

Improving GC-MS Method Robustness and Cycle Times Using Capillary Flow Technology and Backflushing

Application Note

Environmental

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Abstract

This application note demonstrates the customer benefits from using Capillary Flow Technology to provide backflushing of high-boiling materials in GC and GC/MS analyses. Benefits include reduction in chromatographic cycle times, a reduction in system column maintenance, and extended GC column life. If a GC/MS system is utilized, the author has experienced an increase in the number of samples analyzed before ion source maintenance is required.



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Introduction

A critical component of the GC/MS analysis of any sample that contains large amounts of matrix material is the sample preparation. Environmental samples such as soils and sediments require not only extraction, but may also require multiple cleanup steps in order to present as clean an extract as possible for injection in to the GC/MS system.

Any remaining matrix in the sample extract can have deleterious effects on the GC sample inlet, column, and the ion source of the mass spectrometer. Traditionally, these high-boiling matrix materials are removed from the capillary column by a long bake-out period after the analytes of interest have eluted. This long bake-out process causes thermal stress to the column and also drives the matrix material towards the ion source, where it will eventually affect system performance. Moreover, should any material remain in the column after the bake-out process, it can cause loss of chromatographic peak shape and retention time shifting of target analytes. This shifting of retention time is particularly troublesome if the mass spectrometer is being used in the selected ion monitoring (SIM) mode (as with a single quadrupole GC/MS) or in the multiple reaction monitoring (MRM) mode (as with a triple quadrupole GC/MS).

This paper demonstrates how high-boiling matrix materials can be removed from the column quickly and effectively – between sample injections – by using capillary flow technology and capillary column backflushing.

Figure 1 shows a schematic diagram of the GC/MS system used. The 15-m analytical column was connected to the EPC split/splitless inlet and a capillary flow technology two-way splitter (p/n G3180B or G1540 option number 889).

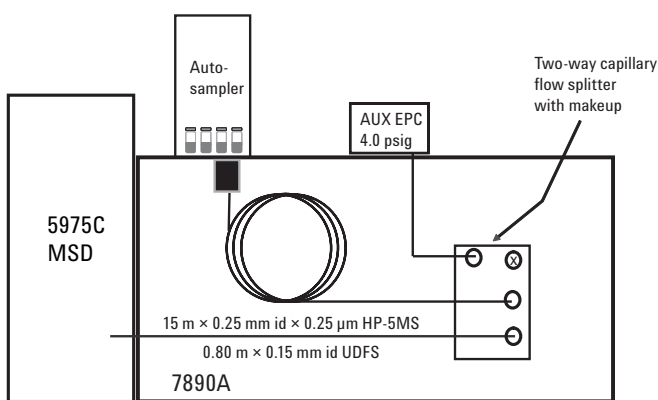


Figure 1. Schematic diagram of GC-MS system.

A short length of uncoated, deactivated fused silica (UDFS) capillary column is used as a restrictor between the splitter and the MS. Note carefully how the connections are made at the splitter. The X represents a port on the splitter plate that is closed off with a SilTite metal ferrule and stainless steel wire plug.

Backflushing in this example was accomplished during a post-run period by a combination of increasing oven temperature, reducing the inlet pressure of the analytical column, and increasing the pressure applied to the splitter plate.

Experimental

The full analytical conditions, both with and without post-run backflush set-points, are shown in Table 1.

Table 1. GC/MS Analysis Conditions

Gas chromatograph	Agilent 7890A
Columns	(1) 15.0 m × 0.25 mm id × 0.25 μm HP-5MS Ultra Inert (19091S-431SI) Inlet Front split/splitless, outlet 2-way Capillary Flow Device (2) 0.80 m × 0.15 mm id uncoated deactivated fused silica inlet two-way capillary flow device at 4.0 psig outlet vacuum
Carrier gas	Helium
Carrier gas mode	Constant pressure
Flow rate	17.18 psi
Injection port	EPC split/splitless
Autosampler	Agilent 7683A
Injection mode	Splitless, purge delay 0.5 min Purge flow 50.0 mL/min at 0.5 min
Injection volume	2.0 μL
Injection port liner	4 mm single-taper splitless liner (5181-3316)
Oven program °C (min)	70 (1) – 50 °C /min – 150 (0) 6 – 200 (0) – 16 – 280 (0) °C
Mass spectrometer	Agilent 5975C MSD
MS interface	280 °C
MS source	230 °C
MS quad 1	150 °C
Backflush conditions (1)	Post-run, 10 min, AUX 60 psig, oven 320 °C
Backflush conditions (2)	Post-run, 6 min, AUX 80 psig, oven 320 °C
Detection mode	EI full scan; mass range 40:550 amu
EI tune	Gain factor = 1

Results and Discussions

Experiment 1: No Backflushing Employed

In the first experiment, an extracted sediment sample was analyzed in full-scan mode to show the extent of the matrix problem. No backflushing was employed.

