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# Determination of polycyclic aromatic hydrocarbons in waters by use of supercritical fluid chromatography coupled on-line to solid-phase extraction with disks

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**Abstract**

The potential of supercritical fluid chromatography (SFC) coupled on-line to solid-phase extraction (SPE) with disks for determining sixteen different polycyclic aromatic hydrocarbons (PAHs) was assessed. A preliminary study of the chromatographic separation was conducted that led to the use of SPE coupled to SFC for improved detection limits. Disks of two different materials, i.e., $C_{18}$ and polystyrene–divinylbenzene, were assayed in terms of the variables influencing the extraction step. $C_{18}$ disks provided the best results, with detection limits ranging from 0.1 to 1.5 $\mu g\ l^{-1}$. The ensuing method was applied to river and tap water, with good repeatability and reproducibility, and no interference from the sample matrix.


*Keywords:* Water analysis; Extraction methods; Environmental analysis; Polynuclear aromatic hydrocarbons

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced by incomplete burning of fossil fuels and other organic materials, as well as from forest fires. As a result, they are widely distributed in soils, air and waters. Their high toxicity and widespread occurrence has led the US Environmental Protection Agency (EPA) to class sixteen of them as priority pollutants, the determination of which in environmental studies is therefore highly important.

This type of compound has so far been determined by using various chromatographic techniques including gas chromatography (GC) [1], high-performance liquid chromatography (HPLC) [2–12] and supercritical fluid chromatography (SFC) [13–15]. HPLC with fluorescence detection is by far the most frequently used choice for this purpose; however, while fluorimetric detectors are highly sensitive, they cannot afford the typically low levels of these compounds (in the parts-per-billion range), so they often call for an extraction–concentration step prior to HPLC analysis. Liquid–liquid extraction is the most common alternative for the detection of PAHs in waters [6]; however, the use of solid-phase extraction (SPE)–HPLC coupling in combination with $C_{18}$ packing materials for this purpose has grown significantly in recent times [16–20].

SFC has aroused increasing interest for environmental analyses on account of the high separation efficiency and short analysis times it provides. Although PAH separation by SFC was explored in

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recent research [21–23], work was focused on the separation and was performed with standard solutions at concentrations of 10–100 mg $l^{-1}$, which, to the authors' minds, does not afford the analysis of real samples, where PAHs occur at concentrations of only a few micrograms per litre. SFC had not been used to date in on-line combination with disk-based SPE. We believed that it could provide a suitable means for lowering existing detection limits for PAHs; also, SPE with supercritical $CO_2$ should be more selective than conventional liquid–liquid extraction and thus avoid potential matrix interferences, as was shown for the determination of phenolic compounds in a previous paper [24].

The purpose of this work was thus to assess the potential of SPE with disks, which have been successfully applied using HPLC and off-line SPE [20], coupled on-line to SFC for the determination of PAHs in water samples. To this end, the chromatographic conditions leading to the highest separation efficiency were established. Then, SPE with two types of disks [$C_{18}$ and polystyrene–divinylbenzene (PS–DVB)] were coupled on-line to SFC. The variables influencing the extraction efficiency (number of disks and drying time) were optimized and breakthrough volumes were determined. The method thus developed was used to analyse river and tap water samples for PAHs.

## 2. Experimental

### 2.1. Reagents

Methanol and isopropanol were of HPLC grade and were purchased from Lab-Scan (Dublin, Ireland). Standards of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene were supplied by Sigma (Madrid, Spain). Stock solutions of 100 mg $l^{-1}$ and the working solutions used for direct injection were made up in methanol in order to avoid miscibility problems with the mobile phase. Working solutions for extraction experiments were prepared by diluting stock solutions with nanopure water and adding 20% isopropanol, to prevent adsorption occurring [20]. Carbon dioxide (SFC grade) and helium (99.999% pure) were purchased from Carburos Metálicos (Barcelona, Spain).

