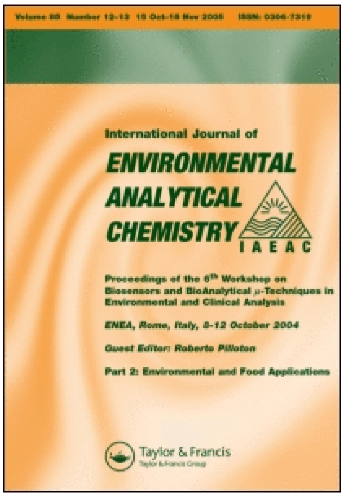

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Comparison of Stir Bar Sorptive Extraction and Solid Phase Extraction as Enrichment Techniques in Combination with Column Liquid Chromatography for the Determination of Polycyclic Aromatic Hydrocarbons in Water Samples

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COMPARISON OF STIR BAR SORPTIVE EXTRACTION AND SOLID PHASE EXTRACTION AS ENRICHMENT TECHNIQUES IN COMBINATION WITH COLUMN LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER SAMPLES

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The commonly used solid-phase extraction (SPE) was compared with the recently developed stir bar sorptive extraction (SBSE) to determine EPA-PAHs from precipitation water samples. SPE was performed using C18 PAH-filled cartridges; magnetic stirring rods 10 mm long and coated with 0.5 mm (24 μL) polydimethylsiloxane were used for SBSE. Determination was performed by high performance liquid chromatography and fluorescence detection.

The investigations were performed at a concentration level of 30 ng/L, adjusted to actual PAH concentration levels of precipitation water. The recoveries ranged between 54% (SBSE) and 20% (SPE) respectively and about 100%, while the standard deviation ($n = 5$) varied in the range of 4.7–13.5% (SBSE) and 3.6–16.9% (SPE) except for the more volatile compounds acenaphthene and fluorene. The detection limits calculated were between 0.4 and 5.0 ng/L. Both techniques were applied to study the PAH contents of precipitation water of several polluted sites in the city of Halle (Saxony-Anhalt, Germany). The advantages and disadvantages of the methods used are discussed.

Keywords: Stir bar sorptive extraction; Solid phase extraction; Column liquid chromatography; Water analysis; Polycyclic aromatic hydocarbons

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of environmental pollutants. PAHs are formed during the incomplete combustion or pyrolysis of organic matter. They originate from both natural and anthropogenic sources and are

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ubiquitous and persistent in the environment. The carcinogenic and/or mutagenic properties of some of these compounds and the resulting human health risk [1] requires sensitive and reliable methods for the determination of PAHs [2]. The most common method for PAH analysis from aqueous samples is solid-phase extraction (SPE) combined with HPLC or GC [3–5]. Nonpolar interactions via van der Waals forces are used to adsorb the target analytes on octadecyl-bonded silica followed by elution of the analytes with small amounts of a suitable organic solvent.

Some 10 years ago solid phase microextraction (SPME) [6] based on polydimethylsiloxane (PDMS) as extraction medium was introduced. In this case the enrichment step is characterised by partitioning the analytes between the PDMS phase and the sample matrix. Although SPME using PDMS fibres is a simple and rapid technique, its applicability is limited. Recent studies [7] described low recoveries obtained for solutes with $K_{\mathrm{ow}} < 10{,}000$. This disadvantage can partially be compensated for by using fibres based on adsorption (e.g. carbowax-divinylbenzene), but these fibres only have a limited number of surface sites where adsorption can take place. Consequently the range of linear dependence is limited and extraction is frequently influenced by matrix effects. In response to these results, a new approach using stir bars coated with 50–300 µL PDMS was recently developed [8]. The authors documented the effective extraction of volatile and semi-volatile organic compounds from aqueous samples using the SBSE-thermodesorption-GC/MS technique. Because of the lower phase ratio between the aqueous and the PDMS phase compared to the SPME procedure, noticeably higher recoveries of the SBSE extraction were obtained, especially for volatile compounds.

Popp *et al.* [9] first described the combination of SBSE extraction and solvent desorption with subsequent liquid chromatography for PAH analysis from water samples. The results obtained demonstrate that SBSE combined with solvent desorption as well as the combination of SBSE and thermodesorption are eminently suitable for pre-concentrating PAHs from aqueous samples.

