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Analysis of BTEX in Water with a CAR(WR)/PDMS 95 µm SPME Fiber

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Abstract

The CAR(WR)/PDMS 95 µm SPME fiber was selected for the analysis of BTEX and MTBE in drinking water due to its selectivity for gases and low molecular weight compounds. The CAR(WR)/PDMS 95 µm SPME fiber maintained a linearity (R^2) of > 0.99, and a calibration accuracy between 98.8 to 100.9% over the calibration range for each target analyte. The method detection limit (MDL) and limit of quantitation (LOQ) for all compounds were < 0.80 and < 2.39 ppb respectively.

Introduction

The production of safe drinking water is an important issue, and legislation has established allowed levels of chemical substances in drinking water, whether they occur naturally, as deliberate additions, or as contaminants.

Organic compounds in water derive from three major sources:

- The breakdown of naturally occurring organic materials
- Domestic and economic activities, and
- Reactions that occur during water treatment and distribution

Domestic and economic activities may be the source of many synthetic organic chemicals (SOCs) from wastewater discharges, agricultural runoff, urban runoff, and leachate from contaminated soils. Most of the organic contaminants identified in water supplies as having adverse health concerns are part of this group.[1]

One broad group of volatile organic compounds (VOCs) that have been found in drinking water includes compounds found in petroleum products, especially aromatics like benzene, toluene, and xylenes.[2] Major sources of these compounds include leaks in fuel and gasoline tanks and piping due to deficient installation or corrosion, especially in old underground storage tanks.

Benzene, toluene, ethylbenzene, and xylene (BTEX) isomers are monocyclic aromatic hydrocarbons, that have 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. These compounds are also the major water-soluble constituents of petroleum derivatives (gasoline).[3]

Due to concerns about the toxicological properties of benzene and related compounds, there is an interest in developing a simple and specific analytical procedure to measure the levels of these compounds water. Solid phase microextraction (SPME) is a convenient technique used for the analysis of volatile and semivolatile compounds in liquid samples.

Experimental

To avoid loss of volatile molecules, it is best to perform these additions as quickly as possible (preferably within a temperature regulated laboratory).

Calibration preparation

Two standard solutions were prepared for the analysis of BTEX in water with the CAR(WR)/PDMS 95 µm SPME fiber.

- An internal standard (ISTD) solution was prepared at 2.5 µg/mL in water containing: dibromofluoromethane (CAS# 1868-53-7); toluene-d8 (CAS# 2037-26-5), and 4-bromofluorobenzene (CAS# 1072-85-1).

- A calibration standard solution was prepared at 2.5 µg/mL in water containing: (*tert*-Butyl methyl ether (MTBE); CAS# 1634-04-4); benzene (CAS# 71-43-2); toluene (CAS# 108-88-3); ethylbenzene (CAS# 100-41-4); m-xylene (CAS#108-38-3); p-xylene (CAS# 106-42-3); and *o*-xylene (CAS# 95-47-6).

1. Weigh approximately 4 ± 0.05 g of salt (NaCl) into each 20 mL headspace vial (p/n 5188-6537). The addition of NaCl increases 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.

2. Add 10 mL of Milli-Q 18.2 Ω water.

3. Add 25 µL of the ISTD solution to the sample, and cap (p/n 8010-0139).

4. Add a varying volume of the calibration standard solution to different water samples to create calibration levels, see Table 1.

5. Vortex the sample for 30 seconds to mix well and dissolve NaCl.

6. Place the vial on the sample rack for analysis.

Table 1. Calibration standard preparation procedure.