Before any sediment was injected, a system blank (no injection) followed by a 2- μ L solvent blank was made. In the absence of the actual hexane solvent used to prepare the

sediment extract, hexane that was not particularly clean was used. The TICs are shown overlaid in Figure 2, system blank in black, and solvent blank in gray. These chromatograms show that the system is free from high-boiling matrix material.

Following the blanks, a single injection of the sediment extract was made without backflushing; the TIC is shown in Figure 3. Note the very high abundance of the matrix and that when the analysis finishes, there is still a significant amount of matrix material to elute from the column.

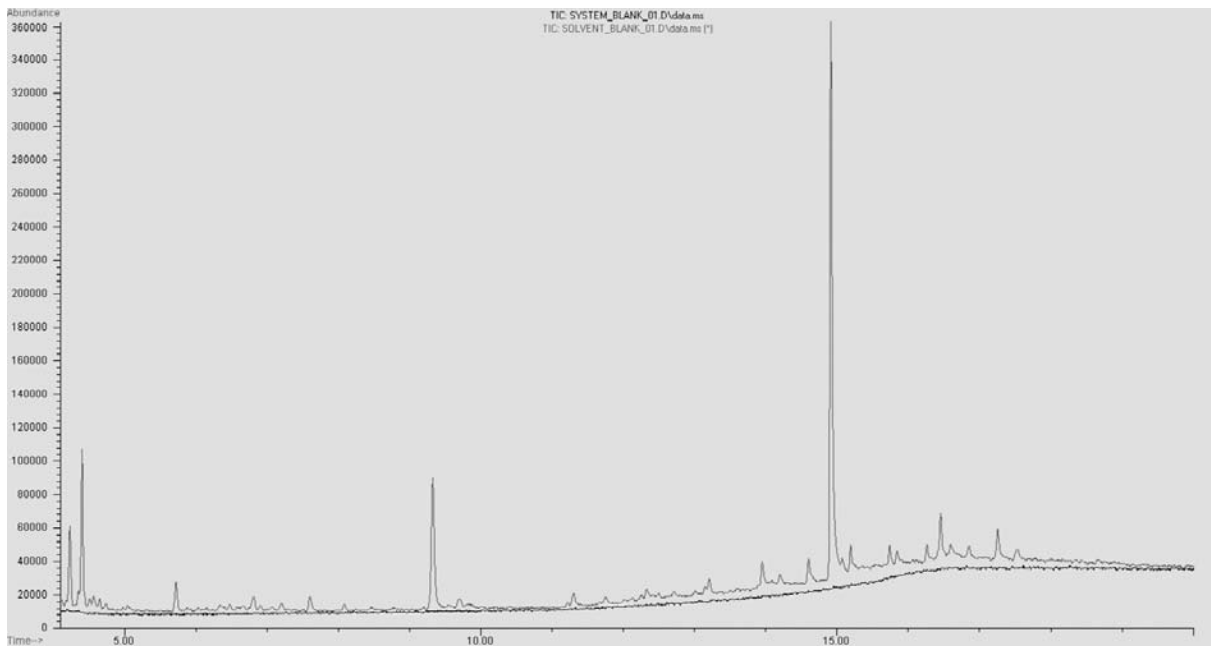


Figure 2. System blank and solvent blank TICs.

