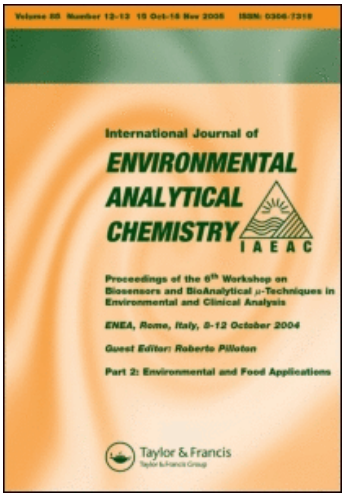

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Determination of Polycyclic Aromatic Hydrocarbons in Water by Solid-Phase Extraction Membranes

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER BY SOLID-PHASE EXTRACTION MEMBRANES

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A method for determining sixteen PAHs, which are included in the US Environmental Protection Agency list of priority pollutants is described. The procedure involves column liquid chromatography with fluorescence and UV detection and off-line concentration with solid-phase extraction membranes. In this study, two different membranes are tested, C18 and SDB. Different steps for cleaning and conditioning the membranes to prevent interfering peaks in the chromatogram were studied. The use of an organic solvent and Brij-35 as surfactant to prevent the analytes from being adsorbed on inner walls or surfaces is studied. The method enables these compounds to be determined in tap and river water samples at low ng l^{-1} levels.

KEY WORDS: Polycyclic aromatic hydrocarbons, high-performance liquid chromatography, solid-phase extraction membranes, tap and drinking water analysis.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment, as a result of natural or man-home incomplete combustion of organic materials. Several PAHs which contain from four to six fused rings are known to be carcinogenic or mutagenic and their presence in different matrices needs to be controlled, particularly in water[1,2]. According to a proposal by the Commission of European Communities about the quality of water for human consumption, the sum of concentrations of 6 PAHs must not exceed 0.2 $\mu g\ l^{-1}$ and 0.01 μg^{-1} for benzo[a]pyrene[3]. The Environmental Protection Agency also established a list of organic compounds containing sixteen PAHs for monitoring in effluent waters[4].

Determining PAHs in water samples is difficult for several reasons, mainly because of their low solubility in water which means they tend to adsorb on the walls and surfaces with which they come into contact, but also because light, residual chlorine and biodegradation, can change their concentration; thus introducing considerable losses during sampling and storage[5–7].

Due to the usual low levels in real samples, a preconcentration step prior to analysis is required. Both solid-phase extraction (SPE)[8–14] and liquid-liquid extraction (LLE)[15–16] have been reported to enrich PAHs from water. However, solid-phase extraction has more advantages because it is faster, does not require large volumes of volatile organic solvents, allows to concentrate PAHs from larger volumes of water, and is more efficient than the traditional liquid-liquid technique. To prevent the adsorption of PAHs on the walls of the water containers, some authors add an organic solvent such as methanol or

acetonitrile to the sample[14,17,18] while others add surfactants to the aqueous media to increase its solubility[14,17,19–21]

PAHs are commonly analyzed by gas chromatography (especially capillary gas chromatography) in combination with FID or MS detector[22–25] or by HPLC with fluorescence detection[13,14,16,26,27]. Capillary gas chromatography is known to have much higher resolution than HPLC methods, but nowadays, HPLC can easily separate the 16 EPA priority PAHs.

This paper describes a method for preconcentrating and determining these PAHs in water. Systematic studies were made of the off-line preconcentration of these compounds, using two different solid-phase extraction membranes, C18 and SDB. The effect of stabilizing the sample with 2-propanol and Brij-35 on recovering the PAHs was also studied. The performance of the method was checked with tap and river water.

EXPERIMENTAL

Chemicals

The sixteen EPA priority PAHs studied are: (1) naphtalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benz[*a*]anthracene, (10) chrysene, (11) benzo[*b*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene, (14) dibenz[*a,h*]anthracene, (15) benzo[*ghi*]perylene and (16) indeno[*1,2,3-cd*]pyrene. They were all supplied by Sigma. A standard solution of 500 mg l^{-1} was prepared by weighing 5 mg of each compound and dissolving in a volumetric flask with 10 ml of acetonitrile. To determine recovery values in the solid-phase extraction studies, standard solutions were prepared daily by diluting this standard solution with Milli-Q quality water (Millipore, Bedford, MA,USA).

