PAL SPME Arrow: An Evolutionary Step Forward for Solid-phase Microextraction (SPME)

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1) Introduction

Since its development in 1989 by Pawliszyn & Belardi [1], solid-phase microextraction (SPME) has received significant attention for its unique capabilities: The inherent cleanup functionality, which separates the desired analyte molecules from their matrix, the simultaneous pre-concentration effect for these analytes, leading to improved detection limits compared to simple liquid-injection and last, but not least, the possibility of sampling not only from the sample solution but also from its headspace with the same device without any further instrumental requirements. The ability of this technique to accomplish all of these features without the use of any organic solvents has led it to become the predominant microextraction technique on the analytical market today [2-4]. Its use is not limited only to the research field but it is also implemented in routine analysis.

Apart from its many advantages, SPME also has drawbacks, including the limited mechanical robustness of the fibre [5-8] and the rather small sorption phase volume of the commercially available fibres [4,6,9]. In order to overcome the latter disadvantage, the SPME related technique of stir bar sorptive extraction (SBSE) was developed. SBSE provides a significantly larger extraction phase on the order of 100 µL compared to about 1 µL with classical SPME, but loses the advantage of full automation, as the SBSE bar has to be recovered from the sample, dried and introduced into a thermodesorption unit in a manual process.

Recently, a novel SPME related extraction device named PAL SPME Arrow was developed. It is a completely redesigned, automatable fibre, and combines the advantages of the classical SPME fibre and SBSE, while remediating the disadvantages of these techniques. A graphical representation of a PAL SPME Arrow is shown in Figure 1 alongside a classical SPME fibre. Its properties will be discussed in the results section of this article.

Polycyclic aromatic hydrocarbons (PAHs) are abundant environmental contaminants originating both from anthropogenic as well as natural sources, which typically involve incomplete combustion processes such as forest fires or burning of fossil fuels [8,9]. Their analysis in environmental sampling is widespread due to the many regulations that exist to monitor these organic pollutants.

In the context of increasing analytical demands, PAHs were used as representative and well studied analytes to determine to which extent PAL SPME Arrow surpasses the limitations of classical SPME fibres without compromising the original SPME advantages.

Polydimethylsiloxane (PDMS) was used as common sorption phase material [12], because just like the aforementioned analytes, it enables effective comparison of results with literature.

PAL SPME Arrow is based on a stabilising stainless steel inner rod that runs continuously through the entire fibre, carrying the cylindrically shaped sorption phase and connecting the upper parts of

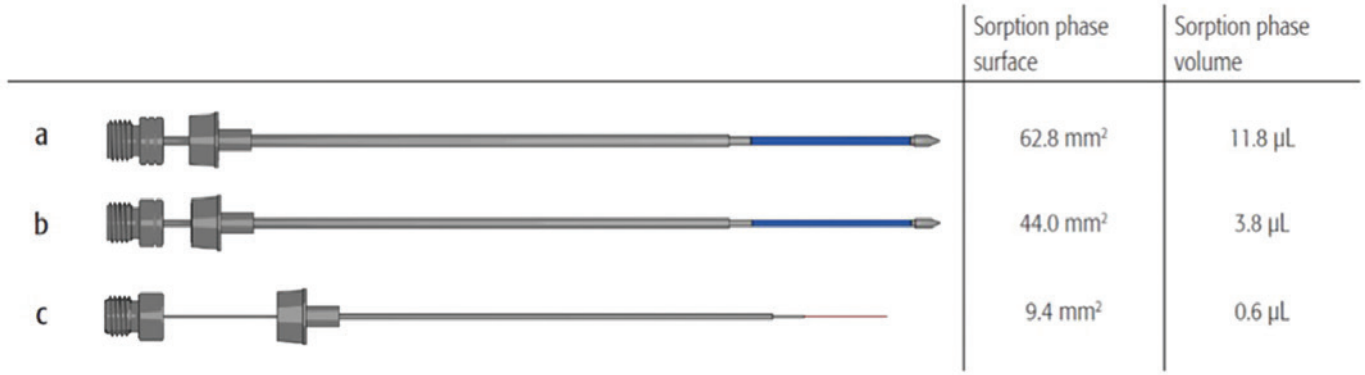

Figure 1. Sketch of a classical SPME fibre and a novel PAL SPME Arrow 1.5 mm (top), PAL SPME Arrow 1.1 mm (middle) and a classical SPME fibre (bottom). In case of the classical fibre, the sorption phase is attached to a fused silica backbone, while the PAL SPME Arrow is made practically entirely of stainless steel

