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Determination of polycyclic aromatic hydrocarbons in waste water by off-line coupling of solid-phase microextraction with column liquid chromatography

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Abstract

A new method for the determination of polycyclic aromatic hydrocarbons (PAHs) in waste water using solvent-free solid-phase microextraction (SPME) is described. The PAHs are extracted with a 100 μm polydimethylsiloxane (PDMS) fiber, desorbed in 40 μl acetonitrile and measured with LC and fluorescence detection. The detection limits of this very simple method under the given conditions (extraction from 5 ml sample, extraction time 1 h) are in the range of 1–6 ng l^{-1}. The standard deviations ($n=6$) at a concentration level of 0.8 μg l^{-1} are between 1.8 and 14.4%. The procedure was used for the determination of PAHs in contaminated water samples.

Keywords: Solid-phase microextraction; Polynuclear aromatic hydrocarbons

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and some of their derivatives represent a complex class of important environmental pollutants originating from a wide variety of natural and anthropogenic sources. PAHs are generally formed during incomplete combustion or pyrolysis of organic matter and contaminate the environmental compartments as air, soil and water. Main sources of PAH emissions are domestic coal heating, coke production, open fires, but also vehicle exhaust and oil combustion.

The preferred method for analyzing PAHs in the aquatic environment is the solid-phase extraction (SPE) combined with column liquid chromatography (LC) or gas chromatography (GC) [1–4]. In many cases SPE is coupled to the analytical equipment to form a fully automatic system. Brouwer et al. [2] showed, that fluorescence detection used on a 10-ml sample resulted in detection limits ranging between 0.5 ng l^{-1} (anthracene) and 70 ng l^{-1} (fluorene). Recoveries of over 90% were obtained at the 100 ng l^{-1} level. The total analysis time was 50 min. In recent years, a new extraction technique, the solid-phase microextraction (SPME) has been developed. It was initially investigated for the gas-chromatographic analysis of volatile and semi-volatile organic compounds [5–9]. The first application of SPME for

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LC was described by Chen and Pawliszyn [10], who used a specially designed interface. Polycyclic aromatic hydrocarbons were selected as test analytes to evaluate this interface. Other SPME–LC couplings with various interfaces have been applied for the determination of PAHs [11] and other compounds [12–16]. Meanwhile a SPME–LC interface from Supelco has been made commercially available. Because the volume of the desorption chamber used is about 90 μl, peak broadening is difficult to avoid.

The aim of this work is to show that the off-line coupling of SPME and LC-fluorescence detection without an interface is a useful tool for the determination of PAHs in contaminated water. The procedure is simple to use, provides excellent peak shapes and low detection limits, and should be easy to automate by, for example, combining of a commercial SPME autosampler with a conventional autosampler of an LC device. Applied in this way, the technique may provide an alternative to the on-line SPE–GC or SPE–LC-procedures.

2. Experimental

2.1. Chemicals

Acetonitrile (HPLC, Ultra Gradient Grade), which was the solvent used and HPLC water were purchased from Baker. PAH standard materials were obtained from Supelco.

2.2. Preparation of standard solutions

The method was optimized and validated with 15 of the EPA–PAHs (except acenaphthylene). Concentrated solutions were prepared in acetonitrile. For SPME samples, 5 μl of these solutions was directly added to 5 ml water. Hence the proportion of acetonitrile in each sample did not exceed 0.1% (v/v).

2.3. SPME procedure

Fibers coated with 100 μm polydimethylsiloxane (PDMS) were obtained from Supelco. Before being used the fibers were conditioned for 1 h in the injector of a gas chromatograph under a nitrogen or helium stream at a desorption temperature of 250°C and under stirring exposed in acetonitrile for 5 min.

