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Rapid screening of polycyclic aromatic hydrocarbons (PAHs) in waters by directly suspended droplet microextraction-microvolume fluorospectrometry

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ABSTRACT

A rapid and simple screening method for polycyclic aromatic hydrocarbons (PAHs) in water samples is proposed. The method is based on the combination of a miniaturized sample preparation approach, namely, directly suspended droplet microextraction (DSDME), and microvolume fluorospectrometry. Benzo[a]pyrene (BaP) was used as the model compound for screening purposes. Under optimal conditions, a detection limit of 0.024 $\mu g\,L^{-1}$ and an enrichment factor of 159 were obtained for BaP in 5 min. The repeatability, expressed as relative standard deviation (RSD), was 4.9% ($n = 8$). The unreliability region of the screening method was 0.54–0.67 $\mu g\,L^{-1}$, by using a cut-off value of 0.6 $\mu g\,L^{-1}$ of BaP. Finally, the proposed method was applied to the *in situ* achievement of the binary "yes/no" response for PAHs in different water samples and recovery studies were performed at three different levels, with BaP recoveries in the range of 93–104%.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants containing two or more condensed aromatic rings. From the existing PAHs, 16 compounds have been classified by the U.S. Environmental Protection Agency (EPA) as priority pollutants due to their toxicity, being benzo[a]pyrene (BaP) the most powerful carcinogen [1]. Due to its toxicity and environmental significance, BaP is often used alone to evaluate the risk [2]. The determination of PAHs in environmental water samples is not an easy task, as their concentrations in such samples are very low owing to their low solubility. In addition, serious adsorption losses of PAHs during sampling, transport and storage of water samples have been reported in the literature [3,4]. The development of analytical methods that allow rapid and reliable *in situ* field monitoring of PAHs is therefore of great interest.

Screening methodologies are commonly employed to achieve a binary 'yes/no' response in a simple and expeditious way. Routine laboratories are increasingly interested in reducing the number of samples to be analyzed by conventional analytical methods. In this sense, screening methodologies act as a filter, thus avoiding the need to analyze the whole set of samples by a conventional analytical method but a reduced subset of samples showing analyte concentrations above a pre-set concentration threshold. Such strategies have been recently introduced as 'vanguard–rearguard analytical systems' [5,6]. The employment of sample-screening systems (vanguard), eventually followed by confirmatory conventional analytical systems (rearguard), results in a reduction of costs, time and hazards, wherefore vanguard systems are considered green analytical methodologies [7]. Several examples of sample-screening systems can be found in the literature, including PAHs [2,8–10], heavy metals [11], hardness [12], *N*-nitrosamines [13], benzene, toluene, ethylbenzene and xylene in waters [14]; acetone [15] and non-polar heterocyclic amines in urine [16]; or volatile aldehydes [17], sulfonamides [18] and synthetic and natural colorants in foods [19].

Current sample preparation approaches are directed towards their miniaturization and automation, in accordance with the green analytical chemistry (GAC) principles [7]. Hence, several analytical methods have been developed for the determination of PAHs on the basis of solid phase microextraction (SPME) and related approaches [20–23]. On the other hand, the miniaturization of conventional liquid–liquid extraction has led to the development of different microextraction modes embraced under the term 'liquid-phase microextraction' (LPME) [24]. LPME approaches are nowadays considered as broad-spectrum sample preparation techniques as a result of the complementary capabilities of the different LPME modes. These miniaturized sample preparation approaches allow the achievement of large enrichment factors, being characterized by their simplicity and economy. In addition, the organic solvent

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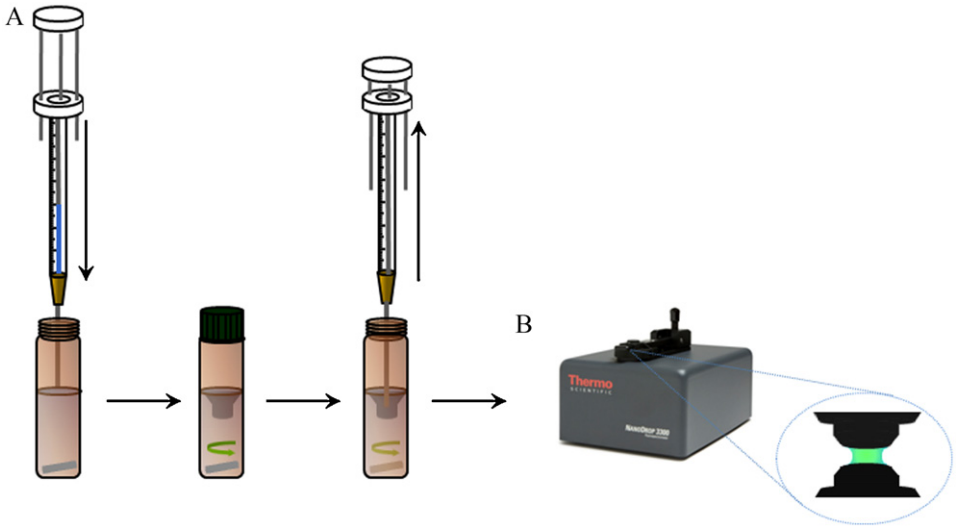

