Determination of polycyclic aromatic hydrocarbons in surface water by column liquid chromatography with fluorescence detection, using on-line micelle-mediated sample preparation

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Abstract

Column liquid chromatography with fluorescence and diode-array UV detection has been used for the trace-level determination of sixteen EPA-priority polycyclic aromatic hydrocarbons. The procedure involves on-line micelle-mediated preconcentration on selective sorbents. Using Brij-35 as the surfactant, unwanted adsorption of the analytes on inner walls or surfaces is prevented. The system has been used for the analysis of surface water samples, and detection limits typically are at the low- to sub-ng/l level. The system is robust and repeatability is excellent.

1. Introduction

Within the international Rhine Basin Program (Amsterdam/Waldbronn) [1], we have recently developed several methods for the determination of organic pollutants in surface water [2–8]. These pollutants, mainly polar pesticides, usually are preconcentrated on-line on small pre-columns, with subsequent separation by means of column liquid chromatography (LC) and diode-array UV or MS detection. To extend the scope of these methods we have now attempted to develop an on-line reversed-phase LC system for the determination of non-polar pollutants.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants. They are formed by incomplete combustion of organic matter and thus enter the environment from a wide variety of sources. Because of their mutagenic and carcinogenic nature, their determination in a variety of matrices has become an important task, particularly in water pollution control. The determination of PAHs in aqueous samples is rather difficult as their concentration in water is extremely low due to their low solubility. Besides, because PAHs tend to adsorb on walls and surfaces with which they come into contact, serious losses often occur during sampling and storage [9–12]. As a result of the toxicity of the PAHs, according to Dutch law [13], the tolerance levels in surface water are rather low (200 ng/l total). In order to detect the PAHs at these low levels in water, a concentration step is generally required by means of liquid–liquid extraction (LLE) [9,14–17] or solid-phase extraction (SPE) [16–19]. The latter

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technique is gaining popularity, because unlike LLE, SPE does not require large volumes of (toxic) organic solvents, analysis times can be decreased significantly, and on-line and/or automated procedures are easily designed.

Recently, several sorbents have been introduced for the selective sorption of PAHs from aqueous samples [20–24]. These sorbents, which predominantly are of the copper phthalocyanine trisulphonate type, display specific hydrophobic and steric interactions with PAHs, which contain three or more fused rings. In this study several of these special phases for the sorption of PAHs were tested.

PAHs are commonly analysed by reversed-phase LC with UV and/or fluorescence detection [25–27] or by gas chromatography (GC) in combination with a flame ionization or MS detector [20,28–30]. Nowadays LC is used more often, because this technique is ideally suited for the determination of non-volatile PAHs. Moreover, with the 16 US Environmental Protection Agency (EPA)-priority PAHs LC often provides a ready separation, whereas GC techniques show a lack in resolution for several PAHs [20].

In order to avoid the —rather notorious— sorption problems often encountered during sampling and storage of PAHs, it is necessary to develop a method that increases their solubility. Normally this is achieved by adding organic solvents to the sample [9,12,31]. However, recently increasing attention has been devoted to the use of surfactants as solubilizers [31–36]. Surfactant molecules are amphiphilic, having a polar and a non-polar moiety. Because of their amphiphilic nature, surfactant molecules can dissolve in water as monomers, or be incorporated with other surfactants to form a micelle. The concentration at which they start to form micelles is termed the critical micelle concentration (CMC). The CMC which is dependent on factors such as, e.g., surfactant nature, temperature, ionic strength and the presence of organic additives, is the concentration at, or concentration range over which solution properties like surface tension show an abrupt change in value. When the hydrophobic part of the amphiphile is a hydrocarbon chain —as is normally true—, the micelles will consist of a hydrocarbon core with polar groups at the surface, which serve to maintain solubility in water. The hydrocarbon chains in such micelles are generally regarded as disordered, so that the hydrophobic core is in effect a small volume of a liquid hydrocarbon. The ability to dissolve hydrophobic substances is the simplest evidence for the liquid-like nature of the micelle interior.

In this study we have used the solubilizing properties of several ionic and non-ionic surfactants, to solve the problems arising from the low solubility of PAHs in water and their sorption to surfaces, and set up an on-line trace enrichment–LC system with fluorescence detection.

2. Experimental

2.1. Reagents and materials

All PAHs were from Radiant Dyes Chemie (Wermelskirchen, Germany). HPLC gradient-grade acetonitrile and HPLC-grade methanol were obtained from J.T. Baker (Deventer, Netherlands). Sodium dodecyl sulphate (SDS) was purchased from Merck (Darmstadt, Germany). Brij-35 came from Fluka (Buchs, Switzerland). Cetyl trimethylammonium chloride was obtained from Kodak (Rochester, NY, USA). All aqueous solutions were prepared with demineralized water, purified with a Milli-Q (Millipore, Bedford, MA, USA) ultrafiltration system. Stock solutions of the PAHs were prepared by dissolving about 3 mg of analyte in 15 ml of methanol. As a result of the low solubility of dibenz[a,h]anthracene and benzo[ghi]perylene in methanol, these analytes were dissolved in acetonitrile. Surface water samples were spiked by dilution of the stock solutions to the appropriate concentration. In most instances, prior to analysis, the surface water samples were filtered over a 0.45-μm filter (Schleicher & Schüll, Dassel, Germany).

