Delivering the Right Results

Evaluation of a Liquid Cryogen-Free Thermal Modulator for GCxGC

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INTRODUCTION

A common limitation of the cryogenically-cooled thermal modulator for GCxGC is its consumption of liquid cryogen. In the LECO GCxGC thermal modulator utilizing liquid nitrogen as a cryogen, the liquid nitrogen is utilized to chill a jet of dry nitrogen gas,which is then used to focus effluent from the first dimension column in the modulator. A jet of hot air is then used to desorb this focused effluent as a narrow plug onto the second dimension column. In situations where resources or space are limited, the elimination of a large cryogen dewar could be desirable, from both an expenditure and laboratory real estate viewpoint. In this work, a dual-stage quad-jet thermal modulator, which does not use liquid cryogen, is described and evaluated for use in GCxGC. In this thermal modulator, a closed-loop chiller utilizing a cold-probe is used in place of a dewar of liquid nitrogen to cool the dry nitrogen gas for use in the cold jet. The Consumable-Free (CF) Modulator's usable range is for compounds with volatilities n-C_8 ≥ ~n-C_{40}. The CF Modulator's performance as it relates to modulator setup and methodology was evaluated for an analysis of diesel fuel. Peak widths for biphenyl will be used as a gauge of performance.

DIFFERENCES: CF MODULATOR VS. LN_2 MODULATOR

The basic design of the thermal modulator is relatively unchanged. It is a dual stage, quad-jet thermal modulator. There are three significant design changes from the liquid nitrogen (LN_2) modulator.

- The dewar containing the liquid nitrogen has been removed and replaced with a closed-loop chiller utilizing a cold-finger. The chiller's minimum operating temperature is -80 °C. The temperature of LN_2 is -196 °C.
- The shape of the cold jets has been changed from a cylindrical tube on the LN_2 modulator to a fan shape on the CF modulator. This is intended to focus the cold jet on the column due to the decrease in cooling capacity.
- The electronics controlling the modulator, modulator block heating, and secondary oven have been moved from the auxiliary controls on the Agilent Gas Chromatograph with the LN_2 modulator to an external "piggy-back" electronic control box for the CF modulator system.

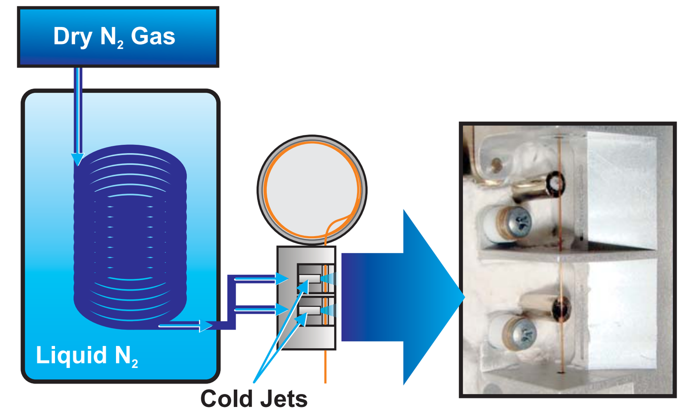

Figure 1. A schematic of the cooling system and modulator on the thermal modulator utilizing LN_2. The cold jets on this system are cylindrical.

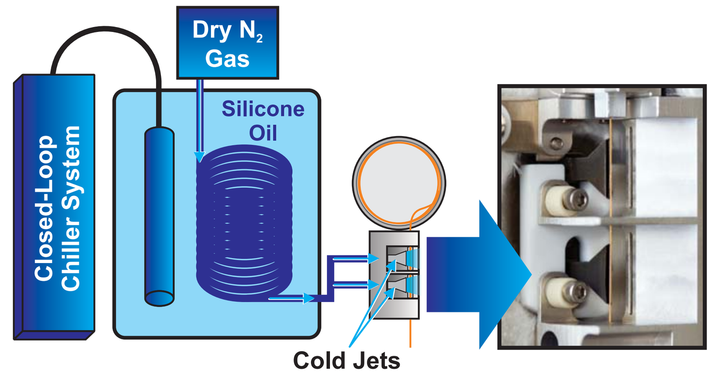

Figure 2. A schematic of the cooling system and modulator on the thermal modulator utilizing the closed-loop chiller. The cold jets on this system are fan-shaped to better focus the cooled N_2 gas onto the column.

