Prefractionator for Reliable Analysis of the Light Ends of Crude Oil and other Petroleum Fractions

Application Note

Hydrocarbon Processing

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Abstract

A precolumn backflush system based on capillary columns using midpoint pressure control is described. Midpoint backflush is made possible with a Capillary Flow Technology (CFT) purged union controlled by an AUX EPC channel on the Agilent 7890A GC system. The key application discussed is prefractionation of crude oil that provides a high resolution separation of the C4 to C12 cut. A general backflush method using Polywax 500 is presented to illustrate the backflush concept.

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Introduction

The concept of backflushing in gas chromatography has been a mainstay of many petrochemical and gas analysis applications for over 40 years. Most use some implementation of a packed or micropacked precolumn connected to a mechanical valve. The analytical separation can then be done with either a packed or capillary column while the precolumn is backflushed to vent. Now precolumn backflush can be implemented in capillary only systems using either a standard split/splitless inlet or multimode inlet (MMI). Any application where sample components elute (or in some cases never elute) after the last compound of interest is a good candidate for a backflush implementation.

Process engineers and chemists working in the petroleum industry often have a need to analyze in detail the lighter fraction of a wide boiling raw material or feedstock. While GC is always the separation method of choice for petroleum and petrochemical samples, real limitations exist concerning the boiling point range or maximum carbon number that can be accommodated by a given capillary column. Many petroleum materials contain high boilers that can never elute. Analysis time can also be an issue even for compatible samples and columns because heavy material may require 60 minutes or longer to elute from the column. Now, the analysis of wide range petroleum material such as crude oils can be easily optimized, providing a high resolution time optimized separation for only the fraction required.

Crude oil analysis serves as an excellent example. A detailed analysis of the hydrocarbons in the C4 to C12 fraction is extremely valuable to the process engineer looking for the best method of refining the material. It is also valuable for determining the crude oil's value. Typically prefractionator or precolumn backflush GC configurations are based on packed precolumns and mechanical valves that can require specialized inlets. These systems require frequent maintenance, can suffer from poor thermal control, and are not optimized for high resolution separations. Agilent offers a unique solution based on a simple in-oven Capillary Flow Technology (CFT) device, the Purged Union (p/n G3186-60580). An MMI, AUX module, and FID complete the required hardware on the Agilent 7890A GC system. The configuration is compatible with all GC detectors including the MSD.

Experimental

A diagram of the basic system is shown below in Figure 1. The MMI is used in temperature programmed split mode to assist with cleaning out the liner during backflush while an AUX channel controls analytical column flow. Injection is handled by the 7693A Tower and Tray system where basic sample prep (mixing, dilution, and heating) is used for automated sample prep.

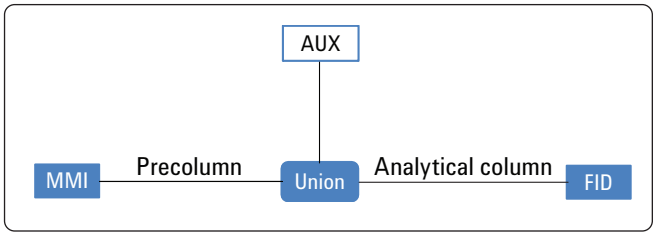

Figure 1. Basic precolumn backflush configuration with purged union.

Parameters for crude oil analysis of C4 to C12/C13

Sample:	Various crude oils
Inlet:	Multimode, 250:1 split
Inlet program:	250 °C (0.3 min) to 425 °C (60 min) at 200 °C/min
Oven program:	35 °C (10 min) to 160 °C (1 min) at 1 °C/min then 15 °C/min to 240 °C
Column 1:	2 m × 0.32 mm deactivated retention gap
Column 1 Flow:	0.9 mL/min in constant flow mode
Column 2:	100 m x 0.25 mm, 0.5 µm DB-Petro
Column 2 Flow:	1.2 mL/min in constant flow mode
Backflush after C12:	1.3 min approx.

Parameters for wide boiling range generic method

Sample:	Polywax 500
Inlet:	MMI, 10:1 split
Inlet program:	350 °C (0 min) to 425 °C (20 min)
Oven program:	50 °C (0 min) to 355 °C (5 min) at 15 °C/min
Column 1:	1 m x 0.53 mm deactivated retention gap
Column 1 Flow:	9 mL/min
Column 2:	5 m x 0.53 mm × 0.15 µm DB-HT
Column 2 Flow:	12 mL/min
Backflush times:	Various

The general procedure for precolumn backflush can be illustrated using a wide boiling range sample such as Polywax 500 (PW 500) where backflushing at specific carbon numbers can be easily accomplished. Setup panes for the PW500 analysis are shown in Figures 2A and 2B for precolumn and analytical column, respectively. Note that backflush is triggered by programming a rapid pressure drop at the inlet to the precolumn, which is the MMI in this example. First, defining the inlet and outlet sources for the columns is critical. The inlet to the precolumn is the MMI and the outlet an Aux channel. For the analytical column, the inlet is the Aux and FID the outlet.

