Characterization of a Temperature and Flow Programmable Microfluidic Pre-Column for Gas Chromatography.

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Introduction

Recent advances in microfluidics and surface coating technologies have enabled the fabrication of modular flow chips for use in gas chromatography. The flow chips can be used to construct application-specific flow paths for a variety of GC applications. For example, an uncoated deactivated microfluidic flow chip can be placed in the flow path between the GC inlet and analytical column. This flow chip can function as either a retention gap or guard column (i.e. 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 upon volatility. Combining thermal control with pneumatic control to induce flow reversal can be used for eliminating matrix before introduction into the analytical column. In this paper, the selectivity of a microfluidic guard chip will be explored detail. Examples of guard chip programing for trapping and backflushing soil matrix will be 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 post-column backflush flow-chip for mass spectrometry. The GC was interfaced to a single quadrupole 5977 mass spectrometer. The guard chip serves as a microfluidic precolumn by providing a deactivated flow path of about 1 meter in length and 0.5 mm in diameter. Temperature control of the guard chip is independent of the GC column and is conductively heated by a low thermal mass ceramic heater and convectively cooled by a high velocity blower (Figure 1). With the post column backflush module installed, the flow in the GC column and guard chip could be reversed during backflushing.

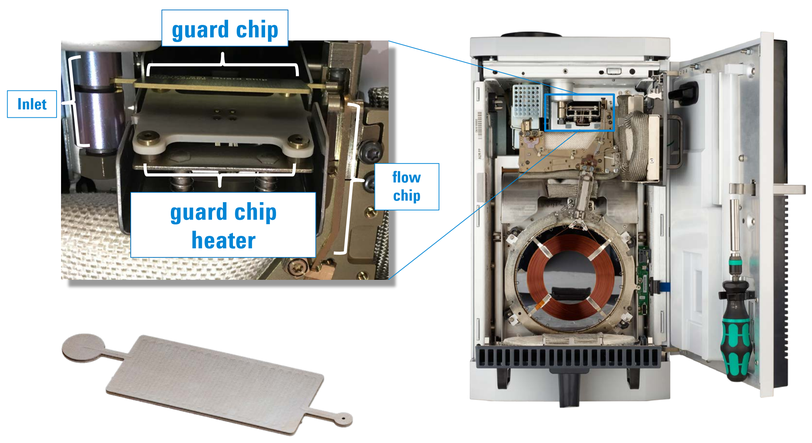

Figure 1. Intuvo GC and microfluidic precolumn (i.e. guard chip)

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 isothermal with the GC following an oven program (Figure 2). The results for the injection of C10 to C40 are shown in Figure 3. At 40 °C, C10 through C14 are not retained on the guard chip with C16 partially retained. At 350 °C, C10 through C40 are passed through the guard chip and eluted from the column. With the guard chip following the oven program, recovery of C10 through C40 are quantitatively recovered (Figure 4).

