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.
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 desorption, 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

<table>
<thead>
<tr>
<th>Vial #</th>
<th>Name</th>
<th>Water (mL)</th>
<th>NaCl ±0.05 (g)</th>
<th>+ISTD (pL)</th>
<th>ISTD (µg/L)</th>
<th>+Cal. sol. (pL)</th>
<th>BTEX (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>0</td>
<td>Blank</td>
</tr>
<tr>
<td>2</td>
<td>STD 1</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>5.0</td>
<td>0.83</td>
</tr>
<tr>
<td>3</td>
<td>STD 2</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>5.0</td>
<td>0.83</td>
</tr>
<tr>
<td>4</td>
<td>STD 3</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>10.0</td>
<td>1.67</td>
</tr>
<tr>
<td>5</td>
<td>STD 4</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>15.0</td>
<td>2.49</td>
</tr>
<tr>
<td>6</td>
<td>STD 5</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>20.0</td>
<td>3.32</td>
</tr>
<tr>
<td>7</td>
<td>STD 6</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
<td>25.0</td>
<td>4.16</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Vial #</th>
<th>Name</th>
<th>Water sampled (mL)</th>
<th>Residual water (mL)</th>
<th>NaCl ±0.05 (g)</th>
<th>+ISTD (pL)</th>
<th>ISTD (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Sampling blank</td>
<td>20</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
</tr>
<tr>
<td>12</td>
<td>Sample “A”</td>
<td>20</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
</tr>
<tr>
<td>13</td>
<td>Sample “B”</td>
<td>20</td>
<td>15</td>
<td>6</td>
<td>25</td>
<td>4.16</td>
</tr>
</tbody>
</table>

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.

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>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>Chloro-benzene</th>
<th>Ethyl-benzene</th>
<th>m/p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT (min)</td>
<td>7.63</td>
<td>12.54</td>
<td>16.04</td>
<td>17.13</td>
<td>17.58</td>
<td>18.62</td>
</tr>
<tr>
<td>CV (%)</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>
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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Published in UK, September 29, 2010
SI-01251