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Analysis of Low-Level PAHs in Drinking Water with an Agilent PAL3 equipped with SPME ARROW

Authors

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Abstract

This Application Note describes a quick analytical method for the determination of polycyclic aromatic hydrocarbons (PAHs) in drinking water. The method presented rapidly samples PAHs in drinking water without compromising the sensitivity necessary to achieve the low detection limits required by regulatory organizations.

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, and to protect human health, 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, and less sample manipulation and solvent consumption.

The Agilent SPME Arrow is a new technology for microextraction, combining trace level sensitivity with high mechanical robustness.

Figure 1. Dimensions of a PAL3 SPME Arrow 1.5 mm (a), 1.1 mm (b), and SPME fiber (c) in comparison.

Experimental

An Agilent 7890B GC equipped with a split/splitless inlet, an Agilent 5977B GC/MSD equipped with an extractor source with a 9 mm drawout plate (to increase linearity), and an Agilent PAL3 RSI 120 autosampler (product number G7368A) with an SPME Arrow (product number F7377A) were used for this series of experiments. The fiber type chosen for this study was 100 µm polydimethylsiloxane (PDMS) with a sorption phase volume of 3.8 µL. This gave six times more phase volume compared to a standard fiber. This was necessary to achieve the lowest possible sensitivity.

GC method	
Inlet liner	SPME Arrow liner
Column	Agilent DB-EUPAH, 30 m x 0.25 mm x 0.25 µm (part number 122-9632)
Inlet temperature (°C)	280
Oven program	40°C (2min), 20°C/min to 260°C, 6°C/min to 335°C (2min)
Transfer Line (°C)	320
5977B GC/MSD parameters	
Acquisition mode	SIM
Source temperature (°C)	320
Quadrupole temperature (°C)	150
PAL3 RSI 120 autosampler method	
Sample extraction time (min):	30
Sample desorption time (min):	5
Extraction temperature (°C):	40
Incubation time (agitator) (min):	5
Stirrer speed (rpm):	500
Predesorption conditioning time (min):	15
Fiber conditioning station temperature (°C):	280
Postdesorption conditioning time (min):	15

Table 1. Chromatographic Conditions.

The standard used to set up the method, create a calibration curve, and to validate the system was the Agilent PAH analyzer calibration sample kit (p/n G3440-85009). The following are the PAHs included in the standard with a concentration of 10.0 µg/mL:

Compound name	m/z	Compound name	m/z
Naphthalene	128	Fluoranthene	202
Naphthalene, 1-methyl-	142	Pyrene	202
Naphthalene, 2-methyl-	142	Benz[a]anthracene	228
Biphenyl	154	Chrysene	228
Naphthalene, 2,6-dimethyl-	156	Benzo[b]fluoranthene	252
Acenaphthylene	152	Benzo[j]fluoranthene	252
Acenaphthene	154	Benzo[k]fluoranthene	252
Naphthalene, 2,3,6-trimethyl-	170	Benzo[e]pyrene	252
Fluorene	166	Benzo[a]pyrene	252
Dibenzothiophene	184	Perylene	252
Phenanthrene	178	Dibenz[a,h]anthracene	278
Anthracene	178	Indeno[1,2,3-cd]pyrene	276
Phenanthrene, 1-methyl-	192	Benzo[ghi]perylene	276

Table 2. List of compounds present in the PAH analyzer calibration sample kit.

The internal standards listed in Table 3 each had a concentration of 50 µg/mL.

Compound name	m/z
Naphtalene-d_8	136
Acenaphthene-d_{10}	162
Anthracene-d_{10}	188
Chrysene-d_{12}	240
Perylene-d_{12}	264

Table 3: Internal standards.

Samples were prepared using HPLC grade water; all samples had a total volume (solvent plus standard) of 15 mL. Six standards at 1.0, 5.0, 25, 50.0, and 200 ng/L were prepared and used to create a calibration curve. [3], [4], [5]