### 2.2. Apparatus and procedure

A G1205A model supercritical fluid chromatograph from Hewlett-Packard (Palo Alto, CA, USA), equipped with a diode array detector, was used. The instrument was operated in the downstream mode. The volume used for direct injections was 5 μl (full loop). The following columns were tested: 125×4.6 mm Envirosep-PP (particle size, 5 μm) and 150×4.6 mm Spherisorb ODS2 (particle size, 5 μm) from Phenomenex (Torrance, CA, USA); 250×4.6 mm Partisil ODS (particle size, 10 μm) from Sugelabor (Madrid, Spain); and 150×4.0 mm Tracer PAHs $C_{18}$ (particle size, 5 μm) from Teknokroma (Barcelona, Spain). The modifier (methanol) gradient was initially held at 0% for 1 min, then raised at 7% $min^{-1}$ to 10%, which was held for 2 min, and finally raised at 20% $min^{-1}$ to 50%, which was held for a further 8 min. The flow-rate used was 2.5 ml $min^{-1}$. The outlet pressure was kept constant at 200 bar during analyses. The oven temperature was set at 40°C. For single wavelength monitoring, which was used to calculate all data, the detection was set at the optimum wavelength for each compound studied. The spectra were recorded between 210 and 350 nm.

On-line trace enrichment was carried out with Empore, $C_{18}$ and PS–DVB disks, all purchased from 3M (St. Paul, MN, USA), using a stainless steel membrane disk holder constructed in the workshop of the Free University of Amsterdam. A cutting device was used to obtain small membrane disks from the original 47 mm disks and these were arranged in the holder. In both cases, the sample was prepared by adding 20% isopropanol and the corresponding standard addition.

Two six-port rotary valves [25] from Rheodyne (Cotati, CA, USA) were arranged serially and were used to carry out the different steps of the preconcentration process, namely, conditioning and activation of the disks, retention of the analytes, and drying and elution of the analytes. Firstly, the preconcentration system was washed with methanol and then the disks were cleaned-up and conditioned with 10 ml of

methanol. After washing the tubes with water containing 20% isopropanol, the disks were activated with 10 ml of the same solution and again the tubes were cleaned with the sample solution. Then different sample volumes were preconcentrated, depending on the sorbent used. Before elution, the disks were dried with 5 bar of helium for the optimized time according to the type of sorbent. The analytes trapped in the disks were desorbed in the backflush mode and on-line transferred to the analytical columns.

When river or tap water was analyzed, samples were filtered through a 0.45-μm filter (MFS, Pleasanton, CA, USA) before analysis.

## 3. Results and discussion

### 3.1. Chromatographic separation

The chromatographic separation was assayed with different columns consisting of $C_{18}$ material of variable dimensions and degrees of polymerization. No individual column succeeded in resolving the mixture of the sixteen PAHs studied. We therefore considered using several serially arranged columns and tested various combinations.

The best results were obtained by serially connecting a 150×4.6 mm Spherisorb ODS2 column and a 125×4.6 mm Envirosep-PP column, both packed with 5 μm particles. Changes in column temperature and $CO_2$ pressure resulted in no significant variation of the selectivity or the retention parameters. A temperature of 40°C and a pressure of 200 bar were thus selected as optimal. The modifier content in the supercritical fluid was found to be the most influential parameter; the above-mentioned gradient was required in order to ensure the resolution of all of the mixture's components. The flow-rate of the mobile phase was 2.5 ml $min^{-1}$, which resulted in an analysis time of 14 min, which is shorter than that most commonly obtained using HPLC [20]. Lower flow-rates gave rise to unacceptably long chromatographic times and peak broadening or even fully overlapped peaks for the phenanthrene–anthracene couple.

The detection limits, calculated at a signal-to-noise ratio of three, ranged from 0.1 mg $l^{-1}$ for naphthalene to 0.8 mg $l^{-1}$ for benzo[*ghi*]perylene. The linearity range was similar for all of the compounds (0.8–12.0 mg $l^{-1}$), except for pyrene, benzo[*k*]-fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene and benzo[*ghi*]perylene (1.5–12.0 mg $l^{-1}$) and indeno[1,2,3,-*cd*]pyrene (1.5–8.4 mg $l^{-1}$).

