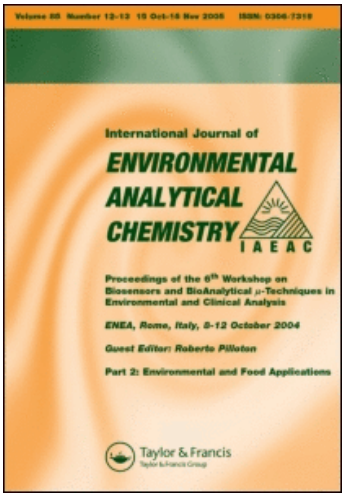

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

On-Line Trace Enrichment and HPLC Determination of Polycyclic Aromatic Hydrocarbons in Water

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To cite this Article Vila, L. E. Vera-A and Covarrubias, R.(1994) 'On-Line Trace Enrichment and HPLC Determination of Polycyclic Aromatic Hydrocarbons in Water', International Journal of Environmental Analytical Chemistry, 56: 1, 33 — 47
To link to this Article: DOI: 10.1080/03067319408044415
URL: http://dx.doi.org/10.1080/03067319408044415

Intern. J. Environ. Anal. Chem., Vol. 56, pp. 33-47
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ON-LINE TRACE ENRICHMENT AND HPLC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER

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(Received, 27 May 1993; in final form, 12 July 1993)

A fast and simple method for the determination of trace levels of polycyclic aromatic hydrocarbons in water is proposed. Problems arising from the adsorption of the heaviest hydrocarbons on vessels, filters and connection tubes have been mostly overcome by addition of acetonitrile to the sample before the preconcentration step. Recoveries >70%, RSD <10% and limits of detection ranging from 1.2 µg/l (naphthalene) to 4 ng/l (anthracene, fluoranthene and benzo(k) fluoranthene) were obtained with spiked water samples.

KEY WORDS: Polycyclic aromatic hydrocarbons, On-line trace enrichment, Water analysis.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), an important class of apolar compounds, are mainly introduced in the environment as a result of incomplete combustion of different materials, in particular petroleum fuels. These compounds are known to be strongly carcinogenic, specially the PAHs fraction containing 4 or more aromatic rings[1]. Although their solubility in water is very low, in the µg/l range, some of them have been found to be toxic at this concentration level. Therefore, very strict limits have been set for their total concentration in drinking and surface waters.

Traditional methods for the isolation of hazardous organic compounds, such as PAHs, from water for their LC or GC analysis are variations of the acid/base/neutral liquid-liquid extraction. This procedure involves large volumes of expensive solvents, several sample-handling steps and extensive labor and time.

Today, on-line concentration/analysis techniques, based on Solid Phase Extraction (SPE) with small precolumns coupled to high efficiency LC-columns, are one of the most powerful alternatives for the analysis of trace compounds in aqueous matrixes. Many applications of the technique to the determination of organic pollutants in drinking, surface and wastewaters

have been reported[2–9]. Compounds on a wide polarity range, including phenols[4,5], anilines[6]; herbicides[7,8] and pesticides[9], have been determined at ppb or (sub)ppb levels in water.

On the other hand, there are few reports on the application of SPE techniques, in on-line or off-line modes, to the preconcentration of strongly hydrophobic compounds from water. This fact seems surprising considering that this type of solutes are easily adsorbed on octadecyl bonded silicas, the most popular packing used for the extraction of organics from water. However, a strong hydrophobicity can be a severe drawback in some cases. Subra *et al.*[10,11] found that SPE methods were not adequate to recover very hydrophobic solutes from water because of their inefficient solubilization or their possible adsorption on the vessels and connection tubes. Thome *et al.*[12] reported the application of C-18 microcolumns for the off-line trace enrichment of PCBs from water, but they found that it was necessary to treat the glassware with dimethylchlorosilane to prevent adsorption of the compounds on the inner surfaces of glass vessels. Other works[13,14] report significant losses of analytes by adsorption on cellulose acetate membranes or other types of filters. This problem could be mitigated by addition of methanol to the water sample prior to filtration.

In the case of unsubstituted PAHs, only the lightest members of the group (≤ 4 aromatic rings) have been preconcentrated from water using off-line SPE[15,16]; no reports were found on the application of SPE for 5 or 6-ring PAHs.

In this paper we propose a methodology for the on-line trace enrichment of unsubstituted PAHs from water. Ten PAHs, including compounds from 2 to 6 aromatic rings, were used to develop the method. Because of the great differences of hydrophobicity among the members of the group, it was necessary to design two procedures for sample preparation: one for the analysis of 2-ring PAHs, the other for heavier ones. The only difference between them is the volume of organic solvent added to the sample before the preconcentration step.

EXPERIMENTAL

Chemicals

HPLC-grade acetonitrile, from Prolabo, and organic free Type-1 water, from a Nanopure deionizer (Barnstead Thermolyne Corp.), were used to prepare all the solutions and eluents.

The ten PAHs used in this work: Naphthalene (N), Fluorene (Fl), Phenanthrene (Ph), Anthracene (A), Fluoranthene (F), Pyrene (P), Benzo(a)Anthracene (B(a)A), Benzo(k)Fluoranthene (B(k)F), Dibenzo(ah)Anthracene (DBA) and Benzo(ghi)Perylene (B(ghi)P), were obtained from Accustandard. Each reference standard solution (0.2 mg/ml of each individual compound in methanol or methylene chloride) was dissolved in 25 ml of acetonitrile to give a concentration of 8 mg/l. A stock mixture of PAHs was made up from these solutions, or adequate dilutions of them, to give the following final composition (ppb): N 960, Fl 256, Ph 384, A 64, F 64, P 256, B(a)A 64, B(k)F 64, DBA 128 and B(ghi)P 64, in acetonitrile-water 65 : 35 v/v.

