The Influence of Modulation Period Changes on Slightly Resolved Components Using Variable Modulation in GCxGC

Cory Fix and Joe Binkley | LECO Corporation, St. Joseph, Michigan

Introduction

Variable modulation is a relatively new concept in the field of comprehensive two-dimensional gas chromatography (GCxGC), where the method developer can change the modulation period throughout the course of the analysis. In general, variable modulation can be used to ensure multiple subpeaks are produced from narrow, early eluting peaks with a short modulation period, while later on providing additional peak capacity to accommodate the strongly retained, late eluting compounds. It was discovered during a variable modulation project involving polycyclic aromatic hydrocarbon (PAH) analysis that the timing of the modulation period transition to a new period would affect the subpeak profile of the analytes eluting afterwards, which was especially noticeable in the contour plots of slightly resolved critical pair analytes. Additional work studying and investigating this phenomenon is presented here.

Modulation Phase Theory

The phase of a modulated peak (not to be confused with the stationary phase of the modulator) is a way to describe the relationship between the timing of the modulator's second-dimension injection events as the unmodulated analyte band passes through it and the resulting pattern of subpeaks produced at the detector. A phase of 0° indicates a symmetrically modulated peak with one large central subpeak, while a phase of 180° indicates a symmetrically modulated peak with the two largest subpeaks being equal in height and area. Most modulated peaks in real-world analyses tend to have an asymmetric phase in between these two extremes. Figure 1 displays conceptual diagrams for peaks modulated with: (A) a 0° phase; (B) a 180° phase; (C) an in-between phase. The red dashed line indicates the plane of symmetry in diagrams A and B.

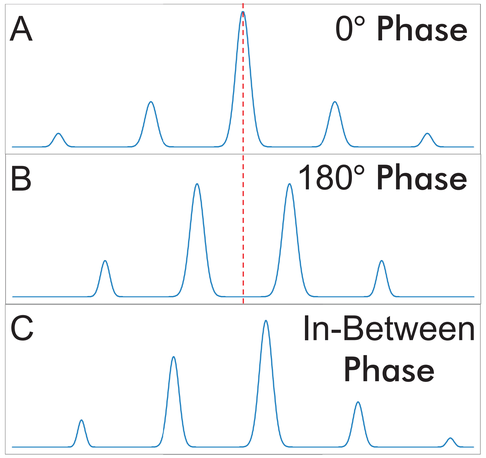

Figure 1. Conceptual diagrams of a peak modulated with different phases. (A) corresponds to 0° phase, (B) corresponds to 180° phase, and (C) corresponds to an asymmetric phase in between.

Experimental Methodology

The data presented here was produced using the LECO Pegasus® 4D TOFMS, a GCxGC-TOFMS instrument with variable modulation control in the ChromaTOF® software package, allowing the instrument user to control the modulation period as easily as one controls a temperature program.

The PAH standards mixture consisted of a 2000 µg/mL phenanthrene-d10 in dichloromethane internal standard (Restek #31045), 500 µg/mL EPA Method 8310 PAH mixture in acetonitrile (#31841), and 1000 µg/mL decafluorobiphenyl in acetonitrile standard (#31842).

The variable of interest that was incrementally changed for this experiment was the time of the transition between a modulation period of 2 s and a modulation period of 3 s. All other conditions were held constant and are described in Table 1. After the sequence of five runs at different transition times was complete, a second sequence was performed to make sure that the modulation phases were reproducible and not completely random. While the slightly resolved benzo(b)fluoranthene and benzo(k)fluoranthene analytes experienced a modulation period of 3 s during their modulation in all cases, altering the time of the 2 s to 3 s transition would alter the modulation phase enough to produce visibly different contour plot representations of these two compounds.

Carrier Gas	Helium using corrected constant flow control
Injection Volume (µL)	1
Split Ratio	Splitless
Flow Rate (mL/min)	1.4
Primary Column	30 m x 0.25 mm x 0.25 µm Rxi-1ms
Secondary Column	1 m x 0.10 mm x 0.10 µm RTX-17
Primary Oven Ramp	50°C for 0.5 min then 10°C/min to 100°C then 5°C/min to 300°C with 5 min hold
Secondary Oven Ramp	+10°C offset from primary oven
Modulator Offset	25°C
Initial Modulation Period Profile	2 s period (0.4 s hot) - 0 to 2250 s 3 s period (0.5 s hot) - 2250 to 2598 s 5 s period (0.8 s hot) - 2598 s to end
Transfer Line Temperature	270°C
Ion Source Temperature	200°C
Mass Spec Detector Voltage (V)	1600
Mass Spec Acquisition Delay (s)	500
Mass Range (m/z)	50-500
Acquisition Rate (spectra/s)	100
Electron Energy for EI (V)	-70
Collection/Processing Software	ChromaTOF 4.34

Table 1. Experimental conditions for the variable modulation PAHs project.

Results

Figure 2 displays the overall variable modulation GCxGC-TOFMS TIC contour plot. The PAH peaks are labeled according to Table 2 provided below. Two critical pairs of interest are 15 and 16 (benzo(b)fluoranthene and benzo(k)fluoranthene) and 18 and 19 (indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene). Changing the modulation period during the run leads to a contour plot exhibiting a step function aspect, readily identifying the regions where modulation period transitions occur.

