Simplified Backflush Using Agilent 6890 GC Post Run Command

Application Note

Gas Chromatography

Author

Matthew S. Klee
Agilent Technologies
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

A simple way to perform backflush with gas-phase microfluidic devices using the Agilent 6890 gas chromatograph is described. By selecting the microfluidic pressure source as the "inlet" for "Column 2" in the Column Configuration screen, one can then set a backflush pressure and time in Post Run. Several advantages ensue, including the ability to backflush in methods that use Constant Flow mode.

Introduction

One way to significantly reduce cycle times in GC analysis is to backflush late-eluting compounds from the column. "Backflush" is a term used for the reversal of flow through a column such that sample components in the column are forced back out the inlet end of the column.

Applications where backflushing can provide the most benefits are:

- Methods where sample components of interest elute early, but a longer temperature ramp is required to remove later-eluting components from the column
- Methods where high-boiling matrix components contaminate the column, requiring frequent maintenance, such as trimming the head of the column

There are many ways that backflushing is beneficial:

- Cycle times (total time to run a sample and be ready to run the next sample) are improved
  - Run time is reduced
  - Cool down time is reduced (cooling down from a lower temperature)
- Data file sizes are smaller
- Data quality is better
  - Column bleed is reduced (from lower exposure to high temperatures)
  - Ghost peaks (due to carryover into subsequent runs) are eliminated
- Columns last longer
  - High-boilers do not build up on column
  - Column is spared exposure to highest temperatures
- Calibrations and system suitability are maintained for longer periods
- MSD source is not exposed to high-boiling components (less source cleaning required, a given tune will last longer, etc.)
- Columns can be conditioned in backflush mode to prevent MSD source contamination

- Electrical power is saved (lower temperature maximum and time at high temperatures, less air conditioning power required to keep room cool because GCs don't produce as much heat)
- Less gases are used (less time per sample = less carrier gas per sample)

There are several ways that one might program pressure changes with the Agilent 6890 and 6850 GCs to do backflush. The simplest is to use a Post Run program. There are several advantages to using the Post Run program:

- Data acquisition automatically ends (the MSD source and detector are turned OFF).
- Pressure changes are ballistic (as fast as they can be established) rather than at the 99.99 psi/min maximum controlled inlet pressure program rate.
- Constant Flow mode can be used during the analysis. Negative flows (such as what happens during backflush) are not accepted as set points by 6890 GC software and firmware, so only pressure programs can be used during the run. However, pressure programs are not allowed when using Constant Flow mode (mixed modes are not allowed).
- Changes can be made to the analytical part of the method (involving, for example, pressures, temperatures, times, and ramps) without needing to change Post Run backflush set-points.
- Post Run conditions are executed even if a run is stopped. Runs that are stopped will have remaining components backflushed, thereby quickly and effectively readying the column for subsequent use.

Backflushing can be accomplished with any of the microfluidic devices listed in Table 1.

Table 1. Microfluidic Devices

Microfluidic Device	Accessory Kit	Option
QuickSwap no-vent for MSD	G3185B	885 6890 or 6850 instruments
Purged 2-way splitter	G3180B	889 6890 or 6850 instruments
Purged 3-way splitter	G3183B	890
Dean's switch for multidimensional heart cutting	G2855B	888 6890 or 6850 instruments

For MSD users, QuickSwap is of a high interest and was the gas-phase microfluidics device chosen for the examples shown here. QuickSwap attaches to the column end of the MSD transfer line and is supplied by a secondary pressure source, typically Auxiliary Pressure channel #5. A restrictor resides within the MSD transfer line to limit total flow to the MSD. The restrictor size is chosen based on what is appropriate for the analysis at hand and the MSD system being used. The analytical column attaches to the GC-oven side of QuickSwap. See Figure 1.

Typically, operational pressure for QuickSwap is between 1 and 4 psig, depending on the application and the chosen restrictor. One configures the "outlet pressure" of Column 1 (the analytical column) to be the set point pressure of the microfluidic device (for example, QuickSwap, Aux #5). Note that the 6890 and 6850 GC firmware only allow outlet pressures ≤4 psig. Column flow will then be correctly reflected in the setup and display screens. A higher inlet pressure will be needed to

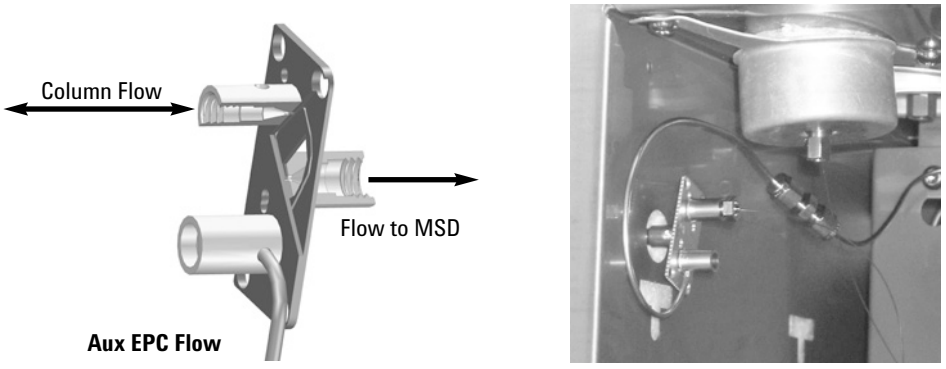

Figure 1. QuickSwap flow pattern on the left, and a QuickSwap installation in a 6890 GC on the right.

establish the same flow (similar retention time) as that of a column directly connected to the MSD because of the higher column outlet pressure.

To accomplish a backflush, the column outlet pressure must be raised higher than that of its inlet. For minimum backflush times, the inlet pressure should be minimized and the outlet pressure maximized. There are limits, however. The minimum controlled inlet pressure is limited by the backpressure created by the flow through the split vent trap (column backflush flow + inlet purge gas flow). 1.0 psig is usually achievable with a purge flow ≤50 mL/min under most backflush conditions, and was used in the examples shown here.

Column outlet pressure maximum during backflush is limited by the maximum allowable flow to the MSD when it is not acquiring data. The maximum allowable flow to the MSD depends on the type of vacuum pump. Because of the limited pumping capacity of diffusion pumps, backflush should only be done with turbopump systems. Practically, one must stay below an ion gauge reading of 10^{-3} torr. Table 2 provides estimates for maximum allowable flows based on pump type.

Table 2. Maximum Gas Flows for Turbopumps

Pump	Maximum He Flow
Standard turbo and performance turbo with dry pump	25 mL/min
Performance turbo	100 mL/min

In order to be allowed to set pressures for a backflush in Post Run, one must configure a second column (Column 2). One can simply repeat the configuration used for Column 1 (dimensions, column description, etc.) as Column 2, but instead of an inlet, one would select QuickSwap (Aux #5) as the inlet pressure source. Once this is done, one can set a high Post Run pressure for Column 2. The Post Run pressure for column 1 (the inlet) would be set low (for example, 1 psig).