The stock mixture and dilutions of it: 1/2, 1/4, 1/8, 1/20, 1/40 and 1/80 were used to spike water samples (400 µl in 75 ml of pure water). They also were injected in the chromatograph to calculate PAHs recovery in each experiment.

Apparatus and materials

Percolation of water samples through the precolumn was performed with a Beckman 110A isocratic pump (preconcentration pump), which was modified to replace the Teflon tubing of the inlet line with a 1/8″ O.D. stainless steel tubing.

Precolumn elution and HPLC analysis were carried out with a Varian 5000 binary gradient system equipped with a Varian LC-100 variable wavelength spectrophotometer and a Gilson 121 filter fluorometer (305–395 nm excitation and 430–470 nm emission filters). Quantitative measurements of peak areas were made with Hewlett-Packard 3396A integrators.

A 7125 Rheodyne valve with a nominal 100 µl loop was used for the injection of standard PAHs mixtures. Loop calibration was performed *in situ* by injection of an excess volume of a perchloric acid solution of known concentration, which was displaced from the loop with 20 ml of pure water. The liquid collected at the valve exit was titrated with a standard NaOH solution. Results from 3 measurements gave the following values: Loop volume = 113 µl Relative Standard Deviation = 0.83%

A 7000 Rheodyne valve, with a precolumn placed at the position corresponding to the loop, was inserted between the 7125 Rheodyne injector and the HPLC column. This assembly allows the switching between two operating arrangements (Figure 1):

Position (A).—Sample concentration in the precolumn and simultaneous HPLC analysis of a standard PAHs mixture.

Position (B).—Precolumn elution and analysis of the sample.

Samples were prepared in amber glass bottles (~ 75 ml) fitted with a screw cap lined with Teflon. For the application of this method, water samples must be collected in this type of bottle at the sampling site. A minimum of two bottles filled up with the same sample is required for a complete analysis.

A Millipore glass filter holder with a nylon 66 membrane (0.4 µm pore size) was used for sample filtration. Before use, the membrane was soaked in acetonitrile for several hours, then, it was placed in the filter holder and rinsed with 10 ml of fresh acetonitrile and 20 ml of pure water.

Stationary phases and columns

The analytical column was a 15 cm × 4.6 mm I.D. stainless steel column home-packed with 5µ Spherisorb ODS-2 from Phase Separations.

The precolumn, 2 cm × 2 mm I.D. from Upchurch Scientific, was also home-packed with Spherisorb ODS-2. The packing procedure was as follows: with the precolumn seated over the hole of a stopper in the neck of a filtering flask, vacuum was applied and a thin slurry of the stationary phase was dropwise poured into the tube with a micropipette until the packing reached its top. This vacuum assisted packing procedure permitted us to obtain very reproducible precolumns. Extracolumn band broadening due to the precolumn was similar to that produced by a direct 100 µl injection of a standard in the HPLC column.