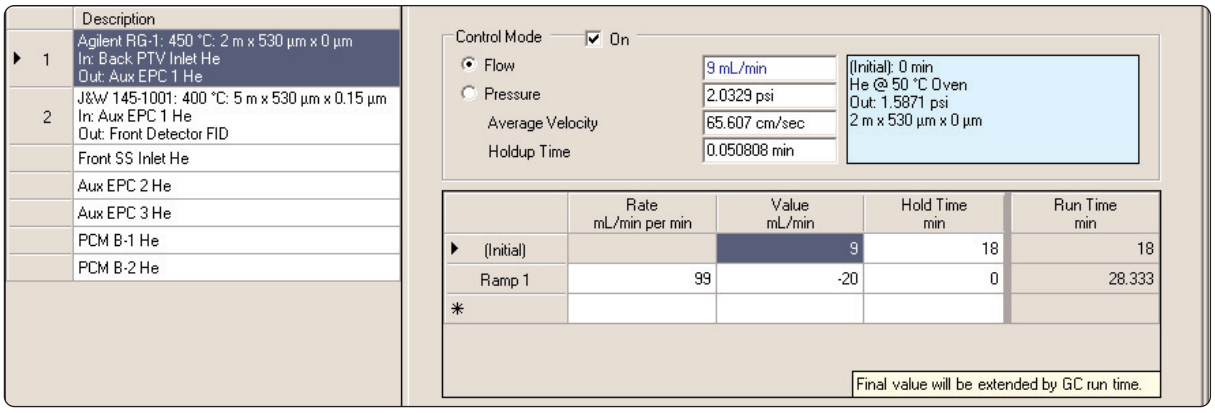

Figure 2A. Precolumn flows. Backflush starts at 18 min in this example.

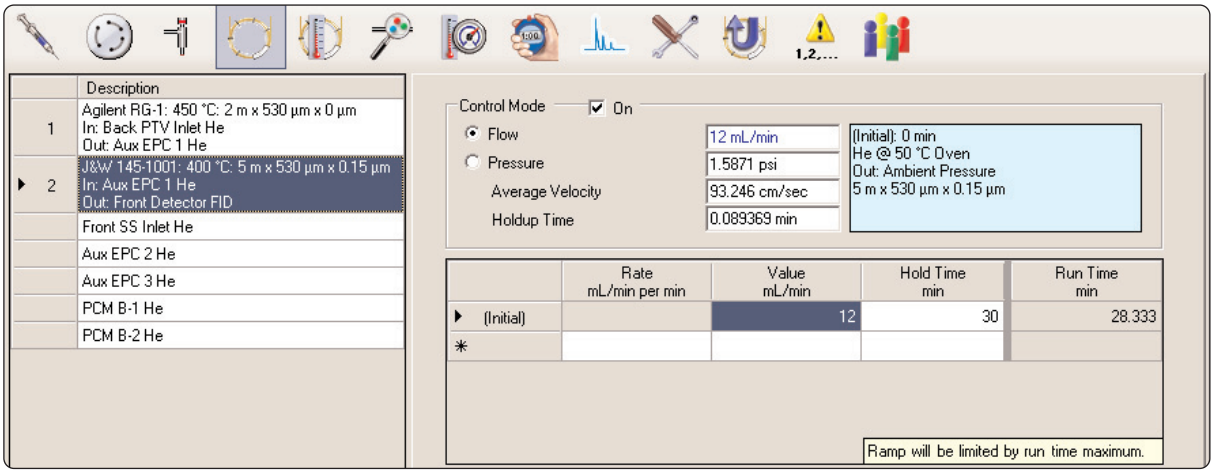

Figure 2B. Analytical column flow set at 12 ml/min for the entire run.

Note that at certain backflush times, only part of the last hydrocarbon is transferred to the analytical column. This occurs because individual compounds will be spread out and distorted on the precolumn. Backflush times can usually be fine tuned to make a clean cut with the polyethylene fragments that make up PW500 since they occur at even carbon numbers only (Figure 3).