### 3.2. Solid-phase extraction process

In order to lower the above detection limits, preconcentration of the PAHs by SPE with two different types of disks was assayed. The extractor was coupled on-line to the supercritical fluid chromatograph; the effects of the different experimental variables were examined and breakthrough volumes were calculated.

To study the influence of the number of disks, the membranes were activated with 10 ml of methanol and 10 ml of nanopure water containing 20% isopropanol. Then, a volume of 5 ml of a standard solution containing 6.0 μg $l^{-1}$ of each compound and 20% isopropanol was preconcentrated. Disks were initially dried for 10 min and after that, the retained analytes were eluted by the mobile phase. The number of disks tested were three, five and eight (the maximum possible with the holder used) with both sorbents. The best recoveries with both $C_{18}$ and PS–DVB were obtained by using eight disks, however, some PAHs were still recovered in proportions below 60% with PS–DVB disks. The recoveries obtained with eight disks of $C_{18}$ were higher than 86%, although for some PAHs, recoveries in excess of 100% were obtained as a result of distorted peaks, due to a drying time that was too short.

The optimum drying time for each sorbent was determined using the same SPE process as described above. The number of disks was eight, the value optimized previously. Recoveries obtained for each sorbent and with different drying times are shown in Table 1. Data were calculated using the optimum wavelength for each compound. Drying times of 10 min and longer gave rise to acceptably symmetric peaks, using $C_{18}$ or PS–DVB. However, the recoveries obtained with $C_{18}$ disks and a drying time of 10 min exceeded 100% for some PAHs. This may have been caused by residual solvent (water–isopropanol) altering the detector response, since a drying time of 20 min led to recoveries that were

Table 1
Recoveries (%) obtained using eight disks and different drying times (min) at a fortification level of 0.03 μg

| Peak Label | Compound | Retention time (min) | $C_{18}$ Drying time (min) | | | | | | Poly(styrene–divinylbenzene) Drying time (min) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 5 | | 10 | | 20 | | 5 | | 10 | | 20 | |
| | | | *R* | R.S.D. (%) | *R* | R.S.D. (%) | *R* | R.S.D. (%) | *R* | R.S.D. (%) | *R* | R.S.D. (%) | *R* | R.S.D. (%) |
| 1 | Naphthalene | 1.7 | 88 | 4 | 86 | 4 | 76 | 3 | 86 | 6 | 88 | 4 | 89 | 5 |
| 2 | Acenaphthylene | 2.2 | 120 | 6 | 101 | 5 | 79 | 5 | 50 | 7 | 55 | 7 | 52 | 5 |
| 3 | Acenaphthene | 2.3 | 154 | 4 | 134 | 5 | 83 | 4 | 82 | 5 | 83 | 3 | 83 | 4 |
| 4 | Fluorene | 2.5 | 147 | 3 | 136 | 6 | 94 | 4 | 79 | 7 | 84 | 6 | 85 | 8 |
| 5 | Phenanthrene | 3.2 | 133 | 6 | 118 | 5 | 94 | 5 | 48 | 8 | 58 | 7 | 60 | 6 |
| 6 | Anthracene | 3.4 | 151 | 5 | 130 | 4 | 98 | 6 | 96 | 5 | 97 | 6 | 97 | 6 |
| 7 | Fluoranthene | 4.3 | 189 | 7 | 166 | 5 | 102 | 5 | 81 | 5 | 93 | 4 | 60 | 5 |
| 8 | Pyrene | 5.0 | 185 | 4 | 157 | 3 | 108 | 3 | 74 | 4 | 76 | 6 | 81 | 5 |
| 9 | Benz[*a*]anthracene | 6.5 | 198 | 8 | 178 | 7 | 103 | 7 | 65 | 7 | 65 | 7 | 64 | 8 |
| 10 | Chrysene | 7.1 | 210 | 7 | 196 | 8 | 107 | 6 | 58 | 6 | 60 | 7 | 60 | 7 |
| 11 | Benzo[*b*]fluoranthene | 8.4 | 204 | 5 | 189 | 4 | 106 | 5 | 65 | 5 | 63 | 6 | 50 | 6 |
| 12 | Benzo[*k*]fluoranthene | 8.7 | 167 | 4 | 143 | 4 | 79 | 4 | 90 | 5 | 94 | 5 | 80 | 4 |
| 13 | Benzo[*a*]pyrene | 9.7 | 174 | 6 | 154 | 5 | 99 | 5 | 55 | 7 | 57 | 6 | 53 | 6 |
| 14 | Dibenz[*a,h*]anthracene | 10.9 | 169 | 7 | 145 | 8 | 81 | 7 | 39 | 8 | 47 | 9 | 38 | 7 |
| 15 | Indeno[1,2,3-*cd*]pyrene | 12.6 | 106 | 5 | 102 | 6 | 95 | 5 | 48 | 5 | 54 | 4 | 50 | 4 |
| 16 | Benzo[*ghi*]perylene | 13.0 | 187 | 8 | 160 | 7 | 101 | 6 | 53 | 7 | 55 | 6 | 52 | 5 |