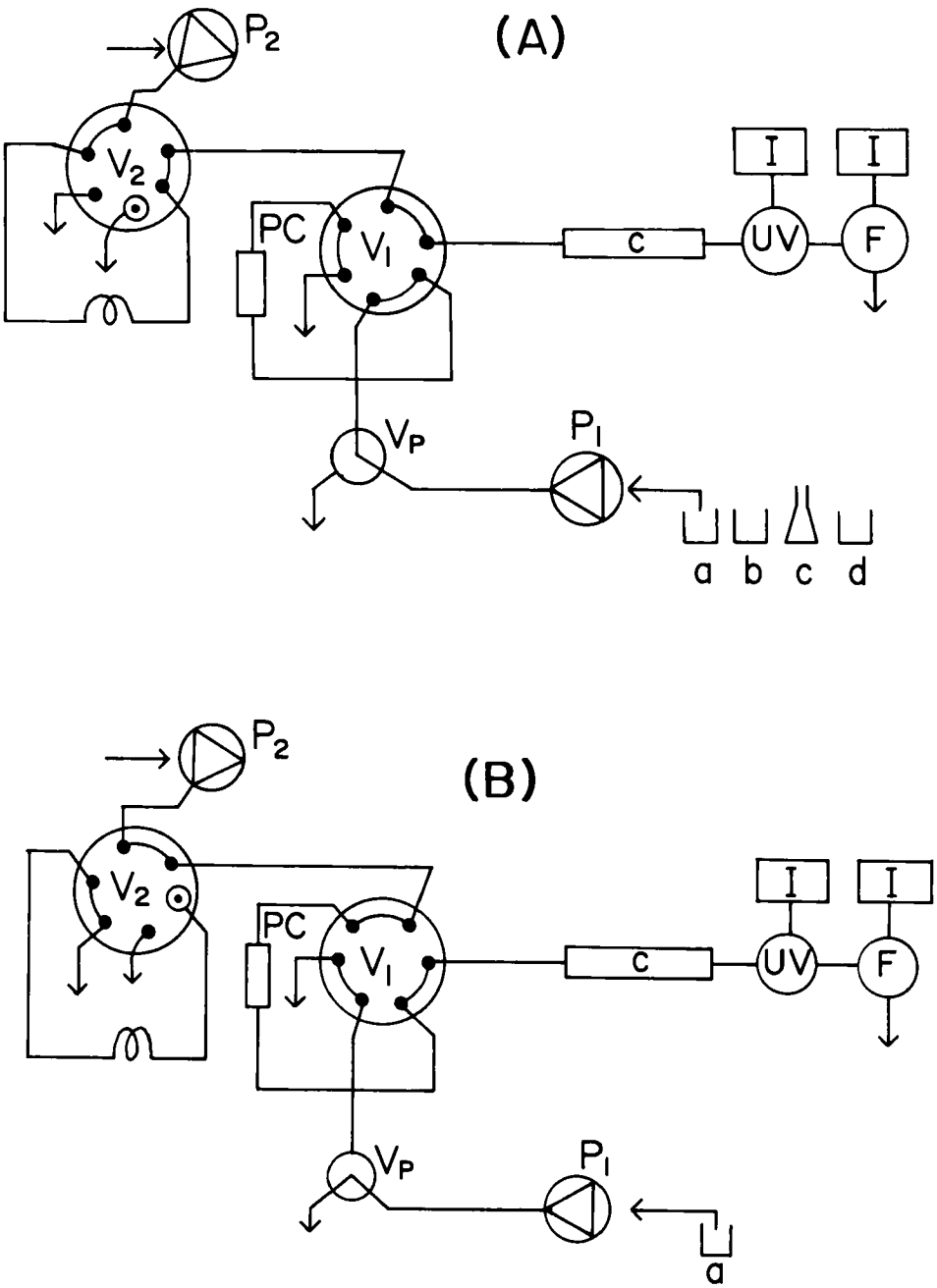


Figure 1 On-line system. (A) Regeneration of the precolumn and concentration of the sample. (B) Backflush elution of the precolumn and HPLC analysis. P1: isocratic pump; P2: gradient system; V1,V2: switching valves; Vp: purge valve; PC: precolumn; C: HPLC-column; UV,F: UV and Fluorescence detectors; I: integrator; a,b,c,d: solvent and sample reservoirs.

PROCEDURE

Breakthrough curves

Solutions of naphthalene or anthracene in various acetonitrile-water mixtures were used to measure breakthrough volumes of these analytes in the precolumn. First, the precolumn directly coupled to the UV detector was equilibrated with the adequate solvent mixture, then, the solution of the analyte, at mg/l (naphthalene) or µg/l (anthracene) levels, was percolated while the absorbance of the eluate was recorded.

Preconcentration and analysis

Figure 1 shows the scheme of the experimental assembly used for sample preconcentration and analysis.

Preliminary experiments proved that a considerable proportion of the heaviest PAHs was adsorbed on the surface of Teflon or other plastic materials, even in the presence of relatively high contents (25%) of acetonitrile in the sample. Therefore, the inlet Teflon tubing of the preconcentration pump was replaced with a stainless steel tubing. Besides, it was not possible to adapt a selecting valve at the pump inlet because the valve body and its channels are manufactured with Teflon. Instead, a stainless steel purge valve was installed just before the inlet port of the 7000 Rheodyne valve in order to completely fill and rinse the lines and the pumphead with the adequate solvent, or with the sample, before pumping it to the precolumn.

The following procedure for sample preconcentration and analysis was adopted:
With the switching valves in the position shown in Figure 1A, the precolumn is rinsed with 10 ml of pure acetonitrile (reservoir a), equilibrated with 20 ml of the adequate acetonitrile-water mixture (reservoir b), loaded with exactly 25 ml of the sample prepared as described in the next section (reservoir c), and, finally, flushed with 1 ml of pure water (reservoir d). Next, with the valves in the position shown in Figure 1B, the analytes trapped in the precolumn are backflush desorbed and transferred to the analytical C-18 column by an acetonitrile gradient. When the analysis is finished, the valves are switched to their first position and a new cycle begins with the next sample. Experimental conditions for preconcentration and HPLC analysis are summarized in Table 1.

It is interesting to remark that, while the preconcentration procedure is carried out, a simultaneous analysis of a calibrating standard injected in valve 2 can be performed.

Sample preparation

Preliminary preconcentration/analysis experiments using different acetonitrile-water mixtures placed in the reservoir of the preconcentration pump, where they were spiked with PAHs, gave the following results:
Recovery of PAHs dissolved in pure water was too low except for 2-ring hydrocarbons. If PAHs were dissolved in acetonitrile-water 5:95 v/v, the recovery of 2 and 3-ring compounds

Table 1. Experimental conditions for on-line concentration and analysis of polyaromatic hydrocarbons

PRECONCENTRATION
Precolumn (20×2 mm I.D.) packed with 5μ Spherisorb ODS-2
Regeneration:
10 ml of acetonitrile + 20 ml of acetonitrile-water mixture 5:95 v/v for 2-ring PAHs analysis or 23:77 v/v for other PAHs
Sample Loading: 25 ml
Flushing: 1 ml of pure water
Flow: 2 ml/min Room Temperature

ANALYSIS
Column (150×4.6 mm I.D.) packed with 5μ Spherisorb ODS-2
Flow: 1 ml/min Room Temperature
Gradient Elution: A = acetonitrile-water 10:90 v/v
B = acetonitrile