A 250 × 4.6 mm I.D. analytical column packed with 5 μm Supelcosil LC-PAH octadecyl-bonded silica came from Supelchem (Leusden, Netherlands). Laboratory-made stainless-steel pre-

columns (10 mm × 3 mm I.D.) were slurry-packed manually with several packing materials using methanol as the slurry liquid. Several packing materials were provided by Professor Dr. K.-S. Boos (Ludwig-Maximilians-Universität, Munich, Germany). Since no commercial trade names are known for these materials, they are indicated as "Boos glass" and "Boos silica", respectively. "Boos glass" is a diol-modified porous glass support with a particle diameter of 30–60 μm chemically modified with a copper phthalocyanine trisulphonic acid derivative, and "Boos silica" is a diol-modified silica with a particle diameter of 20 μm chemically modified with the same copper phthalocyanine trisulphonic acid moiety. The Blue Pearls packing material, a copper phthalocyanine trisulphate-modified polymethacrylamide, was a gift from Dr. M. Geisert (Johannes-Gutenberg-Universität, Mainz, Germany). Precolumns (20 mm × 3.0 mm I.D.) packed with ChromSpher π were a gift from Chrompack (Middelburg, Netherlands). Bondesil octadecyl-bonded silica (40 μm)

was purchased from Analytichem (Harbor City, CA, USA).

2.2. Set-up and procedures

The LC system consisted of two Gynkotek (Germering, Germany) Model 300 pumps to deliver the aqueous sample and methanol–acetonitrile (50:50, v/v) for cleaning and wetting the precolumn. An HP 1090 (Hewlett-Packard, Waldbronn, Germany) LC gradient system was used to deliver the mobile phase. Two six-port switching valves were laboratory-made. For absorbance detection an HP 1040 diode array detector was used. The data were evaluated by a Hewlett-Packard Pascal Workstation using the Chemstation software. For fluorescence detection a programmable HP 1046A detector with a xenon flashlamp, was used. When using this detector the chromatograms were recorded by a Kipp & Zonen (Delft, Netherlands) Model BD8 recorder.The total analytical set-up is shown in Fig. 1. Pump P1 delivers the methanol–acetoni-
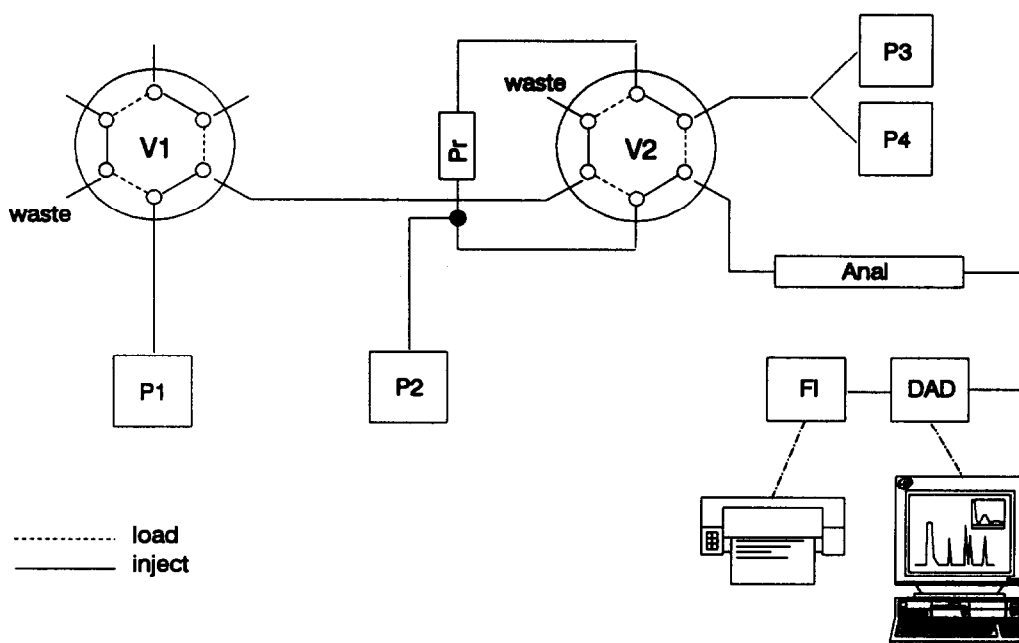

Fig. 1. Set-up of on-line trace enrichment–LC–UV–fluorescence system. P1 = Pump delivering wetting solvent and sample; P2 = pump delivering Milli-Q water; P3, P4 = mobile phase pumps; Pr = 10 × 3 mm I.D. precolumn; Anal = 250 × 4.6 mm I.D. analytical column; DAD = diode-array UV detector; Fl = fluorescence detector;V1, V2 = valves.

