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Sensitive determination of polycyclic aromatic hydrocarbons in water samples using monolithic capillary solid-phase extraction and on-line thermal desorption prior to gas chromatography–mass spectrometry

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ABSTRACT

A methacrylate-based monolithic capillary column has been evaluated for the preconcentration of polycyclic aromatic hydrocarbons (PAHs) from environmental water samples. For this purpose, the monolyte was *in situ* synthesized in a 6 cm × 0.32 mm id fused-silica capillary. The microextraction unit was fitted to a micro-HPLC pump to pass 10 mL of sample. The isolated pollutants were eluted by means of 10 μL of methanol, the organic phase being directly collected in a specific interface that can be fitted to the injection port of the gas chromatograph without modification. The interface allows the on-line thermal desorption of the PAHs, avoiding the dilution and providing enough sensitivity to reach the legal limits established for these pollutants in the matrices selected. The limits of detection achieved for 10 mL of water ranged between 2.8 ng/L (indeno(1,2,3-cd)pyrene) and 11.5 ng/L (acenaphthene) with acceptable precision (between 4.5 and 18.2% RSD). The method was applied to the determination of the selected PAHs in tap, river waters and sewage, being fluoranthene and pyrene detected in all of them at concentrations lower than the legal limits established for these compounds in the matrices assayed.

1. Introduction

Analytical laboratories can use a large variety of highly sensitive analytical instruments for the analysis of samples of different nature. However, sample treatment still remains as the main limitation to improve the productivity of an analytical laboratory. Great efforts have been made in this field, the most recent dealing with the miniaturization of the preliminary operations of the analytical process. Reducing the size in this context presents several advantages related with the reduced consumption of sample and reagents, easy automation and on-line coupling with instrumental techniques (mainly chromatography and electrophoresis) [1]. The conventional liquid–liquid (LLE) and solid-phase extraction (SPE) techniques currently have their miniaturized approaches which are successfully employed in different application fields [2,3].

Solid-phase microextraction (SPME) implemented in a tube, needle or tip requires the immobilization of an active coating (usually of polymeric nature) in the inner surface of the extraction device [1]. Burger and Munro proposed in 1986 the use of an open tubular fused silica capillary coated with activated carbon or powdered porous organic polymer for the determination of volatile organic compounds using thermal desorption and gas chromatographic separation [4]. Although the first application involved gas chromatography (GC), several disadvantages were identified, mainly concerning the low capacity of the stationary phase for analytes retention and the limitation on sample flow rate due to system overpressure, being limited to sample volumes lower than 3 mL and flow rates in the range 0.4 mL/min. Moreover, it requires rather complicated instrumental setups to prevent traces of water from entering the chromatographic system. However, the miniaturization technology was found to be more adequate for liquid chromatographic and electrophoretic separations, being the applications in the on-line and in-line modalities widely reported in the scientific literature. However, the low capacity of the microextraction units still remains as a disadvantage [5–10].

Monolithic columns are highly attractive for preconcentration purposes. Monoliths can be synthesized directly inside the capillary and anchored to the wall through chemical bonding, avoiding the need of frits [11,12]. The monolith itself consists of a rigid macroporous structure which can be prepared by polymerization of a precursor mixture *in situ*. Silica monoliths are made through the condensation of alkylsilanes via sol–gel chemistry, while polymer-based monoliths (including acrylate, methacrylate, acrylamide and styrene) are prepared by polymerizing monomers and cross-linkers

