

Characterization of a Temperature and Flow-Programmable Microfluidic Precolumn for Gas Chromatography

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Abstract

This Application Note investigates the temperature control of Agilent Intuvo Guard Chips as a means of improved separation and selectivity in GC. Temperature adjustments, both isothermal and pulsing, are shown to influence Guard Chip solute trapping. Temperature-induced retention and backflushing of the Guard Chip can enable the removal of lower volatility solutes prior to column separation. This form of backflushing is also demonstrated to be more efficient than traditional postcolumn backflushing.

Introduction

Recent advances in microfluidics and surface coating technologies have enabled the fabrication of modular Intuvo Flow Chips for use in gas chromatography (GC). These Flow Chips can be used to construct application-specific flowpaths for a variety of GC applications. For example, an uncoated, deactivated microfluidic Flow Chip can be placed in the flowpath between the GC inlet and analytical column. This Flow Chip can function as either a retention gap or guard column (with the integration of a Guard Chip) analogous to an uncoated deactivated precolumn used in traditional GC. However, unlike traditional GC, independent thermal control can be used to selectively and quantitatively retain or mobilize solutes based on volatility. Combining thermal control with pneumatic control to induce flow reversal can be used for eliminating matrix before introduction into the analytical column. This Application Note explores in detail, the selectivity of a microfluidic Guard Chip. Examples of Guard Chip programming for trapping and backflushing soil matrix are demonstrated for the analysis of semivolatile organic compounds.

Experimental

All experiments were performed on the Agilent Intuvo 9000 GC equipped with a multimode inlet, single GC column, and a Flow Chip for postcolumn backflush in mass spectrometry (MS). The GC was interfaced to a single quadrupole Agilent 5977A MSD. The Guard Chip serves as a microfluidic precolumn by providing a deactivated flowpath of approximately 1 m in length and 0.5 mm in diameter. Temperature control of the Guard Chip is independent of the GC column, involving conductive heating by a low thermal mass ceramic heater and convective cooling by a high velocity

blower (Figure 1). With the postcolumn backflush module installed, the flow in the GC column and Guard Chip could be reversed during backflushing.