Solid-phase extraction is the preferred enrichment technique for the determination of polycyclic aromatic hydrocarbons in atmospheric precipitation (rainfall, snow, etc) [5,10–12]. The small PAH levels of such samples require the pre-concentration of greater sample volumes for a suitable enrichment efficiency.

The aim of this study was to examine the combination of SBSE extraction and solvent desorption in comparison with conventional SPE technique for water analysis regarding the sensitivity and capability of both methods for PAH determination from precipitation samples.

EXPERIMENTAL

Chemicals and Samples

Throughout all the experiments, the PAH Mix No. 9 (Dr. Ehrenstorfer, Augsburg, Germany) containing the 16 EPA-PAHs in acetonitrile (each 100 µg/mL) was used. Acetonitrile (HPLC ultra gradient grade), methanol, methylene chloride, benzene (all for organic trace analysis) were supplied by Merck (Darmstadt, Germany). The SPE sorbent C18 PAH (special modification of octadecyl based on silica gel with 60 Å pore diameter, pore size 45 µm, surface area $500\,\mathrm{m^2g^{-1}}$, not endcapped, 14% carbon) was obtained from Macherey-Nagel (Düren, Germany).

Pure water (MILLI-Q Plus, Millipore GmbH Eschborn, Germany) was used to prepare the samples.

Calibration solutions (10, 20, 50, 100, 200 ng/L) were prepared in ACN. 10μL of each standard solution was always directly added to 10 mL of pure water, so that the concentration of ACN did not exceed 0.1% (v/v).

To evaluate the efficiency of the procedures, pure water samples were spiked with the EPA-PAHs (each 30 ng/L). Subsequently the procedures were applied to monthly precipitation water samples from several polluted sites in Halle (Saxony-Anhalt) collected in November/December 2000 and January 2001.

The HPLC method was optimised and validated with 14 of the EPA-PAHs (except acenaphthylene and naphthalene). The reasons for excluding these individual compounds are: acenaphthylene is not detectable with fluorescence detection and naphthalene due to its volatile properties and its wide spread distribution led to carry over in HPLC-FD.

SBSE Procedure

Before being reused or used for the first time, the stir bars or “twisters” (Gerstel GmbH, Mühlheim, Germany) were conditioned by first placing them in vials with 1 mL of a solution of methanol and methylene chloride (1 : 1, v/v) for 5 min. Then the solution was refreshed and the procedure repeated three times. Subsequently the stir bars were dried at room temperature in a desiccator and heated at 250°C in a moderate nitrogen stream.

For enrichment, the stir bars (usually 6 pieces simultaneously) were placed in 10 mL water samples in a 10 mL glass vial and stirred at 850 rpm. The exposure time was 60 min. After the extraction step, the stirrers were removed with clean tweezers and dried with lint-free tissue. Then they were each placed into a 2 mL vial with an insert (250 μL, glass, flat bottom). For the desorption of PAHs, the inserts were filled with 160 μL of a mixture of ACN and water (4 : 1, v/v) and kept for 10 min at room temperature. After desorption the stir bars were removed using a magnetic rod. To analyse the PAHs, the insert vials were placed into the autosampler of the HPLC device.

SPE Procedure

Solid phase extraction was performed using a conventional BAKER SPE System (Mallinckrodt Baker, Griesheim, Germany) with vacuum manifold and multiple glass cartridges. The SPE procedure was as follows: 2 g of the SPE sorbent C18 PAH was placed between two glass fibre frits in 6 mL cartridges. The sorbent was conditioned successively with 6 mL of methanol and 6 mL of purified water. The precipitation water samples were filtered through GF 6 glass fibre filters (Schleicher & Schuell, Darsel, Germany), which allows particles with diameters even smaller than 1 μm to be deposited. Each 500 mL of both spiked pure water and filtered precipitation water samples mixed with 5 mL of methanol to avoid wall effects were sucked through the cartridge at a flow rate of about 15 mL min^{-1}. The loaded sorbent material was dried overnight in a gentle argon stream and eluted with a mixture of ACN and benzene (3 : 1, v/v). Elution was performed in two steps: first the sorbent layer was wetted with 2 mL of the eluent for about 30 min to enable the analytes to interact with the sorbent