All analytes were placed in 5 ml vials with glass-coated impellers and sealed with Teflon-lined septa and hole caps. The advantage of glass-coated impellers for the extraction of PAHs compared to Teflon-coated stirring bars has been established in previous investigations [17]. The vials were filled with 5 ml water samples (the headspace volume being 2 ml). The speed of the magnetic stirrer (Heidolph MR 3002) was always about 950 r.p.m. The PAHs were extracted by exposing the fiber in the water sample. All extractions were carried out at room temperature. To avoid the vial being heated up during longer extraction periods, a thermally isolating material was placed between the bottom of the vial and the stirrer plate. After use the vials and the stirring bars were rinsed three times with acetone and dried with ultra-pure nitrogen.

The compounds were desorbed by exposure of the PDMS fiber in 40 μl acetonitrile using 0.1 ml conical inserts for crimp top vials (Chrompack). The smallest amount of solvent is 40 μl, which enables the fiber to be completely immersed. A measure of 2 μl acetonitrile was injected with the desorbed PAHs by means of the autosampler of the LC device used.

2.4. Instrumental

For PAH analysis, an HP 1100 system with a programmable fluorescence detector (HP 1046A) was used. The PAHs were separated on a Vydac 201 TP 52 column (250×2.1 mm ID). The conditions were as follows: Acetonitrile and water were used as mobile phase at a flow-rate of 0.4 ml min^{-1}. The composition gradient started with 50% water and 50% acetonitrile, then the acetonitrile content was increased to 60% (0–2 min), 90% (2–13.5 min) and 95% (13.5–19 min). This level was held constant for 7 min until the end of the analysis. The temperature was 22°C. The following excitation (ex) and emission (em) wavelength program was used for detection: naphthalene (λ_{ex} 221 nm, λ_{em} 337 nm), acenaphthene, fluorene (λ_{ex}, 227 nm, λ_{em} 315 nm), phenanthrene, anthracene (λ_{ex} 252 nm, λ_{em} 372 nm), fluoranthene, pyrene (λ_{ex}, 237 nm, λ_{em}, 440 nm), benzo(a)anthracene, chrysene (λ_{ex} 277 nm, λ_{em}, 393 nm), benzo(b)fluoranthene (λ_{ex}, 258 nm, λ_{em}, 442

nm), benzo(k)fluoranthene, benzo(a)pyrene (λ_{ex}, 266 nm, λ_{em}, 415 nm), dibenz(a,h)anthracene, benzo(g,h,i)perylene (λ_{ex}, 295 nm, λ_{em}, 425 nm), indeno(1,2,3)pyrene (λ_{ex}, 251 nm, λ_{em}, 510 nm).

3. Results and discussion

As SPME is an equilibrium process, the first thing to be done is usually to determining the extraction time profiles of the analytes. Fig. 1 shows the profiles of the more volatile compounds for extraction times of 0.5, 1, 2, 3 and 4 h, while Fig. 2 contains the profiles of the semivolatile PAHs. Apart from naphthalene, the equilibrium times of the volatile compounds are about 2 h; within the limits of error, the peak areas for naphthalene are independent of the extraction time — meaning that the extraction time is lower than 0.5 h. In the case of the semivolatile compounds the equilibrium time is higher. For pyrene, chrysene and benzo(a)anthracene, equilibrium is reached between 3 and 4 h, while the equilibrium time for the other compounds is higher than 4 h. To minimize the analysis time an extraction time of 1 h was chosen, even though an extraction time of 4 h would result in higher extraction yields.

Desorption performed over 2, 5, 10 and 15 min as described above (experimental part). As it was found that the peak areas of the extracted compounds only increased to 5 min desorption time, this time was chosen for all further experiments. Negative effects caused by the swelling of the polymer coating were not observed.

Carryover was controlled by a triple repetition of the desorption procedure using 40 μl pure acetonitrile in each case. The analysis of the three extracts showed a very low carryover. The values in the second extract were between 0.3% (benzo(a)anthracene) and 1.3% (acenaphthene). After the second desorption carryover was negligible.

