

HPLC Determination of Polycyclic Aromatic Hydrocarbons in Tap Water with On-Line Preconcentration

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A simple on-line preconcentration technique, gradient HPLC separation, and UV photodiode array detection have been used for the determination of fifteen polycyclic aromatic hydrocarbons, included in the EPA norm, in the tap water. The preconcentration was done with the C-18 precolumn ($\varnothing(\text{particle}) = 5 \mu\text{m}$). Recoveries of all polycyclic hydrocarbons at the ppt range have been found over 90 %.

Polycyclic aromatic hydrocarbons (PAH's) naturally occur in various organic materials, e.g. crude oil, asphalt, and some minerals. The main source of PAH's is the pyrolysis of crude oil fractions and the production of coke or tar [1]. Some of them, especially benzo[a]pyrene and dibenzo[a,h]anthracene are well known carcinogens [2].

The solubility of PAH's in water would be expected to be very low (mg dm^{-3} range), due to their nonpolar nature and relatively high molecular mass [3]. The higher amounts of PAH's in water samples as expected can be explained by the adsorption of PAH's onto particulate matter or solubilizing by micelles [4].

The HPLC method for the determination of PAH's from the water samples usually consists of an extraction step (liquid—liquid extraction by a suitable organic solvent [1, 5—7] or a solid phase extraction on the various type of sorbents [4, 8—13]), a separation step, and a detection. For the appropriate separation of 16 PAH's included in the EPA norm, the use of RP stationary phases and programmed analysis with fluorescence or UV detection is suitable [14—17].

The aim of this work was to use the on-line preconcentration and gradient elution with photodiode array detection (DAD) for the determination of 15 PAH's at the low ppt range in the tap water.

EXPERIMENTAL

Reversed phase HPLC was performed on Waters Assoc. model 501 pumps (Fig. 1, 1, 2) with a Vydac — $5 \mu\text{m}$, C-18 column (length = 250 mm, inner diameter = 4.6 mm) (3) and a Waters Assoc. photodiode array detector, model 990 (4). On-line

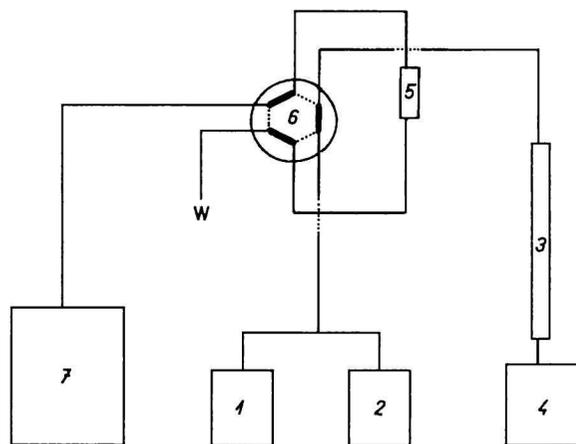


Fig. 1. The scheme of experimental apparatus. For details see Experimental. — Load position of a valve, inject position.

preconcentration system consisting of a Valco six-port valve (6), Separon — $5 \mu\text{m}$, C-18 column (Tessek, Prague) (length = 30 mm, inner diameter = 4.6 mm) (5) and HPLC pump HPP model 4001 (7) was used in the backflush mode. The apparatus is shown in Fig. 1.

The standards of 15 PAH's listed below were purchased from Supelco (USA), the acetonitrile for gradient was from Merck (Germany), and the twice distilled water was used in laboratory.

Stock standard solution was prepared by dissolving of the analytes in acetonitrile for gradient (0.1 mg cm^{-3}). Working standard solutions of the test compounds were prepared by diluting the stock solution with redistilled or tap water to a concentration $0.005\text{—}5 \mu\text{g dm}^{-3}$. All stock and working standard solutions were stored at 4°C in the dark.

On-line preconcentration of 15 PAH's was performed using the apparatus shown in Fig. 1. The preconcentration method consisted of the following steps:

- flushing the C-18 precolumn with 15 cm³ of pure acetonitrile to avoid the memory effect,
- injection of 75 cm³ of a spiked tap water with a flow rate of 3 cm³ min⁻¹,
- after column switching, focusing the displacement of PAH's zone from the precolumn into the analytical column using gradient elution (Table 1) and the backflush mode.

Table 1. The Composition of the Gradient Mobile Phase

t/min	$\varphi(A)$ /vol. %	$\varphi(B)$ /vol. %
0	100	0
3	100	0
18	0	100
27	0	100
30	100	0

$\varphi(A)$ = 50 vol. % acetonitrile in water, $\varphi(B)$ = 100 vol. % acetonitrile.

RESULTS AND DISCUSSION

The breakthrough volume was determined only for the most polar compound from the selected group of PAH's (naphthalene). Naphthalene was dissolved in the redistilled water at a spiking level of 1 $\mu\text{g cm}^{-3}$ and the breakthrough volume was determined by on-line monitoring of eluent. The breakthrough volume for naphthalene was higher than 100 cm³. According to this fact the application of 75 cm³ of the sample is satisfactory also for the other components, at the same concentration, the polarities of which are lower than that of naphthalene.

The recovery is a function of the flow rate, the volume applied into the precolumn, the concentration of the analyte, and the efficiency of the desorption step. The choice of the volume applied into the precolumn (75 cm³), which is lower than the breakthrough volume of the most polar component, and backflush mode during on-line preconcentration step, satisfied high recoveries of all PAH's. The recoveries of 15 PAH's are listed in Table 2.

