Application Brief

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Examination of Lower Molecular Weight PAHs in Drinking Water Using Agilent PDMS SPME Fibers

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large class of organic compounds containing two or more fused aromatic rings. PAHs are considered compounds of concern by every environmental organization; their concentration in water is strictly regulated.

Solid phase microextraction (SPME) has become one of the most widely used extraction technologies for environmental, food, and clinical analyses. It is well suited for automated sample preparation, resulting in reduced time per sample, less sample manipulation, and less solvent consumption.[1]

Experimental

Samples were prepared by adding 25 µL of PAH standard (2.5 ppm) to 10 mL of water in a 20 mL screw top headspace vial (part numbers 5188-6537 and 5188-2759). The samples were vortexed before placement on the PAL RTC rail system.

SPME

In SPME, analytes establish equilibria among the sample matrix, the headspace above the sample, and a polymer coating on a fused silica fiber. Extracted analytes are thermally desorbed from the fiber to a capillary GC column. The SPME fiber of choice for the analysis of PAHs in drinking water was the 100 µm polydimethylsiloxane (PDMS). The 100 µm coating thickness is designed for low molecular weight (MW) and volatile compounds with MWs between 60 and 275. Table 1 shows the SPME headspace parameters.

GC/MS analysis

PAHs in water were extracted using SPME headspace with a PAL RTC rail system. This was combined with an Agilent 7890B GC system, coupled with an Agilent 5977B High Efficiency Source GC/MSD (Figure 2).

Figure 2. The PAL RTC rail system combined with an Agilent 7890B GC and an Agilent 5977B GC/MSD.

Table 1. SPME headspace parameters.

Parameters	Value
Script Name	ARROW-STD-V2.0
Tool	SPME 1
SPME Fiber Phases (Figure 1)	PDMS 7 µm (p/n 5191-5870) PDMS 30 µm (p/n 5191-5871) PDMS 100 µm (p/n 5191-5872)
Incubation Time	5 minutes
Stirrer	Heatex Stirrer 1
Heatex Stirrer Speed (Agitation)	1,000 rpm
Heatex Stirrer Temperature (Extraction Temperature)	40 °C
Agitator	None
Sample Extract Time	10 minutes
Extraction Temperature	40 °C
Sample Vial Penetration Depth	40 mm
Sample Vial Penetration Speed	20 mm/s
Inlet Penetration Depth	40 mm
Inlet Penetration Speed	100 mm/s
Injection Signal Mode	Before fiber expose
Sample Desorption Time	4 minutes
Conditioning Port	SPMEArrowCond 1
Pre-Desorption Conditioning Time	5 minutes (analytical run)/ 60 minutes (precondition)
Fiber Conditioning Station Temperature	275 °C
Post-Desorption Conditioning Time	0 minutes
GC Cycle Time	5 minutes (set for sequence overlap)

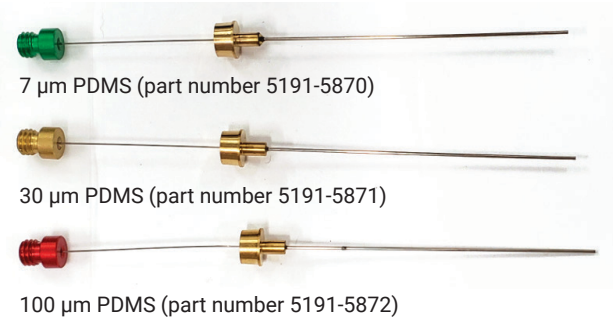

Figure 1. PDMS SPME fibers.

Table 2. Agilent 7890B GC settings.

Parameter	Value
Inlet Liner	Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id (p/n 5190-4048)
Injection Mode/Temperature	Splitless/270 °C
Oven Program	40 °C (hold 2 minutes); 20 °C/min to 260 °C (hold 0 minutes); 6 °C/min to 296 °C
Equilibration Time	0.5 minutes
Control Mode	Constant flow (1 mL/min)
Column	Agilent J&W DB-EUPAH, 30 m, 0.25 mm, 0.25 µm GC column (p/n 122-9632)
Septum Purge Flow Mode	Standard at 3 mL/min
Purge Flow to Split Vent	15 mL/min at 0.35 minutes
Agilent 5977B GC/MS Conditions	
Transfer Line	280 °C
Acquisition Mode	SIM (Table 3)
Solvent Delay	2 minutes
Tune File	atune.u
Gain	1
MS Source Temperature	280 °C
MS Quad Temperature	150 °C

Table 3. Agilent 5977B GC/MS SIM parameters.

