Analysis of BTEX in Natural Water with SPME

Application Note

Environmental

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Introduction

Benzene, toluene, ethylbenzene and xylene (BTEX) isomers are monocyclic aromatic hydrocarbons, which 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. Moreover, these compounds are the major water-soluble constituents of petroleum derivatives (gasoline). During tire burning, benzene and toluene are the two components, which have the highest exhaust emission factor.

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Instrumentation and Conditions

GC with FID

Detector temperature: 300 °C

Work-range: 10

Injection technique: Agilent 1093 (SPI) on-column injector

Injection temperature: 290 °C, isothermal, equipped with a 0.75 mm SPME Insert

Autosampler with automated SPME and needle heater

Column: Agilent CP-Sil 5CB (p/n: CP8770)

Temperature: 30 °C, hold 4 min, 4 °C/min to 130 °C, hold 1 min

Carrier: Helium 5.0 @ 3.0 mL/min

Fiber: 75 µm Carboxen/PDMS

Extraction/analysis times: pre-incubation time 5 min@ 400 rpm (35 °C), 24 min extraction time @ 250 rpm, 4 min desorbtion, 1 min bake-out time @ 300 °C

Working mode: SPME extraction is performed in the headspace to improve extraction sensitivity. Samples are injected without performing a septum purge.

Reagents and Materials

PVOC Mixture 3 in MeOH

Chlorobenzene "neat" 99.9 % (ISTD)

Methanol, GC Grade

Water, Suprapur Grade

20 mL Headspace screw vial ND18

Silicone blue/PTFE white screw cap

Sodium chloride, RPE grade

Description

Calibration standards:

Into different 20 mL calibration vials weigh approximately 6 ± 0.05 g of salt and 15 mL of suprapur water. Prepare an internal standard (ISTD) solution at 2.5 µg/mL in water.

25 µL of this solution is transferred to each calibration vial (final concentration in the water: 4.156 µg/L). Then prepare the calibration standards in these vials by adding different volumes of a calibration standard solution in water at 2.5 µg/mL (prepared from the PVOC Mixture 3 ampoule) of benzene, toluene, ethylbenzene, p-xylene and o- xylene. Close the vials and shake vigorously for 30 sec to dissolve the salt. Table 1 shows a short recapitulation of the procedure for this first preparation.

Table 1. Short STD preparation procedure

Vial #	Name	Water	NaCl ±0.05	+ISTD (µL)	ISTD (ug/L)	+Cal. sol. (µL)	BTEX (µg/L)
1	Blank	15 mL	6 g	25	4.16	0	Blank
2	STD 1	15 mL	6 g	25	4.16	5.0	0.83
3	STD 2	15 mL	6 g	25	4.16	5.0	0.83
4	STD 3	15 mL	6 g	25	4.16	10.0	1.67
5	STD 4	15 mL	6 g	25	4.16	15.0	2.49
6	STD 5	15 mL	6 g	25	4.16	20.0	3.32
7	STD 6	15 mL	6 g	25	4.16	25.0	4.16

Sample treatment:

Samples are collected in the precleaned 20 mL vials, and closed with the correct septa and caps. During sampling, all air bubbles must be eliminated from the vial. If the analysis is performed within fourteen days, it is not necessary to preserve the samples (by adding 1 drop of HCl 1:1). A "sampling blank" collection on-site is recommended using suprapur water.
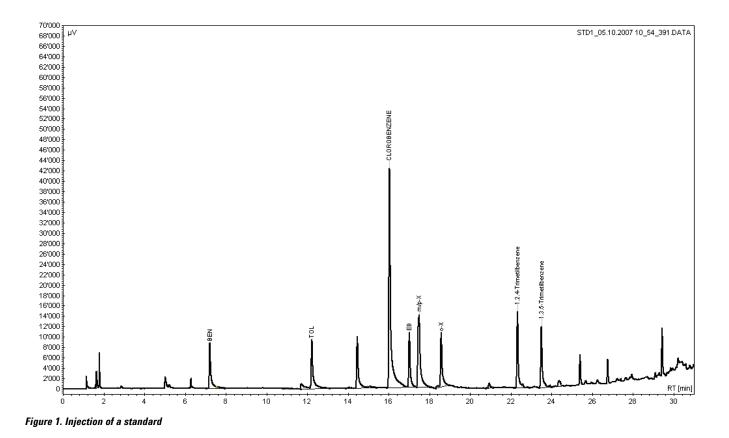
Open the vials, remove 5 mL of water and discard it, add 6 ± 0.05 g of salt, and 25 µL of the ISTD solution at 2.5 µg/L. To avoid a loss of more volatile molecules, it is better to perform these additions as quickly as possible. Shake vigorously for 30 sec and analyze. Table 2 illustrates a short sample preparation procedure.

Table 2. Short sample preparation procedure.