Calibration was performed by extraction of spiked HPLC water samples with five calibration levels (0.01 μg l^{-1}, 0.1 μg l^{-1}, 0.4 μg l^{-1}, 0.8 μg l^{-1}, l.0 μg l^{-1}). A chromatogram of the calibration point 0.8 μg l^{-1} is given in Fig. 3. The limits of detection (LODs) were defined as three times the standard deviation of baseline noise. The LODs (see Table 2) estimated for spiked HPLC water are in the lower ng l^{-1} range. The low sample amounts of 2 μl injected

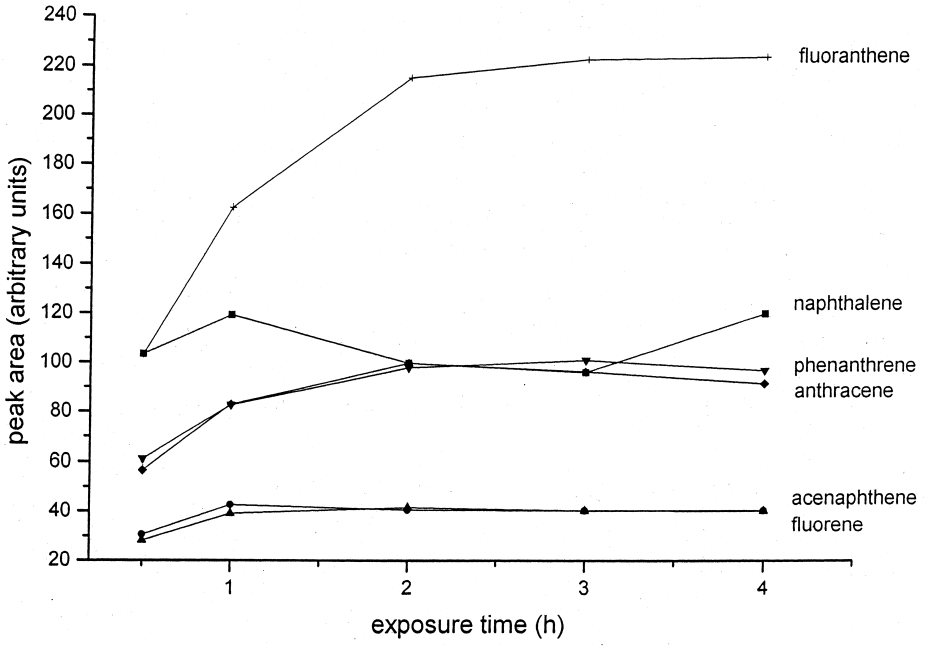

Fig. 1. Exposure time profiles of selected two ring to four ring PAHs.