Milli-Q quality water, acetonitrile HPLC gradient-grade and 2-propanol were from Scharlau (Barcelona, Spain) and Brij-35 was supplied by Fluka (Buchs, Switzerland). Anhydrous sodium sulphate from Probus (Barcelona, Spain) dichloromethane Pestanal grade from Riedel-de-Haën (Seelze, Germany) and Ethyl acetate purchased from Probus (Barcelona, Spain) were used. A 10% solution of Na_2SO_3 purchased from Scharlau (Barcelona, Spain) was used to remove the free chlorine before adding the standard solution to tap water.

Equipment

Analyses were performed on a HP series 1050 liquid chromatograph (Waldbronn, Germany) equipped with an injector valve which had a sample loop of 20 µl with a HP 1046A programmable fluorescence detector used in series with a HP series 1050 ultraviolet-visible detector. Chromatographic data were collected and recorded on a HP Chemstation version A.01.01. The analyses were carried out with a 150 × 4 mm Tracer PAH C18 reverse-phase column from Teknokroma (Barcelona, Spain) with a particle size of 5 µm.

Chromatographic conditions

The chromatographic separation was carried out with a Tracer PAHs analytical column. In the mobile phase Milli-Q water was used as solvent A and acetonitrile as solvent B. A

two step gradient elution analysis was used. For five minutes there was an isocratic elation of 50% acetonitrile which rose linearly to 100% after 50 minutes. The flow rate was 1.5 ml min^{-1} and the temperature was 30°C. For more sensitive detection of the different PAHs, optimum excitation and emission wavelengths had to be used for each component and for this purpose a wavelength detection program was developed (Table 1). With an UV detector, a wavelength was established at 228 nm to obtain optimum response for acenaphthylene.

Sample preparation

Off-line solid-phase membrane extraction was carried out using a standard Millipore 47-mm filtration apparatus. The membrane extraction disks were Empore disks manufactured by 3M (St. Paul, MN, USA). The disks were 47 mm in diameter and 0.5 mm thick and each disk contained about 500 mg of C18-bonded silica or styrene-divinylbenzene copolymer (SDB).

Prior to the extraction procedure, the disks were conditioned. In this process, for C18 disks, 20 ml of organic elution solvent (dichloromethane/ethyl acetate/acetonitrile in a ratio of 50/30/20 v/v/v) was added to the filtration reservoir and drawn slowly through the disk by applying a slight vacuum. After drawing air through the disk for five minutes, 20 ml of acetone/water mixture in a ratio of 80/20 v/v was added and drawn slowly through the filtration disk. Then 10 ml of Milli-Q water was added before the extraction process of the sample.

The styrene-divinylbenzene copolymer (SDB) disks were conditioned with 20 ml of acetone, 20 ml of acetonitrile and 20 ml of dichloromethane. After each addition a vacuum was applied to remove interfering compounds from the disk. Then, 20 ml of Milli-Q water was added and drawn through the disk as a step prior to sample preconcentration.

After this step, samples with organic modifiers or surfactants to prevent compounds of interest from being adsorbed were passed through the disk. Then, the excess of water was removed from the disk by a few minutes of full vacuum. After this operation, the PAHs trapped in the disk were collected using 2 × 15 ml of a mixture of dichloromethane, ethyl acetate and acetonitrile (5030/20)(v/v/v). The extract was dried over anhydrous sodium sulphate to eliminate residual water and transferred to a concentration tube marked at 1 ml. Using a rotary evaporator from Büchi (Flavil, Switzerland), the mixture was evaporated under vacuum and at room temperature to

Table 1 Fluorescence detection conditions used to analyse PAHs.

Time (min)	*Wavelength (nm)*	
	Excitation	*Emission*
0	220	330
8	215	322
12	250	368
15.5	236	440
17.5	232	420
21	265	396
28	255	420
35	300	410
37.5	230	450

about 0.5 ml. The extract was adjusted to 1 ml with acetonitrile and injected into the chromatograph with a 20 µl loop.