How much time is needed to backflush?

It was found that for a typical column used for capillary GC-MS, the high-boilers ("late eluters") actually are backflushed first from the column, with the "least retained" components being the last to be backflushed. An example of this effect is shown in Figure 2. For this, ever-increasing backflush times were used, followed by reestablishment of forward flow to see what had not been backflushed from the column.

During the backflush experiments in Figure 2, the oven temperature was paused at 169 °C (the temperature at 10 min in the temperature program) for the duration of the backflush period. At the conclusion of each backflush, the temperature program was resumed. The ever increasing backflush periods are easily seen from the widening gaps starting at 10 min.

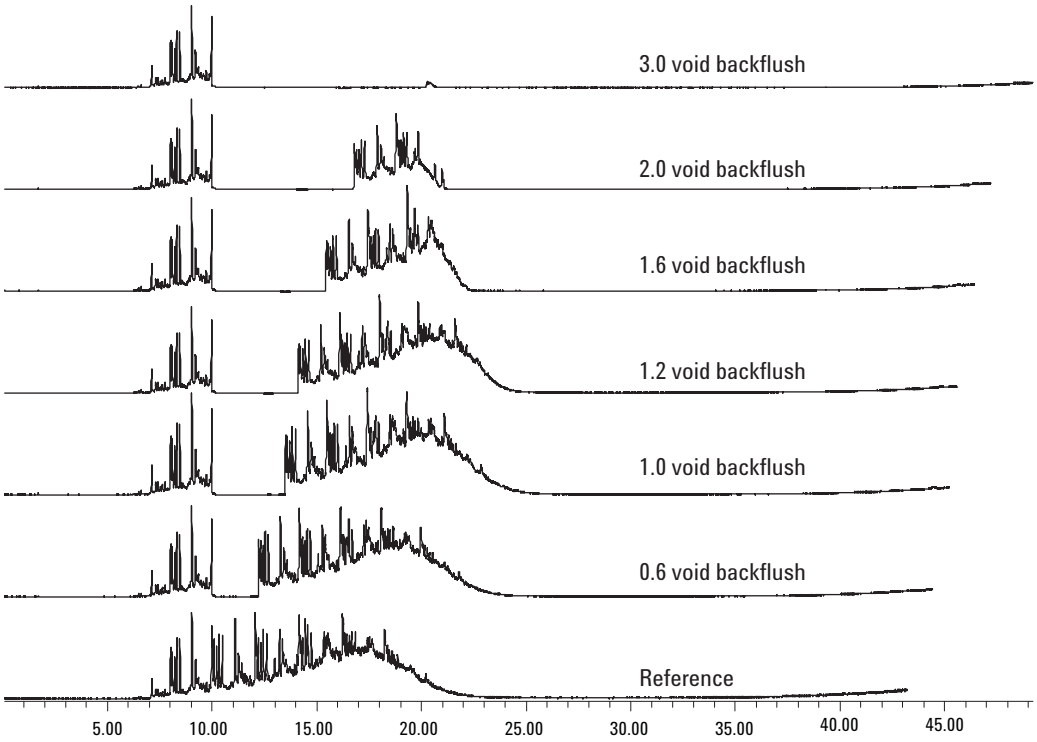

Figure 2. Successive chromatograms with increasing backflush times.

Actual void time was determined by injecting air under isothermal (169 °C) conditions, with inlet and outlet pressures the same as those used during backflush (only reversed).

As can be seen, a small amount of "least retained" components still remain after 3 void times. Something between 3 and 4 void times would be enough for the conditions used (10 °C/void time oven ramp rate). The minimum number of void times required to remove all components from the column depends on several factors, including, but not limited to:

- Temperature program rate
- Column dimensions
- Carrier gas type
- Pressure drop prior to backflush
- Pressure drop during backflush
- Manner of pressure change (programmed or ballistic)

Therefore, the simple rule for temperature-programmed analysis is that one should backflush for at least 5 void times. A void time (also known as holdup time) is determined using backflush conditions and a software tool such as Flow Calculator or Method Translator (available for download from Agilent website). Plug in the column dimensions, the oven temperature of the time backflush is started, the "inlet" pressure (that of the microfluidic device), and the "outlet" pressure (that of the inlet during backflush). Find the "holdup" or "void" time and multiply by 5. That is the time required to be sure all components have been
backflushed from the column.

First, set a Post Run time and temperature in the Oven screen. Shown in Figure 3, a temperature of 170 °C was set because that corresponded to the approximate oven temperature at 10 min in the original temperature program when the backflush was to occur. One and a half minutes was chosen for the backflush period because this corresponds to approximately 5 void times under the conditions chosen.

Once a Post Run time and temperature is established, one can set the Post Run pressures for both the inlet and QuickSwap from the Columns panel. See Figure 4. To set the backflush pressure for QuickSwap, select the radio button for Column 2 and set the pressure in the Post Run line at the bottom of the run table. Here, a pressure of 85 psi was selected because it will minimize the time required to backflush the column. Using Flow Calculator or Method Translator, one can input the value of 85 psi inlet pressure, 1 psi outlet pressure (15.496 absolute) and see that void time is approximately 0.3 min at an oven temperature of 170 °C.