Fig. 1. Schematic representation of the DSDME-microvolume fluorospectrometric system used for the screening of PAHs: (A) DSDME of PAHs; (B) fluorescence spectra acquisition.

consumption and waste generation per analysis can be considered negligible. A number of publications concerning the determination of BaP and related PAHs in waters making use of different LPME approaches have been reported [25–31]. However, LPME approaches have been scarcely employed with screening purposes [32,33] and, to the best of our knowledge, this is the first report on the development of an LPME-based screening method for PAHs.

The aim of this work is to propose a rapid screening method based on the combination of a miniaturized liquid-liquid extraction approach, namely, directly suspended droplet microextraction (DSDME) [34], and a portable microvolume fluorospectrometer for PAHs in water samples.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Deionized water obtained from a Milli-Q water purifier (Millipore, Molsheim, France) was used throughout. A standard solution of benzo[a]pyrene (BaP) (100 mg L^{-1}) in CH_2Cl_2 was purchased from Supelco (Bellefont, PA, USA). Anthracene (Ant), fluoranthene (Flt), phenanthrene (Phe) and pyrene (Pyr) were supplied by Sigma–Aldrich (Milwaukee, WI, USA). Stock solutions were prepared by dissolution in ethanol (Merck, Darmstadt, Germany). Working standard solutions were prepared by appropriate dilution of the corresponding stock solution with methanol (Merck).

Toluene (Panreac, Barcelona, Spain), xylene (Fluka, Buchs, Switzerland), *n*-hexane (Merck) and 1-octanol (Merck) were tried as extractant phases.

NaCl (Merck) was used to evaluate the effect of the ionic strength of the sample on the extraction of BaP.

2.2. Apparatus

Fluorescence measurements were performed using a Nanodrop® (Thermo Scientific, Wilmington, DE, USA) model ND-3300 fluorospectrometer. The technical specifications of the instrument are outlined in a previous work [35]. Fluorescence measurements were carried out at 406 nm, using the UV LED as excitation source (excitation maximum at 365 nm).

2.3. DSDME procedure

A 5-mL water sample was introduced into a 7-mL amber vial together with a stir bar (10 mm × 3 mm). The sample was stirred at 1200 rpm in order to produce a benign vortex at the top of the sample solution. Then, 35 μL of toluene was injected at the bottom of the vortex and the vial was capped to minimize the evaporation of the solvent during the extraction process. After 5 min, the cap was removed and an aliquot of the extract was taken with a microsyringe while stirring to maintain the vortex. Finally, 2 μL of the extract was placed between the pedestals of the portable microvolume fluorospectrometer in order to obtain the corresponding analytical signal. A schematic diagram of the steps involved in the DSDME procedure and its combination with the microvolume fluorospectrometer is shown in Fig. 1.

3. Results and discussion

3.1. Fluorescence parameters

The selection of optimal excitation and emission wavelengths is of great importance for sensitive monitoring of PAHs. The cuvetteless microvolume fluorospectrometer used in this work provides three different LEDs (UV, blue and white) as excitation sources that cover a broad wavelength range (365–650 nm). Thus, a 2-μL drop of a 250 μg L^{-1} BaP solution was used to obtain the corresponding fluorescence emission spectra using the aforementioned excitation sources. The UV LED (365 ± 10 nm) provided the largest fluorescence intensity for BaP. Thus, the excitation/emission wavelength pair 365/406 nm was selected as optimum.

3.2. Optimization of DSDME

DSDME is based on the use of a microvolume of a low-density extractant phase in order to extract and preconcentrate the target analytes from a continuously stirred sample solution [34]. The impact of experimental variables on the DSDME procedure was evaluated. Thus, type and volume of extractant phase, stirring rate, extraction time, as well as the addition of NaCl to the sample, were optimized independently. Method optimization was carried out using a concentration of 3 μg L^{-1} of BaP. Three replicates were performed in all cases.