RESULTS AND DISCUSSION

The detection of the 16 PAHs with good sensitivity requires the combination of UV and fluorescence detection. One of them (acenaphthylene) must be detected with a UV detector because its response to fluorescence is low[14]. To this end, absorbance wavelength was set at 228 nm to detect acenaphtylene at its maximum value, and for the rest of the compounds a program with different excitation and emission wavelengths was performed. Table 1 shows the program that was used and Figure 1 shows the

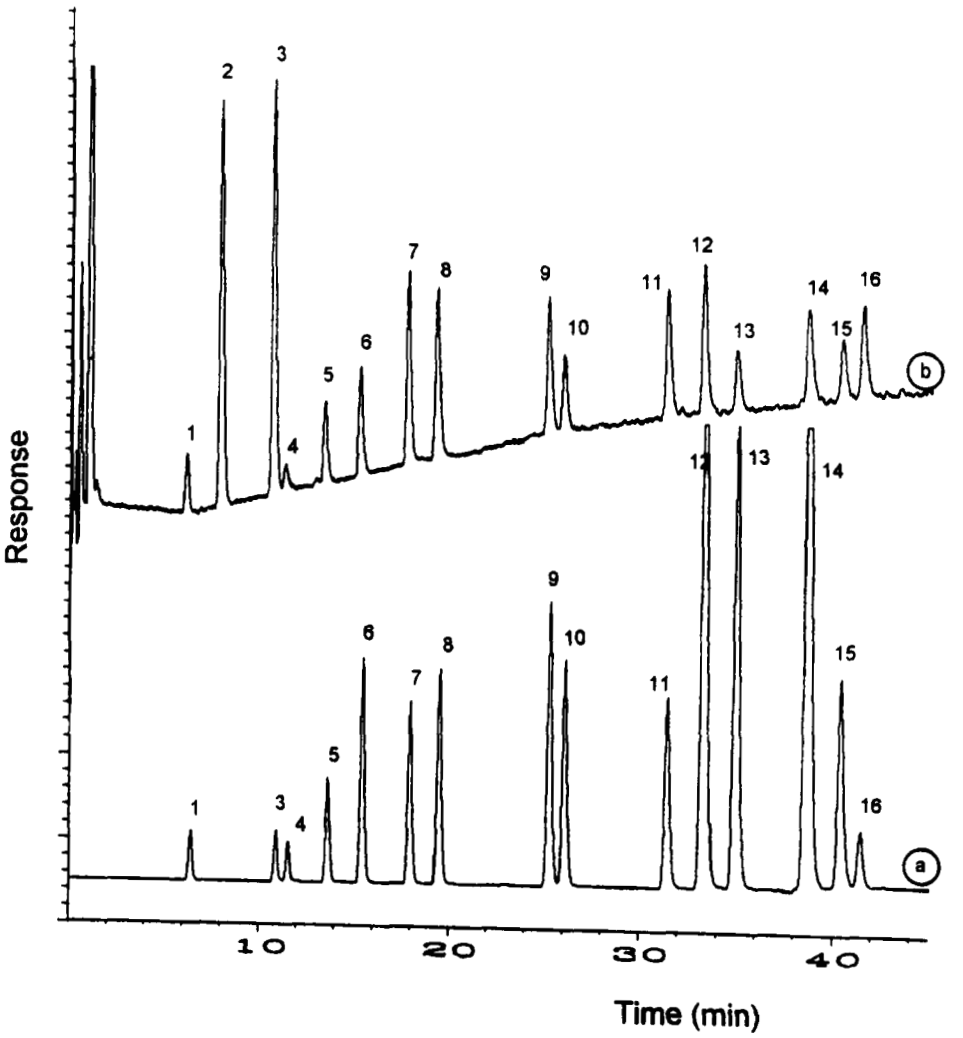

Figure 1 Chromatogram of 0.2 mg l^{-1} of the standard solution. a) fluorescence detection and b) UV detection. (For experimental conditions see text).

chromatogram of the standard solution of 0.2 mg l^{-1} of the sixteen PAHs obtained with both detectors.

The response linearity was determined by direct injection and in a concentration range between 0.01–1 mg l^{-1}. Good linearity was observed for all compounds with a correlation coefficient higher than 0.9990. The detection limits were between 0.1 and 3.0 μg l^{-1} for a signal to noise ratio of 3, except for acenaphthylene that was 25 μg l^{-1}.

Although chromatographic methods with fluorescence detection provide good detection limits for PAHs, preconcentration step must be introduced to decrease these values. Systematic research has been carried out to find a quick, simple and reproducible method for preconcentrating PAHs in water using membrane disks which have many advantages over cartridges when large sample volumes are to be analyzed. In this comparative study, styrene-divinylbenzene and octadecyl bonded silica membranes were used.