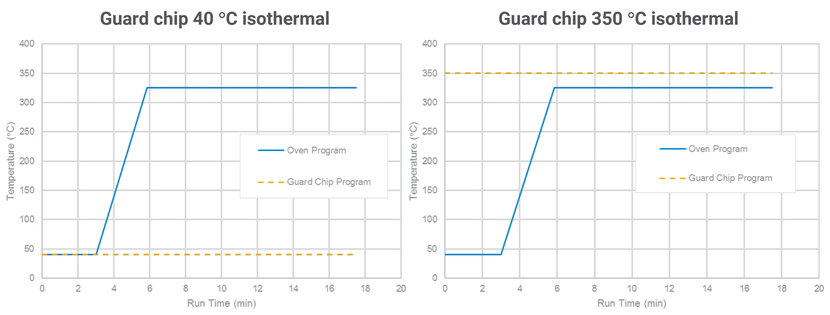

Figure 2. Programing curves for the guard chip heater and column oven

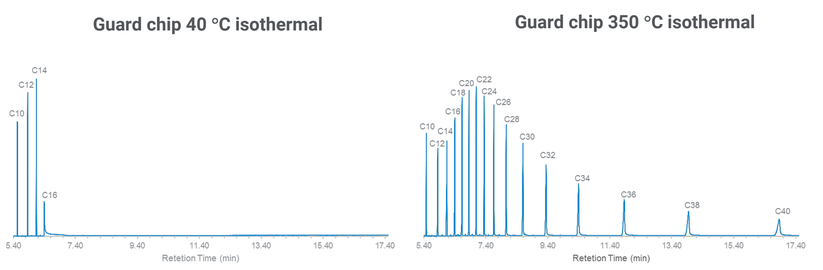

Figure 3. Chromatograms with isothermal guard chip settings

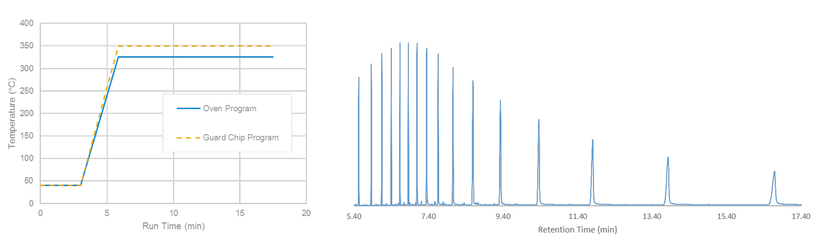

Figure 4. Ramped guard chip and GC oven result in quantitative recovery of C10 to C40.

Results and Discussion

Guard Chip Pulsing Experiments

The guard chip temperature was programed at 300 °C/min to 350 °C and then rapidly cooled (i.e. temperature pulsed). Figure 5 shows the guard chip and GC pulsing programs and the associated chromatogram. Recovery of C10 to C40 with the pulsed guard chip was the same as running the guard chip isothermally hot at 350 °C and following the GC oven program.

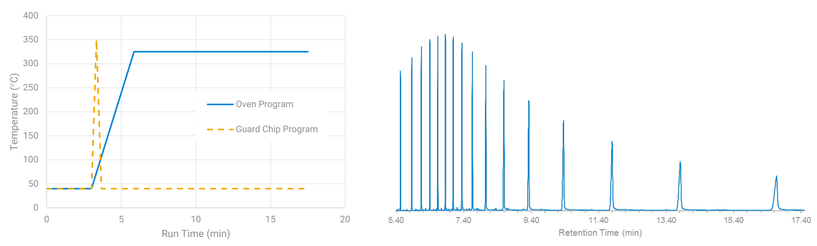

Figure 5. Guard chip pulsing experiment and C10 to C40 recovery.

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, 130 °C showing the selectivity of temperature pulsing.

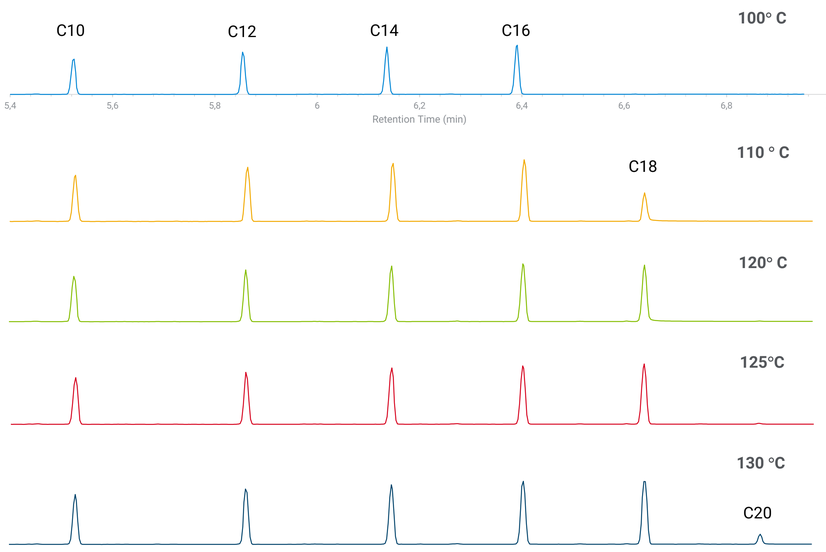

Figure 6. Guard chip pulsing to different final temperatures

Additional experiments were carried out pulsing the guard chip to final temperatures of 100 to 310 °C in increments of 5 °C. The temperatures at which each alkane was partially volatilized and fully volatilized was 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.