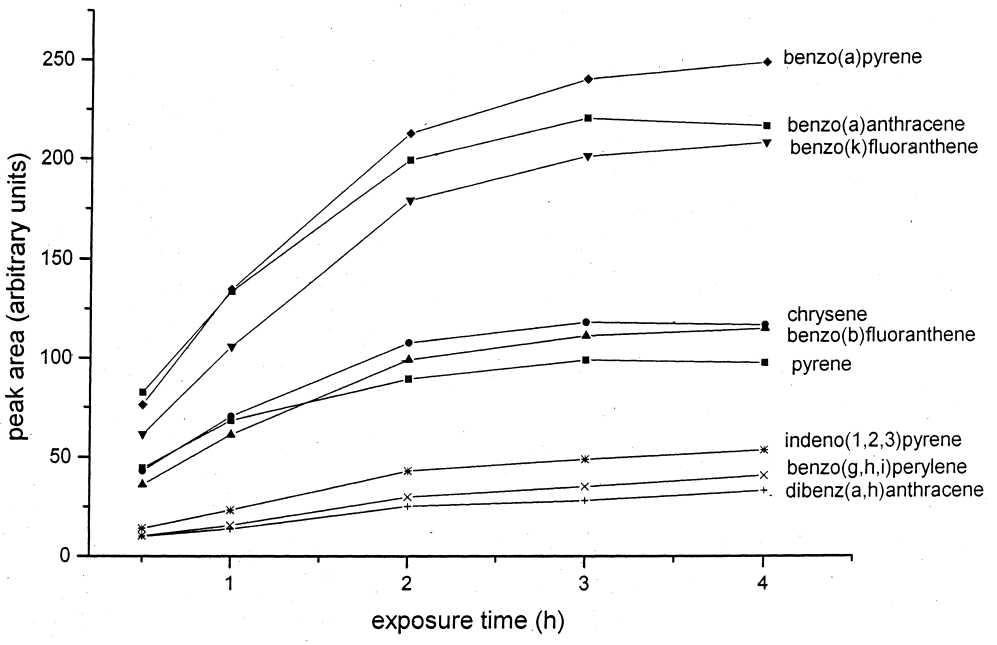

Fig. 2. Fig. 2. Exposure time profiles of selected four ring to six ring PAHs.

using the autosampler of the LC-device ensure symmetrical peak shapes with the chosen 2.1 mm ID Vydac column. On the other hand, 2 μl sample represents just 5% of the extracted analytes. Preliminary investigations performed with a 4.6-mm ID column showed that in this case a sample injection of 30 μl is possible. This means that 75% of the sample extract can be injected and the detection limits can be further improved, although the solvent consumption considerably increases. Because a further improvement of the very low detection limits was not as important for us as low solvent consumption, the investigations were performed with the 2.1-mm ID column. In comparison to on-line SPE–LC procedures (e.g. [2]), which enable over 90% analyte introduction, the method described has two disadvantages: first, that SPME is an equilibrium method and the amount extracted is much lower than 90%, and second, the additional limitation that the total sample mass cannot be injected. The advantages of the procedure described are its simplicity and the very low solvent consumption.

The linear ranges for the most hydrophobic compounds were limited to the calibration point 0.8 μg l^{-1}, which is probably due to the low water solubility of these compounds. For the less hydrophobic compounds (naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene), the extension of the linear dynamic range was much higher. With the exception of naphthalene, all the correlation coefficients were between 0.996 and 0.999. The relative standard deviations (RSD) for the calibration point 0.8 μg l^{-1} and six extractions are given in Table 1. The values are between 1.8 and 14.4%. The method developed for the determination of PAHs was applied to contaminated water samples — groundwater from the Bitterfeld industrial area, pump water from a gas station and groundwater from the area of the disused hydrogenation plant in Zeitz. To ensure that the calibration data can be transferred to actual samples, some of the contaminated waters were spiked with different concentration levels of PAHs. Comparison of the results showed that within the limits of error, the values of the spiked clean water and actual water samples were identical. Matrix effects did not influence the results. Table 2 lists the LODs determined for spiked HPLC water and the concentrations of the PAHs analyzed with the off-line SPME/LC. A chromatogram of the groundwater from Bitterfeld is shown in Fig. 4. The chromatogram is marked using