As a first step, a preliminary test was carried out to select an appropriate eluent to desorb PAHs from the disk. For this study, 100 ml of a standard solution of 5 μg l^{-1} of each compound was passed through a C18 disk and eluted twice with 15 ml of different organic solvent. Then, the organic solvent was dried over anhydrous sodium sulphate to eliminate residual water, concentrated under vacuum at room temperature to approximately 0.5 ml and diluted to 1 ml with acetonitrile before being injected into the chromatograph. To avoid adsorption losses, all glassware was rinsed with organic solvent before preparing the standard samples.

Elution with common organic solvents such as acetonitrile, ethyl acetate or dichloromethane leads to a low recovery of the PAHs especially for compounds which have more than three rings. After several experiments with different solvents, the best recoveries were obtained with a mixture of dichloromethane, ethyl acetate and acetonitrile in the ratio 50/30/20 (v/v/v).

When low concentrations of these compounds have to be analyzed, organic solvent or micellar media is usually added to prevent the adsorption process. In this study 2-propanol was preferred to other organic solvents such as methanol or acetonitrile and results are compared with those obtained when Brij-35 is used as surfactant.

In this study, 100 ml of Milli-Q water spiked with 0.5 μg l^{-1} of fifteen PAHs studied and 29 μg l^{-1} of acenaphthylene was passed through conditioned C18 and SDB disks and eluted twice with 15 ml of organic mixture, concentrated under vacuum to 0.5 ml, eluted to 1 ml with acetonitrile and injected into the chromatograph. The same experiment was carried out adding 10% and 15% of 2-propanol to this standard solution before extraction. Table 2 shows the recovery values obtained in these experiments.

Better results were obtained when an organic solvent was added to the sample, particularly for compounds with high retention times. For these compounds, values near to 95% for C18 and 85% for SDB disks were obtained if 15% of 2-propanol was added to the sample. On the other hand, lower recoveries were obtained for more polar compounds when this organic solvent was added. In this case, the best results were obtained with no organic media or with only 10% of 2-propanol. The use of C18 or SDB disks did not give very significant differences when analyzing these compounds in the range studied, but the best results were obtained when a C18 disk was used with 15% of 2-propanol.

Similar experiments were performed using micellar media with Brij-35 since this is a better additive from the environmental point of view. Different concentrations from 1.10^{-4} M to 1.10^{-3} M were added to the water samples in order to decrease the PAHs adsorption on the walls of the container. This concentration is higher than its critical micellar concentration (CMC). Table 3 shows the results obtained in different experiments, where the best results were obtained at 3.10^{-4} M for the more polar

Table 2 Influence of the percentage of 2-propanol in the sample on PAHs using C18 and SDB membrane extraction. (Results are the mean of three determinations) (See text for conditions)

Compound	*Recovery and RSD (%) in the presence of 2-propanol*					
	0%		*10%*		*15%*	
	C18	*SDB*	*C18*	*SDB*	*C18*	*SDB*
Naphthalene	86 ± 3.1	89 ± 3.0	80 ± 5.2	75 ± 7.6	70 ± 7.2	62 ± 8.7
Acenaphthylene	83 ± 4.3	85 ± 3.1	80 ± 5.5	80 ± 4.5	75 ± 6.1	65 ± 7.6
Acenaphthene	85 ± 3.3	87 ± 3.6	83 ± 4.5	82 ± 4.3	81 ± 5.6	70 ± 6.3
Fluorene	87 ± 3.5	85 ± 4.1	85 ± 3.5	80 ± 5.5	86 ± 5.8	73 ± 6.3
Phenanthrene	84 ± 4.0	88 ± 3.2	92 ± 3.0	90 ± 3.2	95 ± 3.2	78 ± 5.7
Anthracene	79 ± 5.2	81 ± 3.1	85 ± 3 4	75 ± 4.5	93 ± 3.1	78 ± 5.5
Fluoranthene	75 ± 5.0	70 ± 4.9	92 ± 3.1	80 ± 4.8	97 ± 3.0	79 ± 4.8
Pyrene	74 ± 6.1	70 ± 5.2	92 ± 3.2	75 ± 5.6	97 ± 3.3	71 ± 5.8
Benzo(*a*)anthracene	64 ± 7.5	52 ± 7.6	72 ± 4.6	82 ± 4.7	98 ± 3.4	85 ± 4.3
Chrysene	71 ± 6.8	53 ± 8.2	75 ± 5.2	80 ± 3.5	99 ± 3.2	84 ± 3.8
Benzo(*b*)fluoranthene	66 ± 7.4	45 ± 8.7	74 ± 6.3	77 ± 4.7	99 ± 3.1	85 ± 4.1
Benzo(*k*)fluoranthene	74 ± 6.9	50 ± 7.8	85 ± 4.1	78 ± 5.6	95 ± 3.2	88 ± 4.0
Benzo(*a*)pyrene	54 ± 8.7	44 ± 8.6	75 ± 5.2	69 ± 7.5	95 ± 4.0	85 ± 4.2
Dibenz(*a,h*)anthracene	59 ± 8.8	39 ± 8.9	77 ± 5.6	73 ± 7.7	97 ± 3.3	72 ± 5.6
Benzo(*ghi*)perylene	60 ± 8.3	37 ± 10.	81 ± 4 8	70 ± 8.3	97 ± 3.1	82 ± 4.8
Indeno(*1,2,3-cd*)pyrene	63 ± 7.9	40 ± 9.4	90 ± 3.3	75 ± 8.0	93 ± 3.1	80 ± 6.2

