APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Using the PreVent System in Time-Saver Mode with the AutoSystem XL Gas Chromatograph and the TurboMass Mass Spectrometer

Overview

A mass spectrometer is an increasingly popular choice for a gas chromatographic detector. It is responsive, highly selective and can be used in almost all gas chromatographic applications. Unfortunately, these strengths also lead to one of the main weaknesses of gas chromatography/mass spectrometry (GC/MS) – risk of contamination by sample residue, leaks in gas fittings, impurities in carrier gas suppliers, etc. The analyst must take special precautions when using a GC/MS system, to minimize the risks of any such contamination.

The PerkinElmer® PreVent™ system, which has been used to enhance the chromatographic performance in many applications using conventional GC detectors, can also be used with the PerkinElmer TurboMass™ Mass Spectrometer GC detector. No additional parts are required to use the standard PreVent accessory with the TurboMass.

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Figures 1 and 2 show the two PreVent configurations that can be used with the TurboMass MS.

Figure 1 shows the PreVent device installed in a Split/Splitless or Programmable Split/Splitless (PSS) injector. This configuration is independent of the detector type and is used with the TurboMass in the same way as any other GC detector.

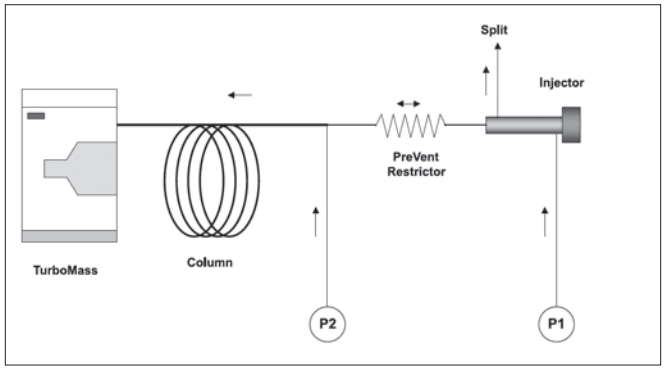

Figure 1. GC/MS with PreVent configured in the Column Isolation mode.

Figure 2 shows the PreVent device installed between the GC column and the TurboMass MS detector in Time-Saver mode and is the subject of this application note. The situation here is different from conventional GC detectors for the following reasons:

1. The restrictor outlet is under vacuum.
2. The detector is more remote from the GC oven and so needs a longer restrictor.
3. Only a low flow of carrier gas into the detector can be tolerated.

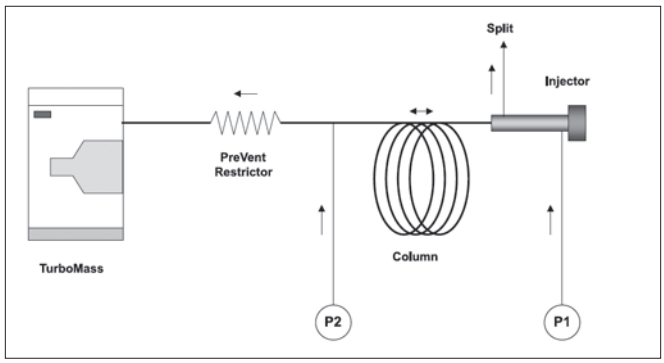

Figure 2. GC/MS with PreVent configured in the Time-Saver mode.

Fortunately, these three points can be easily addressed by using a 40-cm length of 0.075-mm i.d. deactivated fused silica restrictor tubing within the TurboMass MS heated transfer line. This tubing is included in the standard PreVent accessory kit.

Figure 3 shows the expected flow rate of helium through this restrictor as the PreVent midpoint pressure and transfer line temperature are varied. These plots are based on theoretical expectations and should be used for guidance only. The internal diameter of the fused silica restrictor tubing may not be exactly 0.075 mm because of manufacturing variances and, as gas flow rate is proportional to the fourth power of the internal diameter, some deviations from these plots would be expected in practice.