TIME (min)	0	2	18	30	40	50
%B	33	33	40	70	92	92

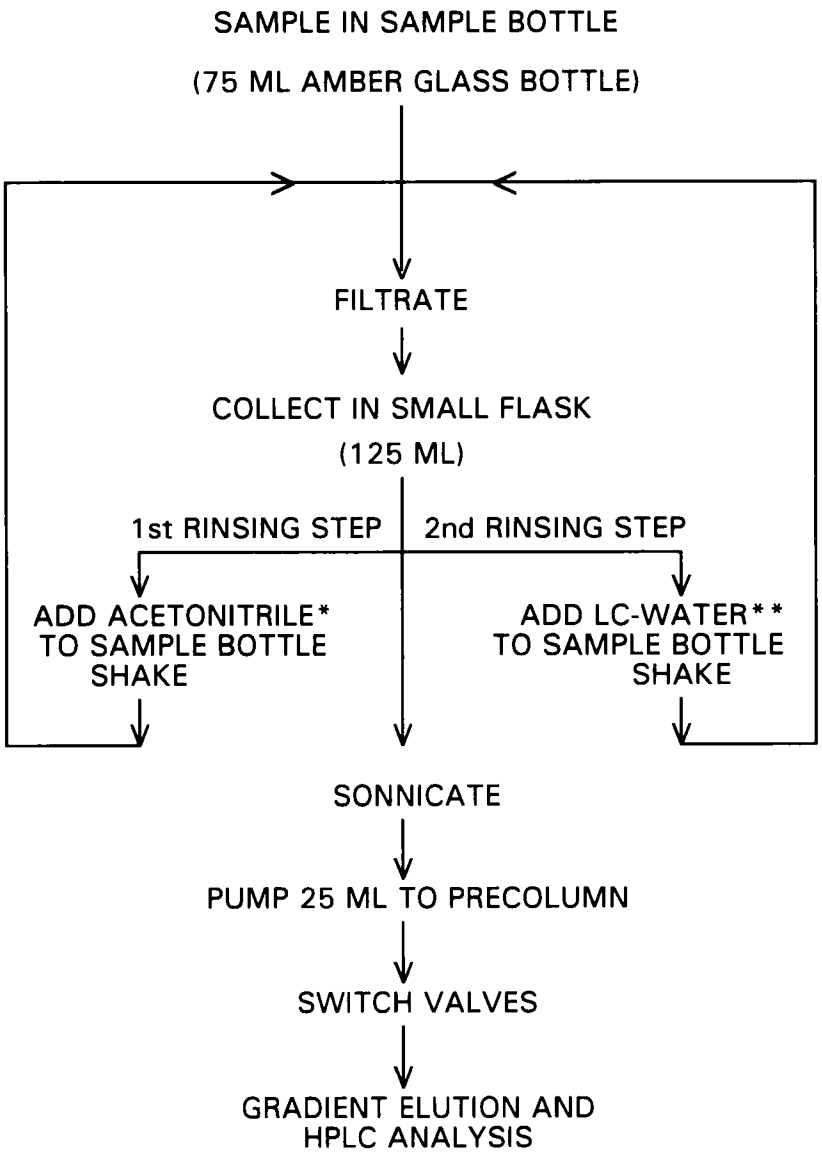
UV Detection: λ = 262 nm (0-38.5 min); λ = 288 nm (>38.5 min)
Fluorescene Detection: Excitation Filter 305–395 nm
Emission Filter 430–470 nm

increased but it remained too low for heavier solutes. A good recovery of ≥3-ring PAHs was obtained with solutions containing 25% of acetonitrile. However, in these conditions the recovery of 2-ring PAHs significatively decreased.

These observations indicate that a significant amount of all PAHs, specially of the heaviest ones, is adsorbed on the inner walls of glass vessels and metallic tubing when they are dissolved in pure water. Their degree of adsorption decreases as the content of acetonitrile in the sample increases. On the other hand, addition of acetonitrile to the aqueous sample severely limits the volume of solution that can be concentrated without exceeding the breakthrough volumes of 2-ring PAHs in the precolumn. Therefore, in order to have good recoveries and high sensitivity in the analysis of all PAHs, it is necessary to employ two different procedures for sample preparation, one for the analysis of 2-ring hydrocarbons and the other for heavier ones.

Considering that the sample to be analyzed is initially in the glass sample bottle, where PAHs adsorption also occurs, the following procedure for sample preparation before its preconcentration was adopted:

1) General Step.—The sample bottle with the sample is hand-shaken to homogenize its content. Then, the sample is slowly poured into the funnel of the filtering unit using a glass rod to direct the liquid to the center of the filter in order to minimize its contact with the walls of the funnel. A very slight vacuum is applied during this operation to avoid losses of the most volatile compounds. The filtered sample and rinsing liquids (see below) are collected in a small vacuum flask (125 ml) which is gently stirred and sonnicated for 3 minutes. The flask is directly used as reservoir of the preconcentration pump.



*** 5 ML FOR 2-RING PAHs; 23 ML FOR ≥3-RING PAHs**

**** 20 ML FOR 2-RING PAHs; 2 ML FOR ≥3-RING PAHs**

Figure 2 Methodology for sample preparation and on-line concentration/analysis.

