

Benefits of a novel automated SPME technology for the detection of environmental pollutants at trace level in water

Manuela Bergna (1), Tommaso Albertini (1), Flavio Bedini (1), Fausto Pigozzo (1), Giulia Riccardino (1), Jason Cole (2) and Lori Dolata (2)
(1) Thermo Fisher Scientific, Rodano, Italy (2) Thermo Fisher Scientific, Austin, TX

ABSTRACT

Solid Phase Micro Extraction (SPME) is widely used as a valid solvent-free extraction technique for the analysis of an extended range of pollutants in environmental aqueous samples.

However, since its introduction, SPME has retained its main limitations of reduced fiber phase volume and mechanical robustness, the latter one restricting the wide adoption of this technology in automated systems.

The novel SPME Arrow design has been optimized to provide larger phase volume and fiber diameter thus overcoming both disadvantages and delivering higher extraction efficiency, increased sample throughput and robustness.

In this study, the SPME Arrow technology is presented for the determination of the 16 EPA regulated Polycyclic Aromatic Hydrocarbons in water using a Thermo Scientific™ Trace™ 1310 Gas Chromatograph and Thermo Scientific™ ISQ™ Series Single Quadrupole GC-MS systems. Results obtained with SPME Arrow are showed that demonstrate its enhanced capability to reach low detection limit and mechanical reliability compared to classic SPME.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are complex mixtures of compounds originating from incomplete combustion of natural deposits, artificial sources and cooking processes. They are considered worldwide spread organic pollutants as they can leach from air particles to ground and groundwater. Since they are considered to be carcinogenic, teratogenic and mutagenic, they are listed as priority pollutants in all the environmental protection agencies drinking-water criteria^{1,2}.

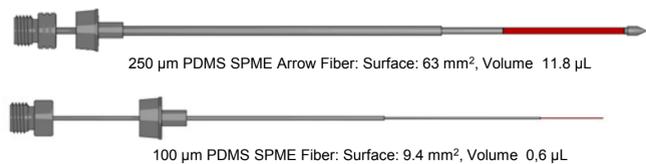
As PAHs are present in trace level in environmental matrices, a suitable extraction method is necessary to achieve adequate detection limits. Among the numerous extraction methods developed over the years, SPME is widely used to recover semi-volatiles organic compounds from water and wastewater: in this technique, a fiber coated with an organic phase, such as polydimethyl-siloxane (PDMS) is used for sampling the analytes from headspace or liquid phase and then thermally desorbed into the GC injector. Compared with typical liquid-liquid extraction or solid-phase extraction methods, SPME offers numerous advantages: it eliminates solvent usage and disposal and integrates multiple steps into a single procedure, thus reducing the risk of analyte loss. Furthermore, SPME method has been fully automated, making it an appropriate method for routine analysis.

However, in spite of these advantages, SPME has two main drawbacks: a relatively small sorption volume phase and a limited mechanical robustness of the fiber.

Some years ago, Baltussen et al.³ introduced a technique that uses a stir bar coated with PDMS material, called stir bar sorptive extraction (SBSE). The SBSE uses a larger amount of PDMS relatively to the SPME fiber, thus increasing the recovery of analytes and therefore the sensitivity. However, SBSE doesn't benefit of the full automation as the stir bar has to be recovered from the sample, dried and introduced in a thermal desorption unit manually.

Recently, a novel SPME extraction device has been introduced named SPME Arrow which consists of a steel rod coated with larger amount of sorbent material than the traditional SPME fiber (Figure 1). The rod ends in a sharp and solid tip that allows it to easily penetrate into the injector and vials septa. A second steel tube protects the fiber during the transfer processes and when the device is not in use, thus also eliminating the risk of contamination from ambient air. This innovative design finally delivers a more robust and reliable mechanical solution thus combining the advantages of the classical SPME with those of SBSE.

Figure 1. Design of SPME Arrow and comparison with classical SPME



MATERIALS AND METHODS

Sample preparation

Parameter optimization and calibration were carried out using a PAH standard solution at 2000 mg/L (Restek® SV Calibration mix # 5). From the standard solution, three solutions at 0.1, 1.0 and 10.0 µg/L were prepared (Methanol Chromasolv®) and diluted in MilliQ® water to prepare calibration solutions ranging from 1.0 to 500 ng/L. 15 mL calibration solution were pipetted in 20 mL headspace vials. Calibration curves were run in triplicate from different vials in order to avoid sample depletion due to repeated extractions.