trile mixture, and the aqueous sample, containing either micelles or an organic solvent, at a flow-rate of 1 ml/min. After every change of solvent in pump P1, the first 2 ml of solvent are flushed to waste via valve V1 ("load" position) in order to remove the remaining solvent from the tubing. Pump P2 is used when micelle-mediated samples are analysed, *viz.* to deliver Milli-Q water (2.5 ml/min). The precolumn (Pr) is percolated with 5 ml of the methanol–acetonitrile mixture to condition the packing material and, next, 5 ml of Milli-Q water. Subsequently, the precolumn is loaded with 10 ml of sample (at 3 ml/min), by switching valve V1 to the "inject" and valve V2 to the "load" position. Next valve V2 is switched to the "inject" position, and the analytes are desorbed by the LC gradient. The gradient was prepared by mixing water (A) and acetonitrile (B). The gradient profile for the desorption of the analytes from the precolumn and subsequent analysis on the analytical column was: A–B (60:40) (0 min) which was held constant for 5 min, and subsequently changed linearly to 100% B in 30 min. The separations were carried out at ambient temperature, at a flow-rate of 1.5 ml/min, using pumps P3 and P4. Detection was carried out by a time-programmable fluorescence detector in series with a diode-array UV detector.

3. Results and discussion

Since the PAHs selected as test solutes, which are all EPA-priority pollutants [16,19], widely differ in polarity a gradient LC system has to be used for their separation. The gradient profile recommended by Supelco for use with their analytical column gave complete baseline separation of all analytes, and was therefore used in this study.

As regards detection, since a time-programmable fluorescence detector and a diode-array UV detector were used in series, optimal excitation and emission, or absorbance, wavelengths could be applied for all compounds. As is well known, from among the present set of analytes only acenaphthylene does not display native fluores-

cence at all, and fluorene shows a rather weak signal. Since fluorescence detection is much more sensitive —and, for all other PAHs, also much more selective— than UV detection, the latter mode was only used for acenaphthylene ($\lambda = 230$ nm). Since the diode-array UV detector was not available during the initial stages of this project, acenaphthylene was not included in all parts of the present study. However, it was included in the final testing and validation stages. The time schedule used for fluorescence detection is given in Table 1. Typical chromatograms using the set-up of Fig. 1 are given in Fig. 2.

In order to study the potential of (selective) trace enrichment, five different packing materials were tested using the set-up of Fig. 1, Boos silica, Boos glass, Chromspher π, Blue Pearls and an octadecyl-bonded silica; the first four are selective sorbents, whereas the last one can be considered non-selective. Initial experiments were carried out using Boos silica, a sorbent which has been shown to have an excellent sorption ability and high specificity for aromatic compounds containing at least three fused benzene rings [21], for trace enrichment. A series of 10-ml preconcentrations of standard solutions of the analytes was performed without the addition of surfactants or organic modifiers (pump P2 not included in the analytical system). Low and irreproducible PAH recoveries, due to adsorption of the analytes on the PTFE tubing, switching valves, sample bottles and/or pumping heads, which were previously reported by other authors [12,31], were immediately encountered.

3.1. Solubilizing effect of an organic modifier and micellar agents

To overcome the problems outlined above it is necessary to enhance the solubility of the PAHs in water. Two options were tested: the addition of an organic solvent to the sample or the use of micellar media. As can be seen from Table 2 the recoveries of the late-eluting analytes, which are expected to show the strongest adsorption, increase from *ca.* 10 to 50% when 25% of methanol is present in the sample solution, while a most rewarding increase was also obtained for

Table 1
Fluorescence detection conditions used for on-line trace enrichment–LC of 16 priority PAHs

Compound		Time (min)	Wavelength (nm)	
No.	Name		Excitation	Emission
1	Naphthalene	0	218	357
2	Acenaphthylene			
3	Acenaphthene	17.1	226	359
4	Fluorene			
5	Phenanthrene	19.2	250	350
6	Anthracene	21.0	250	425
7	Fluoranthene	22.4	234	440
8	Pyrene			
9	Benz[a]anthracene	26.0	286	405
10	Chrysene	28.1	265	405
11	Benzo[b]fluoranthene	29.8	250	420
12	Benzo[k]fluoranthene	31.8	238	460
13	Benzo[a]pyrene	33.2	294	460
14	Dibenz[a,h]anthracene	34.6	298	420
15	Benzo[ghi]perylene			
16	Indeno[1,2,3-cd]pyrene	38.8	246	490

the central group (phenanthrene–chrysene), viz. from 15–40% to 80–100%. However, the early-eluting compounds unfortunately show rapidly decreasing recoveries upon going from 0 to 15% and, again, from 15 to 25% of organic modifier. Obviously, while the presence of 25% methanol in the sample certainly is not sufficient for one half of the analytes to really prevent adsorption, less than 15% causes insurmountable problems for the more polar PAHs.

