The Use Of Automated Backflush on the 7890A/5975A GC-MS System

Setup Example Using Biomarkers

Application

Hydrocarbon Processing

Authors

Courtney Milner and Russell Kinghorn
BST International
41 Greenaway Street
Bulleen, VIC 3105
Australia

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

Abstract

The use of column backflushing in capillary gas chromatography has been sparingly used over the years, primarily due to its added complexity and demands on data system control for use in automated/routine laboratories. The potential of backflushing has been demonstrated in a gamut of applications from environmental, refining, and residues in food where high boiling point and complex matrices are commonplace. This application describes the setup, use and tricks and tips for implementing backflushing on the 7890A/5975A GC-MS system, with the specific example of monitoring biomarkers in crude oil.

Introduction

Until recently, the implementation of capillary column backflush has required a cumbersome conglomeration of parts and separate controllers. The nonintuitive combination of manual pressure regulators, timers, stand-alone valve controllers, and experimentally determined GC setpoints conspired against chromatographers with interest in attempting it. The few who were successful on a given system would rarely consider implementing backflush routinely, even if their efforts met with success the first time. Considerable improvements in implementation of backflush became available with the 6890 GC and 6890/5973 GC MSD systems [1–6]. With the release of the Agilent 7890A/5975A GC-MS system with ChemStation version E.01.00, implementation of capillary column backflush has never been easier. Full electronic control of all backflush parameters is possible in a manner never before offered in a GC-MS system. At the same time, major advancements in fluidic devices now greatly improve the mechanical aspects of implementing routine capillary column backflush.

The benefits of backflush in capillary gas chromatography are myriad:

- More samples/day/instrument
- Better quality data
- Lower operating costs
- Less frequent and faster GC and MSD maintenance
- Longer column life
- Less chemical background

When a mass spectrometer (MS) is employed, a key additional benefit is that backflushing high-boiling components from the capillary column and out of the inlet to waste (usually via a split/splitless inlet or PTV) prevents them from being deposited in the ion source. This improves detection limits for sub-

sequent samples (less background) and greatly increases the number of samples that can be run before ion source cleaning is required.

As illustrated by the many prior examples (see references), backflush technology is relevant in many areas, including the geochemical/hydrocarbon area, wherein samples generally span a large boiling point range and analyses are typically long yet contain only one or two compounds of specific interest. Biomarker determination in crude oils is such an example where backflush can provide several significant benefits. Analytical run times are greatly reduced; high-boiling, less important components are removed from the system and prevented from reaching the mass spectrometer; and the column is exposed to much lower final oven temperatures. In this application, backflushing on a 7890A/5875 system is presented to show the new setup screens and increased ease of setting up backflush conditions.

Experimental

Table 1 shows the analytical conditions used in a traditional GC-MS analysis of crude oil. The boiling point range of this oil sample is very wide (spanning C_4 to C_{50}), with the target components of interest eluting around 30 minutes in a 74-minute analysis (see Results and Discussion).

Table 1. Original Analytical Method Conditions

Column	HP5-MS 30 m × 0.25 µm × 0.25 µm; part number 19091S-433
Carrier gas	Helium, constant flow mode; 1.2 mL/min
Split/splitless inlet	340 °C, split 30:1
Oven	50 °C (1 min) → 320 °C at 5 °C/min hold for 20 minutes
Analysis time	74 min
Sample	Crude oil in CS_2, 1-µL injection
MSD	Scan = 35–700 u Samples = 2^2 Source = 300 °C Quad = 150 °C Transfer line = 320 °C

A 3-way purged splitter (Agilent part number G3183B) Capillary Flow Technology device was used for this application, in part to demonstrate its flexibility. The device has a purge and four connections (Figure 1). As used herein, only two of the ports were used, one for the column outlet (port 3) and the other for the restrictor to the MSD (port 4). The other two ports (1 and 2) were plugged with solid wire instead of column connections. Very reliable connections are a feature of Capillary Flow Technology devices because of the use of soft metal ferrules. Care needs to be taken when making these connections, but the process is very straightforward and easily learned. The manuals provided with the various Capillary Flow Technology devices contain explicit instructions.

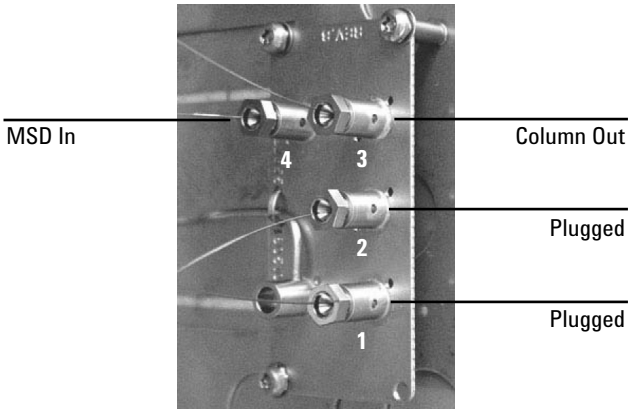

Figure 1. 3-way purged splitter. The column outlet was attached to port 3 and the MSD restrictor was attached to port 4. Ports 1 and 2 were plugged.

