A Comparison of the Performance of Two Chromatographic and Three Extraction Techniques for the Analysis of PAHs in Sources of Drinking Water

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Abstract

The aim of this work is to establish a sensitive and reliable method for the analysis of the 16 priority Environmental Protection Agency-defined polycyclic aromatic hydrocarbons (PAHs) found in water samples. Gas chromatography (GC)–mass spectrometry (MS) and high-performance liquid chromatography (HPLC)–fluorescence detection (FLD)-UV techniques are optimized to obtain an adequate resolution of all compounds. Validation of the methods is carried out, and a good performance is observed for both techniques. The HPLC–FLD-UV technique is somewhat more sensitive than the GC–MS technique for the determination of PAHs; thus, the HPLC–FLD-UV method is used to follow up both the solid-phase extraction (SPE) analysis using cartridges and discs and the liquid–liquid extraction (LLE), which are also evaluated for the extraction of the PAHs. Low recoveries between 43% and 79% are obtained using SPE cartridges, and higher values are obtained using SPE discs (56–96%) and LLE (60–105%). Better results are obtained using the LLE technique, and, thus, analysis of real water samples is carried out using this technique. LODs between 0.6 and 21 ng/L and relative standard deviations less than 15% are obtained using a spiked water sample analyzed using the full LLE HPLC–FLD-UV method.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic pollutants that are primarily released into the environment by the incomplete combustion of fossil fuels and the burning of vegetation and other organic materials (1–3). Because of their mutagenic and carcinogenic properties, these compounds are of interest in several environmental compartments, such as the atmosphere, soil, or natural water (4). The major routes of exposure to PAHs for the general population are from food and ambient and indoor air. The use of open fires for heating and cooking can increase exposure to PAHs. Where there are elevated levels of contamination from coal tar coating of water pipes, PAH intake from drinking water can equal or even exceed that obtained from food (2). The main source of PAH contamination in drinking water is from the coal tar coating of drinking water distribution pipes, which is used to protect the pipes from corrosion. However, washout from the atmosphere from precipitation or water runoff from the street and other surfaces are also pathways that bring PAHs into surface waters (5). Fluoranthene is the most commonly detected PAH in drinking water, and it is mainly associated with coal tar linings of cast iron or ductile iron distribution pipes (2).

Based on their toxicity, several PAHs are included in "priority" lists and are currently regulated in a number of countries. The US Environmental Protection Agency (EPA) has established a list of 16 PAHs that are "consent decree" priority pollutants (5). In drinking water, the US EPA has established a maximum contaminant level of 0.2 µg/L for benzo(a)pyrene (6), though the World Health Organization (WHO) has established a benzo(a)pyrene guideline contaminant value of 0.7 mg/L (2). A European Union Directive pertaining to water intended for human consumption proposes that the sum of the concentration of benzo(b)-fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene must not exceed 100 ng/L and limits the maximum concentration to 10 ng/L for benzo(a)pyrene (7). In Mexico, PAH levels are not regulated in drinking water, and these compounds are considered only for wastewater (8,9).

Several reference methods have been proposed for the analysis of PAHs, with the most common being high-performance liquid chromatography (HPLC) coupled with two detectors: a fluorescence detector (FLD) and a UV detector. Gas chromatography (GC) with a mass spectrometer (MS) is also used. Specific analytical protocols are described in detail in the US EPA Methods 550, 610, and 525 (10–12). Most methods use liquid–liquid extraction (LLE) to extract water samples (13–16) and solid-

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phase extraction (SPE) (13–15, 17–19), and, more recently, a solid phase microextraction (SPME) method has been developed (20–24).

In this work, a comparison in the performance of two chromatographic techniques (HPLC–FLU-UV and GC–MS) is carried out. The SPE and LLE techniques were evaluated during the sample treatment, and LLE HPLC–FLD-UV was applied in the analysis of real samples.

Experimental

Chemicals, reagents, and standards

All the reagents and chemicals used were HPLC-grade. The dichloromethane used was obtained from EMD Chemicals Inc. (Gibbstown, NJ), and the acetonitrile used was obtained from Fisher Scientific (Hampton, NH). The deionized water used was obtained using a Milli-Q water purification system (Millipore, Bedford, MA).