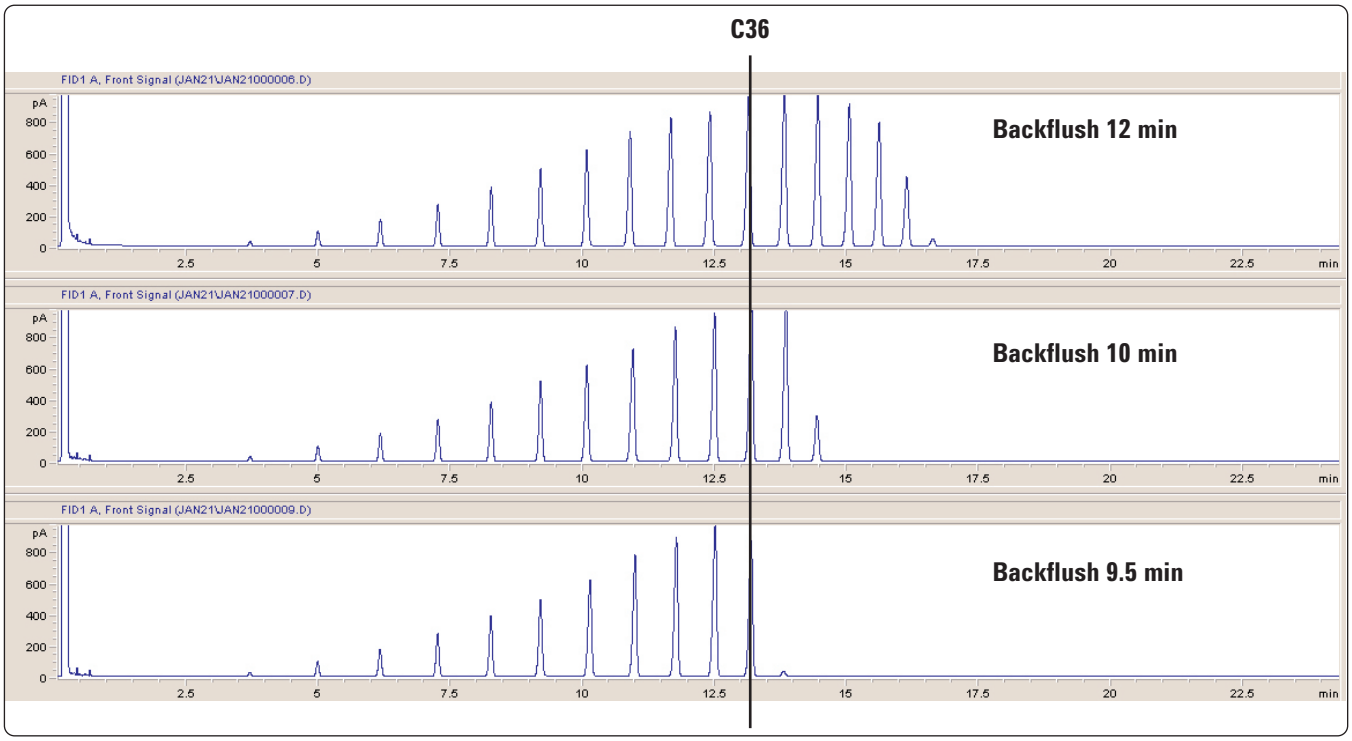

Figure 3. Polywax 500 chromatograms at three backflush times.

A plot of backflush time versus carbon number can be constructed as shown in Figures 4A and 4B. While a polynomial curve fit is best (Figure 4A), a linear regression will give a very good prediction of an appropriate backflush time at any desired carbon number (Figure 4B). The equation

BF Time = (Carbon number – 5.56)/3.68

can be used to give very close to ideal times for the columns and conditions stated here. Any change in the parameters would require a new equation. When developing a new applicatin three to four points would be enough to establish the relationship between carbon number and backflush time using an appropriate test mixture. This is easily done using a ChemStation sequence for fast method optimization.

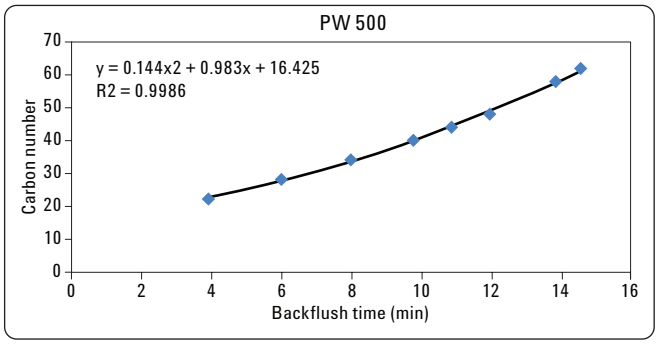

Figure 4A. Polynomial fit.