Results and Discussion

Linearity was calculated using the above-mentioned standards. The SPME Arrow PDMS fiber was able to extract every PAH and showed good linearity. For each compound, $R^2 >= 0.999$ was achieved in the calibration range between 1 and 200 ng/L, except for dibenz[a,h] anthracene, for which $R^2 >= 0.99891$ was achieved.
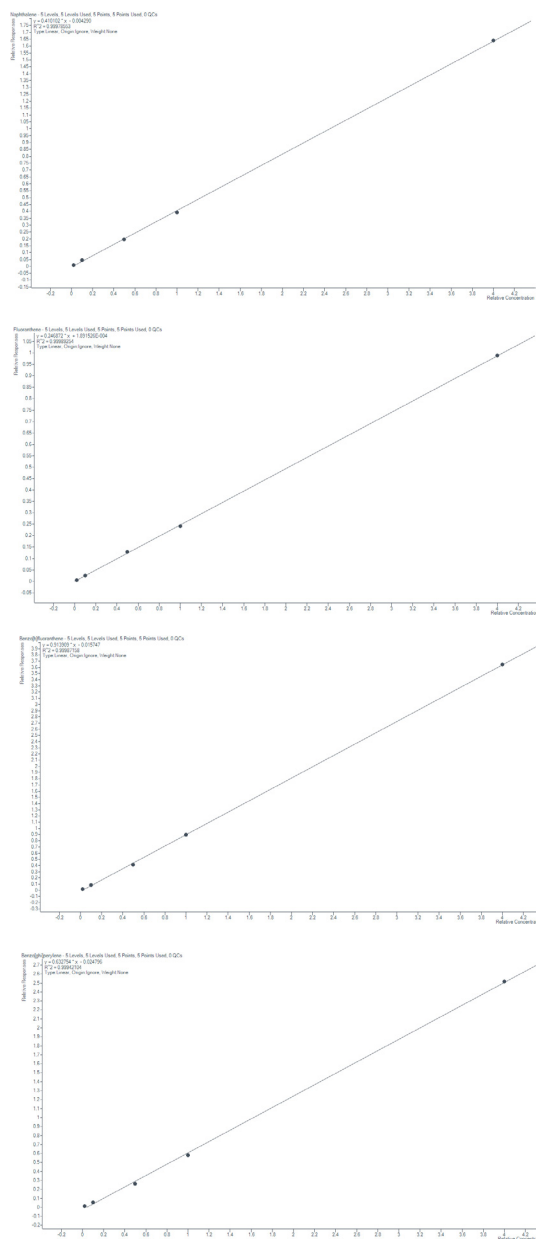

Figure 2. Calibration curves for naphthalene, fluoranthene, benzo[b]fluoranthene, and benzo(ghi) perylene.

The reproducibility of the system was calculated in alignment with the NS30 document [6], with 11 injections of a 10 ng/L standard solution. The results are shown in Table 4.

Compound name	R2	RSD%	Compound name	R2	RSD%
Naphthalene	0.99979	3.56	Fluoranthene	0.99989	6.22
Naphthalene, 1-methyl-	0.99995	4.85	Pyrene	0.99986	3.99
Naphthalene, 2-methyl-	0.99994	5.06	Benz[a]anthracene	0.99954	3.67
Biphenyl	0.99999	6.8	Chrysene	0.99991	8.03
Naphthalene, 2,6-dimethyl-	0.99992	7.81	Benzo[b]fluoranthene	0.99960	7.49
Acenaphthylene	0.99953	6.44	Benzo[j]fluoranthene	0.99984	6.15
Acenaphthene	0.99976	8.09	Benzo[k]fluoranthene	0.99928	4.58
Naphthalene, 2,3,6-trimethyl-	0.99998	7.58	Benzo[e]pyrene	0.99992	6.75
Fluorene	0.99986	7.75	Benzo[a]pyrene	0.99992	6.75
Dibenzothiophene	0.99979	6.14	Perylene	0.99919	5.47
Phenanthrene	0.99992	6.95	Dibenz[a,h]anthracene	0.99891	4.86
Anthracene	0.99985	6.95	Indeno[1,2,3-cd]pyrene	0.99962	5.76
Phenanthrene, 1-methyl-	0.99982	5.35	Benzo[ghi]perylene	0.99942	6.92

Table 4. Calibration results of reproducibility testing.

Conclusions

The SPME Arrow fiber shows excellent robustness. More than 200 samples where run with the same fiber for the development of this Application Note. The SPME Arrow, coupled with a 7890B GC and 5977B GC/MSD extractor source, enables the detection of PAH in drinking water at levels below 1 ng/L. The SPME Arrow shows great reproducibility, with an average area of RSD% < 7.5 for all the PAH investigated in this study. Excellent linearity was achieved for all compounds in the calibration range of 0.5 to 200 ng/L, with R^2 >=0.999 for all PAHs (dibenz[a,h]anthracene R^2=0.99891).

References

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