Name	SIM Ion	Dwell
1-Methylnaphthalene	142	15
2-Methylnaphthalene	142	15
Acenaphthene	154	15
Acenaphthylene	152	15
Anthracene	178	15
Benzo[a]pyrene	252	15
Benzo[b]fluoranthene	252	15
Benzo[k]fluoranthene	252	15
Dibromofluoromethane	111	15
Fluoranthene	202	15
Fluorene	166	15
Naphthalene	128	15
Phenanthrene	178	15
Pyrene	202	15
Toluene-d_8	98	15

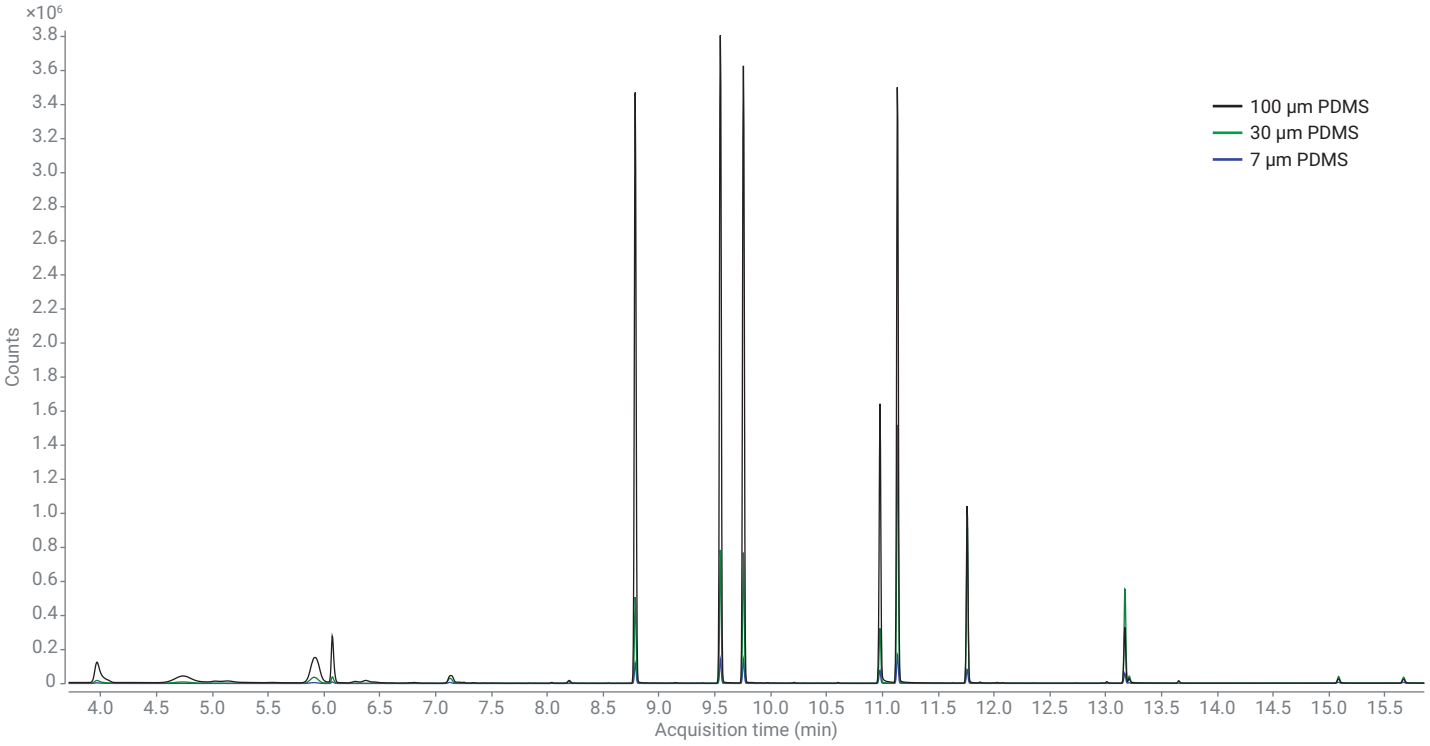

Figure 3. SIM chromatogram of PAHs with PDMS fibers (black trace = 100 µm; green trace = 30 µm; blue trace = 7 µm).