the device to its solid tip. This tip is specially designed to allow gentle penetration of injector- and sample-vial septa (about 30% lower force required to penetrate a septum compared to a conventional SPME fibre). It also retains the sorption phase, which is attached to the inner rod, and furthermore enables PAL SPME Arrow's capability to enclose this sorption phase during transfer processes. This is an important difference to the traditional SPME fibre, which only allows for the retraction of the latter, with its outer capillary more open to external, potentially adverse influences such as contaminations from ambient air.

Furthermore, an open capillary faces significant resistance during penetration processes, in contrast to a PAL SPME Arrow in its closed state. Its outer capillary rests against the solid tip, resulting in a homogeneously closed fibre since both parts possess the same diameter.

Classical SPME fibres can cause coring of injector septa due to their open tubular tip [4]. Based on our own experiences, the GC septa should be replaced after approximately 100 injections to avoid leakages when using SPME, however using the PAL SPME Arrow, the wear of injector septa was reduced due to the specially designed tip. Despite the enlarged diameter compared to the classical fibre, the GC septa did not need to be replaced for at least 200 injections without coring, abrasion or leakage of the GC septa.

PAL SPME Arrow demonstrated faultless mechanical reliability over the entire course of these studies (not a single failure was observed that could be contributed to the fibre itself). In our experience, classical SPME fibres are more fragile, typically requiring replacement after 100 to 200 injections due to bending of the fibres. These values seem to be typical and are also encountered in literature [5,7,8].

The SPME Arrows' mechanical robustness is due to the increased diameter of the fibres' outer capillary, which is 1.1 or 1.5 mm, in contrast to approx. 0.7 mm in case of the classical gauge 23 SPME fibre.

2) Experimental

A PAH standard (SV Calibration Mix #5 / 610 PAH) purchased from Restek (Bellefonte, PA) was used to prepare the samples. The standard contains 16 PAHs in methylene chloride at a concentration of 2 g L^{-1}. Analytical grade methanol (KMF Laborchemie, Lohmar, Germany) and lab water from a Purelab Ultra analytic water purification system (Elga LabWater, Celle, Germany) were used as solvents for stock, standard and sample preparation. From the PAH calibration mix, a methanolic stock solution with a concentration of 1 mg L^{-1} was prepared and stored in a 20 mL amber screw cap headspace vial, with silicone/PTFE septa (BGB Analytik, Boeckten, Switzerland) ensuring that there was no headspace within the vial, in the refrigerator at 4°C. From this stock solution, aqueous standard dilutions were prepared and stored in the same manner. Hamilton glass syringes (Hamilton, Bonaduz, Switzerland) and Blaubrand® bulb pipettes (Brand, Wertheim, Germany) were used for stock, dilution standard and sample preparation. The PDMS tubes which were used as extraction phases for PAL SPME Arrows were also obtained from BGB Analytik.

All analyses were carried out on a Shimadzu GCMS-QP2010 Ultra (Shimadzu Deutschland GmbH, Duisburg, Germany). Thermal desorption of the extracted analytes was carried out using a split/splitless injector set to a temperature of 280°C. The injector was equipped with a Restek (2 mm i.d. x 5 mm o.d. x 95 mm length) splitless liner (BGB Analytik, Boeckten, Switzerland). The thermal desorption time was 5 minutes and after a splitless time of 6 minutes, the split ratio was set to 10:1.