The plots in Figure 3 can be used to estimate the nominal midpoint pressure required to deliver the total column effluent to the detector. For instance, with a 0.250-mm internal diameter column, the nominal helium carrier gas flow rate would be about 1 mL/min. With a transfer line temperature of 200 °C, we would expect to see a midpoint pressure of about 20 psig. The gas pressures for PreVent operation are set up in the same way as for any other detector according to instructions given in the operating manual.

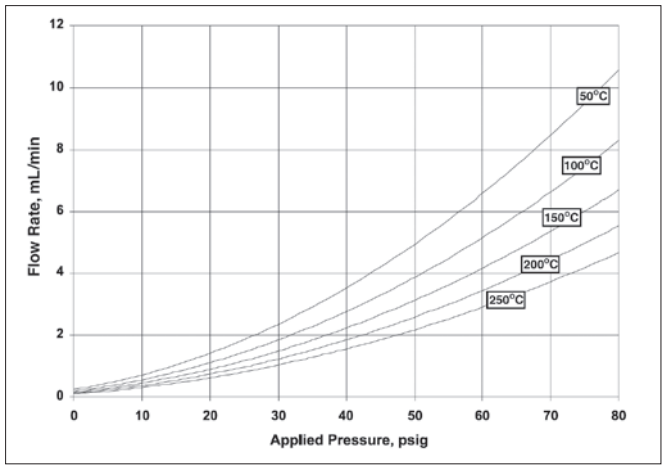

Figure 3. Plots of expected flow rates (adjusted to 20 °C and 1 atmosphere) of helium carrier gas through the PreVent TurboMass restrictor versus inlet pressure at various temperatures with a vacuum applied to the outlet.

The PreVent device is installed into the TurboMass MS as shown in Figure 4. The PreVent 'injector' T-piece is screwed onto the 1/16" fitting at the end of the standard TurboMass MS transfer line with the fused silica restrictor inserted through it, through the heated transfer line and directly into the TurboMass ion source. The end of the restrictor is exposed beyond the T-piece to enable the column to be threaded over it with the aid of an hourglass guide. Figures 5 to 9 show details of the installation. Figure 10 shows a detail of the column-restrictor interface. Because the restrictor is inserted directly into the end of the capillary column, there are no issues with active sites or dead volumes and optimum chromatographic performance is assured.

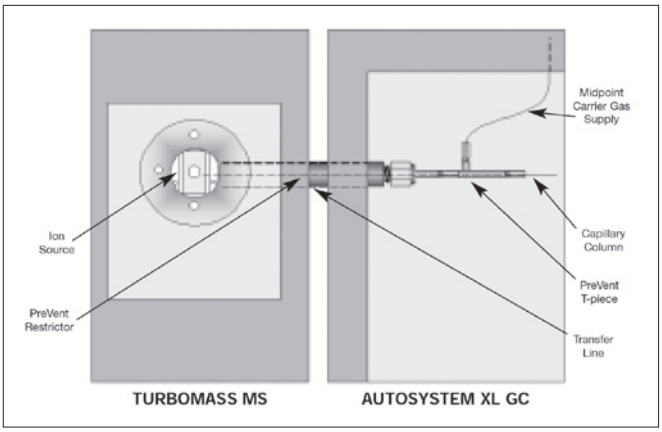

Figure 4. Diagram showing PreVent device installed into the TurboMass MS detector.

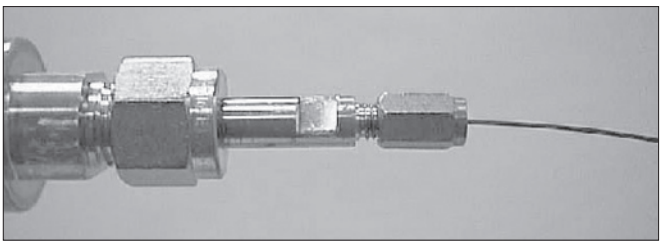

Figure 5. Normal connection of column to TurboMass MS transfer line.