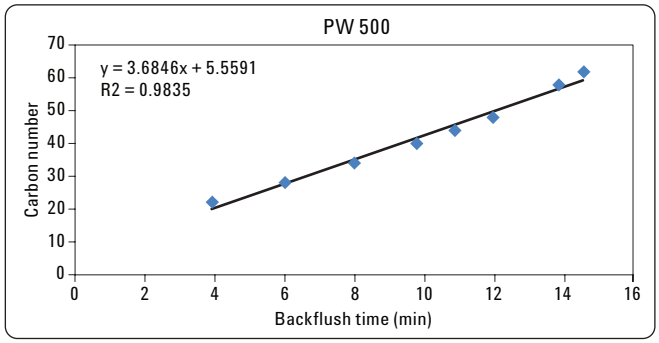

Figure 4B. Linear regression.

Discussion

Crude oil analysis is used as an example to show system setup and typical results. The precolumn usually consists of a short piece of deactivated fused silica, and the analytical column is chosen to provide sufficient separation power for the application. The columns used for crude oil analysis are 2 m × 0.32 mm deactivated retention gap, and 100 m × 0.25 mm × 0.50 µm DB-PETRO for the pre and analytical columns, respectively. Many possibilities exist for choice of pre and analytical columns for customizing the system for a particular application. Attention must be given to the pressure differential between

the inlet and aux to assure stable operation when choosing columns and conditions. Differences less than 0.1 psig must be avoided.

To begin system setup, the EPC channels must first be zeroed. This is necessary because the pressure difference between the MMI pressure and the Aux pressure may be as small as 0.1 psig. This can be seen in Figure 5 where the flow calculator is used to determine the flow settings for the crude oil prefractionation system. Flow calculator software can be downloaded from the Agilent web site. [1]

Next the "Quick swap" PID constants need to be uploaded to the Aux channel. This is done with the LMD Update Utility Tool for the 7890A. Flow or pressure is set first for the analytical column controlled by an Aux channel, then Flow or pressure is set for the precolumn controlled by the MMI. As a general rule, the precolumn flow should be set between 70% and 85% of the analytical column flow.

Fine tuning the backflush time is easily done by running a sequence of several methods with a slightly different backflush time in each using a mix of hydrocarbons from C5 to C17 (p/n 5080-8769). A given hydrocarbon will elute from the uncoated precolumn at a lower temperature than it would from the analytical column. Exactly how much lower is highly dependent on the phase ratio of the analytical column. Therefore it is best to start with a relatively quick backflush and then adjust the time upwards to allow all of the desired boiling point range to pass into the analytical column for separation. As shown in Figure 6, the area of the C13 peak increases as the backflush time is lengthened. The final desired backflush time is reached once the area becomes constant (BF = 1.30 min).