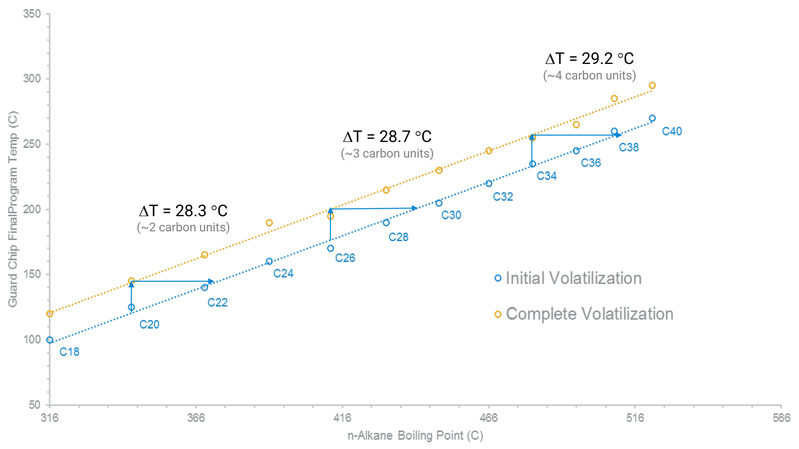

Figure 7. Guard chip pulsing boiling point and carbon number selectivity

Guard Chip Pulsing with Backflush

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

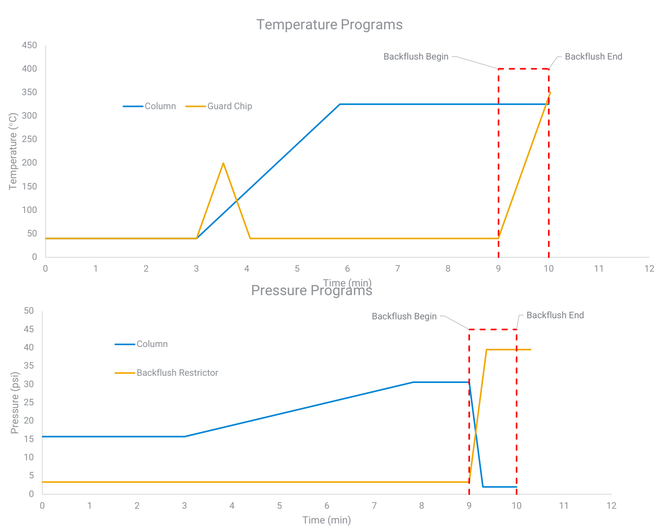

Figure 8. Temperature and pressure program used for backflushing

Results and Discussion

Guard Chip Pulsing with Backflush

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 upon the method parameters in Figure 8. The pulse temperature of 200 °C quantitatively releases C10 to C26 with partial volatilization of C28. The subsequent blank run shows that the backflush was successful at removing C28 through C40.

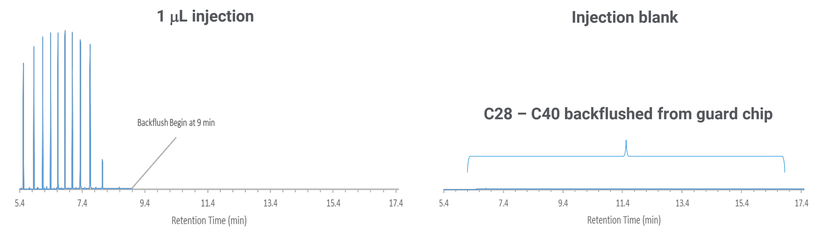

Figure 9. Chromatograms demonstrating guard chip pulsing with backflushing

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 post-column 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 will 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 programed to follow the column programing. Using guard chip pulsing, backflush was complete in 30 seconds compared to 3.5 minutes using traditional backflush.