compounds and 1 $.10^{-4}$ M for the less polar ones. However, an organic solvent gives better recovery values than micellar media. For this reason, 15% of 2-propanol was used further on.

The highest volume that can be preconcentrated, with good recovery values was also investigated. Table 4 shows the results obtained using C18 and SDB membranes when the water volume was increased to 1000 ml and 15% of 2-propanol was added. There were important losses for only three more polar compounds mainly when the C18 membrane disk was used. Obviously, when a high volume of sample was analyzed, SDB enable these more polar compounds to be concentrated with higher recovery values than C18.

The background signal of an aqueous solution containing 15% of 2-propanol with a SDB membrane disk was studied. In this case, 1000 ml of Milli-Q water with 15% of 2-propanol was passed through the disk and eluted twice with 15 ml of the solvent mixture, concentrated under vacuum to 0.5 ml and diluted to 1 ml with acetonitrile. No interfering peaks were observed when low concentrations of the compounds of the interest had to be identified.

In order to determine the capacity of the disk, different concentrations between 500 ng l^{-1} and 5 ng l^{-1} of the sixteen PAHs were studied by preconcentrating a volume of 1000 ml Milli-Q water. Good recoveries were obtained for all compounds in this range of concentrations. With this sample volume, the detection limits of the method for a signal to noise ratio of 3 were between 0.2 ng l^{-1} for dibenz(*a,h*) anthracene and 3.7 ng l^{-1} for fluorene for the fluorescence detector, and 25 ng l^{-1} for acenaphtylene.

The method was used to determine these compounds in tap and river waters. No interference from the background signal was observed, so the identification and the quantification of PAHs in extracts are reliable if there is no matrix interference. On the other hand, the recovery values were similar to the ones obtained with Milli-Q water in the analysis of the tap and river waters spiked at the same level of concentrations as the previous study.

Table 3 Influence of the percentage of Brij-35 in the sample on PAHs using C18 membrane extraction (Values are the mean of three determinations)(See text for conditions).