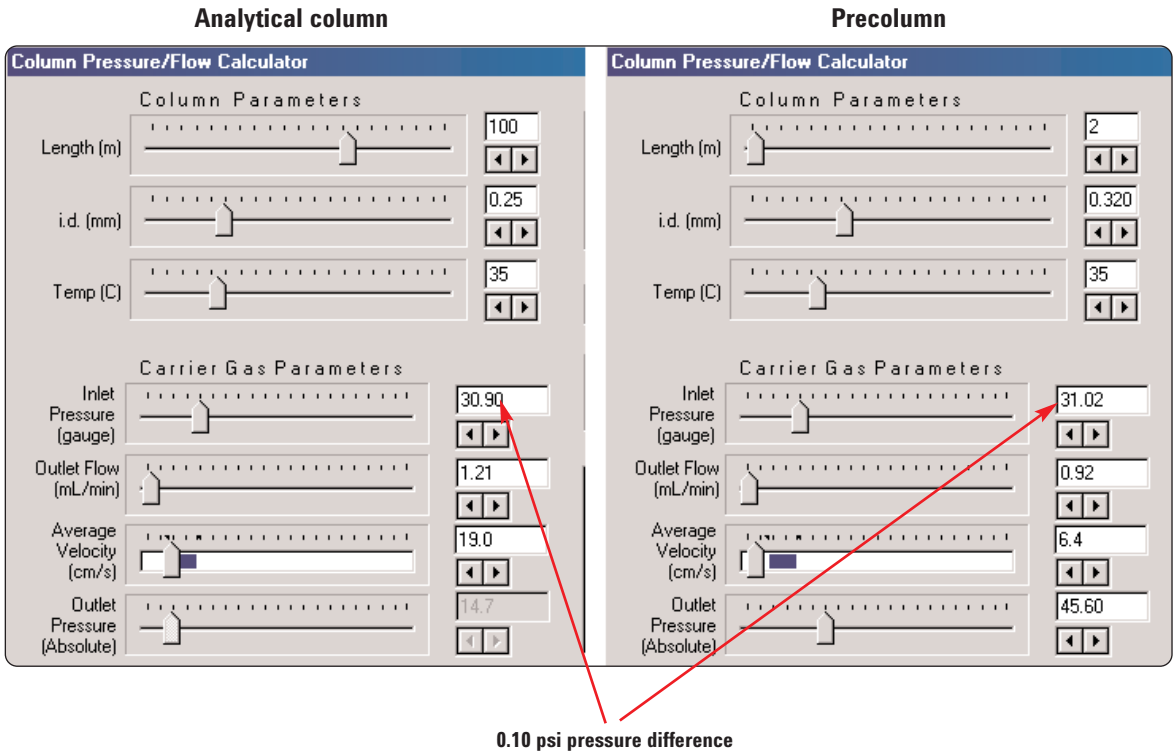

Figure 5. Pressure and flow setting for the analytical column (left pane) and precolumn (right pane).

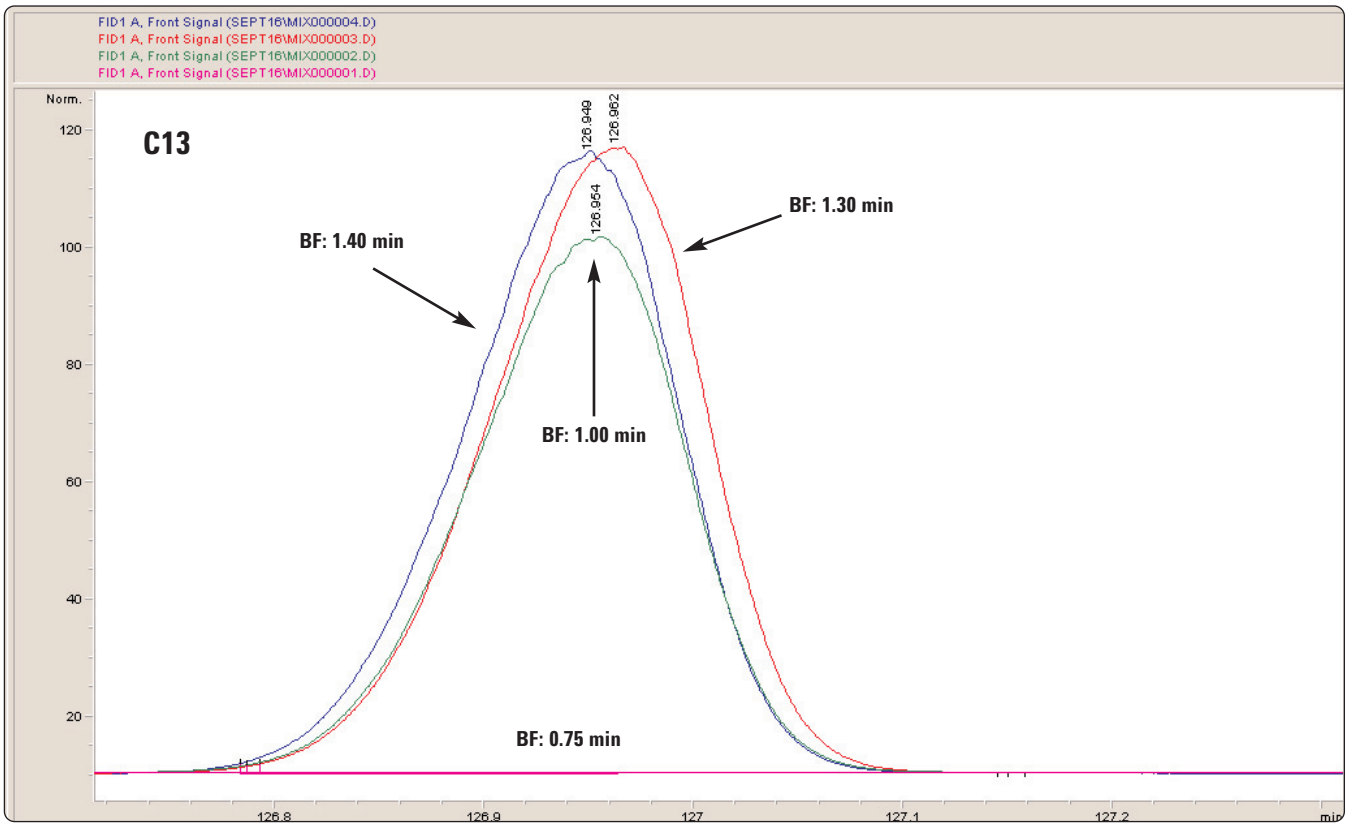

Figure 6. Fine tuning backflush time for ending transfer at C13. Trace at baseline: BF = 0.75 min, Peak at height of 100pa: BF = 1.00 min, Peaks at 117 pa: BF = 1.3 min and 1.4 min.

