

# OPTIMISING OF THE COLUMN, TEMPERATURE, AND PRESSURE FOR INCREASED RESOLUTION AND PERFORMANCE FOR THE SEPARATION OF ALKANES AND AROMATICS FOR ASTM D5186 AND D6550 USING SFC

SFC is well established for enantiomeric separations and purifications in the pharmaceutical industry as well as for fuel analysis of gasoline and diesel using the ASTM D5186 and D6550 methods. Both ASTM methods use a silica column for the separation, while D6550 secondarily employs a silver column for retention of the olefins after the alkanes and aromatics are separated. In addition to these methods, GC is often used for analysis for the alkanes, but this application will show this is also possible using SFC.

The first step in optimising the resolution for the ASTM methods is evaluating the available silica columns. Recent advances in column technology have provided numerous new phases and particles including small particle HILIC columns. These new columns were compared to traditional 5µm columns to determine which is the best for this analysis.

The second step in improving the system performance is evaluating the retention behavior by adjusting system parameters on the best columns as determined in the previous step. As with HPLC the column temperature is controlled in SFC, but this change in temperature alters the density of CO<sub>2</sub> compared to a change in viscosity in HPLC producing a different effect on the separation in SFC. One additional and unique parameter in SFC is the back pressure, which is not controlled in HPLC, but can be adjusted in SFC to optimise a separation. The parameters of pressure and temperature were evaluated below to determine their effect on the resolution.

With the optimised column, temperature and pressure determined, the system was evaluated for ASTM 5186 and ASTM 6550 methods. In these methods the individual components within each class (non-aromatics, mono-aromatics, poly-aromatics) are not identified, but simply grouped to determine the percentage of each group. Recent interest in further separation and identification of the components within those compound classes has led to additional research.

Non-aromatic hydrocarbons are very difficult to retain as seen in the above-mentioned methods. In order to identify the components in the non-aromatics, a significant increase in retention is required. Unique to SFC is the ability to join columns inline to increase the effective length of the separation column. This will be performed to increase the retention and resolution of the non-aromatics for further identification.

## Experimental

Equipment		Conditions	
CO <sub>2</sub> Delivery Pump:	PU-2080-CO <sub>2</sub>	CO <sub>2</sub> Flow rate:	2.0 – 3.0 mL/min
Autosampler:	XLC-3159AS	Column/FID Splitter Temp.:	200°C
Column/FID Splitter Oven:	GC-FID	FID Temperature:	350°C
Back Pressure Regulator:	BP-2080	Injection volume:	0.5 - 1 µL

## Results

### Column Evaluation

Figure 1 shows the comparison of the 6 silica columns from various manufacturers at 120bar back pressure. The JASCO column is the only one that shows any separation of hexadecane and cyclohexane and clearly shows the most resolution between those peaks and the toluene and naphthalene peaks. Figure 2 shows this same comparison at 200bar and again the separation of hexadecane and cyclohexane is the best and the resolution between those peaks and toluene and naphthalene is the largest.