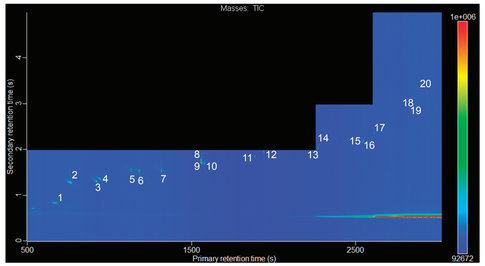

Figure 2. TIC contour plot of the variable modulation GCxGC-TOFMS analysis of the PAH standards mixture. The numbered peaks correspond to the analytes listed in Table 2.

Analyte	Peak #	Unique Mass	Avg t_r'	Avg t_r''	pg
decafluorobiphenyl	1	334	625	0.75	2.3
naphthalene	2	128	685	1.06	0.7
2-methylnaphthalene	3	142	778	1.06	1.5
1-methylnaphthalene	4	142	790	1.09	1.1
acenaphthylene	5	152	895	1.20	1.2
acenaphthene	6	153	920	1.19	1.7
fluorene	7	166	995	1.19	2.3
phenanthrene-d10	8	188	1120	1.33	2.5
phenanthrene	9	178	1120	1.34	2.0
anthracene	10	178	1130	1.31	2.1
fluoranthene	11	202	1285	1.43	1.8
pyrene	12	202	1315	1.50	1.8
benzo(a)anthracene	13	228	1480	1.59	6.4
chrysene	14	228	1485	1.62	23.5
benzo(b)fluoranthene	15	252	1625	2.16	20.4
benzo(k)fluoranthene	16	252	1630	2.16	4.7
benzo(a)pyrene	17	252	1670	2.57	25.1
indeno(1,2,3-cd)pyrene	18	276	1875	4.08	48.4
dibenzo(a,h)anthracene	19	276	1880	4.05	93.6
benzo(ghi)perylene	20	276	1928	4.72	150.0

Table 2. List of PAH standards analyzed with pg detection limits extrapolated based on S/N = 5.

Figure 3 displays ten contour plot representations of the slightly-resolved benzo(b)fluoranthene and benzo(k)fluoranthene analytes, with two duplicates for each of five different transition times. In each figure, the time of the transition between a 2 s modulation period and a 3 s modulation period is listed. The cyclical nature of the phase shifting is evident since rows 2 and 5 (i.e. t = 2252 and 2258 s) exhibit very similar contour plots with poorer resolution for the rows in between. Even though the modulation period transition occurs ~300 s before these analytes reach the modulator, there is a clear influence on the contour plot peak shape.

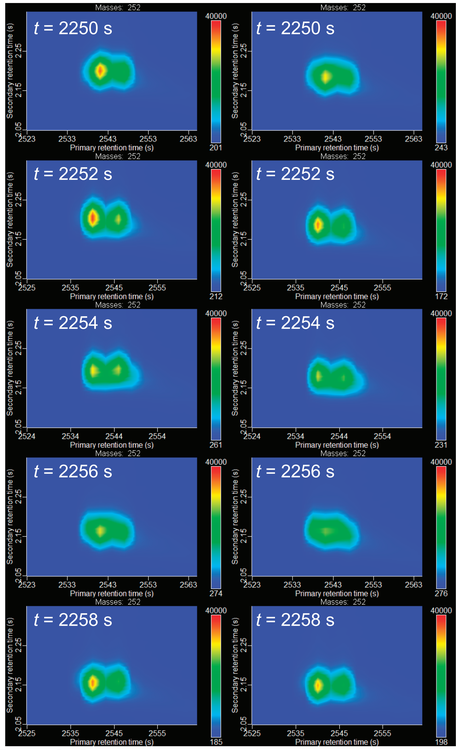

Figure 3. Contour plot representations of benzo(b)fluoranthene and benzo(k)fluoranthene with different modulation period transition timing. The time of each 2 s to 3 s modulation period change is provided by t.

Figure 4 displays the overlaid 1D chromatograms of the analytes of interest to demonstrate the reproducibility of the modulation phases. As was shown in Figure 3, the subpeak profile of t = 2252 s and t = 2258 s are very similar, demonstrating the cyclical nature of the modulation phases.

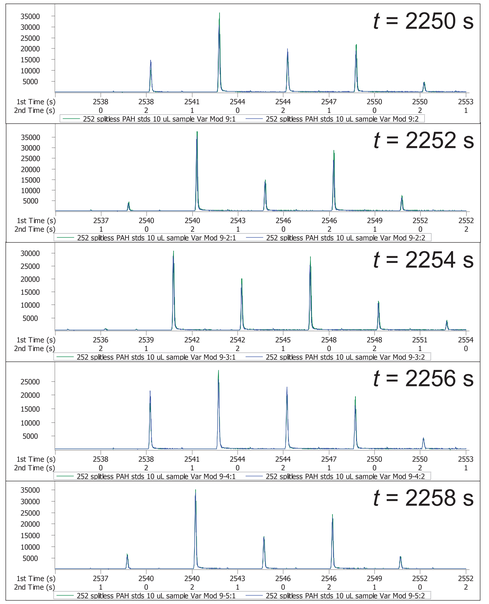

Figure 4. Overlaid 1D representations of benzo(b)fluoranthene and benzo(k)fluoranthene with different modulation period transition timing. The time of each 2 s to 3 s modulation period change is provided by t.

Conclusions

Variable modulation is a relatively new capability of the ChromaTOF software platform, allowing GCxGC users to further optimize their separations with tuned modulation periods. One of the previously unforeseen aspects of this new capability is how altering the modulation period during the run can affect the subsequent eluting peaks that pass through the modulator. While trying to force a particular modulation phase on a pair of closely eluting peaks is exceedingly difficult, knowing that slight alterations in the modulation period transition timing can significantly change the modulation phase allows for some additional fine-tuning of the separation where problematic critical pairs exist.