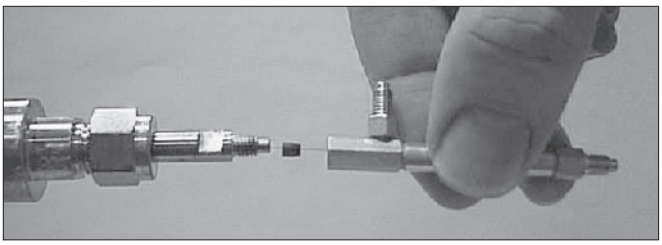

Figure 6. Column is detached and PreVent adapter is attached to TurboMass MS transfer line with fused silica restrictor pushed through into ionizer.

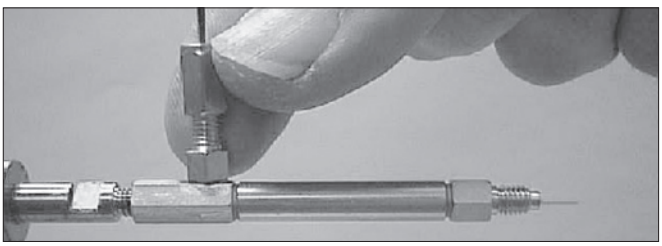

Figure 7. Restrictor is sealed within adapter with end protruding. Midpoint gas supply is connected to port on adapter.

Figure 8. Hourglass guides restrictor into capillary column.

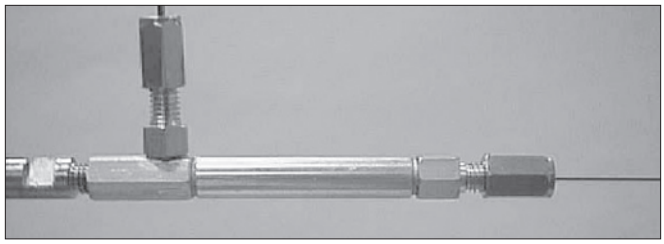

Figure 9. Installation completed.

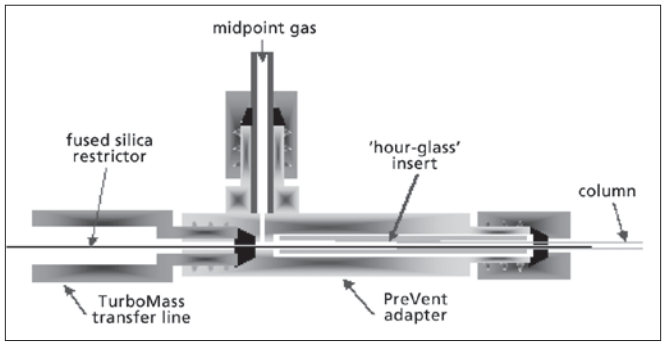

Figure 10. Detail of column-restrictor interface at end of TurboMass MS transfer line.

Once installed, this PreVent configuration allows the capillary column to be backflushed, offering the following benefits:

- Allow injector maintenance without having to cool the GC/MS transfer line or vent the mass spectrometer.
- Allow a degraded section of column to be removed from its inlet without the need to cool the GC/MS transfer line or vent the mass spectrometer.
- Provide for easier column replacement.
- Reduce risk of air entering the detector in the event of a leak or column breakage.
- Prevent column bleed from entering the detector while conditioning or when the system is idle.
- Allow the injector liner and quartz wool packing to be deactivated *in situ*.
- Reduce analysis times by eliminating the need for extensive temperature programming to elute unwanted, less volatile sample residue from the column.
- Increase the life of a column by eliminating temperature programming completely.
- Remove potential contaminants before they reach the detector.

It will also have the added benefit of maintaining a constant flow of carrier gas into the MS detector in both forward flow and backflush modes during temperature programming.