Sample	Sample Volume (mL)	NaCl (± 0.5 g)	Volume ISTD Added (µL)	ISTD Concentration (µg/L)	Volume Calibration Standard Added (µL)	Calibration Standard Concentration (µg/L)
ISTD Blank	10	4	25	6.25	0	Blank
Cal Level 1	10	4	25	6.25	5	1.25
Cal Level 2	10	4	25	6.25	5	1.25
Cal Level 3	10	4	25	6.25	10	2.5
Cal Level 4	10	4	25	6.25	15	3.75
Cal Level 5	10	4	25	6.25	20	5
Cal Level 6	10	4	25	6.25	25	6.25

Sample preparation

Sample treatment: Samples were collected in precleaned 20 or 40 mL vials and sealed with the correct septa and caps. During sampling, all air bubbles must be eliminated from the vial. If the analysis is performed within 14 days, it is not necessary to preserve the samples (by adding one drop of HCl 1:1).

1. Weigh approximately 4 ± 0.05 g of salt (NaCl) into each 20 mL headspace vial.

2. Add 10 mL of sample to the vial.

3. Add 25 µL of the ISTD solution to the sample and cap (6.25 µg/L in the sample).

4. Vortex the sample for 30 seconds to mix the sample well and dissolve NaCl.

5. The sample is ready for analysis.

Solid Phase Microextraction (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. Because the analytes are not diluted with solvent, minimum detection limits are improved relative to solvent extraction procedures. Peak symmetry and resolution are maintained.

The extraction by SPME is influenced by several factors:

- Sample matrix
- Agitation
- Temperature
- The amount of sample
- The size of the headspace vial
- The ratio of the headspace to the aqueous phase, and
- The position of the coated fiber in the HS

Table 2 shows the SPME headspace parameters used for this BTEX in water application.

Table 2. SPME headspace parameters.

Script Name	ARROW-STD-V2.0
Tool	SPME 1
SPME Fiber Phase	CTC CAR(WR)/PDMS 95 µm (Figure 1)
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	24 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
Predesorption Conditioning Time	5 minutes (analytical run)/ 60 minutes (precondition)
Fiber Conditioning Station Temperature	297 °C
Postdesorption Conditioning Time	0 minutes
GC Cycle Time	5 minutes (set for sequence overlap)

Figure 1. CAR(WR)/PDMS 95 µm SPME fiber.

GC/FID/MS analysis

The analysis of BTEX in water was 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. PAL RTC rail system combined with an Agilent 7890B GC and 5977B High GC/MSD.

Table 3. 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, 0.75 mm id (p/n 5190-4048)
Injection Mode/Temperature	Splitless/290 °C
Oven Program	30 °C (hold 4 minutes); 4 °C/min to 100 °C (hold 0 minutes)
Equilibration Time	0.5 minutes
Control Mode	Constant flow (3 mL/min; 1.4 mL/min into MSD)
Column	Agilent J&W CP-Sil 5 CB GC column, 30 m, 0.25 mm, 1.00 µm (p/n CP8770)
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)
Septum Purge Flow Mode	Standard at 3 mL/min
Purge Flow to Split Vent	15 mL/min at 0.75 minutes
GC/FID Parameters (Constant Makeup and Fuel Flow)	
Makeup Gas	He
Heater	300 °C
Air Flow	400 mL/min
H_2 Flow	40 mL/min
Make up flow	25 mL/min
Agilent 5977B GC/MS Conditions	
Transfer Line	260 °C
Acquisition Mode	Scan
Solvent Delay	4 minutes
Tune File	atune.u
Gain	1
MS Source Temperature	280 °C
MS Quad Temperature	150 °C

Results and discussion

SPME is a convenient technique used for the analysis of volatile and semivolatile compounds in liquid samples. For the analysis of BTEX in water, the CTC CAR(WR)/PDMS 95 µm was chosen due to its selectivity for gases and low molecular weight compounds (30−225 g/mol).

Calibration

Calibration and linearity are used to determine the accuracy of a laboratory test.

Table 4. Compound R^2 values (Linear; Origin: Ignore; Weight: None).