Careful consideration must be made before a restrictor internal diameter (ID) and length are chosen for a backflush application. Parameters such as detector type (atmospheric pressure versus vacuum), vacuum pumping capacity (for example, diffusion pump, standard and performance turbo molecular pumps), and Capillary Flow Device pressure and desired split ratio (if splitting detector effluent to multiple detectors) must all be taken into consideration. Such considerations are described in detail in a previous application [1].

In this example with a 5975A MSD, a deactivated restrictor of 1 m × 0.18 mm id (such as Agilent part number 160-2615-1) provided a balanced match for this application.

Table 2 shows the analytical conditions used for this backflush application, and Figures 2 to 7 show the software setup screens for the 7890A/5975A GC-MS system with MSD ChemStation revision E.01.00 software.

Table 2. Backflush Analytical Method Conditions

Column	HP5-MS 30 m × 0.25 µm × 0.25 µm part number 19091S-433
Carrier gas	Helium, constant flow mode; 1.2 mL/min
Split/splitless inlet	340 °C, split 30:1
Oven	50 °C (2 min) → 205 °C at 5 °C/min no hold
Backflush restrictor	1m × 0.18 mm deactivated capillary column tubing
Aux 3 pressure	1 psi
Backflush pressure	75 psi
Analysis time	31 min + 5.47 post run at 205 °C Total time = 36.47 min
Sample	Crude oil in CS_2, 1-µL injection
MSD	Scan = 45–700 u Samples = 2^2 Source = 300 °C Quad = 150 °C Transfer line = 320 °C

By setting up the required analytical column and restrictor with the correct inlet and outlet connections (Figures 2 to 4), the software automatically calculates the inlet pressure required to maintain analytical column flow. By selecting the "evaluate" button (Figure 5), the backflush pressure required for a predetermined number of column "sweeps" or "void volumes" is calculated, displayed for review, and uploaded to the analytical method along with the GC oven hold time (Figures 6 to 8). As a general guide, 10 void volumes is effective for most applications. As few as two void times can effectively backflush a capillary column under certain conditions (for example, high oven ramp rates prior to backflush). However, some applications may require more than 10 void volumes to backflush everything, so the onus is on the user to validate appropriately backflush times for a given application. A blank run (that is, pure solvent as sample) following a sample run with backflush is helpful during method validation to see that all components are effectively removed from the analytical column by the chosen backflush conditions.

In this application, a 75 psi backflush pressure resulted in a backflush flow of approximately 6 mL/min through the capillary column and 75 mL/min into the performance turbo molecular pump. A figure shown later in this application illustrates that these backflush conditions were effective.

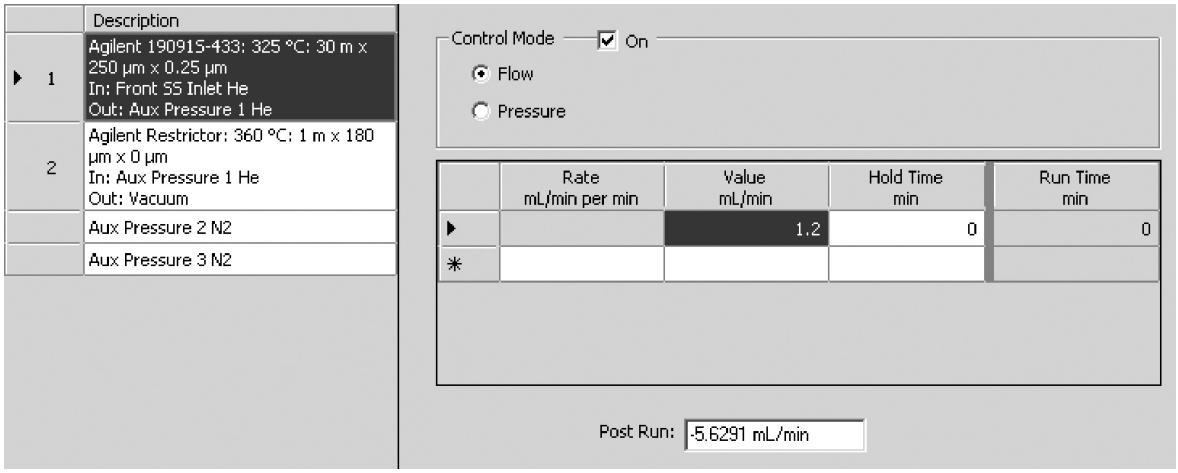

Figure 2. Software setpoints for the analytical column.

