PAL SPME Arrow for the determination of volatile organic compounds in water by GC-MS after headspace-solid-phase microextraction (HS-SPME) according to German standard method DIN 38 407-41

Andreas Kremser[1], Guenter Boehm[2]

[1]University of Duisburg-Essen, Faculty of Chemistry, Instrumental Analytical Chemistry, Universitätsstraße 5, 45141 Essen, Germany;
[2]CTC Analytcis AG, Industriestrasse 20, 4222 Zwingen, Switzerland

Introduction

The German standard DIN 38 407-41 describes a method for the analysis of volatile compounds from aqueous samples by headspace-solid-phase microextraction (HS-SPME). Analytes are volatile, organic compounds (VOCs), fuel constituents (BTEX) and methyl-tert.-butylether (MTBE). The method allows for the detection of such contaminants in drinking-, ground- and surface waters by gas chromatography coupled to mass spectrometry (GC-MS). With the small sample volumes of 10 mL, the working range of the original method is 0.01 to 100 µg L^{-1} , with the lowest reported detection limits in the range of approx. 10 ng L^{-1} [1].

PAL SPME Arrow

The novel PAL SPME Arrow (see Table 1) combines the advantages of the classical SPME fiber with the benefits of extraction techniques providing larger sorption phase volumes such as stir bar sorptive extraction (SBSE).
It thereby avoids the inherent drawbacks of both techniques such as limitations in method automation in case of SBSE, as well as the small sorption phase volumes and the lacking fiber robustness of classical SPME fibers[2].
Using SPME Arrow instead of SPME fibers fulfills the DIN method's requirements. The major advantages when switching from the classical SPME fiber to PAL SPME Arrow are prolonged fiber lifetimes and an improved method sensitivity.

Validation data

Validation of the method was carried out for a representative, exemplary set of analytes which are contained in DIN 38 407-41 standard either directly, or as structurally similar compounds (Tables 2 & 3). Examined were linearity (linear correlation coefficient), repeatability (in terms of e.g. the relative standard deviation or RSD) and the limits of detection (LOD). They were determined in two concentration ranges: In the range between 10 and 1 ng L^{-1} and the range between 100 and 10 ng L^{-1}. Calibration results are depicted in tables 2 and 3. PDMS was used as sorption phase, sorption phase dimensions were: 20 mm length, 250 µm of thickness and a volume of 10.2 µL (Part No: ARR15-P-250/20-P1).

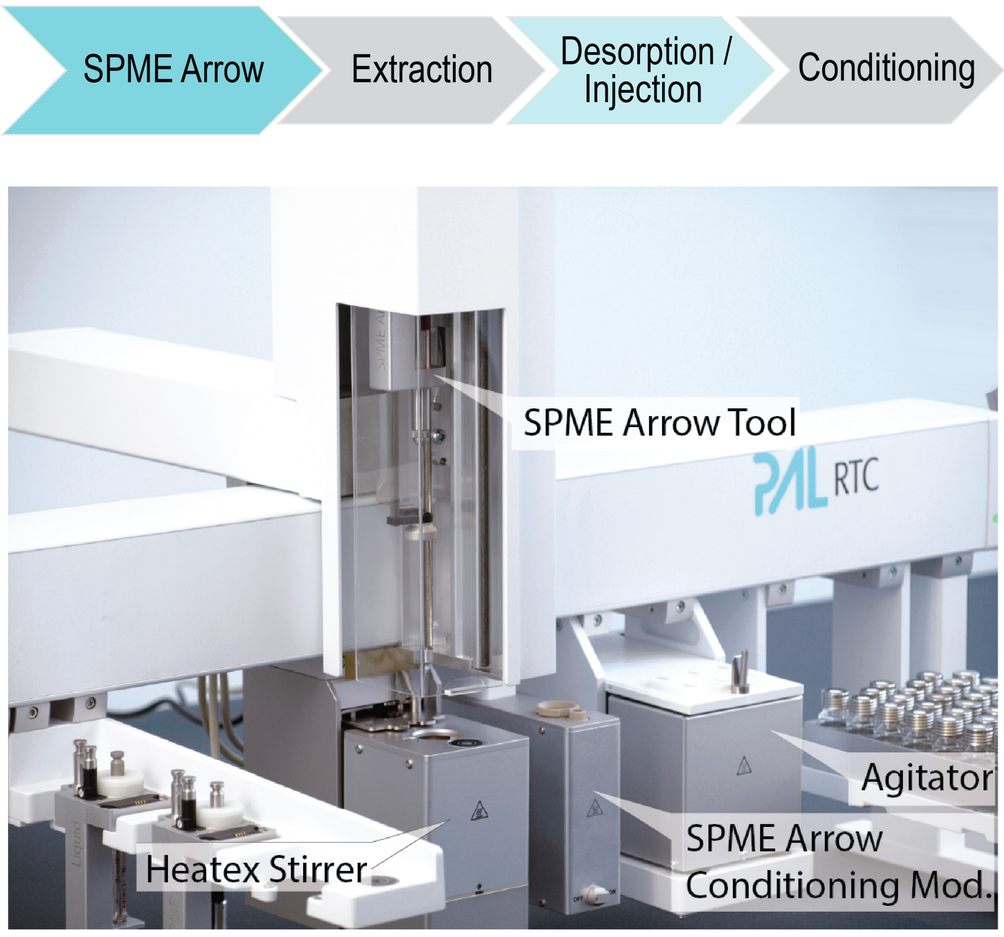
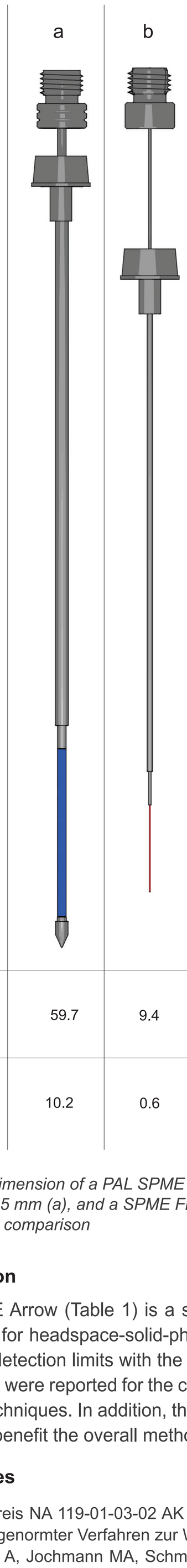