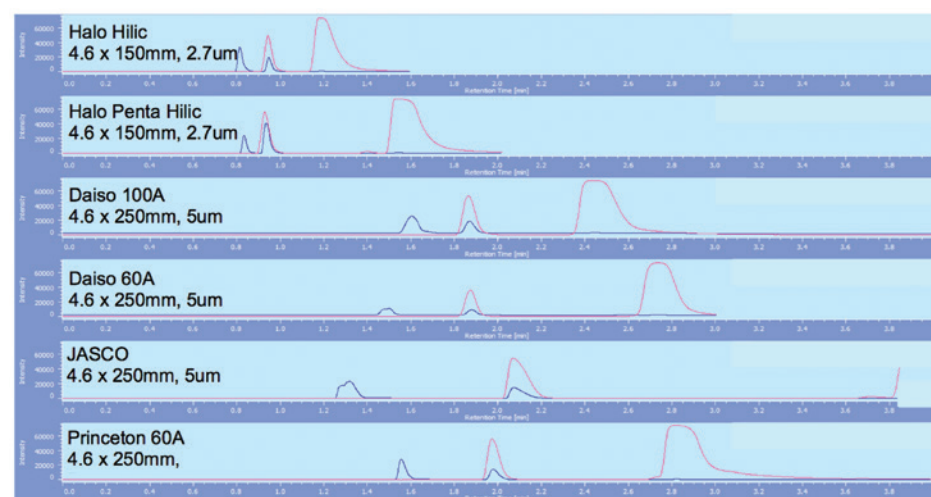


Figure 1: Silica Column Comparison. Back Pressure 120bar. Blue line = FID, Pink line = UV at 225nm. Peaks: 1. Hexadecane, 2. Cyclohexane, 3. Toluene, 4. Naphthalene.

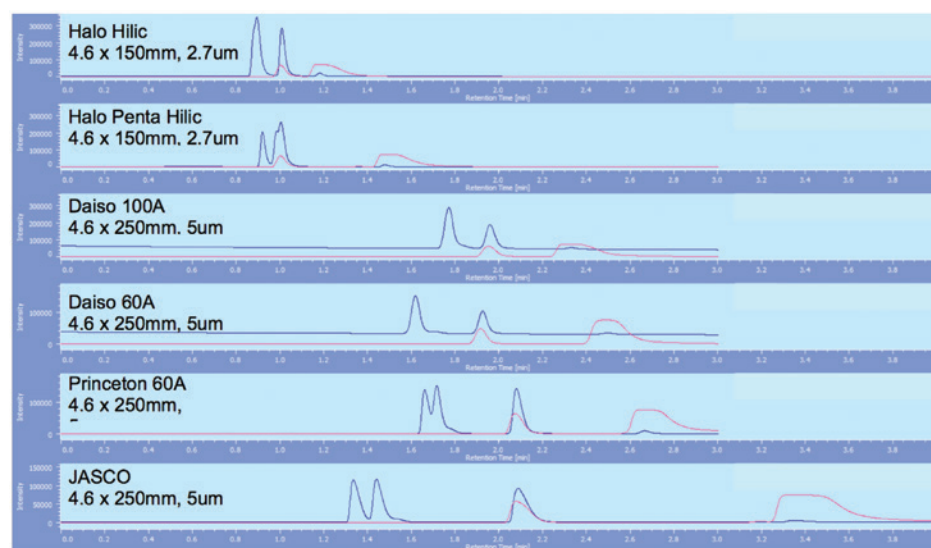


Figure 2: Silica Column Comparison. Back Pressure 200bar. Blue line = FID, Pink line = UV at 225nm. Peaks: 1. Hexadecane, 2. Cyclohexane, 3. Toluene, 4. Naphthalene

As the Princeton 60A and the JASCO columns were the only ones to show separation of hexadecane and cyclohexane, those were further evaluated at a few other pressures. As the resolution of those peaks increased when running at 200bar compared to 120bar, 150bar and 250bar were run to confirm the trend and also that higher pressure led to the best separation.

