K.45 Learnings from the modulation of methane in GCxGC with a flow modulator

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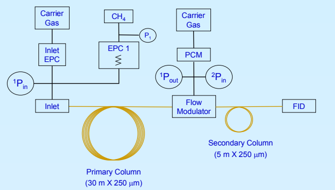
Abstract

One benefit of flow modulators is that they allow one to modulate methane as easily as less-volatile components. This in turn provides an opportunity to use methane as a hold-up time marker when investigating fundamental chromatographic phenomena in GC×GC. By bleeding a small amount of methane into the primary column carrier gas supply (Figure 1), an aliquot of methane is injected with each sample slice during each cycle. Having a methane peak indicating hold-up time in each cycle provides a very-accurate reference that can be used to track flow trends, retention factors as a function of temperature and ramp rate, initial peak widths, wrap around, etc. [1].

Through visualization of the hold-up time in 2D space, relative retention behavior and retention trends become faster and easier to investigate and interpret. Some long-held assumptions (e.g., that stationary phase bleed is a good indicator of hold-up time) are seen to be false.

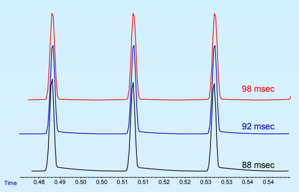
When using the approach to do fundamental retention studies one can not escape the fundamental trappings of capillary chromatography. Loss of He through fused-silica at high temperatures and low flows can cause significant errors [2].

Modulation of Methane using EPC and a Flow Modulator



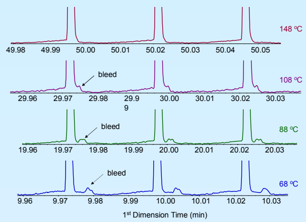
Methane is doped into the primary column carrier gas ahead of the inlet. Flow exits the primary column and enters the flow modulator, filling the sample channel at low flow rate (e.g., 1 mL/min). Meanwhile, a high flow of methane-free carrier gas feeds the secondary column (e.g., 20 mL/min). During sample transfer, a solenoid is briefly switched to direct the high flow through the sample channel to sweep it to the secondary column. Compression of the peak in time occurs due to the ratio and of secondary column flow to primary (approximately 20:1).

Modulator timing optimization is simplified



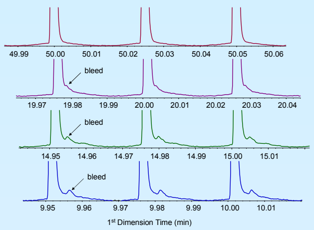
Flow modulator cycle time and transfer time need to be optimized. The typical process requires sample injection and temperature-programmed runs lasting several minutes. With modulated methane short isothermal runs of < 1 min can be used with no sample needs to be injected

Bleed Retention, Apolar-Apolar



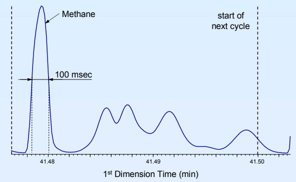
Retention of stationary phase bleed on the second column is easily visualized because of the presence of the methane void peak.

Bleed Retention, Apolar-Polar

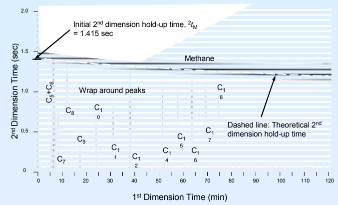


Silicone bleed from the primary column is less retained on a carbowax secondary column than a silicone based secondary column. Compare these results to those at the less.

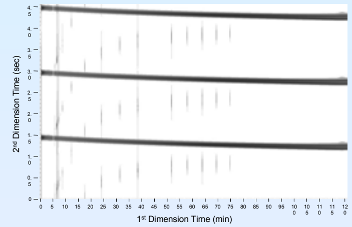
2nd Dimension slices look similar to those from Thermal Modulators



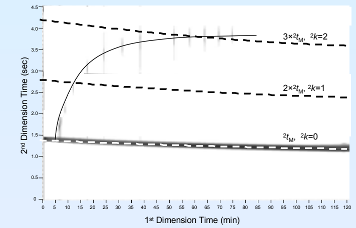
A 1.5 s section (one cycle time) slice from analysis of diesel on apolar–polar column combination. The flow-modulated methane peak provides not only a direct measure of hold-up time, but also shows initial peak width and shape. In this example, the methane peak is 100 ms wide at half height.



