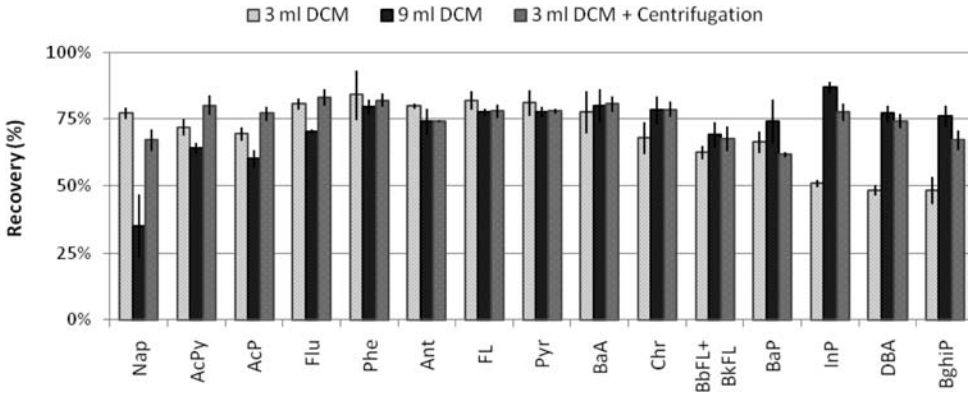

Figure 6. Comparison between recoveries obtained for elution on cartridge (3 and 9 mL of DCM) and elution with centrifugation using only (3 × 1 mL) DCM. Sample volume was 500 mL with 0.05 μg/L of analyte. Cartridges were dried with 2 min of centrifugation followed by 10 min under vacuum.

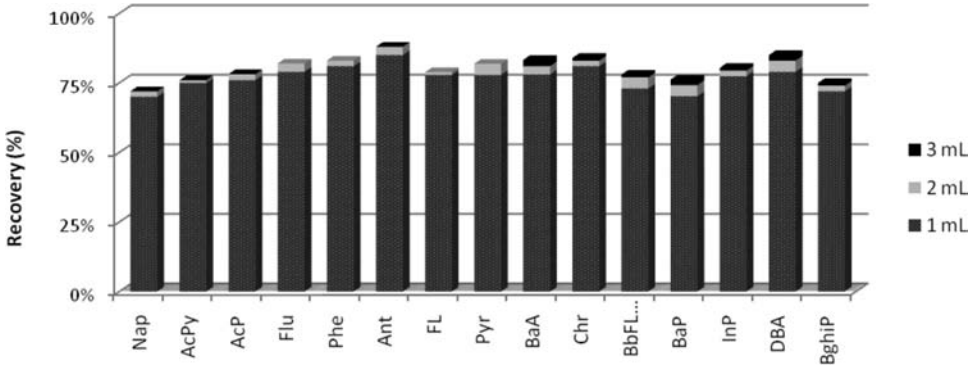

Figure 7. Recoveries of the 16 PAHs in each 1 mL of DCM. Sample volume was 500 mL with 0.05 μg/L of analyte. Cartridges were dried with 2 min of centrifugation followed by 10 min under vacuum.

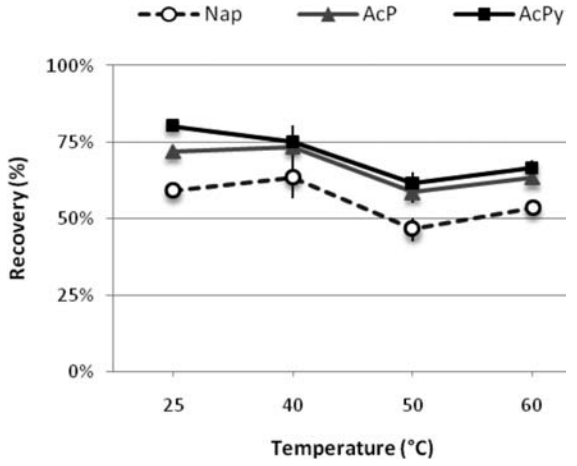

Figure 8. Effect of evaporation temperature (25, 40, 50, and 60 °C) on recoveries of Nap, AcPy, and AcP for the concentration of 1 mL of DCM containing 0.05 μg of each analyte.

3.5.1. Temperature Effect. Heating should be supplied to the sample to obtain a rapid and efficient evaporation. In the absence of any external heating source, the sample under nitrogen flow evaporates and cools until the vapor pressure is very low and the evaporation slows dramatically. The applied temperature is a critical factor during the evaporation step because overheating can lead to high losses of the more volatile two- and three-ring PAHs.

For reasons of simplicity the three more volatile PAHs (Nap, AcPY, and AcP) were selected to determine the optimal operating conditions. Triplicate samples of 1 mL of DCM containing 0.05 μg of each analyte were concentrated at 25, 40, 50, and 60 °C, and the results are illustrated in Figure 8.

A decrease in recoveries was observed with temperature. Recoveries of Nap, AcPy, and AcP were by 11−14% lower for a temperature above 40 °C. Therefore, to avoid losses of the LMW PAHs during the evaporation step, a temperature lower than 40 °C is recommended. A temperature of 35 °C was chosen as optimal for the elimination of DCM during the optimization of concentration conditions by Fladung.[16]

3.5.2. Type and Initial Volume of Solvent: Effect of the Addition of Isooctane. The type and initial volume of solvent are directed by the previous elution step. A low initial volume can reduce 9−10 times the evaporation period, from 45 min for 9 mL to <5 min for 1 mL of DCM.