Injector Maintenance

Figure 11 shows some detector selective ion traces taken on the TurboMass while the injector was stripped down, the liner removed and repacked, a new septum fitted and the injector reassembled. No evidence of ingress of oxygen, nitrogen, water or carbon dioxide is apparent – only a very minor disturbance to the background signal is observed as the carrier gas pressure re-equilibrates following re-assembly of the injector. Using PreVent in this manner saves the analyst about 1 hour in time otherwise spent waiting for the detector to pump-down and cool beforehand and re-equilibrate afterwards.

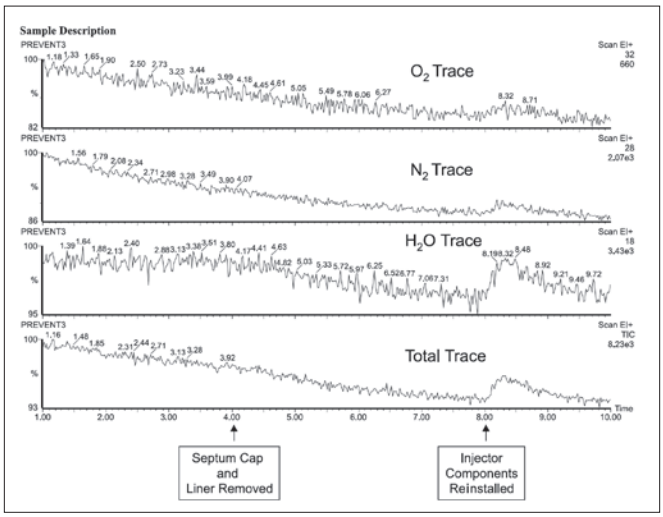

Figure 11. Background signal on TurboMass MS while the injector is being serviced.

Figure 12 shows isothermal chromatography of a simple test mix performed before and after injector liner exchange – no apparent differences in peak retention time, area or shape are apparent.

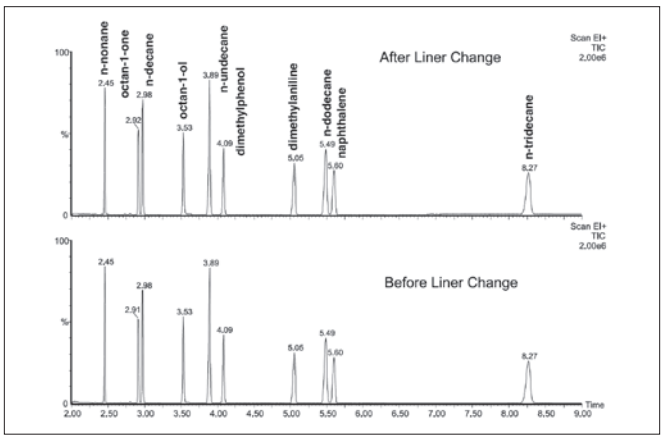

Figure 12. Isothermal chromatography of a simple test mix before and after injector liner replacement. Column: 30 m x 0.25 mm x 0.25 µm PE-5 at 140 °C.

In the same way, the column may be disconnected from the injector while the mass spectrometer is still active. This enables a piece of degraded column to be removed with a minimum of disturbance to the system.

Columns do age in use, particularly if dirty samples are being analyzed, and often performance can be recovered by cutting just a short section from the inlet end of the column.

Column Exchange

One of the most critical steps in the setup of a GC/MS system is the correct placement of the end of the column within the detector ion source so that the transfer line fittings are clean and leak-tight.

In the case of PreVent in the Time-Saver mode, a fused silica restrictor tube within the transfer line replaces the column. This restrictor remains in place if the column is removed and replaced with another and so physical installation is considerably simplified.

When the GC column is removed from the system, the end of the PreVent restrictor is exposed to air. The impedance of the restrictor is sufficient to allow the vacuum inside the detector to be maintained while the column is absent. It is, therefore, possible to exchange columns without venting the system. This is another feature of the PreVent system that saves the analyst time when using a GC/MS. To prevent possible oxidation of the restrictor inner walls or the detector interior components, it is still necessary to cool the detector and transfer line before removing the column.

