HIGH SPEED GAS CHROMATOGRAPHY ANALYSIS FOR BENZENOID HYDROCARBONS USING GC-17AV3

Introduction

"High Speed Gas Chromatography" is a recent advance in separation science that dramatically can reduce analysis run times without sacrifice to analytical performance. This technology allows some separation times to be reduced from minutes to seconds. Several developments have made high speed GC possible. These include the improvement in the production of narrow bore (≤0.1 mm I.D.) capillary columns by the column manufacturers and the introduction of advanced flow and pressure control by the instrument manufacturers.

Narrow bore columns have very high efficiency and provide a greater number of theoretical plates over a given column length. For example, a 0.1mm I.D. column has approximately 8600 theoretical plates/meter while a 0.25mm I.D. column has approximately 3300 theoretical plates/meter. This greater number provides the 0.1 mm I.D. column with more than twice the efficiency of a 0.25mm I.D. column. The higher efficiency allows for the use of shorter columns that decreases the analysis time, yet still provides good resolution of the compounds. When using narrow bore columns, higher pressures are required to obtain adequate flow rates, therefore a GC with digital control of gases may be needed. With digital control of the gas flow pressure programming takes full advantage of the narrow bore column and further reduces analysis times.

This application note examines a set of benzenoid hydrocarbon compounds using high speed GC. Some typical analytical conditions encountered in traditional capillary column GC are compared to the conditions used for high speed GC using a 0.1 mm I.D. column. Technical suggestions for performing high speed GC are also provided.

Experimental

The following instrumentation was used for the examples with the 0.1 mm I.D. and 0.32 mm I.D. columns: GC-17Av3 Gas Chromatograph, AFC-17H High Pressure/High Flow Controller, SPL-17 Split/Splitless Injection Port, FID-17 Flame Ionization Detector, AOC-20i Autoinjector, and Class-VP Data Acquisition System. A standard mix that contained benzene, toluene, m-xylene, o-xylene, and p-cymene was purchased from Supelco (Bellefonte, PA) and was diluted to a concentration of 100 ppm. A second standard of 2 mg/mL containing benzene, toluene, o-xylene, and m-xylene was made from neat materials purchased from Aldrich Chemical Company (Milwaukee, WI). Analysis conditions for each of the chromatograms are found in Tables 1 and 2.