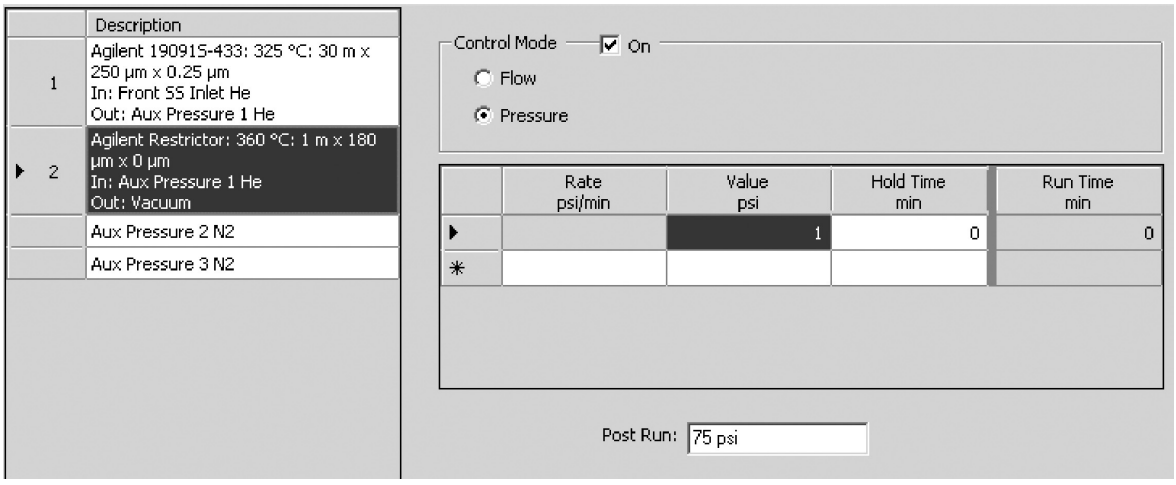

Figure 3. Software setpoints for the restrictor to the MSD.

	Description
▶ 1	Agilent 19091S-433: 325 °C: 30 m x 250 µm x 0.25 µm In: Front SS Inlet He Out: Aux Pressure 1 He
2	Agilent Restrictor: 360 °C: 1 m x 180 µm x 0 µm In: Aux Pressure 1 He Out: Vacuum

Figure 4. Column inlet and outlet conditions.

