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Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples

Bita Kolahgar*, Andreas Hoffmann, Arnd C. Heiden

Gerstel GmbH & Co. KG, Aktienstrasse 232–234, D-45473 Mülheim an der Ruhr, Germany

Abstract

The technique of stir bar sorptive extraction is used for the determination of polycyclic aromatic hydrocarbons (PAH) in aqueous samples. The PAHs are extracted with 10-mm stir bars (Gerstel Twister) coated with 0.5 mm polydimethylsiloxane and analyzed with a gas chromatography–mass spectrometry system. The influence of methanol and hyamine addition to the samples for preventing wall effects is investigated at 100 ng/l. The results indicate improved sensitivity using hyamine addition to the samples. The optimal extraction time was found to be between 3 and 4 h. The reproducibility of the method, as determined by nine replicate measurements, is between 5 and 15% at 10 ng/l and between 3 and 9% at 50 ng/l. Carry-over, which was evaluated at 500 ng/l by desorbing the same Twister three times, seems to be negligible for most of the compounds. In worst cases, carry-over of up to 7% was found for indeno[1,2,3]pyrene, dibenz[*a*,*h*]anthracene, and benzo[*g*,*h*,*i*]perylene. The technique shows excellent linearities for 5 point calibrations. Detection limits are between 0.1 and 2 ng/l.

Keywords: Stir bar sorptive extraction; Extraction methods; Water analysis; Polycyclic aromatic hydrocarbons

1. Introduction

Polycyclic aromatic hydocarbons (PAHs) are important priority organic pollutants. They emanate primarily from coal- and oil-burning plants and vehicle emissions as combustion products and are most likely adsorbed onto smoke particles settling on all kinds of surfaces, where they are transferred by rainfall into the aquatic environment.

Preferred methods for the determination of PAHs in aquatic samples are solid-phase extraction (SPE) or liquid–liquid extraction (LLE) combined with liquid chromatography (LC) or gas chromatography (GC) [1–4]. In both cases analytes are extracted from the aqueous phase and dissolved into an organic solvent. This solvent is then evaporated to a small volume to concentrate the analytes and lower detection limits. Solvent evaporation can be eliminated when a programmed-temperature vapourizer (PTV) inlet is used and large-volume injection (LVI) applied [5]. The process of extraction is on the one hand, time consuming, tedious, and can lead to errors of contamination or spillage; on the other hand, extractions require, especially in the case of LLE, the use of large amounts of organic solvents and often produce even more toxic waste. State-of-the-art procedures should be designed to minimize or completely avoid solvent consumption.

Arthur and Pawliszyn [6] developed a technique called solid-phase microextraction (SPME), where a fiber, coated mainly with polydimethylsiloxane (PDMS), is used for sampling. The fiber is after-

*Corresponding author. Tel.: +49-208-765-030; fax: +49-208-765-0333.

E-mail address: bita_kolahgar@gerstel.de (B. Kolahgar).

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wards thermally desorbed to introduce compounds into the GC typically in the splitless mode. This approach has limitations including limited capacity of the fiber and potential contamination of the SPME needle assembly when sampling complex liquid matrices. Baltussen et al. [7] introduced a technique that uses a stir bar coated with PDMS material that is called stir bar sorptive extraction (SBSE). Due to a larger amount of PDMS relative to the SPME fiber, this technique increases the recovery of analytes and therefore enhances sensitivity.

In recent years, SPME and SBSE in combination with LC have been applied to the extraction of PAH in water samples [8,9].

The aim of this study was to apply SBSE to the determination of PAHs in aqueous samples. The extracted PAHs are thermally desorbed and introduced into a GC–MS system for separation and analysis.

For optimization of the procedure, the influence of extraction time and stabilizers like methanol and hyamine are investigated. Reproducibilities using different stir bars, linearities and detection limits are described.

2. Theoretical

The recovery of an analyte from a sample extracted by a sorptive process in equilibrium can be described from the following equation [7].

$$\frac{m_S}{m_0} = \frac{\left(\frac{K_{OW}}{\beta}\right)}{1+\left(\frac{K_{OW}}{\beta}\right)}$$

where m_S, amount of analyte in the PDMS phase; m_0, total amount of analyte originally present in the water sample; K_{OW}, octanol–water partition coefficient; phase ratio $\beta = V_W/V_S$; and V_W, V_S, volume of water and PDMS phase.