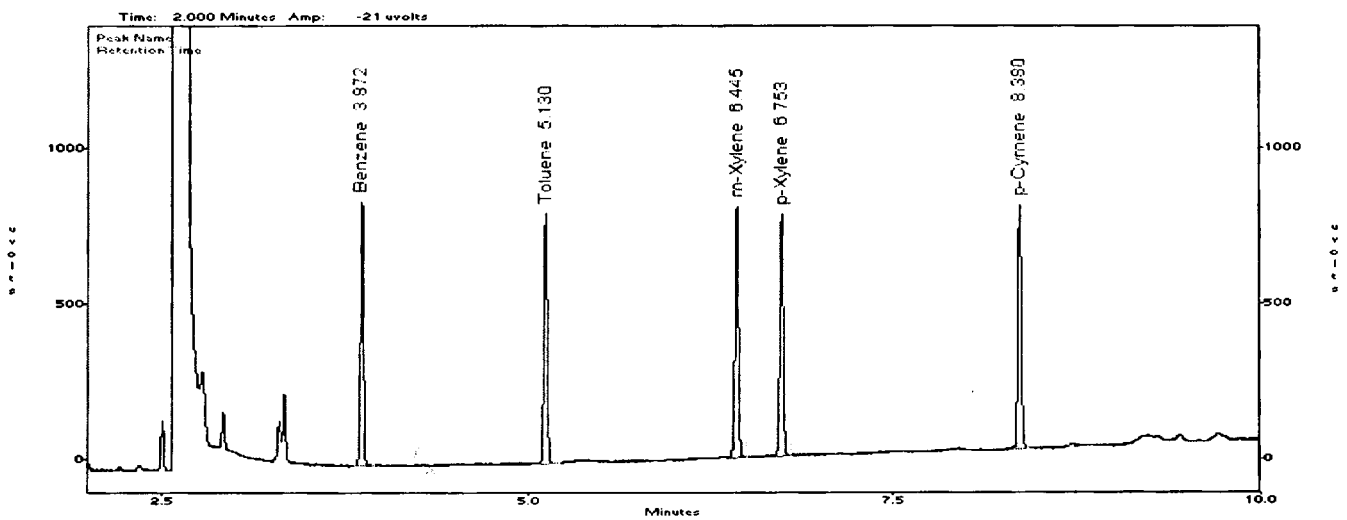

Figure 1 - Typical Benzenoid Hydrocarbon Analysis with 0.32mm I.D. Column

Column:	Supelco SPB-1 30 m × 0.32 mm × 1.0 µm
Carrier:	Helium at 30 cm/sec at 40°C 60 kPa for 1 min 60 kPa to 77 kPa at 1.9 kPa/min
Oven :	40°C for 1 min 40°C to 175°C at 15°C/min
Injector:	Split 1:30, 1µL, 300°C
Detector:	FID, 300°C Helium makeup gas at 30 mL/min

Table 1 – Typical Analytical Conditions with 0.32 mm I.D. Column

Column:	J&W DB-5 10 m × 0.1 mm × 0.1 µm
Carrier:	Hydrogen at 124 cm/sec at 35°C 416 kPa to 970 kPa
Oven:	35°C to 100°C at 40°C/min
Injector:	Split 1:10, 1µL, 340°C
Detector:	FID, 360°C Helium makeup at 30 mL/min