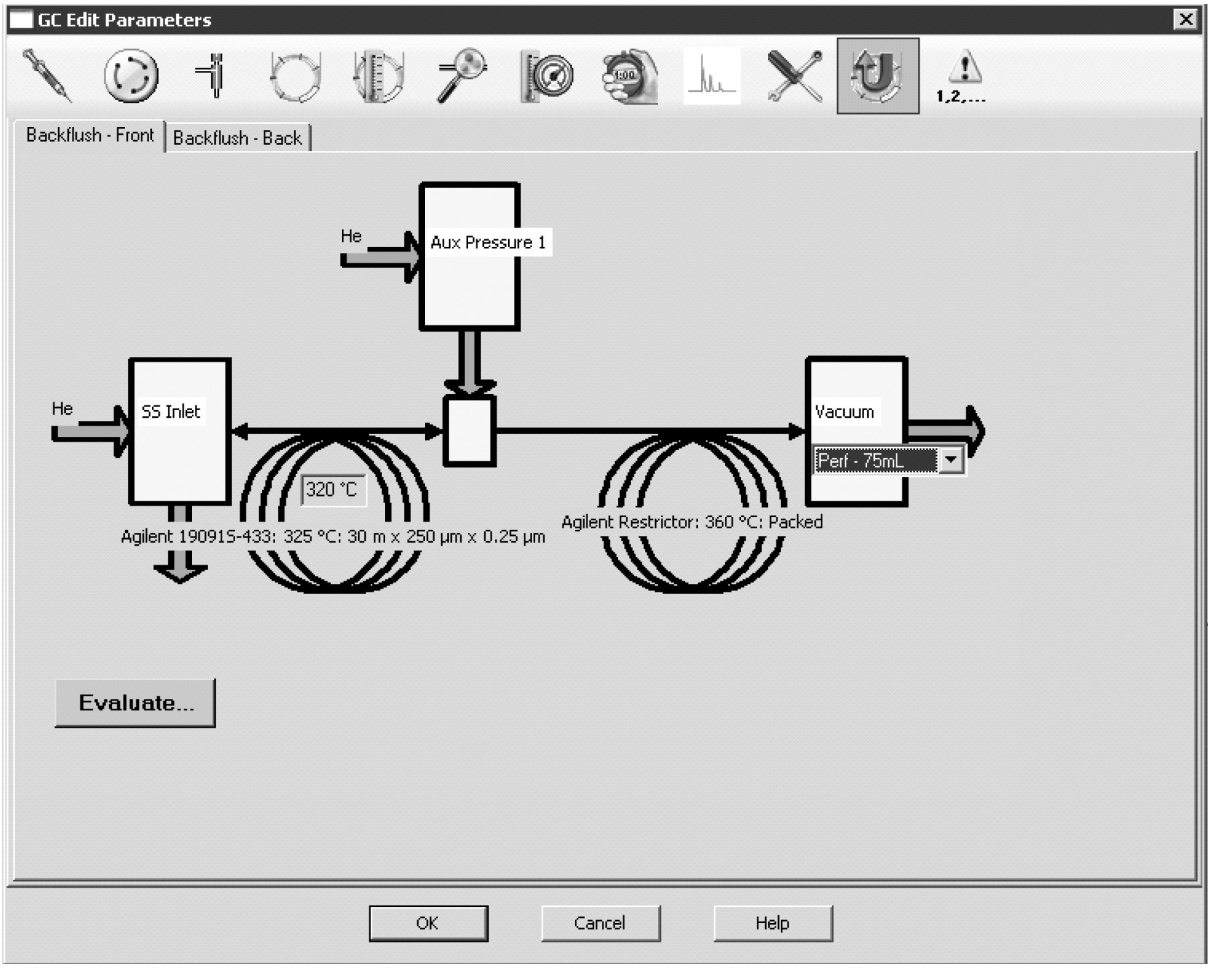

Figure 5. Interactive setup for backflush conditions in ChemStation.

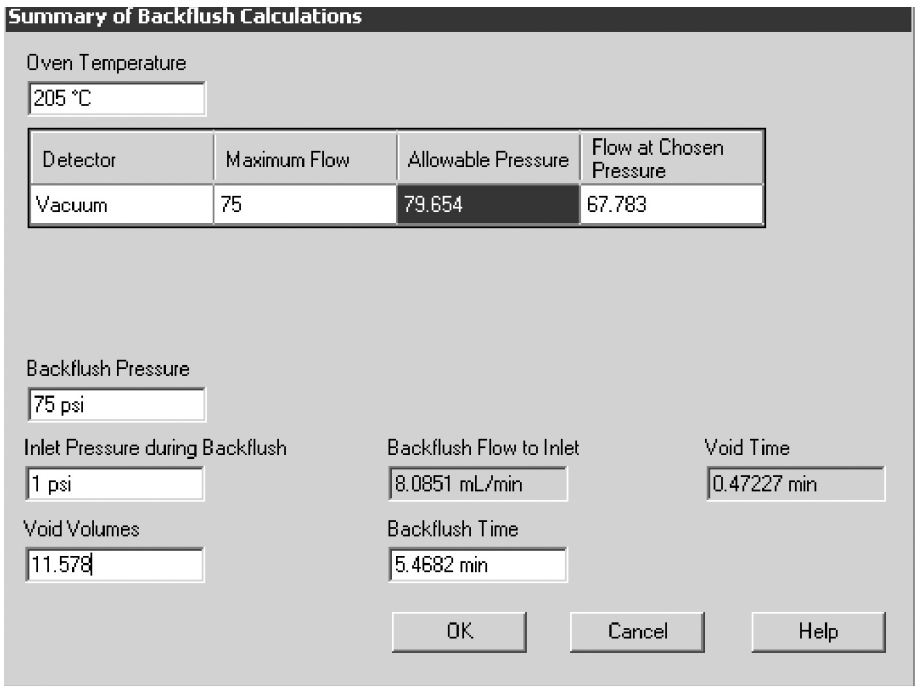

Figure 6. Conditions uploaded to method setpoints.

Results and Discussion

The profile seen in Figure 9 is typical of many crude oils with complex distribution over a large boiling point range, with a large number of unresolved components. Another feature is the long tail of high-boiling components that must be eluted after the compounds of interest. Figure 10 illustrates the three components of interest: a series of three methylbenzothiophenes through an extracted ion chromatogram (EIC) of *m/z* 198.