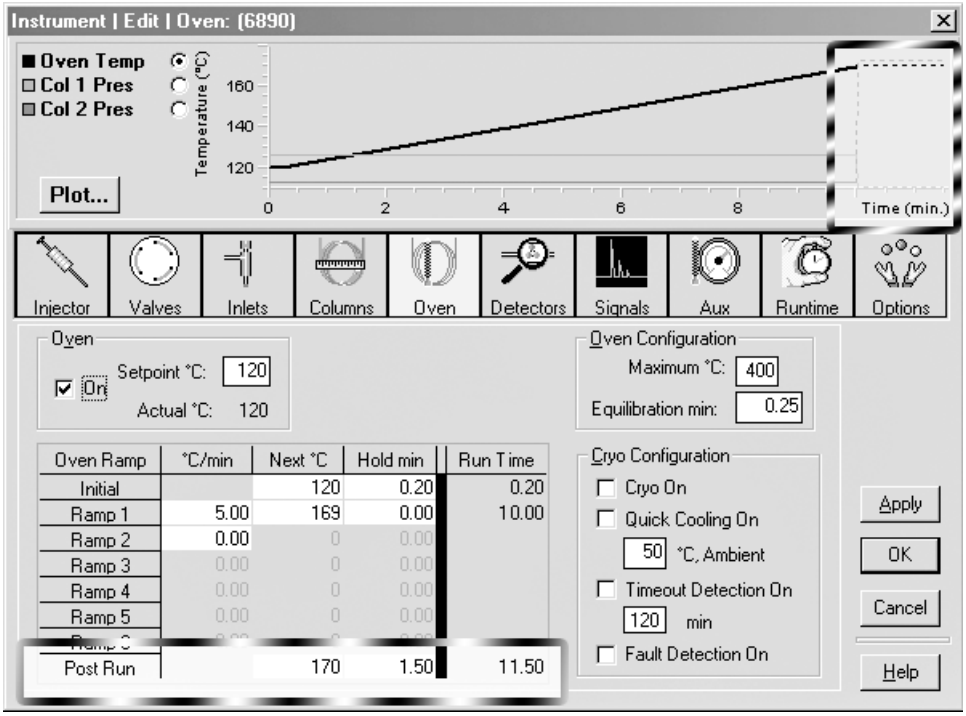

Figure 3. Oven screen, used to set up oven temperature ramp and Post Run time and temperature.

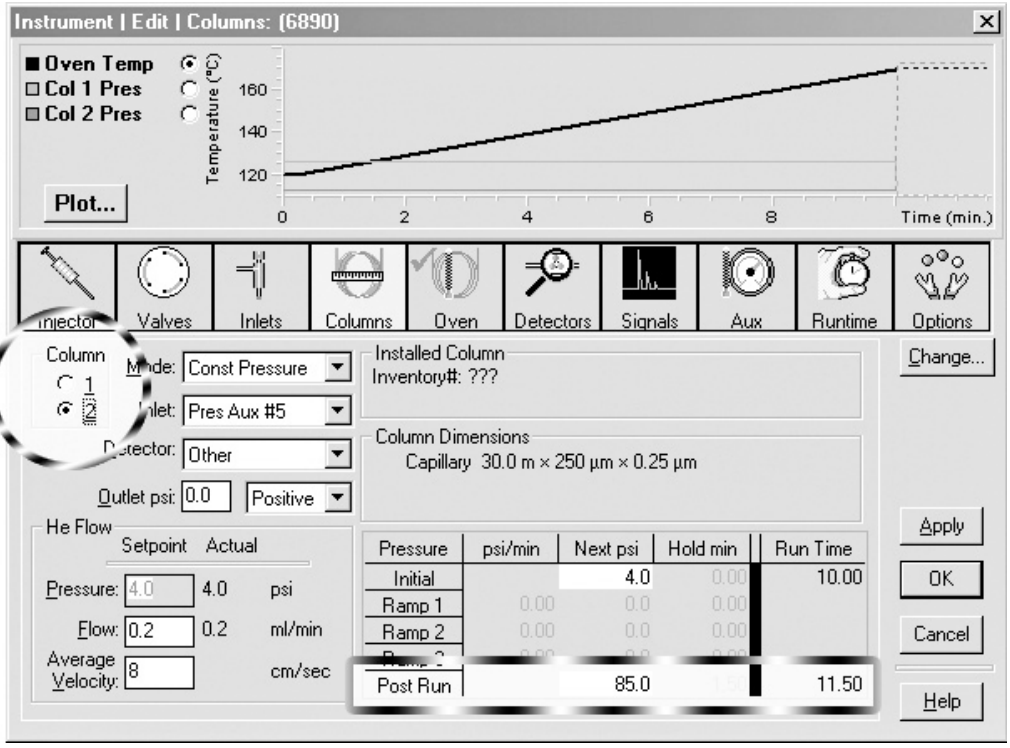

Figure 4. Columns screen, used to set up Post Run pressure and flow conditions.

Then, by clicking on the Column 1 radio button, one can set the low inlet pressure for backflush. See Figure 5. In this example, 1 psi was set. Remember to check that the low pressure can be controlled under backflush conditions and that sufficient split flow is set to sweep backflushed components out of the inlet to the split vent trap (30 < flow < 100 mL/min are recommended).

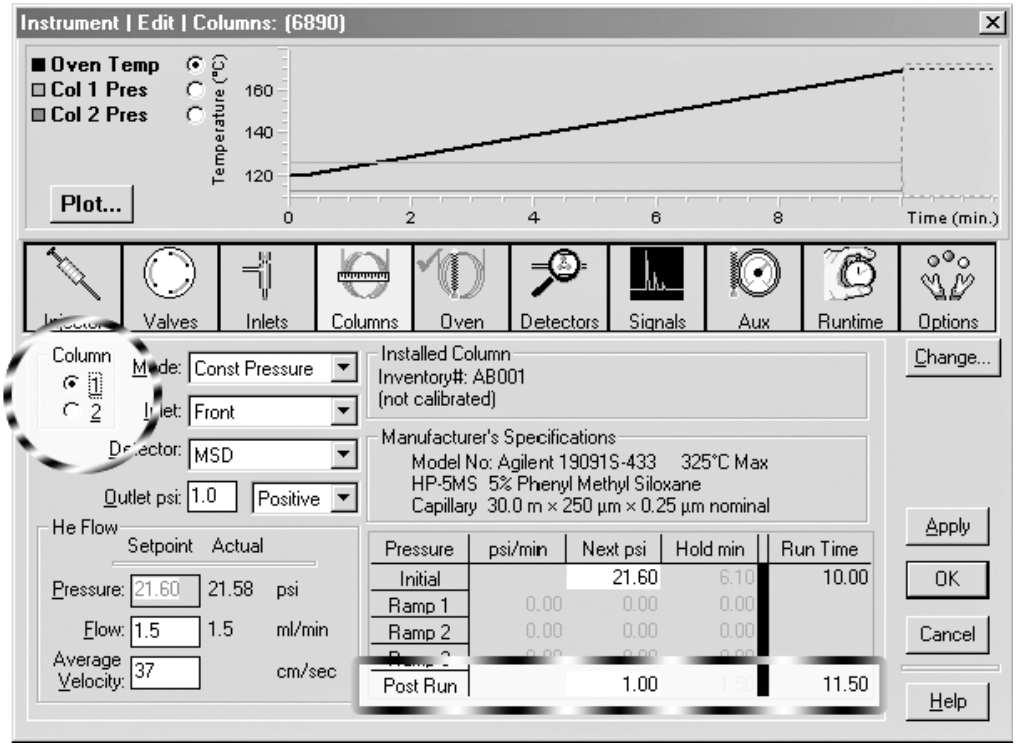

Figure 5. Columns screen, used to set a low inlet pressure for backflush.

Will backflushing through the inlet cause problems?