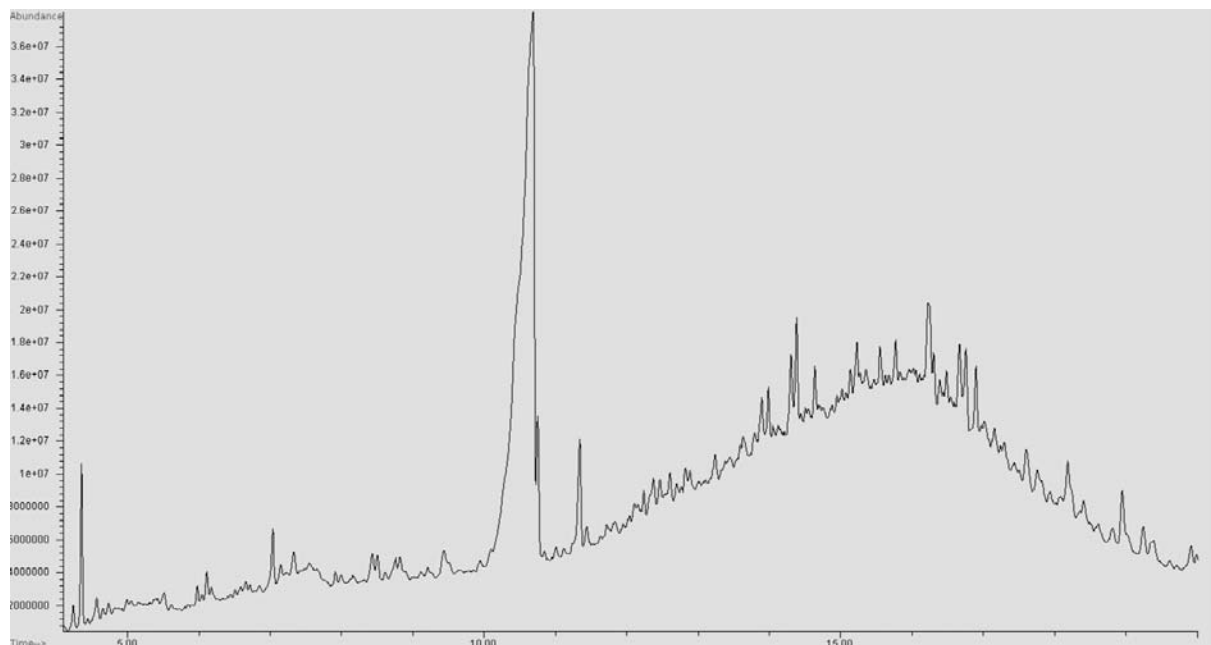


Figure 3. Sediment extract TIC.

The sediment extract injection was followed by a series of hexane blank injections. The first seven hexane blank TICs are shown overlaid in Figure 4 with the solvent blank before the sediment was injected into the GC/MS system.

The original solvent blank TIC is shown in black, the eighth solvent blank TIC after the sediment injection is shown in gray.

Figure 5 shows that after the eighth solvent blank injection, the system has almost recovered to the level of background before the sediment sample was injected.