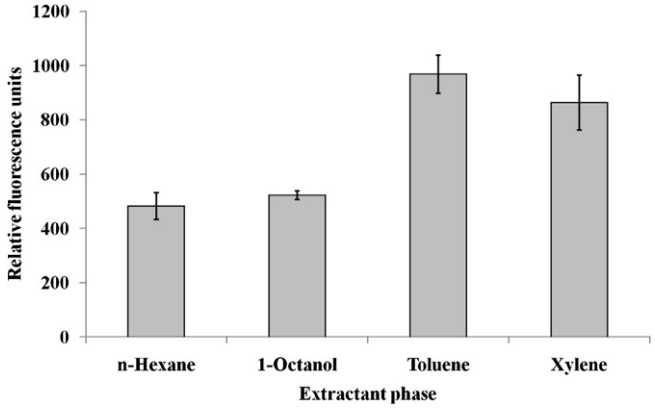

Fig. 2. Effect of the type of extractant phase on the DSDME of BaP. DSDME conditions: extractant phase volume, 40 μL; stirring rate, 1050 rpm; extraction time, 4 min. Error bars represent the standard deviation for $N = 3$.

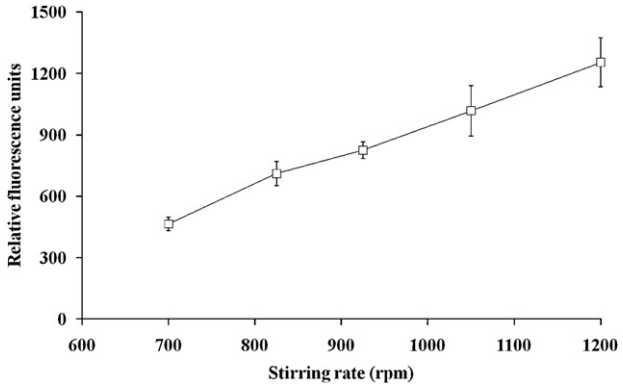

Fig. 4. Effect of the agitation of the sample solution on the DSDME of BaP. DSDME conditions: extractant phase, toluene; extractant phase volume, 35 μL; extraction time, 4 min. Error bars represent the standard deviation for $N = 3$.

3.2.1. Nature of the extractant phase

Extractant phases potentially useful in DSDME must be immiscible with water and show lower density than water. In order to achieve the highest enrichment factor, appropriate extractant phases must be compared on the basis of their extraction efficiency, selectivity, evaporation and dissolution rates. In this work, several organic solvents with different physicochemical properties, namely, *n*-hexane, toluene, xylene and 1-octanol, were tested as potential extractant phases of BaP. The results of this study can be shown in Fig. 2. As expected from the aromatic structure of BaP, toluene and xylene provided the highest extraction efficiency for BaP. Toluene was finally selected as the extractant phase in subsequent experiments.

3.2.2. Extractant phase volume

The extractant phase volume can affect the achievable enrichment factor (EF) of target analytes in DSDME in accordance with the equation:

$$\mathrm{EF} = \frac{K}{1 + K(V^{\mathrm{extr}}/V^{\mathrm{w}})} \quad (1)$$

where K is the distribution coefficient, V^{extr} is the extractant phase volume and V^{w} is the sample volume. Hence, the lower the extractant phase volume, the larger the potential enrichment factor. The impact of the toluene volume on the DSDME of BaP was tested in the range of 30–80 μL. The results of this study are shown in Fig. 3. As expected from Eq. (1), the analytical signal increased significantly as the extractant phase volume was reduced to 30 μL. Lower toluene volumes were not studied in this work due to the difficulty to uptake the enriched drop into the syringe at the end of the DSDME process. Thus, a 35 μL volume of toluene was selected as optimum since it ensures a high sensitivity and a low organic solvent consumption per analysis.

3.2.3. Stirring rate

The selection of an appropriate stirring rate of the sample solution is key in DSDME. In general terms, the agitation of the sample affects the diffusion of target analytes into the microdrop, and therefore, the employment of high stirring rates allows the achievement of large extraction efficiencies. The effect of the agitation of the sample solution was evaluated in the range of 700–1200 rpm. As shown in Fig. 4, an almost linear increase on the analytical signal was obtained by increasing the stirring rate up to 1200 rpm. The effect of larger stirring rates on the extraction efficiency of BaP was not evaluated in this work since unstable agitation and dispersion of the organic solvent through the sample solution was observed. Hence, 1200 rpm was chosen as the optimum stirring rate.