Instrumentation

A Thermo Scientific™ TriPlus™ RSH™ autosampler was equipped with the new SPME Arrow tool, an incubator module for sample pre-equilibration, a Heatex Stirrer module for sample extraction and an SPME Arrow conditioning station. Samples were introduced into a Trace 1310 Gas Chromatograph equipped with an instant-connect SSL injector and coupled with a Thermo Scientific™ ISQ™ LT Single Quadrupole Mass Spectrometer in SIM mode using electron ionization (EI). Due to the larger diameter of the SPME Arrow fiber, an injector head and septum nut with an enlarged hole are required.

Sample separation was achieved using a Thermo Scientific™ TG-5 SiIMS 30 m X 0.25 mm I.D. X 0.25 µm film capillary column. The GC, MS and autosampler method setup is described in Table 1 below.

Table 1. GC/MS and Autosampler setup.

TRACE 1310 GC System Parameters		TriPlus RSH Autosampler – SPME Arrow Parameters	
Inlet (°C):	280	Incubation Temperature (°C):	35
Liner:	Arrow liner 1.8 mm I.D.	Incubation Time (min):	15
Inlet module and mode:	SSL, splitless	Incubation speed (rpm):	500
Splitless time (min):	8	Extraction Temperature (°C):	35
Purge Flow (mL/min):	5, stopped during desorption	Extraction Time (min):	60
Carrier Gas (mL/min):	He, 1.2	Stirring speed (rpm):	750/1500
Oven Temperature Program		Fiber Conditioning Temperature (°C):	250
Temperature (°C):	35	Fiber Conditioning Time (min):	15
Hold Time (min):	5	Fiber Depth in Vial (mm):	55
Rate (°C/min):	80		
Temperature 2 (°C):	150		
Rate (°C/min):	80		
Temperature 3 (°C):	250	ISQ LT Single Quadrupole MS Parameters	
Rate (°C/min):	10	Transfer Line Temperature (°C):	310
Temperature 4 (°C):	305	Source Temperature (°C):	350
Hold Time (min):	15	Ionization Mode:	EI
		Electron Energy (eV):	70
		Acquisition Mode:	SIM

SPME fiber selection and extraction procedure

The PDMS coating was chosen because it is reported in literature to be commonly used for PAH extraction with both SPME and SBSE.

Three different SPME fibers were used to compare extraction efficiency: a PDMS SPME Arrow fiber (250 µm x 20 mm, 11.8 µL), a PDMS SPME Arrow fiber (100 µm x 20 mm, 3.8 µL) and a classic SPME PDMS fiber (100 µm x 10 mm, 0.6 µL).

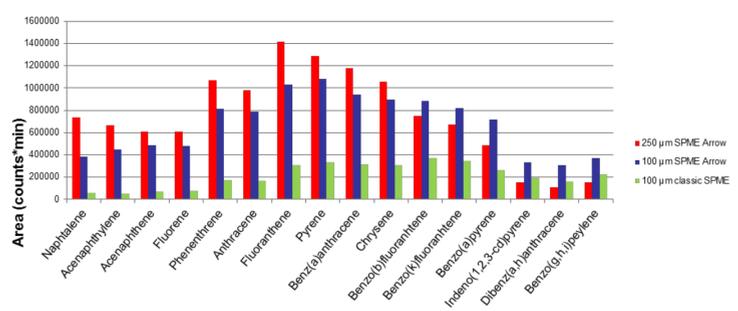
Extraction was performed by Direct Immersion setting the parameters listed in Table 1 except for classic SPME where the agitation speed during extraction was set at 250 rpm to limit the risk of fiber damaging.

RESULTS

The effect of the enlarged sorption phase volume was evaluated comparing the extraction efficiency of the SPME Arrow fibers with the classic SPME fiber (Figure 2).

