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Development of a new sorptive extraction method based on simultaneous direct and headspace sampling modes for the screening of polycyclic aromatic hydrocarbons in water samples

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ABSTRACT

A new straightforward and inexpensive sample screening method for both EPA and EU priority polycyclic aromatic hydrocarbons (PAHs) in water has been developed. The method is based on combined direct immersion and headspace (DIHS) sorptive extraction, using low-cost disposable material, coupled to ultraperformance liquid chromatography with fluorescence and UV detection (UPLC-FD-UV). Extraction parameters, such as the sampling mode, extraction time and ionic strength were investigated in detail and optimized. Under optimized conditions, water samples (16 mL) were concentrated in silicone disks by headspace (HS) and direct immersion (DI) modes simultaneously, at room temperature for 9 h for the majority of the 24 studied compounds. Ultrasound-assisted desorption of extracted analytes in acetonitrile was carried out also at room temperature. The optimized chromatographic method provided a good linearity ($R \geq 0.9991$) and a broad linear range for all studied PAHs. The proposed analytical procedure exhibited a good precision level with relative standard deviations below 15% for all analytes. Quantification limits between 0.7 and 2.3 $\mu g\ L^{-1}$ and 0.16 and 3.90 $ng\ L^{-1}$ were obtained for compounds analyzed by UV (acenaphtylene, cyclopenta[c,d]pyrene and benzo[j]fluoranthene) and fluorescence, respectively. Finally, the proposed method was applied to the determination of PAHs in different real tap, river and wastewater samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a broad group of organic compounds which have received much attention over the years because of their wide distribution in the environment as well as their well-known carcinogenic and mutagenic properties [1,2]. Due to the ubiquity of PAHs and their potential deleterious effects on human health, these compounds have been often monitored in air, soil, water, foods and beverages [3]. On the basis of risk assessment, 15 PAHs have been identified as priority hazardous substances by the European Union (EU) [4]. Moreover, in 2005, the Joint FAO/WHO Experts Committee on Food Additives appended to the list a 16th compound (benzo[c]fluorene, B[c]F) also considered as genotoxic. To distinguish this list from the set of 16 US EPA PAHs [5], the term "15+1 EU priority PAHs" is commonly used. The list of these PAHs comprises of B[c]F, cyclopenta[c,d]pyrene (CP[c,d]P), benz[a]anthracene (B[a]A), chrysene (Chry), 5-metylchrysene (5-MC), benzo[j]fluoranthene (B[j]F), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenzo[a,l]pyrene (DB[a,l]P), dibenzo[a,h]anthracene (DB[a,h]A), benzo[g,h,i]perylene (B[g,h,i]P), indeno[1,2,3-c,d]pyrene (I[1,2,3-c,d]P), dibenzo[a,e]pyrene (DB[a,e]P), dibenzo[a,i]pyrene (DB[a,i]P) and dibenzo[a,h]pyrene (DB[a,h]P). Because of the continued development of European legislation in this area, analytical methodology for multiple PAHs in water and other types of samples is required in order to get a clearer picture of human exposure.

A variety of analytical methods have been used for determining trace concentrations of PAHs in water samples. Aside from the classical liquid–liquid extraction (LLE), alternative sampling methods like solid phase extraction (SPE) [6], solid phase microextraction (SPME) [7], stir bar sorptive extraction (SBSE) [8] and silicone rods and tubes sorptive methods [9] have been developed. These procedures, based on equilibrium extraction, exhibit several advantages over LLE, regarding sample preparation speed and allows for improved sample throughput by parallel analyses [10].

The most widely used sorptive extraction phase is polydimethylsiloxane (PDMS). Absorptive interactions are much weaker compared to adsorption on active surfaces. Therefore, analyte desorption can be performed under softer conditions, such as

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lower temperature and shorter desorption times and the degradation of unstable analytes is significantly impaired as compared to adsorptive processes [9,11].

Among the PDMS extraction techniques, solid-phase microextraction (SPME) has been widely used to extract PAHs from water samples [12–14]. Stir bar sorptive extraction (SBSE) which is more recent, has also been used for that kind of extraction [15–17]. In addition to PDMS coated fibers and stir bars (Twisters), PDMS is also available in bulk formats (sheets, tubes and rods). Silicone materials in form of rods (SRs) and tubes (STs) for the enrichment of organic compounds have been employed by Popp et al. [18,19]. In terms of analyte extraction the SRs and STs are similar to SPME and SBSE. Additional advantages of using bulk PDMS or equivalent materials as sorbent are the possibility of customizing the volume of polymer for each particular application, the availability of different formats and the very low cost of the sorbent in comparison with SPME fibers and Twisters. The latter feature makes it possible to use a new piece of sorbent for each extraction, which avoids problems associated with carry-over and cross contamination, allowing simultaneously processing as many samples as desired, and providing the possibility of considering the disposable sorbent material for analyte storage purposes [9].

The aim of this work was to develop and optimize a new one shot procedure based on sorptive extraction coupled with UPLC-FD-UV for determination of the 16 EPA priority PAHs and the "15+1" EU priority PAHs in water samples. The 24 PAHs are naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), fluoranthene (Flt), pyrene (Pyr), B[c]F, CP[c,d]P, B[a]A, Chry, 5-MC, B[j]F, B[b]F, B[k]F, B[a]P, DB[a,l]P, DB[a,h]A, B[g,h,i]P, I[1,2,3-c,d]P, DB[a,e]P, DB[a,i]P and DB[a,h]P.

