



# A novel and cost-effective method for the determination of fifteen polycyclic aromatic hydrocarbons in low volume rainwater samples



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## ABSTRACT

A novel single-step method was developed for the determination of 15 polycyclic aromatic hydrocarbons (PAHs) at ultratrace levels in rainwater by on-line in-tube solid-phase microextraction (IT-SPME) coupled to high-performance liquid chromatography-photodiode array-fluorescence detection. This paper is focused on a study of the IT-SPME coupling and optimization, its application to rainwater and other environmental waters and the stability of PAH rainwater solutions. In order to solve the different extractive behavior of PAHs, several IT-SPME parameters were optimized, with the type and percentage of organic modifier playing a decisive role. In the kinetic study on stability of PAH solutions, the organic modifier has proven to be effective as a preservative, avoiding the loss of the higher-molecular weight PAHs. The proposed method presents a wide interval of linearity ( $10\text{--}1500\text{ ng L}^{-1}$ ) and a good relative standard deviation between 3.4% and 14.6% for the PAHs analyzed. Detection and quantification limits between  $2.3$  and  $28\text{ ng L}^{-1}$  and  $5.7$  and  $65\text{ ng L}^{-1}$  were obtained respectively, taking into account the values of the procedure blanks. Recoveries for different kinds of real water samples were within the range of 72–110%. Low and medium-molecular weight PAHs predominate in daily and monthly rainwater samples analyzed. In comparison with other methods reported, the proposed method achieves a significant reduction of the sample volume, the organic solvent consumption and time of sample treatment, allowing a cost-effective analysis of environmental waters. The method is especially suitable for samples from the precipitation events of low intensity or short duration for which sample volume is limiting.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) containing two or more fused aromatic rings [1]. They are basically generated by incomplete combustion and pyrolysis processes involving hydrocarbons (fossil fuels and wood), either from natural or anthropogenic sources [2,3]. Some of them have genotoxic (carcinogenic, mutagenic, teratogenic) properties [4], due to the interaction between their metabolites and DNA [1,5]. PAHs are widely present in the environment (water, air and soil) at low concentrations. The analysis of PAHs at ultratrace level in environmental matrices usually requires several steps of sample treatment, which can be significant time-consuming processes, and they involve high consumption of organic solvents and losses of analytes [6].

The relevance of rainwater in environmental studies is related to spatial and temporal balances of pollutants and their exchange between different environmental compartments. Particularly, PAHs are incorporated into soil, water systems, biota and food chains by wet deposition. Rainwater scavenges the PAHs present in the atmosphere in vapour and particulate phase. Their incorporation into rainwater depends on several factors, such as temperature or amount of precipitation. For some pollutants, the relationship between their concentration levels and amount of precipitation has been interpreted by hyperbolic and exponential models [7,8]. Thereby, the highest concentration of pollutants is found in the initial precipitation, and the following rainfall (with lower concentration) dilutes the sample. A similar relationship was found between PAHs concentration in particulate and precipitation phases [7]. Furthermore, short-time breaks in rainfall have also an influence on the pollutants levels over a day, and may cause fluctuation of data in long sampling periods. These investigations suggest that smaller sample volumes and a shorter sampling period than those used in classical monitoring can be required. For example, regional differences in pollutants levels

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were only observed in the initial rainfall, so large volume samples are not suitable to study them [8]. Furthermore, if the sampling is done in remote areas, the stability of the sample during transport and its conservation has to be controlled. The routine analysis of PAHs in rainwater is usually accomplished using traditional multi-step methods, which typically involve liquid-liquid extraction, purification and evaporation, and a large consumption of solvents and time.

In-tube solid-phase microextraction (IT-SPME) is a sample preparation technique that can be easily coupled on-line to high-performance liquid chromatography (HPLC), combining sample treatment and determination in a single step. Since its introduction, IT-SPME has demonstrated its ability to analyze complex samples in the environmental, clinical and food fields [9–14]. PAHs analysis has been carried out by IT-SPME coupling HPLC with a fluorescence detector [9,11]. However, 15 USEPA priority PAHs could not be determined in a single run due to different behaviors between lower-molecular weight and higher-molecular weight PAHs, doubling sample, reagents and time consumption.

The aim of this work is the development of a novel method for the determination of ultratrace 15 USEPA priority PAHs in environmental waters (particularly in rainwater). For this purpose, a miniaturized extraction technique (IT-SPME) coupled to liquid chromatography with fluorescence detection, which combines extraction, purification and concentration in a single-step, was employed. Evaporation steps are unnecessary. Good concentration factors were achieved by the addition of an appropriate organic modifier which also behaves as a preservative. The sample volume (less than 5 mL), consumption of toxic and expensive organic solvent (0.75 mL) and time of sample treatment (7 min) are significantly reduced with respect to classical methods turning it into a simple, rapid and cost-effective method. Its application to samples collected from short-duration precipitation events is especially suitable due to the low sample volume required and good sensitivity achieved. From a methodological point of view, the used configuration combining a six-port injection valve and autosampler allows a higher throughput of the instrumental laboratory. On the other hand, the stability of PAH aqueous solutions is not good, as noticed during the development of this work. However, to the best of the authors' knowledge very few studies have been carried out on this subject, and none in rainwater. Therefore, this work also presents a novel study about the stability of PAH rainwater solutions. Finally, the single-step method was applied to rainwater samples from a region with abundant rainfall (northwest of the Iberian Peninsula) [15] and several environmental samples (spring, river and lake) from a local area in which there was an open-pit coal mine.