Extraction with a phase like PDMS has the advantage that it is a pure sorptive process and no adsorptive processes take place.

Table 1 shows the predicted octanol–water partition coefficients (log K_{OW}) and the calculated recoveries for the compounds under consideration in this work. The K_{OW} values are calculated from the SRC KowWin Software, which is available from Gerstel (Mülheim an der Ruhr, Germany). Recoveries are calculated on the basis of a 10-ml sample volume and the 10-mm stir bars with a phase thickness of 0.5 mm (24 μl PDMS).

Table 1
Log K_{OW} values for PAH as predicted from "SRC K_{OW}Win" ver 1.66 as well as calculated recoveries

Compound	CAS Number	Log K_{OW}	Recovery (%)
Naphthalene	[91-20-3]	3.17	83
A-Methylnaphthalene	[90-12-0]	3.72	93
2-Methylnaphthalene	[91-57-6]	3.72	93
Acenaphthylene	[208-96-8]	3.35	95
Acenaphthene	[83-32-9]	4.15	95
Fluorene	[86-73-7]	4.02	97
Phenanthrene	[85-01-8]	4.35	99
Anthracene	[120-12-7]	4.35	99
Fluoranthene	[206-44-0]	4.93	100
Pyrene	[129-00-0]	4.93	100
Benzo[*a*]anthracene	[56-55-3]	5.52	100
Chrysene	[218-01-9]	5.52	100
Benzo[*b*]fluoranthene	[205-99-2]	6.11	100
Benzo[*k*]fluoranthene	[207-08-9]	6.11	100
Benzo[*a*]pyrene	[50-32-8]	6.11	100
Indeno[1,2,3]pyrene	[193-39-5]	6.70	100
Dibenz[*a*,*h*]anthracene	[53-70-3]	6.70	100
Benzo[*g*,*h*,*i*]perylene	[191-24-2]	6.70	100

From Table 1 it is obvious that SBSE will theoretically lead to almost quantitative extractions for most of the compounds.

3. Materials and methods

3.1. Chemicals and standards

The PAH calibration mix (20 μg of each compound/ml methanol) and hyamine were delivered by Sigma–Aldrich (Taufkirchen, Germany). For the analysis, HPLC water was spiked with the PAH standard to concentration ranges between 1 and 100 ng/l. The PAH mix contained the compounds listed in Table 1.

HPLC grade water and methanol were supplied by Promochem (Wesel, Germany).

3.2. Sample preparation

The stir bars were pre-conditioned before use by treating with acetonitrile for cleaning and thermal desorption in a special tube conditioner (Gerstel TC) at 300 °C in a nitrogen stream (100 ml/min) for 1 h.

The PAHs were extracted with stir bars of 10 mm in length and 0.5 mm in film thickness (Gerstel) from 10-ml samples in crimped 10-ml headspace vials at a stirring speed of 500 rpm and at ambient temperature.

After extraction, stir bars were removed with magnetic tweezers, cleaned with a lint-free tissue, placed in an empty glass thermal desorption tube (187 mm×4 mm I.D.) and thermally desorbed in a thermal desorption system (TDS 2, Gerstel).

3.3. Analysis

All experiments were performed on a gas chromatograph (6890, Agilent Technologies, Wilmington, DE, USA) with a mass selective-detector (5973, Agilent Technologies, Palo Alto, CA, USA), a PTV inlet (CIS 4, Gerstel), and an automated thermal desorption system (TDS 2/TDS A, Gerstel). All data were analyzed using target ions in the extracted ion mode. As target ions we used the molecular ions for the PAHs under consideration.

The analysis conditions were: TDS: splitless, 20 °C, 60 °C/min, 300 °C (10 min), transfer line 320 °C; PTV: glass wool insert, split 10:1, −150 °C, 12 °C/s, 300 °C (5 min); GC column: HP5-MS (Agilent), 30 m×0.25 mm I.D., d_f=0.25 μm; GC oven: 40 °C, 10 °C/min, 320 °C (2 min); GC pneumatics: constant flow =1 ml/min; MS, scan 35–400 amu, transfer line 280 °C.