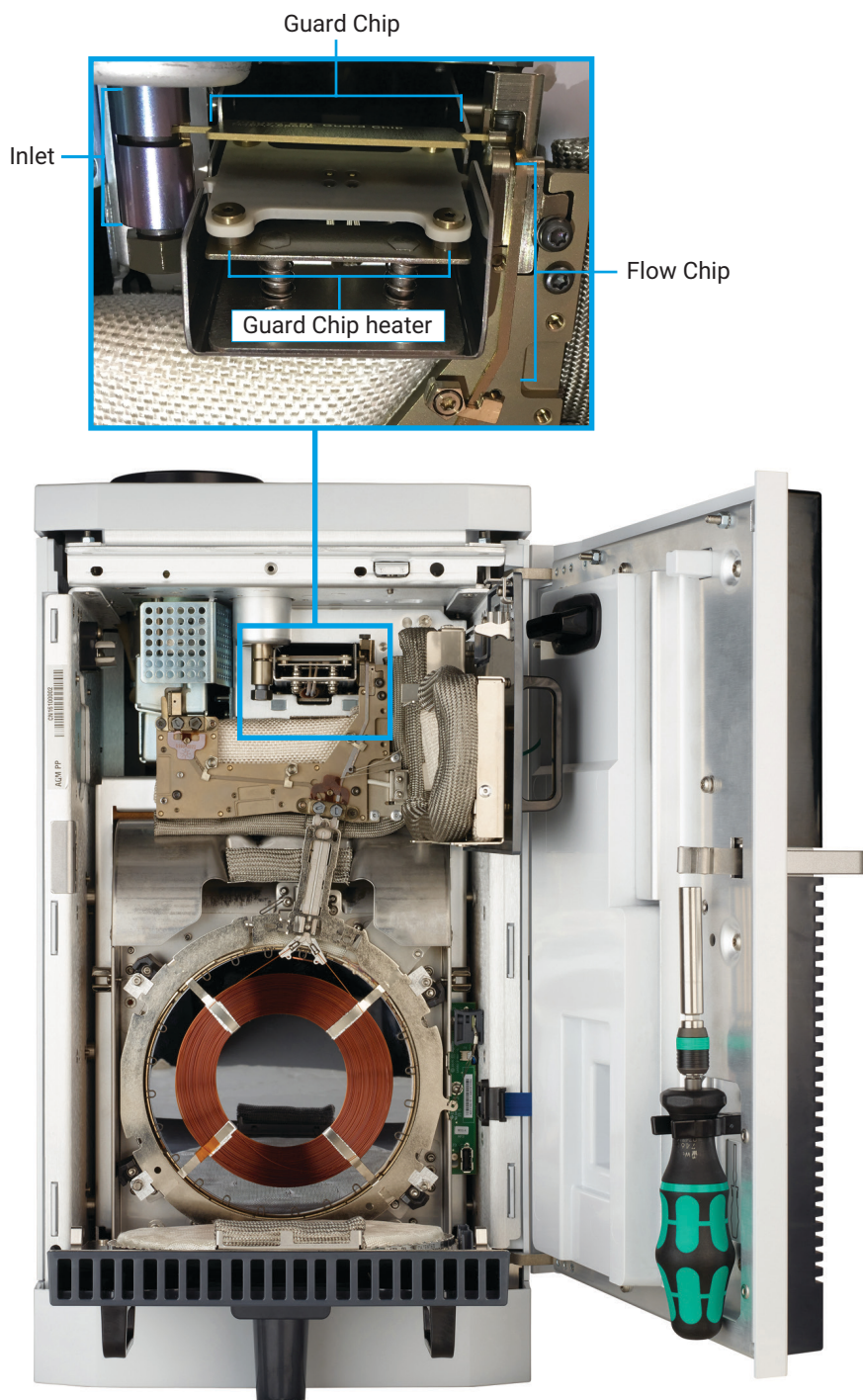


Figure 1. Intuvo GC and microfluidic precolumn (that is, Guard Chip).

Samples

- **Alkane standard:** Alkane standard mixture for performance tests of GC systems (C₁₀–C₄₀, Sigma-Aldrich, p/n 68281)
- **Sample extract:** Composite dichloromethane soil extract donated from ESC Lab Sciences (Mt. Juliet, TN)

Results and discussion

Guard Chip trapping experiments

Initial experiments were carried out to determine the thermal trapping capabilities of the Guard Chip. Two GC runs were made, one with the Guard Chip at 40 °C and another at 350 °C (both isothermal) with the GC following an oven program (Figure 2).

Instrument conditions

Parameter	Value
GC	9000 Intuvo GC with simple MS flowpath
MS	5977A MSD with EI Extractor source
Column	Agilent J&W DB-UI 8270D Intuvo GC column, 30 m × 0.25 mm, 0.25 μm (p/n 122-9732-INT)
Liner	Ultra Inert, splitless, single-taper liner with glass wool (p/n 5190-2293)
Injection volume	1 μL
Inlet	Split/splitless 280 °C Purge 60 mL/min at 0.5 minutes Septum purge switched flow mode 3 mL/min
Guard Chip program	Varied
Column temperature program	Varied
Bus temperature	310 °C
Flow	1.2 mL/min constant flow
Transfer line temperature	320 °C
Ion source temperature	320 °C
Quadrupole temperature	200 °C

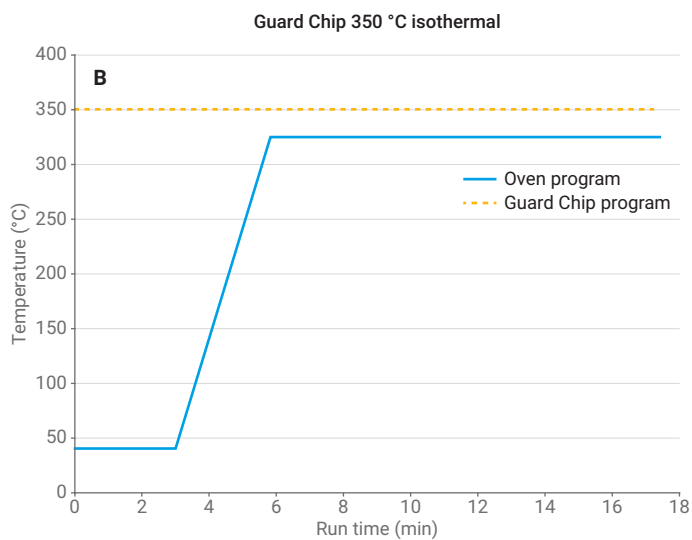
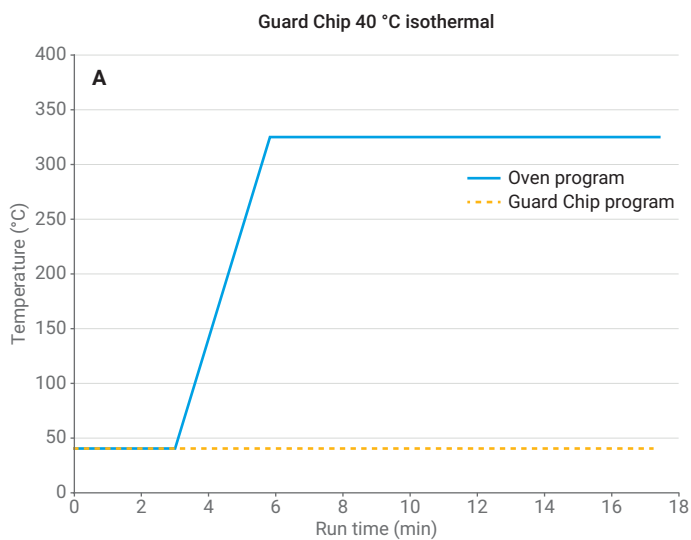