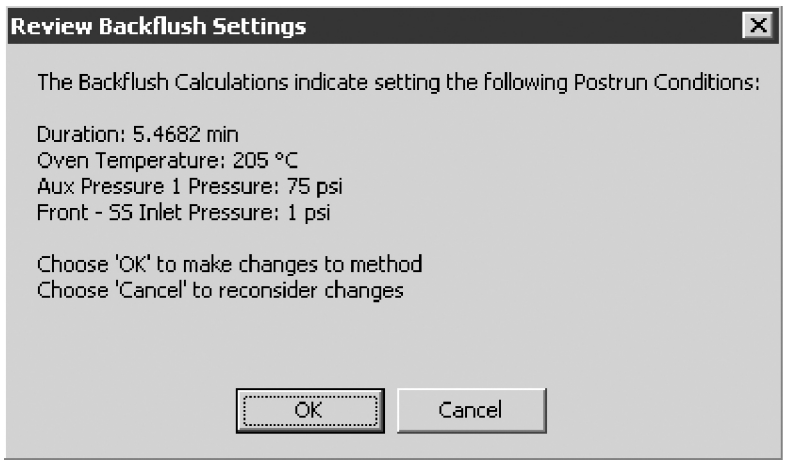

Figure 7. Conditions uploaded to method setpoints.

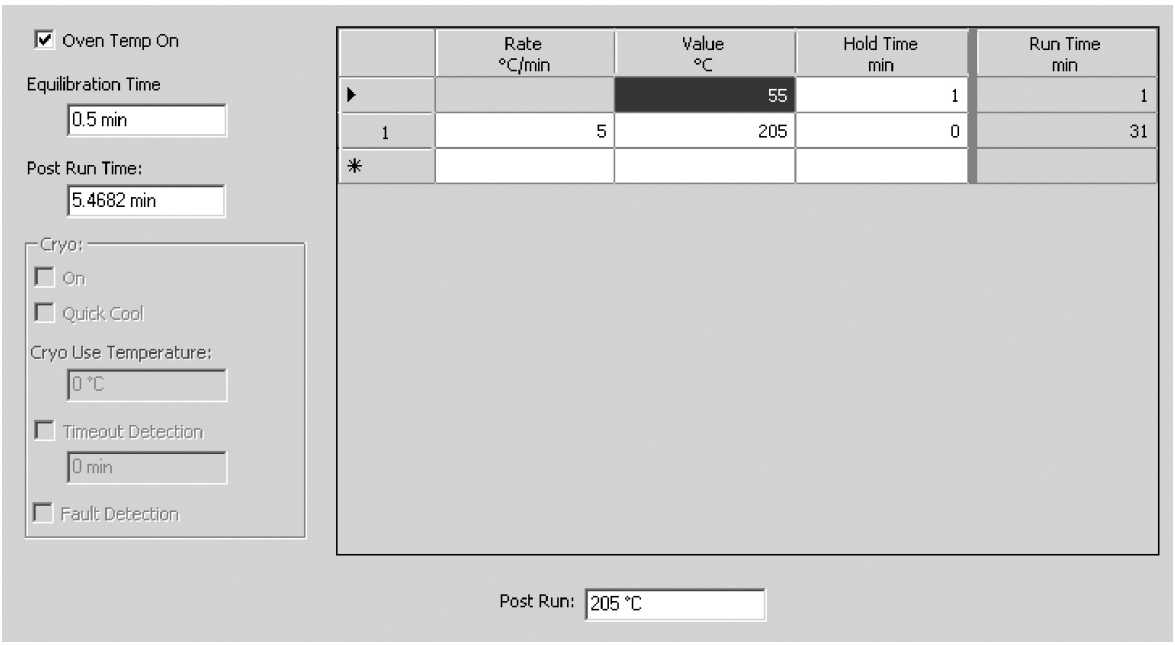

Figure 8. Note that the post-run time has been updated automatically.

Figure 11 shows the chromatogram from another run that includes a backflush immediately after the benzothiophenes had eluted.

In order to validate the efficacy of the backflush, a full-length analysis was undertaken with pure solvent immediately after the backflush run. It

