Capillary Flow Technology for GC/MS: A Simple Tee Configuration for Analysis at Trace Concentrations with Rapid Backflushing for Matrix Elimination

Application

Environmental, Drug Testing, and Forensics

Author
Harry Prest
Agilent Technologies Inc.
5301 Stevens Creek Blvd.
Santa Clara, CA 95051
USA

Abstract

Capillary Flow Technology devices offer the potential to enhance GC/MSD operation and robustness. In operation, they can allow rapid service of the GC column and inlet, including liner and septum, without venting or subjecting the MSD to air. In terms of robustness, late eluting compounds can be removed from the column by "backflushing," which forces components to retreat through the column into the injection port before they damage the MSD source or compromise the next analysis. This leads to higher analytical integrity as both the column phase and the MSD can be protected. This application describes a simple arrangement for Capillary Flow Technology devices that provides ventless maintenance features with highly accelerated backflushing and minimal losses in the MSD signal. This solution supports GC analysis in constant flow mode with pressure pulsed injections and is recommended for all MSD users (in both electron impact or chemical ionization modes), including those with diffusion pump systems.

Introduction

The introduction of Electronic Pressure Control (EPC) was a major advance for GC and especially GC/MS analysis. EPC allowed development of the constant flow mode of analysis, which generates chromatographic peaks of consistent width (time) and allows optimization of MS cycle times to meet either qualitative or quantitative requirements. Also, splitless injections gained pressure pulsing or ramped flow modes, which lowered the analytes' residence time in the hot injection port and confined the expansion of the injection solvent (avoiding overfilling of the liner). The power of this approach lead to continued evolution of EPC technology with the present state of the art represented in the new 7890A GC.

The recent addition of Capillary Flow Technology (CFT) devices has reinvigorated and recast Deans switching and other pressure control approaches to GC analysis. One such CFT device, the Quick-Swap [1–3], provides two important capabilities to GC/MS:

1) The ability to service and/or replace the entire analytical column or the injection port liner and septum without venting the MSD (yet still retaining high vacuum integrity)

2) The ability to remove from the column late-eluting, highly retained components that elute after the target compounds of analytical interest by reversing the carrier flow direction through the column in what is called “backflushing.” With the oven temperature elevated and the flow reversed, these very high boiling interferences can be pushed off the column into the split vent and thereby prevent degradation of the column phase or the detector.

A schematic representation of the arrangement that makes this possible is shown in Figure 1.
Every new approach has a downside and for QuickSwap it is the additional makeup flow required to purge the QuickSwap device during analysis which dilutes the signal in the GC/MSD. This is not an issue for many users since the sensitivity of the MSD is usually more than adequate. However, analysis at trace concentrations has more stringent requirements and maintaining a signal closely comparable to that of a single continuous column is essential.

Another CFT configuration for GC/MSD applications designed specifically for trace GC/MS analysis where customers do not wish to surrender signal is possible using the QuickSwap or any of several other CFT devices. In this alternate configuration, the CFT device is located in the middle of the analytical column, essentially splitting the column in half. For example, a 15-m column precedes and follows a CFT tee. Schematically this arrangement is illustrated in Figure 2. The auxiliary EPC device adds just enough pressure (flow) to match the flow (pressure) from the first column, so there is little flow addition and therefore less “dilution” and loss in the GC/MSD signal. Backflushing is similarly simple; the pressure or flow is dropped in the first column section while the second section column flow is increased.

Advantages of this pressure controlled tee (PCT) approach are similar to those of QuickSwap, such as:
- Service of injection port liner and septum without venting the MSD
- Column cutback or replacement of the “front” or first column without venting the MSD

But additional advantages of the PCT arrangement over QuickSwap are:
- Minimal or no signal loss (in EI- or CI-MS) is obtained because of the very small additional “makeup” gas flow.
- Constant flow mode and pressure pulsed injections are straightforward.
- This configuration is suitable for diffusion pumped systems and allows backflushing in diffusion pumped systems.
- Backflushing is more rapid and can be initiated earlier.