Vial #	Name	Water sampled	Residual water	NaCl ± 0.05	+ISTD (µL)	ISTD (µg/L)
11	Sampling blank	20 mL	15 mL	6 g	25	4.16
12	Sample "A"	20 mL	15 mL	6 g	25	4.16
13	Sample "B"	20 mL	15 mL	6 g	25	4.16

Results and Discussion

The GC/FID spectrum for a standard and a sample are shown in Figures 1 and 2.
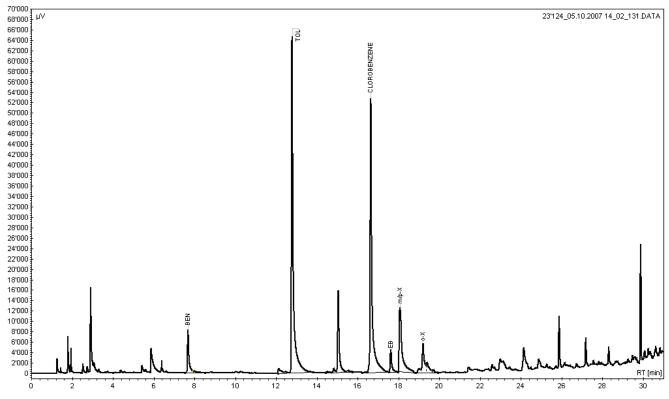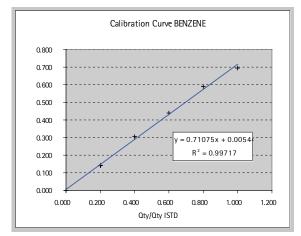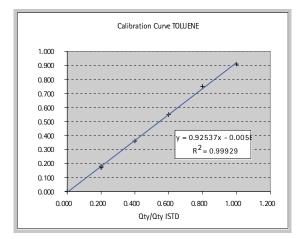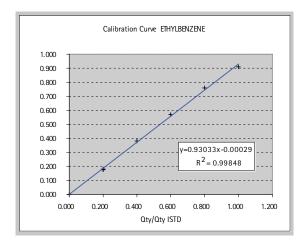
Figure 1. Injection of a standard

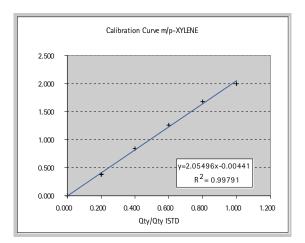*Figure 2. Injection of polluted water*

Linear, 6-point calibration curves for the BTEX compound are shown below.

Calibration Curve BENZENE

$y = 0.71075x + 0.0054$
$R^2 = 0.99717$

Calibration Curve TOLUENE

$y = 0.92537x - 0.0058$
$R^2 = 0.99929$

Calibration Curve ETHYLBENZENE

$y = 0.93033x - 0.00029$
$R^2 = 0.99848$

Calibration Curve m/p-XYLENE

$y = 2.05496x - 0.00441$
$R^2 = 0.99791$

Calibration Curve o-XYLENE

$y = 1.11415x - 0.01647$
$R^2 = 0.99691$

With the same fiber, more than 300 injections were done without loss in performance.

Table 3 shows the variations in retention time for the components studied.

Table 3. Retention times

	Benzene	Toluene	Chloro-benzene	Ethyl-benzene	m/p-Xylene	o-Xylene
RT (min)	7.63	12.54	16.04	17.13	17.58	18.62
CV (%)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

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The sampling error on the volume remaining in the vial (15 mL) was assessed after the removal of 5 mL from the full, plain vial: a test conducted on 21 vials gave an average of 15.1383 mL and a CV of 0.92 %, which can be considered sufficiently accurate.

For the extraction of ISTD, a series of blanks "doped" with differents ISTD concentrations was analyzed (Table 4).

Table 4. Chlorobenzene area variation

ISTD (µg/L)	Samples	% RSD
1.154	53	9.1
4.156	17	6.7
11.543	45	7.3

The determination of the minimum detection limit (MDL) was calculated using the procedure published in Chapter One of SW-846 (EPA): a minimum 3 replicates of a matrix spiked with analytes at a concentration 3-5 times the estimated MDL (= S/N between 2.5 to 5.0) are injected and, for each compound, standard deviations are calculated and multiplied with the one-sided 99 % t-test. After measuring four replies of a standard at 0.21µg/L, the following MDLs were obtained (Table 5).

Table 5. MDLs from SW-846

Compound	MDL (µg/L)
Benzene	0.056
Toluene	0.065
Ethylbenzene	0.043
m/p-Xylene	0.040
o-Xylene	0.075

Precision and accuracy from two independent quality control laboratories were investigated, although not all samples were situated in the calibration range (see Table 6).

Table 6. Precision and accuracy results (IN-and-OUT calibration range).

	Benzene	Toluene	Ethyl-benzene	m/p-Xylene	o-Xylene
Average (µg/L)	1.66	1.73	1.69	3.77	1.74
Recovery (%)	99.3	103.3	101.4	113.1	104.2
RSD (%)	6.9	2.8	5.5	6.4	6.4
Average (µg/L)	3.52	3.46	3.52	3.64	4.07
Recovery (%)	105.7	103.9	105.7	109.3	(122.3)
Average (µg/L)	4.82	4.99	4.96	4.79	4.71
Recovery (%)	96.4	99.8	99.2	95.8	94.2
Average (µg/L)	6.89	6.80	6.90	6.78	6.81
Recovery (%)	103.5	102.1	103.6	101.8	102.3
Average (µg/L)	8.28	8.24	8.30	8.29	8.00
Recovery (%)	99.5	99.1	99.8	99.7	96.2

Conclusion

Global results illustrate that SPME-extraction is an excellent method to extract BTEX from water samples. Due to the fiber's properties, it is very important to find and adjust correctly extraction / injection parameters. With such molecules, any cross-contamination between samples was demonstrated, even at higher concentrations.

It is possible to increase the sensitivity for toluene (x1.6), ethylbenzene (x4.5), m/p-xylene (x9) and o-xylene (x4) by using a DVB-CAR-PDMS fiber. However, with such fiber, benzene is less sensitive (factor x0.7). Use of DVB-CAR-PDMS fiber will be of interest in the analysis of more high-boiling substances (such as trimethylbenzenes) with a loss in the lighter ones (methyl tert-butyl ether, benzene).

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