3.2.4. DSDME time

In DSDME, the extraction efficiency is highly dependent on the extraction time. As can be observed from Fig. 5, the analytical signal increased with the DSDME time in the whole studied range (0.5–8 min). Larger extraction times were not evaluated due to the reduced extract volume that remained at the end of the extraction process as a result of its partial dissolution. Even though 8 min

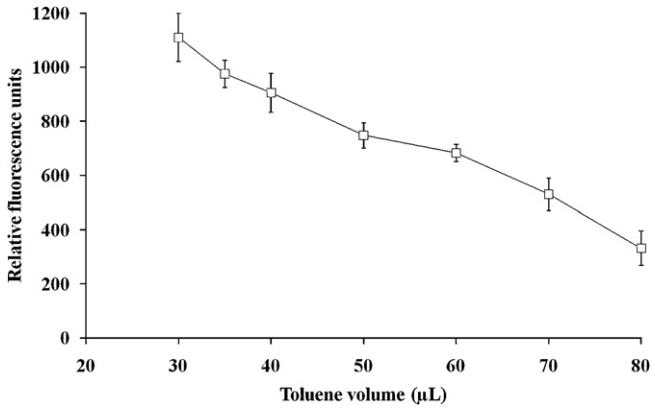

Fig. 3. Effect of the toluene volume on the DSDME of BaP. DSDME conditions: extractant phase, toluene; stirring rate, 1050 rpm; extraction time, 4 min. Error bars represent the standard deviation for $N = 3$.

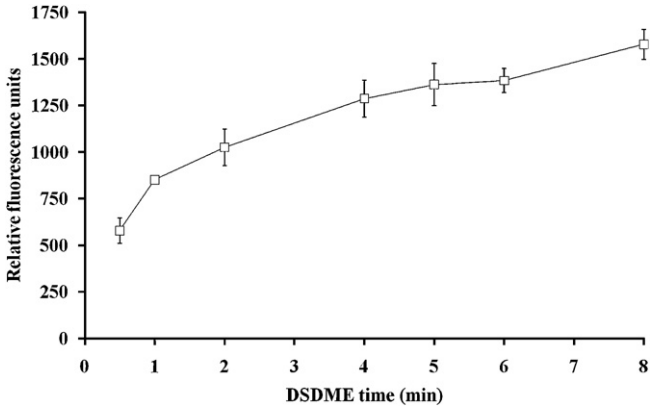

Fig. 5. Effect of the extraction time on the DSDME of BaP. DSDME conditions: extractant phase, toluene; extractant phase volume, 35 μL; stirring rate, 1200 rpm. Error bars represent the standard deviation for $N = 3$.

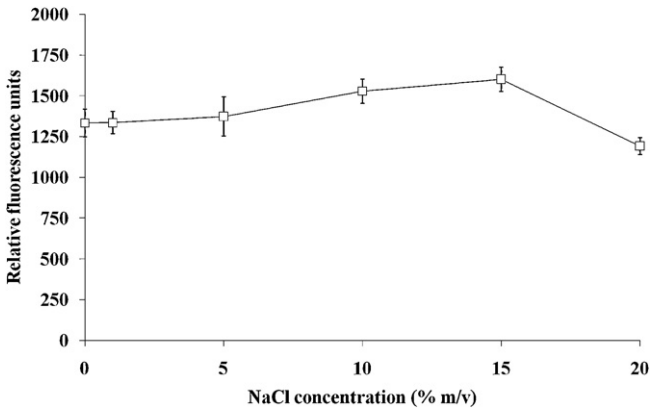

Fig. 6. Effect of the addition of NaCl on the DSDME of BaP. DSDME conditions: extractant phase, toluene; extractant phase volume, 35 μL; stirring rate, 1200 rpm; extraction time, 5 min. Error bars represent the standard deviation for $N = 3$.

provided the higher sensitivity, a 5 min DSDME time was selected for subsequent experiments, since in such conditions the enriched extractant phase is more easily retracted back into the syringe and the sample throughput is enhanced.