Disposable silicone in disks format, sampling simultaneously in direct immersion and headspace (DIHS) modes, was chosen as extractant phase and the influence of different experimental parameters (e.g. sampling mode, stirring rates, extraction time, etc.) on the analyte recoveries was investigated optimizing the operating conditions. Chromatographic conditions have been also optimized in order to obtain the satisfactory separation of 24 studied PAHs. Finally, the applicability of the developed procedure was tested for the determination of PAHs in some real tap, river and wastewater samples.

2. Materials and methods

2.1. Reagents, standards and materials

The disposable silicone sorbent was purchased from Goodfellow (Bad Nauheim, Germany) in sheets with a thickness of 0.6 mm. Silicone provided by Goodfellow is not pure PDMS but a phenyl-vinyl-methyl-polysiloxane (so-called PVMQ silicone Rubber). Disks (5 mm diameter × 0.6 mm thickness, 12 μL volume) were obtained by cutting the silicone sheet with a sharp hollow punch (internal diameter 5 mm). The obtained pieces were weighed and those differing by more than 2% in weight were discarded. Before being used for analytes extraction, disks were sonicated three times (5 min each) with methanol–acetone (1:1, v/v) mixture and then were conditioned overnight at 200 °C. Finally the pieces of silicone were sonicated three times (5 min each) with acetonitrile (ACN) and stored dry in sealed bags before use.

ACN and methanol (gradient-grade, Lichrosolv), and 2-propanol (analysis grade), were supplied by MercK (Darmstadt, Germany). Ultrapure water was produced by means of a Milli-Q Gradient A-10 system (Millipore, Billerica, MA, USA). Potassium carbonate and potassium hydrogenum carbonate were purchased from Sigma-Aldrich (Madrid, Spain). Sodium chloride (NaCl) was supplied by Prolabo (Fontenay-Sous-Bois, France). EPA-610 Polycyclic aromatic hydrocarbons mixture was supplied by Supelco (Bellefonte, PA, USA). 5-MC (10 μg mL^{-1}), DB[a,l]P (10 μg mL^{-1}), CP[c,d]P (10 μg mL^{-1}), B[c]F (10 μg mL^{-1}), DB[a,e]P (10 μg mL^{-1}), DB[a,i]P (10 μg mL^{-1}) and DB[a,h]P (10 μg mL^{-1}) were from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Durapore filters (Millex GV, 13 mm, 0.22 μm) were supplied by Millipore.

2.2. Samples and sample preparation

Spiked and non-spiked ultrapure, tap, and river waters samples, and both raw (influent) and treated (effluent) wastewater samples were used in this study. All samples were used directly without preliminary filtration. Ultrapure and tap waters were obtained directly in the laboratory when needed. River water samples were collected in different points in Galicia (northwest Spain). Sewage water samples were obtained from the inlet and outlet of an urban wastewater treatment plant in operation near Santiago de Compostela (~100,000 inhabitants), equipped with a primary and aerobic secondary treatment, and which receives mostly municipal non-industrial wastewaters. Spiked samples were prepared by adding a standard solution of analytes at levels between 0.12 ng mL^{-1} and 2.5 ng mL^{-1}, depending on the considered compound.

Extractions were carried out in 22 mL capacity glass vials furnished with PTFE-lined septa (covered with aluminum foil) and aluminum caps. Vials and caps were supplied by Sugelabor (Madrid, Spain).

Under optimized conditions, 16 mL of water was transferred to extraction vials containing 4 g (25%w/v) of sodium chloride, 1 mL of 2-propanol (i-prOH) and a PTFE covered stirrer (6 mm × 3 mm). Analytes were extracted by night (c.a. 15 h approximately) at room temperature, with 5 silicone disks immersed directly in the stirred sample (900 r.p.m) and a sixth silicone disk in the headspace of the sample, fixed to the septum of the vial with a stainless steel pin (i.d. 0.4 mm). After extraction, the silicone disks were removed with clean tweezers, rinsed with ultrapure water and transferred into a small vial containing 0.25 mL of ACN and desorbed during 5 min in an ultrasonic (US) bath. Then, 0.1 mL of the obtained ACN extract was taken and diluted with 0.1 mL of water to match the initial mobile phase composition in the UPLC separation program. This diluted solution was filtered through a 0.22 μm Durapore filter and 5 μL was injected into the UPLC system.

2.3. Chromatographic method (UPLC-FD-UV)

UPLC chromatographic separations were developed in a system comprising a quaternary pump (Acquity H Class, Waters), an UV–vis diode array and a fluorescence detector (FD) in series (Waters, Singapore). The autosampler has a temperature controller for the samples and is fitted with a flow through needle system. Analytical column temperature was controlled with an integrated oven module. The analytical column was a 50 mm × 2.1 mm I.D. Zorbax Eclipse PAH Rapid Resolution HT C_{18} column, (particle size 1.8 μm). A filter guard cartridge (2.1 mm × 0.2 μm) was used to protect the analytical column (Waters, USA). Empower 2.1 Software was used for data acquisition.

A binary solvent system made of ACN and water was used for chromatographic separations. The gradient elution program was as follows: initial conditions, 47% ACN for 0.5 min, then a linear ramp to 80% ACN in 4.9 min and finally another linear ramp to 100% ACN in 1.9 min, holding in 100% ACN for 3.7 min.

The flow rate was also programmed. Initially it was set at 0.6 mL min^{-1} during 7.3 min, and then increased to 0.9 mL min^{-1} for 0.2 min, holding at 0.9 mL min^{-1} for 3.5 min. The column