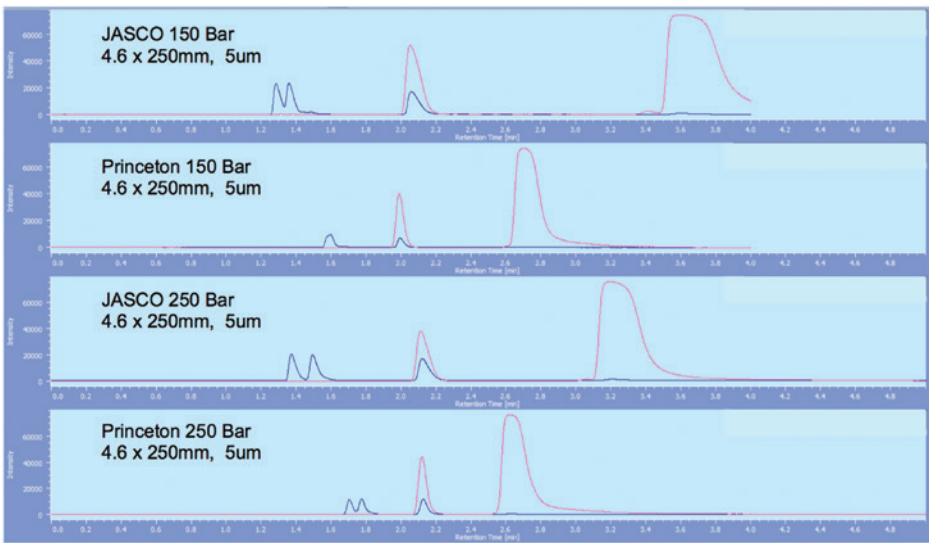


Figure 3: Princeton and JASCO Silica Column Comparison. Blue line = FID, Pink line = UV at 225nm. Peaks: 1. Hexadecane, 2. Cyclohexane, 3. Toluene, 4. Naphthalene.

As illustrated in figure 3, an increase in pressure led to better resolution and 250bar was proven to be the best back pressure on both columns, with the JASCO column proving to be the best. As the pore size of the JASCO column is 30A, a Princeton 30A was compared as well as a Phenomenex Kinetex HILIC column using a simplified 3 component mix. As shown in figure 4 the difference between the Princeton 30A and Princeton 60A is significant as the separation of hexadecane and cyclohexane is drastically improved. The Kinetex® column did not show much retention of any of the peaks. As the pore size was 100A that was likely a factor in the insufficient resolution of hexadecane and cyclohexane, but also the toluene retention time was less than the Halo Penta HILIC.

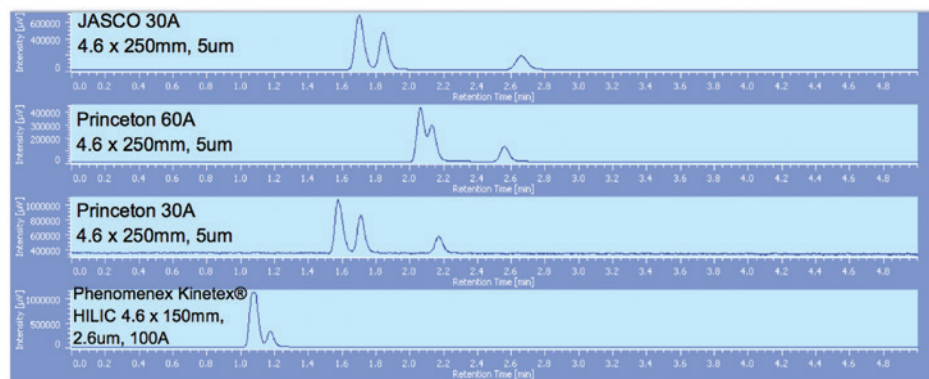


Figure 4: Silica Column Comparison. Back Pressure 250bar. Peaks: 1. Hexadecane, 2. Cyclohexane, 3. Toluene

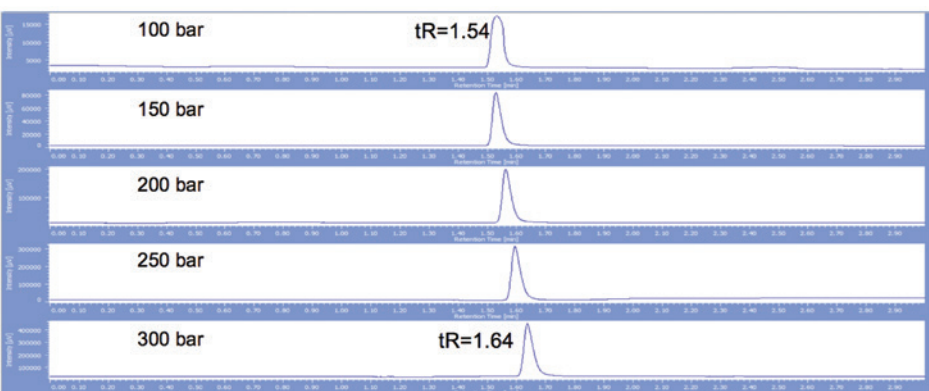


Figure 5: Hexadecane Retention Time Comparison at 35C and Various Back Pressures.