## 2. Material and methods

### 2.1. Apparatus

The chromatographic system (Waters, Mildford, MA, USA) consisted of a 2695 Alliance module and two detectors in series: a photodiode array detector, DAD (Waters 996), and a scanning fluorescence detector (Waters 474), with the software Empower 2.0. A six-port injection valve (Rheodyne Model 7725i) was coupled for the IT-SPME procedure.

### 2.2. Reagents and materials

A PAH Calibration Mix containing naphthalene (Naph), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Ft), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysen

(Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBa,hA), benzo[*ghi*]perylene (Bg,h,iP) and indeno[1,2,3-*cd*]pyrene (IP) ( $10 \mu\text{g mL}^{-1}$  each in acetonitrile) was obtained from Supelco (Bellafonte, USA). Working solutions were prepared from the commercial solution. All solutions were stored at  $-18^\circ\text{C}$  in amber glass vials (Waters, Mildford, MA, USA, and Supelco, Steinheim, Germany).

All solvents were of Gradient HPLC grade. Acetonitrile (J. T. Baker, Phillipsburg, USA, and Scharlau, Barcelona, Spain), 2-propanol HPLC (Panreac, Barcelona, Spain) and tetrahydrofuran (Merck, Darmstadt, Germany) were filtered through  $0.45 \mu\text{m}$  PTFE membranes (Teknokroma, Barcelona, Spain). Water was Milli-Q quality, filtered through  $0.20 \mu\text{m}$  nylon membranes (Millipore, Darmstadt, Germany).

### 2.3. Sampling and filtration of aqueous samples

Rainwater samples (daily [24 h] and monthly) were collected at two air monitoring stations: at the University Environmental Institute (suburban area in Liáns-Oleiros, A Coruña, Spain), and an industrial area in Arteixo, A Coruña, Spain. All rainwater samples were collected using a silanized glass sampler (DEPOBULK<sup>®</sup>, Lab-Service Analytica, Bologna, Italy), they were filtered through pre-calcinated MK360 Munktell quartz filters (4.7 cm diameter) and they were later stored at  $-18^\circ\text{C}$  until analysis.

The samples of lake water (Lake As Pontes), river water (Eume river) and spring water (Ribeira Nova spring), were collected at As Pontes de García Rodríguez, A Coruña, Spain. There is a thermal power plant near the sampling points. These samples were filtered through Discmic<sup>®</sup>-13HP syringe filters (PTFE,  $0.50 \mu\text{m}$ , 13 mm) purchased from Advantec MFS (Dublin, CA, USA). After the aqueous sample was filtered, 15% (proportion of the final volume) of tetrahydrofuran was passed through the filter.

### 2.4. In-tube SPME procedure

For the IT-SPME-HPLC-FLD procedure, the loop of the six-port injection valve was replaced by a 70 cm-long GC capillary column TRB-5 (95% poly(dimethylsiloxane)-5% poly(diphenylsiloxane),  $0.32 \text{ mm i.d.}$ ,  $3 \mu\text{m}$  thickness) purchased from Teknokroma (Barcelona, Spain). Capillary connections were facilitated by the use of a 2.5 cm sleeve of 1/16 in. polyether ether ketone (PEEK) tubing at each end of the capillary. In load position, 5 mL of a sample or PAHs solution were passed through the capillary at flow-rate of  $0.7 \text{ mL min}^{-1}$ , followed by  $60 \mu\text{L}$  of Milli-Q water to displace the remaining sample in the capillary. The run is started by programming a sample volume equal to zero for the autosampler. At the time the gradient starts, the valve is rotated to the inject position, and mobile phase passes through the capillary, desorbing analytes.

Between runs, the sample syringe is rinsed with methanol and acetonitrile (filling it twice with each solvent), while the valve and capillary are flushed with 2.5 mL of acetonitrile before loading the next sample.

### 2.5. Chromatographic conditions

The analytical column was a Waters<sup>®</sup> PAH C18 ( $250 \times 4.6 \text{ mm i.d.}$ ,  $5 \mu\text{m}$ ). The gradient elution mode was used, with an acetonitrile/water mixture (Fig. 1). The column temperature was set to  $32 \pm 5^\circ\text{C}$  and fluorescence programmed conditions are shown in Fig. 1. DAD data were recorded between 210 and 400 nm. Under these conditions, the 15 PAHs are detected within 38 min.

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