*R*=Recovery (%).

Table 2
Recoveries (%) obtained for different sample volumes, all of which were spiked with 0.03 μg of each compound

| Compound | $C_{18}$ Volume (ml) | | | | | | | | Poly(styrene–divinylbenzene) Volume (ml) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 5 | | 10 | | 25 | | 50 | | 5 | | 10 | |
| | R | R.S.D. (%) | R | R.S.D. (%) | R | R.S.D. (%) | R | R.S.D. (%) | R | R.S.D. (%) | R | R.S.D. (%) |
| Naphthalene | 76 | 3 | 71 | 3 | 68 | 5 | 62 | 4 | 8 | 2 | 60 | 6 |
| Acenaphthylene | 79 | 4 | 77 | 2 | 58 | 8 | 40 | 8 | 55 | 3 | 45 | 8 |
| Acenaphthene | 83 | 5 | 83 | 4 | 84 | 4 | 75 | 5 | 83 | 4 | 76 | 4 |
| Fluorene | 94 | 3 | 86 | 3 | 76 | 4 | 68 | 5 | 84 | 2 | 53 | 3 |
| Phenanthrene | 94 | 6 | 95 | 5 | 93 | 7 | 93 | 6 | 58 | 5 | 48 | 7 |
| Anthracene | 98 | 5 | 106 | 4 | 100 | 8 | 102 | 7 | 97 | 4 | 69 | 5 |
| Fluoranthene | 102 | 6 | 94 | 5 | 93 | 7 | 64 | 4 | 93 | 4 | 61 | 6 |
| Pyrene | 108 | 4 | 99 | 2 | 101 | 3 | 101 | 4 | 76 | 4 | 60 | 1 |
| Benz[*a*]anthracene | 103 | 7 | 102 | 8 | 105 | 6 | 107 | 6 | 65 | 1 | 44 | 4 |
| Chrysene | 107 | 8 | 97 | 6 | 108 | 7 | 105 | 8 | 60 | 8 | 49 | 9 |
| Benzo[*b*]fluoranthene | 106 | 3 | 98 | 3 | 104 | 5 | 100 | 3 | 63 | 6 | 49 | 5 |
| Benzo[*k*]fluoranthene | 79 | 4 | 78 | 5 | 80 | 3 | 99 | 6 | 94 | 3 | 61 | 5 |
| Benzo[*a*]pyrene | 99 | 5 | 86 | 4 | 87 | 7 | 85 | 6 | 57 | 4 | 46 | 3 |
| Dibenz[*a,h*]anthracene | 71 | 6 | 73 | 7 | 71 | 8 | 75 | 7 | 47 | 6 | 28 | 9 |
| Indeno[1,2,3-*cd*]pyrene | 95 | 4 | 79 | 4 | 78 | 6 | 71 | 5 | 54 | 5 | 57 | 5 |
| Benzo[*ghi*]perylene | 101 | 7 | 97 | 7 | 94 | 8 | 91 | 9 | 55 | 4 | 39 | 8 |

R=Recovery (%).

