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, that have a moderate solubility in water (benzene: 1600 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. 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 Arrows, 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 a par for both techniques. In addition, the improved mechanical reliability of PAL SPME Arrow can be expected to assist the analytical method accuracy and precision.

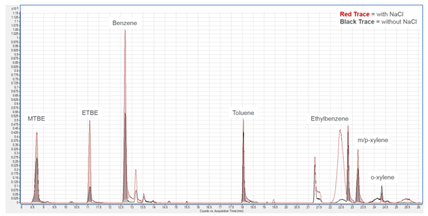
BTEX application

Both an SPME Fiber and an SPME Arrow were chosen for the analysis of BTEX in drinking water:

85 µm CAR WR/PDMS Fiber

120 µm CAR WR/PDMS Arrow

5 mL of sample was added to 2 g (±0.05 g) NaCl in a 20 mL HS vial.



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).

Methodology

SPME-GC/FID/MSD

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

PAL RTC rail system, combined with an Agilent 7890B GC and 5977B High GC/MSD.

Agilent 7890B GC Settings	
Turn top assembly	Agilent 7890 GC turn top assembly enlarged ID – inert (p/n G3452-60930)
Inlet liner	Inlet liner, Ultra Inert, splitless, straight, 2 mm id (p/n 5190-6168)
Inj. mode/temp	Splitless/290 °C
Control mode	Constant flow (1 mL/min; 1.4 mL/min into MSD)
Column	J&W CP-Sil 5 CB GC column, 30 m, 0.25 mm, 1.00 µm (p/n CP8770)
Oven program	30 °C (hold 4 min); 4 °C/min to 130 °C (hold 1 min)
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 min
Heatex stirrer speed (agitation)	1000 rpm
Heatex stirrer temp (extraction temp)	40 °C
Sample extract time	3 min
Sample desorption time	4 min
Conditioning time	10 min
Conditioning temp	297 °C

FID Parameters	
Make up gas	He
Heater	300 °C
Air flow	400 mL/min
H2 flow	40 mL/min
Make up flow	25 mL/min
(Constant make up and fuel flow)	

Agilent 5977B MS Conditions	
Transfer line	260 °C
Acquisition mode	Scan
Solvent delay	7.5 min
Tune file	atune.u
Gain	1
MS source temp	280 °C
MS quad temp	150 °C

References

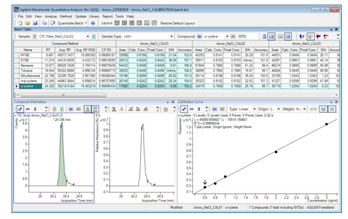
Analysis of BTEX in Natural Water with SPME. Agilent Application Note SI-01251. September 2010.

Results

Data analysis

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

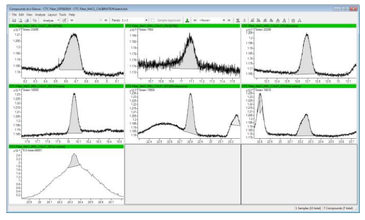
MassHunter quant batch view of 85 µm CAR WR/PDMS Fiber calibration (benzene shown)



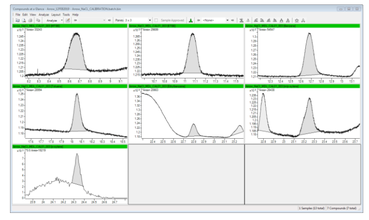
MassHunter quant batch view of 120 µm CAR WR/PDMS Arrow calibration (o-xylene shown)

Table 1. R2 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



85 µm CAR WR/PDMS Fiber MDL replication (BTEX targets shown)



120 µm CAR WR/PDMS Arrow MDL replication (BTEX targets shown)

Table 2. Avg. 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

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

	Sample 1 Filtered H2O	Sample 2 Tap H2O	Sample 3 Lab Sink H2O
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	None detected	None detected	None detected

Conclusions

Salting out: The addition of NaCl increased the extraction efficiency for the analytes of interest. This is 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 a 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).

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