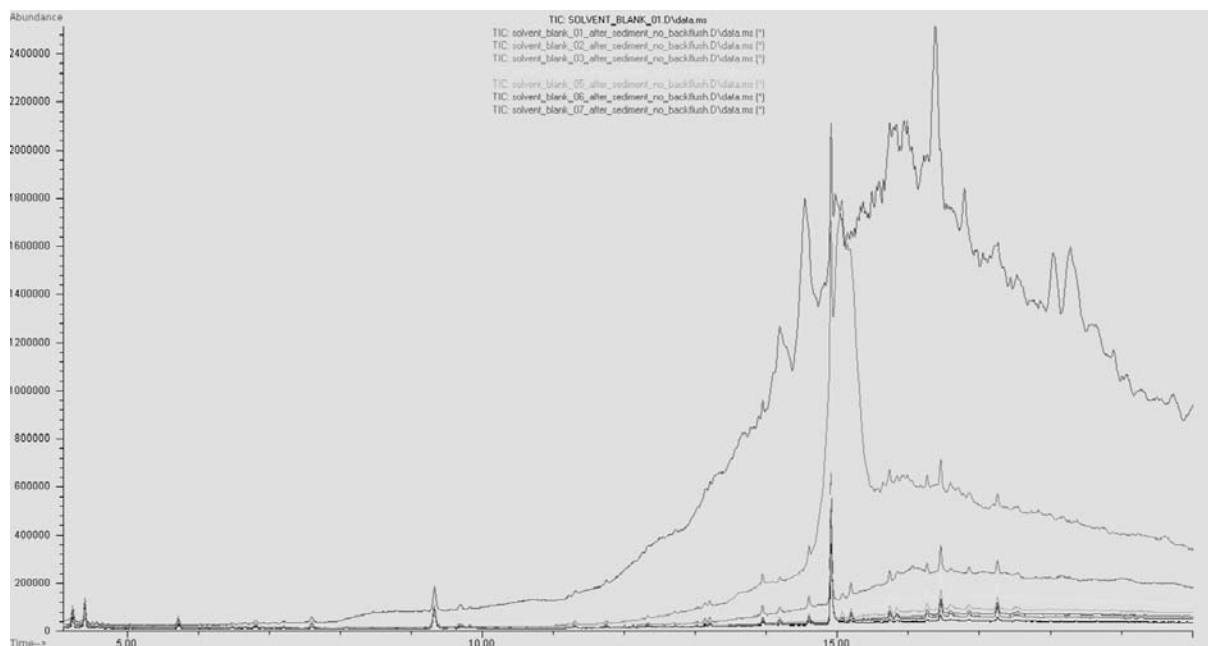


Figure 4. Successive solvent blank injections.

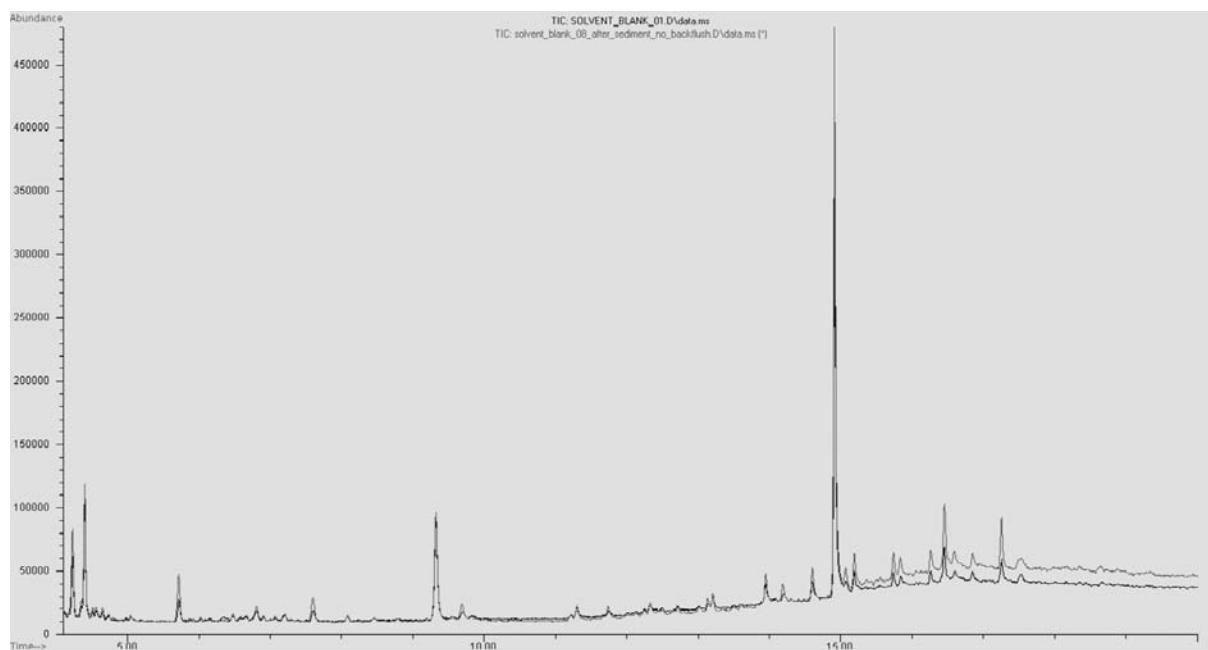


Figure 5. Eighth solvent blank and original solvent blank TICs

Experiment 2: Backflushing Employed

Backflushing was enabled during a post-run period by increasing column oven temperature, reducing the inlet pressure of the analytical column, and increasing the gas pressure applied to the splitter plate.

The 7890A instrument control software includes simple and easy-to-use screens to help set up post-run backflushing conditions. Figure 6 shows the configuration of columns and connections with the GC oven.