The analyte separation was accomplished on a 30 m x 0.25 mm Rxi®-PAH column (Restek, Bellefonte, PA) with a 0.1 µm film thickness. As carrier gas Helium 5.0 (Air Liquide, Oberhausen, Germany) with a flow of 1.5 mL min^{-1} was used. The GC temperature program started with a 5 minute period at a constant temperature of 40°C, followed by a first temperature ramp of 50°C min^{-1} up to 110°C, a second ramp of 5°C min^{-1} to 240°C and a third ramp of 50°C min^{-1} to a final temperature of 320°C, which was maintained for 5 minutes for cleanup purposes. The transfer line and ion source were both set to 250°C, respectively. The compounds eluted between 8.7 min to 49.5 minutes, with naphthalene-d8 eluting first and benzo(ghi) perylene eluting last.

Sample extraction was performed by a PAL RTC autosampler, which was equipped with SPME fibres (100 µm x 10 mm, 0.6 µL) and PAL SPME Arrows (e.g. 250 µm x 20 mm, 10.2 µL) (all from CTC Analytics AG, Zwingen, Switzerland). Due to the larger diameter of PAL SPME Arrow in contrast to traditional SPME fibres, the openings of the PAL tool needle guide, the GC injector and the SPME fibre conditioning station had to be widened to approximately 1.8 mm.

The sample vials contained 19 mL of water and were stored in their tray at room temperature (23°C). Prior to extraction they were transferred to a self-constructed stirring station based on an IKA-Mag RCT basic (IKA-Werke GmbH & Co KG, Staufen, Germany). In this station, samples were continuously stirred at 1500 rpm and 35°C, initially to allow temperature pre-equilibration for 10 minutes and afterwards during sample extraction. Simultaneous to the first five minutes of sample pre-equilibration time, the SPME fibre or PAL SPME Arrow was preconditioned in the SPME fibre conditioning station at 200°C under a stream of nitrogen 5.0.

At the conclusion of the pre-equilibration time, the sample vials' septa were pierced by the fibre and the sorption phase was immersed into the continuously stirred sample for 70 min. The sample vial penetration depth was thereby set to 55 mm, in order to ensure constant and complete immersion of the sorption phase.

Once extraction was completed, the fibre was transferred into the GC injector for thermal desorption at 280°C. Subsequently, it was cleaned for 15 min in the SPME fibre conditioning station at 200°C. The samples in PAL RTC sequence were handled in a staggered manner so that the subsequent equilibration and extraction was carried out during the GC run of the previous sample in order to reduce overall analysis time.

3) Results and discussion

To determine the extraction efficiency of the enlarged sorption phases of PAL SPME Arrow, a comparison with classical SPME fibres was performed. To this end, the depletion SPME method [13] was used to determine the extracted percentages of analytes out of a sample with an initial concentration of 50 ng L^{-1} for a single extraction. The latter was either carried out by a classical SPME fibre or a PAL SPME Arrow, which was available in different phase dimensions. This method is based on performing depletion extractions by extracting and measuring samples multiple times. The declining, logarithmical peak areas are then plotted against the number of consecutive extractions, yielding a linear regression, whose slope b then enables calculation of the extracted percentage E from log (1-E) [13].

The results of these experiments are summarised in Figure 2 for various available sorption phase dimensions and illustrate the advantages of the increased sorption phase volumes of PAL SPME Arrow.