4. Results and discussion

4.1. Influence of methanol and hyamine

As indicated by many authors, PAH losses to glass walls can be prevented by using methanol or hyamine (an ionic tenside) [10–12]. The influence of 10% methanol [12] and hyamine in a concentration of 10 μg/l [11] on PAH recovery in aqueous solutions is examined. Heiden et al. [12] investigated the influence of methanol concentration on PAH recovery. It was found that addition of methanol increases the recovery of PAH in water but the methanol concentration (10 and 20%) made no significant difference. The authors recommend a methanol concentration of 10%.

The influence of methanol and hyamine on PAH recovery is investigated in this study at 100 ng/l (Table 2). The results can be compared for three different solvents: pure water, water with methanol, water with hyamine.

As shown in Table 2 the best results are obtained by using hyamine. Therefore, the subsequent measurements are performed using hyamine in a concentration of 10 μg/l.

4.2. Extraction time

To optimize the extraction time, 100 ng/l standards containing hyamine were used. The extraction time was varied between 1 and 21 h (1, 1.5, 2, 3, 4, 5, 6, and 21 h). The results are shown in Fig. 1 for benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3]anthracene, and benzo[*g,h,i*]perylene as examples.

It was found that peak areas increased until 3 h of extraction and remained nearly constant until 4 h. After 4 h of extraction, the peak areas decreased and increased again at an extraction time of 21 h. The reason for the decrease at 5 and 6 h is not clear and should be investigated in a future study.

As a result, the remaining investigations were performed using an extraction time of 210 min (3.5 h).

4.3. Carry-over

Carry-over is investigated by desorbing the same Twister, containing 500 ng/l PAH, three times. More than 90% of all PAH are desorbed in the first desorption step. In the worst cases, carry-over of up to 6–7% were found in the second desorption for the higher boiling compounds indeno[1,2,3]pyrene, dibenz[*a,h*]anthracene, and benzo[*g,h,i*]perylene.

4.4. Reproducibility

Nine replicate measurements at 10 and 50 ng/l

Table 2
Influence of methanol and hyamine on the recovery of 100 ng/l PAH in aqueous solutions

Compound	Peak area		
	100% HPLC Water	10% Methanol	10 μg/l Hyamine
Naphthalene	20 472	20 215	23 856
A-Methylnaphthalene	11 293	12 456	13 700
2-Methylnaphthalene	10 881	11 776	12 968
Acenaphthylene	13 732	17 223	21 610
Acenaphthene	12 704	13 273	15 343
Fluorene	16 856	18 091	20 270
Phenanthrene	31 598	35 551	37 610
Anthracene	17 172	24 155	30 071
Fluoranthene	25 590	31 111	31 191
Pyrene	24 063	30 665	33 743
Benzo[*a*]anthracene	5887	13 277	14 306
Chrysene	10 375	17 864	17 610
Benzo[*b*]fluoranthene	1646	5893	6928
Benzo[*k*]fluoranthene	2241	6408	7106
Benzo[*a*]pyrene	975	3026	4146
Indeno[1,2,3]pyrene	79	656	1010
Dibenz[*a,h*]anthracene	1160	2971	4264
Benzo[*g,h,i*]perylene	971	3136	4532

were performed. Problems due to carry-over on the Twister can be neglected, since each Twister is used once, the results represent the inter-Twister reproducibilities (see Table 3).

At 10 ng/l, a poorer precision is found for the higher boiling compounds, probably due to either insufficient migration in or desorption from the PDMS phase.