As an alternative solution, we studied the solubilizing effect of micelles on hydrophobic compounds. SDS, cetyl trimethylammonium chloride (CTACl) and polyoxyethylene lauryl ether (Brij-35) were tested in this study. Their properties are given in Table 3. Analyte recoveries after preconcentration of 10 ml of surface water, spiked at the 25 μg/l level, on Boos silica were determined at different surfactant concentrations, both below and above the CMC. As is evident from Table 4 the addition of Brij-35 has a positive influence on analyte recovery even below the CMC, especially for the late-eluting compounds. This is not surprising since Brij-35 has a rather high molecular mass and can therefore be expected to interact with

the analytes even when micelle formation has not taken place. With increasing concentration of Brij-35, the recoveries of the late-eluting PAHs increase significantly, but the earlier-eluting analytes already display a slow decrease in recovery due to early breakthrough. [The recoveries of the most polar PAHs are rather low in Table 4 because of the selectivity of Boos silica (cf. above).] From Table 4 it can also be seen that increasing the Brij-35 concentration from $3 \cdot 10^{-4}$ to $6 \cdot 10^{-4}$ M causes a decrease of recovery for all analytes. Obviously, since micelles act as a kind of modifier, breakthrough will occur when too high surfactant concentrations are used.

The above experiments were repeated with CTACl and SDS as micellar media. However with these charged surfactants, at concentrations above the CMC cloud formation occurred, a phenomenon that was not observed for Brij-35. Similar results were reported by Becker et al. [37]. Many ionic amphiphiles readily form crystalline precipitates at elevated salt concentrations, thereby preventing the formation of micelles, below a characteristic temperature, the critical micellar temperature. For e.g. SDS, in the presence of 0.15 M sodium ions, this critical
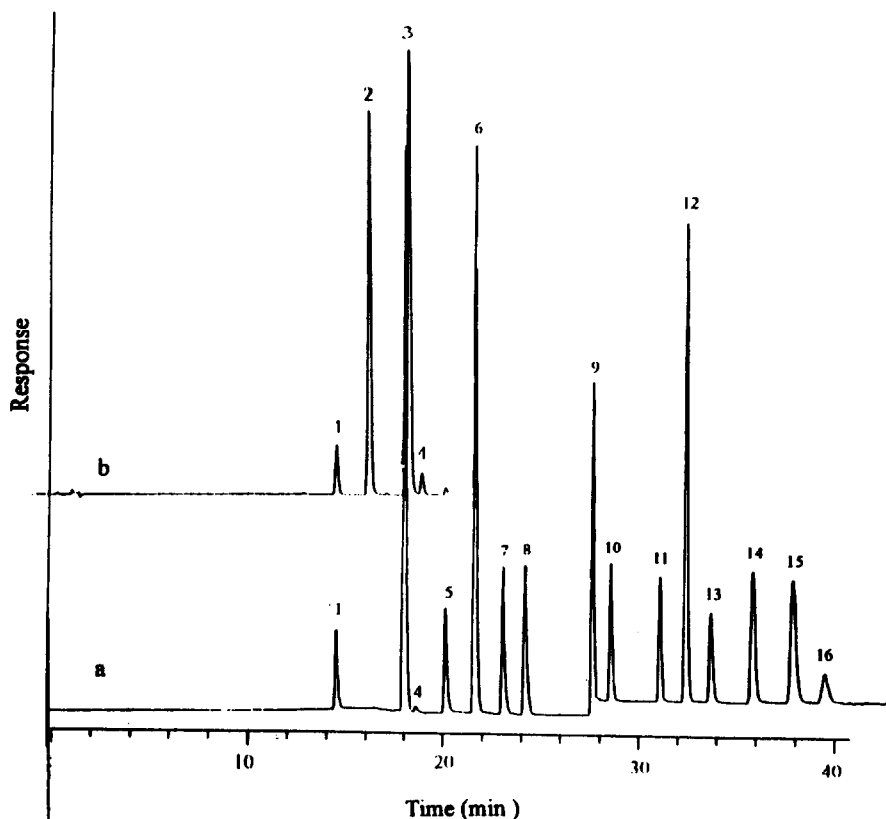
Fig. 2. LC–UV–fluorescence chromatograms of standard mixture of PAHs after loop injection; (a) fluorescence detection (25 μl; 40 μg/l of each PAH); (b) diode-array UV detection (25 μl; 10 mg/l of each PAH). For peak assignment, see Table 1. For conditions, see text.

temperature is 23°C. Since salt concentrations in surface water samples show both spatial and temporal levels, and often are rather high, ionic surfactants obviously are not a proper choice for the present type of study.

Since the addition of $3 \cdot 10^{-4}$ M Brij-35 to the sample solution gave the best results, this concentration was used in further work.