Compound	*Recovery and RSD (%)*							
	1.10^{-4} M		*3.10^{-4} M*		*6.10^{-4} M*		*1.10^{-3} M*	
	C18	*SDB*	*C18*	*SDB*	*C18*	*SDB*	*C18*	*SDB*
Naphthalene	37 ± 9.7	62 ± 6.5	45 ± 7.9	59 ± 5.6	40 ± 7.4	63 ± 6.5	14 ± 10.8	27 ± 10.5
Acenaphthyltene	42 ± 8.9	5'9 ± 7.6	60 ± 5.6	55 ± 6.2	38 ± 8.4	65 ± 6.5	20 ± 10.6	66 ± 6.7
Acenaphthene	40 ± 7.8	63 ± 6.7	59 ± 6.4	59 ± 5.1	36 ± 8.7	65 ± 6.2	15 ± 10.9	62 ± 7.2
Fluorene	39 ± 9.5	59 ± 7.8	83 ± 4.2	49 ± 7.2	34 ± 9.2	56 ± 7.6	22 ± 9.8	52 ± 8.3
Phenanthrene	72 ± 7.6	60 ± 8.8	85 ± 4.1	55 ± 6.7	70 ± 6.5	72 ± 5.4	38 ± 8.7	58 ± 8.3
Anthracene	71 ± 8.5	59 ± 9 5	75 ± 5.3	50 ± 7.2	62 ± 6.8	54 ± 7.1	35 ± 8.4	50 ± 8.7
Fluoranthene	42 ± 9.7	63 ± 8.3	>100 ± 8.7	43 ± 8 3	73 ± 6.5	58 ± 7.6	18 ± 10.8	49 ± 9.1
Pyrene	52 ± 8.6	58 ± 8.9	>100 ± 9.2	41 ± 8.8	88 ± 4.2	57 ± 7.9	45 ± 8.5	45 ± 8.6
Benzo(*a*)anthracene	57 ± 8.8	55 ± 7.8	66 ± 5.3	42 ± 8.9	63 ± 5.8	56 ± 6.7	42 ± 8.3	46 ± 8.2
Chrysene	56 ± 9.4	58 ± 8.9	74 ± 4.6	41 ± 9 3	68 ± 5.4	63 ± 7.8	32 ± 9.4	45 ± 8.5
Benzo(*b*)fluoranthene	59 ± 9.2	53 ± 8.5	61 ± 5.7	41 ± 9.4	53 ± 6.2	45 ± 8.6	35 ± 9.7	40 ± 9.2
Benzo(*k*)fluoranthene	64 ± 8.4	57 ± 9.3	56 ± 6.8	45 ± 7.9	52 ± 7.1	47 ± 8.5	25 ± 10.4	40 ± 9.3
Benzo(*a*)pyrene	65 ± 7.9	49 ± 9.7	54 ± 7.1	44 ± 8.4	44 ± 8.6	48 ± 8.9	17 ± 10.8	45 ± 8.9
Dibenz(*a,h*)anthracene	66 ± 6.8	55 ± 9.2	38 ± 9.3	45 ± 7.9	28 ± 10.4	48 ± 9.3	15 ± 10.5	41 ± 7.8
Benzo(*ghi*)perylene	65 ± 8.7	45 ± 9.8	35 ± 10.3	36 ± 9.5	27 ± 10.5	42 ± 9.2	15 ± 10.6	33 ± 8.6
Indeno(*1,2,3-cd*)pyrene	77 ± 7.2	50 ± 8.7	40 ± 9.6	41 ± 7.2	36 ± 9.8	45 ± 9.0	20 ± 9.8	37 ± 8.8

Table 4 Recovery dependence on sample volume spiked at 1 μg l^{-1} using C18 and SDB membrane disks. (Values are mean of three determinations)

Compound	*Volume of sample with 15% of 2-propanol*							
	100 ml		*250 ml*		*500 ml*		*1000 ml*	
	C18	*SDB*	*C18*	*SDB*	*C18*	*SDB*	*C18*	*SDB*
Naphthalene	70 ± 6.5	45 ± 8.7	58 ± 8.3	52 ± 7.8	29 ± 11.3	48 ± 7.5	13 ± 15.4	60 ± 7.2
Acenaphthyltene	77 ± 5.8	50 ± 9.6	65 ± 7.2	57 ± 8.2	47 ± 6.8	49 ± 8.2	27 ± 9.8	59 ± 8.3
Acenaphthene	81 ± 5.7	56 ± 8.9	75 ± 6.7	58 ± 8.5	76 ± 4.7	50 ± 9.3	50 ± 8.7	69 ± 6.5
Fluorene	86 ± 4.8	58 ± 8.8	81 ± 5.4	60 ± 7.5	82 ± 4.1	80 ± 5.4	66 ± 7.6	70 ± 6.3
Phenanthrene	95 ± 3.1	78 ± 6.4	90 ± 4.2	81 ± 4.6	98 ± 3.1	95 ± 3.4	91 ± 3.4	90 ± 4.5
Anthracene	93 ± 3.2	71 ± 6.5	90 ± 4.3	73 ± 5.7	93 ± 3.2	90 ± 3.3	93 ± 3.2	85 ± 5.4
Fluoranthene	97 ± 3.0	79 ± 5.8	91 ± 3.7	82 ± 4.2	97 ± 3.0	92 ± 3.2	89 ± 4.3	87 ± 4.8
Pyrene	97 ± 3.2	81 ± 4.2	89 ± 4.3	87 ± 3.6	97 ± 3.2	94 ± 3.7	79 ± 5.6	89 ± 4.7
Benzo(*a*)anthracene	98 ± 3.5	85 ± 4.1	95 ± 3.2	88 ± 3.8	100 ± 3.5	95 ± 3.6	98 ± 3.1	91 ± 4.0
Chrysene	100 ± 6.5	84 ± 3.5	95 ± 3.1	89 ± 3.2	100 ± 3.4	94 ± 4.0	89 ± 4.2	90 ± 3.9
Benzo(*b*)fluoranthene	99 ± 4.5	85 ± 3.7	95 ± 3.2	89 ± 3.1	100 ± 3.2	92 ± 4.1	98 ± 3.3	88 ± 4.3
Benzo(*k*)fluoranthene	95 ± 5.2	88 ± 3.2	94 ± 3 5	92 ± 3.0	95 ± 3.5	95 ± 4.2	95 ± 3.0	90 ± 4.5
Benzo(*a*)pyrene	95 ± 4.3	83 ± 4.0	93 ± 4.0	86 ± 3.6	97 ± 4.1	94 ± 3.8	97 ± 3.2	90 ± 4.6
Dibenz(*a,h*)anthracene	97 ± 3.5	82 ± 4.1	87 ± 4.3	85 ± 4.5	96 ± 4.0	90 ± 4.3	90 ± 4.3	86 ± 5.6
Benzo(*ghi*)perylene	97 ± 3.1	82 ± 3.8	92 ± 3.6	86 ± 4.5	100 ± 3.4	93 ± 3.7	97 ± 3.0	90 ± 4.8
Indeno(*1,2,3-cd*)pyrene	93 ± 3.7	80 ± 3.9	94 ± 3.2	84 ± 4.5	96 ± 3.3	91 ± 3.2	96 ± 3.0	88 ± 5.2

