Application Note

Sample Preparation

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Determination of VOCs in Water by GC/MS after Headspace-Solid-Phase Microextraction (HS-SPME)

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Introduction

Benzene, toluene, ethylbenzene, and xylene (BTEX) isomers are monocyclic aromatic hydrocarbons, which have a moderate solubility in water (benzene: 1,600 mg/L; toluene: 500 mg/L; ethylbenzene and xylenes: 160 mg/L). They are constituents of mineral oil products, and are used in many industrial processes as solvents. Moreover, these compounds are the major water-soluble constituents of petroleum derivatives (gasoline). During tire burning, benzene and toluene are the two components that have the highest exhaust emission factor.

Traditionally, headspace-SPME is a reliable and advantageous sampling method for the determination of VOCs in water. With the introduction of the PAL SPME Arrow, VOCs in water can now be detected at least one order of magnitude lower than its SPME fiber predecessor. Method repeatability and linearity are on par for both techniques. In addition, the improved mechanical reliability of PAL SPME Arrow can assist the analytical method accuracy and precision.

BTEX Application

A SPME Fiber and a SPME Arrow were chosen for the analysis of BTEX in drinking water (Figure 1).

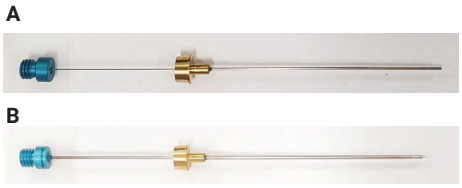

Figure 1. A) 85 µm CAR WR/PDMS Fiber. B) 120 µm CAR WR/PDMS Arrow (p/n 5191-5859).

The application called for the addition of a 5 mL sample to 2 ±0.05 g of NaCl in a 20 mL HS vial (Figure 2).

Methodology

SPME-GC/FID/MSD

The analysis of BTEX in water was extracted using a SPME headspace, with a PAL RTC rail system, combined with an Agilent 7890B GC system, coupled with an Agilent 5977B High Efficiency Source GC/MSD.

Figure 3. PAL RTC rail system combined with an Agilent 7890B GC + 5977B High GC/MSD.

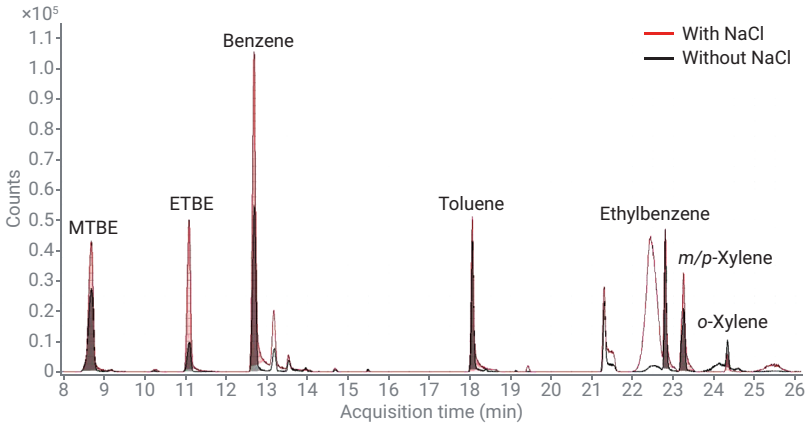

Figure 2. Chromatogram of 0.8 ppb BTEX standard analyzed by a 120 µm CAR WR/PDMS SPME Arrow with NaCl (red trace) and without NaCl (black trace).

Instrument parameters

Agilent 7890B GC Settings	
Turn Top Assembly	Agilent 7890 Turn Top Assy Enlarged id – Inert (p/n G3452-60930)
Inlet Liner	Inlet liner, Ultra Inert, splitless, straight, 2 mm id (p/n 5190-6168)
Injection Mode/Temperature	Splitless/290 °C
Control Mode	Constant flow (1 mL/min; 1.4 mL/min into MSD)
Column	Agilent J&W CP-Sil 5 CB, 30 m × 0.25 mm, 1.00 µm (p/n CP8770)
Oven Program	30 °C (hold 4 minutes); 4 °C/min to 130 °C (hold 1 minute)
MSD Restrictor	Fused silica tubing, 1.7 m, 0.15 mm (p/n CP801505)
FID Restrictor	Fused silica tubing, 0.7 m, 0.25 mm (p/n CP802505)