3.2. Other sorbents

Next to Boos silica, three further selective packing materials were tested, namely Boos glass, Chromspher π and Blue Pearls. Boos glass differs from Boos silica only in backbone (glass vs. silica); therefore rather similar results were expected. However, compared with Boos silica,

the analyte recoveries with Boos glass were significantly lower (cf. Table 5). The larger particle size of the glass support (30–60 μm) compared with the silica-based (20 μm) material, which results in a diminished surface area and, thus, a decreased sorption efficiency for the analytes, probably is the explanation. The sorption of aromatic compounds on Blue Pearls [22] is also based on the selective interaction of copper phthalocyanine moieties with π electrons of the analytes. Compared with the other packing materials tested analyte recoveries were rather low with the Blue pearls. They were below 10% for all analytes when 10-ml samples were preconcentrated (cf. Table 5). Since after desorption from the precolumn, the analyte peaks were rather sharp, it is obvious that the

Table 2
Influence of percentage methanol in sample on PAH (25 μg/l) recoveries after preconcentration of 10 ml Milli-Q water on a 10 × 3 mm I.D. precolumn containing Boos silica

Compound	Recovery (%) in presence of:		
	0% MeOH	15% MeOH	25% MeOH
Naphthalene	18	10	5
Acenaphthene	55	40	21
Fluorene	73	51	27
Phenanthrene	42	76	80
Fluoranthene	21	73	100
Anthracene	41	70	83
Pyrene	17	76	100
Benz[a]anthracene	16	34	99
Chrysene	16	33	81
Benzo[b]fluoranthene	14	12	53
Benzo[k]fluoranthene	14	15	53
Benzo[a]pyrene	13	10	47
Dibenz[a,h]anthracene	11	10	57
Benzo[ghi]perylene	7	10	29
Indeno[1,2,3-cd]pyrene	7	10	28

low recoveries were not caused by slow elution but that the retention power of the Blue pearls was insufficient to trap the PAHs. Therefore this material was not used in further work.

As regards the Chromspher π material, no details concerning its composition have been disclosed by the manufacturers. However, the sorbent is claimed to show high retention for aromatic compounds and to possess high selectivity [38]. Comparison of the results obtained with Chromspher π and Boos silica showed that recoveries for the late-eluting compounds were comparable (ca. 75%) while recoveries for the early-eluting analytes were significantly improved (90% for Chromspher π vs. 40% for Boos silica). Although back pressure over the

Chromspher π precolumn was rather high (ca. 30 bar per ml/min) as a result of the small particle size of the sorbent (5 μm), no negative influences were observed with respect to the total analytical procedure.

The results for the four selective π–π interaction-based sorbents were compared with that for a non-selective C_{18}-bonded silica, most commonly used in our laboratory. It was found that recoveries for most analytes were comparable to those of the Chromspher π precolumn. All 16 EPA-priority PAHs, including the most polar one, naphthalene, had recoveries over 80%, as can be read from Table 5, where the three analytes typically represent the early-, in-between and late-eluting PAHs, respectively.

Table 3
Properties of surfactants used in this study

Surfactant	Type	Molecular mass	CMC (M)	Aggregation number
SDS	Anionic	288	$8.3 \cdot 10^{-2}$	62
CTACl	Cationic	320	$8.0 \cdot 10^{-4}$	78
Brij-35	Neutral	1182	$1.0 \cdot 10^{-4}$	40

Table 4
Influence of surfactant concentration on recovery of PAHs, after 10-ml preconcentration on a 10×3 mm I.D. Boos silica precolumn

Compound	Analyte recovery (%; $n = 2$) at Brij-35 concentration ($\times 10^{-4}M$) of				
	0.0	0.5	1.1	3.0	6.0
Naphthalene	18	15	13	12	12
Acenaphthene	55	53	55	39	32
Fluorene	73	75	83	54	38
Phenanthrene	42	37	52	84	75
Anthracene	41	38	55	80	69
Fluoranthene	21	23	48	91	84
Pyrene	17	20	46	99	88
Benz[a]anthracene	16	20	46	94	64
Chrysene	16	19	45	94	62
Benzo[b]fluoranthene	14	26	49	82	54
Benzo[k]fluoranthene	14	23	48	81	54
Benzo[a]pyrene	13	24	49	81	52
Dibenz[a,h]anthracene	11	30	53	62	31
Benzo[ghi]perylene	7	29	32	50	31
Indeno[1,2,3-cd]pyrene	7	28	32	50	31

For LC conditions, see section 2.2.

3.3. Disruption of micelles

in order to obtain the high recoveries reported above, relatively high surfactant concentrations were needed. Since surfactants act as a modifier, it is obvious that distribution of the analytes over the precolumn occurs, which will result in peak broadening, especially for those compounds which have strong interaction with the micelles. However, micelles have one major advantage: when the concentration drops below the CMC, they disrupt immediately. By using pump P2 (cf.

Fig. 1) for the addition of water we were able to break up the micelles just before the precolumn, still taking advantage of the solubilizing effect during preconcentration, but preventing them to act as a modifier on the precolumn. This procedure was tested for the C_{18}, Chromspher π and Boos silica precolumns. Samples of 10 ml, containing $3 \cdot 10^{-4}$ M Brij-35 were preconcentrated at 1 ml/min, adding water to the micelle-mediated sample (via P2 and a T-piece) at a flow-rate of 2.5 ml/min. This results in a final concentration of $0.85 \cdot 10^{-4}$ M Brij-35, which is

Table 5
Recovery data for a selected number of PAHs after 10-ml preconcentration of Milli-Q water, containing $3 \cdot 10^{-4}$ M Brij-35, on different precolumns

Packing material	Recovery (%)		
	Acenaphthene	Benz[a]anthracene	Dibenz[a,h]anthracene
Boos silica	39	94	62
Boos glass	18	28	26
Chromspher π	90	88	78
Blue pearls	8	9	6
C_{18}	92	90	85

somewhat lower than the CMC (*cf.* Table 3), just before the precolumn. The results obtained for all precolumns tested were quite satisfactory, with recoveries of over 90%, and often 95%, for most compounds (*cf.* Table 6) although, of course, low recoveries were found with Boos silica for the PAHs having less than three aromatic benzene rings. Only the non-selective C_{18} precolumn retains naphthalene quantitatively. Furthermore, by disrupting the micelles before the precolumn, band broadening is distinctly reduced, presumably as a result of a diminished breakthrough for the *late*-eluting PAHs (*cf.* data for Boos silica in Tables 4 and 6).

