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BTEX: Complete Resolution in Under 6.5 Minutes

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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 nonpolar 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, CA, USA) ZB-5, 30m x 0.32mm x 0.25µm; ZB-50, 30m x 0.32mm x 0.50µm; ZB-WAX, 30m x 0.32mm x 0.50µm and ZB-1, 100m x 0.25mm x 0.50µm. Carrier Gas was UHP grade helium. Hydrogen for FID was UHP grade and air was purified using a Dominic 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 analyzed. The first prepared by diluting a stock solution of equal parts (v/v) of 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 34cm/sec. The oven program increased from 60°C to 75°C at 15°C/min to 90°C at 3°C/min. ZB-WAX and ZB-50 programs were then held for 3 minutes while the ZB-5 program was increased to 190°C at 25°C/min. ZB-1 parameters were 35°C for 14 minutes to 60°C at 1.1°C/min for 19 minutes to 280°C at 2°C/min for 5 minutes. Inlet and detector temperatures were 225°C and 300°C, respectively. FID conditions consisted of hydrogen flow of 40mL/min, airflow of 450mL/min, and a helium makeup flow of 40mL/min. Injection volumes were 0.2µL with a split of 20:1.

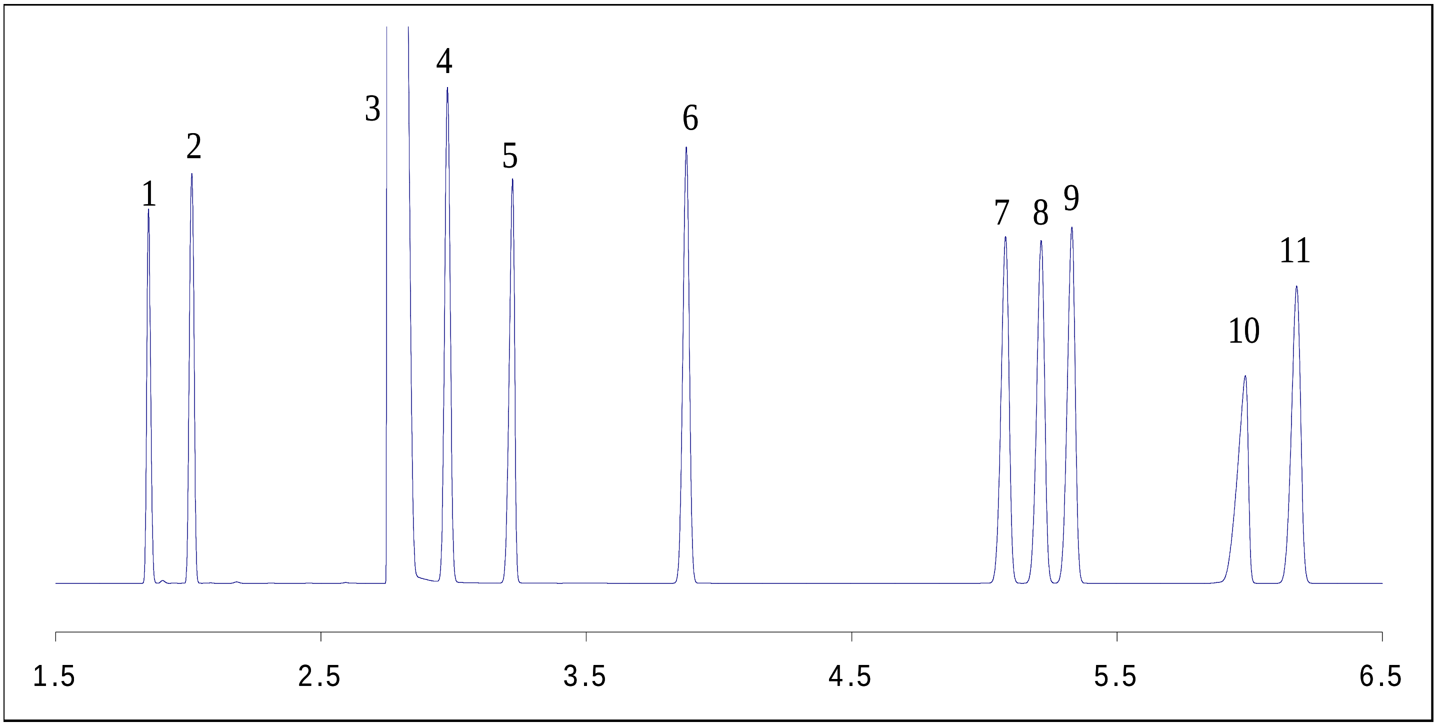

Figure 1. BTEX solution and four alkane markers were separated using a ZB-WAX 30m x 0.32mm x 0.50µm column. 1 = pentane, 2 = heptane, 3 = solvent (methylene chloride), 4 = benzene, 5 = decane, 6 = toluene, 7 = ethylbenzene, 8 = m-xylene, 9 = p-xylene, 10 = dodecane, 11= o-xylene.

Results

A solution containing BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) with pentane, heptane, decane, and dodecane as retention markers was analyzed 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 seven minutes with all BTEX components eluting in under 6.5 minutes.