Figure 1: PAL SPME Arrow Tools and Modules on a PAL RTC, full automation of the extraction/injection process



	a	b
Sorption phase surface [mm^2]	59.7	9.4
Sorption phase volume [µL]	10.2	0.6

Table 1: Dimension of a PAL SPME Arrow 1.5 mm (a), and a SPME Fiber (b) in comparison

Compound-name	LOD (ng L^{-1})	Repeatability (RSD) (%)	Linearity coefficient
Trichloroethylene	1.35	4.54	0.99998
Dibromomethane	13.22	4.35	0.99994
Chlorobenzene	1.80	6.07	0.99999
Ethylbenzene	1.40	5.68	0.99966
1,2-Dimethylbenzene	3.69	4.65	0.99866
n-Propylbenzene	0.84	4.71	0.99839
Bromobenzene	1.00	3.94	0.99949
sec-Butylbenzene	2.11	1.63	0.99570
1,3-Dichlorobenzene	0.78	4.23	0.99748
p-Isopropyltoluene	1.28	3.21	0.99172
1,2-Dichlorobenzene	0.68	3.49	0.99665
n-Butylbenzene	1.76	3.30	0.99518
1,2,3-Trichlorobenzene	1.27	3.15	0.99417

Table 2: Method parameters for PAL SPME Arrow in a calibration range of 10 to 1 ng L^{-1}, determined from five replicate measurements

Compound-name	LOD (ng L^{-1})	Repeatability (RSD) (%)	Linearity coefficient
Methylene Chloride	1.1	3.6	0.99902
1,2-Dichloroethene	3.8	4.6	0.99821
Carbon Tetrachloride	2.0	0.7	0.99552
Benzene	2.3	8.0	0.99174
Trichloroethylene	3.2	1.1	0.99842
Dibromomethane	0.9	1.3	0.99768
Toluene	4.1	3.4	0.99453
Tetrachloroethylene	1.9	2.4	0.99848
Ethylbenzene	3.4	7.7	0.99996
1,1,1,2-Tetrachloroethane	3.1	5.4	0.98555
m-Xylene	0.7	0.9	0.99555
o-Xylene	3.3	7.5	0.99778
Styrene	4.8	4.8	0.99685
Isopropylbenzene	4.1	3.5	0.99756
n-Propylbenzene	4.0	3.0	0.99799
4-Chlorotoluene	3.4	2.2	0.99786
1,2,3-Trimethylbenzene	3.0	8.8	0.99459
2-Chlorotoluene	3.5	10.0	0.99922
Sec-Butylbenzene	3.3	7.2	0.99658
1,2,3-Trimethylbenzene	4.3	4.8	0.99542
tert-Butylbenzene	2.9	7.2	0.99570
1,3-Dichlorobenzene	2.3	4.8	0.98752
1,4-Dichlorobenzene	2.1	5.3	0.99021
n-Butylbenzene	3.2	3.7	0.99246
1,2-Dichlorobenzene	2.0	4.9	0.99716
1,2,4-Trichlorobenzene	4.0	4.8	0.99719
Naphthalene	3.9	4.7	0.99240

Table 3: Method parameters for PAL SPME Arrow in a calibration range of 10 to 1 ng L^{-1}, determined from five replicate measurements

Conclusion

PAL SPME Arrow (Table 1) is a suitable tool for fulfillment of the German standard method DIN 38 407-41 for headspace-solid-phase microextraction of volatile analytes from aqueous samples. Obtained detection limits with the novel device are at least one order of magnitude better than the values that were reported for the classical SPME fiber. Method repeatability and linearity are on par for both techniques. In addition, the improved mechanical reliability of PAL SPME Arrow can be expected to benefit the overall method stability over prolonged, automated measurement series.

References

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[2] Kremser A, Jochmann MA, Schmidt TC (2015) PAL SPME Arrow—evaluation of a novel SPME device for freely dissolved PAHs in water. Anal Bioanal Chem 408 (3):943-952
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