Figure 3. A LECO Pegasus® 4D utilizing the LN_2 modulator (left) and a LECO Pegasus 4D utilizing the CF Modulator (right). Note the absence of the liquid nitrogen dewar (to the left of the autosampler) on the CF Modulator system.

EXPERIMENTAL CONDITIONS

The following chromatograms show system performance for identical injections of pump diesel. Two modulation locations were evaluated, the start of the secondary column (conventional) and the end of the primary column. The reason for evaluating modulating on the end of the primary column was to determine if the lower linear carrier gas velocity in the primary column would facilitate enhanced trapping performance (< n-C_8). The expected trade-off for trapping of more volatile compounds would be increased injection peak width and less ideal peak shapes, especially for less volatile compounds.

Sample
- Pump Diesel (neat)

Inlet Conditions

– Inlet Type:	PTV
– Inlet Mode:	Split
– Split Ratio:	100:1
– Inlet Temperature:	250°C
– Injection Size:	200 nL

GC Conditions

– Primary Column:	50 m x 0.20 mm ID x 0.5 µm df DB-PONA
– Secondary Column:	1.7 m x 0.10 mm ID x 0.1 µm df DB-Wax
– Carrier Gas:	Helium
– Carrier Gas Flow:	1.5 mL/min Corrected Constant Flow
– Primary Temperature Program:	100°C, hold for 0.2 min Ramp at 1.5°C/min to 240°C, hold for 20 minutes (LN_2 Modulator) Ramp at 2.0°C/min to 240°C, hold for 20 minutes (CF Modulator)

GCxGC Conditions
- Modulation Location, Modulator Period, Modulator Offset, Secondary Oven Offset, and Hot Pulse Timing are variable. See each figure for these conditions.