SPME Headspace Parameters	
Incubation Time	5 minutes
Heatex Stirrer Speed (Agitation)	1,000 rpm
Heatex Stirrer Temperature (Extraction Temperature)	40 °C
Sample Extract Time	3 minutes
Sample Desorption Time	4 minutes
Conditioning Time	10 minutes
Conditioning Temperature	297 °C

FID Parameters	
Makeup Gas	He
Heater	300 °C
Air Flow	400 mL/min
H_2 Flow	40 mL/min
Makeup Flow	25 mL/min
(Constant Makeup and Fuel Flow)	

Agilent 5977B MS Conditions	
Transfer Line	260 °C
Acquisition Mode	Scan
Solvent Delay	7.5 minutes
Tune File	atune.u
Gain	1
MS Source Temperature	280 °C
MS Quad Temperature	150 °C

Results and discussion

Data analysis

The analysis of BTEX in water was extracted using SPME headspace, with a PAL RTC rail system, combined with a 7890B GC system coupled with a 5977B High Efficiency Source GC/MSD.

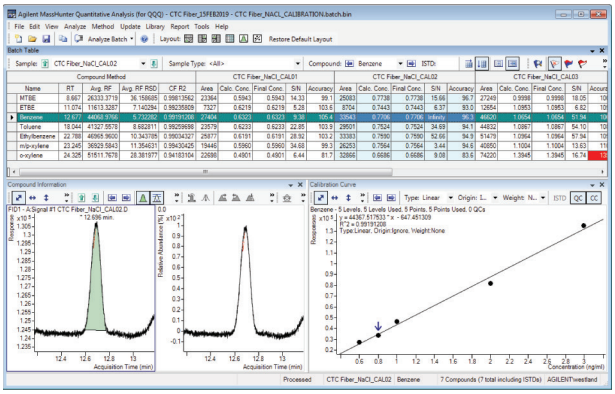

Figure 4. MassHunter Quant Batch view of 85 µm CAR WR/PDMS Fiber calibration (benzene shown).

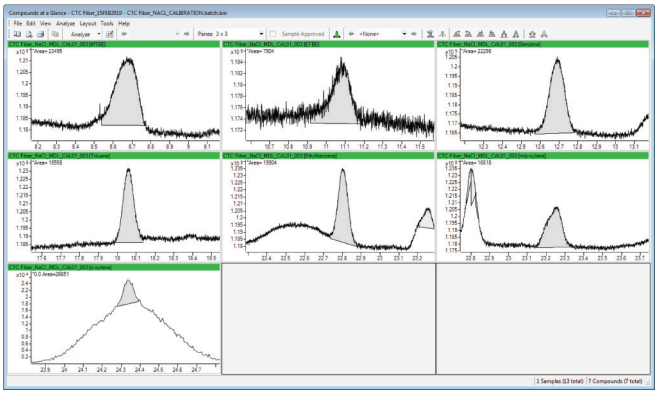

Figure 6. An 85 µm CAR WR/PDMS Fiber MDL replication (BTEX targets shown).

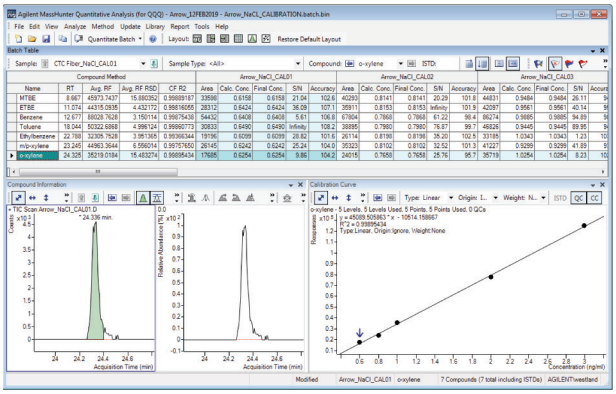

Figure 5. Agilent MassHunter Quant Batch view of 120 µm CAR WR/PDMS Arrow calibration (*o*-xylene shown).