Easily Protect the Analytical Column with Backflush

Without backflush, a crude oil sample would contaminate and render the 100 m column useless. Setting the system to perform a backflush of the precolumn after approximately C12 has transferred to the 100 m column allows a high resolution separation to occur while the heaver fraction of the crude oil is backflushed through the MMI's split vent. The MMI is also programmed to 425 °C to assist in cleaning the inlet liner during backflush. A single taper liner with glass wool is used (Agilent p/n 5183-4647). ChemStation screens showing setup conditions for the pre and analytical columns are shown in Figures 7A and 7B, respectively.

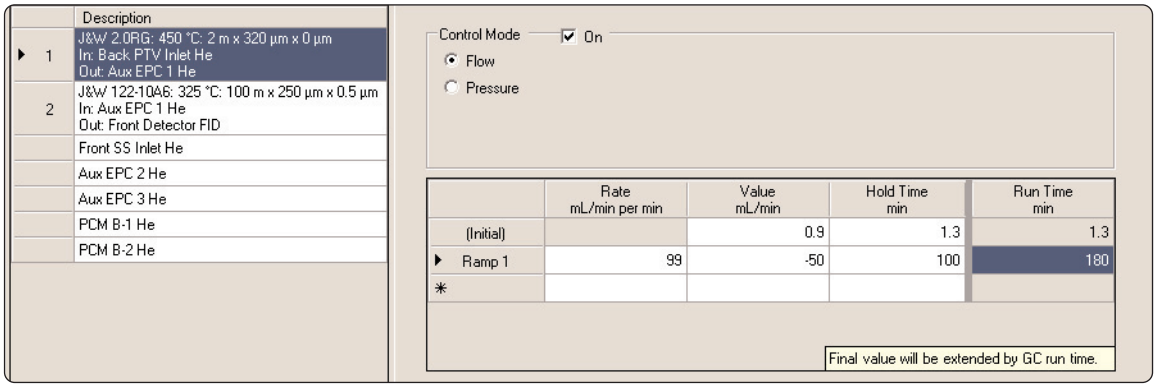

Figure 7A. Precolumn set to backflush at 1.3 min.

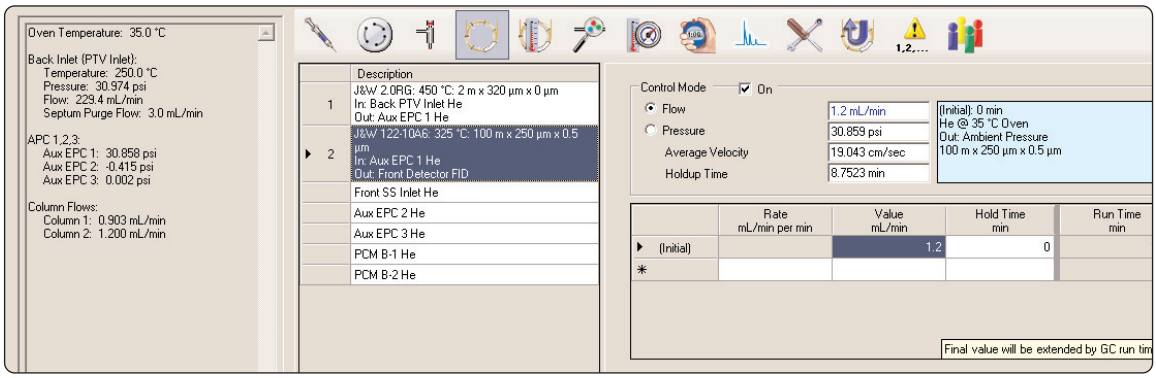

Figure 7B. ChemStation panes for configuring backflush and column flow.