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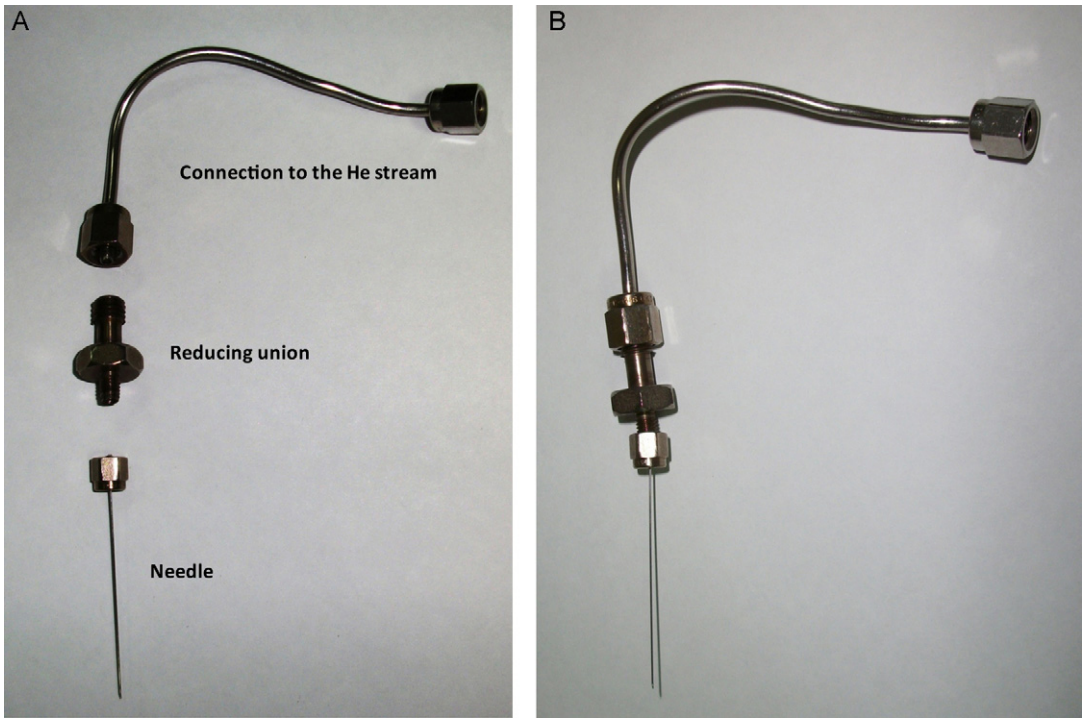

Fig. 1. Photographs of the elements (A) and interface assembly (B) for the on-line thermal desorption of PAHs.

in the presence of porogenic solvents. The use of both silica and polymer monoliths for preconcentration and solid-phase extraction has been described as less common applications of these chromatographic supports [13–17]. In this context, sol–gel coated capillaries have been used for the preconcentration of analytes belonging to different chemical classes prior to gas chromatographic separation [18,19].

In this paper, we have evaluated the applicability of such combination for the sensitive determination of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. These compounds are priority pollutants, being the legal limits established by the legislation in the low nanogram per liter level. The sensitivity of the methodology has been dramatically improved because the analytes were collected from the monolithic column in a specific interface which permits their direct thermal desorption in the injection port of the gas chromatograph. Several parameters affecting to the design of the interface were evaluated and the final configuration employed commercial stainless steel pieces. The setup is cheap and does not require any special injector configuration. Moreover the temperature can be controlled by means of a heating block or an external heated air stream.

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade or better. Polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benzo-anthracene, benzo(k) fluranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene) were purchased from Sigma–Aldrich (Madrid, Spain). Stock standards solutions of each analyte were prepared in methanol (Scharlab, Barcelona, Spain) at a concentration of 500 mg/L and stored at 4 °C.

Working solutions of PAHs were prepared by dilution of the stocks in Milli-Q water (Millipore Corp., Madrid, Spain) or methanol as required.

The reagents employed for the preparation of the monolithic columns, butyl methacrylate (BMA), ethylene dimethacrylate (EDMA), lauroyl peroxide (LPO), 3-(trimethoxysilyl)propyl methacrylate, 2-propanol (2-PrOH) and formamide were purchased from Sigma–Aldrich (Madrid, Spain).

Uncoated fused-silica capillaries with 435 μm od × 320 μm id (Polymicro Technologies, Phoenix, AZ, USA) were used.

River, tap water and sewage samples were collected in different locations of Córdoba in amber-glass bottles without headspace. The samples were stored in the dark at 4 °C and filtered through a 0.45 μm Nylon filter prior to analysis.

2.2. Instrumentation

For analytes preconcentration and elution, a micro-HPLC pump Jasco 1585 (Jasco Analítica Spain, Madrid, Spain) was employed. For the thermal desorption of analytes and their on-line introduction in the chromatographic system, an interface developed by our research group, shown in Fig. 1, was used. It consists of a reducing union 1/16 in. Swagelok, 1/8 in. Swagelok (Supelco, Madrid, Spain) with a needle screwed in the lower part to facilitate its coupling with the injector of the gas chromatograph. The upper part is connected to the carrier gas during the desorption step, being the flow rate controlled by a millimetre valve. A small cotton bead was placed in the inner body of the reducing union for the retention of the methanol containing the eluted analytes.