Figure 2. Programming curves for the Guard Chip heater and column oven.

Figure 3 shows the results for the injection of C_{10} to C_{40} . At 40 °C, C_{10} through C_{14} are not retained on the Guard Chip, with C_{16} partially retained. At 350 °C, C_{10} through C_{40} are passed through the Guard Chip and eluted from the column. With the Guard Chip following the oven program, recovery of C_{10} through C_{40} is quantitative (Figure 4).

Guard Chip pulsing experiments

The Guard Chip temperature was programed at 300 °C/min to 350 °C, then rapidly cooled (that is, temperature pulsed). Figure 5 shows the Guard Chip and GC pulsing programs and the

associated chromatogram. Recovery of C_{10} to C_{40} with the pulsed Guard Chip was the same as running the Guard Chip isothermally at 350 °C or following the GC oven program.

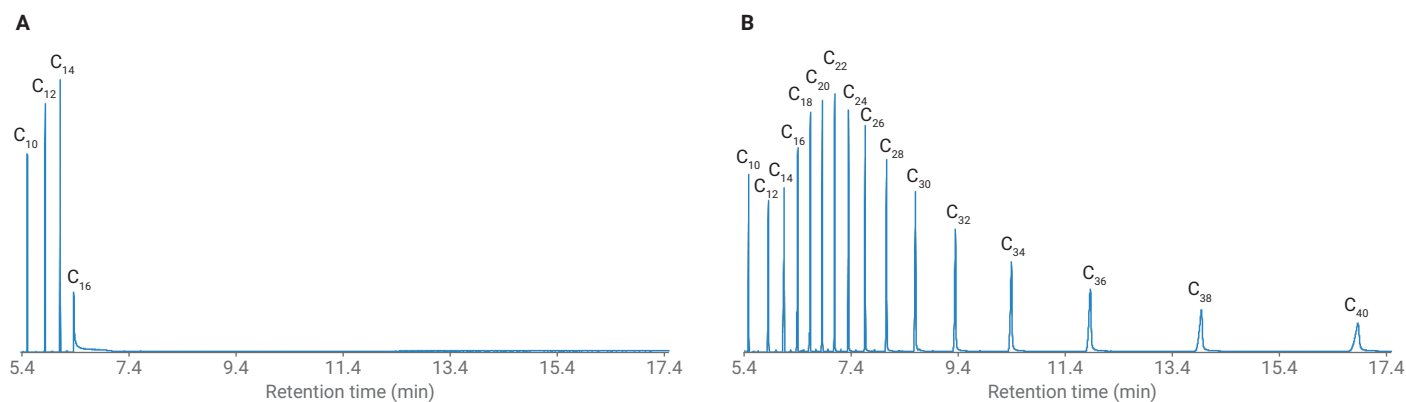


Figure 3. Chromatograms with isothermal Guard Chip settings.