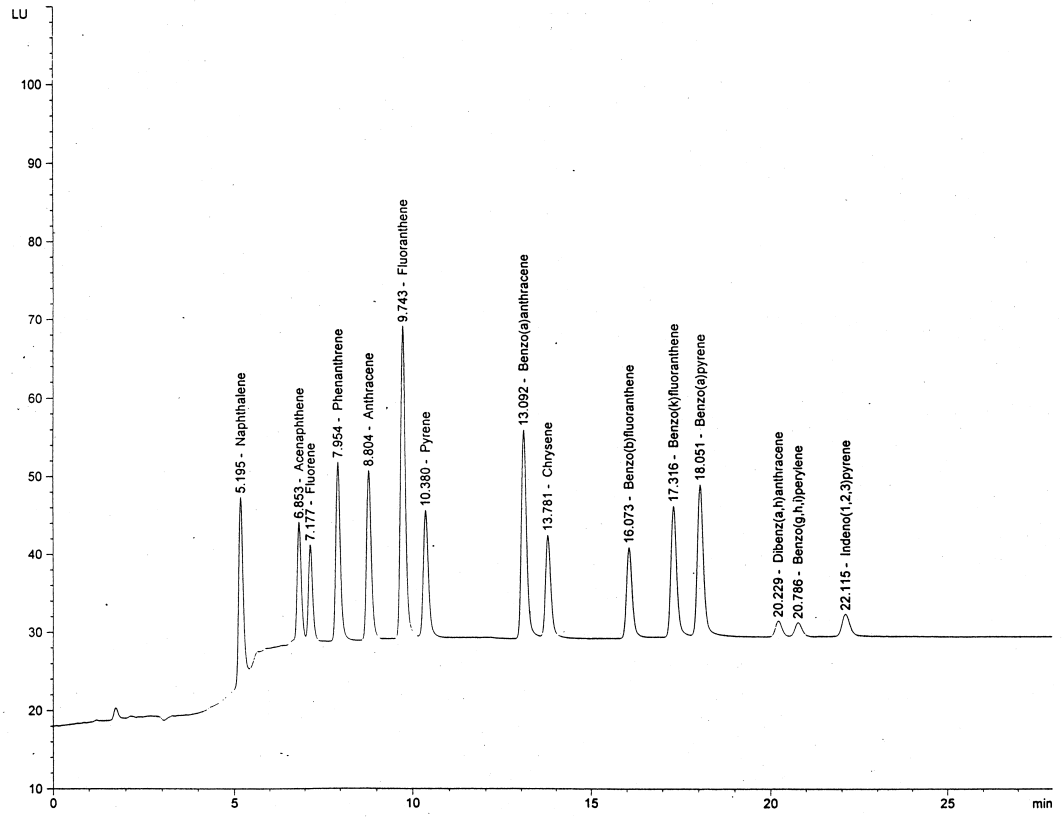

Fig. 3. Chromatogram of a spiked HPLC water sample (calibration level 0.8 μg l^{-1}) using SPME from a 5 ml sample, desorption in 40 μl acetonitrile and injection of 2 μl extract.

two different scales, with the peaks from benzo(k)-fluoranthene to indeno(1,2,3)pyrene being zoomed. It can be seen that the benzo(k)fluoranthene is not completely separated from an unknown compound and that the indeno(1,2,3)pyrene peak is overlapped to such a content by another compound that quantitation is not possible.

The results show, that the described off-line method can be used to the analyze PAHs in water samples. Because of the possibility of automation (an

Table 1
Reproducibility of SPME of 5 ml 0.8 μg l^{-1} spiked HPLC water with a 100 μm PDMS fiber

Compound	RSD (n=6) (%)	Compound	RSD (n=6) (%)
Naphthalene	5.9	Chrysene	7.7
Acenaphthene	3.0	Benzo(b)fluoranthene	8.6
Fluorene	1.8	Benzo(k)fluoranthene	8.4
Phenanthrene	4.1	Benzo(a)pyrene	4.9
Anthracene	4.5	Dibenz(a,h)anthracene	14.4
Fluoranthene	6.2	Benzo(g,h,i)perylene	11.8
Pyrene	7.3	Indeno(l,2,3)pyrene	9.5
Benzo(a)anthracene	5.9		

Table 2
Limits of detection (LODs) estimated from spiked HPLC water and concentrations of PAHs in analyzed water samples