This application details some configurations and provides an example of backflushing.
A number of devices can be used in this approach and those arrangements will be cited later, but for these experiments the instrument configuration was as follows:

- 7890A GC with split/splitless ports in front and back and a 7683B ALS
- 5975C MSD with performance turbomolecular pump
- 2 HP-5ms 15 m × 0.25 mm id × 0.25 µm film columns (19091S-431)
- CFT device: 2-way unpurged splitter (G3181-60500) with SilTite ferrules and nuts
- CFT GC mounting hardware: dual-wide mounting bracket (G2855-00140) or single-wide mounting bracket kit (G2855-00120)
- Deactivated 0.25 mm id column approximately 1 m long
- 2 CFT blanking plugs (G2855-60570 or as G2855-20550 with G2855-20593)

As an overview of the configuration, the 1-m column was connected to the back injection port and to the first position on the CFT splitter using the appropriate SilTite fittings. (This CFT device has three connection points and is really best thought of as a simple tee reminiscent of glass Y- or T-connectors and will be referred to as a “CFT device” or “CFT tee” from here forward).

One of the 15-m HP-5ms columns was connected at the uppermost position on the CFT tee and the other end through the transfer line into the MSD as usual. The other 15-m HP-5ms column was connected to the midpoint of the CFT device and the front injection port.

In detail, the arrangements were as follows. The CFT tee was attached to the forward position on the mounting hardware on the right side in the GC oven. The 1-m long section of guard column was wound on a spare column cage and hung on the column hanger in the back of the oven. (This could simply be added to one of the 15-m HP-5ms column...
cages to avoid the extra cage.) Using a Vespel/graphite ferrule, one end was connected to the back injection port and the other end to the lowest connection of the CFT device with a SilTite ferrule and nut. The other two CFT tee connections were sealed with CFT blanking plugs and the back injection port was pressure tested as described in the 7890A Advanced User Guide (part number G3430-90015).

One of the 15-m columns was then hung on the cage carrying the 1-m column and installed with one end through the MSD transfer line. Since this column (column #2) can be expected to have a rather long life as it will be protected by the upstream column, a SilTite ferrule is recommended for the transfer-line seal. These ferrules do not develop leaks as the transfer-line temperature is cycled; however, the Vespel/graphite ferrules can shrink and develop leaks. (Note that if the surface of the transfer line is very worn it may fail to seal well, in which case the Restek Agilent interface cleaner [P/N 113450] can be used to resurface the sealing surface if very carefully employed). The other end of this GC column was connected to the uppermost connection on the CFT tee with the SilTite ferrule.

The “upstream” 15-m GC column (column #1) was hung on the other 15-m column cage and installed in the front split/splitless injection port with a Vespel/graphite ferrule, liner, and BTO septum, as usual. The other end was connected to the CFT tee middle post and, after temporarily removing the other connected columns, blanked off and pressure tested as above.

All connections were then re-established to the CFT tee with the 1-m column in the lower position; the front, first column (#1) connected in the middle position; and the rear, second or MSD column (#2) in the uppermost connection. Helium was supplied to both the front and back ports, and a helium leak detector was used to check for any leaks.

A picture of the arrangement is shown in Figure 3.
**GC Configuration**

The GC can be configured in several ways. However, for instructional purposes and those of these experiments, the GC was configured as follows:

Column #1: 30 m × 0.25 mm id × 0.25 µm column
Inlet: Front injection port: pulsed splitless mode, split flow
15 mL/min
Outlet: MSD (vacuum)
Mode: Constant flow

Column #2: 15 m × 0.25 mm id × 0.25 µm column
Inlet: Back injection port: split mode, split flow 15-mL/min
Outlet: MSD (vacuum)
Mode: Constant flow

The flows were set to 1.2-mL/min, all zones were left cold, and the MSD power was turned on. With the MSD and GC zones still “cold,” the MSD background was checked to be sure m/z 28 was decreasing, indicating that the system was tight. Only after there was confidence that there was no leak were other zones brought up to temperature.