Figure 2 shows the chromatogram obtained when 1000 ml of tap water with 15% of 2-propanol was preconcentrated with a SDB membrane and injected into the chromatograph after the concentration step and the same sample spiked with a standard solution of 10 ng l^{-1} and 29 ng l^{-1} of acenaphtylene. Before the standard addition, the residual chlorine was removed by adding 300 µl of a 10% Na_2SO_3 solution for each 100 ml of water. The studied compounds could not be positively identified in the range studied.

Figure 3 shows the same procedure applied to a river water (Ebro). In this case, and using a fluorescence detector, a peak with the same retention time as naphthalene was obtained, at a concentration of 8 ng l^{-1}.

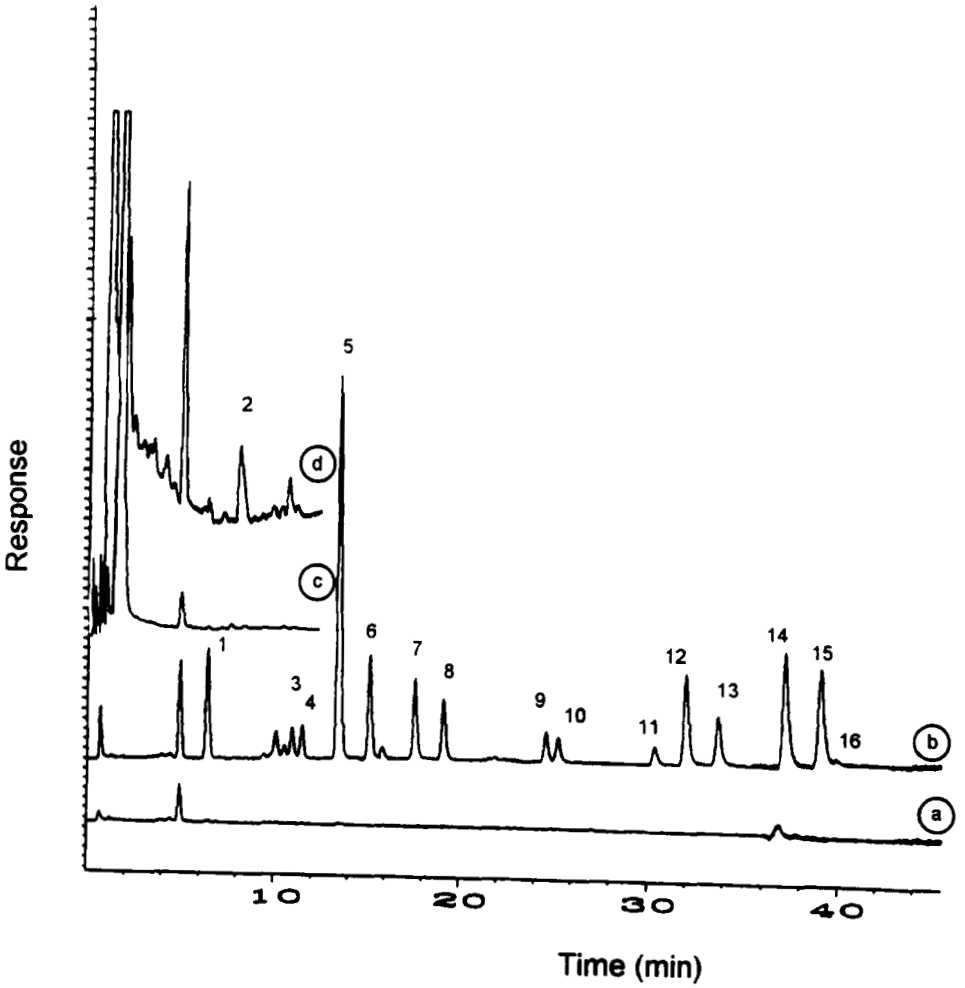

Figure 2 Chromatogram obtained in the analysis of tap water. a) tap water with fluorescence detection, b) tap water spiked with 10 ng l^{-1} of fifteen PAHs and 29 ng l^{-1} for acenaphtylene with fluorescence detection, c) tap water with UV detection and d) tap water spiked with the same standard solution with UV detection