A common question from backflush neophytes is "Will I cause problems by backflushing high-boiling components back through the inlet?" Backflushing is only done with inlets that are purged, for example, split/splitless or PTV. These inlets have been designed to handle all sample components when doing split injections and when venting after splitless injection. To that end, these inlets have replaceable split-vent traps that are designed to handle whatever passes through the inlet. All sample components that make it into the column have already passed through the inlet once; there is no reason to believe that there would be a problem arising from them passing back through the inlet a second time, as long as a reasonable split vent (pure) gas flows to help backflushed components move to the split vent trap.

Gas Saver mode provides added independence to method

One way to ensure that a reasonable flow purges through the inlet during backflush is to use Gas Saver Mode. This achieves independence from both the conditions that are used during injection and the mode of injection (such as, splitless versus split). Here, we did a split injection at high split ratio with high associated split flow (617 mL/min). Gas Saver was activated at 3 minutes into the run, with a split flow reduced to 75 mL/min. If Gas Saver had not been used in this method, then the high vent flow associated with the high split ratio may have disallowed the pressure of the inlet to get down to the 1 psi set point (there is a small pressure drop through the split vent trap that might become notable at high split vent flow rates). See Figure 6.

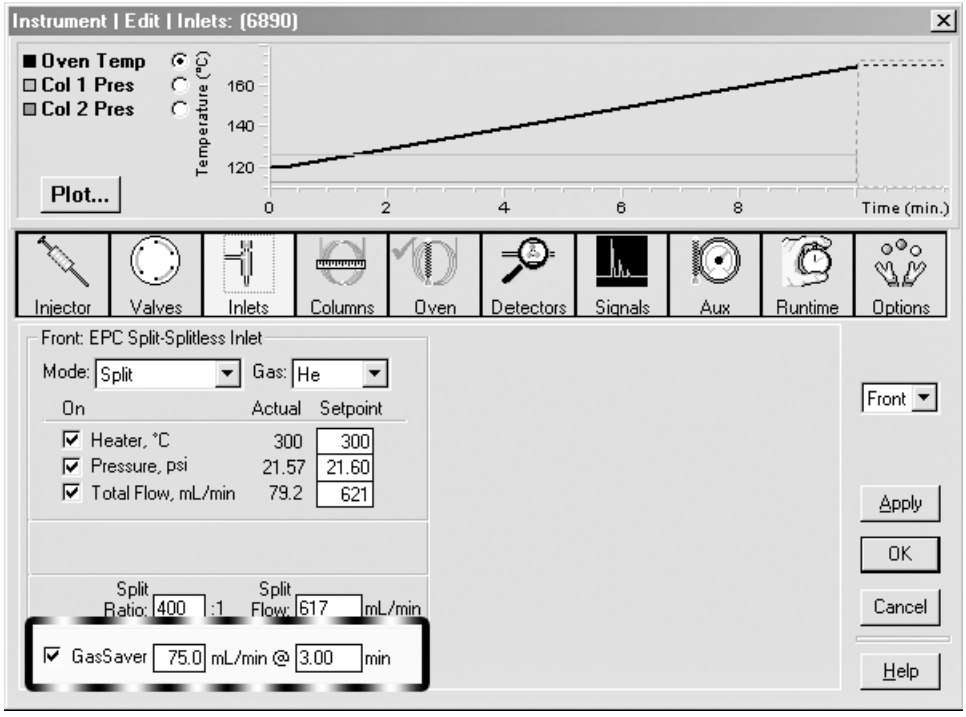

Figure 6. Inlets screen, displaying Gas Saver settings.

Instrumental

Below is an example listing of conditions used to perform a Post Run backflush (such as those shown in the Discussions section).

Oven

Initial temp:	120 °C (On)
Initial time:	0.20 min

Temperature Ramp for Original:

No.	Rate	Final temp	Final time
1	5.00	330	1.00
2	0.0 (Off)		

Post temp:	70 °C
Post time:	0.00 min
Run time:	43.20 min

Temperature Ramp for Backflush:

No.	Rate	Final temp	Final time
1	5.00	169	0.00
2	0.0 (Off)		

Post temp:	170 °C
Post time:	1.50 min
Run time:	10.00 min

Front Inlet (Split/Splitless)

Mode:	Split
Initial temp:	300 °C (On)
Pressure:	21.60 psi (On)
Split ratio:	400:1
Split flow:	617.1 mL/min
Total flow:	621.5 mL/min
Gas saver:	On
Saver flow:	75.0 mL/min
Saver time:	3.00 min
Gas type:	Helium

Column 1

Capillary column

Model number:	Agilent 19091S-433
	HP-5MS 5% phenyl methyl siloxane
Max temperature:	325 °C
Nominal length:	30.0 m
Nominal diameter:	250.00 µm
Nominal film thickness:	0.25 µm
Mode:	Constant pressure
Pressure:	21.60 psi
Nominal initial flow:	1.5 mL/min
Average velocity:	37 cm/sec
Inlet:	Front Inlet
Outlet:	MSD
Outlet pressure:	1.00 psi

Column 2

Capillary column

Nominal length:	30.0 m
Nominal diameter:	250.00 µm
Nominal film thickness:	0.25 µm
Mode:	Constant pressure
Pressure:	4.00 psi
Nominal initial flow:	0.2 mL/min
Average velocity:	8 cm/sec
Inlet:	Aux 5 Pressure Controller
Outlet:	(unspecified)
Outlet pressure:	0.00 psi

Aux Pressure 5

Description:	QuickSwap
Gas Type:	Helium
Driving Column 2	
Initial pressure:	4.00 psi (On)

Post Run

Post Time:	1.50 min
Oven Temperature:	170 °C
Column 1 Pressure:	1.0 psi
Column 2 Pressure:	85.0 psi

Front Injector

Sample washes:	2
Sample pumps:	3
Injection volume:	0.10 µL
Syringe size:	5.0 µL
Preinjection solvent A washes:	0
Preinjection solvent B washes:	0
Postinjection solvent A washes:	2
Postinjection solvent B washes:	0
Viscosity delay:	0 sec
Plunger speed:	Fast
Preinjection dwell:	0.00 min
Postinjection dwell:	0.00 min

5973 Performance Electronics MSD with Performance Turbo

General Information	
Tune file	atune.u
Acquisition mode	Scan
MS Information	
Solvent delay	0.00 min
EM absolute	False
EM offset	0
Resulting EM voltage	1776.5

Scan Parameters	
Low mass	28.4
High mass	800.0
Threshold	10
Sample number 1	A/D Samples 2
MSD Heated Zones	
MS quad	200 °C
MS source	300 °C

Results and Discussion

Two valved musical-instrument lubricants and a reference diesel fuel were analyzed. These were chosen for comparison because they had unique chromatographic and compositional features. A backflush time of 10 minutes was chosen. The analytical run ended at 10 min and was followed by a post-run backflush of 1.5 min. Based on the QuickSwap restrictor and MSD used, pressure conditions were determined that would minimize the time for 5 void times to complete. This was with QuickSwap pressure of 85 psi and inlet pressure of 1 psi.