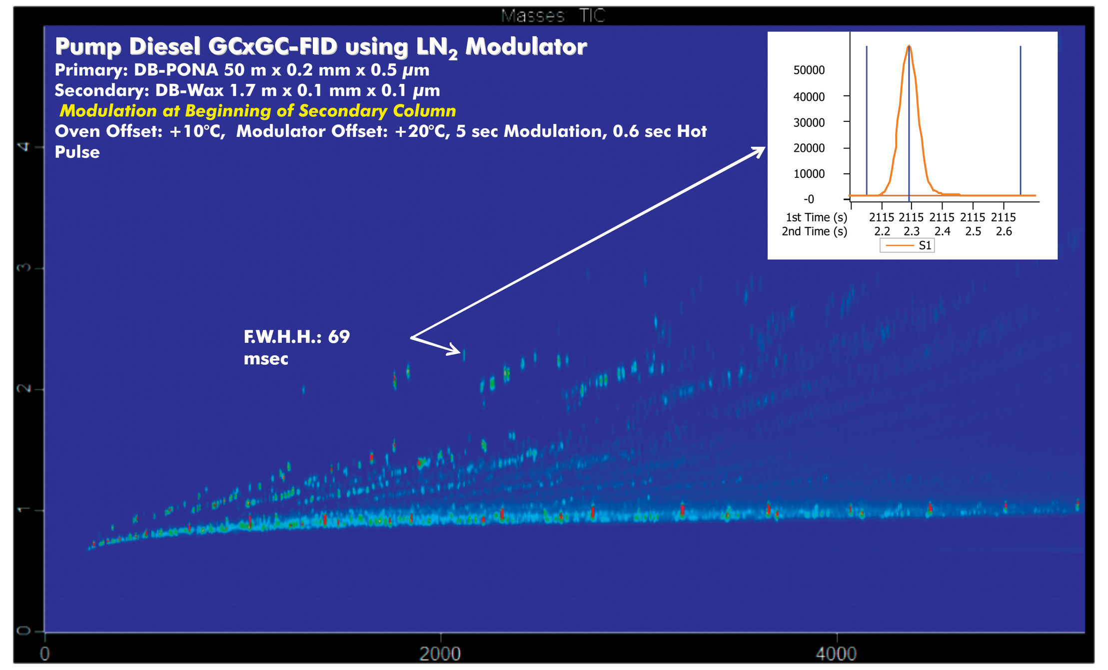

Figure 4. A contour plot of a sample of pump diesel run on a GCxGC system utilizing the LN_2 modulator. The column ensemble was set-up so that modulation occurred on the beginning of the secondary column. The Full Width at Half-Height (F.W.H.H.) for biphenyl is indicated. The modulated 1D trace of the base peak for biphenyl is shown in the upper right.

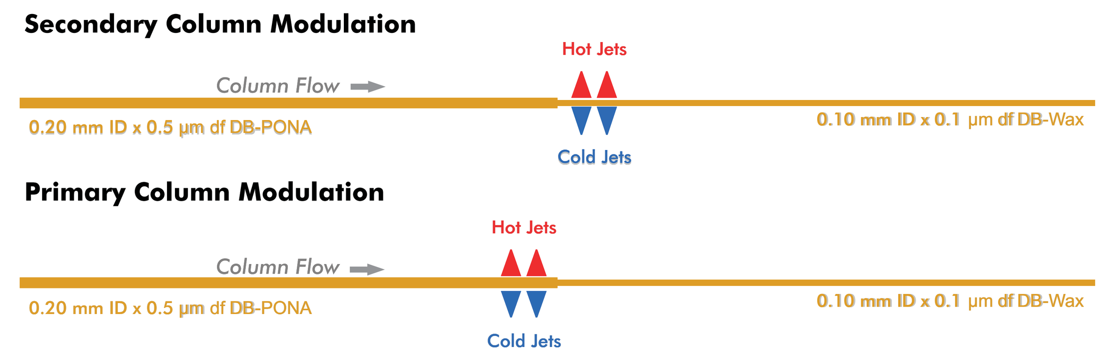

Figure 5. This figure shows the configuration difference between modulation on the secondary column and modulation on the primary column. Modulating on the secondary column is the normal mode of operation.