The monolithic column was connected to the pump by means of a stainless steel internal union (Valco, Houston, US) fitted with a peek adapter (Supelco, Madrid, Spain).

GC/MS analyses were carried out on an Agilent (Palo Alto, CA) HP6890 gas chromatograph equipped with an HP5973 mass spectrometric detector based on a quadrupole analyzer and an electronmultiplier detector. System control and data acquisition was achieved with an HP1701CA MS ChemStation (also from Agilent). The injector was maintained at 225 °C with a 1:10 split ratio. Helium (2 purity grade, Air Liquid, Seville, Spain) was used

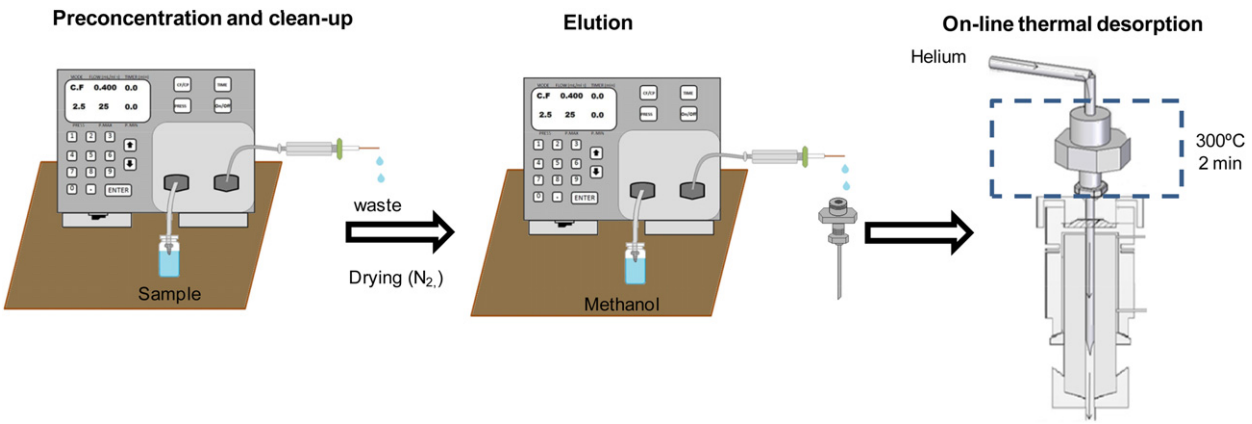

Fig. 2. Schematic diagram of the proposed analytical method.

as carrier gas at a flow rate of 1 mL/min. Gas chromatographic separations were performed on a fused silica capillary column (30 m × 0.25 mm id) coated with 5% phenylmethyl-polysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The column temperature program was as follows: 2 min at 60 °C, raised up to 240 °C at 35 °C/min, then immediately ramped at 12 °C/min up to 330 °C and kept finally at 330 °C for 2.5 min. The quadrupole mass spectrometer detector was operated in selected ion monitoring mode, recording the following fragment-ion: 128 (from 2.50 to 7.00 min), 154 (from 7.00 to 7.35 min), 166 (from 7.35 to 8.00 min), 178 (from 8.00 to 9.00 min), 202 (from 9.00 min to 10.50 min, 228 (from 10.50 to 12.50 min), 252 (from 12.50 to 14.50), and finally 276 (from 14.50 to the end of the chromatogram). The MS source and quadrupole temperatures were kept at 230 and 150 °C, respectively.

2.3. Preparation of the polymer monolith in a fused silica capillary

To ensure covalent attachment of monolithic beds to the inner capillary wall, a previous surface modification of this wall was performed with 3-(trimethoxysilyl)propyl methacrylate [20]. Monolithic columns were prepared using a polymerization mixture composed by 20 wt% monomers (50 wt% BMA and 50 wt% EDMA) and 80 wt% porogens (50 wt% 2-PrOH and 50 wt% formamide) in the presence of 0.3 wt% of LPO. This polymerization mixture was sonicated for 10 min and purged with nitrogen for 10 min more. Next, the modified capillaries were filled with polymerization mixture up to a length of 6 cm. Then, the capillaries were introduced into an oven at 70 °C for 24 h. After polymerization and using a HPLC pump, the resulting columns were flushed with methanol to remove the pore-forming solvents and any possible unreacted monomers or oligomers.