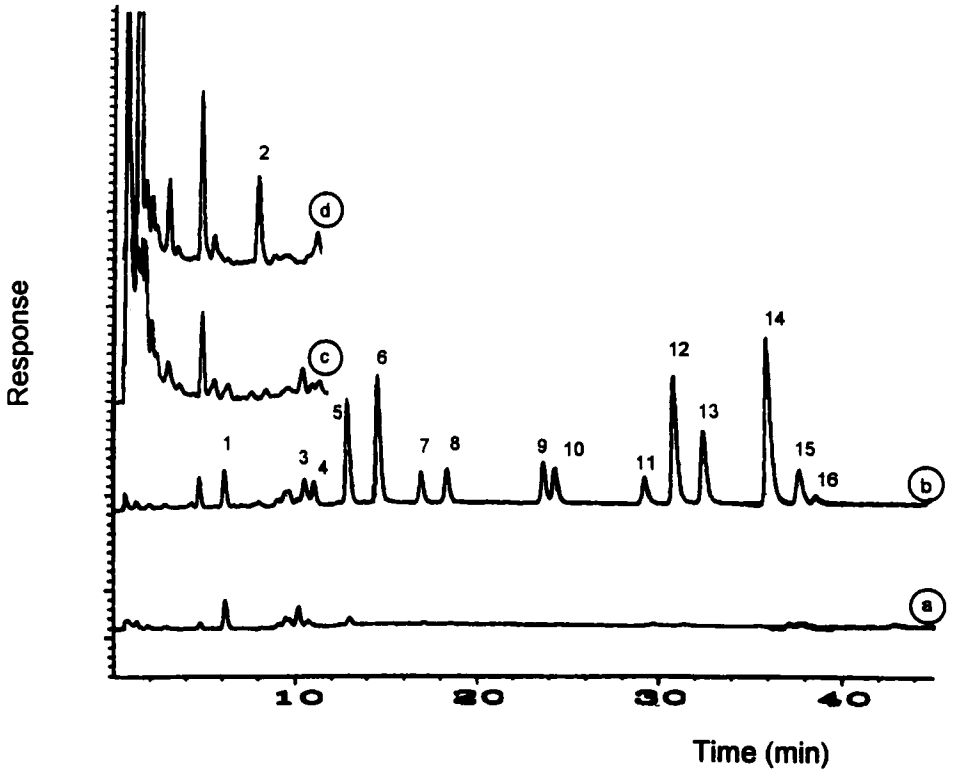

Figure 3 Chromatogram obtained in the analysis of river water (Ebro). a) river water with fluorescence detection, b) the same sample spiked with 10 ng l^{-1} of fifteen PAHs and 29 ng^{1} l for acenaphtylene with fluorescence detection, c) river water with UV detection and d) river water spiked with the same standard solution with UV detection.

CONCLUSIONS

The use of membrane disks and HPLC-with fluorescence and UV detection gives good results in terms of linearity and detectability, with limits of detection between 0.2 ng l^{-1} and 3.7 ng l^{-1}. SDB extraction disks gave better recoveries than C18 extraction disks when the volume of sample was1000 ml, mainly for compounds which elute first.

The use of 2-propanol as organic solvent in the aqueous solution increases PAHs preconcentration recoveries from water. Better results were obtained when this organic solvent was used instead of micellar media with Brij-35, although the latter should be recommended from the environmental point of view.

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