To carry out GC–MS analysis, a standard mixture of the 16 priority EPA PAHs [acenaphthene (ACE), acenaphtylene (ACY), anthracene (ANT), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BPY), benzo(a)pyrene (BaP), chrysene (CHR), dibenzo (a,h)anthracene (DBA), fluoranthene (FLT), fluorene (FLU), indeno(1,2,3-cd)pyrene (IND), naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR)] at a concentration of 2000 µg/mL in methylene chloride–benzene (1:1 v/v), a mixture of deuterated internal standards (IS) (acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}) at a concentration of 500 µg/mL in acetone, and deuterated surrogate standard perylene-d_{12} in methylene chloride at a concentration of 2000 µg/mL were purchased from Supelco (Bellefonte, PA). For LC, a standard mixture of the PAHs in an acetonitrile–methanol (9:1) was used at concentrations between 20 and 1000 µg/mL, obtained from Supelco. Stock standard solutions of PAHs were prepared in methylene chloride (100 µg/mL) for the GC–MS experiments and in acetonitrile (concentration = 1–50 µg/mL) for the HPLC experiments. Working solutions were obtained by dilution. All the solutions were stored in amber glass vials at 4°C.

GC

GC–MS analysis was performed using an Agilent 6890/5973 GC–MS system (Agilent, Palo Alto, CA) equipped with a split/splitless injection port, electronic ionization, and a quadrupolar mass analyzer. A PTE-5 fused-silica capillary column (30 m × 0.25-mm i.d., × 0.25-µm film thickness) was used (Supelco). Helium was used as the carrier gas at a flow rate of 1.1 mL/min. The injector was maintained at 280°C, and injection was carried out in the splitless mode.

The GC oven program began at 70°C, was held for a period of 1 min, before being ramped at 25°C/min to 340°C, and was held at that temperature for a period of 3.2 min. The MS was operated in the electron impact ionization positive mode (V = 70 eV), and quantitative analysis was carried out in the selected ion-monitoring mode. The ion source was maintained at 230°C, and the quadrupole was maintained at 150°C. The MS system was tuned using perfluorotributylamine. Table I shows the molecular and confirmation ions monitored for each compound, as reported by Martinez et al. (17).

A quantitative analysis of PAHs was performed using the IS method. Calibration curves, prepared in methylene chloride, were constructed using five analyte concentrations between 0.25 and 1.25 µg/mL. However, in the case of BbF, the concentration ranged from 0.10 to 1.00 µg/mL. The internal and surrogate standards were added to all calibration standards at a concentration of 2 µg/mL.

Liquid chromatography

HPLC–FLD-UV separation was carried out using a 2690 separation module equipped with a quaternary solvent delivery system, an autosampler, a column heater, a 2475 programmable FLD, and a 2996 UV diode-array detector (DAD) from Waters (Milford, MA). The column used was a Supelcosil LC PAH (250 × 4.6 mm, 5 µm; Supelco) connected to a guard column Symmetry C_{18} (20 × 3.9 mm, Waters).

Gradient elution was used to achieve the optimum separation of the PAHs. Solvent A was water, and solvent B was acetonitrile. The elution program contained a linear gradient from 60% to 100% of solvent B in a period of 12 min, followed by an isocratic step held for a period of 11 min. The flow rate was 1.5 mL/min, and the temperature of the column was maintained at 27°C. The column was equilibrated between runs, with the initial mobile phase being 7 min long. The PAHs were monitored using the fluorescence detector, with only ACY being recorded using the UV–DAD at a wavelength of 228 nm. The excitation and emission wavelengths were changed during the run to obtain the highest sensitivity for all compounds, with the wavelength program being: 8.5 min λ_{ex} at 224 nm and λ_{em} at 330 nm, followed by 2 min λ_{ex} at 254 nm and λ_{em} at 323 nm, 1.5 min λ_{ex} at 250 nm and

Table I. Molecular and Confirmation Ions Used for the Selected Ion Monitoring GC–MS Analysis

Compound	Molecular ion	Confirmation ions
NAP	128	127, 129
ACY	152	151, 153
ACE-d_{10} (IS)	164	162, 160
ACE	154	153, 152
FLU	166	165, 167
PHE-d_{10} (IS)	188	94, 189
PHE	178	176, 179
ANT	178	176, 179
FLT	202	201, 203
PYR	202	200, 203
BaA	228	226, 229
CHR-d_{12} (IS)	240	120, 236
CHR	228	226, 229
BbF	252	253, 126
BkF	252	253, 126
BaP	252	253, 126
PER-d_{12} (SURR)	264	260, 265
IND	276	138, 277
DBA	278	139, 276
BPY	276	138, 277

λ_{em} at 366 nm, 1 min λ_{ex} at 252 nm and λ_{em} at 400 nm, 0.7 min λ_{ex} at 235 nm and λ_{em} at 420 nm, 0.8 min λ_{ex} at 236 nm and λ_{em} at 390 nm, 1.5 min λ_{ex} at 270 nm and λ_{em} at 385 nm, 5 min λ_{ex} at 299 nm and λ_{em} at 430 nm, and finally, 1.4 min λ_{ex} at 305 nm and λ_{em} at 480 nm.