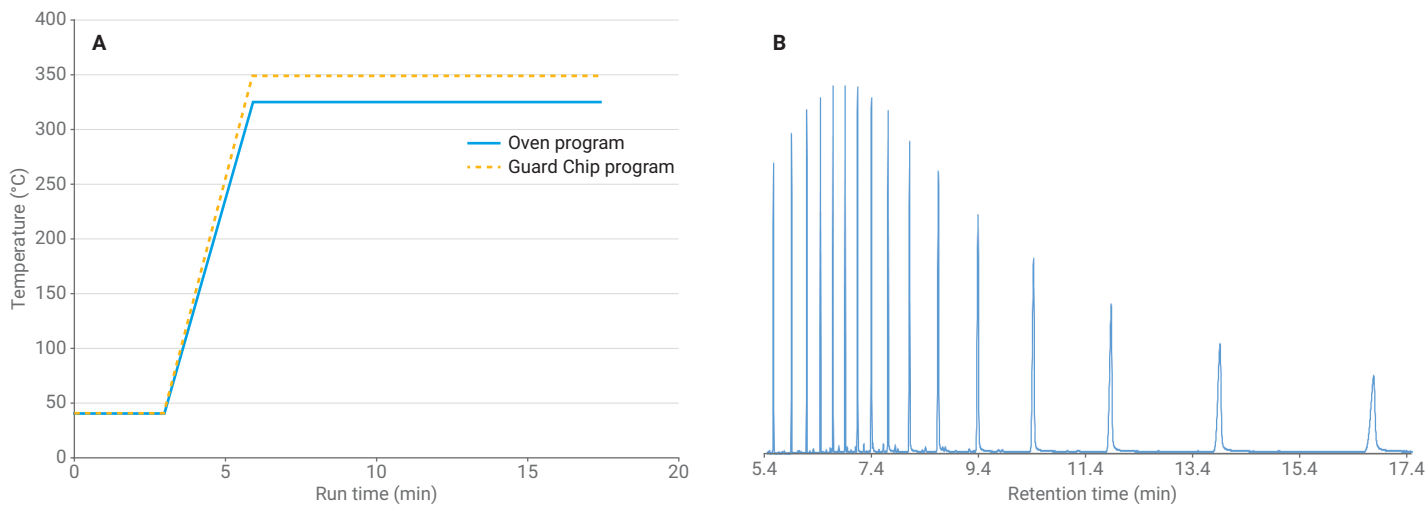


Figure 4. Ramped Guard Chip and GC oven result in quantitative recovery of C_{10} to C_{40} .

Guard Chip pulsing selectivity

The Guard Chip temperature was pulsed to different final temperatures and rapidly cooled. Figure 6 shows a series of chromatograms with the Guard Chip

pulsed to 100, 110, 120, 125, and 130 °C, demonstrating the selectivity of temperature pulsing.

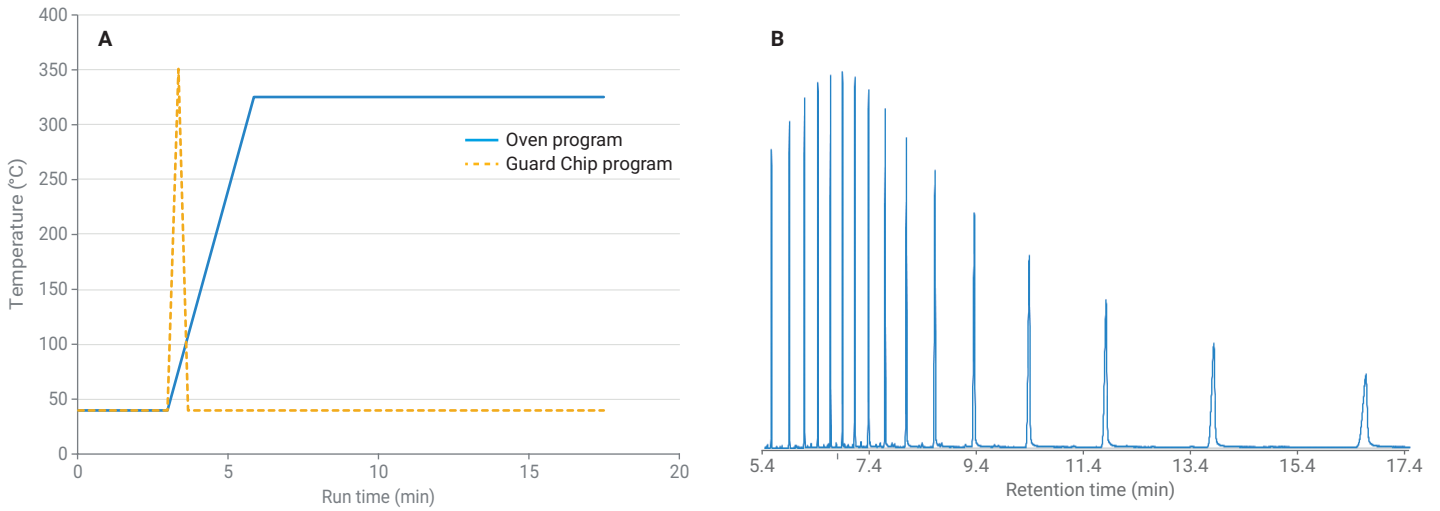


Figure 5. Guard Chip pulsing experiment and C₁₀ to C₄₀ recovery.