As an illustration Fig. 3 shows the trace enrichment LC–fluorescence chromatograms obtained after 10-ml preconcentrations of river Rhine water spiked at the 100 ng/l level, on Boos silica, Chromspher π and C_{18}-bonded silica. The figure clearly illustrates the selectivity of Boos silica, especially in the early part of the chromatogram and in the 14–17 min retention time range. The large early-eluting peaks which are due to humic substances in surface water, are almost completely absent. The other two sorbents, although less selective, have the advantage that the relatively polar PAHs are efficiently trapped and can thus be detected and quantitated at low levels. Final experiments were performed with the C_{18}-bonded silica precolumn. Fig. 4 shows the on-line trace enrichment–LC–fluorescence/UV chromatograms after preconcentration of 10 ml of river Meuse water spiked at the 100 ng/l (fluorescence) and 500 ng/l (UV) level.

Calibration curves were constructed for all analytes in surface water samples over the range 0.01–20 μg/l. The curves (six data points; $n = 2$) were linear with R^2 values of over 0.995, except for naphthalene (0.985). The somewhat lower R^2 value for naphthalene is probably due to the well known fact that this compound easily evaporates from aqueous solutions.

In order to determine the precision of the analytical procedure, river Rhine water spiked with a mixture of all test solutes at the 100 ng/l level (fluorene and acenaphthylene: 2 μg/l) were analysed ($n = 6$). The average R.S.D. was 3.5% (range 1.0–8.5%), which is quite satisfactory for these low concentration levels. The

Table 6
Recovery data for different sorbents after preconcentration of 10 ml micelle-mediated surface water samples, spiked with PAHs (100 ng/l), with disruption of micelles

| Compound	Recovery (%; $n = 2$)		
	C_{18}	Boos silica	Chromspher π
Naphthalene	96	4	78
Acenaphthene	100	22	97
Fluorene	97	26	97
Phenanthrene	100	94	97
Anthracene	100	97	99
Fluoranthene	99	94	95
Pyrene	99	100	90
Benz[a]anthracene	100	93	100
Chrysene	100	94	100
Benzo[b]fluoranthene	91	92	90
Benzo[k]fluoranthene	93	92	92
Benzo[a]pyrene	90	94	93
Dibenz[a,h]anthracene	92	100	100
Benzo[ghi]perylene	94	100	100
Indeno[1,2,3-cd]pyrene	94	100	100

For experimental conditions, see text.
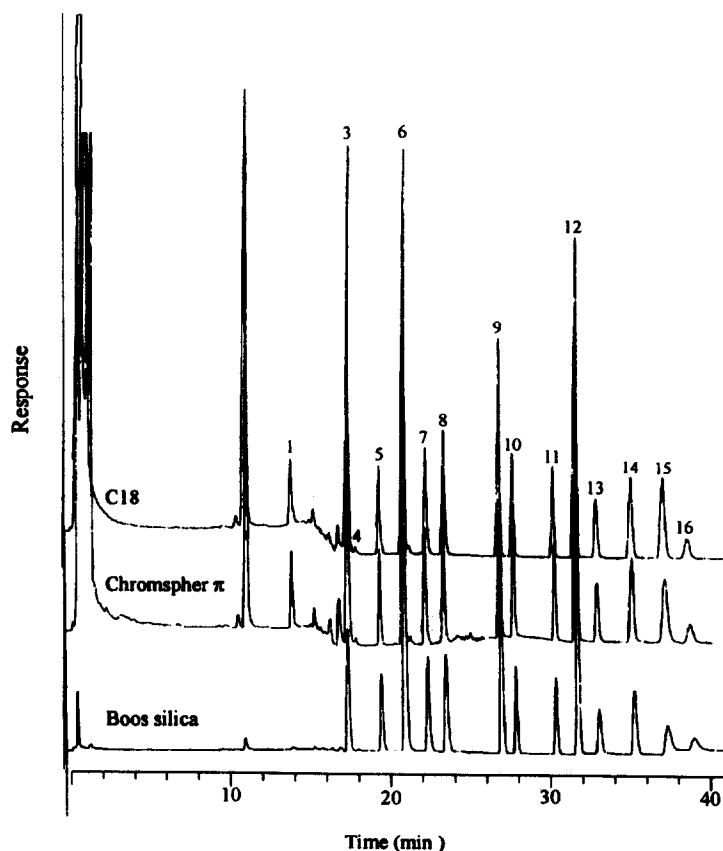
Fig. 3. On-line trace enrichment–LC–fluorescence chromatograms of 10 ml surface water, containing $3 \cdot 10^{-4}$ M Brij-35, spiked at the 100 ng/l level with all PAHs, using Boos silica, Chromspher π, or C_{18}-bonded silica precolumns. For peak assignment, see Table 1.