The samples were analyzed using the external calibration method. Calibration curves were constructed in acetonitrile at five concentration levels in the range 2.5–12.5 ng/mL for the most diluted analytes (ANT, BbF, and BkF) and 125–625 ng/mL for the most concentrated analyte (ACE).

SPE

SPE was carried out using both cartridges and disks. Supelclean Envi-18 (6 mL, 1 g) cartridges and Envi-18 DSK 47 mm SPE disks were obtained from Supelco. Extraction using cartridges was carried out using a Supelco Visiprep System, and extraction using disks employed a Supelco Disk TM Holder Manifold. Samples of Milli-Q water spiked with PAHs at concentrations between 0.010 and 0.500 µg/L were used to evaluate the performance of the SPE procedure.

The general scheme used for SPE extraction was the same for both cartridges and disks. Conditioning was carried out with 5 mL of methylene chloride followed by 5 mL of methanol and 10 mL of Milli-Q water. Water samples (250 mL) were then percolated through the extraction device. The stationary phase was left to dry completely, and then PAHs were recovered by successive elutions using 4, 3, and 3 mL of dichloromethane. Anhydrous sodium sulfate was added to the resulting extracts to eliminate any water residue. After filtration, the extracts were evaporated under nitrogen and reconstituted with 250 µL of acetonitrile for LC analysis.

LLE

Samples of Milli-Q water spiked with PAHs at concentrations between 0.010 and 0.500 µg/L were used to evaluate the performance of the LLE extraction.

A 250-mL water sample aliquot was transferred to a 500-mL separatory funnel, and 15 mL of methylene chloride was added. The separatory funnel was shaken for a period of 2 min, and the organic layer was separated and collected in a 50-mL flat-bottomed flask containing 2 g of anhydrous sodium sulfate. The extraction step was repeated twice, and the resulting extracts were combined. The combined extract was concentrated to a volume of approximately 1 mL using a rotary evaporator (BM 200, Yamato Scientific, Tokyo, Japan), and the extract was then evaporated under nitrogen gas to near dryness and then reconstituted in 250 µL of acetonitrile for chromatographic analysis.

Results and Discussion

Selection of the analytical method

As previously described, both the GC–MS and HPLC–FLD-UV techniques were evaluated with the aim of determining which was the most sensitive for the analysis of PAHs. In both cases, the working conditions were optimized to obtain a good separation for all the compounds. Achieving an adequate resolution between peaks was a challenging task because of the differences in the chemical properties of the PAHs. In fact, a number of methods do not include the 16 EPA priority PAHs, nor do they separate all the analytes, and quantitation is achieved with unresolved pairs (3,11,13,16,25–27). In this method, the established GC–MS and HPLC–FLD-UV conditions provided an excellent separation of PAHs, which allowed the individual quantitation of each compound. It must be noted that when compared with other reports (13,17,20,22), our GC–MS method achieved an important reduction in the analysis time of at least two times.

The performance of both chromatographic methods was evaluated by establishing the quality parameters. These parameters were determined using standard solutions, and the results

