BTEX: Complete Resolution in Under 6.5 Minutes

Kory Kelly and Bruce Harder, Phenomenex Inc., Torrance, California, USA.

Introduction

BTEX (benzene, toluene, ethylbenzene and xylenes) are volatile aromatic hydrocarbons with toxic properties. Exposure to BTEX can cause neurological, respiratory, genetic and excretory system damage. Use of BTEX has persisted despite toxic properties because of the extent of applications in which they have been used in the past. BTEX chemicals are commonly large constituents (~18%) in gasoline and petroleum products and are extensively (megatons per year) used as solvents and reactants in many industrial and manufacturing processes.

Analysis for BTEX results from the need for quality assurance of solvents/reactants and environmental applications to quantify BTEX contaminated soil and water samples. Because BTEX chemicals are used in a wide variety of applications, analysis of BTEX compounds can vary according to the properties of the sample matrix. Common matrices range from non-polar alkane mixtures to more polar aromatic hydrocarbon samples.

The purpose of this application note is to show the resolution that is achieved for BTEX and alkanes with capillary columns of different stationary-phase polarities and conditions.

Experimental

Instrumentation: Analysis was performed using an HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, California, USA) with flame ionization detection (FID) and equipped with HP Chemstation software (Version A.09.01) used for data analysis and a G2614A autosampler from Agilent. The GC columns used for analysis were Zebron (Phenomenex, Torrance, California, USA) ZB-5, 30 m × 0.32 mm × 0.25 µm; ZB-50, 30 m × 0.32 mm × 0.50 µm; ZB-WAX, 30 m × 0.32 mm × 0.50 µm and ZB-1, 100 m × 0.25 mm × 0.50 µm. Carrier gas was UHP-grade helium. Hydrogen for FID was UHP-grade and air was purified using a Domnick Hunter ZA3500 (EST Analytical, Fairfield, Ohio, USA) with an additional moisture trap with 13X molecular sieve. All chemicals were of HPLC grade.

Sample preparation: Two samples were analysed. The first was prepared by diluting a stock solution of equal parts (v/v) pure BTEX constituents to 10% in methylene chloride. The second was prepared by diluting a stock solution of equal parts (v/v) pure BTEX, pentane, heptane, decane and dodecane to 10% in methylene chloride.

Chromatographic conditions: A constant flow of helium carrier gas was set to 34 cm/s. The oven programme increased from 60 °C to 75 °C at 15 °C/min to 90 °C at 3 °C/min. ZB-WAX and ZB-50 programmes were then held for 3 min while the ZB-5 programme was increased to 190 °C at 25 °C/min. ZB-1 parameters were 35 °C for 14 min to 60 °C at 1.1 °C/min for 19 min to 280 °C at 2 °C/min for 5 min. Inlet and detector temperatures were 225 °C and 300 °C, respectively. FID conditions consisted of a hydrogen flow of 40 mL/min, airflow of 450 mL/min and a helium make-up flow of 40 mL/min. Injection volumes were 0.2 µL with a split of 20:1.

Results

A solution containing BTEX (benzene, toluene, ethylbenzene and xylenes) with pentane, heptane, decane and dodecane as retention markers was analysed on ZB-1, ZB-5, ZB-50 and ZB-WAX columns to demonstrate the effect of polarity on the retention of compounds and determine the most effective column for the separation of these chemicals. Results for the ZB-WAX are shown in Figure 1. All peaks are fully baseline resolved including the meta and para-xylene isomers (peaks 8 and 9). The retention time of the most retained peak is under 7 min with all BTEX components eluting in under 6.5 min.

The solution was analysed using a ZB-50 column and results are shown in Figure 2. In this figure, all chemicals are eluted in under 8.5 min with all BTEX eluted in under 5 min. Complete separation of BTEX did not occur; in particular, ethylbenzene, p-xylene and m-xylene are not baseline separated. Temperature programming was unable to resolve the xylenes and resulted in longer run times.

Figure 3 shows the same solution run on a ZB-5 column with the same dimensions. In this instance, resolution of meta and para-xylene is poor as these components co-elute. Resolution is achieved for all other compounds. The retention of the less polar

![Figure 1: BTEX solution and four alkane markers were separated using a ZB-WAX 30 m × 0.32 mm × 0.50 µm column.](image-url)

Peaks: 1 = pentane, 2 = heptane, 3 = solvent (methylene chloride), 4 = benzene, 5 = decane, 6 = toluene, 7 = ethylbenzene, 8 = p-xylene, 9 = m-xylene, 10 = dodecane, 11 = o-xylene.
Environmental alkanes is much greater and required an increased temperature ramp at the end of the oven programme (up to 190 °C). Even with
the higher oven temperature, the retention time of dodecane remained >8.5 min.

A ZB-1, 100 m × 0.25 mm × 0.50 µm column was installed and conditions were as for a gasoline range organic (GRO) analysis. The BTEX solution was injected and a portion of the resulting chromatogram is represented in Figure 4 showing that m-, and p-xylene (peaks 2 and 3) are mostly resolved with complete resolution of ethylbenzene (peak 1). All other peaks were completely resolved.

Conclusions
Chromatograms were acquired for BTEX chemicals as they might be encountered when analysing common environmental samples. BTEX found in gasoline samples are accompanied by many compounds with varying properties. These samples are analysed on a 100 m ZB-1 column and show near full resolution of para- and meta-xylene. Mixed samples that contain BTEX are commonly analysed using a ZB-5, which shows resolution excepting para- and meta-xylene. Samples with more aromatic content might be analysed using a more polar ZB-50 allowing partial resolution for para- and meta-xylene. The best resolution was achieved using a ZB-WAX column, which showed complete resolution of all BTEX compounds and normal alkane markers.

Ordering Information

<table>
<thead>
<tr>
<th>Order Number</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>7HM-G007-17</td>
<td>ZB-WAX (30 m × 0.32 mm × 0.50 µm)</td>
</tr>
<tr>
<td>7HM-G004-17</td>
<td>ZB-50 (30 m × 0.32 mm × 0.50 µm)</td>
</tr>
<tr>
<td>7HM-G002-11</td>
<td>ZB-5 (30 m × 0.32 mm × 0.25 µm)</td>
</tr>
<tr>
<td>7MG-G001-17</td>
<td>ZB-1 (100 m × 0.25 mm × 0.50 µm)</td>
</tr>
</tbody>
</table>

Peaks:
1 = ethylbenzene, 2 = m-xylene, 3 = p-xylene, 4 = o-xylene.