2.4. Analytical procedure

Fig. 2 schematically shows the steps involved in the proposed analytical method. Aliquots of 10 mL sample or standard solution, containing the target analytes, were placed in a glass vial and pumped through the monolithic column at 0.4 mL/min by means of the microLC pump. The system was washed by passing 5 mL of milli-Q water (0.4 mL/min) through the column. The aqueous phase remaining in the column was eliminated by means of a nitrogen stream. The retained analytes were eluted using 10 μL of methanol, being the organic phase directly collected on a cotton bead placed in the stainless steel interface. The interface was then transferred to the injection port of the gas chromatograph and heated by a focused air stream (generated by a heat gun) at 300 °C for 2 min to achieve the thermal desorption of the analytes. The PAHs were carried from the interface to the chromatographic column by means of the same helium stream used as carrier gas in the chromatographic separation.

3. Results and discussion

3.1. Interface design

For the interface design, several factors were initially taken into account. First of all, we consider that the stainless steel was the most appropriated material among others such as PTFE or other polymers on the basis of its higher thermal conductivity. This fact clearly favours the analyte desorption and transference to the chromatographic column. Among commercially available devices, the Swagelok reducing unions seemed to be an adequate alternative due to their commercial availability and the possibility of a double connection: the upper part for the carrier gas and the lower one for the needle required for the injection port of the gas chromatograph. Among them, we chose the 1/16–1/8 in. for compatibility with the tubing and needle since no differences were observed for the inclusion of the inert material in the central element of the unit.

Next, an inert material was included in the interface to retain the analytes which allows the joint transference to the chromatographic column while prevents the interference of organic solvent in the chromatographic separation. Three different materials were assayed, namely: glass wool, cotton and glass beads. The glass beads were discarded because they produce irreproducible results due to variations in the flow rate of the carrier gas during the heating process. It can be explained by a potential expansion of the beads as result of a temperature increase. The glass wool presents as inconvenient that the fibers can block the needle and thus make useless the interface. Therefore, cotton was selected as the most robust material. However, it must be considered the occurrence of artifacts in the chromatogram as result of the potential degradation of the cotton during the heating step when high temperatures were used.

3.2. Optimization of thermal desorption

The two main variables affecting the thermal desorption, namely temperature and desorption time were studied by adding aliquots of 10 μL of a methanolic standard solution containing the analytes at a concentration level of 500 μg/L to the cotton placed in the interface. For this study, a thermally controlled interface was employed. It consists of an aluminium heating block

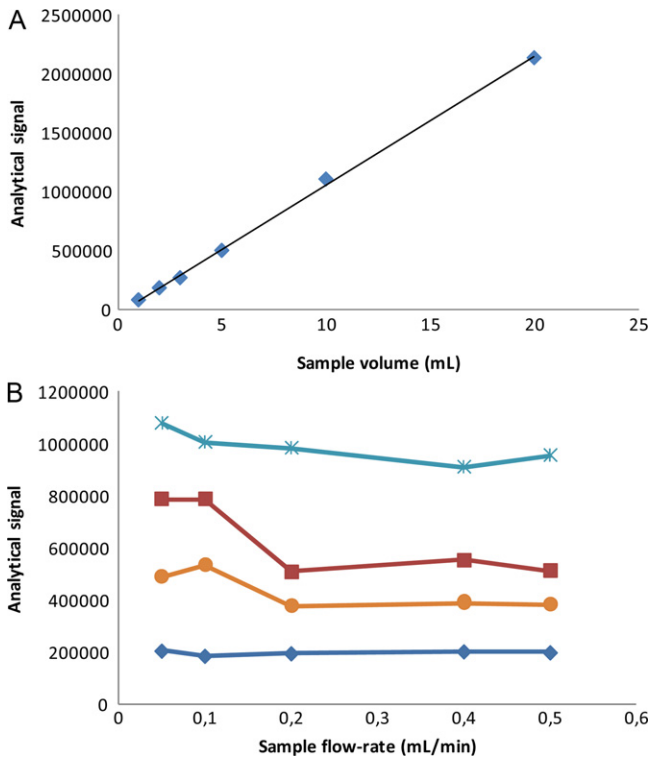

Fig. 3. (A) Influence of the sample volume on the analytical signal, exemplified for pyrene. (B) Effect of the sample flow rate on the analytical signal obtained for a selected group of analytes, ( ) pyrene, ( ) benzo(a)pyrene, ( ) acenaphthene, and ( ) fluorene.

and was provided with a heater and a temperature probe in order to hold the temperature required to carry out the desorption of the analytes and to reduce the equilibration time of the interface.