2D plot (GC Image software) n-alkane mix analyzed on an apolar/apolar column combination at 2 °C/min heating rate (≈ 10 °C/^1t_M) and He carrier gas. Data were processed with a 3.0 s (2 cycles) time second dimension range and then zoomed to 0–2 s range with no offset. The dark line is from the modulated methane and marks hold-up time. The dashed line represents the theoretical hold-up time for the 5.0 m × 250 µm i.d. second dimension column run in constant flow mode. One can see peaks that wrap-around to subsequent periods being displayed below the methane line.

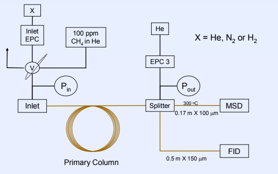


Same n-alkane data plotted with the second axis time scale equal to three cycles (4.5 s). As a consequence of data processing and plotting, peaks repeat in 1.5 s segments on the plot, making it a bit difficult to visualize retention behavior.



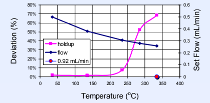
Cleaned up plot for better visualization. Replicate methane lines and reflections of analyte peaks from wrap-around were graphically masked. Dark dashed lines multiples of hold-up time (2×^2t_M, ^2k = 1) and at (3×^2t_M, ^2k = 2) were calculated and added to the plot for reference. A solid line intersecting n-alkane peak maxima was also added to accentuate the retention trend.

Air holdup time measurement configuration

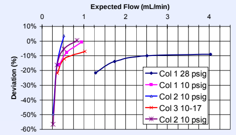


This configuration was used to measure holdup time of the primary column accurately for several carrier gases. Redundant measurements was possible (air and CH_4 by MSD, CH_4 by FID). Repeated valve injections as run time events simplified precision measurements by having all information in a single data file.

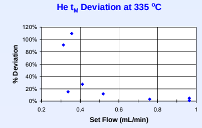
He Holdup Time Devation



Direct He Flow Measurement



He t_M Deviation at 335 °C

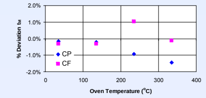


When attempting to determine the accuracy of hold-up time measurement for subsequent studies, it was found that at low flows and high temperatures, the hold-up time measurements for He deviated largely from theory. The behavior is consistent with that described in reference [2].

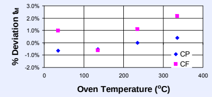
Flow deviation was confirmed by directly measurement with a bubble flow meter

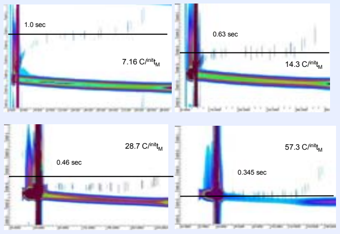
Both N_2 and H_2 carrier gases yielded hold-up time values that were within a couple of a percent of theoretical. As a consequence, future studies aimed at elucidating retention behavior will avoid use of He as the carrier gas.

Quick Holdup Check N_2
32.6 m X 262 µm X 0.25 mm



Quick Holdup Check H_2
32.6 m X 262 µm X 0.25 mm





Retention factor trends are elucidated here as a function of reduced ramp rate.
Col 1 = 32.6 m X 263 µm X 0.25 µm HP-1
Col 2 = 2.0 m X 253 µm X 0.25 µm HP-1
H_2 Carrier, Constant Flow

Conclusion

Flow modulation of methane provides a useful internal reference for hold-up time in the secondary column. Holdup time measurements in the first column (equally important to know for theoretical retention studies) indicated that He is probably not a good choice to continue fundamental studies because of losses through the column at high temperature and lower flows. Early results with N2 and H2 carrier gases appear promising.

References

1. M. S. Klee, L. M. Blumberg, *J.Chrom. A*, 1217 (2010) 1830–1837
2. J. E. Cahill, D. H. Tracy, *J. High Resol. Chromatogr.*, 21/10 (1998) 531-539