For the following examples, a reference chromatogram was acquired with no backflush. Then, analysis was repeated with a backflush at 10 min. Finally, a blank was run under full analysis conditions to determine if any sample components were left on the column.

One valve oil product was unique in that it was a mixture of linear dimethyl siloxane homologs. As such, it was a nice reference sample for development of chromatographic method and backflush conditions. The backflush time of 10 min was chosen because it occurs before elution of the 7 silicon-unit siloxane homolog and is representative of analyses wherein only the volatile components are of analytical importance. See Figure 7.

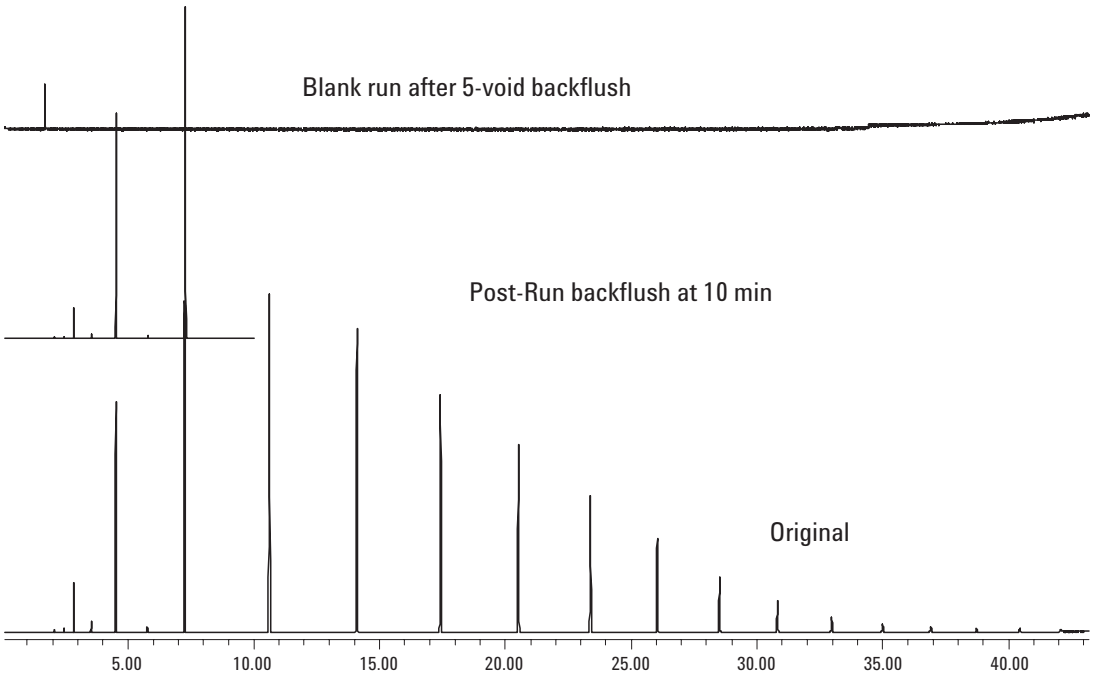

Figure 7. Example chromatograms of a valve oil composed of dimethyl siloxane homologs demonstrating backflush.

Notice from the blank run that the 1.5 min backflush (5 void times) was sufficient to remove all components that eluted after 10 min under the original conditions.

Another valve oil product was a petroleum distillation cut. The initiation of backflush at 10 minutes occurred in the thick of elution of sample components. As can be seen from the blank run, all remaining sample components were effectively removed from the column. See Figure 8.

A diesel sample was chosen to accentuate the removal of high boilers. The diesel had components eluting out past 25 min. The blank run after the backflush analysis demonstrates that all components were effectively removed during the backflush. See Figure 9.

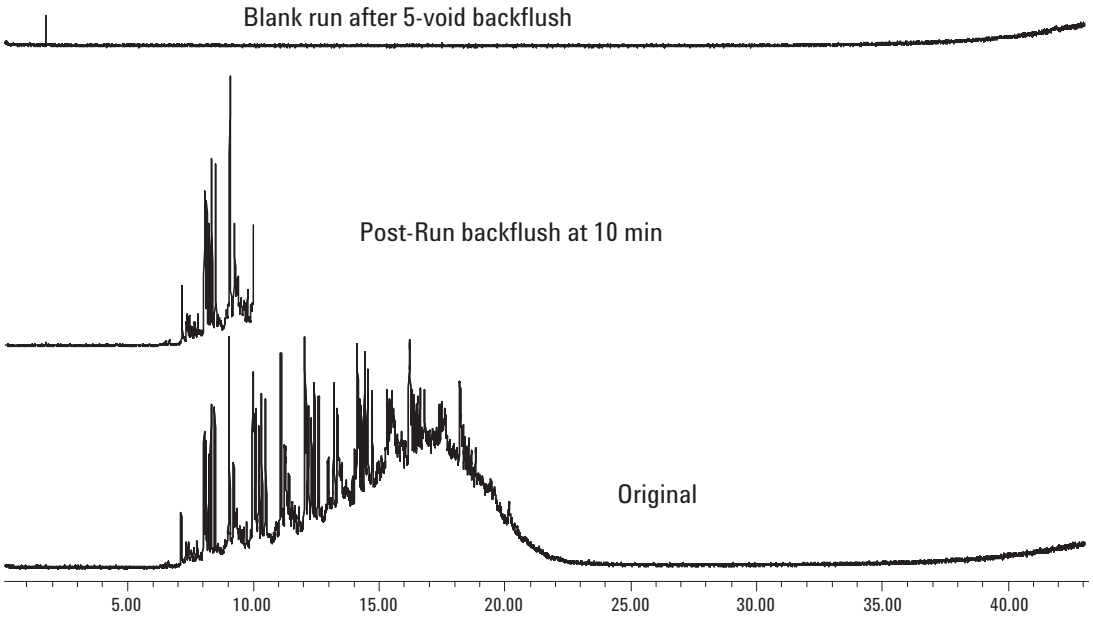

Figure 8. Chromatograms demonstrating backflush efficacy using a valve oil product composed of a petroleum distillation cut.