The desorption temperature was studied within the interval 200–500 °C. The results pointed out that the chromatographic separation was affected at the highest value as very dirty chromatograms were obtained as the likely result of the transference of cotton degradation products from the interface to the chromatographic column. Therefore, 300 °C was selected to evaluate the desorption time which was studied in the interval 30–180 s. The peak areas for the ten PAHs increased when increasing the time up to 120 s, remaining constant over this value, being thus selected as optimum value. This temperature can be also achieved by using an external focused heated air stream.

3.3. Optimization of the extraction conditions

The variables directly related with the extraction step, namely: volumes of sample and eluent as well as flow rates for preconcentration and elution, were studied using aqueous standards containing a selected group of the target analytes at a concentration of 5 μg/L.

The hydrodynamic variables were evaluated in order to maximize the analytical signals for the target compounds. The sample and eluents volumes are critical parameters for the method sensitivity, since they will determine the preconcentration factor. The sample volume was studied within the interval 1–20 mL and the results obtained are represented in Fig. 3A for pyrene. As can be seen, the chromatographic peak areas increased when increasing the sample volume within the studied interval. However, 10 mL were selected as a compromise between sensitivity and sample throughput. The volume of methanol required for analytes elution was studied between 10 and 40 μL with negligible influence in the analytical signal, taking into account that the entire organic fraction is collected in the interface. Therefore, 10 μL was selected for further studies.

The flow-rates for the preconcentration and elution steps were studied between 0.05 and 0.5 mL/min. Fig. 3B shows the variations of the peak areas for a selected group of analytes when different sampling flow rates were used. Two different behaviours were observed, on the one hand, pyrene and fluorene were not affected by this variable, on the other hand a slight decreasing of the peaks areas of the rest of PAHs were observed at flow rates higher than 0.1 mL/min, remaining almost constant over this value. Finally, a flow rate of 0.4 mL/min was fixed in order to increase the sample throughput. Concerning the eluent flow-rate, it was observed that the analytical signal decreased at higher values due to the lower residence time of the methanol in the capillary. Therefore, 0.1 mL/min was chosen as optimum and the column eluent was collected for 6 s (*ca.* 10 μL) on the interface.

3.4. Analytical performance

The analytical features of the proposed method are summarized in Table 1. The calibration graphs for the 10 PAHs selected were constructed by preconcentrating twenty working standards of the mixture prepared in ultrapure water at different concentration (between 12.5 ng/L and 5 μg/L). For all the analytes, the same behaviour was observed since two different linear ranges appeared. The first linear range, obtained for low concentrations, seemed to be very sensitive. In the second linear range (obtained for higher concentrations), the calibration slope was lower (in the range from 3 to 10% respect to the first one).

The method was evaluated in terms of precision, linearity and limits of detection. The precision of the method (repeatability), expressed as relative standard deviation of the peak areas, was calculated from 11 replicates analyses of aqueous standards prepared at a concentration of 50 ng/L. As can be seen in Table 1, the obtained values ranged from 4.5% (pyrene) and 18.2% (naphthalene). These values would be improved by using the corresponding isotopic labelled standards [21]. Linear ranges, method detection limits (MDLs) and enrichment factors are summarized in Table 1 The method detection limits (MDLs) were calculated according to the US-EPA guidance [22] and varied between 2.8 ng/L (indeno(1,2,3-cd)pyrene) and 11.5 ng/L (acenaphthene). These values were lower than those reported by other authors using a silica monolith as extractant phase holder in solvent bar microextraction [23] or similar to those reported for sol–gel coated capillaries or polymeric monolith in a stir bar [18,24] using larger sample volumes.

3.5. Recovery study

The proposed extraction method was applied to the determination of PAHs in a variety of environmental samples, namely: tap and river waters and sewage, collected from different locations. Only fluoranthene and pyrene were detected in all the samples analyzed although the concentration was in all cases lower than the corresponding quantitation limit and the legal limits as well. Fig. 4A shows the gas chromatogram obtained after the analysis of a sewage sample in which the chromatographic signal for fluoranthene and pyrene were observed. Therefore, in order to determine the feasibility of the proposed method, a recovery study was carried out. Thus, aliquots of 100 mL of samples were spiked with 100 ng/L of each compound and left stand for 24 h to facilitate potential analytes interaction with the sample matrix. Each sample was analyzed by quintuplicate; the results obtained are listed in Table 2. As can be seen, acceptable recovery values ranged between 69 ± 9%