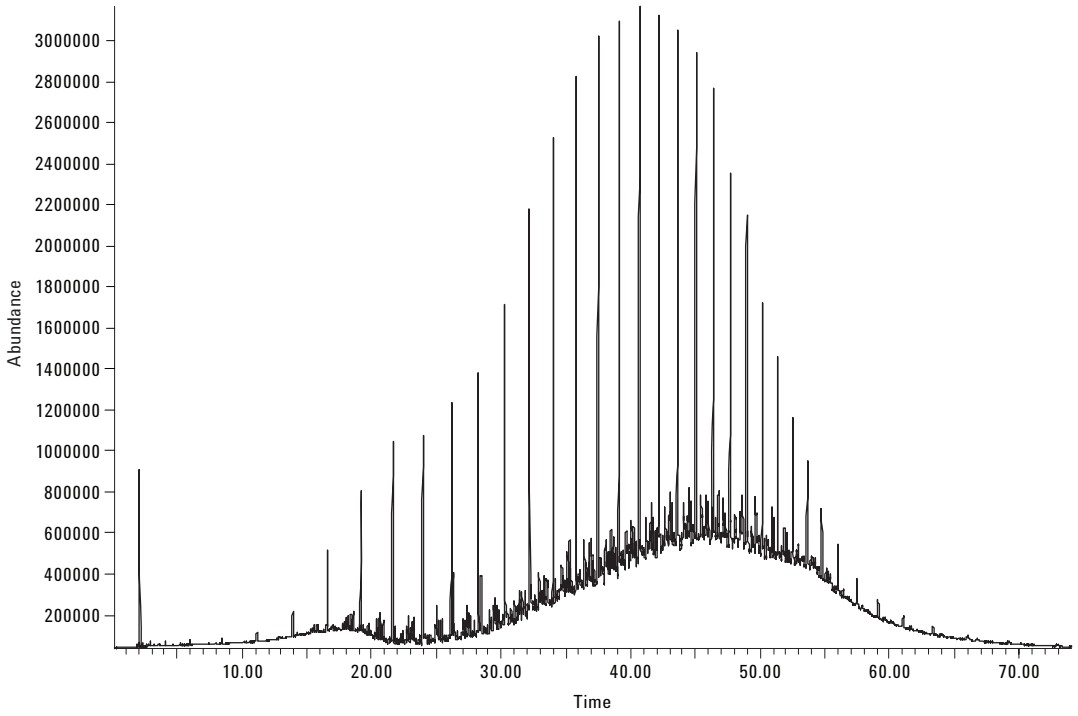

Figure 9. Total ion chromatogram (TIC) of normal analysis. Peaks of interest (benzothiophenes) are obscured by the high concentration of hydrocarbons.

can be seen from Figure 12 that no residual high-boiling components remained in the capillary column after the backflush from this blank solvent injection. Also, there are no residual biomarkers at *m/z* 198. All material (representing over 50% of the sample introduced into the column) eluting after 31 minutes was effectively backflushed.

Figure 13 shows the EIC (*m/z* = 198) for both the normal run and the backflushed runs, showing that no material was lost and retention times were not changed by implementing the backflush.

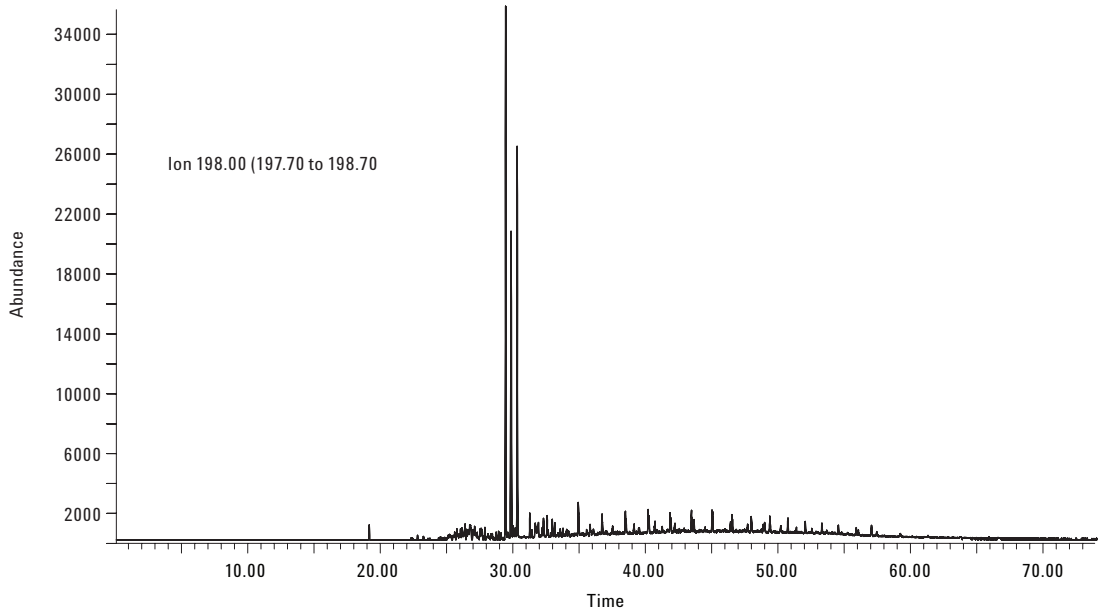

Figure 10. EIC of *m/z* 198 ion. The three methylbenzothiophene peaks of interest at approximately 30 minutes are easily visualized.