The solution was analyzed using a ZB-50 column and results are shown in Figure 2. In this figure, all chemicals are eluted in under 8.5 minutes with all BTEX eluted in under five minutes. 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.

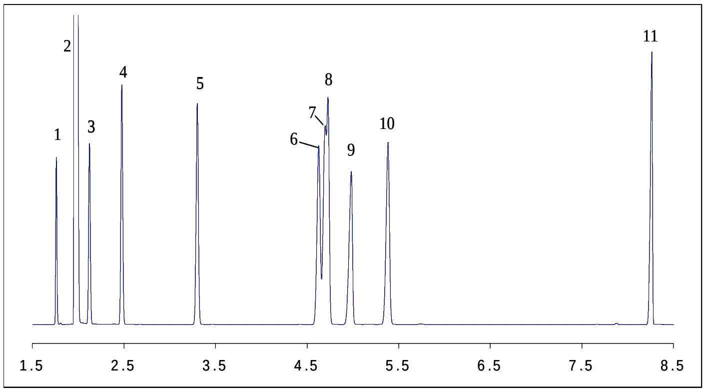

Figure 2. BTEX solution with markers on ZB-50. 1 = pentane, 2 = solvent (methylene chloride), 3 = heptane, 4 = benzene, 5 = toluene, 6 = ethylbenzene, 7 = m-xylene, 8 = p-xylene, 9 = o-xylene, 10 = decane, 11 = dodecane.

Figure 3 shows the same solution run on a ZB-5 column with the same dimensions. In this case, 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 alkanes is much greater and required an increased temperature ramp at the end of the oven program (up to 190°C). Even with the higher oven temperature, the retention time of dodecane remained >8.5 minutes.

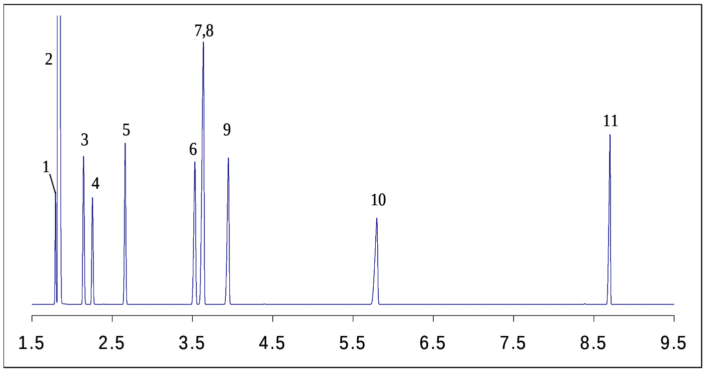

Figure 3. BTEX solution with markers on ZB-5. 1 = pentane, 2 = solvent (methylene chloride), 3 = benzene, 4 = heptane, 5 =toluene, 6 = ethylbenzene, 7 = m-xylene, 8 = p-xylene, 9 = o-xylene, 10 = decane, 11 = dodecane.

A ZB-1, 100m x 0.25mm x 0.50µm 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.

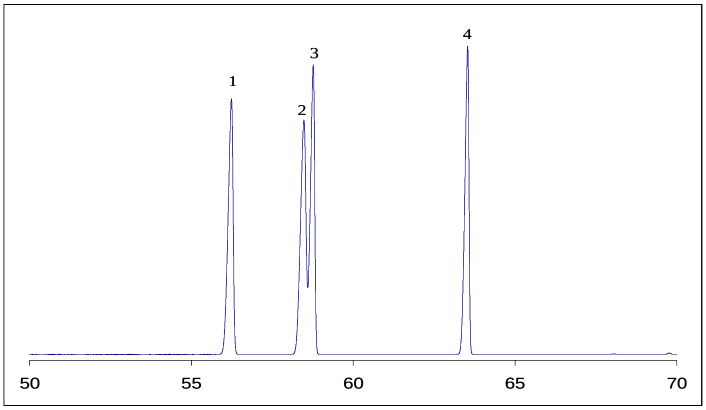

Figure 4. Portion of BTEX solution with markers on ZB-1 100m x 0.25mm x 0.50µm column, 1 = ethylbenzene, 2 = m-xylene, 3 = p-xylene, 4 = o-xylene.

Conclusions

Chromatograms were acquired for BTEX chemicals as they might be encountered when analyzing common environmental samples. BTEX found in gasoline samples are accompanied by many compounds with varying properties. These samples are analyzed on a 100m ZB-1 column and show near full resolution of para- and meta-xylene. Mixed samples that contain BTEX are commonly analyzed using a ZB-5 which shows resolution excepting para- and meta-xylene. Samples with more aromatic content might be analyzed 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

Order Number	Description
7HM-G007-17	ZB-WAX - 30m x 0.32mm x 0.50µm
7HM-G004-17	ZB-50 - 30m x 0.32mm x 0.50µm
7HM-G002-11	ZB-5 - 30m x 0.32mm x 0.25µm
7MG-G001-17	ZB-1 - 100m x 0.25mm x 0.50µm