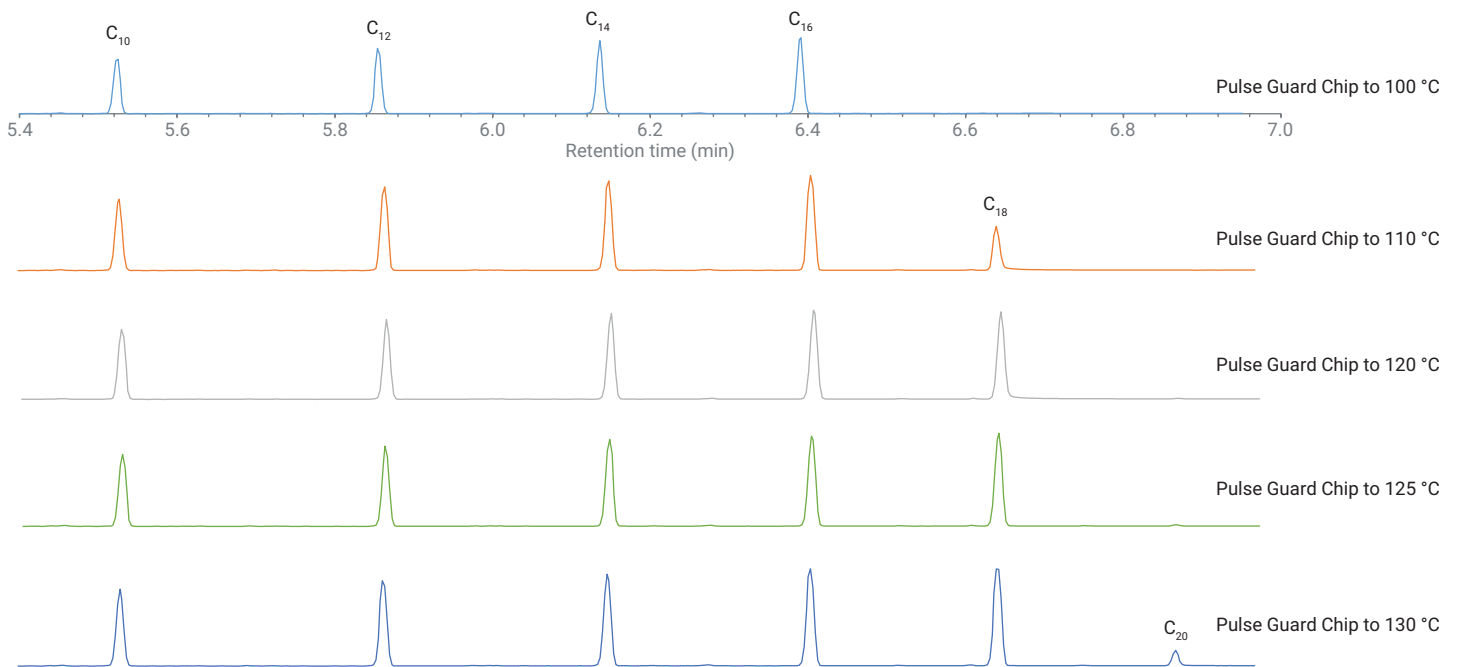


Figure 6. Guard Chip pulsing to different final temperatures.

Additional experiments were carried out by pulsing the Guard Chip to final temperatures of 100 to 310 °C in 5 °C increments. The temperatures at which each alkane was partially volatilized and fully volatilized were plotted against the corresponding boiling point of each alkane (Figure 7). This plot is a measure of the selectivity of Guard Chip pulsing across the boiling point range. This can be used to estimate the final pulsing temperature required to volatilize or retain compounds on the Guard Chip.

Guard Chip pulsing with backflush

Guard Chip pulsing was combined with postcolumn backflushing. During backflush, the column flow is reversed to push low volatility compounds out of the column and split vent trap. Backflushing has been demonstrated to improve retention time reproducibility and column lifetime. Figure 8 shows the temperature and pressure programs used for backflushing.

Based on the selectivity curve in Figure 7, a pulse temperature of 200 °C should volatilize C₁₀ to C₂₆ while C₂₈ through C₄₀ are retained. Figure 9 shows the chromatograms based on the method parameters in Figure 8. The pulse temperature of 200 °C quantitatively releases C₁₀ to C₂₆ with partial volatilization of C₂₈ (A). The subsequent blank run (B) shows that the backflush successfully removed C₂₈ through C₄₀.