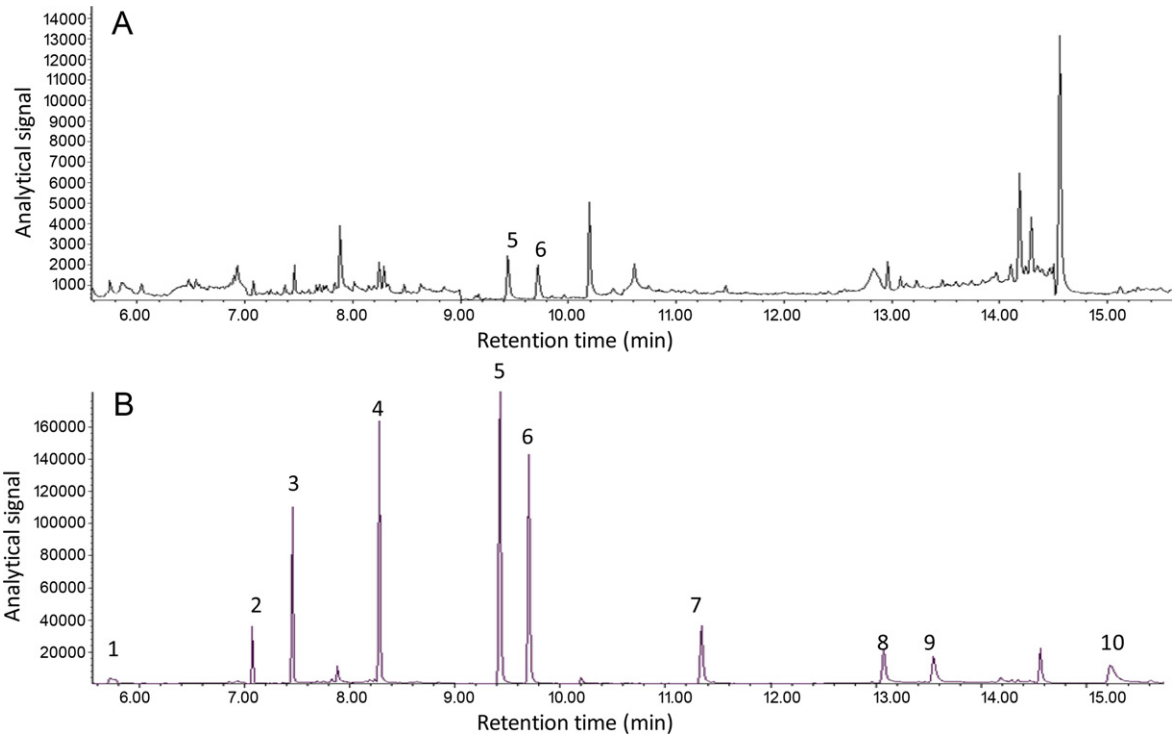

Fig. 4. (A) SIM chromatogram obtained for the analysis of a sewage sample analyzed following the proposed method. Peaks: (5) fluoranthene, (6) pyrene. (B) SIM chromatogram obtained after the analysis of a spiked (10 ng/L) river water analyzed following the proposed procedure. Peaks: (1) naphthalene, (2) acenaphthene, (3) fluorene, (4) anthracene, (5) fluoranthene, (6) pyrene, (7) benzo-anthracene, (8) benzo(k)fluranthene, (9) benzo(a)pyrene, (10) indeno(1,2,3-cd)pyrene.

(anthracene) and 95 ± 5% (benzo-anthracene). Additionally, the tap water sample was spiked with the analytes at concentrations covering the whole calibration range (100, 200 and 2000 ng/L) and treated as previously described. The results are summarized in Table 3 and show the good performance of the method within the dynamic interval. Fig. 4B shows a representative chromatogram of a spiked river water sample processed following the proposed method.

Table 1
Analytical figures of merit obtained for the 10 PAHS using the proposed extraction method.