2) Rinsing step for 2-ring PAHs analysis.—5 ml of pure acetonitrile are poured into the empty sample bottle, the cap is fitted and the bottle is energically shaken. Then, the solvent is passed through the membrane previously employed to filter the sample. A glass rod is used to direct the liquid to the lower sides of the funnel, which were wetted with the sample in the previous filtration. Vacuum is completely stopped during this operation to maximize the contact of acetonitrile with the filter and the funnel base. Afterwards, 20 ml of pure water are used for a final rinse of the sample bottle and the filter.
3) Rinsing step for ≥3-ring PAHs analysis.—The procedure is similar to the previous one but 23 ml of pure acetonitrile and 2 ml of pure water are used for rinsing.

After this procedure, 25 ml of the "prepared sample" (containing 75 ml original sample + 25 ml rinsing solvents) are preconcentrated and analyzed. The complete methodology is summarized in Figure 2.

For the application of this method to "real" samples, the sample bottle must be filled up with the water to be analyzed. This means that the original sample volume will be between 73 and 77 ml. The method can accept sample volumes between these limits without any modification. However, to calculate PAHs concentrations, the initial sample volume must be known. The water meniscus on the side of the sample bottle is marked before beginning the sample preparation procedure for later determination of sample volume.

RESULTS AND DISCUSSION

Breakthrough volumes

Breakthrough volumes were determined at 1% of the height of breakthrough curves, according to (11). Table 2 shows the results obtained from different experiments.

These results indicate that ~25 ml of a sample containing 5% of acetonitrile can be safely percolated through the precolumn because the breakthrough volume of naphthalene, the less retained compound, is higher than this volume. However, in these conditions the heaviest PAHs still are notably adsorbed on the walls of vessels. A better choice for hydrocarbons with ≥3 aromatic rings is to concentrate 25 ml of a sample containing 23% of acetonitrile.

Figure 3 shows breakthrough curves of naphthalene at different concentrations in acetonitrile-water 5:95 v/v. The retention volume of the solute in the precolumn, which

Table 2. Breakthrough volumes of naphthalene and anthracene in the precolumn

Acetonitrile-water mixtures containing Naphthalene (1.2 mg/l) or Anthracene (138 µg/l). Detection: UV 254 nm. Flow: 1.5 ml/min. Room Temperature

	ACETONITRILE CONTENT (%)				
COMPOUNDS	5	10	20	23	25
Naphthalene	32.4	19	7.7		
Anthracene			57	31	24