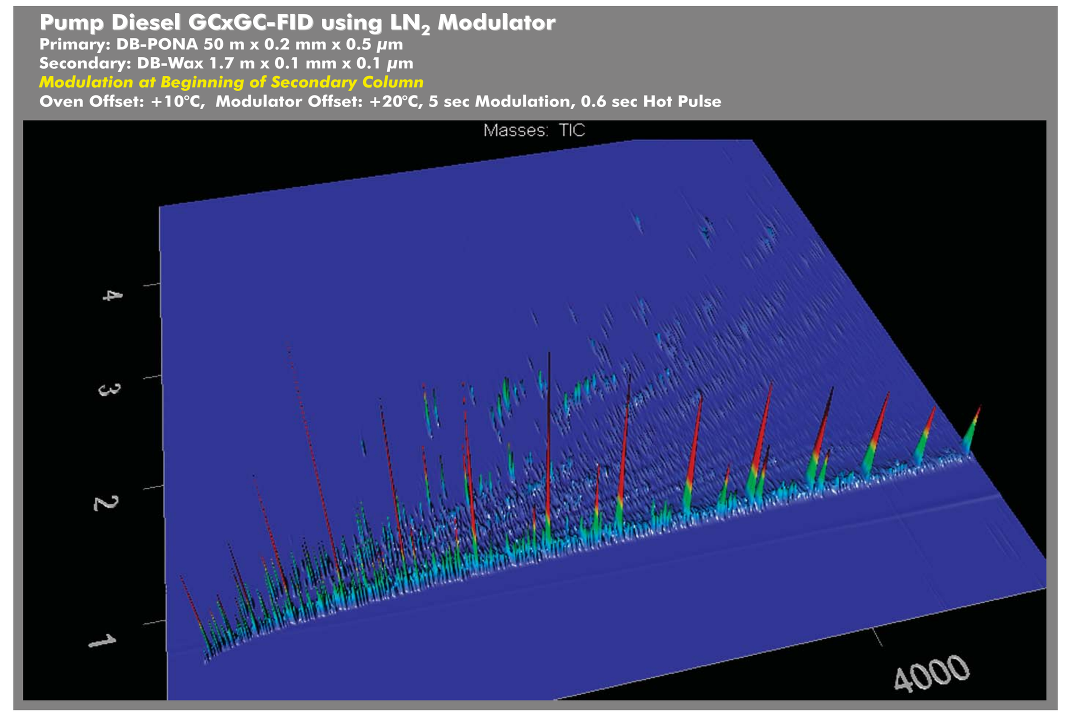

Figure 6. A 3D surface plot of a sample of pump diesel run on a GCxGC system utilizing the LN_2 modulator. The column ensemble was set-up so that modulation occurred on the beginning of the secondary column.

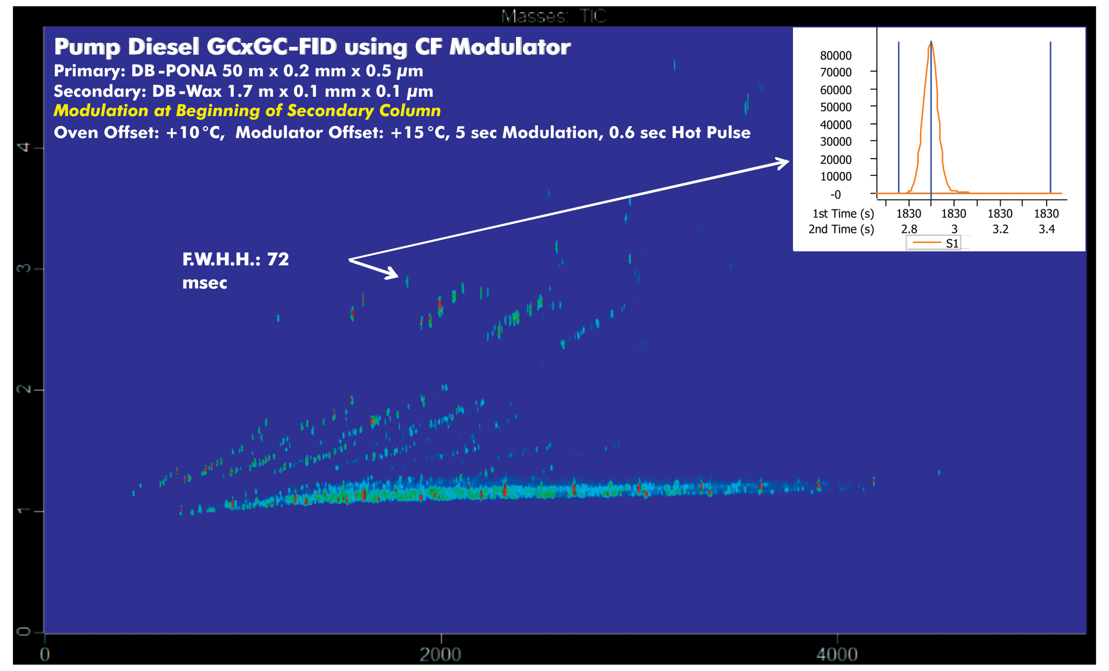

Figure 7. A contour plot of a sample of pump diesel run on a GCxGC system utilizing the CF modulator. The column ensemble was set-up so that modulation occurred on the beginning of the secondary column. The F.W.H.H. for biphenyl is indicated. The modulated 1D trace of the base peak for biphenyl is shown in the upper right.