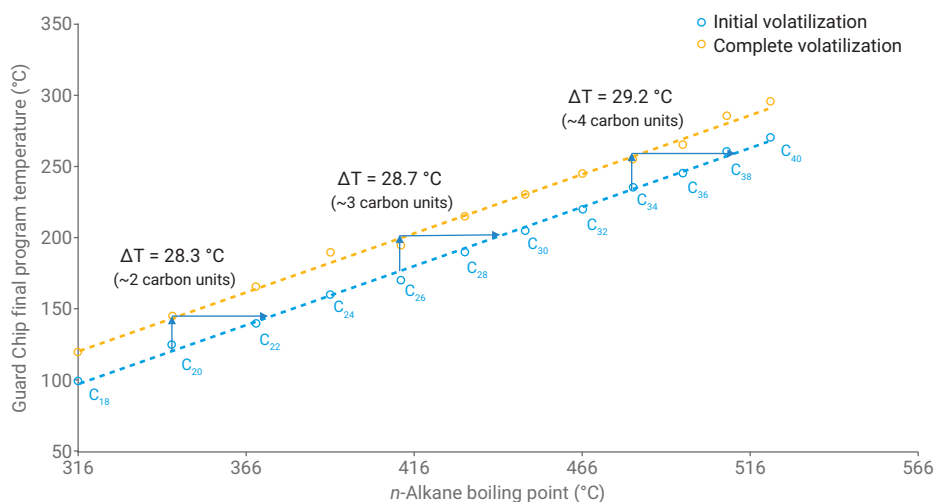


Figure 7. Guard Chip pulsing boiling point and carbon number selectivity.

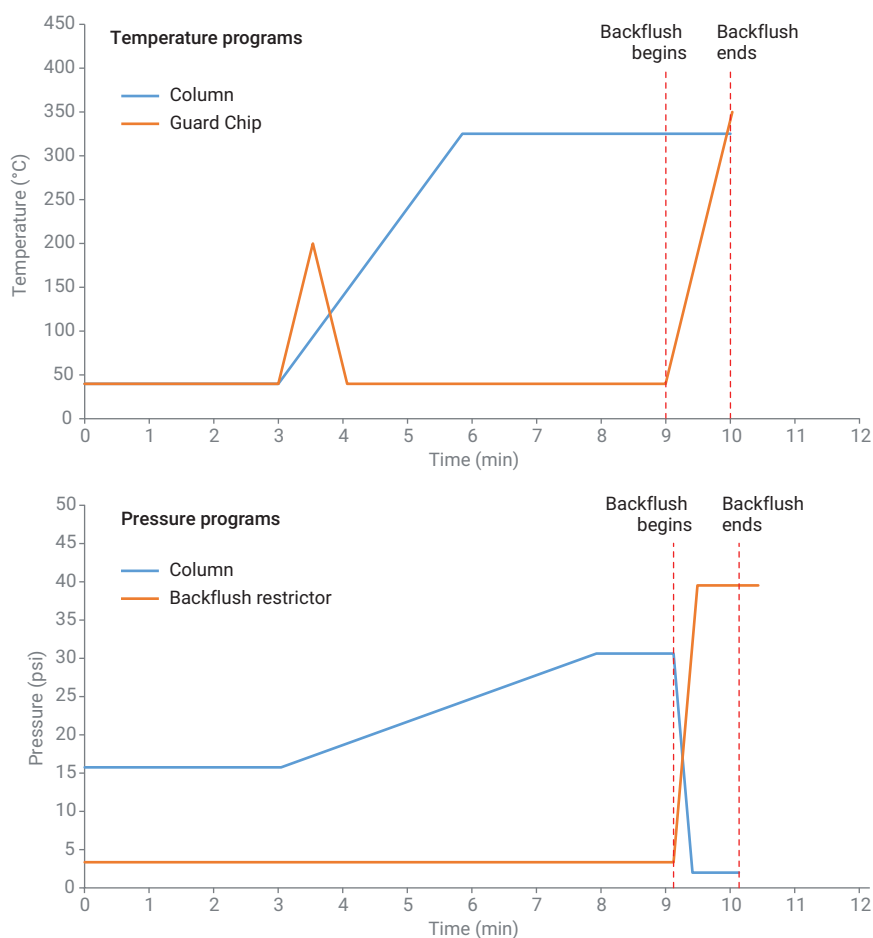


Figure 8. Temperature and pressure program used for backflushing.

Since Guard Chip pulsing can effectively release or trap compounds on the Guard Chip depending on upper pulsing temperature, it is a more efficient means of implementing postcolumn backflush. In traditional GC, where the guard column is in the same oven as the analytical column, solutes or matrix intended for backflushing will migrate through the guard column to the analytical column, and require a longer time to backflush. If these solutes or matrix compounds can be isolated on the Guard Chip, then backflush time should be reduced. Figure 10 shows the time required to backflush C₂₈ through C₄₀ using Guard Chip pulsing and a traditional GC approach where the Guard Chip temperature was programmed to follow the column programming. Using Guard Chip pulsing, backflush was completed in 30 seconds compared to 3.5 minutes using traditional backflush.