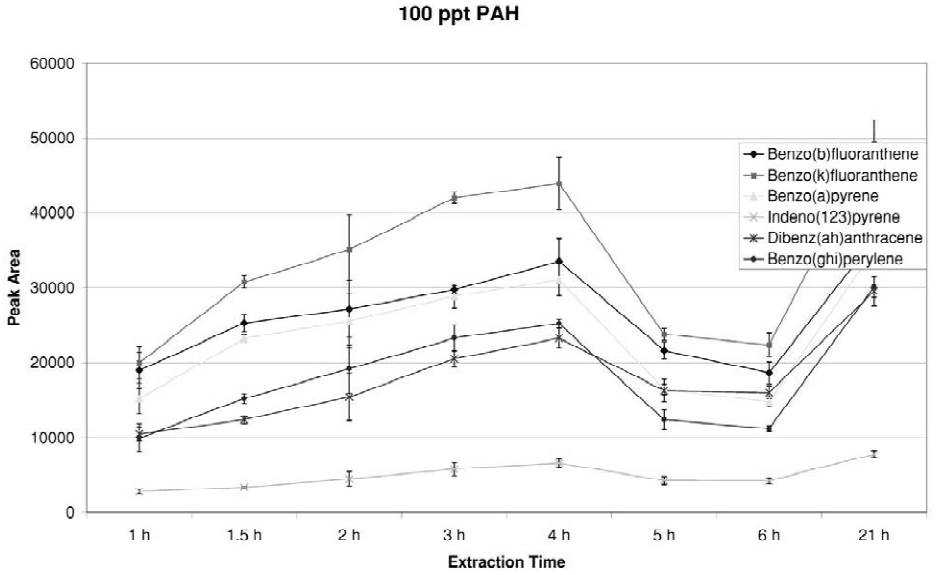

Fig. 1. Dependence of PAH recovery (100 ng/l PAHs) on extraction time. The points are averages of three measurements and the error bars indicate the standard deviations.

Table 3
Reproducibilities as well as sensitivities, linearities, and detection limits as calculated from five-point calibrations

Compound	Reproducibility (%) at 10 ng/l	Reproducibility (%) at 50 ng/l	Linearity	Sensitivity [area/(ng/l)]	Detection limit (ng/l)
Naphthalene	12	9	0.98782	165	0.5
A-Methylnaphthalene	7	4	0.99219	114	0.6
2-Methylnaphthalene	5	4	0.99410	114	0.8
Acenaphthylene	8	5	0.99780	182	0.3
Acenaphthene	10	3	0.99707	135	1.5
Fluorene	9	4	0.99872	178	2.0
Phenanthrene	11	5	0.99948	303	0.8
Anthracene	15	6	0.99865	207	1.2
Fluoranthene	10	4	0.99946	260	0.1
Pyrene	9	3	0.99971	256	0.7
Benzo[*a*]anthracene	8	5	0.97860	103	0.2
Chrysene	6	5	0.98527	137	0.2
Benzo[*b*]fluoranthene	10	5	0.92903	55	0.3
Benzo[*k*]fluoranthene	6	4	0.97357	96	0.5
Benzo[*a*]pyrene	10	6	0.92543	54	1.2
Indeno[1,2,3]pyrene	12	9	0.99894	22	1.4
Dibenz[*a,h*]anthracene	14	7	0.99995	89	0.3
Benzo[*g,h,i*]perylene	14	7	0.99848	74	0.2

At 50 ng/l, the reproducibilities are better than 10% for all compounds.

4.5. Calibration

Five-point calibrations were performed at 1, 5, 10, 50, and 100 ng/l. Table 3 gives the obtained sensitivities, linearities and detection limits. The regression coefficients (r^2) show good linearities in the concentration range under consideration. The detection limits, which are calculated by 3 σ (standard deviation of the peak areas in blank runs) divided by the sensitivities, are between 0.1 and 2 ng/l. The detection limits in Table 3 are theoretical statistical values basing on the fluctuations of the baseline in the blank runs and the sensitivity of the method (slope of the calibration curve). Practically, the quantitation limit is dependent on the smallest peak that can be safely integrated. The quantitation limit of PAHs in this study is found to be around 1 ng/l.

5. Conclusion

SBSE, combined with GC–MS analysis, can be applied to the analysis of PAH traces in aqueous samples. The reproducibility of the applied SBSE method for PAH analysis using different Twister is below 10% at 50 ng/l. Detection limits are between 0.1 and 2 ng/l.

The only disadvantage is that, at the present time, the sample preparation steps are not fully automated.

For routine analysis, extraction times of 210 min seem to be rather long, however multiple sample extractions can be performed in parallel. Therefore, the throughput is only dependent on the instrument run time. The sample introduction into the thermal desorption system is fully automated.

The method can be attractive for the analysis of other groups of compounds e.g. pesticides, herbicides, and phenols.

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