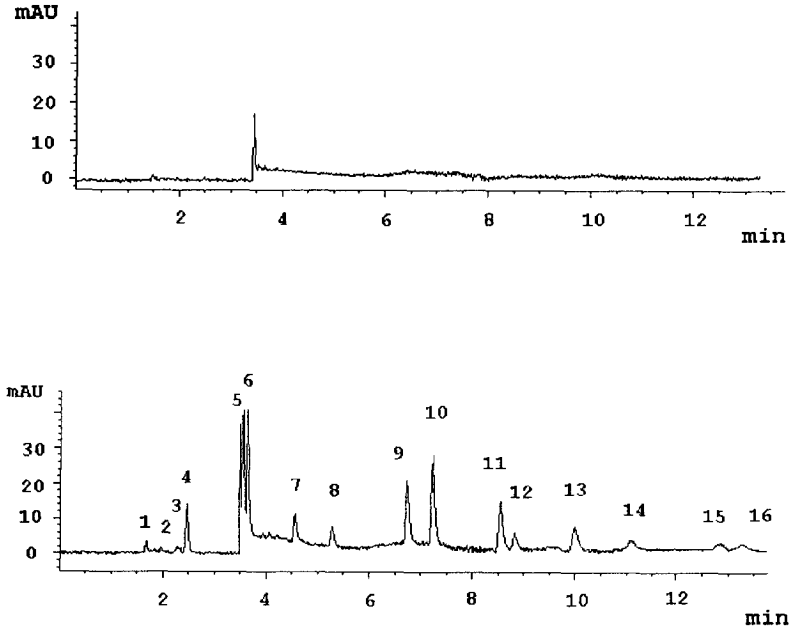


Fig. 1. Chromatograms (254 nm) of tap water. (A) Blank, (B) tap water spiked with 0.03 μg of each compound. $C_{18}$ disks were employed. See Table 1 for peak labelling.

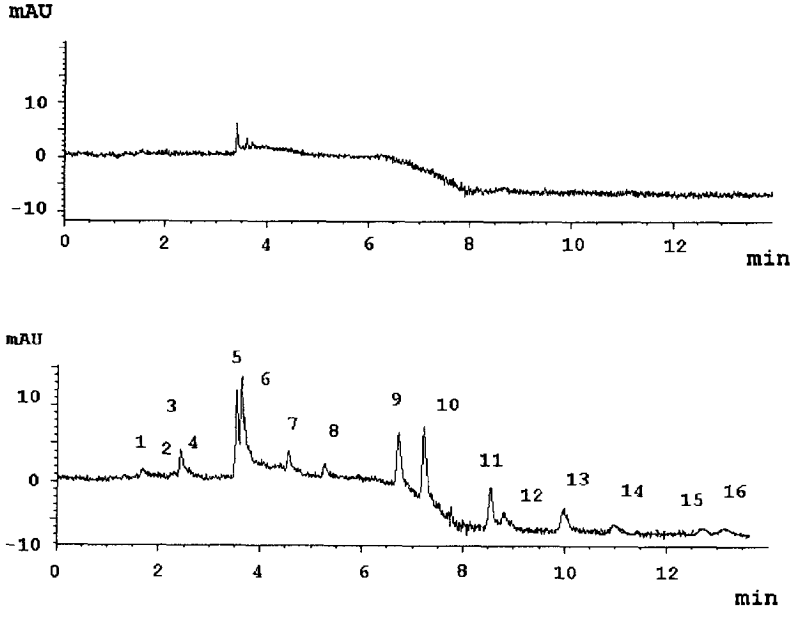


Fig. 2. Chromatograms (254 nm) of river water. (A) Blank, (B) river water spiked with 0.03 μg of each compound. $C_{18}$ disks were used. See Table 1 for peak labelling.