Breakthrough volumes in ml

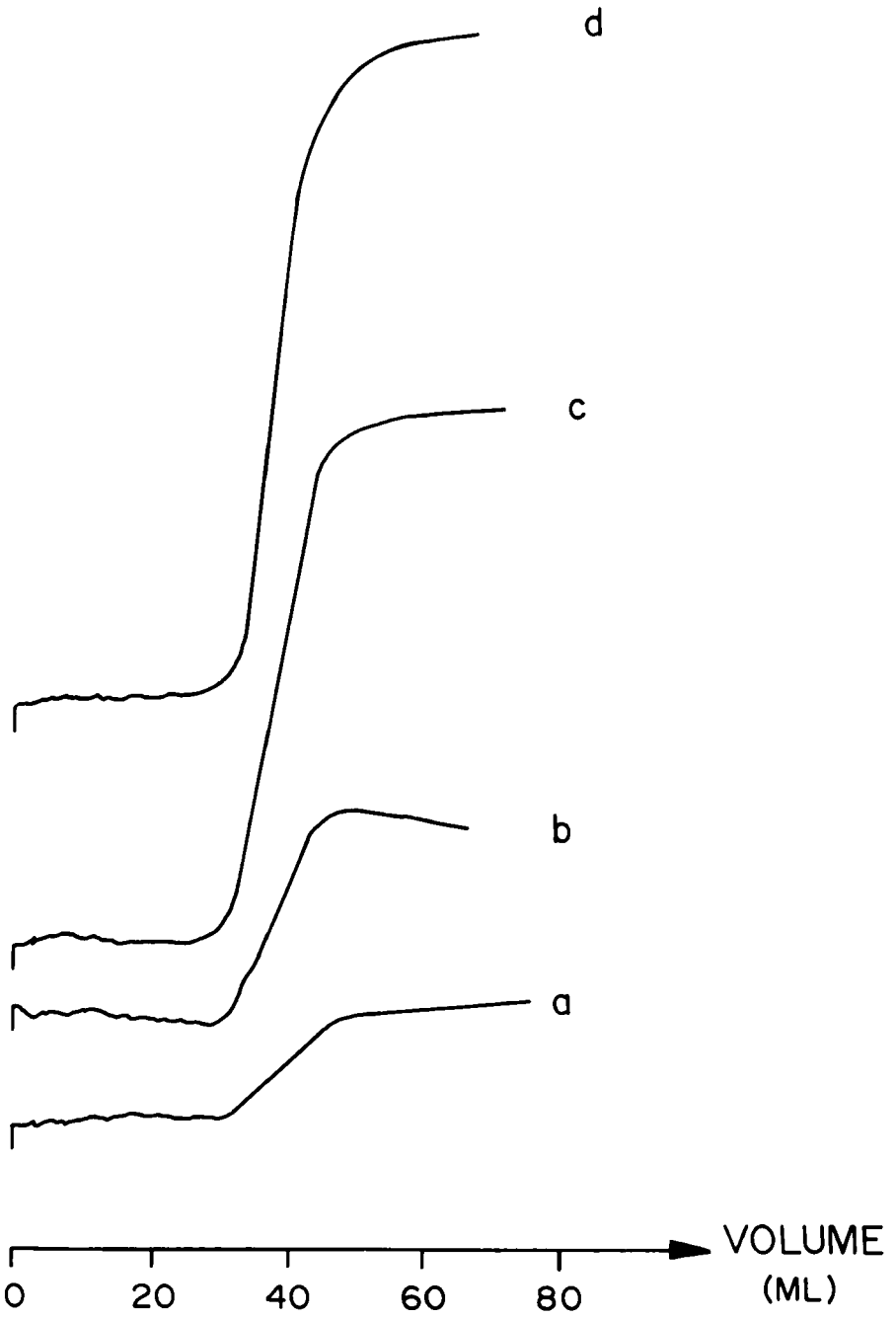


Figure 3 Breakthrough curves of Naphthalene at different concentrations, a: 290 ppb, b: 580 ppb, c: 1160 ppb, and d: 5800 ppb, in acetonitrile-water 5:95 v/v. Detection: UV 280 nm; sensitivity: 0.005 AUFS; attenuation: 2 (a, b, and c) or 4 (d).

corresponds to the inflexion point of the curve, is the same in all the experiments. Thus, overloading of the precolumn does not occur even at naphthalene concentrations as high as 5.8 ppm.

On-line concentration and analysis

The transfer of PAHs from water to reversed-phase packings is very easy because of their strong hydrophobicity. However, it is just this property which renders extremely difficult the design of an adequate procedure for sample pretreatment. In fact, strongly hydrophobic compounds are easily adsorbed not only by RP-packings but by almost all materials which happen to be in contact with their aqueous solutions: glassware, metallic tubing, filters and, specially, Teflon or polypropylene materials. Therefore, extreme care must be exerted to analyze this kind of solutes in water samples because losses of the analytes and cross contamination from one sample to the other can easily occur.

The following precautions, issued from observations accumulated during this work, are recommended for the determination of PAHs in water using on-line SPE techniques:
1st—Replace all plastic materials with glass or stainless steel.
2nd—Containers, filters, and other materials which have been in contact with the aqueous sample during its pretreatment must be rinsed with pure acetonitrile to recover adsorbed compounds. This solvent must be added to the sample before the preconcentration step, therefore use a small volume for rinsing.
3rd—Employ the minimum number of vessels. Do not use high volume flasks or bottles.
4th—To avoid cross contamination, carefully clean all glassware after each experiment. The tubing and pumphead of the preconcentration pump must be thoroughly rinsed with pure acetonitrile.

The procedure described in the experimental section for sample preparation and preconcentration was designed considering these precautions.

Table 3 shows the accuracy and precision obtained when 5 identical water samples were analyzed using the proposed method. Actually, 10 samples were treated, 5 of them using the procedure for 2-ring PAHs and the same number using the procedure for heavier PAHs. Recoveries were calculated by comparison with a direct injection of the PAHs stock solution in the analytical column. In fact, 100 µl of the stock contained the same amount of each PAH as 25 ml of the "prepared sample" (sample + rinsing solvents). However, peak areas had to be corrected because the loop volume did not correspond to its nominal 100 µl value but to 113 µl.

These results show that all polyaromatic hydrocarbons, from 2 to 6 aromatic rings, can be determined with acceptable accuracy and precision at low ppb or ppt concentration levels in water. The recovery of ≤4-ring PAHs is very good but the recovery of the heaviest ones shows a clear tendency to decrease as the number of aromatic rings increases. This means that a small portion of these highly hydrophobic solutes remains undoubtedly adsorbed on the surface of vessels, filters, or tubing during the pretreatment of the sample. Therefore, extreme precautions must be taken to avoid cross contamination.

A series of experiments with samples spiked with dilutions of the PAHs stock solution permitted us to determine the Method Detection Limit (MDL) and the Method Quantifica-

Table 3. Accuracy and precison of the method*

Compound	*Concentration* μg/l	*Detection* (%)	*Recovery* (%)	*RSD***
N[1]	5.12	UV	88	5.4
Fl[2]	1.37	UV	90	6.7
Ph[2]	2.05	UV	110	7.4
A[2]	0.34	F	97	1.8
F[2]	0.34	F	101	3.7
P[2]	1.37	UV	113	5.6
B(a)A[2]	0.34	F	97	4.7
B(k)F[2]	0.34	F	82	5.9
DBA[2]	0.68	F	81	7.9
B(ghi)P[2]	0.34	F	75	7.3

1—Sample with 5% acetonitrile 2—Sample with 23% acetonitrile
* Average from 5 independent samples
** RSD = Relative Standard Deviation

tion Limit (MQL) for each PAH. The former corresponds to the compound concentration in water that produces a signal of 3-times the baseline noise when the sample is analyzed using this method. For the latter, the conditions: recovery ≥70% and relative standard deviation (RSD) ≤10% were arbitrarily set. Three identical samples were analyzed for each concentration level. Results are reported in Table 4.

Figure 4 shows chromatograms obtained from the analysis of LC-grade water spiked with PAHs, each at a concentration corresponding to its "Limit of Quantification" as reported in Table 4. The sample was prepared according to the procedure for ≥3-ring PAHs, therefore the recovery of naphthalene (peak 1) is very low. Pyrene (peak 6) and dibenzoanthracene (peak 9) can be detected with similar sensitivity by UV or fluorescence detectors using the conditions reported in Table 1. However, pyrene elutes just after fluoranthene (peak 5), whose sensitivity by fluorescence detection is ~15-times higher; thus, the UV chromatogram was preferred to quantify pyrene.