Compound	LOD ($\mu g\ l^{-1}$)	Contaminated ground water Bitterfeld ($\mu g\ l^{-1}$)	Pump water ($\mu g\ l^{-1}$)	Contaminated ground water Zeitz ($\mu g\ l^{-1}$)
Naphthalene	0.002	21.6	167.7	45.6
Acenaphthene	0.002	0.2	2.9	0.3
Fluorene	0.002	0.004	7.4	0.6
Phenanthrene	0.001	0.04	1.6	0.04
Anthracene	0.001	0.06	0.05	0.004
Fluoranthene	0.001	0.01	0.1	<0.001
Pyrene	0.001	0.005	0.1	0.002
Benzo(a)anthracene	0.001	0.003	0.004	<0.001
Chrysene	0.001	0.004	0.005	<0.001
Benzo(b)fluoranthene	0002	0.006	0.002	<0.002
Benzo(k)fluoranthene	0.001	0.002	0.001	<0.001
Benzo(a)pyrene	0.001	0.004	0.002	<0.001
Dibenz(a,h)anthracene	0.004	0.006	<0.004	<0.004
Benzo(g,h,i)perylene	0.006	0.006	<0.006	<0.006
Indeno(1,2,3)pyrene	0.003	n.q.[a]	<0.003	<0.003

[a] n.q.: not quantifiable.

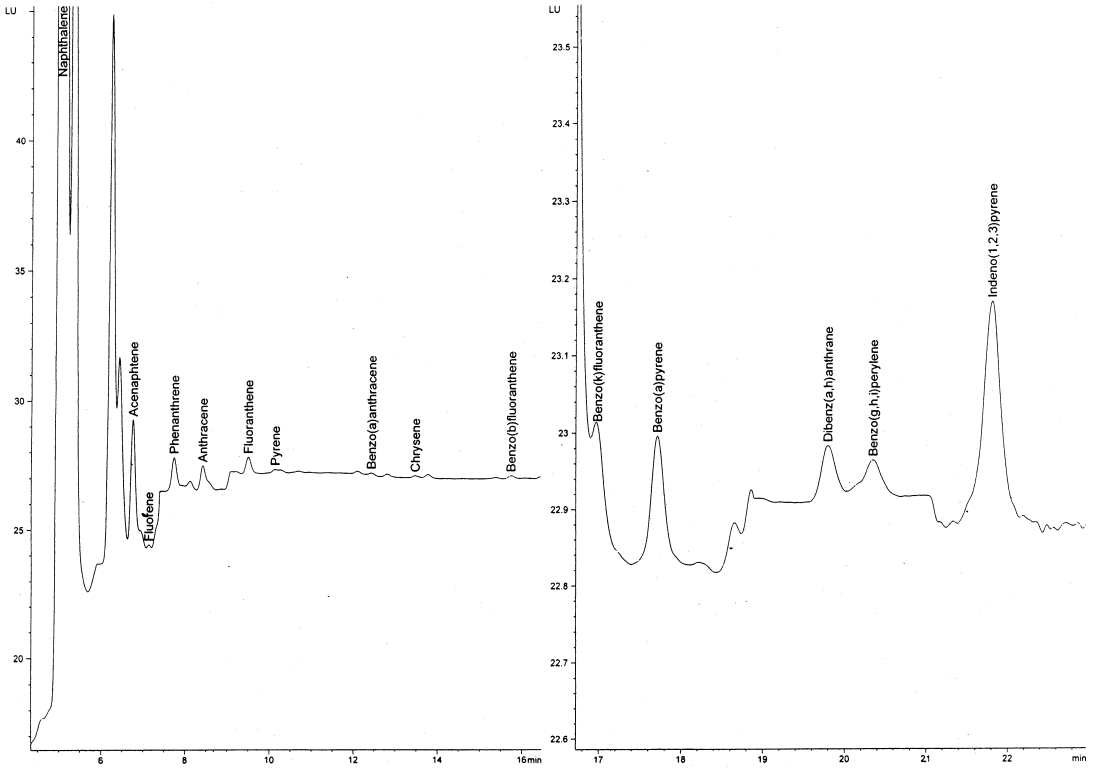

Fig. 4. Chromatogram of contaminated groundwater from an industrial site in Bitterfeld using SPME from a 5 ml-sample, desorption in 40 μl acetonitrile and injection of 2 μl extract.

SPME autosampler must be directly coupled to a conventional LC autosampler) without an additional interface, this method could be attractive not only for the determination of PAHs but also for other future applications.

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