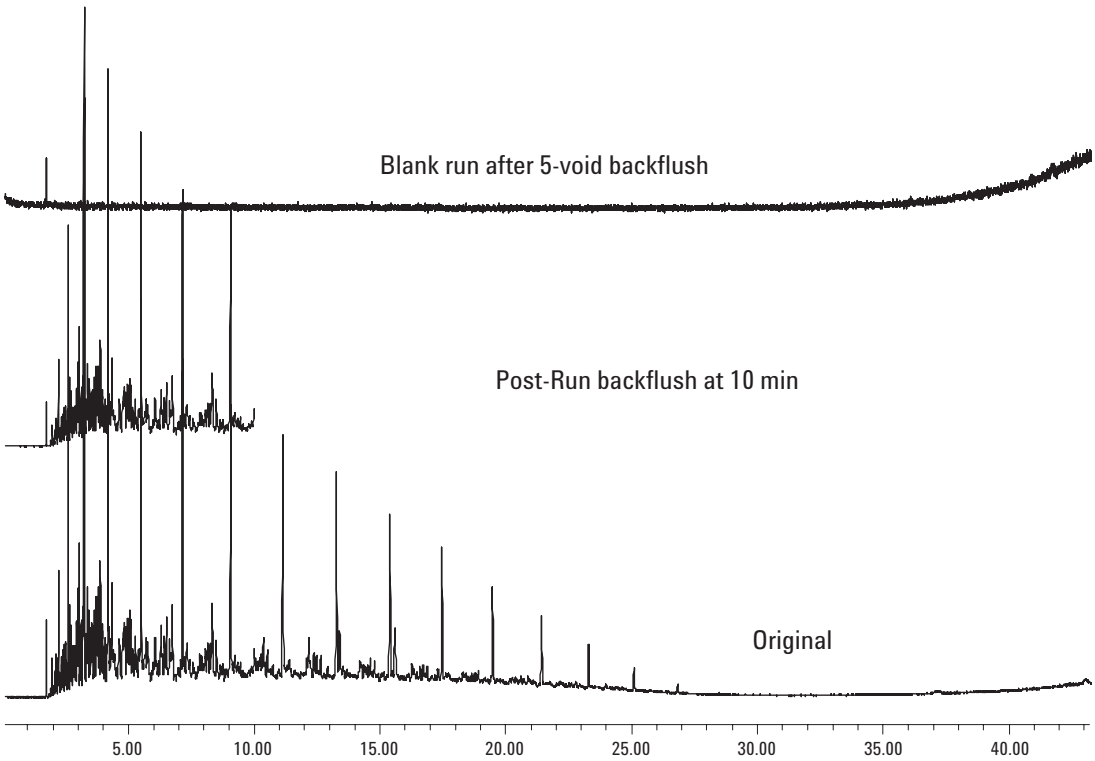

Figure 9. Example chromatograms of NIST 2724b reference diesel demonstrating backflush efficacy.

Time Savings

For the examples shown, cycle time was improved by both reducing run time and by stopping the oven temperature program at the time of backflush. This allowed the oven to cool from a lower temperature to starting conditions, saving time. See Table 3.

Table 3. Example of Time Saved Using Backflush

	Run time (min)	Cool down time (min)	Total (min)
Original	43.2	3.47	
Backflush	11.5	1.90	
Savings	31.7	1.57	33.27

Approximately 31.5 min run time was saved and another 1.5 min during cool down, for a total savings of approximately 33 min. If one were to need to run multiple samples, it is clear that lab productivity would significantly increase by incorporating a backflush.

Constant Flow Mode

A similar method was developed with basically the same conditions as those used earlier, except that 1 mL/min Constant Flow mode was employed. When in Constant Flow mode, the setup screens for Post Run backflush are slightly different than for Constant Pressure mode. The differences are highlighted below. See Figures 10–12.

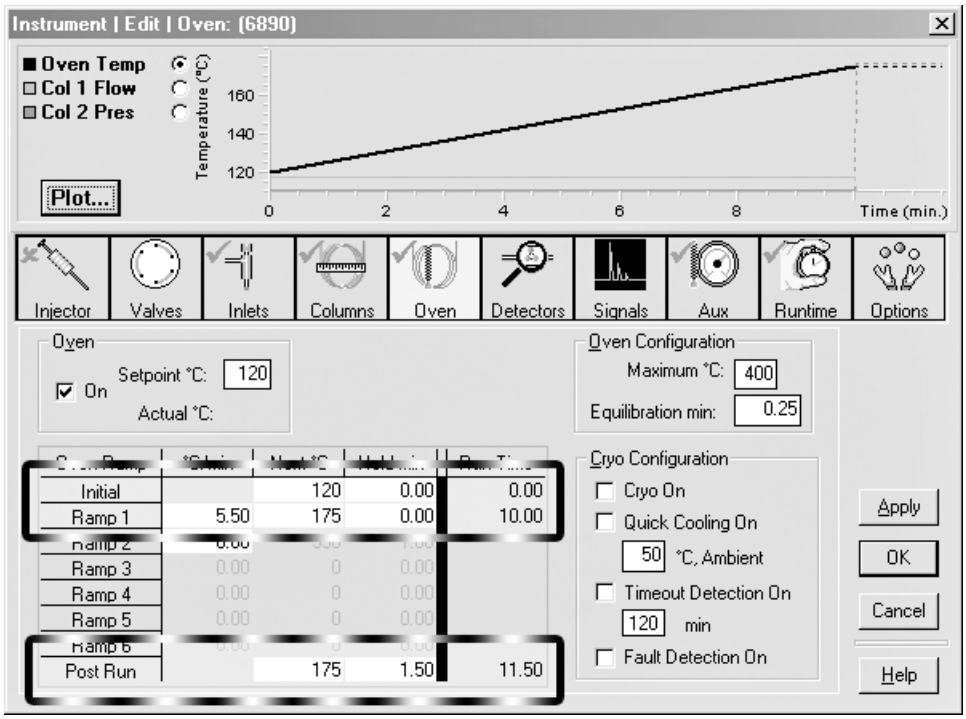

Figure 10. Oven setup screen for Constant Flow application.

First, the initial hold time was set to 0.0 min (0.2 min originally) for no other reason but that the initial hold was unnecessary. The temperature ramp rate was increased to 5.5 °C/min instead of the 5.0 °C/min used originally. This combination of change in initial hold and in ramp rate meant that the desired 10 min end of run/initiation of backflush corresponded to an oven temperature of 175 °C instead of the 169 °C in the Constant Pressure example.

For Post Run backflush in Constant Flow mode, Column 1 set points have a special requirement because the carrier gas terms are specified in flow instead of pressure. To ensure that the inlet pressure drops during backflush, one must ensure that the "column outlet pressure" is set to the ≤4.0 psi value you choose for the inlet backflush conditions (1 psi in this example) and set the value for column flow during backflush to 0.0. The system will then use the "Outlet" pressure set point as the inlet pressure during Post Run.