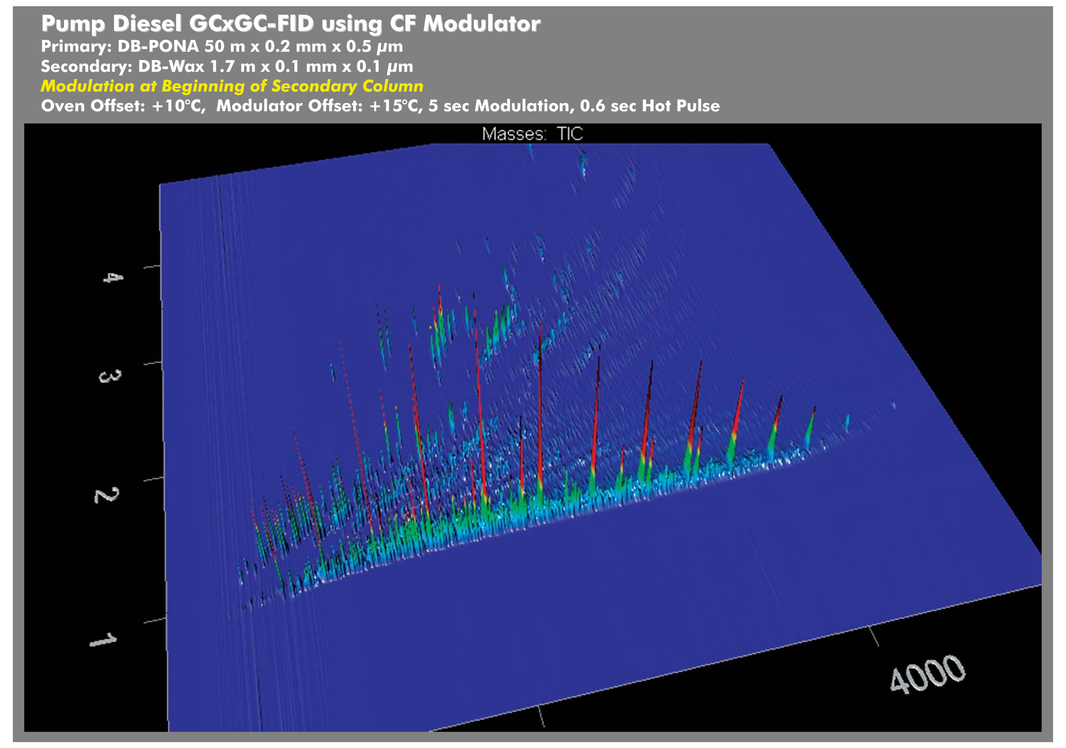

Figure 8. A 3D surface plot of a sample of pump diesel run on a GCxGC system utilizing the CF modulator. The column ensemble was set-up so that modulation occurred on the beginning of the secondary column.

The LN_2 modulator's useable range is C_4 to C_{40}. The CF modulator's useable range is listed as C_8 to C_{40}. The higher minimum temperature of the CF system, as opposed to the LN_2 system, provides less effective focusing. In the following chromatograms, the columns were repositioned so that the end of the primary column would be in the modulator. The idea is that the lower linear velocity of the carrier gas would allow analytes a longer residence time in the cold jet's focusing zone, thereby allowing for the trapping of compounds with volatilities < n-C_8. The trade-off for enhanced trapping capability would be a decrease in injection performance, due to the lower carrier gas linear velocity causing the desorbed peak to take longer to be cleared from the modulator.