Table 2 – High Speed Analytical Conditions with 0.1 mm I.D. Column

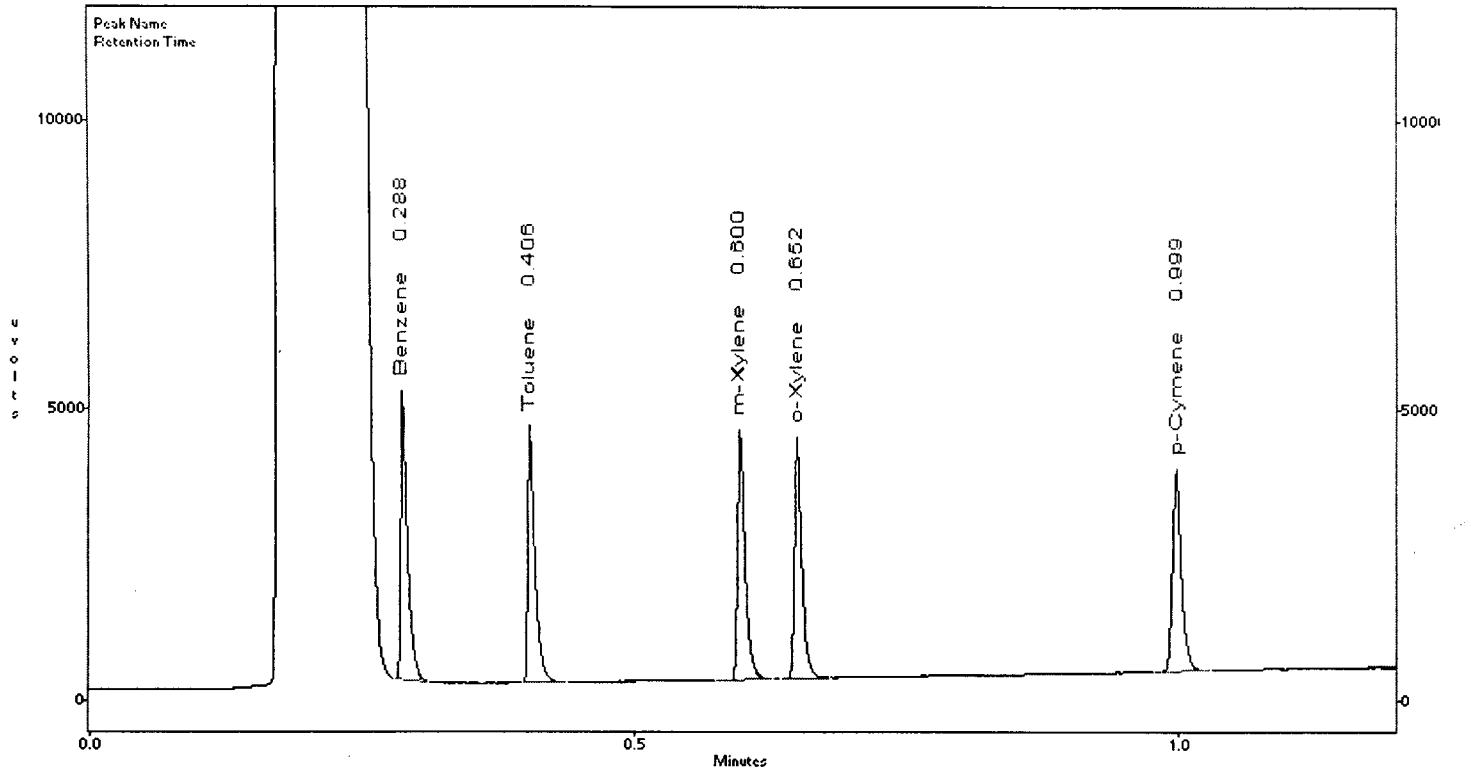

Figure 2 – High Speed Benzenoid Hydrocarbons Analysis with 0.1mm I.D. Column

Results

The chromatographic results for the benzenoid hydrocarbon compounds using a 0.32mm I.D. column with typical conditions are illustrated in Figure 1. The compound, o-xylene, elutes at 6.75 minutes. Using a 0.1mm I.D. narrow bore column o-xylene elutes in 0.65 minutes and is seen in Figure 2.

While decreasing analysis times, high speed GC remains reproducible in terms of both response and retention time. Table 3 lists retention time data and Table 4 lists response data for 7 replicate analysis using the 0.1 mm I.D. column and the following high speed conditions: carrier-56cm/sec helium at 35°C, 416 kPa to 890 kPa at 400 kPa/min; oven-35°C to 85°C at 40°C/min; injector-split 1:200, 0.7 µL, 280°C; detector-FID, 300°C, helium makeup at 30 mL/min.