### Temperature and Pressure

Figure 5 and figure 6 show that the retention time increases as the back pressure is increased for both hexadecane and cyclohexane. However the magnitude of this increase is different for each. Hexadecane at 100bar elutes at 1.54 minutes and has poor peak shape, while cyclohexane elutes earlier at 1.46 minutes. The peak shape sharpens as the back pressure is increased for hexadecane, but notice the retention time only increases to 1.64 minutes at 300bar compared to later cyclohexane elution at 1.70 minutes. Effectively if these two compounds were in the same mixture their elution order would reverse showing the importance of the back pressure.

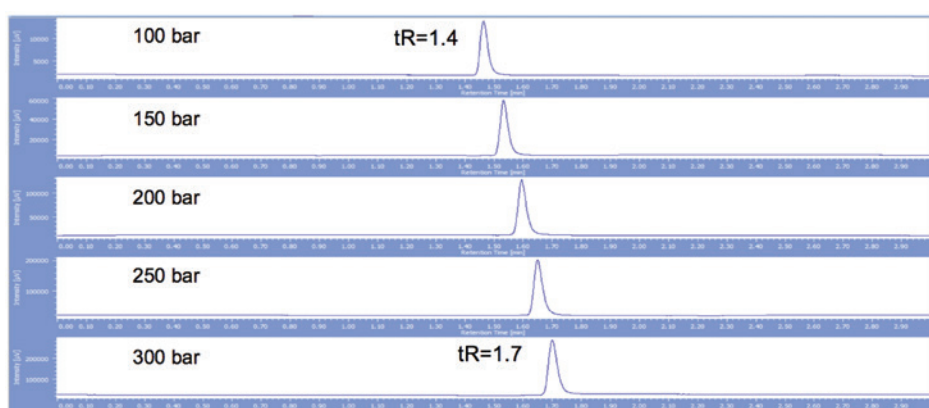


Figure 6: Cyclohexane Retention Time Comparison at 35C and Various Back Pressures.

Figure 7 shows the retention behavior of toluene at various temperatures and various pressures. The retention time does not vary between 35°C and 45°C with the exception at 100bar yielding a slightly longer retention. Although the retention times do not vary, the peak shape is certainly sharper at 35°C. At 55°C the peak shape mimics that broader peak shape seen at 45°C, but the retention time decreases slightly, with the exception of 100bar where the retention time increases. This same data set was repeated using benzene as the sample and the exact same retention behavior was displayed. With benzene, peak broadening was also evident at 45°C and 55°C compared to 35°C, but was much less significant.

The retention time increases as the pressure is increased from 150 bar, up to 300 bar with both 100% CO<sub>2</sub> and 90% CO<sub>2</sub> : 10% methanol as plotted in figure 5 and seen in figures 3 and 4. The retention time trend is identical for both with 10% methanol as expected producing earlier elution. At 100 bar, however, the retention time does not follow the trend when the mobile phase is 100% CO<sub>2</sub>, and toluene has longer retention as the temperature is increased from 35°C to 45°C to 55°C. This suggests that there is a significant difference in the mobile phase (100% CO<sub>2</sub>) density at 100bar for 35°C and 55°C producing very different retention times. The presence of 10% methanol, which is in the liquid phase, inhibits the density change leading to retention times that follow the trends seen at higher pressures.