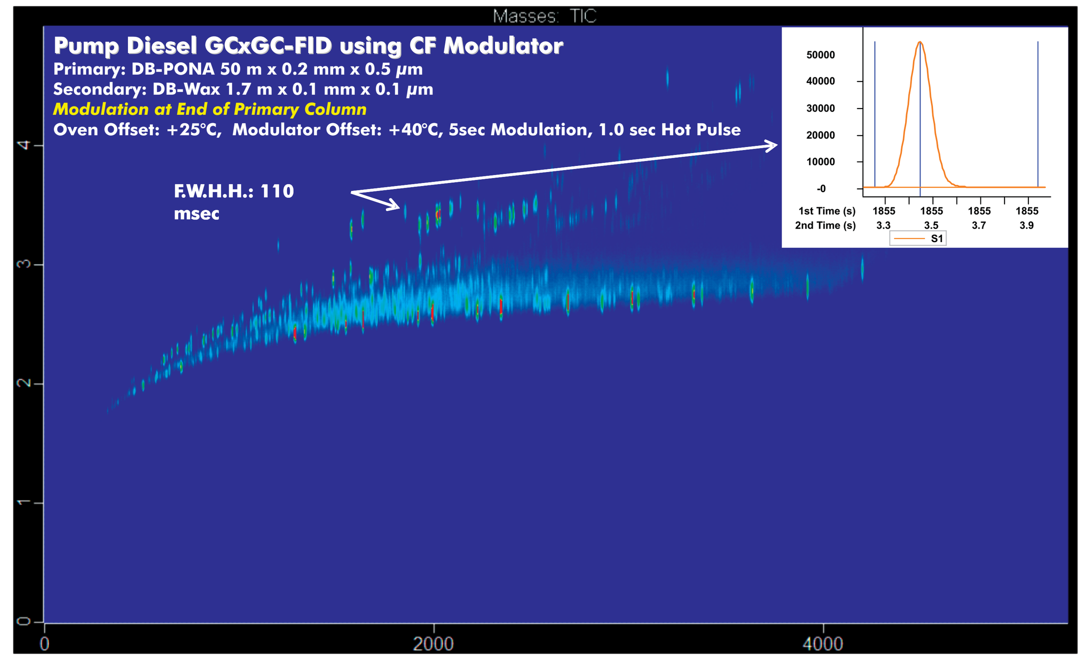

Figure 8. A contour plot of a sample of pump diesel run on a GCxGC system utilizing the CF modulator. The column ensemble was set-up so that modulation occurred on the end of the primary column. The FF.W.H.H. for biphenyl is indicated. The modulated 1D trace of the base peak for biphenyl is shown in the upper right.