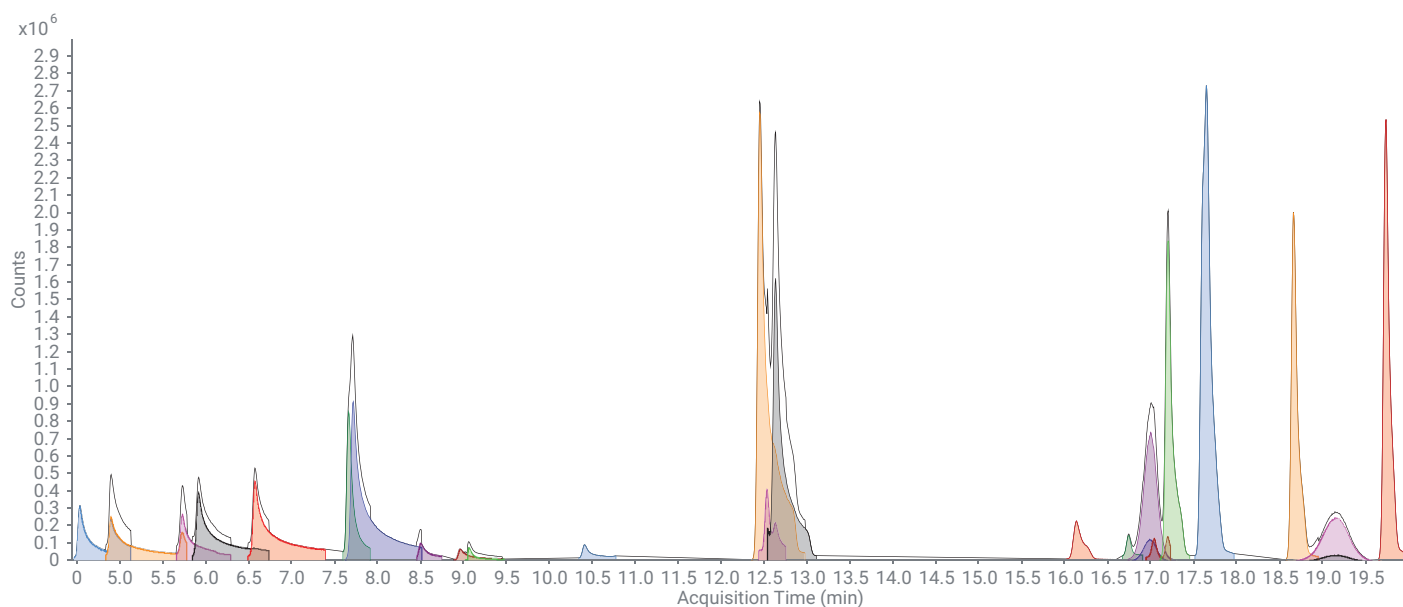| Compound	R^2
MTBE	0.9950
Benzene	0.9900
Toluene	0.9990
Ethylbenzene	0.9990