Results and discussion

PDMS fiber comparison

The 100 µm PDMS coating thickness is recommended for low molecular weight or volatile compounds (Figure 4). Nonpolar high molecular weight compounds (MW 125 to 600; Figures 5 and 6) are more effectively extracted with a 7 µm PDMS fiber. The 30 µm polydimethylsiloxane tends to be used for nonpolar semivolatiles (MW 80 to 500).

100 µm PDMS fiber reproducibility

Replicate injections were performed on three different PDMS 100 µm fibers from two different batches. Percent RSDs were calculated for each fiber, then averaged together. Each set of replications maintained %RSDs lower than 25%. Table 4 shows the averaged results.

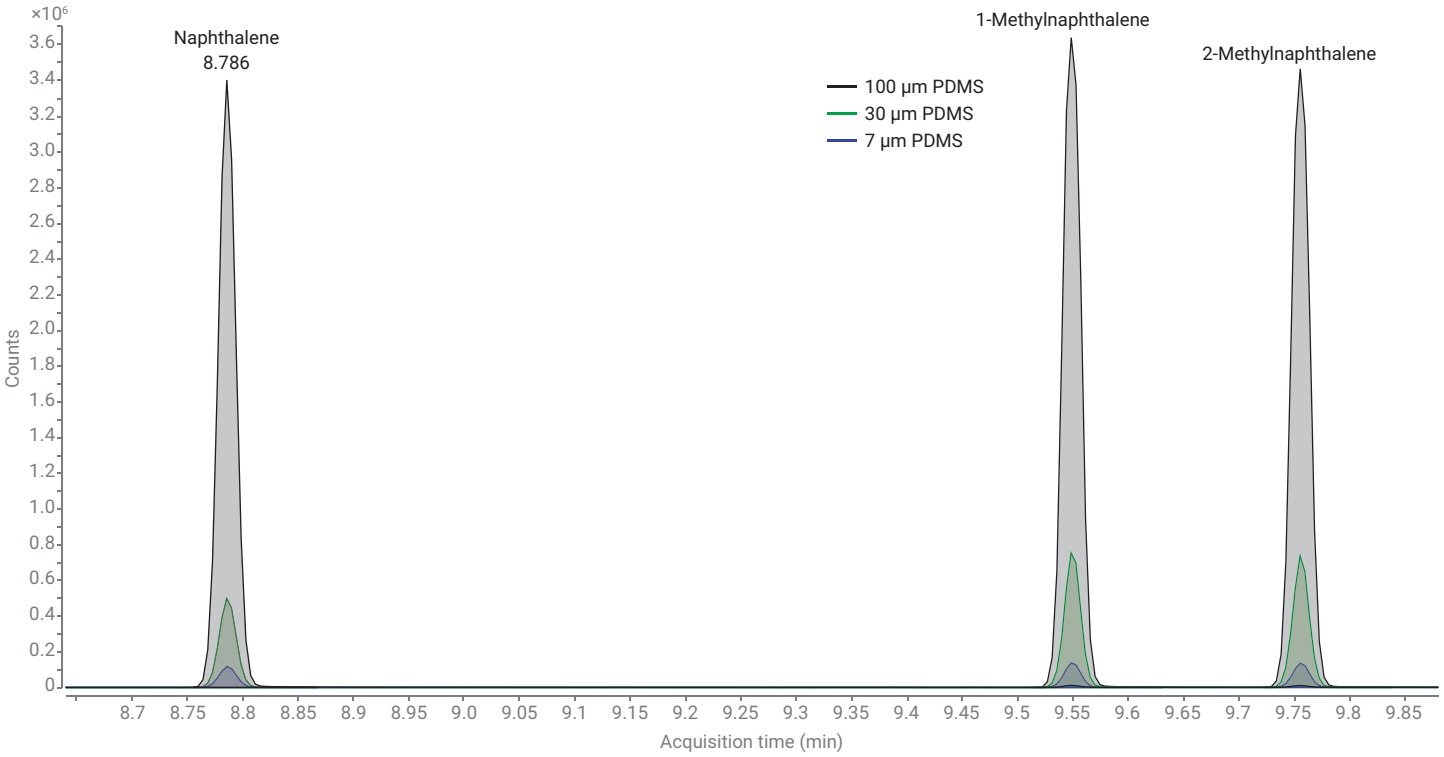

Figure 4. SIM chromatogram of naphthalenes with PDMS fibers (black trace = 100 µm; green trace = 30 µm; blue trace = 7 µm).

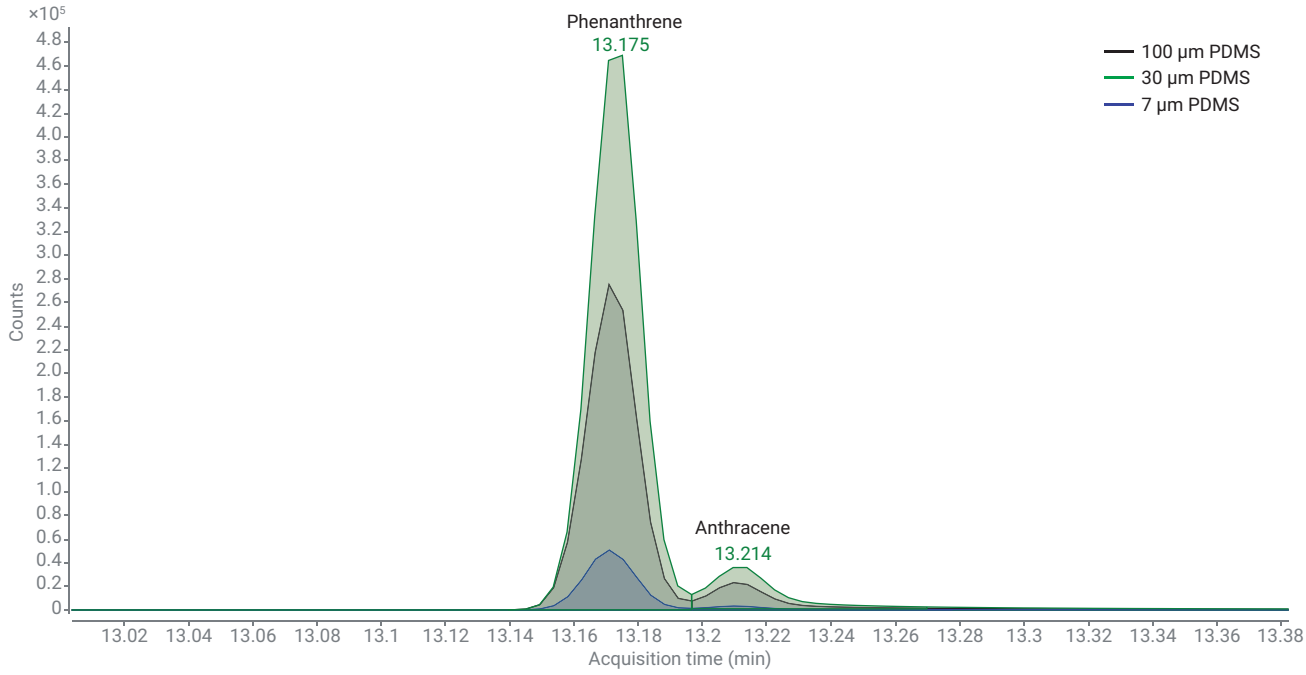

Figure 5. SIM chromatogram of phenanthrene and anthracene with PDMS fibers (black trace = 100 µm; green trace = 30 µm; blue trace = 7 µm).