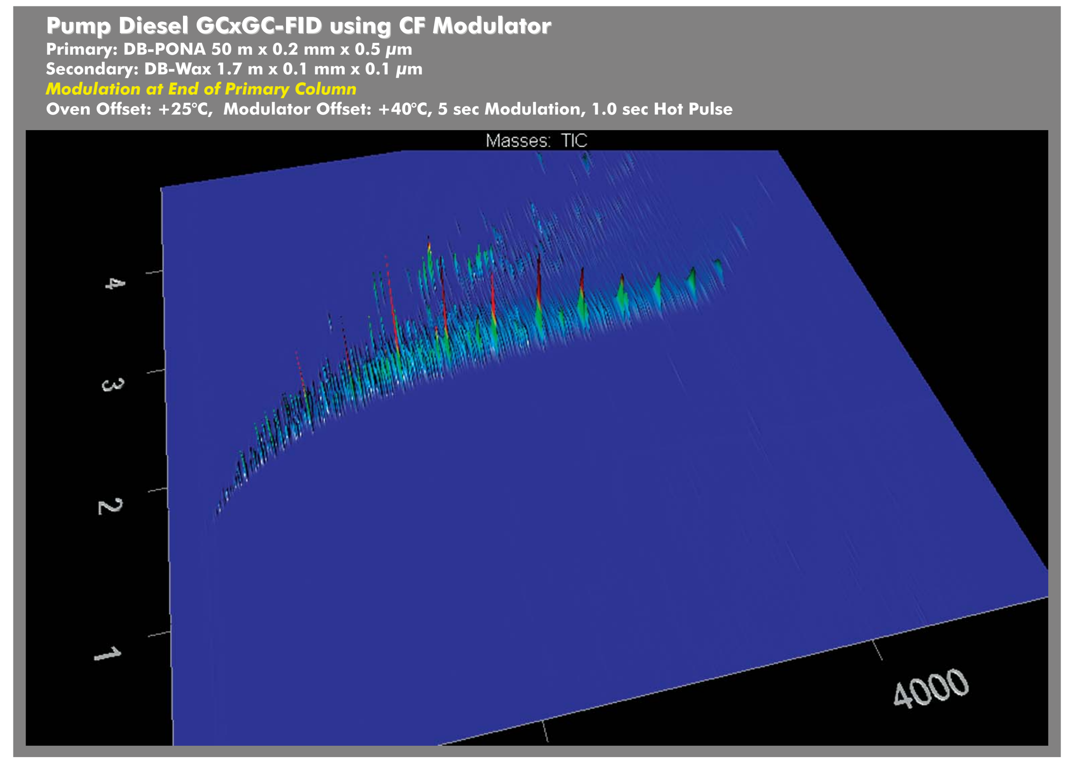

Figure 10. A 3D surface plot of a sample of pump diesel run on a GCxGC system utilizing the CF modulator. The column ensemble was set-up so that modulation occurred on the beginning of the secondary column.

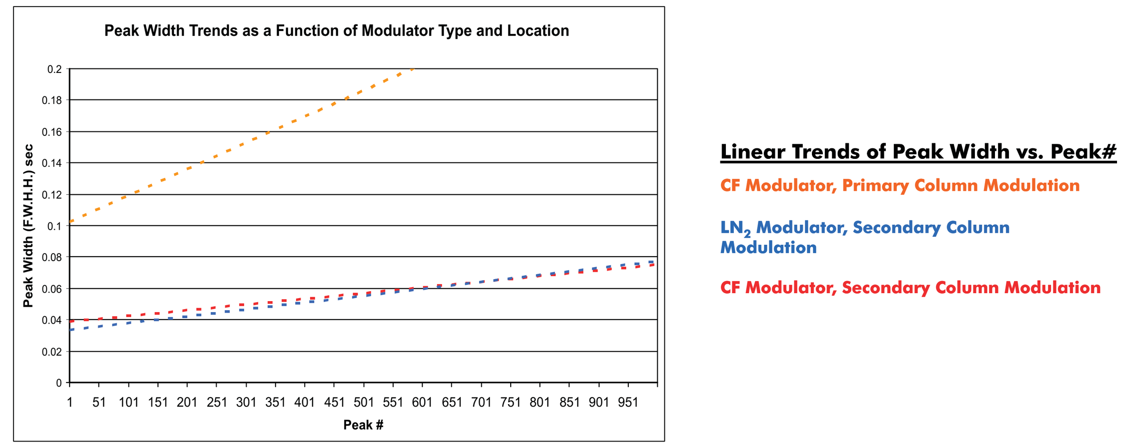

Figure 11. A graph showing the linear trends of F.W.H.H. as a function of Modulator Type and Modulator Location. Peak widths were comparable for both modulator types when modulated on the beginning of the secondary column. Peak widths for the CF Modulator when modulating on the end of the primary column showed a significant increase in peak width as those modulated on the beginning of the secondary column.

CONCLUSIONS

The Consumable-Free Modulator for GCxGC is an effective option for GCxGC applications in its workable volatility range. This modulator still requires the use of dry gases for the hot and cold jets, but has eliminated the need for the use of liquid cryogens. The CF Modulator also utilizes a new "piggy-back" electronics control box. This makes available the auxiliary GC controls that had been previously used to control GCxGC functions. Another added advantage brought about through the use of this control box is that there is now available the ability to vary hot pulse timing during the course of an analysis. This allows for the use of short hot pulses, to increase trapping efficiency, for more volatile compounds earlier in the analysis and then shifting to longer hot pulses, to increase desorption efficiency, later in the analysis. For applications where the compounds of interest are in the C_8 > C_{40} range, the Consumable-Free Modulator has demonstrated performance similar to that of a LN_2 modulator equipped system and in the case of less volatile compounds may show improved peak width over those of the LN_2 modulator equipped system. This is due to the higher trapping temperatures in the CF Modulator. These higher temperatures enable the trapped effluent plug to be re-volatilized more efficiently and results in narrower peaks on the secondary column.