	Analytical figures				
	Linear ranges (ng/mL)	R^2[a]	MDL (ng/L)[b]	RSD (%)[c]	EF[d]
Naphthalene	0.02–0.10 0.1–5.0	0.999 0.981	5.4	18.2	46 ± 1
Acenaphthene	0.035–0.500 0.5–5.0	0.999 0.988	11.5	7.6	19 ± 2
Fluorene	0.012–0.050 0.05–5.00	0.999 0.998	4.5	5.8	154 ± 4
Anthracene	0.012–0.100 0.1–5.0	0.998 0.990	3.6	6.0	228 ± 3
Fluoranthene	0.03–0.05 0.05–5.00	0.990 0.980	9.8	5.1	162 ± 4
Pyrene	0.012–0.100 0.1–5.0 0.012–0.050	0.999 0.990 0.999	3.9	4.5	148 ± 0
Benzo-anthracene	0.05–5.00 0.025–0.100	0.980 0.999	3.8	7.4	141 ± 8
Benzo (k)fluoranthene	0.1–5.0	0.980	7.7	9.2	125 ± 14
Benzo (a) pyrene	0.030–0.1 0.1–5	0.996 0.999	9.0	10.3	97 ± 14
lndeno(l,23-cd)pyrene	0.012–0.100 0.1–5.0	0.994 0.990	2.8	10.2	54 ± 1

[a] Regression coefficient.
[b] MDL: method detection limit.
[c] RSD: relative standard deviation.
[d] EF: enrichment factor.

Table 2
Recovery study of the proposed method for the determination of 10 PAHs in three different water and sewage samples (concentration added 100 ng/L).

Samples	Tap water R (%) ± SD, n = 5	River water R (%) ± SD, n = 5	Sewage R (%) ± SD, n = 5	Average values R (%), n = 15
Naphthalene	95 ± 15	99 ± 15	74 ± 10	89
Acenaphthene	83 ± 6	72 ± 6	90 ± 8	82
Fluorene	99 ± 6	87 ± 5	69 ± 4	85
Anthracene	65 ± 4	62 ± 4	80 ± 5	69
Fluoranthene	87 ± 5	87 ± 5	69 ± 4	81
Pyrene	88 ± 4	88 ± 4	70 ± 3	82
Benzo-anthracene	98 ± 7	98 ± 7	89 ± 6	95
Benzo (k) fluoranthene	87 ± 8	98 ± 10	71 ± 7	85
Benzo (a) pyrene	84 ± 9	83 ± 9	81 ± 9	83
Indeno(1,2,3-cd)pyrene	57 ± 6	58 ± 6	53 ± 6	56

Table 3
Recovery study of the proposed method for the determination of 10 PAHs in tap water at three concentration levels.

Analyte	100 ng/L R (%) ± SD, n = 5	500 ng/L R (%) ± SD, n = 5	2000 ng/L R (%) ± SD, n = 5
Naphthalene	95 ± 15	84 ± 12	85 ± 10
Acenaphthene	83 ± 6	96 ± 7	93 ± 8
Fluorene	99 ± 6	84 ± 4	82 ± 4
Anthracene	65 ± 4	78 ± 6	78 ± 5
Fluoranthene	87 ± 5	95 ± 7	87 ± 4
Pyrene	88 ± 4	86 ± 4	92 ± 3
Benzo-anthracene	98 ± 7	90 ± 6	93 ± 7
Benzo (k) fluoranthene	87 ± 8	89 ± 10	81 ± 7
Benzo (a) pyrene	84 ± 9	82 ± 9	85 ± 9
Indeno(1,2,3-cd)pyrene	57 ± 6	60 ± 6	59 ± 5

4. Conclusions

The analytical method presented in this article combines an extraction procedure based on a monolithic capillary with the GC/MS determination. Monolithic polymer was prepared in a fused silica capillary by *in situ* polymerization and investigated as an adsorbent for the preconcentration of PAHs. The butyl methacrylate monolith adsorbent is mechanically stable and no frits or other special structures are needed to retain them in place. In addition, owing to the smaller size of the capillary column, only a small volume of eluent is needed. The methanolic extract containing the PAHs is directly collected into a specific interface, which can be adapted to the injection port of the gas chromatograph for analytes thermal desorption. The proposed interface is an alternative to the large volume injection approach since no especial configuration for the injector is required. Method detection limits in the range 2.8–11.5 ng/L were obtained by using 10 mL of sample. The method is highly reproducible and robust. The lifetime of the monolithic capillary is also relevant. In fact, it can be used for *ca.* 3 months without performance losses and significant backpressure (28–45 bar). The present investigation demonstrates the satisfactory applicability of polymer monolith as a capillary sorbent. Further research would involve the fully automation of the extraction procedure and the on-line coupling with the gas chromatograph.

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