TABLE I Excitation (λ_{ex}) and emission (λ_{em}) wavelengths for determination of PAH

Compound	*Abbreviation*	λ_{ex} (nm)	λ_{em} (nm)
Acenaphthene	Ace	237	315
Fluorene	Flu	237	315
Phenanthrene	Phe	244	360
Anthracene	Ant	252	372
Fluoranthene	FLU	237	460
Pyrene	PYR	237	385
Benz(a)anthracene	BaA	277	376
Chrysene	CHR	277	376
Benzo(b)fluoranthene	BbF	258	442
Benzo(k)fluoranthene	BkF	255	420
Benzo(a)pyrene	BaP	255	420
Dibenz(a,h)anthracene	DBahA	300	415
Benzo(g,h,i)perylene	BghiP	300	415
Indeno(1,2,3-c,d)pyrene	INP	250	495

material. Subsequently the analytes were eluted with an additional 2 mL of the ACN–benzene mixture. Before PAH analysis, the eluate was evaporated to dryness and dissolved in 1 mL of acetonitrile.

HPLC Conditions

Polycyclic aromatic hydrocarbons determination was carried out using a HP 1050 (Hewlett Packard, Palo Alto, CA, USA) equipped with a wavelength programmable fluorescence detector. The separation of PAHs was performed in a LiChroCART 250-3 (250 mm × 3 mm i.d.) column filled with LiChrospherPAH 5 μm (Merck, Darmstadt, Germany). Acetonitrile–water containing 50% (v/v) acetonitrile was used as mobile phase. The ACN content was linearly increased within 3 min to 60% and between 3 and 14 min continuously to 100%. This level was maintained for 24 min (until the end of the analysis). The flow-rate of the mobile phase was 0.50 mL min^{-1}. Injection volumes of 50 μL (SBSE) and 10 μL (SPE) respectively were used. HPLC analysis was performed at 20°C. The fluorescence wavelengths are given in Table I. The PAH levels in the extracts were quantified using external calibration.

RESULTS AND DISCUSSION

Comparison of the Efficiency of the SBSE and SPE Procedures

In this study the SBSE procedure described by Popp *et al.* [9] was compared with customary SPE techniques used for PAH water analysis [13] with respect to investigating precipitation samples. In this context the SBSE conditions were as follows: 10 mL sample volume, one-step extraction, extraction time 60 min, desorption of the enriched PAHs in 160 μL of an ACN–water mixture (4 : 1, v/v) for 10 min at room temperature. The ACN–water mixture chosen enables the injection of 50 μL of the extract into the HPLC system without the deterioration of the peak shape.

To calculate the reproducibility of the procedure, pure water samples spiked with 30 ng/L of each EPA-PAH were extracted with five different twisters. The results obtained using the specified SBSE procedure are given in Table II. The recoveries

TABLE II Recoveries, relative standard deviations (RSD) and detection limits (LOD) of EPA-PAHs in spiked water samples with both SBSE-HPLC and SPE - HPLC procedures

Compound	*Recovery* [%] ($n = 5$)		*RSD* [%] ($n = 5$)		*LOD* (ng/L)	
	SBSE	*SPE*	*SBSE*	*SPE*	*SBSE*	*SPE*
Ace	61.9	59.8	5.5	41.1	2.0	5.0
Flu	99.3	68.0	5.0	19.2	2.0	5.0
Phe	71.3	86.9	4.7	6.9	0.8	5.0
Ant	57.9	70.4	4.8	7.8	0.8	1.0
FLU	76.9	97.1	5.6	3.6	0.4	0.8
PYR	71.5	74.6	5.2	6.9	0.8	1.2
BaA	71.4	58.3	6.0	6.8	1.8	0.7
CHR	80.9	59.7	7.5	6.9	3.8	1.2
BbF	74.0	45.8	7.4	10.3	1.7	1.2
BkF	74.0	45.9	8.0	13.2	1.0	0.6
BaP	54.0	39.1	7.7	16.9	1.4	1.4
DbahA	71.7	37.5	12.7	12.5	5.0	2.7
BghiP	61.2	19.2	13.5	5.6	5.0	3.0
INP	69.1	26.7	12.8	13.4	5.0	3.8