m/p-Xylene	0.9968
o-Xylene	0.9959
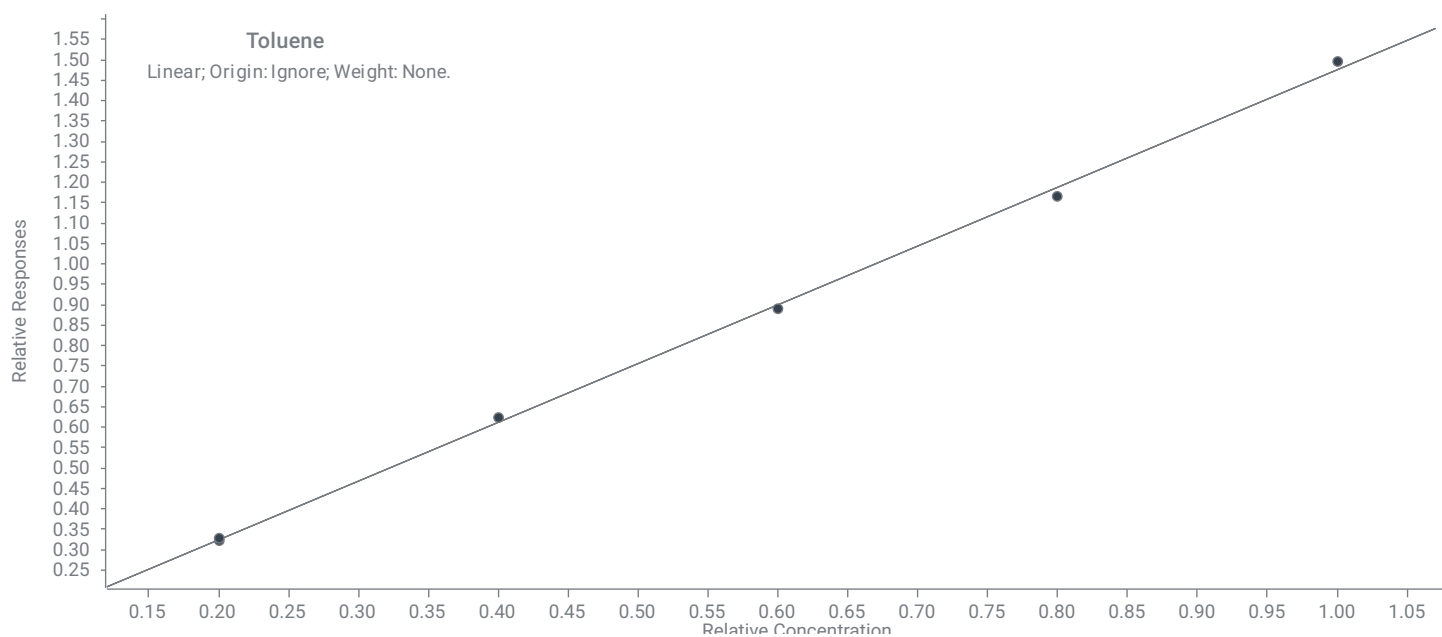
Figure 3. Toluene linear calibration curve.