Table II. Quality Parameters Obtained Using the GC–MS and HPLC–FLD–UV Techniques

	GC–MS					HPLC–FLD-UV				
Compound	Linear range (ng/mL)	Determination coefficient (r^2)	Response factor RSD (%)	LOD (ng/mL)	LOQ (ng/mL)	Linear range (ng/mL)	Determination coefficient (r^2)	Response factor RSD (%)	LOD (ng/mL)	LOQ (ng/mL)
NAP	250–1,250	0.9994	5.13	34.80	104.40	62.5–312.5	0.9997	2.78	6.23	18.70
ACY	250–1,250	0.9990	3.68	42.71	128.13	62.5–312.5	0.9990	3.30	10.83	32.49
ACE	250–1,250	0.9991	6.02	41.50	124.50	125.0–625.0	0.9990	3.01	21.19	63.56
FLU	250–1,250	0.9991	4.47	41.40	124.20	12.5–62.5	0.9993	3.07	1.82	5.45
PHE	250–1,250	0.9996	6.52	80.49	241.47	5.0–25.0	0.9976	3.20	1.34	4.03
ANT	250–1,250	0.9980	3.57	61.08	183.24	2.5–12.5	0.9988	2.51	0.47	1.41
FLT	250–1,250	0.9979	3.79	63.50	190.50	6.25–31.25	0.9999	2.20	0.49	1.46
PYR	250–1,250	0.9978	3.89	64.90	194.70	12.5–62.5	0.9998	2.63	1.07	3.21
BaA	250–1,250	0.9986	5.24	51.91	155.73	6.25–31.25	0.9991	3.03	1.00	3.01
CHR	250–1,250	0.9958	6.31	89.19	267.57	6.25–31.25	0.9983	3.38	1.42	4.25
BbF	100–1,000	0.9992	6.89	35.71	107.14	2.5–12.5	0.9980	3.51	0.61	1.83
BkF	250–1,250	0.9966	6.07	79.79	239.37	2.5–12.5	0.9991	2.57	0.41	1.23
BaP	250–1,250	0.9989	7.83	45.35	136.05	6.25–31.25	0.9985	2.99	1.32	3.95
IND	250–1,250	0.9993	4.67	35.99	107.97	6.25–31.25	0.9956	5.87	2.28	6.85
DBA	250–1,250	0.9996	6.50	28.17	84.51	10.0–50.0	0.9993	2.26	3.75	11.24
BPY	250–1,250	0.9990	4.83	42.79	128.37	25.0–125.0	0.9988	2.95	1.89	5.68

obtained are shown in Table II. For each compound, linear ranges were established from the curves constructed by plotting the ratio of the analyte and internal standard areas in GC–MS and the analyte area in HPLC–FLD-UV versus concentration, as can be observed from the data shown in Table II. For both methods, all the PAH compounds showed a linear relationship over the selected concentration range with correlation coefficients > 0.99, and with relative standard deviations (RSDs) for the response factor < 8%. In all cases, slightly higher RSD values were obtained using the GC–MS method.

The limits of detection (LOD) and quantitation (LOQ) were established from the calibration curves. The LODs were estimated from the analytical background response (i.e., the *y*-axis intercept of the regression line) plus three times the standard deviation of this response (28). For the GC–MS technique, the LODs were between 28 and 89 ng/mL (for DBA and CHR, respectively), and for the HPLC–FLD-UV technique, lower values, from 0.41 to 21 ng/mL (for BkF and ACE, respectively), were obtained.

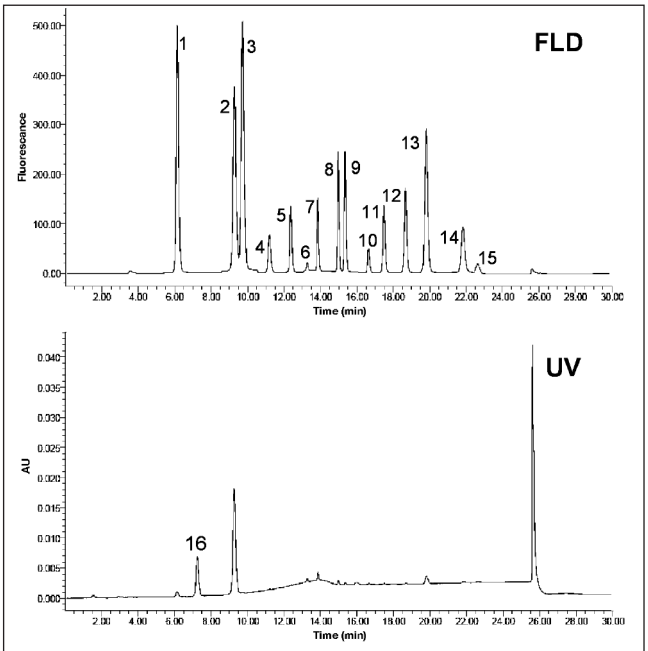

Figure 1. HPLC–FLD-UV chromatograms obtained for a standard solution of PAHs (0.01–0.5 µg/mL). Peak numbers are: 1, NAP; 2, ACE; 3,FLU; 4, PHE; 5, ANT; 6, FLT; 7, PYR; 8, BaA; 9, CHR; 10, BbF; 11, BkF; 12, BaP; 13, DBA; 14, BPY; 15, IND; and 16, ACY.