Table 3
Detection limits and linearity obtained with tap and river water samples ($n=2$)

| Compound | Tap water | | | | | | River water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | LODs (μg/l) | Linearity | $a$ | $S_a$ | $b$ | $S_b$ | LODs (μg/l) | Linearity | $a$ | $S_a$ | $b$ | $S_b$ |
| Naphthalene | 0.2 | 0.4–6.2 | 32.8 | 2.1 | −22.9 | 8.3 | 0.4 | 0.8–6.0 | 30.8 | 1.8 | −27.8 | 7.2 |
| Acenaphthylene | 0.4 | 0.8–6.3 | 13.7 | 0.6 | 2.3 | 2.5 | 0.6 | 0.8–6.2 | 15.1 | 1.0 | 2.7 | 4.2 |
| Acenaphthene | 0.3 | 0.4–6.0 | 32.6 | 2.3 | −21.3 | 9.2 | 0.3 | 0.4–6.2 | 28.9 | 2.1 | −11.9 | 8.3 |
| Fluorene | 0.5 | 0.8–6.3 | 8.2 | 0.2 | 2.2 | 0.8 | 0.7 | 0.9–6.3 | 8.3 | 0.1 | −4.0 | 0.4 |
| Phenanthrene | 0.3 | 0.5–6.0 | 13.2 | 0.7 | −4.8 | 2.6 | 0.4 | 0.7–5.9 | 10.2 | 0.5 | 4.5 | 2.1 |
| Anthracene | 0.3 | 0.4–6.1 | 13.8 | 0.5 | 9.0 | 2.0 | 0.3 | 0.4–6.3 | 16.4 | 1.0 | −1.0 | 4.1 |
| Fluoranthene | 0.5 | 0.8–6.0 | 14.1 | 0.8 | −6.4 | 3.1 | 0.7 | 0.9–6.0 | 11.4 | 0.8 | −0.6 | 3.3 |
| Pyrene | 0.7 | 0.9–6.3 | 11.6 | 0.6 | −4.5 | 2.2 | 0.8 | 0.9–6.0 | 12.4 | 0.6 | −5.6 | 2.3 |
| Benz[*a*]anthracene | 0.3 | 0.4–6.1 | 20.1 | 1.4 | −4.6 | 5.4 | 0.5 | 0.8–6.3 | 18.0 | 1.3 | −1.6 | 5.0 |
| Chrysene | 0.3 | 0.4–6.0 | 15.4 | 0.3 | 13.5 | 1.1 | 0.4 | 0.8–6.0 | 17.0 | 0.8 | −3.5 | 3.1 |
| Benzo[*b*]fluoranthene | 0.8 | 1.5–6.4 | 8.8 | 0.5 | 2.5 | 1.9 | 1.0 | 1.3–6.3 | 8.6 | 0.5 | −2.3 | 1.9 |
| Benzo[*k*]fluoranthene | 1.2 | 1.5–6.1 | 4.6 | 0.3 | 0.5 | 1.3 | 1.5 | 2.0–6.3 | 3.8 | 0.2 | 2.5 | 0.8 |
| Benzo[*a*]pyrene | 1.5 | 2.0–6.0 | 7.4 | 0.4 | 2.7 | 1.5 | 1.5 | 2.0–6.3 | 9.1 | 0.4 | −2.5 | 1.6 |
| Dibenz[*a,h*]anthracene | 0.6 | 0.8–6.0 | 18.3 | 1.0 | 3.2 | 3.9 | 0.7 | 0.8–6.0 | 16.9 | 0.9 | 3.3 | 3.4 |
| Indeno[1,2,3-*cd*]pyrene | 2.5 | 3.0–4.2 | 6.0 | 0.2 | 0.6 | 0.6 | 2.7 | 3.0–4.2 | 5.3 | 0.2 | 1.6 | 0.5 |
| Benzo[*ghi*]perylene | 2.5 | 6.3–3.0 | 5.2 | 0.3 | 0.1 | 1.3 | 2.5 | 3.0–6.0 | 6.2 | 0.4 | 1.3 | 1.6 |

$a$=Slope.
$b$=Intercept.
$S_a$=Standard deviation of the slope.
$S_b$=Standard deviation of the intercept.

closer to 100%. For PS–DVB, similar results were obtained with both drying times. In the light of previous results, drying times of 20 min for $C_{18}$ disks and of 10 min for PS–DVB disks were chosen.