Greater immunity to leakage

If the column fractures or there is some other major leakage upstream of the detector, the PreVent system in Time-Saver mode fully protects the mass spectrometer from any ingress of air. Figure 13 illustrates the principle. The maximum flow of gas vented through such a leak is limited to about 50 mL/min by the impedance of the narrow bore stainless steel tubing, which delivers the midpoint gas to the PreVent adapter. The flow rate of carrier gas from the injector in the event of a leak is limited to the current split flow rate setting. This means that a cylinder of carrier gas will still take many days to exhaust, and so the detector is better protected against loss of carrier gas in the event of a major leak.

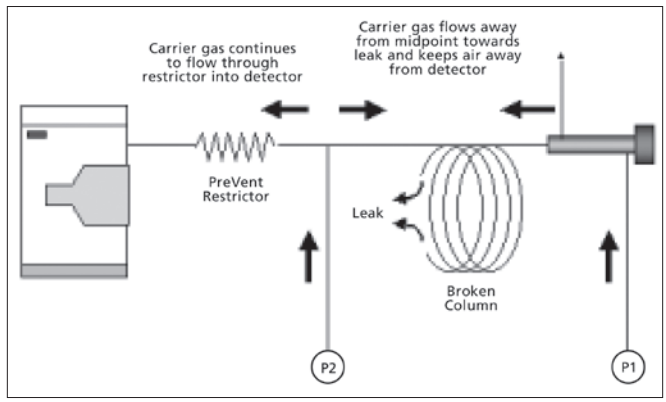

Figure 13. Protection of MS detector from leaks.

Column conditioning, etc.

When a new column is installed, it may contain residual solvents and reagents used during the manufacture of that column. Such compounds may affect the selectivity of that column, produce a high background signal (column bleed) and produce contamination peaks that interfere with subsequent analyses. Such compounds are normally removed by a process called column conditioning where the column is carefully temperature-programmed to bake out the contamination and stabilize the stationary phase. Nowadays, many column vendors will precondition columns prior to shipment to customers. Nevertheless, the prudent chromatographer will always condition a new column prior to use – particularly when a mass spectrometer is being used because of its sensitivity to any residual silanes from the stationary phase.

Columns may also require periodic reconditioning, especially when used with dirty sample matrices, to remove accumulated contamination and recover chromatographic performance.

It is usual to leave the column outlet disconnected from the detector while conditioning the column to prevent the bleed components from becoming deposited in the detector. This is particularly important with a mass spectrometer because of its universal sensitivity and difficulty in cleaning. Unfortunately, once the column is conditioned and connected to the mass spectrometer, the user must then wait for the detector to equilibrate.

The PreVent system enables the column to be conditioned and the detector to equilibrate simultaneously. Because the carrier flow may be reversed in the column, column bleed can be kept away from the detector. Buildup of contamination within the injector is much less likely because of the higher temperatures and carrier gas flow rates within the liner than would be possible within the mass spectrometer.

In situ liner deactivation

For critical applications, especially where trace levels of labile compounds such as pesticides are to be determined, it is important to employ a well deactivated injector liner and packing to reduce the potential loss of analytes during the injection process. There is a variety of materials used for making liners and packing and a variety of deactivation procedures applied to them. The choice is normally dictated by the application, but one of the most commonly used combinations is quartz for the liner and packing and dimethyldichlorosilane (DMCS) for the deactivation.

Typically the quartz liner and quartz wool packing are immersed in a 5% solution of DMCS in a solvent such as toluene for a few hours, rinsed with more toluene, and then rinsed with methanol to deactivate the residual active reagent. The materials are then carefully dried and the quartz wool is inserted into the liner.

The liner is installed into the GC injector and conditioned at an elevated temperature to bake out any residual solvent and reagent. The column and mass spectrometer are clearly at risk from chemical attack during this conditioning stage. This whole process is tedious, takes a long time and is disruptive to the GC/MS system.

The PreVent system in Time-Saver mode not only simplifies the liner installation process but also completely protects both the column and the mass spectrometer during liner conditioning.