Note that precolumn flow (0.9 mL/min) is set to approximately 80% of the analytical column flow. This is a good general rule to follow for method development. The same control mode should be set for both columns, either pressure or flow. Under the conditions used, setting the backflush time at 1.3 min allows up to C12 to pass into the analytical column. A 0.32 mm id precolumn is used instead of one with the same diameter as the analytical column simply because it has more sample capacity and therefore less peak distortion. Peak capacity will be largely dependent on surface area in uncoated retention gaps.

Four crude oils with prefractionation up to approximately C12 are shown in Figure 8. The resulting detailed C4-C12 hydrocarbon analysis provides valuable information to help the process chemist develop the best refining strategy. This system could be coupled with DHA software to provide comprehensive peak identification. The information could also be combined with crude oil simulated distillation for a complete GC sample characterization.

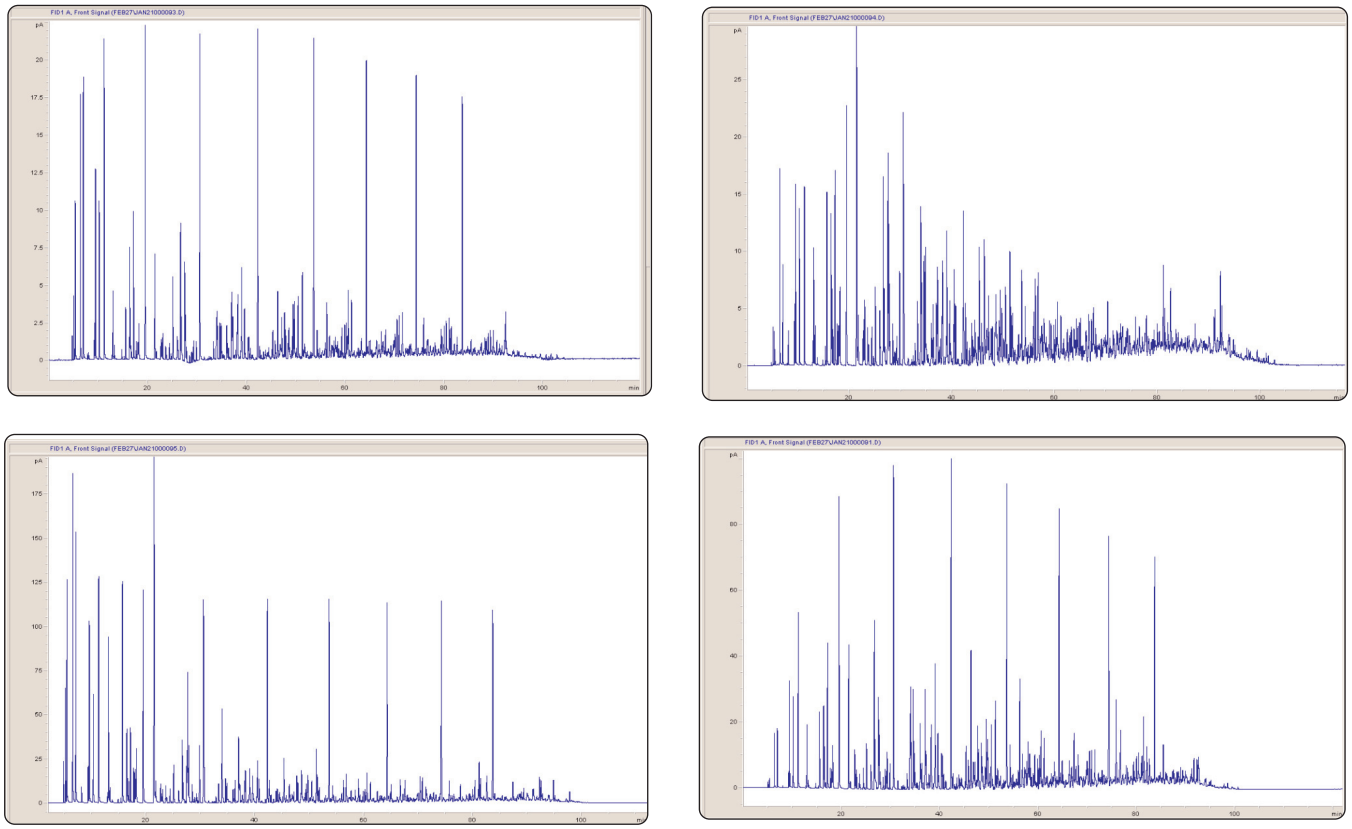

Figure 8. Four crude oils from different regions. Backflushed between C12 and C13.