**Operating with Pressure Pulsed-Splitless Injection**

Figures 4A and 4B show screen captures of the 7890A GC configuration for a standard pressure-pulsed splitless injection with constant flow mode operation; they show the front and back injection port parameters. Remember, the arrangement is set up such that the front port, into which the sample will be injected, is configured as if a 30-m column were installed into the MSD. Typical pressure-pulse conditions are set for these parameters: a 25 psi pulse for 0.5 minutes; split flow on at 0.75 minutes at 50-mL/min; with gas saver on at 2 minutes at 15-mL/min. The general rules apply for pressure-pulsed splitless injections: given a particular liner, inlet temperature, injection volume, and solvent, the expansion of the solvent is confined to a fraction of the interior volume (< 0.75) of the liner by the pressure applied.

Figure 4B shows that the back injection port is in split mode, at 120 °C (to remove water background), with split flow and gas saver set at 15-mL/min flow.
Figure 4B (lower panel). Typical pressure-pulsed splitless injection parameters for constant flow: back injection port (not used for injection but for column control).

Figures 5A and 5B show the constant flow mode settings for the two columns. The front column flow is the typical 1.20 mL/min, but the back column flow is slightly higher at 1.25 mL/min to prevent any backflow. Essentially the additional flow is equivalent to an extra meter of column length.

Figure 5A (upper panel). Typical pressure-pulsed splitless injection parameters for constant flow: First column section (configured as a 30-m column).
Results and Discussion

Figure 6 shows the results for pressure-pulsed splitless injections of octafluoronaphthalene (OFN) at 1-pg/µL acquired in selected ion monitoring (SIM) with the two 15-m column and CFT tee configuration and the standard 30-m continuous column configuration. Both peak height and area remain the same, indicating that there is no loss in signal. This is as expected since no signal dilution is taking place. There is a slight degradation in S/N for the CFT tee results as the background noise is raised by about 35% due to the additional flow controller. The important point is that the signal is preserved at trace levels.

Figure 6. Reconstructed total ion chromatogram (RTIC) of three replicate SIM acquisitions of octafluoronaphthalene using pulsed splitless injection with CFT tee (left profiles) and with a standard 30-m continuous column configuration (right profiles).
**Chromatographic Character**

Beyond preserving signal, the CFT device should exhibit reasonable chromatographic performance. One indication of chromatographic integrity is the peak shape profiles of the fatty acid methyl esters (FAMEs). The result for GC/MS analysis of a FAMEs standard acquired using a metabolomics method is shown in Figure 7 and suggests very little degradation of chromatography using this PCT. This can be expected as the path is deactivated and the path length in the channels in the PCT relative to the linear velocity suggests a relatively rapid transit through the device.

Another common chromatographic test used in organochlorine pesticide analysis (as in USEPA method 8081) examines degradation of 4,4’-DDT and Endrin. This degradation test was developed to indicate the degree of activity of the injection port by examining the amounts of DDD and DDE products of DDT and the ketone and aldehyde products of Endrin. The situation is complicated here as the degradation products can be generated in both the injection port and the CFT tee. How-

![Figure 7](image-url)

*Figure 7. Reconstructed total ion chromatogram (RTIC) of a multicomponent FAMEs standard using pulsed splitless injection with CFT tee (upper) and the reconstructed extracted ion chromatogram (REIC) for m/z 74. The enlarged panel is for octadecanoic methyl ester.*
ever, because those products formed in the injection port and those formed at the CFT device will have different retention times due to differing lengths of column, the degradation contributions from the two origins should be discernable. By analyzing these known breakdown products in the PCT and then injecting the DDT and Endrin agents themselves, an estimate of the activity contributed by the CFT device can be calculated. The upper panel of Figure 8 presents the reconstructed total ion current (RTIC) for the selected ion monitoring (SIM) signals of the four breakdown products. These were acquired in SIM-scan mode with a single SIM group composed of one or two major ions for each compound so there was no time selection for the compounds’ appearance. On the basis of summed areas, the total breakdown for Endrin is less than 13% with the CFT device contributing less than 10% of the total breakdown area or less than 1.2% to the area total. The DDT breakdown is less than 4% for the system; however, the CFT device contributes about 46% of the total observed breakdown and is about double the breakdown generated by the port. It is possible some DDD breakdown is “hidden” under the DDT peak. On the basis of the DDT to DDE contribution from the CFT tee, however, it is likely to increase the breakdown perhaps less than about another 2%. A better study would use on-column injection