The deactivation reaction can also be performed in the vapor phase by injecting DMCS directly into the heated liner while it is installed in the injector. A subsequent injection of methanol deactivates the excess reagent. Residual solvent and reagent are removed by increasing the liner temperature. While this process is taking place, the column and mass spectrometer are still connected but are protected by the PreVent system in Time-Saver mode.

Figure 14 shows a splitless chromatogram of a low concentration column polarity test mix using a new liner freshly packed with untreated quartz wool. The silanol groups present on the surface of the quartz react with the octanol, causing apparent component loss and peak tailing.

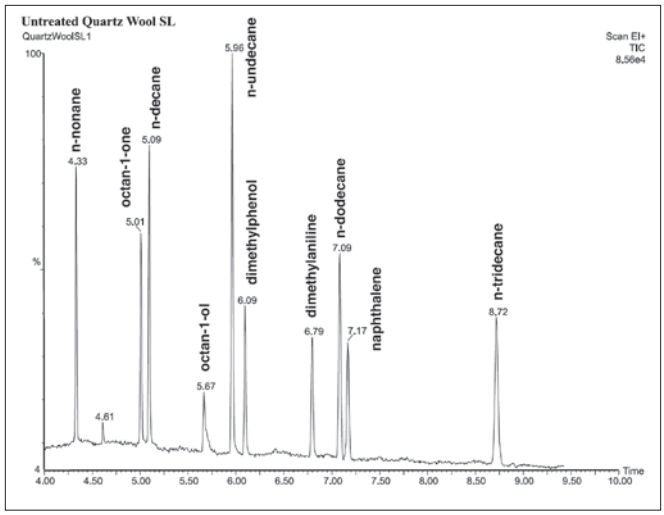

Figure 14. Polarity test mix chromatogram prior to liner deactivation.

Using PreVent to backflush the chromatographic column, this liner was then deactivated at 50 °C by manually injecting 10 µL of a 5% solution of DMCS in toluene 10 mm below the septum with an applied split flow of 20 mL/min. Because the column was being backflushed, none of the DMCS was able to enter it. After 5 minutes, the liner temperature was raised to 150 °C and held for 10 minutes. Two repeat (slow) injections of 10 µL of methanol were then made to deactivate any residual DMCS. Finally, the liner was conditioned by raising its temperature to 325 °C for 30 min.

Figure 15 shows a chromatogram of the test mix on the liner after deactivation. The alcohol peak shape is now much sharper and larger than before the deactivation.

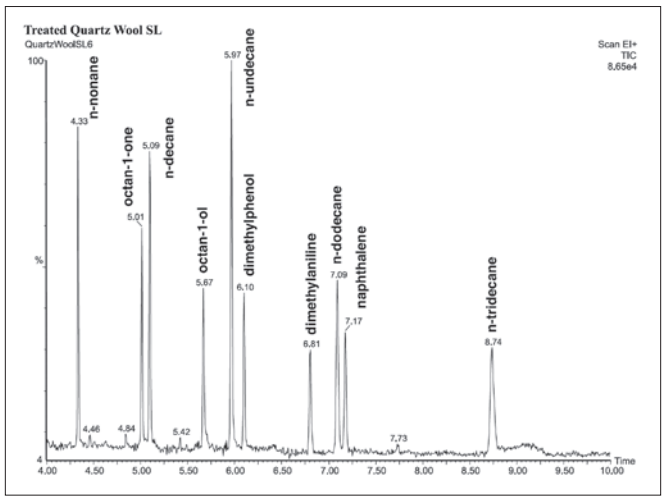

Figure 15. Polarity test mix chromatogram after liner deactivation.

One obvious concern of this approach is the risk that some of the deactivation reagent may find its way into the column and MS detector. Figure 16 shows mass spectra of carrier gas eluting from the column before and immediately after the deactivation. The spectrum of DMCS is also included for reference. There is no evidence of any degradation in the background signal or any indication of any DMCS being present after the deactivation.