varied between 54.0% (BaP) and 99.3% (Flu). The values of the relative standard deviations (RSD) of the PAHs analysed are in the range of 4.7–13.5% for the higher molecular compounds. Taking into account the use of the five different twisters and the low concentrations of the spiked PAHs, these results are satisfactory. Calibration was performed by extracting spiked Milli-Q Plus water samples at five calibration levels (10, 20, 50, 100, 200 ng/L). The detection limits (LOD) given here were defined as concentration giving a signal-to-noise ratio of 3. In the case of acenaphthene, fluorene and phenanthrene, the LOD based on the sum of the mean values of the blanks ($n = 5$) and the triple of the standard deviation. Good linearity of the calibration plots (correlation coefficients between 0.993 and 1.000) was obtained with the exception of DBahA ($r = 0.969$). The estimated LOD values ranged between 0.4 and 5.0 ng/L. The higher LOD values were obtained for the compounds with the highest octanol–water partition coefficient (DBahA, BghiP, INP) because in these cases equilibrium within the extraction time of one hour was not reached.

The SPE procedure was performed with a sample volume of 500 mL to minimise the extraction time. To evaluate reproducibility, pure water was spiked with each 30 ng EPA-PAH, adjusted to the PAH concentrations of actual precipitation samples. To avoid losses of analytes and enable several determinations, the reduced extracts were dissolved in 1 mL of acetonitrile. With pure ACN as solvent, 10 µL of the extract could be injected. Higher sample amounts decreased the peak resolution.

For most of the compounds, recovery was improved by using the SBSE procedure (Table II). In particular, the recoveries of the more hydrophobic PAHs (log $K_{OW} > 5$) were noticeably lower when using SPE compared to SBSE extraction. The recoveries obtained were similar to the results described by other authors. Carrera *et al.* [12] established the extraction efficiencies of PAH standard solutions on two concentration levels 1.5 µg/L and 200 ng/L with sample amounts 2.5 L each. The recoveries were 74–89% at the concentration level of 1.5 µg/L, but recovery efficiency reached of the diluted samples was a lot lower (39–88%). The relative standard deviations reported using SPE are also shown in Table II. With the exception of acenaphthene, the RSD values varied between 3.6 ad 19.2% and tally with the results of both SBSE extraction and other SPE procedures investigated.

Under the chosen conditions, the estimated LOD values of the SPE procedure were similar to those of SBSE and varied between 0.6 and 5.0 ng/L (Table II). The relatively high LOD values of especially acenaphthene, fluorene and phenanthrene resulted from blanks caused by the laboratory air.

Analysis of Precipitation Water Samples

The enrichment techniques described were applied to samples of wet precipitation from various polluted sites located inside the city of Halle in Saxony-Anhalt (Germany): Site I and Site II are located north-east of main arterial roads. Additionally, Site II is affected by the railway near the street. Because the wind here mainly blows from the south-west, these two sites ought to be subject to higher pollution than elsewhere. In contrast, Site III and Site IV are situated inside residential zones with little traffic. These location are considered less polluted.

The sample results were obtained from two collection periods of atmospheric bulk deposition at the described locations in November 2000 and January 2001. The bulk samples were filtered through glass fibre filters (Schleicher and Schuell, Dassel, Germany) to remove particulate matter ≥ 1 µm. For further analysis, only the aqueous phase was used and handled as described above. By way of example, the results of the PAHs analysed from January 2001 are shown in Table III. The total PAH levels of both enrichment techniques tallied satisfactorily except for Site IV. Regarding the low concentrations, most of the values of the individual compounds are also comparable (see Fig. 1). However, higher values were often obtained for the more water-soluble (and more volatile) compounds when SBSE was used. This can be explained by losses of the more volatile PAHs when drying the polluted sorbents and corresponds

TABLE III PAH concentrations in precipitation water of different burdened sites (Halle, Saxonia-Anhalt, Germany) enriched by SBSE and SPE (ng/L)