Figure 7 shows the actual backflushing conditions, namely the post-run oven temperature (320 °C), post-run inlet pres-

sure for the analytical column (1 psig), post-run pressure applied to the splitter device (60 psig), and post-run time (10 minutes). The figure also shows the number of column-volumes of carrier gas that will backflush the analytical column.

Note that using the backflushing conditions shown in Figure 7 (320 °C, column pressure 1 psig, and splitter pressure 60 psig for 10 minutes), that 59.4 column volumes of carrier gas was used to backflush the column during the post-run period. This backflush time may have been more than necessary. Alternate conditions were also investigated and are presented later.

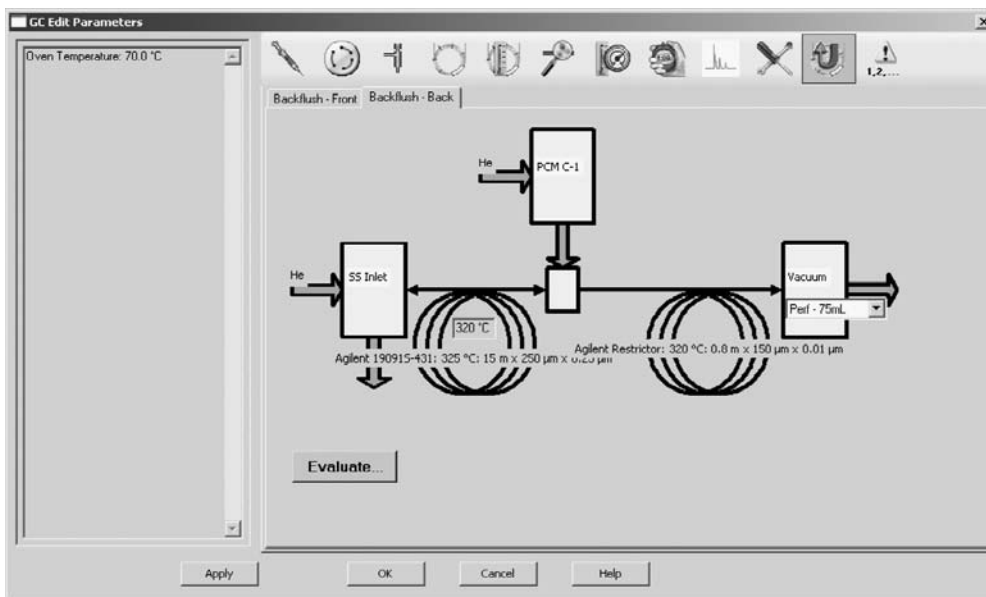


Figure 6. Post-run backflushing screen number 1.

Summary of Backflush Calculations

Oven Temperature
320 °C

Detector	Maximum Flow	Allowable Pressure	Flow at Chosen Pressure
Vacuum	75	130.98	19.719

Backflush Pressure
60 psi

Inlet Pressure during Backflush
1 psi

Backflush Flow to Inlet
7.6986 mL/min

Void Time
0.16817 min

Void Volumes
59.463

Backflush Time
10 min

OK Cancel Help

Figure 7. Post-run backflushing screen number 2.

Before applying the backflush conditions to the method the user is presented with a convenient summary of the backflush conditions. See Figure 8.