Retention time stability

Retention time (RT) stability usually is affected by small variations in column flow, oven temperature, or changes in the chemical composition of the stationary phase.

Table 5. Compound calibration accuracy.

Calibration Concentration (ppb)	MTBE	Benzene	Toluene	Ethylbenzene	*m/p*-Xylene	*o*-Xylene
1.25	105.6	95.1	99.8	99.7	106.2	106.7
1.25	105.6	92.6	101.1	102.4	99.2	100.1
2.50	98.6	97.6	101.8	100.6	99.0	98.3
3.75	92.6	111.9	99.0	99.3	89.6	89.0
5.00	102.0	98.1	98.0	97.9	96.1	95.7
6.25	101.2	97.8	101.3	101.4	102.4	102.8

Figure 4. 2.50 ppb calibrant on column (CAR(WR)/PDMS 95 µm SPME fiber).

Table 6. RT stability.

Compound	Average RT	RT Standard Deviation	RT % RSD
MTBE	4.56	0.02	0.40
Benzene	7.73	0.01	0.18
Toluene	12.63	0.01	0.06
Ethylbenzene	17.20	0.01	0.04
m/p-xylene	17.64	0.03	0.17
o-Xylene	18.66	0.01	0.07

MDLs

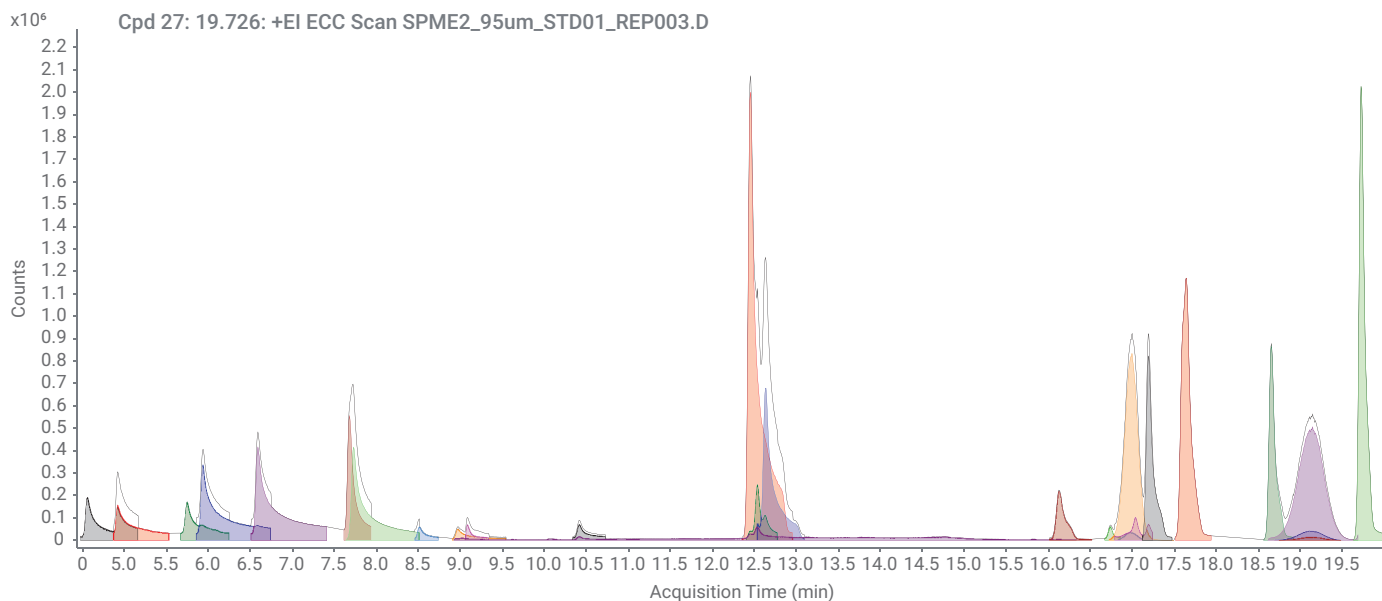The minimum concentration of the compound that can be measured (with 99% confidence) for the analytical method.

Figure 5. 1.25 ppb on column (Replicate #3; CAR(WR)/PDMS 95 µm SPME fiber).

Table 7. MDLs.

Compound	Average Concentration (ppb)	Concentration Standard Deviation	Concentration %RSD	% Recovery	% Error	MDL (ppb)	LOQ (ppb)
MTBE	1.68	0.24	14.22	134.28	34.28	0.80	2.39
Benzene	1.13	0.20	17.98	90.61	9.39	0.69	2.04
Toluene	1.31	0.17	13.09	104.81	4.81	0.58	1.71
Ethylbenzene	1.31	0.14	10.36	104.61	4.61	0.46	1.35
m/p-xylene	1.33	0.09	7.13	106.01	6.01	0.32	0.94
o-Xylene	1.35	0.09	6.68	107.89	7.89	0.30	0.90

Conclusion

This Application Note shows that SPME is a convenient technique for the analysis of volatile and semivolatile compounds in drinking water. The CAR(WR)/PDMS 95 µm SPME fiber was selected for the analysis of BTEX and MTBE in drinking water due to its selectivity for gases and low molecular weight compounds. The CAR(WR)/PDMS 95 µm SPME fiber maintained a linearity (R^2) of > 0.99, and a calibration accuracy between 98.8 to 100.9% over the calibration range for each target analyte. The MDL and LOQ for all compounds were < 0.80 and < 2.39 ppb respectively.

References

1. Almeida, C. M. M., Vilas Boas, L. Analysis of BTEX and other substituted benzenes in water using headspace SPME-GC-FID: method validation. *Journal of Environmental Monitoring*, **2004**, 6, 80–88.

2. AWWA (American Water Works Association), Water Quality & Treatment, A Handbook of Community Water Supplies, *Mc Graw-Hill Handbooks*, 5th edition, **1999**, chapter. 2.

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

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