Compound			*Collection period: January 2001*					
	Site I		*Site II*		*Site III*		*Site IV*	
	SBSE	*SPE*	*SBSE*	*SPE*	*SBSE*	*SPE*	*SBSE*	*SPE*
Ace	12.3	8.83	510	546	232	85.2	318	180
Flu	10.6	12.4	454	687	198	146	326	252
Phe	91.1	71.6	2327	2202	931	623	1436	833
Ant	6.32	5.12	87.9	114	32.1	24.7	48.2	33.4
FLU	74.0	56.4	243	244	147	100	159	88.2
PYR	27.3	31.5	82.1	100	46.5	37.8	49.8	31.9
BaA	< 1.8	4.90	< 1.8	3.40	< 1.8	2.53	< 1.8	2.65
CHR	8.73	10.9	6.57	10.5	4.61	5.44	< 3.8	4.06
BbF	5.49	6.71	5.56	8.51	5.16	6.46	< 1.7	5.82
BkF	2.51	3.93	2.62	5.46	2.51	3.79	< 1.0	3.50
BaP	< 1.4	5.38	4.16	7.35	4.09	5.53	< 1.4	5.27
DBahA	< 5.0	< 2.7	< 5.0	6.16	< 5.0	< 2.7	< 5.0	5.51
BghiP	< 5.0	10.8	< 5.0	16.7	< 5.0	11.0	< 5.0	< 3.0
INP	< 5.0	< 3.8	< 5.0	7.02	< 5.0	4.77	< 5.0	< 3.8
ΣPAH	238	228	3723	3958	1603	1056	2337	1445

Site I: north-east of a main arterial road. Site II: north-east of a main arterial road and railway. Sites III and IV: inside of residential zones with few traffic.

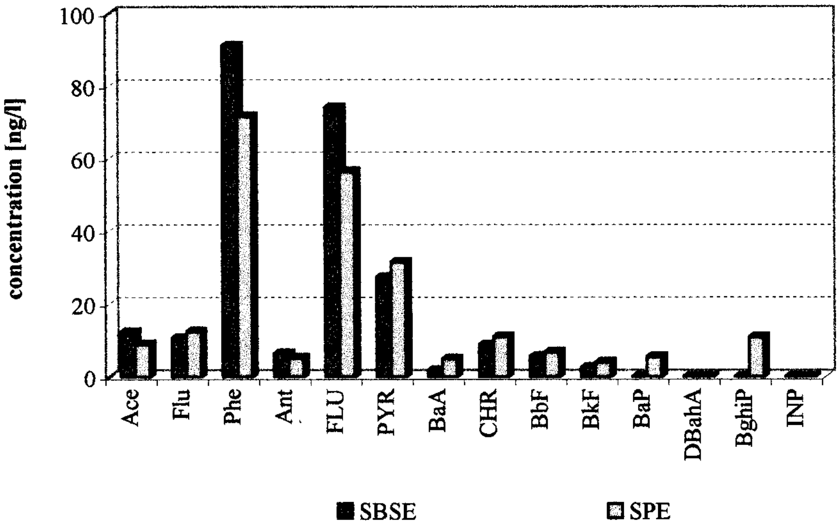

FIGURE 1 Comparison of mean PAH concentration profiles of precipitation water collected in January 2001 from Site I (city of Halle, Saxony-Anhalt) – after enrichment with SBSE and SPE.

to the high relative standard deviations of the SPE reported in Table II. The higher levels from SPE extraction compared to SBSE extraction in the case of more hydrophobic PAHs can be attributed to analytes adsorbed on micro-particles passing through the glass fibre filters (cf. [14,15]).

Compared with other investigations of PAH concentrations in atmospheric residues, the data reported represent the pollution of urban areas. The relatively low PAH levels at the normally more polluted Site I can be explained by the location of this area west of a cemetery and the higher proportion of wind from the east and south-east in January 2001. Leuenberger *et al.* [16] described total PAH contents of 1,500 ng/L in melted snow samples from urban areas in Zurich (Switzerland). Carrera *et al.* [5] investigated atmospheric deposition in several high mountain areas in Europe. The summarised concentrations of 22 PAHs were in the range of 5.6–81.0 ng/L.