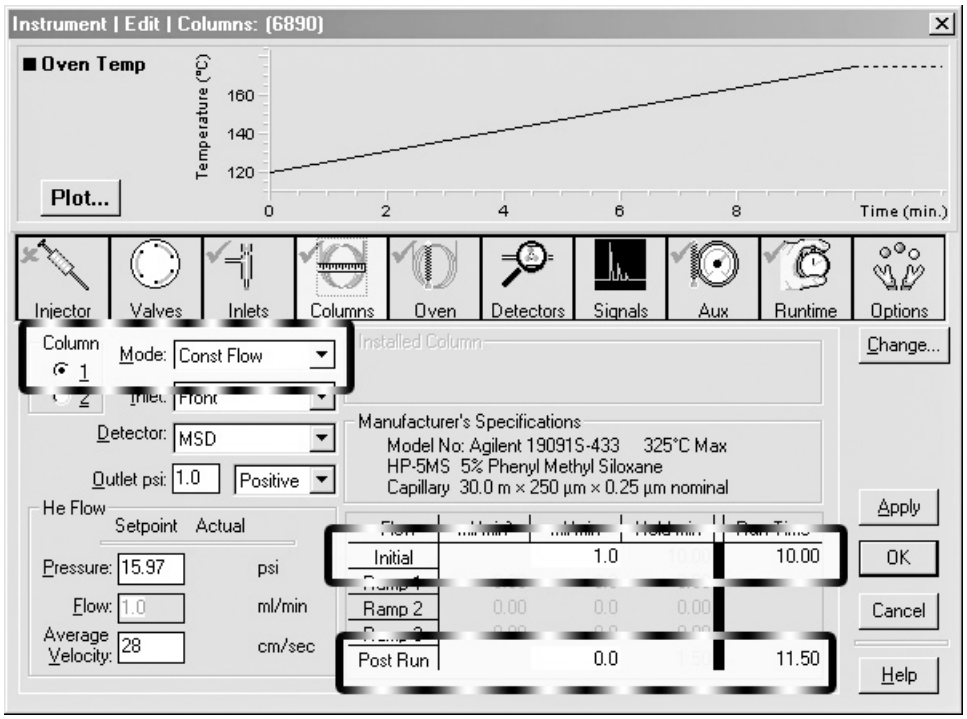

Figure 11. Columns screen for Constant Flow setup.

For Column 1, a 1 mL/min Constant Flow was used.

“Column 2” configuration is the same as in the Constant Pressure case. Constant Pressure mode should be selected, with QuickSwap as the Aux #5 inlet. This will allow a backflush pressure to be set during Post Run.

In this example, 1 psig was used as the pressure for analysis (the same as what was entered as Outlet Pressure for Column 1). A Post Run pressure of 85 psig was entered just as in the Constant Pressure example.

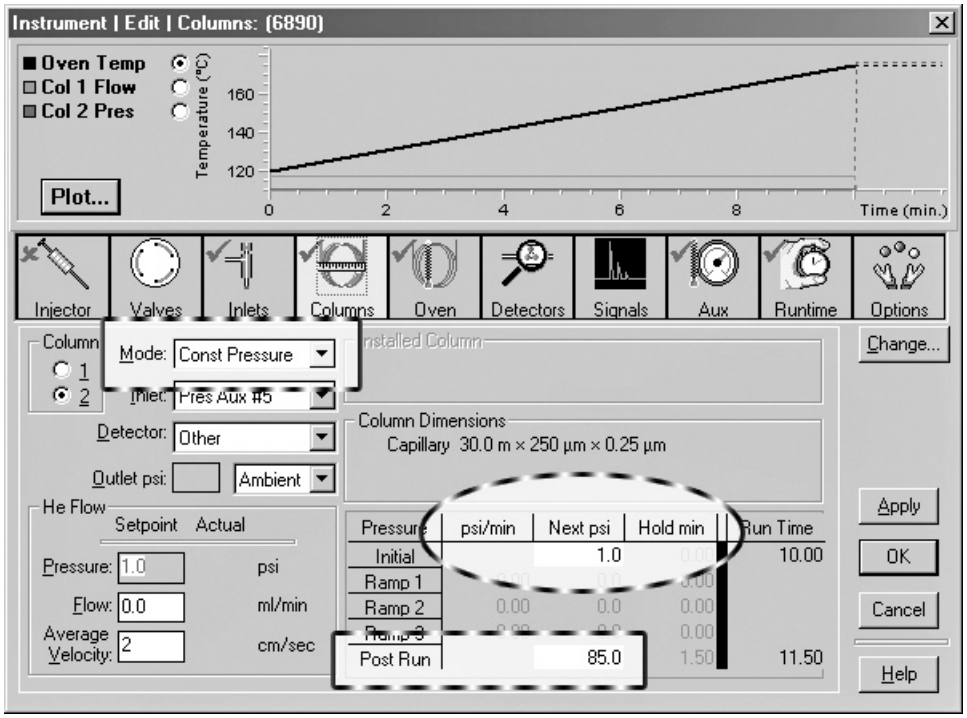

Figure 12. Columns screen for setting initial and Post Run pressure in Constant Pressure mode.

Some results from the above Constant Flow analysis and backflush conditions are shown in Figure 13.

For the homologous series of dimethyl siloxanes in Figure 13, the 1.5 min backflush (approximately 3.3 void times) was clearly sufficient to backflush all components remaining in the column at the conclusion of the 10 min run. This is confirmed in the following example of NIST 2724b diesel fuel. See Figure 14.

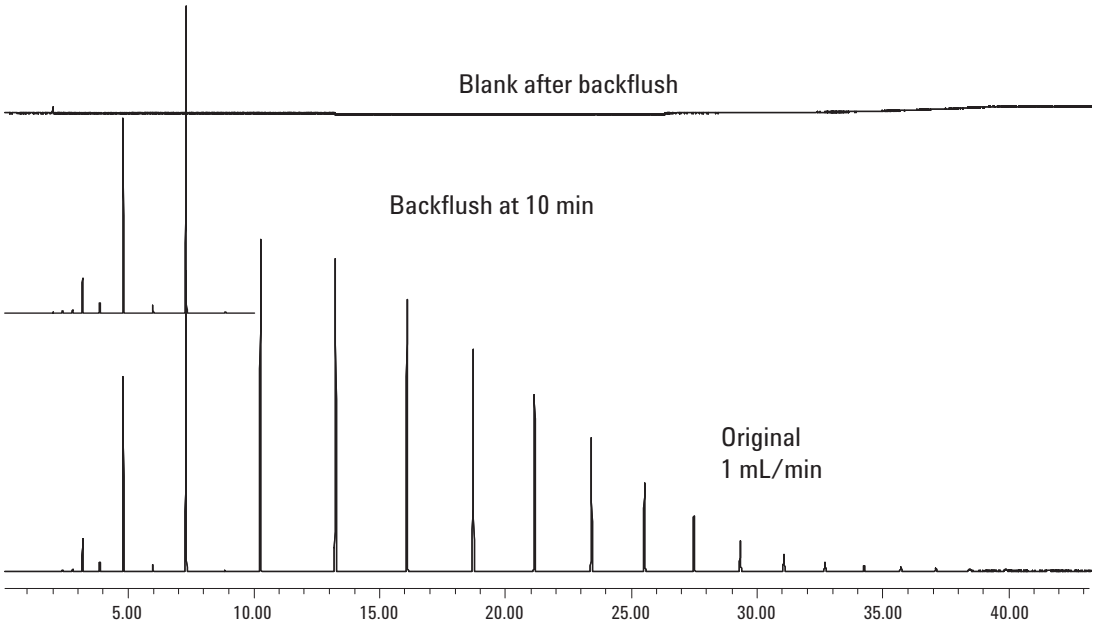

Figure 13. Chromatograms of dimethyl siloxane homologs analyzed under Constant Flow mode conditions and backflush.