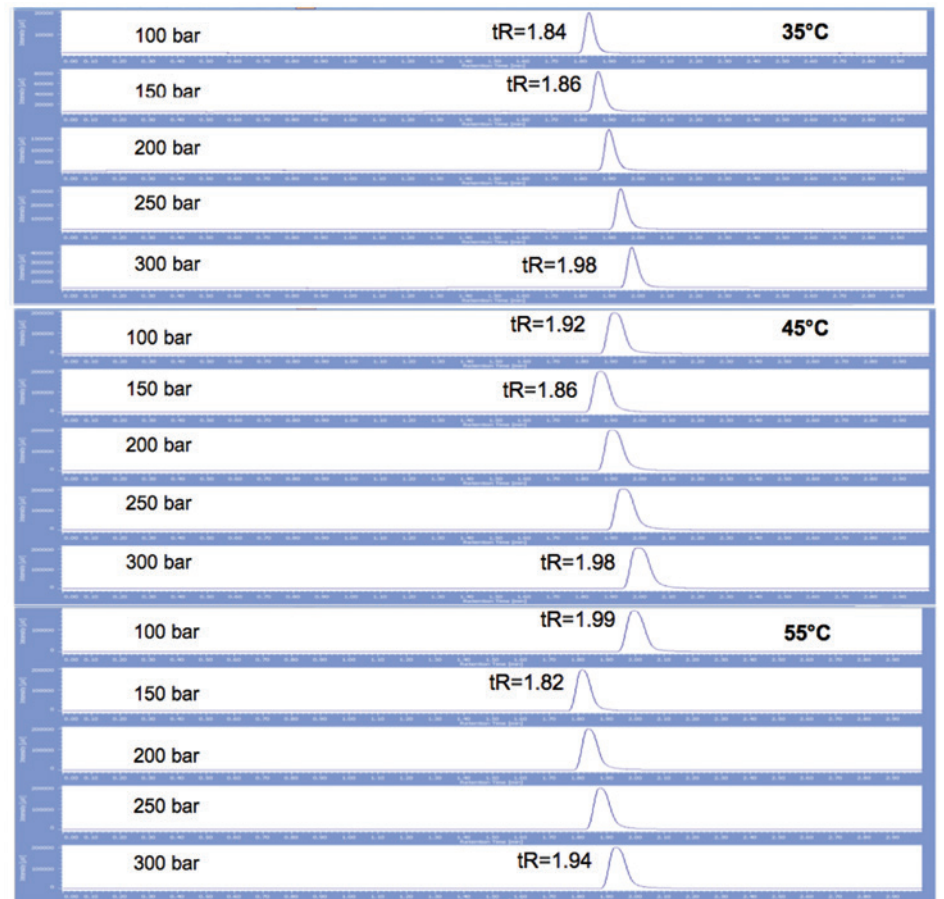


Figure 7: Toluene Retention Time Comparison at Various Temperatures and Various Back Pressures.

### ASTM D6550 Results

Standards were purchased from Spectrum Quality Standards and consisted of individual ampules of 1.0%, 3.5%, 6.0%, 8.5%, 12.0%, 17.0% and 25.0% olefin in a mixture of 75% isooctane : 25% toluene.

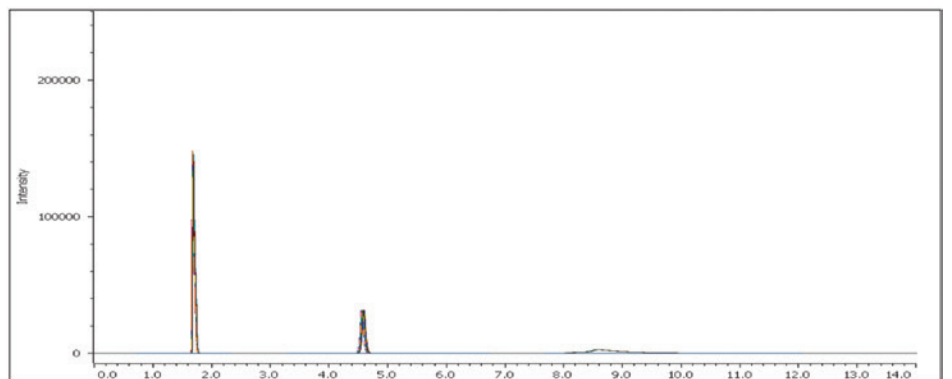


Figure 8: ASTM D6550 Olefin Analysis. Sample is 25% olefins. Overlay of 20 injections.

The overlay of 20 chromatograms of the 25% olefin sample is shown in Figure 8. The zoomed olefin overlay of those 20 injections is shown in Figure 9. The overlay of the olefin peak of the various standards, 1.0%, 3.5%, 6.0%, 8.5%, 12.0%, 17.0% and 25%, is shown in figure 8 and the corresponding calibration curve from those standards is also shown. The linearity of the calibration curve had a correlation coefficient (R) of 0.997.