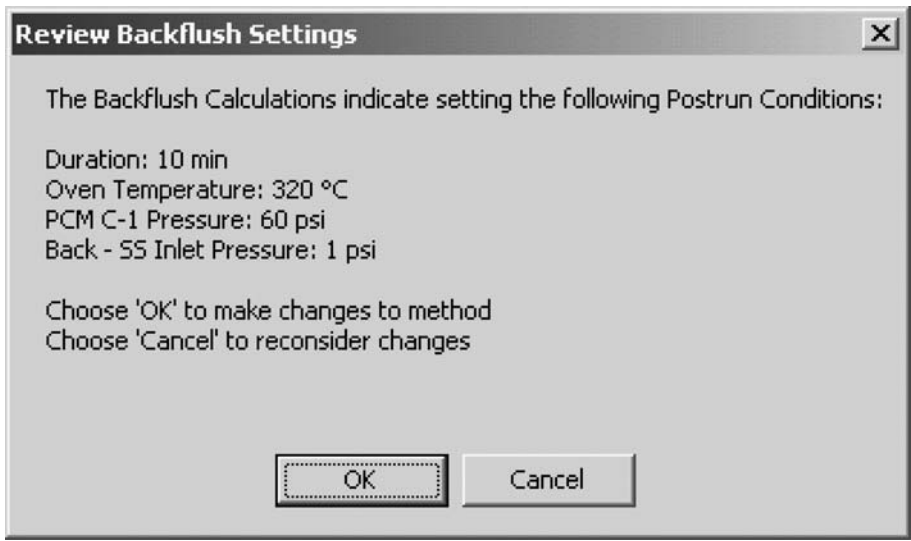


Figure 8. Post-run backflushing screen number 3.

Another injection of the sediment including backflush was made followed by a blank injection of solvent. Figure 9 shows the overlaid TIC of the original solvent blank (black) overlaid on the solvent blank after the sediment injection (gray).

No evidence of any matrix material is indicated, demonstrating that all the high-boiling matrix material had been effectively removed by backflushing.

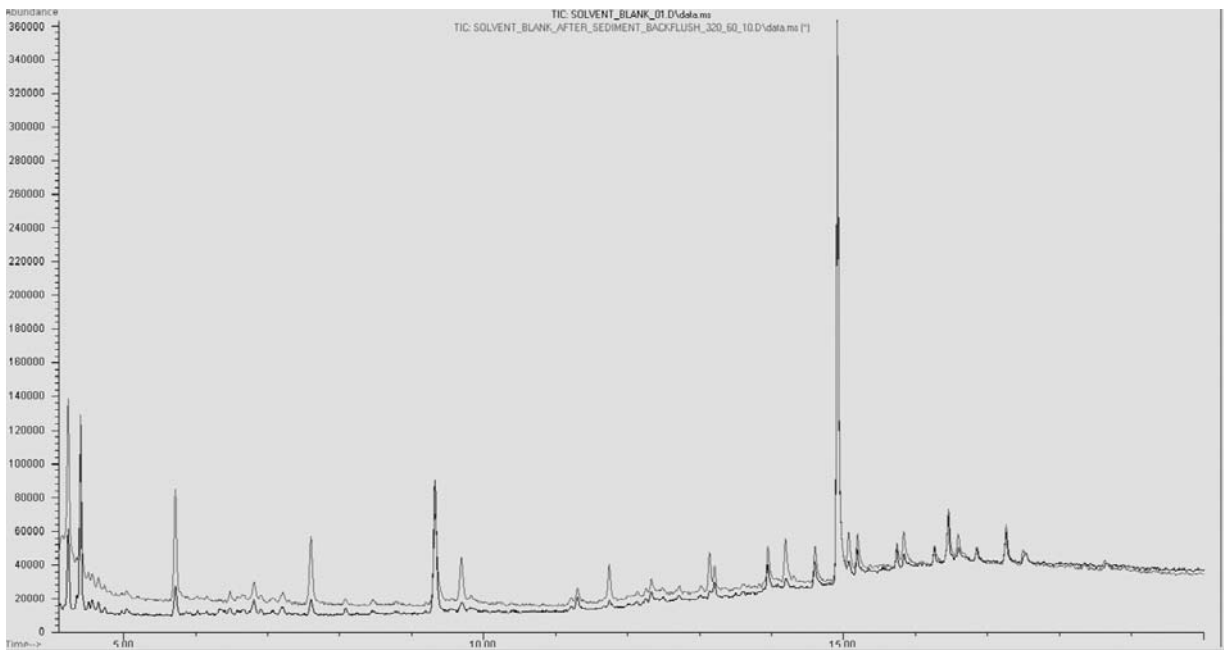


Figure 9. Original solvent blank TIC and solvent blank after sediment injection with post-run backflush (1).

Experiment 3: Backflushing Employed

In order to reduce cycle time for the method, the backflush conditions were modified by increasing the backflush pressure to 80 psig and holding for 6 minutes.

Note that using the backflushing conditions shown in Figure 10 (320 °C, column pressure 1 psig, and splitter pressure 80 psig for 6 minutes), that 46.6 column volumes of carrier gas was used to backflush the column during the post-run period.