Backflush With no Traces of High Molecular Weight Contamination

Figure 9 shows 12 consecutive injections of crude oil and analysis of the C4 to C12 fraction on the DB-Petro column. Retention time repeatability is better than 0.002 min and the baselines show no signs of variability from residual material. This indicates a clean and complete backflush of each run. Typically a liner change should be made after approximately 50 to 75 crude oil injections to be conservative.

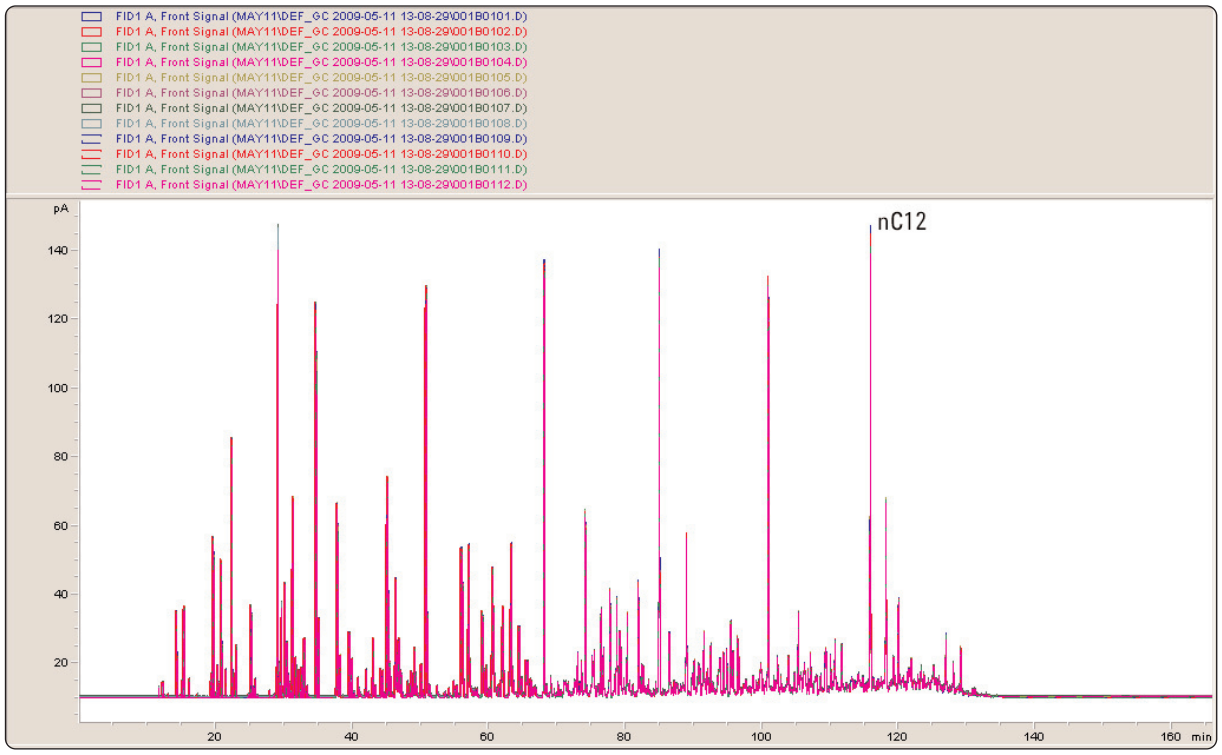

Figure 9. Overlay of twelve runs of crude oil backflushed between C12 and C13.

Conclusions

First and foremost, the system allows GC analysis of many wide molecular weight range samples that otherwise could not be injected without damaging the column or detector. Midpoint pressure control allows the analytical column to run at the desired flow while the precolumn is backflushed during the run. Further, the use of an uncoated precolumn transfers the desired compounds at a low temperature. This has the added benefit of faster backflushing of the heavier material. However, coated precolumns can also be used, and in some applications the use of a thin stationary phase will be advantageous. Columns will have longer lifetimes with improved retention time stability. Many combinations of pre and analytical columns can be used to address just about any GC application where light or early eluting material needs to be separated from heavier material that should not be introduced to an analytical column for either time savings or column protection. Example applications include additives in fuels and biodiesel analysis.

The configuration is compatible with the MSD as high carrier flows to the detector do not occur during backflush. In most cases, even a diffusion pump system can be used since the analytical column is usually of high resolution and the column flow during backflush will be low.

The Agilent 7890A GC system with precise and stable electronic pneumatic control enables midpoint backflush with a variety of column lengths, stationary phases and internal diameters. The CFT purged union designed for leak-free connections, superior inertness, and lack of unswept volumes yields chromatographic performance identical to single column systems.

References

1. Flow Calculator sofware: www.agilent. com/chem/flowcalculator

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

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