detection limits (signal-to-noise ratio 3) in real-life samples were between 0.5 and 15 ng/l, except for acenaphthylene and fluorene (cf. Table 7). It should be added that the detection limits are based on on-line preconcentration of 10-ml samples which were invariably used in this study for reasons of convenience. According to our experience, the breakthrough volumes of all PAHs except naphthalene are significantly higher, viz. at least 25–100 ml. In other words, analyte detectability can, in principle, easily be improved. However, since this was not the major goal of our work, no further optimization in this direction was attempted.

The chromatogram of a blank river Rhine water sample is shown in Fig. 5. In this chromatogram peaks 1 and 5 were tentatively iden-

tified as naphthalene and phenanthrene, respectively. Valuable additional information —which, obviously, was especially required in the case of naphthalene— was obtained by performing a second run with a different excitation/emission schedule. A shift in the excitation wavelength from 218 nm, the optimal wavelength for naphthalene, to 238 nm, a wavelength where naphthalene shows no absorbance at all, indeed resulted in a complete loss of the naphthalene peak (cf. Fig. 5). The calculated concentration levels for naphthalene and phenanthrene, which were invariably present in the numerous surface water samples analysed, were 20 and 10 ng/l, respectively. These data are in agreement with results from the Institute for Inland Water Management and Waste Water Treatment (Lelystad,
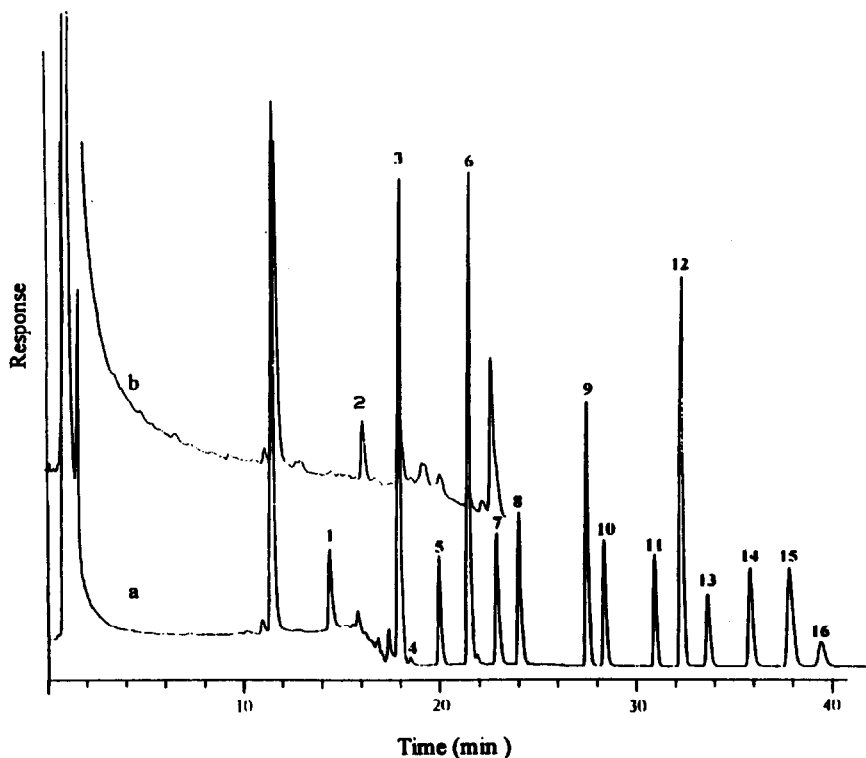
Fig. 4. On-line trace enrichment–LC–fluorescence/diode-array UV chromatograms of 10 ml surface water, containing $3 \cdot 10^{-4}$ M Brij-35 using the C_{18}-bonded silica precolumn. (a) Fluorescence detection (100 ng/l of each PAH); (b) UV detection (500 ng/l of each PAH, $\lambda = 230$ nm). For fluorescence detection conditions and peak assignment, see Table 1.

Netherlands), which indicate PAH concentrations of less than 100 ng/l for all PAHs monitored in surface water samples from the river Rhine [39].