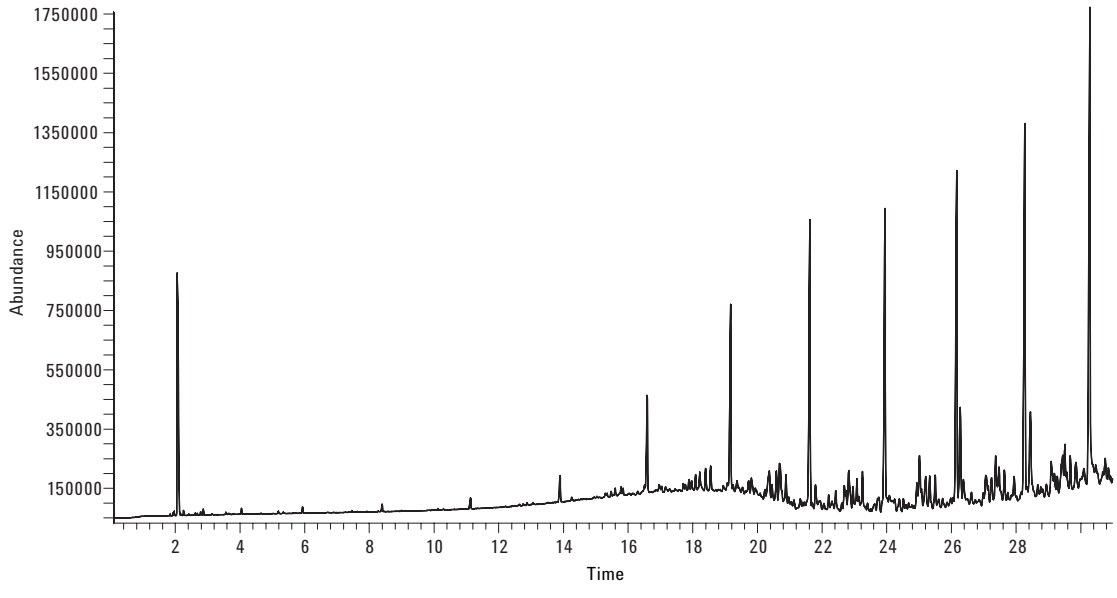

Figure 11. TIC of backflush run; run switched to backflush mode at 31 minutes.

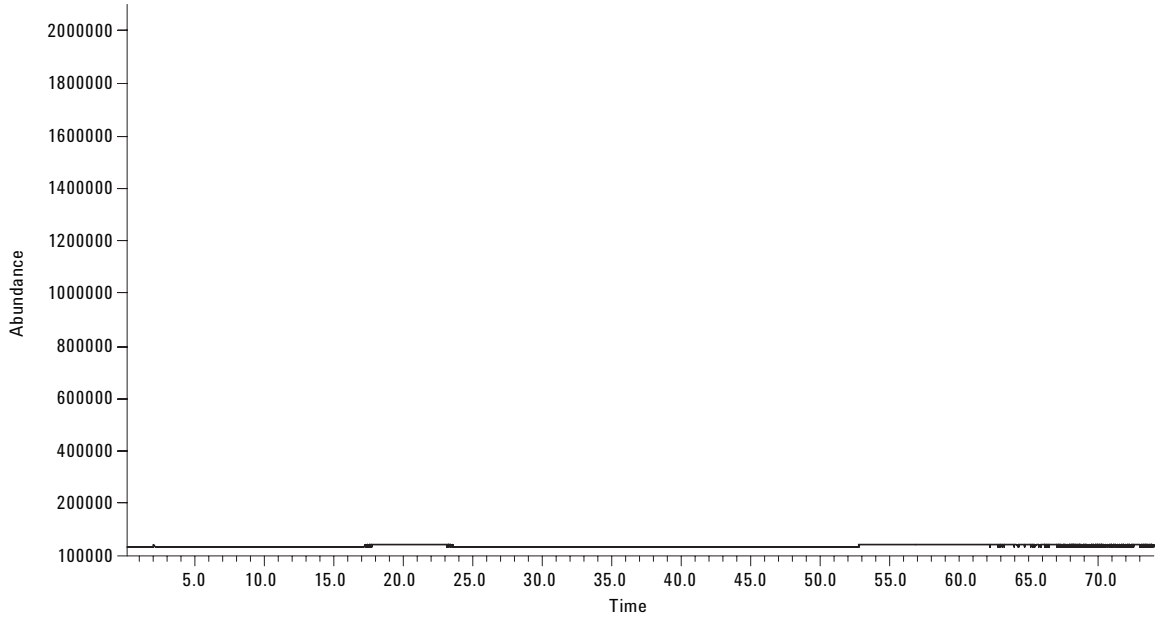

Figure 12. TIC of full run after the backflush with inset of the EIC of *m/z* 198.