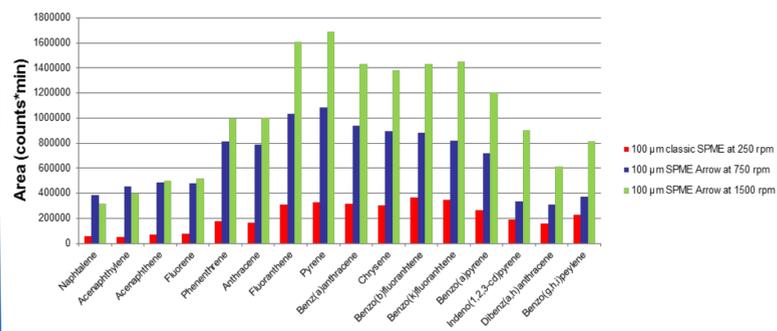
Theoretical calculations based on distribution constant K_{fs} for the analytes' phase transition from the aqueous solution into the PDMS sorption phase⁴ indicate that an improved extraction yield can be expected for lower boiling compounds when a larger sorption phase volume is used while for heavier compounds the difference in extraction efficiency is minimal.

Figure 2. Comparison of PAH extraction (Peak Area) between SPME Arrow (750 rpm) and classic SPME (250 rpm) for 100 ppt standard solution



As expected, both SPME Arrow fibers show a consistent increase in peak areas for the earlier eluting compounds compared with those obtained for the classic SPME as well as a reduced increase for the later eluters. Moreover, the increase of the recovery for the heavier compounds is lower for the 250 µm SPME Arrow fiber than the 100 µm SPME Arrow fiber. The effect of the stirring speed was evaluated for the 100 µm SPME Arrow fiber (Figure 3). Data show that increasing the stirring speed from 750 to 1500 rpm provides a better extraction efficiency for the heavier compounds further improving the extraction yield compared with the classic SPME fiber.

Figure 3. Comparison of PAH extraction between 100 µm SPME Arrow at 750 and 1500 rpm with classic SPME (250 rpm) for 100 ppt standard solution



Linearity, repeatability and MDL were evaluated for the 250 µm and 100 µm SPME Arrow fibers and the 100 starting from these optimized extraction conditions.

Table 2. Linearity in the range 1.0 – 100 ppt, peak area repeatability (%RSD) and MDL calculation for the 100 and 250 µm SPME Arrow fibers.

Compound name	100 µm SPME Arrow fiber			250 µm SPME Arrow fiber			Classic SPME ⁵
	R ²	%RSD (10 ppt)	MDL* (ng/L)	R ²	%RSD (10 ppt)	MDL* (ng/L)	
Naphtalene	0.996	4.89	1.45	0.991	7.22	1.41	2.7
Acenaphthylene	0.999	1.80	0.65	0.999	3.91	0.47	1.8
Avenaphthene	0.998	5.78	1.67	0.998	3.70	0.72	0.9
Fluorene	0.998	4.90	1.36	0.9999	4.19	1.11	3.0
Phenanthrene	0.999	3.02	0.86	1.000	5.54	1.32	2.1
Anthracene	0.999	4.36	1.11	0.999	4.03	1.25	2.1
Pyrene	0.996	1.19	0.27	0.992	2.64	1.20	3.6
Fluoranthene	0.997	1.63	0.37	0.992	2.84	1.15	2.1
Benz(a)anthracene	0.998	2.14	0.68	1.000	6.05	0.78	2.1
Chrysene	0.998	1.64	0.49	1.000	5.16	0.80	1.5
Benzo(b)fluoranthene	0.997	3.94	0.88	1.000	6.54	1.14	2.7
Benzo(k)fluoranthene	0.997	7.67	0.98	1.000	5.67	1.02	1.8
Benzo(a)pyrene	0.996	5.68	1.05	0.999	6.35	1.10	3.6
Indeno(1,2,3-cd)pyrene	0.994	7.75	1.38	0.998	3.25	0.50	3.6
Dibenzo(a,h)anthracene	0.998	9.20	1.46	0.998	2.70	0.58	n.d.
Benzo(g,h,i)perylene	0.994	5.19	1.50	1.000	3.17	0.71	1.8

* MDL values calculated with a 99% confidence interval

CONCLUSIONS

The new SPME Arrow technology was preliminary investigated for the determination of trace level PAHs in water. Both the 100 and 250 µm SPME Arrow fibers showed good recovery, linearity and repeatability.

- The SPME Arrow fiber extended phase volume results in improved extraction yield and sensitivities respect to classic SPME fiber and comparable to those reported for SBSE⁴
- The innovative SPME Arrow fibers' design showed an effective improved robustness and reliability towards mechanical stress even under fast stirring speed overcoming the limitation of the original design
- SPME Arrow technique is fully automated using the TriPlus RSH autosampler providing the advantages for routine laboratories of a high sample throughput and unattended operations

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TRADEMARKS/LICENSING

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