Even when the chosen evaporation conditions were used, relatively low recoveries of LMW PAHs were observed (between 59 and 77%). To try to ameliorate these results, a "solvent keeping" approach was tested, wherein a volume of isooctane was added to each sample of DCM. Isooctane (boiling point = 99.2 °C) is less volatile than DCM (boiling point = 40 °C), in which the samples were dissolved. The object was to verify if LMW PAHs could be successfully concentrated into the residual

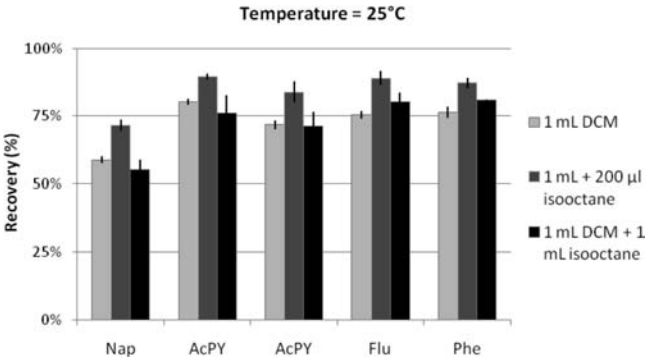

Figure 9. LMW PAH recoveries following concentration from 1 mL of DCM (0.05 μg of each analyte), with and without the addition of isooctane (200 μL and 1 mL) at 25 °C.

isooctane and retained during the elimination of the DCM. A mix containing the LMW PAHs (0.05 μg) was spiked into 1 mL of DCM with and without the isooctane addition (200 μL and 1 mL). The samples were evaporated at 25 °C.

The results presented in Figure 9 show a beneficial effect for the recoveries of the LMW PAHs. When an initial volume of 1 mL of DCM was used, the experiments carried out with the addition of 200 μL of isooctane showed a more pronounced improvement on recoveries than the addition of 1 mL of isooctane.

Isooctane was selected not only for its possibility to capture LMW PAHs during DCM evaporation but also for its low expansion volume after vaporization inside the GC-MS liner. This allows an injection of a higher volume of sample than DCM with an expanded vapor volume not exceeding the capacity limit of the liner.

3.6. Surrogate Standard Recoveries. Recoveries of surrogate standards added to water samples prior to extraction were evaluated as well using the optimal SPE conditions described above. The test was carried out in triplicate. The results, presented in Table 2, indicate average recoveries of 61−94% for the eight deuterated PAHs. The surrogate standards with the lowest and highest molecular weights, Nap-d_8 and B[ghi]P-d_{12}, had lower recoveries. The precision (relative standard deviation) of the recovery was generally better than 10% except for the Nap-d_8 (15%) due to its high volatility.

This work presents for the first time an SPE method using the centrifugation technique for the extraction of PAHs from water samples. The proposed method shows practical environmental and economical advantages in terms of sample preparation time, simplicity, reduction in solvent use, and cost and is particularly suitable for routine applications requiring a high sample throughput. Optimized conditions include the percolation of a sample volume between 500 and 1000 mL on a C18 cartridge and a drying step using centrifugation followed by 10 min under vacuum. The evaluation of the elution parameters demonstrated that 1 mL of DCM with centrifugation was successfully used for the elution of analytes. The concentration was performed at a temperature below 40 °C after the addition of 200 μL of isooctane. Under the optimized conditions, this method showed good recoveries for the 16 U.S. EPA PAHs between 70 and 85% with relative standard deviations between 1 and 14%. Surrogate standard recoveries were similarly between 61 and 94% with relative standard deviations between 2 and 15%.

Table 2. Recoveries and Relative Standard Deviations of Surrogate Standards for the Optimal Conditions

surrogate standard	recovery (%)	relative standard deviation (%)
Nap-d_8	65.6	14.7
Phe-d_{10}	93.8	6.6
Ant-d_{10}	92.2	3.9
FL-d_{10}	92.9	2.2
Chr-d_{12}	87.5	4.0
B[e]P-d_{12}	81.2	8.1
B[a]P-d_{12}	85.5	8.8
B[ghi]P-d_{12}	60.6	9.5

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ABBREVIATIONS USED

AcP, acenaphthene; AcPy, acenaphthylene; Ant, anthracene; BaA, benzo[*a*]anthracene; BaP, benzo[*a*]pyrene; BbFL, benzo[*b*]fluoranthene; BghiP, benzo[*ghi*]perylene; BkFL, benzo[*k*]fluoranthene; Chr, chrysene; DBA, dibenzo[*a*,*h*]anthracene; DCM, methylene chloride; EtOH, ethanol; EU, European Union; FL, fluoranthene; Flu, fluorene; GC-MS, gas chromatograph coupled to mass spectrometer; Hex, hexane; HMW PAHs, high molecular weight PAHs; InP, indeno[1,2,3-*cd*]pyrene; K_w, retention factor of the analyte in water; LC, liquid chromatography; LLE, liquid−liquid extraction; LMW PAHs, low molecular weight PAHs; MeOH, methanol; MMW PAHs, medium molecular weight PAHs; Nap, naphthalene; PAHs, polycyclic aromatic hydrocarbons; Phe, phenanthrene; Pyr, pyrene; RPM, revolutions per minute; SIM, selective ion monitoring; SiO_2-C18, reversed-phase carbon 18 bonded-silica; SPE, solid-phase extraction; U.S. EPA, U.S. Environmental Protection Agency.

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