![Figure 8. CFT tee activity. A: the REIC of a GC-MS SIM acquisition using pulsed splitless injection with the PCT configuration of the expected degradation products of DDT and Endrin at 0.2 ng on column: 4,4’-DDE (DDE), 4,4’-DDD (DDD), Endrin aldehyde (EA), and ketone (EK). B: REIC for an injection of 2.0 ng of 4,4’-DDT and Endrin identifying degradation products. Those with an asterix (*) are attributed to the injection port and due to the CFT device activity such as; from Endrin (5 as ketone) and from 4,4’-DDT (6 as DDE). Note 7 is tentatively identified as DDMU, source unknown.](image-url)
of all components, but the verdict is likely the same: the CFT device has some activity but is comparable to that of other elements (for example, in the inlet and liner). It is worth noting that this CFT device has a very long path compared to others (see the Alternative Configurations section) and that air intrusion in any part of the system will be a major issue in considering activity problems.

Adding Backflush

Figures 9A, 9B, and 9C show the GC parameters for adding backflush. They are quite simple. The oven temperature can remain the same as the temperature at the end of the oven program or can be raised to the isothermal or programmed temperature limits in Post Run for backflushing. Raising the column temperature during Post Run helps condition the column and removes some column bleed but is not necessary. The front column (column #1) flow is dropped to 0.3 mL/min and the back column (column #2) flow is raised to 4 mL/min.

To quickly estimate the duration of the Post-Run time parameter, notice that the back column (column #2) in Figure 9C cites the column Holdup Time at a given flow. At the 1.25-mL/min shown, the Holdup Time is roughly 0.4 minutes. When the column #2 flow is raised to 4 mL/min, the Holdup Time for back flow through column #1 will be less than this (actually around 0.26 min). But estimating that every 0.4 minute the front 15-m column section would be flushed at least once is very conservative and an adequate approximation. Five to 10 column volumes will flush this front 15-m section in less than 2 to 4 minutes, which is relatively rapid. Choose a time in this range (for example, 3 minutes) and test the effectiveness of the backflush method by injecting a sample and follow this with a solvent blank injected under the non-backflush GC/MSD method. There should be no sign of carryover. Extend this Post-Run time if there is carryover or further raise the Post-Run temperature or both. This is a very conservative approach.

Column or Inlet Servicing and Maintenance

To change the liner, septum, cutback the column, or replace the front 15-m column, simply cool the inlet(s) and increase the flow on the back column (column #2) to 4 mL/min and set the front injection port pressure to OFF. It is worth saving this method (such as SERVICE-Front.M). When the head of the column is removed from the injection port, one can confirm that the carrier is flowing back up the column by immersing the tip in liquid.

Figure 9A (upper panel). Adding backflushing in Post Run: oven parameters.
Figure 9B (middle panel). Adding backflushing in Post Run: front column (column #1) parameters.

Figure 9C (lower panel). Adding backflushing in Post Run: back column (column #2) parameters.
This backflow also prevents fines from the column cutting from entering the column. Make the necessary service and reattach and reload the analytical method.

If a completely new 15-m column (#1) is installed, it can be conditioned in situ by setting up the backflow condition with the oven at the conditioning column temperature.

**Advanced Techniques: Concurrent Backflushing**

If the fastest possible total analytical time is the highest priority, one will realize that backflush can begin earlier than the elution of the last component. In other words, backflushing can occur during the analytical acquisition, thereby increasing productivity. After the last compound of interest has passed the CFT tee and entered the back 15-m column, the pressure or flow through the earlier 15-m column can be dropped and compounds will cease moving forward and actually begin to retreat. When the last compound elutes, then the flow in the back column can be raised to complete backflushing. This is demonstrated in Figure 10.

