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

Francisco Pena-Pereira, Isabel Costas-Mora, Isela Lavilla, Carlos Bendicho*

Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

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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

* Corresponding author. Tel.: +34 986 812281; fax: +34 986 812556.
E-mail address: bendicho@uvigo.es (C. Bendicho).

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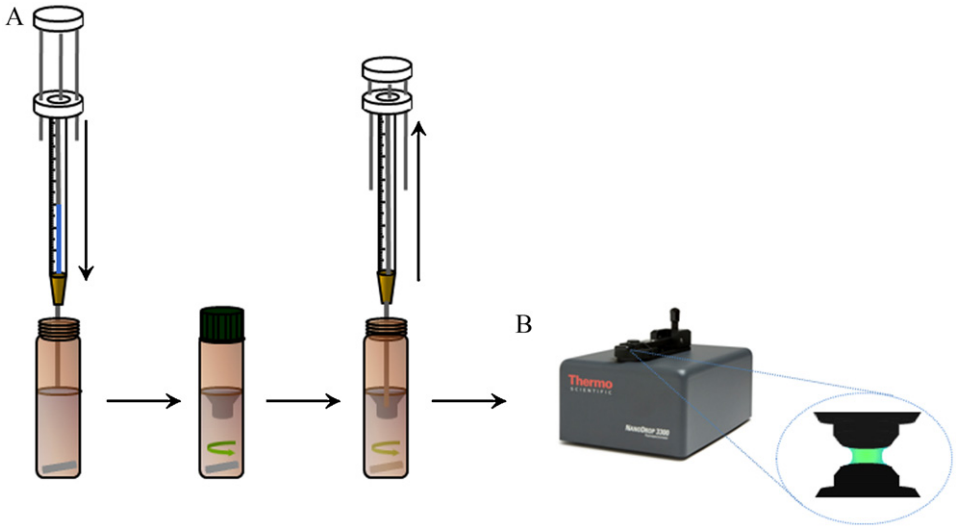

Fig. 1. Schematic representation of the DSDME-microvolume fluorospectrometric system used for the screening of PAHs: (A) DSDME of PAHs; (B) fluorescence spectra acquisition.

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.