Table 4. Limits of detection and limits of quantification

Compound	*Detector*	*MQL** (μg/l)*	*MDL*** (μg/l)*
N	UV	5.12	1.2
Fl	UV	1.37	0.16
Ph	UV	2.05	0.24
A	F	0.043	0.004
F	F	0.043	0.004
P	UV	0.68	0.16
B(a)A	F	0.043	0.017
B(k)F	F	0.043	0.004
DBA	F	0.34	0.034
B(ghi)P	F	0.17	0.009

* MQL = Method Quantification Limit. Conditions: recovery ≥70%, RSD ≤10%
** MDL = Method Detection Limit. Condition: signal/noise = 3

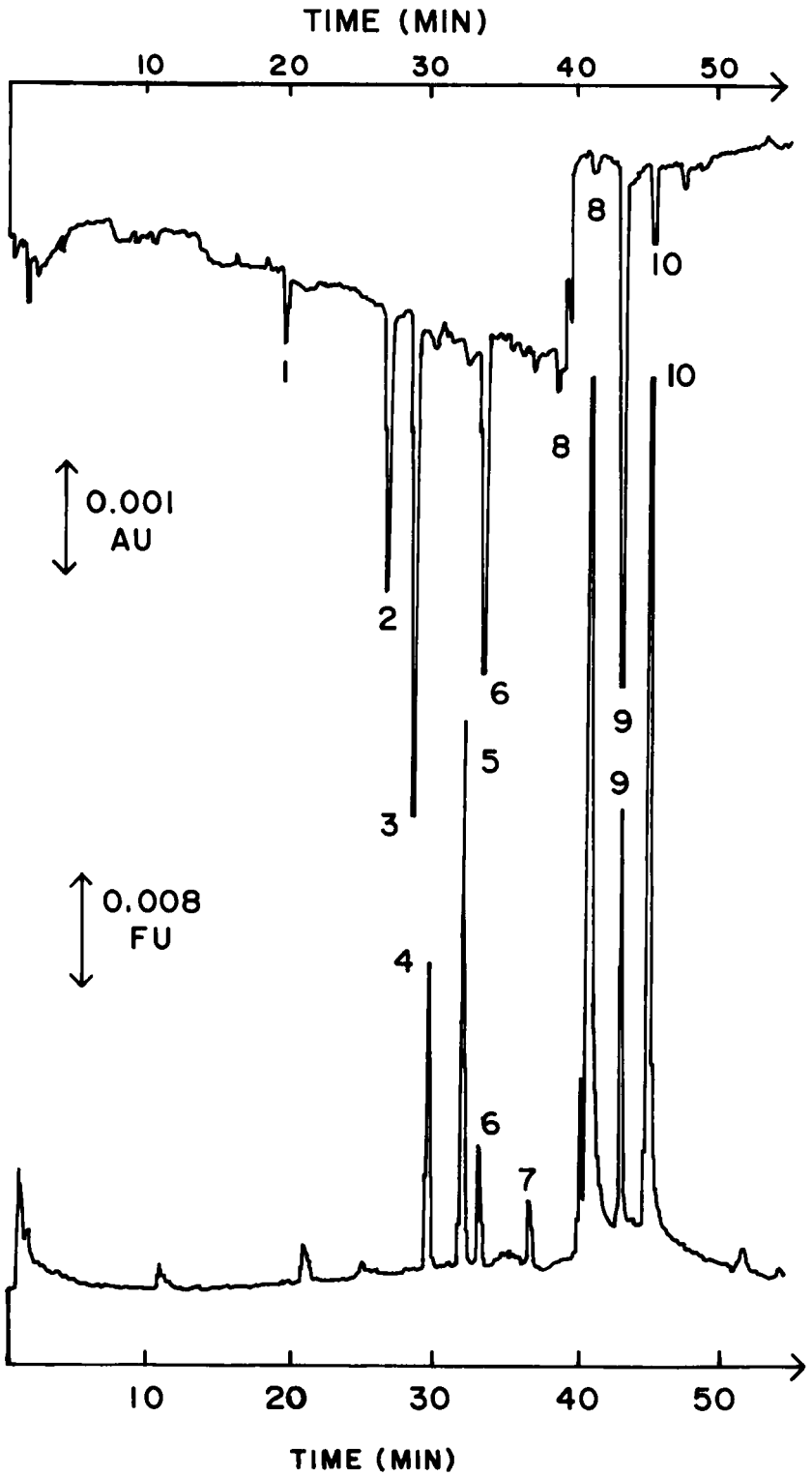


Figure 4 Analysis of water spiked with 10 PAHs, each at a concentration corresponding to its "limit of quantification". Sample prepared using the procedure for analysis of ≥3-ring hydrocarbons. 1: Naphthalene, 2:Fluorene, 3:Phenanthrene, 4:Anthracene, 5:Fluoranthene, 6:Pyrene, 7:Benzo(a)Anthracene, 8:Benzo(k)Fluoranthene, 9:Dibenzo(ah)Anthracene, 10:Benzo(ghi)perylene.