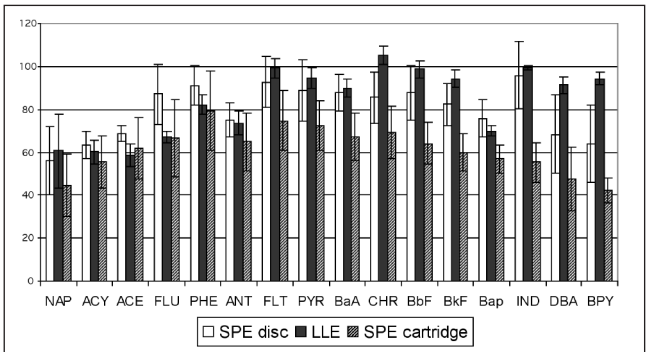

Figure 2. A comparison of the SPE method (discs and columns) and the LLE method.

In the same way, the LOQs were calculated as the analytical background response plus 10 times the standard deviation, and these values were between 84 and 267 ng/mL (for DBA and CHR, respectively) using the GC–MS method and from 1.2 to 64 ng/mL (for BkF and ACE, respectively) using the HPLC–FLD-UV technique.

The data show that accurate results can be achieved using both techniques, but that the HPLC–FLD-UV technique was somewhat more sensitive than the GC–MS technique for the determination of PAHs, enabling detection limits some 2 to 200 times lower for certain compounds. Also, the results compare well with those obtained by other authors, and, for example, Titato et al. (15) obtained values between 0.8 and 30 ng/mL using the HPLC–UV technique, and when using the HPLC–MS technique, Titato et al. achieved a lower sensitivity. In addition, using the GC–MS technique, Filipkowska et al. (13) obtained higher LOD values, between 50 and 300 ng/mL. As better results for the analysis of PAHS were obtained using the HPLC–FLD-UV method, this was selected as the method used to follow up on the analysis. Figure 1 shows the chromatograms obtained for a standard solution of PAHs (0.01–0.50 µg/mL) using the HPLC–FLD-UV method.

Comparison of SPE and LLE

The use of both SPE cartridges and discs and LLE for the extraction of PAHs in water samples was evaluated. Figure 2 shows a comparison of the methods, carried out by extracting the spiked water samples. In spite of the number of important papers dealing with the determination of PAHs in water samples that have been published, there is no general agreement on the best extraction technique for these analytes. Although some authors have used the SPE technique satisfactorily for PAHs in different matrices, such as water (13–15,17–19,25) or sediments (13,17), in this study, the lowest recoveries (43–79%) and the highest RSDs (11–33%) were obtained using the SPE technique with extraction cartridges. On the other hand, the use of disks gave better results, but the recoveries (56–96%) and RSDs (5–28%) were still less satisfactory than those obtained using the LLE method (recoveries of 60–105% and RSDs of 1–28%).

For the SPE method, the results obtained are comparable with those reported by other authors using reversed-phase extraction cartridges and discs (13–15,17–19). In this work, the best recoveries were obtained for the high molecular weight compounds, and the lower recoveries were observed for NAP, ACY, ACE, and FLU. This behavior was also observed by Filipkowska et al. (13), who demonstrated that high losses of the lightest PAHs occur during the evaporation step. In contrast to these data, some authors (14,18) have found better recoveries for the low molecular weight compounds using C_{18} SPE cartridges. It should be noted that not all the published works included the 16 EPA priority PAHs or were able to carry out individual quantitation of all the compounds, as the chromatographic separation was not complete for some analytes. In the case of the LLE technique, the results obtained in this laboratory were better than some recently published studies (13–15), as these authors were not able to analyze the low-molecular-weight PAHs. Moreover, the recoveries obtained are higher than those presented in the described works. Besides exhibiting better recoveries, the LLE

Table III. Determination of PAHs in a Spiked Water Sample Obtained From the Artificial Lake Rodrigo Gómez, Nuevo León, México

Compound	Spiked level (ng/L)	Recovery (%)	RSD (%)	Spiked level (µg/L)	Recovery (%)	RSD (%)	LOD (µg/L)
NAP	0.250	60.75	11.49	0.500	61.65	11.83	3.35
ACY	0.250	65.09	11.80	0.500	70.68	8.11	8.99
ACE	0.500	74.97	13.31	1.000	79.87	9.15	21.29
FLU	0.050	76.62	10.09	0.100	92.54	5.96	1.02
PHE	0.020	77.29	5.30	0.040	125.90	3.46	1.89
ANT	0.010	76.27	4.01	0.020	87.26	3.63	0.59
FLT	0.025	72.91	9.16	0.050	82.22	7.43	0.86
PYR	0.050	86.60	4.31	0.100	93.52	4.73	1.65
BaA	0.025	95.39	9.50	0.050	92.25	5.40	1.38
CHR	0.025	90.11	8.84	0.050	93.03	4.70	0.83
BbF	0.010	89.73	6.71	0.020	93.21	6.60	0.97
BkF	0.010	90.46	7.21	0.020	93.91	6.37	0.83
BaP	0.025	76.98	14.21	0.050	82.53	6.15	3.11
IND	0.025	88.82	4.80	0.050	78.92	13.51	4.59
DBA	0.100	87.68	7.75	0.200	85.83	6.36	5.99
BPY	0.040	91.83	9.12	0.080	85.35	6.40	4.20