3.2.5. Salting out effect

Addition of salt to the sample solution is commonly performed in conventional liquid–liquid extraction to enhance the extraction efficiency of target analytes. In this work, the effect of increasing the ionic strength of the sample by addition of NaCl was evaluated, and the obtained results can be observed in Fig. 6. The addition of NaCl (up to 15% (*m*/*v*)) caused a slight increase in the analytical signal of BaP, while the use of larger concentrations of NaCl caused a negative effect on the extraction efficiency. It is assumed that in DSDME, apart from the 'salting-out' effect, the presence of high concentrations of NaCl in the sample solution can give rise to the modification of the physicochemical properties of the Nernst diffusion film, thus affecting the extraction kinetics of target analytes [36]. Based on the above considerations and for simplicity, no NaCl addition was performed in further experiments.

3.3. Method validation

3.3.1. Analytical performance

Analytical figures of merit were established to characterize the proposed DSDME-microvolume fluorospectrometric method. The equation for the calibration curve of BaP was: $Y = 415.2[\text{BaP}] - 4.2$, where Y is the fluorescence intensity and [BaP] is the BaP concentration expressed in $\mu g\,L^{-1}$. The linear working range was established between 0.1 and 20 $\mu g\,L^{-1}$ of BaP ($n = 8$). The correlation coefficient was $r = 0.9999$.

The detection (LOD) and quantification limits (LOQ), calculated as $3\,s\,m^{-1}$ and $10\,s\,m^{-1}$ (s being the standard deviation of 10 blank measurements and m the slope of the calibration curve), were 0.024 and 0.079 $\mu g\,L^{-1}$ of BaP, respectively.

The enrichment factor, calculated as the ratio between the slopes of the calibration curves obtained by the proposed method and by direct injection of BaP stock solutions in toluene, was found to be 159.

The repeatability of the proposed screening method was tested by performing eight replicate extractions of a 1 $\mu g\,L^{-1}$ BaP solution. The repeatability, expressed as relative standard deviation (RSD), was 4.9%.

When compared with alternative screening methods for PAHs, the proposed methodology is characterized by its minimum consumption of both sample solution and extractant phase per analysis. The high preconcentration factor and sample throughput achieved are also remarkable, being up to 10-fold better than reported [2,8]. The obtained sensitivity and precision is better than reported by cloud point extraction-spectrofluorimetric method [2], although lower than the obtained by sequential injection-variable angle fluorescence with on-line solid-phase extraction [8] and the fluorescence optosensor method [10]. Nevertheless, the proposed method provides the reliable binary "yes/no" response using a cut-off level below the guideline value for BaP in drinking water.

3.3.2. Selectivity of the method

The selectivity of the method was evaluated by applying the optimized DSDME procedure to other selected PAHs, i.e. Phe, Ant, Pyr and Flt. Calibration curves were obtained for the four selected PAHs and the corresponding slopes were compared to that obtained for BaP. Significant differences in the excitation and emission spectra for different PAHs have been reported in the literature. The different sensitivity obtained for the PAHs of interest at any excitation–emission wavelength pair hinders the development of a screening method for total PAHs [2,9]. Hence, it is to be expected that the fluorescence parameters employed in this work would provide differences in the sensitivity for the different PAHs.

A high selectivity was obtained for BaP determination in the presence of Phe and Pyr. In fact, the slope of the calibration curve for BaP was found to be 3400- and 1900-fold higher than the obtained for Phe and Pyr, respectively. On the other hand, reduced selectivity was observed for BaP determination in the presence of Ant and Flt, since the slopes of the calibration curves for such PAHs were found to be similar to that of BaP. As exposed above, these results were expected, bearing in mind the important differences reported for emission spectra of different PAHs when a fixed excitation wavelength is employed.

3.3.3. Determination of the unreliability region of the screening method

To define the unreliability of the screening method, a probability–concentration graph was obtained by analyzing 20 spiked water samples at 10 different BaP concentrations in the range of 0.2–0.9 $\mu g\,L^{-1}$. A false positive is produced when a sample solution containing a BaP concentration lower than the cut-off level gives rise to a positive response, while a false negative is produced when a sample solution containing a BaP concentration higher than the cut-off level gives rise to a negative response [37]. The results are shown in Fig. 7. A cut-off level of 0.7 $\mu g\,L^{-1}$ was initially fixed, since it is the guideline value for BaP in drinking water [38]. In such conditions, an unreliability range of 0.61–0.77 $\mu g\,L^{-1}$ was obtained. When screening methods are employed, it is important to avoid