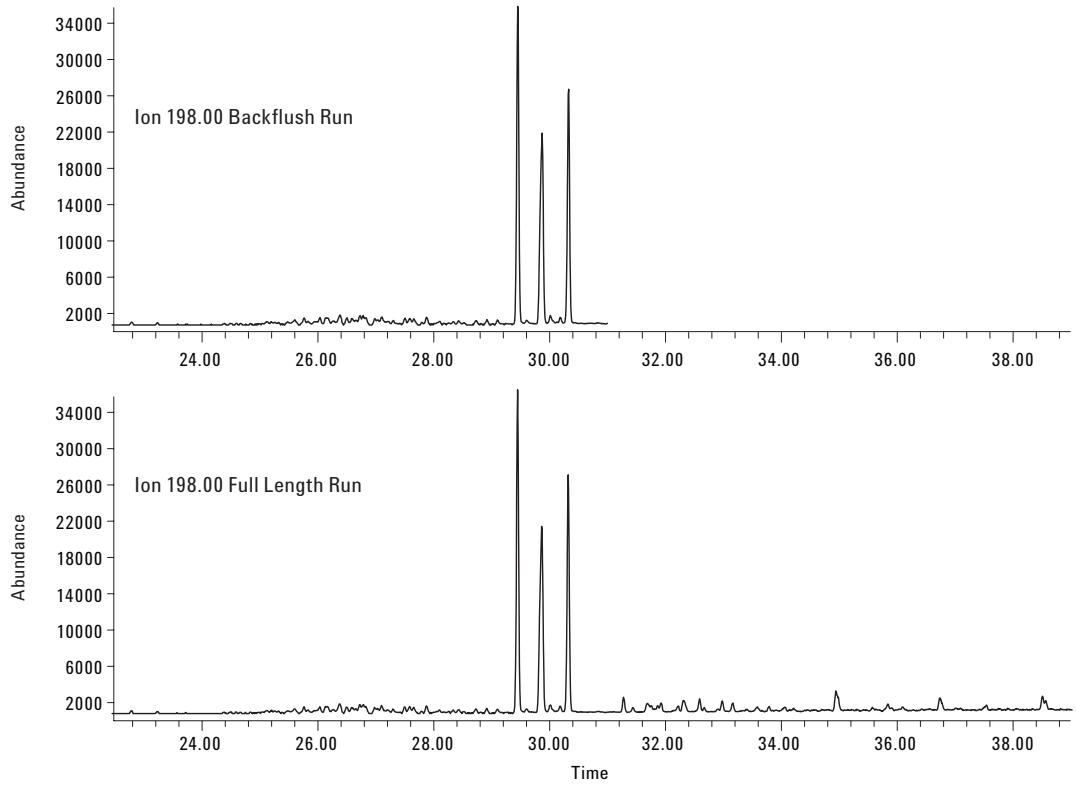

Figure 13. Overlay of EIC of *m/z* 198 from full run and backflush run, showing the exact matching of the analytical portion of each run for the three methylbenzothiophene biomarkers.

Conclusions

This application demonstrates the ease with which backflush can be set up and executed with the 7890A/5975A GC-MS system with EA 01.00 MSD ChemStation. In this example, a total run time saving of 37.5 minutes effectively halved the run time of the original run while ensuring that the analytical column was free from sample carryover. A confirmatory blank run following backflushing substantiates the efficacy of the backflush, verifying removal of all remaining sample components.

References

1. Russell Kinghorn, Courtney Milner, and Matthew S. Klee, "Simplified Backflush Using Agilent 6890 GC," Agilent Technologies publication 5989-5111EN
2. Chin Kai Meng, "Improving Productivity and Extending Column Life with Backflush," Agilent Technologies publication 5989-6018EN
3. Frank David and Matthew Klee, "GC/MS Analysis of PCBs in Waste Oil Using the Backflush Capability of the Agilent QuickSwap Accessory," Agilent Technologies publication 5989-7601EN
4. Frank David and Matthew Klee, "Analysis of Suspected Flavor and Fragrance Allergens in Cosmetics Using the 7890A GC and Capillary Column Backflush," Agilent Technologies publication 5989-6460EN
5. James McCurry, "Enhancements in the Operation and Precision of an ASTM D4815 Analyzer for the Determination of Oxygenates in Gasoline," Agilent Technologies publication 5988-4475EN
6. Mike Szelewski, "Significant Cycle Time Reduction Using the Agilent 7890A/5975A GC/MSD for EPA Method 8270," Agilent Technologies publication 5989-6026EN

For More Information

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

www.agilent.com/chem

Printed in the USA
July 11, 2008
5989-8588EN

Agilent Technologies