As seen from Table 2 the recoveries of all PAH's from the spiked tap water were formed over 90 %. The use of the backflush mode for the desorption of PAH's corresponds with the consideration that the nonpolar PAH's will be retained in the top of the precolumn in a narrow zone. Then they can be replaced into the analytical column by the reverse flow of the mobile phase in a short time without the loss of efficiency [18].

Table 2. Mean Recovery Rate of PAH's from the Spiked Tap Water after On-Line Preconcentration

Compound	ρ	Recovery	Peak
	ng dm ⁻³	%	
Naphthalene	80	93.1	1
Acenaphthylene	98	96.2	2
Acenaphthene	118	94.4	3
Fluorene	150	97.3	4
Phenanthrene	85	93.9	5
Anthracene	72	97.2	6
Fluoranthene	59	97.4	7
Pyrene	90	99.3	8
Benzo[a]anthracene	47	96.3	9
Chrysene	59	95.6	10
Benzo[b]fluoranthene	73	96.5	11
Benzo[k]fluoranthene	47	98.6	12
Benzo[a]pyrene	150	97.4	13
Dibenzo[a,h]anthracene	68	95.6	14
Benzo[g,h,i]perylene	65	98.7	15

The repeatability of the method was tested several times by enriching 75 cm³ of spiked tap water (500 ng dm⁻³). Results are listed in Table 3. The relative standard deviations were less than 15 % in all instances and therefore are acceptable.

Table 3. The Repeatability of Retention Times and Peak Areas of 15 PAH's after On-Line Preconcentration Calculated from 10 Measurements

Compound	Retention time (RSD)/%	Peak area (RSD)/%
Naphthalene	0.40	6.9
Acenaphthylene	0.36	6.1
Acenaphthene	0.41	7.8
Fluorene	0.35	4.5
Phenanthrene	0.38	9.5
Anthracene	0.33	8.5
Fluoranthene	0.27	5.6
Pyrene	0.22	10.6
Benzo[a]anthracene	0.21	7.4
Chrysene	0.18	11.3
Benzo[b]fluoranthene	0.22	6.8
Benzo[k]fluoranthene	0.19	5.4
Benzo[a]pyrene	0.20	7.7
Dibenzo[a,h]anthracene	0.17	9.6
Benzo[g,h,i]perylene	0.24	8.3

The HPLC separation of 15 polycyclic aromatic hydrocarbons after on-line preconcentration from the spiked tap water is shown in Fig. 2 and the chromatogram of the blank sample of the tap water is shown in Fig. 3.

The detection limits for all components were below 100 ng dm⁻³ and for the most dangerous pollutants benzo[a]pyrene and dibenzo[a,h]anthracene they were around 5 ng dm⁻³. Reliable spectral recognition, using DAD, was possible in all instances at the 100 ng dm⁻³ level.

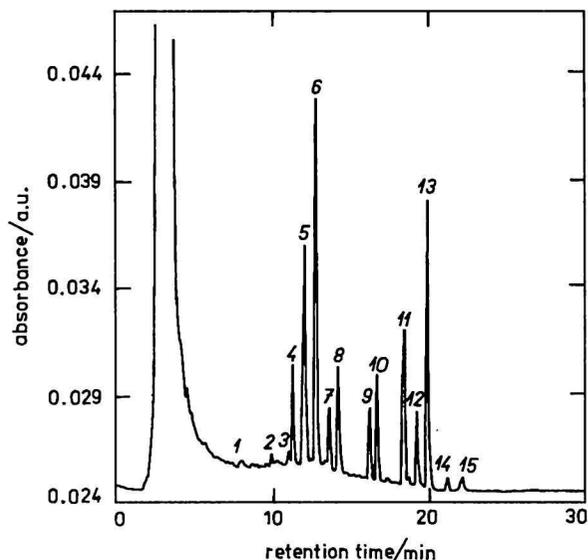


Fig. 2. Chromatogram of the spiked tap water after on-line pre-concentration. For the concentrations and numbering of peaks see Table 2. Mobile phase: see Table 1; flow rate: $1.4 \text{ cm}^3 \text{ min}^{-1}$; UV detection: $\lambda = 254 \text{ nm}$.

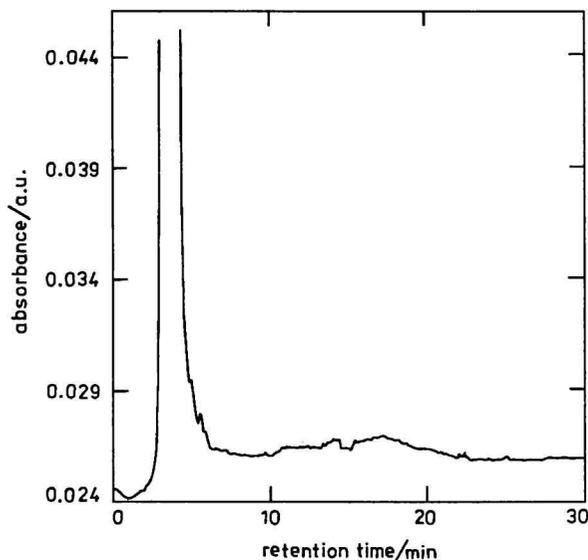


Fig. 3. Chromatogram of a blank tap water after on-line pre-concentration. For the chromatographic conditions see Fig. 2.

CONCLUSION

A simple on-line pre-concentration method for the trace level determination of nonpolar pollutants in tap water is described. The pre-concentration step allows the use of UV photodiode array detector and therefore the spectral recognition of all 15 polycyclic aromatic hydrocarbons is possible at the low level of concentrations. The analytical performance of the system allows to determine the most dangerous polycyclic aromatic hydrocarbons at the low ng dm^{-3} concentration level.

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