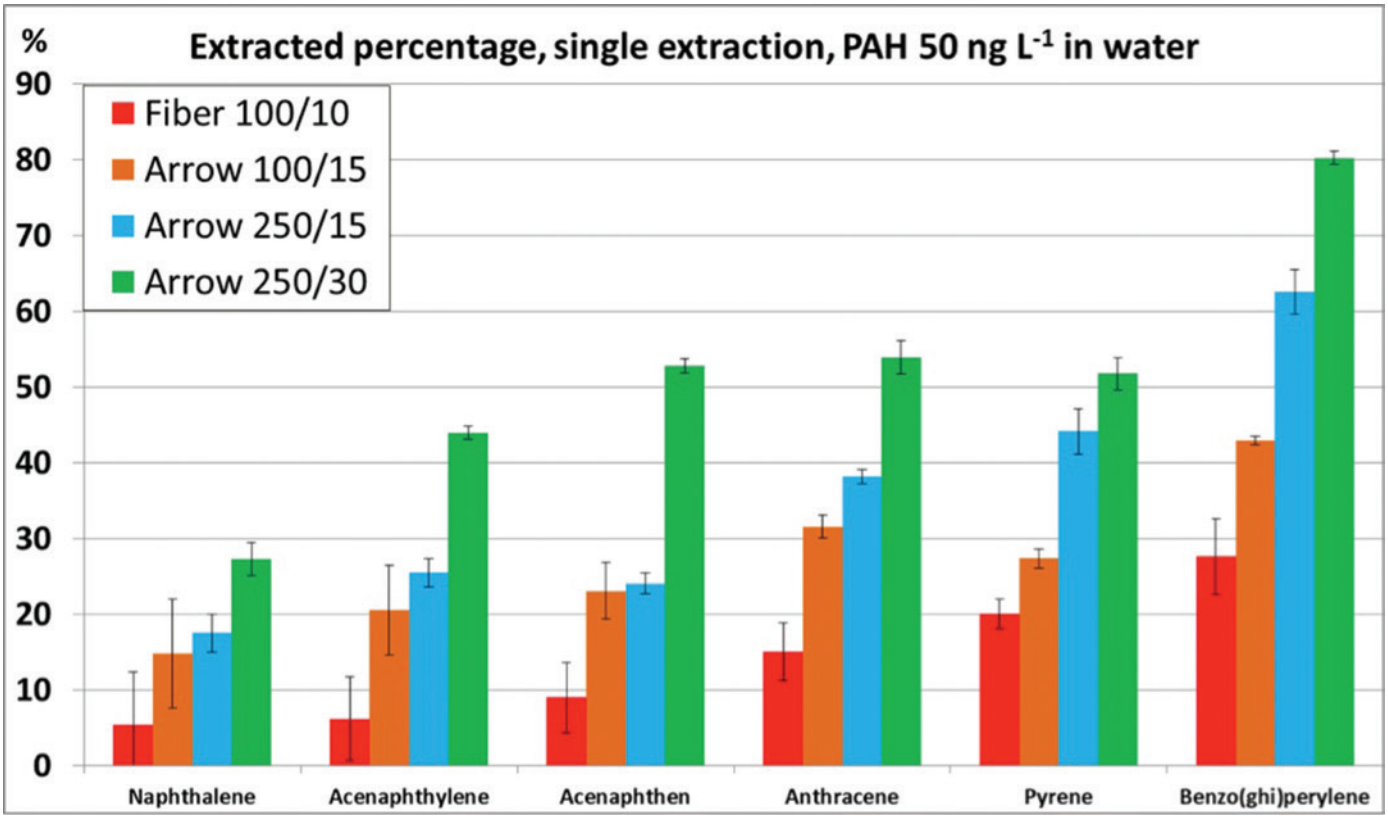

Figure 2: Extracted percentages for exemplary EPA PAH in water with an initial concentration of 50 ng L^{-1}, determined via multiple extractions [13] by different SPME fibres and Arrows showing increased extracted amounts and smaller errors in case of the larger sorption phase volumes

To enable a statistical comparison of achievable detection limits for PAL SPME Arrow with classical SPME fibres, the method detection limits (MDL) were determined according to Keith et al. [14], as well as relative standard deviations. Results are shown in Table 1 for ultrapure water and filtered groundwater.

Using a PAL SPME Arrow (250 µm x 20 mm, 10.2 µL), linear calibrations were obtained in a working range as low as 0.5 to 2.5 ng L^{-1} for all 16 EPA PAHs.

In an unfiltered groundwater sample, the freely dissolved concentration of PAHs measured by PAL SPME Arrow was below the MDL because of sorption to particulate organic matter (POM). The removal of POM (along with sorbed compounds) via filtration, and subsequent spiking of the groundwater samples at 10 ng L^{-1} enabled determination of PAHs with the following exceptions due to matrix interference: Phenanthrene, anthracene, pyrene, fluoroanthene and indeno(1,2,3 cd)pyrene (indicated by slashes in Table 1). The figures obtained with SPME Arrow are compared to previously published data for the analysis of PAHs by SPME and SBSE in table 2.