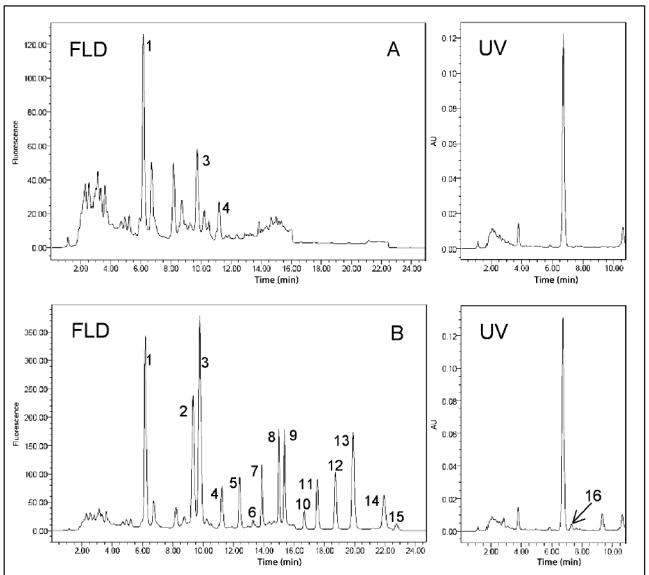

Figure 3. HPLC–FLD-UV chromatograms: a water sample obtained from the artificial Lake Rodrigo Gómez (Nuevo León, México) (A), and the same water sample spiked with PAHs at a concentration level of 0.01 to 0.5 µg/L (B). Peak numbers are 1, NAP; 2, ACE; 3, FLU; 4, PHE; 5, ANT; 6, FLT; 7, PYR; 8, BaA; 9, CHR; 10, BbF; 11, BkF; 12, BaP; 13, DBA; 14, BPY; 15, IND; and 16, ACY.

method had other advantages over the SPE procedure, such as a shorter analysis time and the possibility of processing several samples simultaneously. For these reasons, the LLE method was selected for further analysis.

Analysis of real water samples

The LLE HPLC–FLD-UV procedure was used to determine the PAHs in a water sample obtained from the artificial Lake Rodrigo Gómez, in Nuevo León, Mexico, which is an important drinking-water source for the metro area of Monterrey. Only NAP, at concentrations between 24 and 32 ng/L and FLU and PHE below their LOQs were found in the samples. In addition, a water sample was spiked at two concentration levels and analyzed in quintuplicate following the described procedure, and the recovery was calculated. The resulting data are shown in Table III. As can be observed in Figure 3, which shows the chromatograms obtained from the spiked and unspiked samples, the LLE method combined with the HPLC–FLD-UV method is a highly selective procedure for the analysis of PAHs in water, showing no interferences from other compounds that are potentially present in the sample matrix. No significant effect of the matrix was observed, and the recoveries were similar to those obtained from the Milli-Q water samples.

The LODs were estimated for the presented procedure as described in the chromatographic methods, and the values obtained are shown in Table III. The limits ranged from 0.6 to 21 ng/L and are of the same order of magnitude as those reported using the SPE technique (17–19) and the SPME technique (19,22,23). As can be seen from the data in Table III, the extraction step produced a significant improvement in the detection limits, which were much lower than those obtained by direct injection.

Conclusion

The LLE method, combined with the HPLC–FLD-UV technique, is a good approach for the analysis of low concentrations of PAHs in water samples. The good performance of the GC–MS and HPLC–FLD-UV methods developed was demonstrated, and although both techniques are adequate for the analysis of PAHs in water, a higher sensitivity was achieved using HPLC–FLD-UV. In addition, it was shown that within the extraction procedures evaluated, both SPE using extraction discs and LLE can be applied in the determination of all PAHs, even though the LLE technique gives slightly higher recoveries, lower RSDs, and shorter analysis times.

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