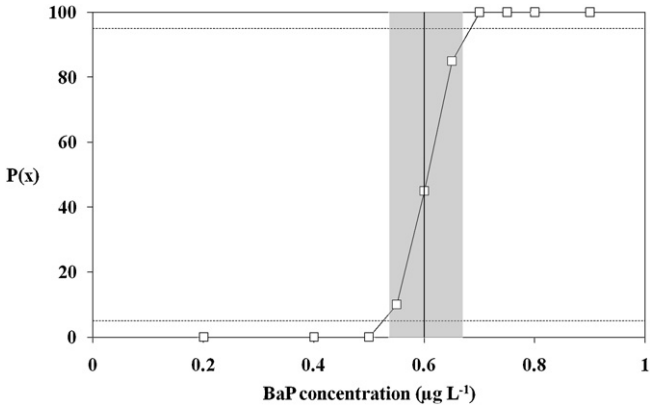

Fig. 7. Real probability–concentration graph for the screening of PAHs in waters for a cut-off concentration value of 0.6 $\mu g\,L^{-1}$ of BaP.

Table 1
Analytical results obtained for the screening of PAHs in fortified waters using the proposed DSDME-microvolume fluorospectrometric method.

Sample	Added concentration ($\mu g\,L^{-1}$)[a]	Screening result[b]	Found concentration ($\mu g\,L^{-1}$)[a,c]	Recovery (%)
Tap	–	Negative	<LOQ	
water	0.2	Negative	0.19 ± 0.01	93 ± 7
	0.4	Negative	0.38 ± 0.01	95 ± 3
	1.0	Positive	0.97 ± 0.02	97 ± 2
Mineral	–	Negative	<LOQ	
water	0.2	Negative	0.20 ± 0.01	98 ± 7
	0.4	Negative	0.41 ± 0.02	104 ± 6
	1.0	Positive	1.00 ± 0.07	100 ± 7
Lake	–	Negative	<LOQ	
water	0.2	Negative	0.20 ± 0.01	101 ± 7
	0.4	Negative	0.41 ± 0.03	104 ± 7
	1.0	Positive	0.98 ± 0.03	98 ± 3

[a] Concentration expressed as BaP.
[b] Cut-off level set at 0.6 $\mu g\,L^{-1}$.
[c] Results expressed as average value ± standard deviation ($N = 3$).

the occurrence of false negatives, since positive and inconclusive samples are commonly confirmed by using a rearguard analytical technique. A slightly lower concentration than the threshold value (0.7 $\mu g\,L^{-1}$ of BaP) must therefore be selected as cut-off level to avoid having a false negative answer [37]. A cut-off value of 0.6 $\mu g\,L^{-1}$ of BaP was found to be a better option, since false negatives are avoided (0.54–0.67 $\mu g\,L^{-1}$). Thus, the cut-off value was set at a concentration of 0.6 $\mu g\,L^{-1}$ of BaP.

3.3.4. Analysis of water samples

The proposed method was applied to the screening of three different water samples (tap water, mineral water and lake water) for PAHs, using BaP as a marker. Water samples were spiked with BaP at three different levels to evaluate the matrix effects. The analytical results obtained are listed in Table 1. As can be seen, the proposed screening method provided suitable qualitative binary responses for the fortified water samples. In addition, recovery studies were performed on the analyzed samples, in accordance with the equation:

$$R(\%) = \left(\frac{[\mathrm{PAH}]_{\mathrm{found}} - [\mathrm{PAH}]_{\mathrm{initial}}}{[\mathrm{PAH}]_{\mathrm{added}}} \right) \times 100 \quad (2)$$

Being $R(\%)$ the recovery value, $[\mathrm{PAH}]_{\mathrm{initial}}$ the original concentration in the sample, $[\mathrm{PAH}]_{\mathrm{added}}$ a well-known concentration of PAHs added to the sample, and $[\mathrm{PAH}]_{\mathrm{found}}$ the concentration obtained after analyzing spiked samples, PAHs being expressed in terms of BaP. Satisfactory relative recoveries were obtained in all cases (93–106%), revealing that the matrices of the analyzed water samples had little effect on the performance of the proposed DSDME method. It should be highlighted that a confirmative analytical method (e.g. the liquid–liquid extraction-gas chromatography standardized method for PAHs in water samples) [39] would be required for positive and inconclusive binary responses.

4. Conclusions

A rapid and simple method that allows the screening of natural waters for PAHs is presented in this work. The method, based on the combination of DSDME and a portable microvolume fluorospectrometry, provides reliable screening data with minimum preliminary operations. The proposed method can be therefore considered a feasible vanguard analytical system for the *in situ* evaluation of the presence or absence of PAHs in water samples.

Acknowledgments

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