Table 1. Validation results obtained with PAL SPME Arrow (250 µm x 20 mm, 10.2 µL) in ultrapure water and groundwater: MDL values (calculated with a 99% confidence interval) and relative standard deviations (RSD)

	Ultrapure water		Filtered groundwater	
Compound	**MDL (ng L^{-1})**	**RSD (%) (at 10 ng L^{-1})**	**MDL (ng L^{-1})**	**RSD (%) (at 10 ng L^{-1})**
Naphthalene	0.3	5.7	1.2	6.9
Acenaphthylene	0.2	6.0	0.9	4.8
Acenaphthen	0.1	7.1	2.3	13.0
Fluorene	0.2	5.6	1.9	10.6
Phenanthrene	0.2	5.5	/	/
Anthracene	0.3	7.6	/	/
Pyrene	0.2	6.4	/	/
Fluoroanthene	0.2	6.2	/	/
1,2-Benzanthracene	0.1	6.2	0.7	3.8
Chrysene	0.1	11.0	0.8	4.3
Benzo(b)fluoroanthene	0.2	10.5	0.6	3.4
Benzo(k)fluoroanthene	0.2	8.6	0.6	3.2
Benzo(a)pyrene	0.3	7.2	0.5	2.4
Indeno(1,2,3 cd)pyrene	0.8	9.2	/	/
Dibenz(ah)anthracene	0.6	11.3	0.7	3.8
Benzo(ghi)perylene	0.8	11.9	0.6	3.4

4) Conclusions

Achieved extraction yields and resulting sensitivities clearly benefit from the enlarged sorption phase volumes of PAL SPME Arrow, when compared to SPME. It has also been shown that the mechanical reliability has been significantly improved as well. As can be concluded by comparison of the above-mentioned results with literature sources, the detection limits are in the range of SBSE techniques without compromising the automatability of the method. PAL SPME Arrow provides analysts with a promising new option for highly reliable extraction technology that provides solutions for sensitive and straightforward measurements of organic pollutants from environmental samples.

5) Disclaimer & Supporting information

The majority of the results presented herein was previously published in a more extensive format [15]. It is accessible as an open-source article for further reference under the following link: http://link.springer.com/article/10.1007%2Fs00216-015-9187-z

Information on the instrumental 'backbone' of PAL SPME Arrow as well as its development process are available in the accompanying PhD thesis, which is accessible under the following link (chapter 2.3):

http://duepublico.uni-duisburg-essen.de/servlets/DerivateServlet/Derivate-42197/Diss_Kremser.pdf

Table 2. MDL and RSD results obtained with PAL SPME Arrow (250 µm×20 mm, 10.2 µL) for PAHs in water in comparison with literature data for classical SPME fibres [16] and SBSE bars [17]

	PAL SPME Arrow		SPME [16]		SBSE [17]	
Compound	**MDL (ng L^{-1})**	**RSD (%) (at 10 ng L^{-1})**	**LOD (ng L^{-1})**	**RSD (%) (at 10 ng L^{-1})**	**LOD (ng L^{-1})**	**RSD (%) (at 50 ng L^{-1})**
Naphthalene	0.3	5.7	2.7	9.0	/	/
Acenaphthylene	0.2	6.0	1.8	6.0	0.1	/
Acenaphthen	0.1	7.1	0.9	3.0	/	/
Fluorene	0.2	5.6	3.0	10.0	0.1	8.3
Phenanthrene	0.2	5.5	2.1	7.0	0.1	1.1
Anthracene	0.3	7.6	2.1	7.0	0.2	2.1
Pyrene	0.2	6.4	3.6	12.0	0.2	/
Fluoroanthene	0.2	6.2	2.1	7.0	0.2	/
1,2-Benzanthracene	0.1	6.2	2.1	7.0	0.2	6.0
Chrysene	0.1	11.0	1.5	5.0	0.2	10.6
Benzo(b)fluoroanthene	0.2	10.5	2.7	9.0	0.1	/
Benzo(k)fluoroanthene	0.2	8.6	1.8	6.0	0.1	/
Benzo(a)pyrene	0.3	7.2	3.6	12.0	0.1	/
Indeno(1,2,3 cd)pyrene	0.8	9.2	3.6	12.0	0.3	/
Dibenz(ah)anthracene	0.6	11.3	/	/	0.3	/
Benzo(ghi)perylene	0.8	11.9	1.8	6.0	0.3	/

6) Acknowledgements

We gratefully acknowledge support by the following companies: CTC Analytics AG, BGB Analytik AG, Shimadzu Europe GmbH.