Guard Chip pulsing with backflush: matrix study

Guard Chip pulsing with backflush was applied to a soil extract. The soil extract contained target PAHs indeno[1,2,3-cd]pyrene and benzo[ghi]perylene, and heavier matrix compounds (likely PAH isomers) eluting after the targets that were not of interest (Figure 11).

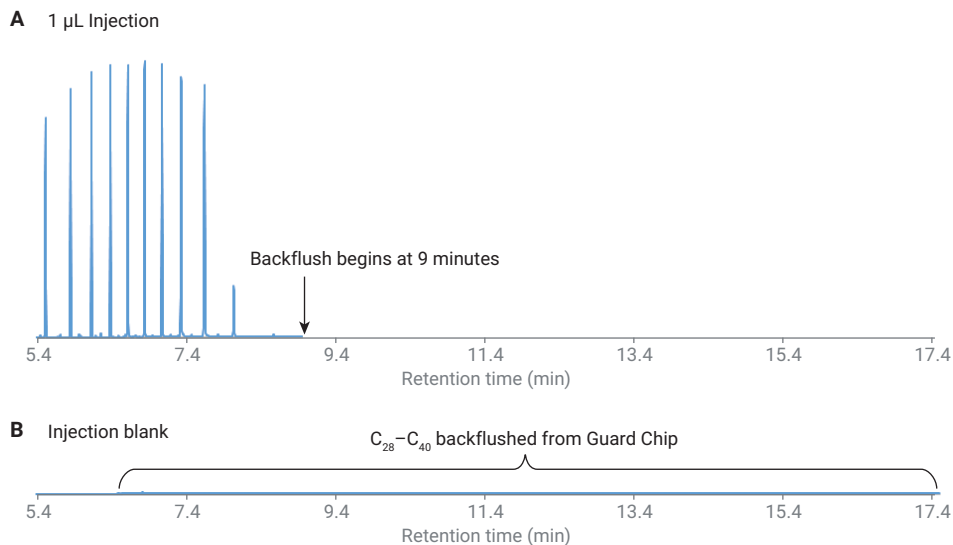


Figure 9. Chromatograms demonstrating Guard Chip pulsing with backflushing.

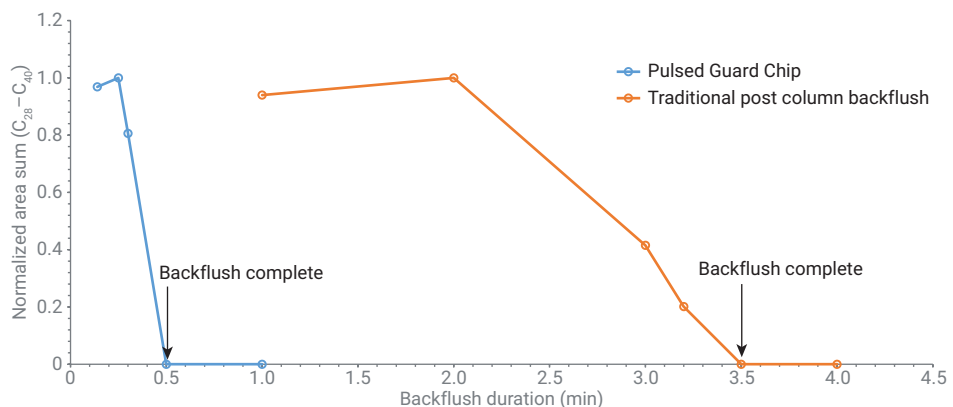


Figure 10. Time savings using Guard Chip pulsing and postcolumn backflush.