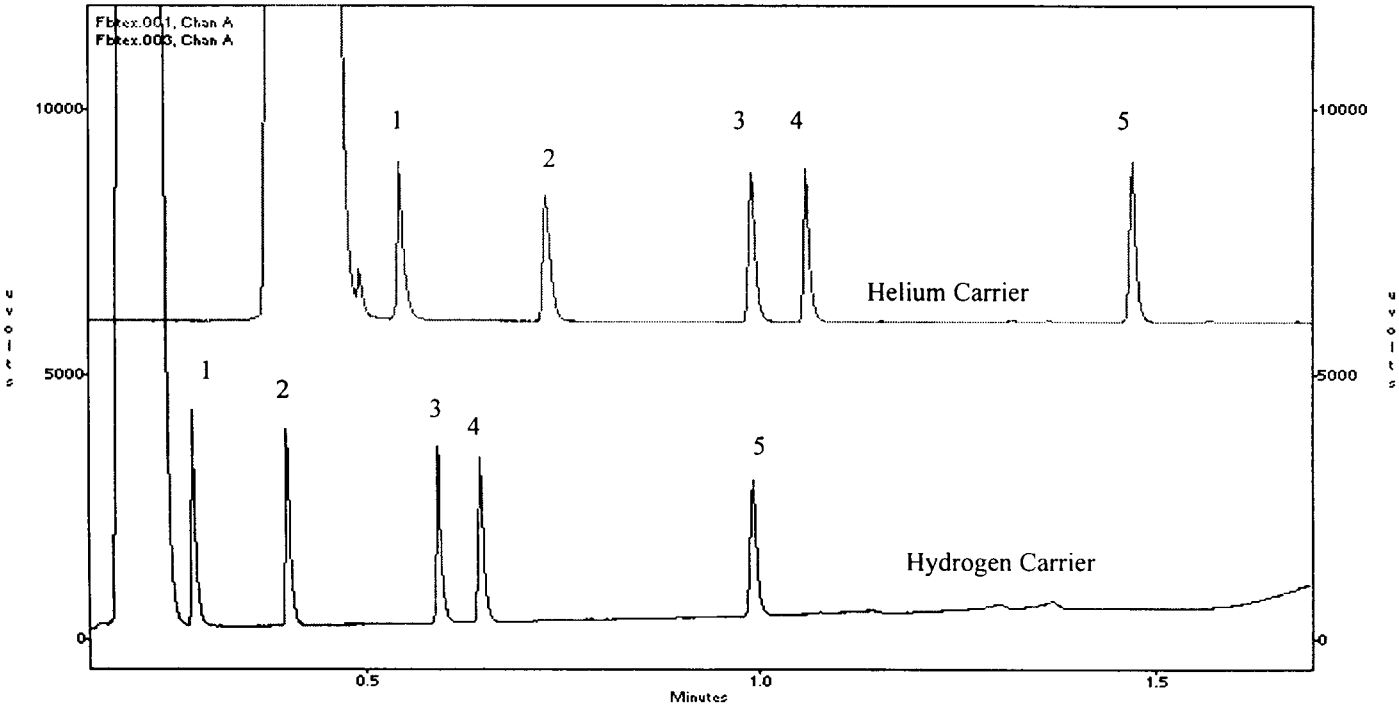

Figure 3 - Comparison of Hydrogen and Helium as Carrier Gas

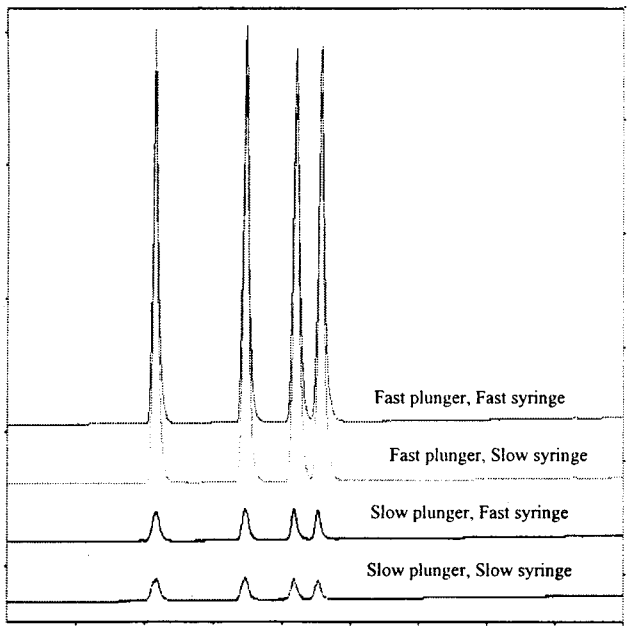

Figure 4 - Comparison of Syringe and Plunger Speeds

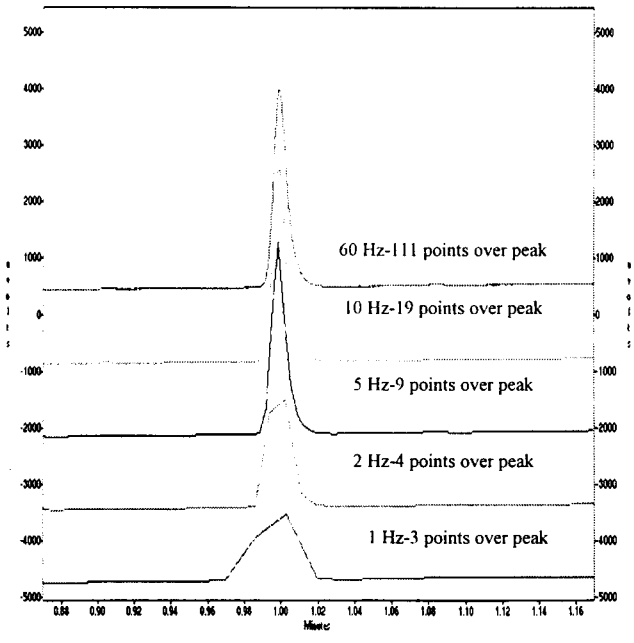

Figure 5 - Comparison of Sampling Frequency

Technical Tips

The following are some suggestions that can assist in setting up a system for performing high speed GC.