7) References

[1] Belardi RP, Pawliszyn JB (1989) The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. Water Pollut Res J Can 24:179-191

[2] Zhang Z, Yang MJ, Pawliszyn JB (1994) Solid-phase microextraction: A new solvent-free alternative for sample preparation. Anal Chem 66:844A-853A

[3] Aulakh JS, Malik AK, Kaur V, Schmitt-Kopplin P (2005) A Review on Solid Phase Micro Extraction - High Performance Liquid Chromatography (SPME-HPLC) Analysis of Pesticides. Crit. Rev. Anal. Chem 35:71-85

[4] Spietelun A, Kloskowski A, Chrzanowski W, Namieśnik J (2012) Understanding Solid-Phase Microextraction: Key Factors Influencing the Extraction Process and Trends in Improving the Technique. Chem Rev (Washington, DC, U S) 113 (3):1667-1685

[5] Bagheri H, Piri-Moghadam H, Naderi M (2012) Towards greater mechanical, thermal and chemical stability in solid-phase microextraction. Trends Anal Chem 34:126-139

[6] Baltussen E, Sandra P, David F, Cramers C (1999) Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. J Microcolumn Sep 11 (10):737-747

[7] Es'haghi Z, Taghizade S, Mazloomi-Bajestani A (2014) Arsenic removal from water/wastewater using nanoparticle-assisted hollow fiber solid-phase microextraction combined with hydride generation–atomic fluorescence spectroscopy. J Iran Chem Soc 11 (5):1421-1428

[8] Kokosa JM, Przyjazny AJ, Jeannot MA (2009) Solvent microextraction: Theory and practice. Wiley, Hoboken, N.J.

[9] Tienpont B, David F, Bicchi C, Sandra P (2000) High capacity headspace sorptive extraction. J Microcolumn Sep 12 (11):577-584

[10] Huang S, He S, Xu H, Wu P, Jiang R, Zhu F, Luan T, Ouyang G (2015) Monitoring of persistent organic pollutants in seawater of the Pearl River Estuary with rapid on-site active SPME sampling technique. Environ Pollut 200:149-158

[11] Purcaro G, Moret S, Conte LS (2013) Overview on polycyclic aromatic hydrocarbons: occurrence, legislation and innovative determination in foods. Talanta 105:292-305

[12] Tsimeli K, Triantis T, Dimotikali D, Hiskia A (2008) Development of a rapid and sensitive method for the simultaneous determination of 1,2-dibromoethane, 1,4-dichlorobenzene and naphthalene residues in honey using HS-SPME coupled with GC-MS. Anal Chim Acta 617 (1-2):64-71

[13] Zimmermann T, Ensinger WJ, Schmidt TC (2006) Depletion solid-phase microextraction for the evaluation of fiber-sample partition coefficients of pesticides. J Chromatogr A 1102 (1–2):51-59

[14] Keith LH, Crummett W, Deegan J, Libby RA, Taylor JK, Wentler G (1983) Principles of environmental analysis. Anal Chem 55 (14):2210-2218

[15] Kremser A, Jochmann MA, Schmidt TC (2016) PAL SPME Arrow - evaluation of a novel solid-phase microextraction device for freely dissolved PAHs in water. Anal Bioanal Chem 408 (3):943-952

[16] Cheng X, Forsythe J, Peterkin E (2013) Some factors affecting SPME analysis and PAHs in Philadelphia's urban waterways. Water Res 47:2331–2340

[17] Pérez-Carrera E, León VML, Parra AG, González-Mazo E (2007) Simultaneous determination of pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in seawater and interstitial marine water samples, using stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry. J Chromatogr A 1170(1–2):82–90