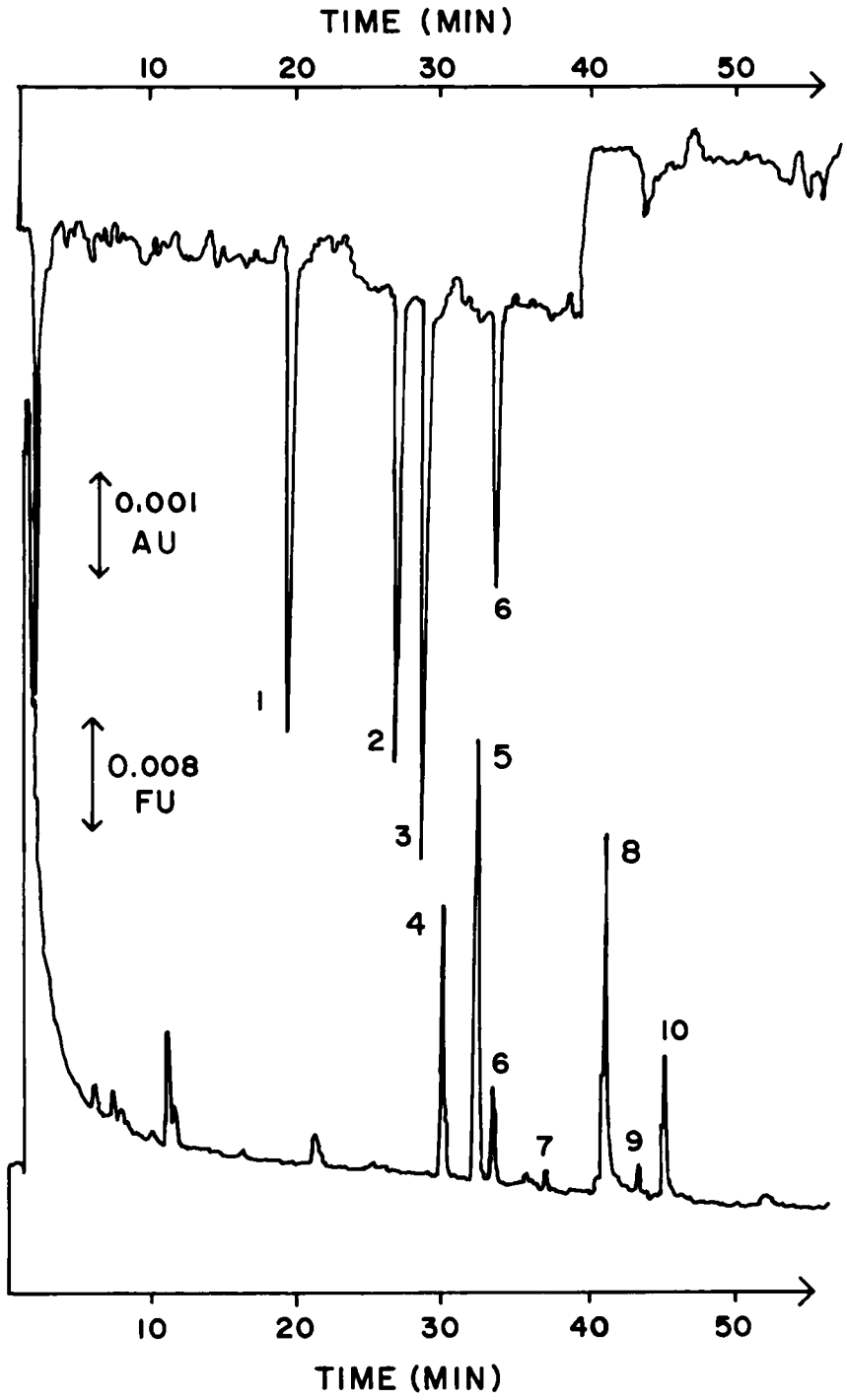


Figure 5 Same as Figure 4 but the sample was prepared using the procedure for the analysis of 2-ring hydrocarbons.

For comparison, figure 5 shows chromatograms obtained from the analysis of a sample identical to the previous one but prepared using the procedure for 2-ring PAHs. The loss of compounds with ≥4-rings is evident but, on the contrary, the recovery of naphthalene is notably higher than before. The recovery of 3-ring compounds is similar in both cases, although anthracene (peak 4) is slightly better recovered using the procedure for ≥3-ring PAHs.

The accuracy, precision, and limits of detection provided by the method proposed in this work are better or, at least, similar to those obtained using conventional liquid-liquid extraction methods for sample preparation. The most interesting advantages of this method are:

Simplicity.—Only 3 operations are necessary for sample preparation: filtration, rinsing of sample bottle and filter, and loading of the precolumn.

Small sample volumes.—Only 75 ml of sample are manipulated instead of 1L required for liquid-liquid extraction methods.

Speediness.—The whole analysis time is only determined by the time required to run 3 HPLC-analysis: standard injection, light PAHs assay, and heavy PAHs assay. Sample preparation is quick enough to be achieved during a run.

CONCLUSION

This work shows that the determination of polycyclic aromatic hydrocarbons, from 2 to 6-rings, at μg/l or (sub)μg/l levels in water can be performed with good accuracy and precision using simple, rapid, and efficient on-line solid phase extraction techniques.

The real problem when dealing with aqueous solutions of these highly hydrophobic compounds is their great tendency to be adsorbed on the walls of glass, plastic, fiber and even metallic materials which are in contact with the water sample. The methodology proposed in this work minimizes losses of PAHs during sample pretreatment and avoids cross contamination.

Acknowledgements

Financial support for this work was provided by grants from the "Dirección General de Asuntos del Personal Académico, Universidad Nacional Autónoma de México".

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