1. Since the GC will likely run at higher pressures than usual, it is critical that the system be leak free. Perform a pressure test on the injection port to be used. To achieve good reproducibility and accuracy the pressure must not change more than 2kPa over 1 hour. More details on performing a pressure test are available in the Shimadzu technical bulletin "If Leaks are your Worst Nightmare...".

2. Be sure that there is adequate pressure set at the regulator on the carrier gas cylinder. Normally, a cylinder pressure of just over 600 kPa (90psi) is recommended. However, in order for the AFC-17H to reach a maximum of 970 kPa the incoming pressure must be at least 150 psi. Also check the tubing lines between the gas cylinder and the GC for leaks.

3. Adjust the purge flow to 3-5 mL/min with the injection port pressure set to the expected operation range. Without adjustment, the purge flow will be too high and will result in low response for the analytes of interest.

4. The choice of carrier gas can also be important. Although safety may be of concern, hydrogen is the carrier gas of choice to achieve the shortest analysis times. Due to the characteristics of the gas at equivalent pressures hydrogen has about twice the linear velocity as compared to helium. For example, using a 0.1 mm I.D. x 10 m column at a temperature of 35°C and initial head pressure of 416 kPa, helium has a linear velocity of 56cm/sec (0.9 mL/min column flow) while hydrogen has a linear velocity of 124 cm/sec (2.0 mL/min column flow). This comparison is seen in Figure 3. The p-cymene (peak 5) elutes at 1.48 minutes with helium carrier and at 0.99 minutes with hydrogen carrier.

5. Using narrow bore columns, injection speed does affect retention time, peak shape, and response. For reproducible results, an autoinjector with variable speeds for the plunger, syringe injection, and syringe dwell time is highly recommended. The faster the injection, the better. As seen in Figure 4, slow plunger speed has a larger deleterious effect than slow syringe speed.

Compound	Benzene	Toluene	m-Xylene	o-Xylene
Run 1	0.481	0.665	0.923	0.995
Run 2	0.481	0.664	0.924	0.996
Run 3	0.480	0.664	0.922	0.994
Run 4	0.481	0.664	0.923	0.995
Run 5	0.481	0.664	0.922	0.995
Run 6	0.481	0.663	0.922	0.995
Run 7	0.481	0.664	0.922	0.994
Average	0.481	0.664	0.923	0.995
Std. Dev.	0.000378	0.000577	0.000787	0.000690
%RSD	0.079%	0.087%	0.085%	0.069%

Table 3 - Retention Times for 7 Replicates (min)

Compound	Benzene	Toluene	m-Xylene	o-Xylene
Run 1	9184	9198	9139	9308
Run 2	9198	9186	9066	9244
Run 3	9013	8974	8863	9032
Run 4	9097	9071	8972	9135
Run 5	9037	9017	8911	9078
Run 6	9373	9370	9252	9425
Run 7	9327	9327	9213	9385
Average	9176	9163	9059	9230
Std. Dev.	138.0	151.1	150.2	152.6
%RSD	1.504%	1.649%	1.658%	1.653%

Table 4 - Response for 7 Replicates (area counts)

6. The sampling frequency of the data collection system is critical to the accurate quantitation and characterization of the chromatographic peaks in high speed GC. For proper integration, 20-25 points over the peak should be collected. A sampling frequency of 60 hertz is adequate for peaks with a base width of 0.36 sec. In Figure 2, benzene is the narrowest peak with a base width of 1.92 sec. At 60 hertz, 115 points were collected over the peak, which is more than enough data for accurate characterization. Figure 5 presents a comparison of sampling frequency for the p-cymene peak.

7. High speed GC may not be the best method for trace analysis due to the narrow bore columns. These columns have limited capacity, 5-10 ng depending on the film thickness. For this reason dirty samples can pose a problem. The smaller size results in contamination accumulating more rapidly, so more maintenance is required for narrow bore columns compared to 0.25 or 0.32 mm I.D. columns. This shortcoming may be overcome with multicapillary columns that offer additional capacity.

- Elizabeth J. Tierney, Ph.D.