The calculations are also very simple. To calculate when the flow (pressure) in the front column (column #1) is to be reduced, simply subtract the Holdup Time (Figure 9C) from the last compound’s

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**Figure 10.** Example of backflushing with flow or pressure control. Upper panel: RTIC of original six-component standard. The third peak is considered the last analyte and the fourth peak the beginning of the late-eluting interferences. Middle panel: RTIC of the same standard with backflushing beginning at 10.1 min (a), where the first 15-m column (column #1) flow is dropped and at (b) where column #2 flow is increased to 4 mL/min. Note that the last analyte is retained but the late eluters never enter the MSD. Lower panel: solvent blank run without backflush after the backflush method which shows no carryover.
elution time. After this last compound has eluted, go into Post Run and set the second 15-m column (#2) flow to 4-mL/min (or the pumping system maximum) with the front column (#1) pressure remaining low and the oven at the final programmed temperature. This can best be accomplished in ramped flow mode or in pressure programming. Do this for two to three column volumes and test with a sample followed by a solvent blank to see if this is sufficient. Experimentation with particular samples will enable setting these requirements more efficiently.

**Conclusions**

**Alternative Configurations**

The CFT is very rich and allows many possible arrangements; these are only a few suggestions or alternatives. The CFT tee used here can be replaced by a purged two-way splitter with one channel plugged (G3180-61500) or even the QuickSwap itself can be moved back from the MSD interface and suspended in the oven.

However, the best CFT tee device appears to be the new Purged Ultimate Union (G3186-60580), Figure 11. As the name describes, this is essentially a union with a gas purging line, making it a very low dead volume tee. It occupies very little space and can be suspended from the column cage, the oven wall, or through the upper GC wall. Preliminary tests of this Purged Ultimate Union using DDT and Endrin have shown very little breakdown. Chromatographic behavior is also very good.

Similarly, the carrier control need not be the back injection port split/splitless module; a Pressure Control Module (PCM) or EPC module can be used. Of the two, the Pressure Control Module may be more convenient.

Most importantly, the CFT tee position itself does not need to be exactly in the middle. The best arrangements can be considered on the basis of selection against components and the rapidity of backflushing. In other words, rapid backflushing suggests a shorter upstream column #1. So another arrangement is at the two-thirds mark or a 10-m column, then the CFT tee, and then a 20-m column to create a 30-m analytical column. Here
backflushing would be nearly 10 times faster than the arrangement with QuickSwap and more than twice as fast as the 15-m column for the same pressure. This would be the best arrangement for the MSD with a diffusion pump. Also, in terms of analytical time, this approach would provide even higher efficiency since 10 column volumes could be flushed in about 2 minutes. If backflushing begins before the analytical run ends (as shown in Advance Techniques and in Figure 10), then in many cases the Post-Run time would be very short or entirely unnecessary, yet still provide sufficient backflushing. This would further reduce total cycle times.

The joined columns need not match in many aspects. For example, a 0.32-mm id may be the first column and a 0.25-mm id the second column. In this situation it will be better to have the columns configured and described as they actually exist in the 7890A. For example, column #1 inlet is the splitless port and the outlet is the PCM module A; column #2 inlet is the PCM module A and the outlet is the MSD. Considerations of capacity, resolution, robustness, etc., can be entertained in several innovative ways to enhance productivity and data quality.

This solution can also be implemented on the Agilent 6890 GC. Of course, the PCT tee configuration is not confined to the Agilent GC/MS detector, but is suitable for other detection schemes as well.

Future software releases will contain a key command that will allow more functionality and greater ease of use: it will allow the user to apply the IGNORE READY = TRUE condition to the EPC device controlling the CFT tee. This will prevent the pressure pulse or other flow conditions from producing a “not ready” condition for the instrument.

References

1. The 5975C Series GC/MSD, Agilent Technologies publication 5989-7827EN
2. Frank David and Matthew S. Klee, “Analysis of Suspected Flavor and Fragrance Allergens in Cosmetics Using the 7890A GC with Column Backflush,” Agilent Technologies publication 5989-6460EN
3. Frank David and Matthew S. Klee, “GC/MS Analysis of PCBs in Waste Oil Using the Backflush Capability of Agilent QuickSwap Accessory,” Agilent Technologies publication 5989-7601EN

(These references are available in the Literature Library at www.chem.agilent.com.)

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