Advantages and Diadvantages of the Applied Extraction Techniques

Both methods described enable to determine traces of polycyclic aromatic hydrocarbons in liquid samples.

The very well investigated SPE technique has become the method of choice for the preparation of aqueous samples and was proposed as a standard technique to enrich and extract aqueous samples for the determination of PAHs by the US EPA [10]. Automation and online applications allow the analytical effort to be minimised and reproducibility to be enhanced.

To reach sufficient detection limits and recoveries for extraction, sample volumes of about 1.0 L were commonly used. Sample volumes smaller than 250 mL were reflected in higher detection limits since the total analyte amount is lower (Carrera *et al.* [12]). The LOD values ought to be further improved by decreasing the extract volume.

The SBSE procedure is very easy to handle and is a process which is nearly solvent-free. No restriction or clean-up procedures are necessary. The low deviations between different stir bars enable the simultaneous extraction of several samples. Since the enrichment of the target analytes is performed in only one step, their losses are minimised. The detection limits (in the ng/L range) and recoveries are comparable or even better than those of similar techniques such as SPME [17,18]. The required sample volumes of 10 mL are very small. The disadvantages of not being fully automated can, due to its good comparability, partly equalised by the simultaneous extraction of several samples. Because of the small sample volumes and easy handling, SBSE can be used as an alternative procedure to SPE for PAH determination in precipitation water samples, even in the case of individual precipitation events with small sample amounts.

Acknowledgement

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References

[1] *Evaluation and Estimation of Potential Carcinogenic Risk of Polynuclear Aromatic Hydrocarbons* (Carcinogen Assessment Group, Office of Health and Environmental Assessment, Office of Research and Development, US Environmental Protection Agency, Washington DC, 1985).

[2] J.J. Santana Rodríges and C. Padrón Sanz (2000). *Analysis*, **28**/**8**, 710–717.

[3] E.R. Brouwer, A.N.J. Hermans, H. Hingeman and U.A.Th. Brinkman (1994). *J. Chromatogr. A*, **669**, 45–57.

[4] I. Liška (2000). *J. Chromatogr. A*, **885**, 3–16.

[5] G. Carrera, P. Fernández, R. Vilanova and J.O. Grimalt (2001). *Atmos. Environ.*, **35**, 245–254.

[6] R.P. Belardi and J.B. Pawliszyn (1989). *Water Pollut. Res. J. Can.*, **24**, 179–188.

[7] J. Beltran, F.J. Lopez, O. Cepria and F. Hernandez (1998). *J. Chromatogr. A*, **808**, 257–267.

[8] E. Balthussen, P. Sandra, F. David and C. Cramers (1999). *J. Microcol. Sep.*, **11**, 737–747.

[9] P. Popp, C. Bauer and L. Wennrich (2001). *Anal. Chim. Acta*, **436**, 1–9.

[10] US EPA-Method 525, In: *Drinking Water*, EPA/600/4-88/039, Office of Research and Development, Washington DC (1988).

[11] R. Reupert and G. Brausen (1994). *Acta Hydrochim. Hydrobiol.*, **22**/**5**, 202–215.

[12] G. Carrera, P. Fernández, R. Vilanova and J.O. Grimalt (1998). *J. Chromatogr. A*, **823**, 189–196.

[13] *PAH from Water* (*Appl.-No.: 301250*), [www http://www.macherey-nagel.com/].

[14] E. Naffrechoux, E. Combet, B. Fanget, L. Paturel and F. Berthier (2000). *Polycyclic Aromatic Compounds*, **18**/**2**, 149–159.

[15] H. Kumata, K. Masuda, J. Yamada and H. Takada (2000). *Polycyclic Aromatic Compounds*, **20**/**1–4**, 39–54.

[16] C. Leuenberger, J. Czuczwa, E. Heyerdahl and W. Giger (1998). *Atmos. Environ.*, **22**, 695–705.

[17] P. Popp, C. Bauer, M. Möder and A. Paschke (2000). *J. Chromatogr. A*, **897**, 153–159.

[18] R.A. Doong, S.M. Chang and Y.C. Sun (2000). *J. Chromatogr. Sci.*, **38**, 528–533.