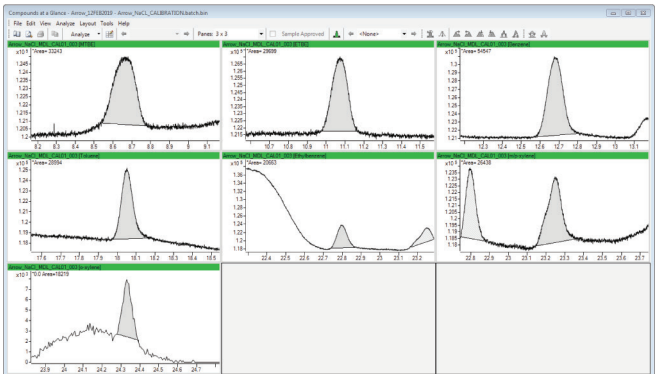

Figure 7. An 120 µm CAR WR/PDMS Arrow MDL replication (BTEX targets shown).

Table 1. R^2 values for MSD calibration curves.

Compound	85 µm CAR WR/PDMS Fiber	120 µm CAR WR/PDMS Arrow
MTBE	0.9981	0.9989
ETBE	0.9924	0.9982
Benzene	0.9919	0.9988
Toluene	0.9926	0.9986
Ethylbenzene	0.9903	0.9937
m/p-Xylene	0.9943	0.9976
o-Xylene	0.9909	0.9990

Table 2. Average area counts of 0.6 ppb replicates.

Compound	Average Response Difference of the Arrow to the Fiber
MTBE	1.4
ETBE	4.2
Benzene	2.3
Toluene	1.6
Ethylbenzene	0.9
m/p-Xylene	1.5
o-Xylene	0.7

Calculated results

Eight replicate samples were prepared at 0.6 ppb, and analyzed by external standard.

Table 3. Results from eight-replicate sample set.

	MTBE		ETBE		Benzene		Toluene		Ethylbenzene		*m/p*-Xylene		*o*-Xylene	
	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow	85 µm Fiber	120 µm Arrow
Avg. Conc. (ppb)	0.639	0.607	0.598	0.655	0.576	0.626	0.569	0.623	0.593	0.638	0.572	0.623	0.692	0.628
Std Dev.	0.068	0.021	0.089	0.015	0.145	0.026	0.131	0.016	0.093	0.025	0.092	0.018	0.074	0.022
% RSD	10.63	3.40	14.90	2.33	25.08	4.18	23.00	2.55	15.62	3.85	16.10	2.83	10.72	3.49
Avg % Error	9.035	3.415	11.931	10.056	19.965	5.340	17.871	4.092	13.348	7.752	12.463	6.573	18.073	7.513
MDL	0.20	0.06	0.27	0.04	0.43	0.08	0.39	0.05	0.28	0.07	0.28	0.05	0.22	0.07
LOQ	0.68	0.21	0.89	0.15	1.45	0.26	1.31	0.16	0.93	0.25	0.92	0.18	0.74	0.22

Conclusion

Salting out

The addition of NaCl increased the extraction efficiency for the analytes of interest. This was due to the decrease of the partition coefficient between the liquid and gas phases, allowing more analytes to readily partition into the headspace.

Calibration

All target analytes were found to have an R^2 value >0.990 when analyzed with the 85 µm CAR WR/PDMS Fiber; however, all target analytes analyzed with the 120 µm CAR WR/PDMS Arrow obtained an R^2 value >0.993. The slight increase of the R^2 value was attributed to an increase in response on the low end of the calibration (0.6 ppb).

Table 4. Results from three selected drinking water samples set with the 120 µm CAR WR/PDMS SPME Arrow.

	Sample 1 Filtered H_2O	Sample 2 Tap H_2O	Sample 3 Lab Sink H_2O
MTBE	<MDL	<MDL	<MDL
ETBE	<MDL	<MDL	<MDL
Benzene	<MDL	<MDL	<MDL
Toluene	<LOQ	<LOQ	<LOQ
Ethylbenzene	<LOQ	<LOQ	<LOQ
m/p-Xylene	<LOQ	<LOQ	<LOQ
o-Xylene	Non detect	Non detect	Non detect

Detection limits

The detection limits for the 85 µm CAR WR/PDMS Fiber ranged between 0.20 to 0.43 ppb; whereas the detection limits for the 120 µm CAR WR/PDMS Arrow ranged between 0.04 to 0.08 ppb.

Reference

1. Analysis of BTEX in Natural Water with SPME. *Agilent Technologies Application Note*, publication number SI-01251, September **2010**.

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Printed in the USA, June 19, 2019
5994-1045EN

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