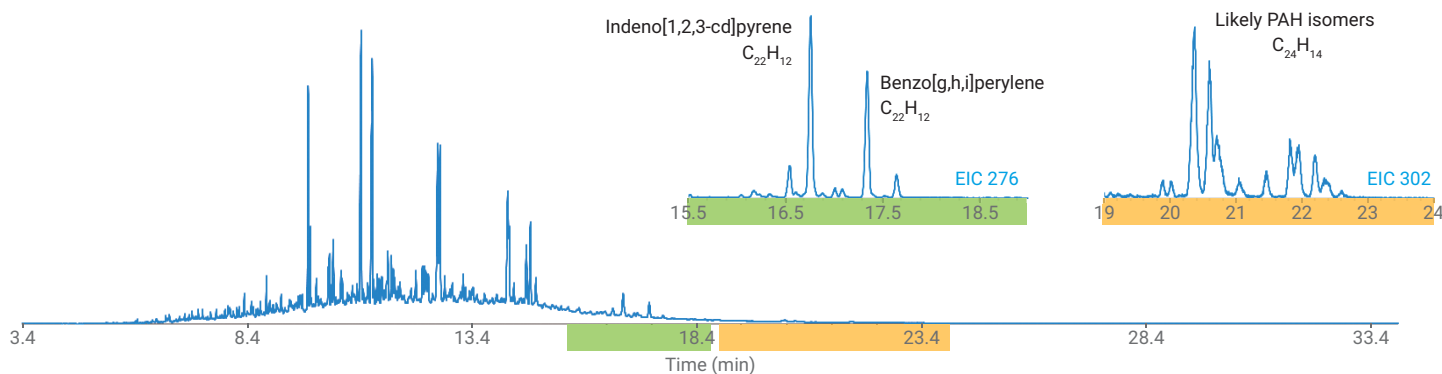


Figure 11. Soil extract with target PAHs and matrix.

To volatilize the target PAHs while trapping the matrix on the Guard Chip, an upper pulse temperature of 250 °C was required with a pulse temperature hold time of three seconds (Figure 12). A backflush time of only one minute was required to remove the matrix from the Guard Chip (Figure 13).

Conclusions

This Application Note provides fundamental information on the function and selectivity of Intuvo Guard Chips. Adjustments to the Guard Chip heating program, both isothermal and pulsing, can add an element of selectivity to solute separation. Precise temperature control can be used to selectively trap compounds on the Guard Chip. Combining Guard Chip temperature pulsing with precise flow programming can be used to backflush lower volatility compounds from the Guard Chip before they enter the column. This approach provides more an efficient use of backflush compared to traditional postcolumn backflushing.

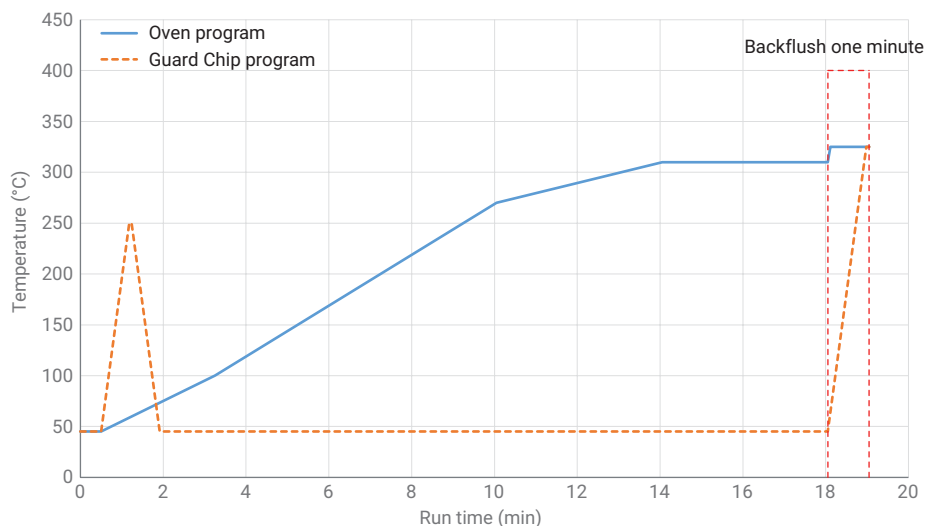
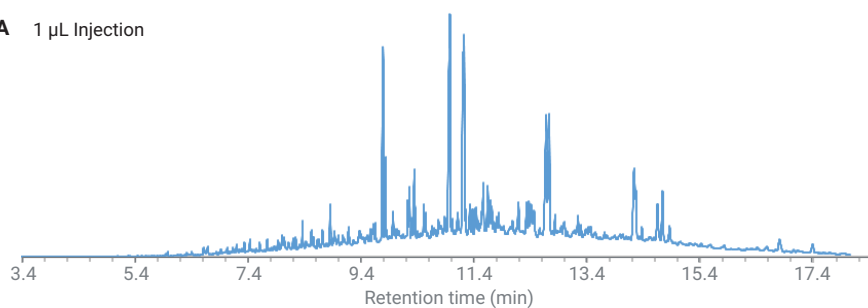


Figure 12. Guard Chip and oven program used for soil matrix.

A 1 μ L Injection



B Injection blank

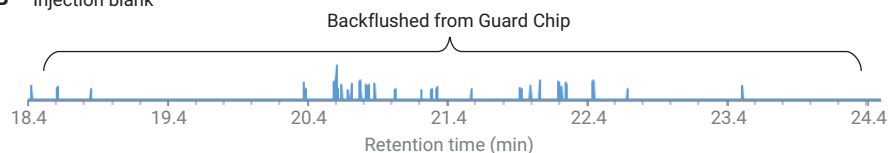


Figure 13. Soil matrix with matrix removal using backflush.