Suspended solids

It is well known that the major part of the PAHs present in surface water is adsorbed on suspended solids. It was therefore briefly tested

Table 7
Detection limits for PAHs, after on-line preconcentration of 10 ml surface water on a 10×3 mm I.D. C_{18}-bonded silica precolumn using gradient LC–fluorescence–diode-array UV detection

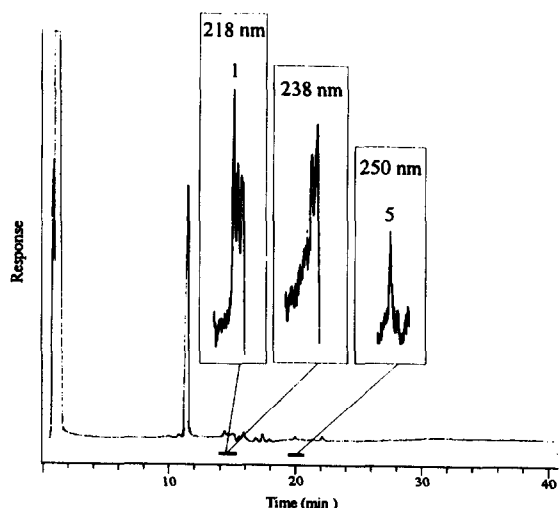| Compound	Detection limit (ng/l)	Compound	Detection limit (ng/l)
Naphthalene	10	Benz[a]anthracene	0.6
Acenaphthylene	150[a]	Chrysene	2
Acenaphthene	0.8	Benzo[b]fluoranthene	3
Fluorene	70	Benzo[k]fluoranthene	0.9
Phenanthrene	4	Benzo[a]pyrene	2
Anthracene	0.5	Dibenz[a,h]anthracene	2
Fluoranthene	5	Benzo[ghi]perylene	2
Pyrene	5	Indeno[1,2,3-cd]pyrene	15

[a] UV ($\lambda = 230$ nm).

Fig. 5. On-line trace enrichment–LC–fluorescence chromatogram of 10 ml of river Rhine water, containing $3 \cdot 10^{-4}$ M Brij-35, using the C_{18}-bonded silica precolumn. The three inserts show blow-ups ($50 \times$) of the identified naphthalene ($\lambda_{ex} = 218$ and 238 nm) and phenanthrene ($\lambda_{ex} = 250$ nm) peaks.

Fig. 6. On-line trace enrichment–LC–fluorescence chromatogram of 10-ml surface water sample —containing 20 mg/l suspended solids, spiked at the 10 ng/l level with the 16 priority PAHs and containing $3 \cdot 10^{-4}$ M Brij-35— using the C_{18}-bonded silica precolumn. For peak assignment, see Table 1. For experimental conditions, see text.

whether the procedure described in this paper for the low-ng/l level determination of PAHs in filtered surface water can also be utilized for non-filtered samples, *i.e.* samples containing suspended solids. In order to find out whether micelles can be used to resolubilize PAHs adsorbed on suspended solids, 2 mg of suspended solids were added to 100 ml of filtered river Meuse water which is a realistic level for surface water. The water sample had been spiked with the PAHs at the 100 ng/l level. After a continuous overnight shake, $3 \cdot 10^{-4}$ M Brij-35 was added and the solution was ultrasonicated for 30 min. Next, 10-ml samples were directly, *i.e.* without any filtration, analysed using the on-line procedure discussed above. Recoveries for all compounds were 50–85% of those found for samples containing no suspended solids. As can be seen from Fig. 6, this is still good enough to obtain detection limits of 10–15 ng/l or lower for all test analytes except acenaphthylene and fluorene. Although the present procedure has not been fully optimized nor tested with different types of suspended solids over a prolonged period of time, the quoted results indicate that
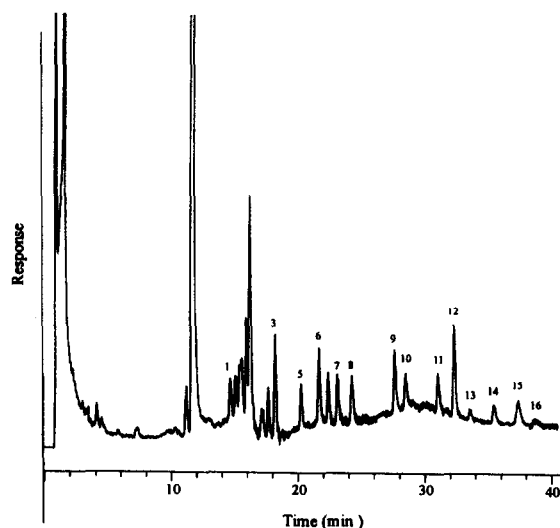
micelle mediation can distinctly be useful in the analysis of non-filtered surface water.

4. Conclusions

A robust and reliable system has been developed for the trace-level determination of 16 PAHs, present on the priority pollutant list of the EPA, in surface water. It involves micelle-mediated preconcentration, which prevents analyte adsorption to *e.g.* glass walls or suspended solids, combined on-line with a (conventional) reversed-phase LC separation and fluorescence or UV detection. Recoveries of over 90% were obtained for all priority PAHs at the 100 ng/l level. The system has been used for four months without any serious maintenance problems. In other words, the practical problems often encountered in the ultra-trace-level determination of the PAHs in real-life samples apparently have been solved.

Phthalocyanine-based sorbents such as Boos

silica proved to be very useful for the trace enrichment of polyaromatic compounds containing three ore more fused benzene rings. Conventional C_{18}-bonded silica and Chromspher π display better trace-enrichment characteristics for the smaller PAHs; however, they possess less selectivity. The present analytical system yields detection limits in the low- to sub-ng/l range for all sixteen priority pollutants when 10-ml surface water samples are used. The total analysis time is 50 min.

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6. References

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