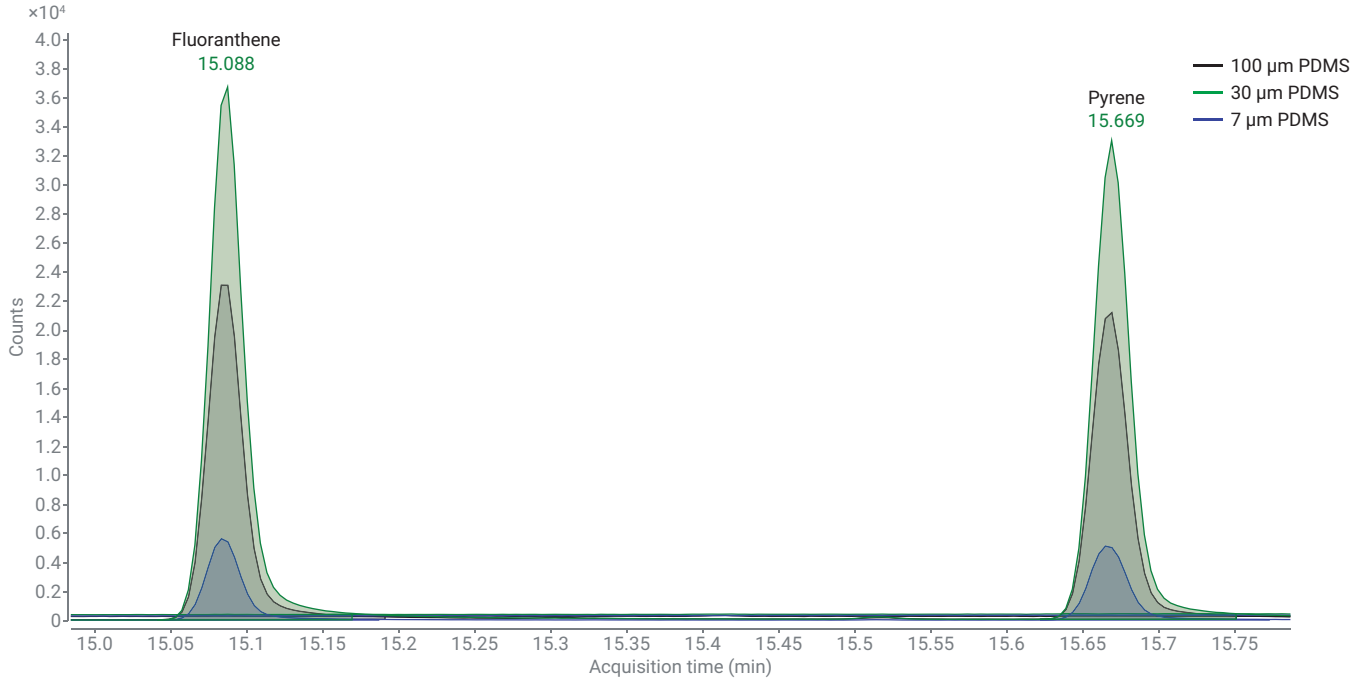

Figure 6. SIM chromatogram of fluoranthene and pyrene with PDMS fibers (black trace = 100 µm; green trace = 30 µm; blue trace = 7 µm).

Reference

1. Godina, L. Analysis of Low-Level PAHs in Drinking Water with an Agilent PAL3 equipped with SPME ARROW. *Agilent Technologies Application Note*, publication number 5994-0590EN, **2019**.

Table 4. Averaged %RSDs for three different PDMS 100 µm fibers.

Compound	Average %RSD
1-Methylnaphthalene	14.33
2-Methylnaphthalene	14.66
Acenaphthene	20.13
Acenaphthylene	19.57
Anthracene	12.37
Benzo[a]pyrene	15.89
Benzo[b]fluoranthene	12.21
Benzo[k]fluoranthene	12.85
Dibromofluoromethane	24.73
Fluoranthene	15.81
Fluorene	9.97
Naphthalene	13.33
Phenanthrene	22.12
Pyrene	15.95
Toluene-d_8	9.03

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