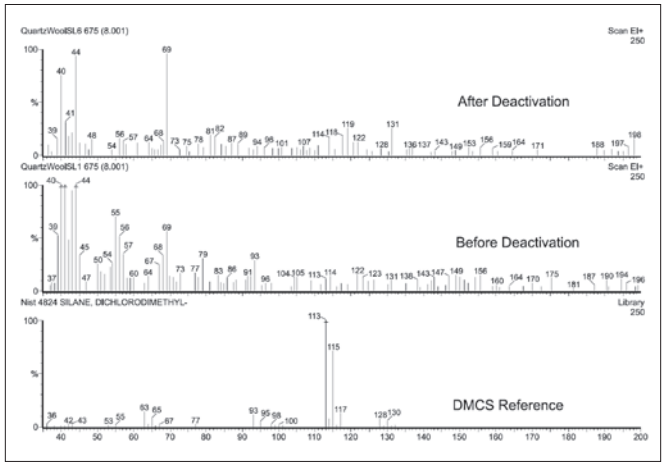

Figure 16. Spectra from background signals taken at 8 minutes in the chromatograms shown in Figures 14 and 15.

Eliminating potential contamination, reducing analysis time and increasing column life

Many applications require the determination of just a few components within a complex sample matrix. In instances where these analytes elute from the chromatographic column earlier than much of the bulk of the sample, the next analysis is delayed until all sample components have eluted from the column. To accelerate the process, it is common to perform an extended temperature program after the analytes have eluted, but this places additional thermal stress on the column and may reduce its operating life. It also dumps all the sample components into the detector where concerns with contamination may arise – especially with a mass spectrometer.

The use of the classical single column backflush technique, as enabled by PreVent in the Time-Saver mode, enables less volatile sample residue to be removed from the column without contacting the detector and often without the need for any temperature programming. Figure 17 illustrates the steps involved.

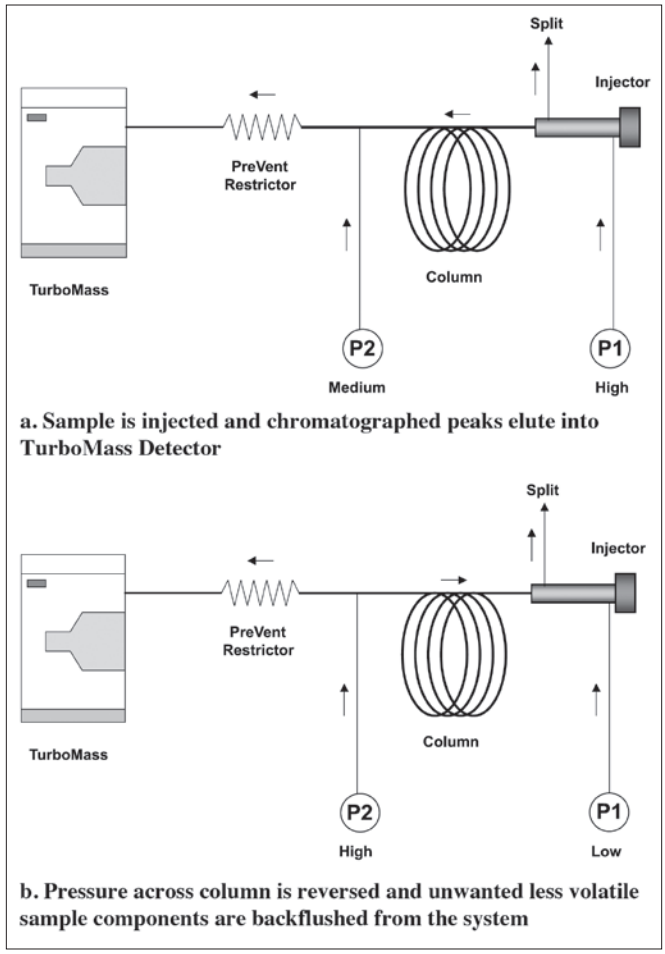

Figure 17. Classical single column backflush with PreVent.