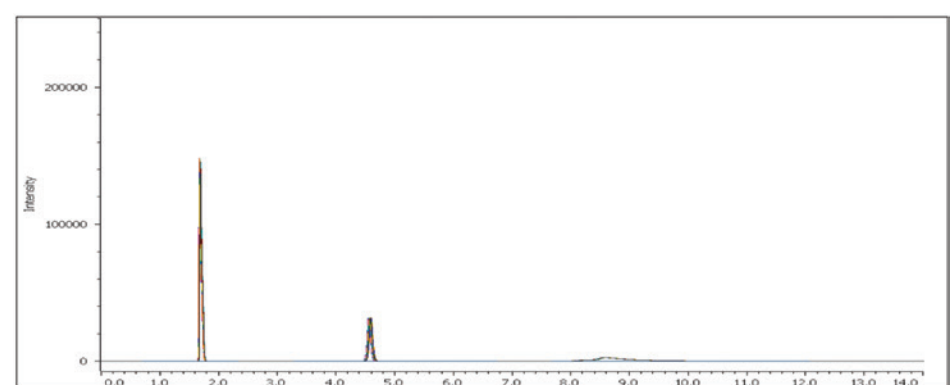


Figure 9: Overlay of 1.0%, 3.5%, 6.0%, 8.5%, 12%, 17%, and 25% Olefins. Calibration curve correlation coefficient (R) was 0.997.

### ASTM D5186 Results

The chromatograms of gasoline and jet fuel under the ASTM D5186 method conditions are shown in Figure 10 and Figure 11. The gasoline was determined to have 59.3% non-aromatics and 40.7% aromatics, while the jet fuel had 81.5% non-aromatics and 18.5% aromatics.

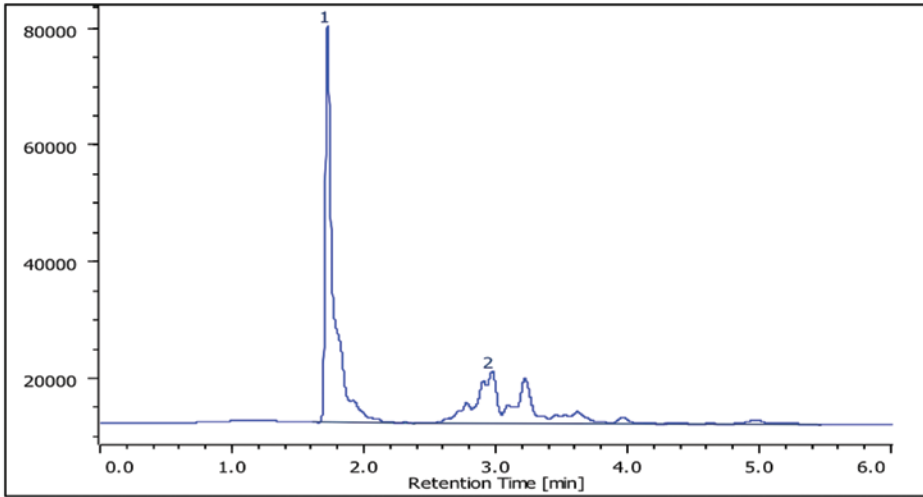


Figure 10: ASTM D5186 Analysis of Commercially Available Gasoline. Non-aromatic 59.3% and aromatic 40.7%.