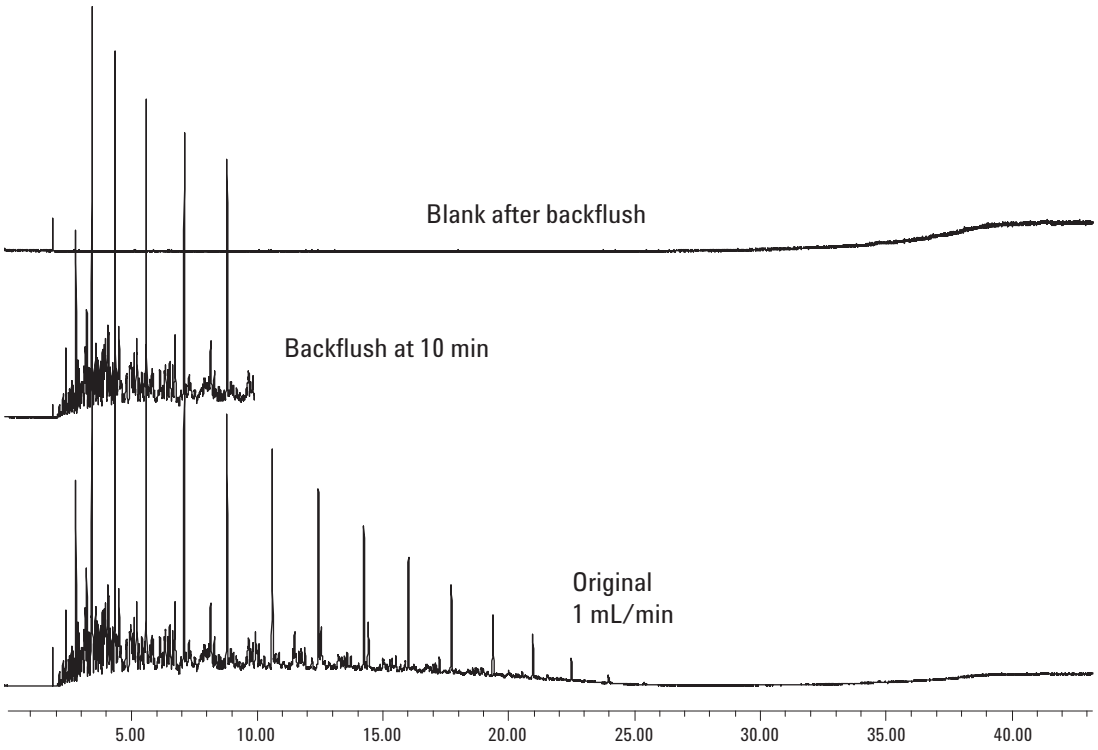

Figure 14. Backflush applied to diesel fuel sample NIST 2724b, analyzed under Constant Flow mode conditions.

Figure 15 is an expanded plot of the diesel fuel example shown in Figure 14. Notice that the baseline on the subsequent blank run after backflush is very clean. This shows that in addition to cycle time improvements, backflushing is an excellent way of improving overall analysis quality by removing all potential ghost peaks emanating from prior sample analyses.

Summary

A simple way to perform backflush with gas-phase microfluidic devices is described and demonstrated using the Agilent 6890 gas chromatograph.

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By selecting the microfluidic pressure source as the "inlet" for "Column 2" in the Column Configuration screen, one can then set a backflush pressure and time in Post Run. Several advantages ensue, including the ability to backflush in methods that use Constant Flow mode.

For More Information

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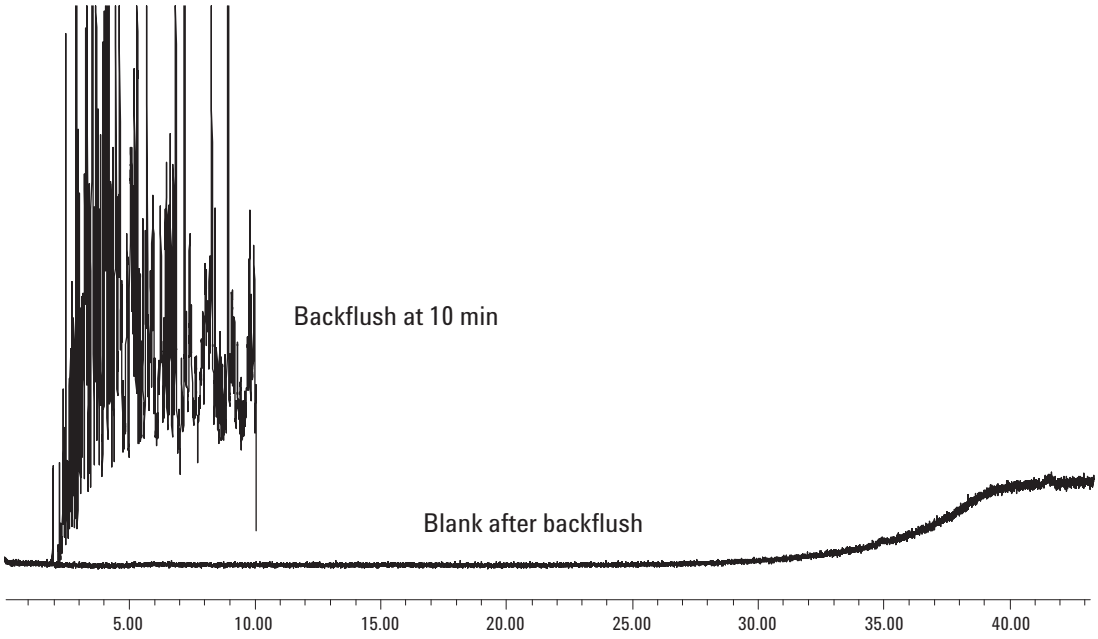

Figure 15. Expanded plot of the diesel fuel example showing excellent clean baseline after backflush.

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