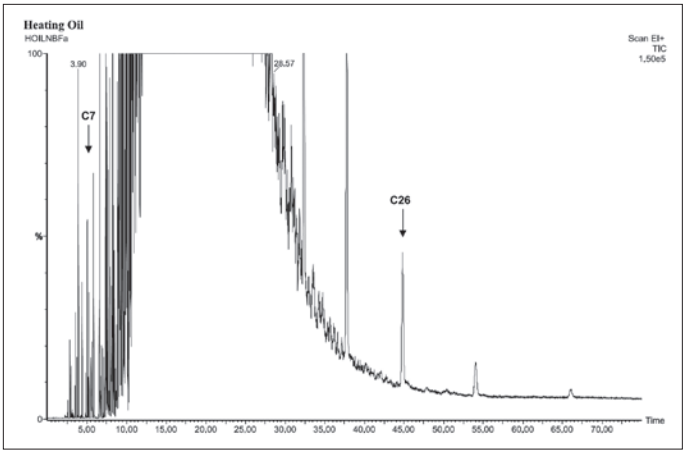

Figure 18. Temperature-programmed chromatogram of a domestic heating oil sample. Column: 30 m x 0.250 mm x 1.0 µm PE-1. Oven: 75 °C for 6 min then 20 °C/min to 250 °C and hold for 60 min. Carrier gas: helium at 12 psig. etection: PerkinElmer TurboMass MS in TIC mode, 35 to 450 Daltons.

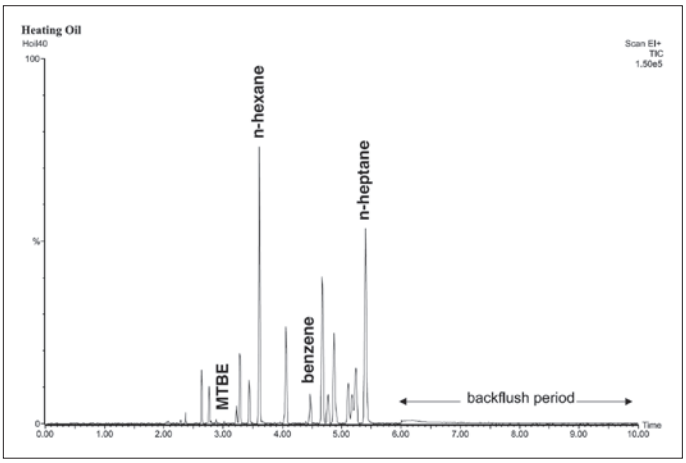

Figure 19. Isothermal chromatogram of volatile compounds in domestic heating oil using PreVent in Time Saver mode to backflush less volatile sample components. Column: 30 m x 0.250 mm x 1.0 µm PE-1. Oven: 75 °C for 10 min. Carrier gas: helium at 45 psig at inlet for 6 min, then 1 psig for 4 min, 33 psig at midpoint for 6 min and then 60 psig for 4 min. Detection: PerkinElmer TurboMass MS in TIC mode, 35 to 450 Daltons.

Figure 18 is an example of an application where the volatile analytes elute early in the chromatography, but the unwanted bulk of the heating oil sample still has to be eluted before the next analysis can be commenced. This 'clean-up' stage requires a temperature program and adds an extra 60 minutes (temperature program time, cooling time and equilibration time) to the chromatographic cycle time.

Figure 19 shows chromatography of the same sample using a method based around the PreVent system. The analysis is now performed isothermally in just 12 minutes (isothermal run time, backflush time and pneumatic equilibration time) representing a six-fold increase in sample throughput and less thermal stress on the column.

Conclusion

This application note is designed to give the reader just a taste of the possibilities the PerkinElmer PreVent system has to offer the mass chromatographer. Although the system is simple in design and use, it effectively addresses many of the operational and performance difficulties associated with many sample types on a GC/MS system.

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