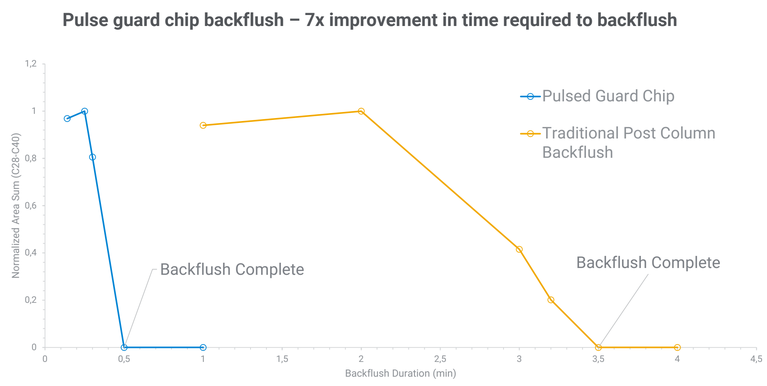

Figure 10. Time savings using guard chip pulsing and post-column backflush

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).

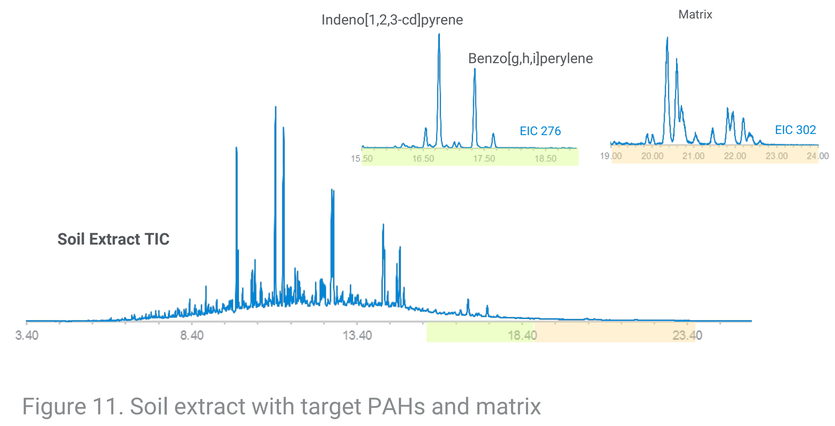

Figure 11. Soil extract with target PAHs and matrix

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 3 seconds (Figure 12). A backflush time of only 1 minute was required to remove the matrix from the guard chip (Figure 13).

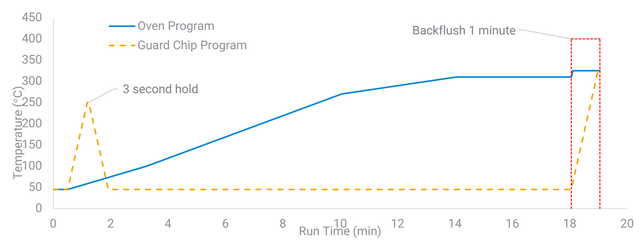

Figure 12. Guard chip and oven program used for soil matrix

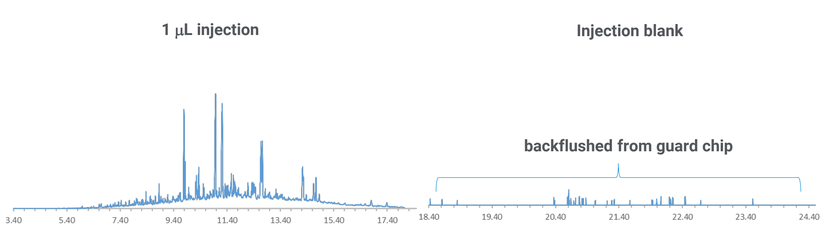

Figure 13. Soil matrix with matrix removal using backflush.

Conclusions

- This work provides fundamental information on the functioning of the guard chip in the Intuvo.
- Precise temperature control can be used to selectively trap compounds on the guard chip.
- Combining guard chip temperature pulsing with precise flow programing can be used to backflush lower volatility compounds form the guard chip before entering the column.
- This approach provides more efficient use of backflush compared to traditional post-column backflush.