Another injection of the sediment was made, followed by a blank injection of solvent. Figure 11 shows the overlaid TIC of the original solvent blank (black) overlaid on the solvent blank after the sediment injection (gray).

No evidence of any matrix material is indicated, demonstrating that all the high-boiling matrix material has been removed by backflushing with the more aggressive conditions as well. These conditions reduced the cycle time for this method 4 minutes compared to the backflushing conditions used in Experiment 1.

Summary of Backflush Calculations

Oven Temperature
320 °C

Detector	Maximum Flow	Allowable Pressure	Flow at Chosen Pressure
Vacuum	75	130.98	31.692

Backflush Pressure
80 psi

Inlet Pressure during Backflush: 1 psi Backflush Flow to Inlet: 12.589 mL/min Void Time: 0.12875 min

Void Volumes: 46.601 Backflush Time: 6 min

OK Cancel Help

Figure 10. Post-run backflushing screen conditions number 2.

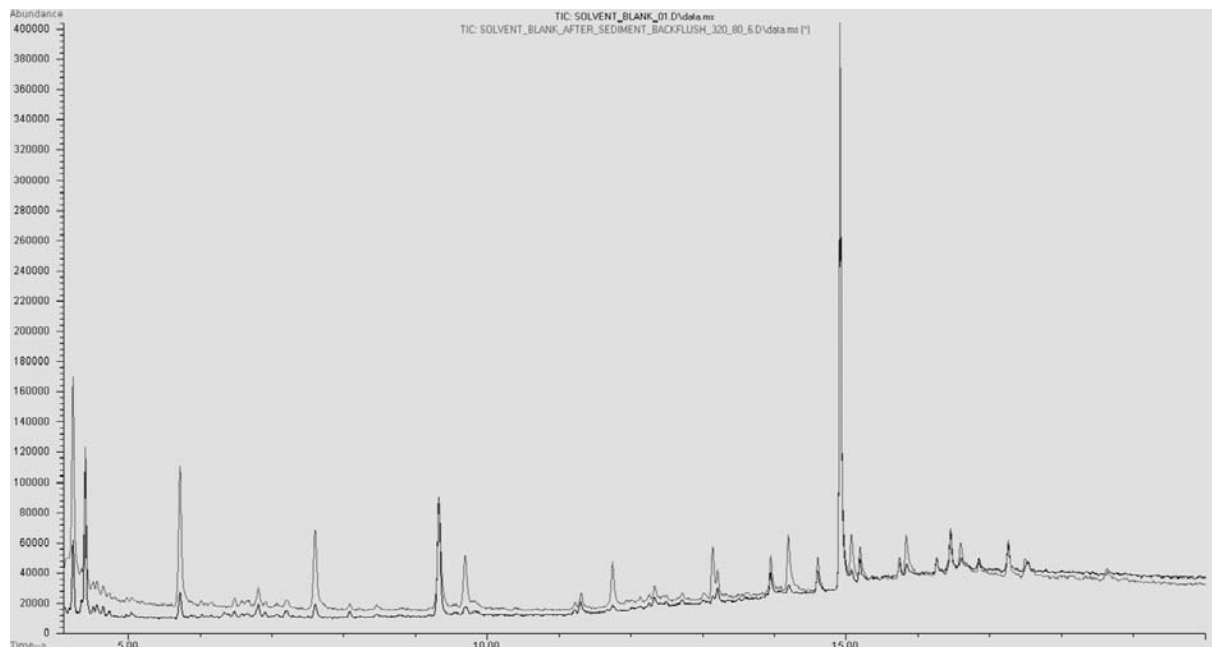


Figure 11. Original solvent blank TIC and solvent blank after sediment injection with post-run backflush (2).

Conclusions

Post-run backflushing was shown to effectively eliminate high-boiling sample matrix in a short amount of time. The major benefits of GC capillary column post-run backflushing include:

- Agilent's capillary flow technology and GC software enable easy and robust setup of GC backflushing.
- Compared to long bake-out periods with flow in the forward direction, a short period of backflushing can remove high-boiling matrix materials more effectively without contaminating the MS ion source.
- Chromatographic cycle time is reduced, columns stay clean, and the integrity of target analyte peak shapes and retention times are maintained.
- For this particular sediment extract the GC column was free of sample matrix after a backflush period of 6 minutes.
- Less system maintenance (ion source cleaning) is required.

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