Under the previously established conditions, breakthrough volumes of the PAHs were determined by preconcentrating different volumes of standard solutions (Table 2). As can be seen, PS–DVB disks

Table 4
Repeatability and reproducibility obtained with tap and river water samples spiked with 0.03 μg of each PAH ($n=5$)

| Compound | Tap water | | River water | |
|---|---|---|---|---|
| | Repeatability R.S.D. (%) | Reproducibility R.S.D. (%) | Repeatability R.S.D. (%) | Reproducibility R.S.D. (%) |
| Naphthalene | 2.9 | 3.5 | 6.2 | 7.0 |
| Acenaphthylene | 2.1 | 5.1 | 5.6 | 7.5 |
| Acenaphthene | 2.4 | 4.7 | 6.8 | 8.3 |
| Fluorene | 5.5 | 5.2 | 5.8 | 5.6 |
| Phenanthrene | 5.1 | 6.9 | 6.3 | 8.3 |
| Anthracene | 5.0 | 6.7 | 5.5 | 6.0 |
| Fluoranthene | 3.5 | 5.6 | 3.9 | 4.2 |
| Pyrene | 2.8 | 6.9 | 6.0 | 7.6 |
| Benz[*a*]anthracene | 4.7 | 5.1 | 4.8 | 6.6 |
| Chrysene | 2.1 | 2.9 | 5.9 | 5.2 |
| Benzo[*b*]fluoranthene | 3.5 | 4.7 | 5.2 | 9.7 |
| Benzo[*k*]fluoranthene | 1.3 | 4.9 | 4.0 | 6.5 |
| Benzo[*a*]pyrene | 2.5 | 2.9 | 2.0 | 5.0 |
| Dibenz[*a,h*]anthracene | 3.8 | 4.9 | 4.8 | 5.9 |
| Indeno[1,2,3-*cd*]pyrene | 3.6 | 6.8 | 6.0 | 9.3 |
| Benzo[*ghi*]perylene | 2.0 | 4.9 | 5.5 | 7.1 |

provided considerably low recoveries even when 5 ml volumes were used, on the other hand, losses of the first eluted compounds were obtained by preconcentrating volumes greater than 10 ml on $C_{18}$ disks. Therefore, sample volumes of 5 and 10 ml were selected for PS–DVB and $C_{18}$ disks, respectively.

It should be noted that, as expected, $C_{18}$ disks provided recoveries (above 70% in all instances) that were higher than those of PS–DVB disks, therefore, we selected $C_{18}$ disks for the preconcentration step.

The detection limits of the ensuing method were calculated at a signal-to-noise ratio of three using the optimum wavelength for each compound. The values obtained varied between 0.1 and 1.5 $\mu g\ l^{-1}$. The linearity range studied was 0.4–6.0 $\mu g\ l^{-1}$. A concentration factor of almost 1000 was achieved.

River and tap water samples were spiked with variable quantities of the PAHs and were analysed using the proposed method. No matrix interference was apparent (Fig. 1 Fig. 2, recorded at 254 nm). The detection limits obtained ranged between 0.2–2.5 $\mu g\ l^{-1}$ for both river and tap water. The linearity ranges (Table 3) were also similar in both cases to those obtained using nanopure water.

The repeatability and between-day reproducibility of the proposed method were estimated by preconcentrating 10 ml of tap water spiked with 0.03 $\mu g$ of each PAH. As can be seen in Table 4, the differences between the values obtained from tap and river water samples are quite small.

## 4. Conclusions

The sixteen priority PAHs in the EPA list were separated in 13 min by using SFC with two serially arranged $C_{18}$ columns. All of the analytes were satisfactorily resolved.

The drying time was found to be highly influential on the SPE combined on-line with SFC. It should be noted that while a drying time of 10 min or longer produced symmetric, undistorted peaks, $C_{18}$ disks required over 20 min of drying for consistent recoveries to be obtained. $C_{18}$ disks provided the best results as regards recovery, with detection limits in the range of 0.1–1.5 $\mu g\ l^{-1}$ when 10 ml of sample were preconcentrated.

The application of the proposed method to the analysis of river and tap water samples for the PAHs studied was not subject to matrix interferences. Also, the reproducibility and repeatability of the analyses were always quite acceptable. Therefore, the method is useful for the determination of PAHs in these types of water samples.

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