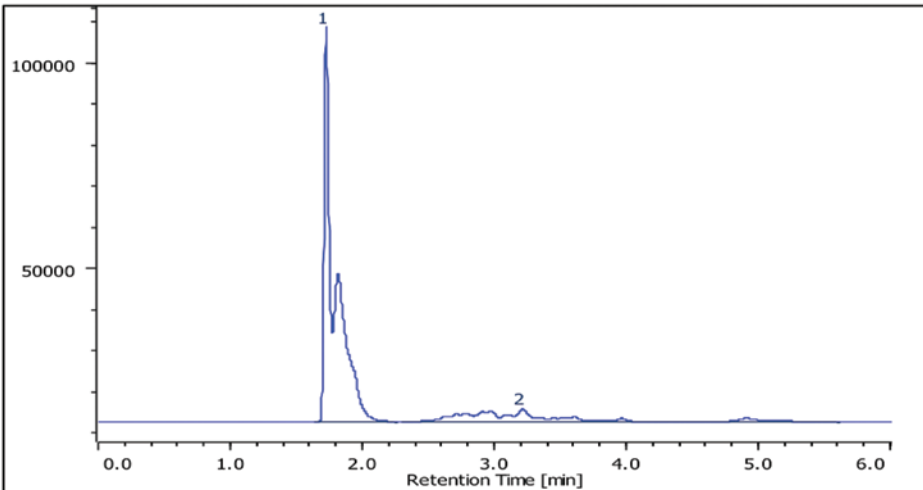


Figure 11: ASTM D5186 Analysis of Jet Fuel. Non-aromatic 81.5% and aromatic 18.5%.

The chromatogram (figure 12) of the non-aromatic hydrocarbon standard mixture is shown below. Besides  $C_5-C_9$  which co-eluted, all of the hydrocarbons were successfully separated and identified. As the BP Calibration standard was diluted in hexane in order to have the FID signal on scale, the strong hexane signal likely contributed to the co-elution of  $C_5-C_9$ .

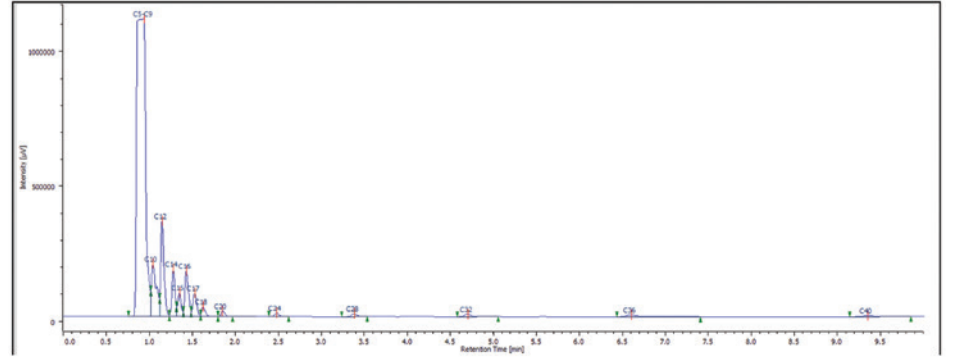


Figure 12: Chromatogram of the BP Calibration standard mixture of hydrocarbons (diluted in hexane before injection). The mixture contained  $C_5-C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{18}$ ,  $C_{20}$ ,  $C_{24}$ ,  $C_{28}$ ,  $C_{32}$ ,  $C_{36}$  and  $C_{40}$ , all of which were identified.

### Conclusion

The pore size is a significant factor in the separation efficiency of the column for the separation of alkanes and aromatics. The JASCO 30A packing material provided the best resolution of hexadecane, cyclohexane and toluene with the Princeton 30A a very close 2nd providing equal resolution of hexadecane and cyclohexane, but less resolution of 5.4 compared to 7.7 on the JASCO silica.

The temperature and pressure studies have not only illustrated how the unique parameter of back pressure plays a significant role in retention time, but also how it can be utilised to optimise a separation when resolution is minimal. Both alkanes and aromatics were more retained at higher pressures, but higher temperatures had the opposite effect on retention and also led to peak broadening. These significant effects from back pressure and temperature provide a user the ability to tune a separation depending on to which class of compounds they are looking to maximise the resolution.

As the results show in the repeatability and reproducibility tables, the SFC-FID exceeds the requirements of the ASTM D6550. Having exceeded the acceptable values, the SFC-FID system can successfully be used for the automated analysis of olefins in gasoline. The ASTM D5186 method was used to successfully analyse commercially available gasoline and jet fuel.

The SFC-FID system offers versatility for high resolution separations of hydrocarbons in a significantly shorter analysis time than provided by GC.

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