Stop-Flow Modulated GCxGC

Product Note

Cost-effective comprehensive GCxGC

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Abstract

A simple, cost-effective technique for flow modulated comprehensive two-dimensional gas chromatography (GCxGC) has been applied on an Agilent 7890. The configuration employs stop-flow modulation where effluent from the first dimension is accumulated in a capillary and re-injected onto the second dimension for orthogonal separation during a selected modulation period. This technique increases the peak capacity from approximately 250 peaks when using single dimension chromatography to over 750 with a signal to noise of 7. Second dimension (^{2}D) peak widths range from 64 to 201 ms, with a median peak width at half maximum of 95 ms. This system allows for dramatically increased separation capability of a GC system.

Introduction

Conventional single-dimensional gas chromatography can be a very powerful technique, but there are separation limitations that often cannot be overcome by changing the phase ratio or length of the column. Commercially available columns have a single stationary phase available for separation, which can be problematic for complex samples that contain mixtures of compounds with varying moieties. Comprehensive two-dimensional gas chromatography introduces a second column with an orthogonal chemistry to perform additional separation. A modulator heart-cuts the effluent of the first dimension and subsequently re-injects that portion onto the second column. The resulting data can be analyzed as a 2D heat map showing separation in two dimensions.

Blended biodiesel is an inherently complex mixture of fatty acid methyl esters (FAMEs), aliphatic hydrocarbons, and aromatic hydrocarbons. Conventional columns cannot separate the aromatic groups from the unsaturated hydrocarbons while also separating all the hydrocarbons by boiling point (Figure 1). It is important to be able to characterize blended biodiesel to assess the effectiveness of manufacturing techniques and the quality of the fuel. When using GCxGC with a non-polar/polar column combination this separation can be realized, but the technique can be cost prohibitive for many laboratories. Here, we have assembled a GCxGC system with differential flow modulation at a fraction of the cost of commercially available systems.

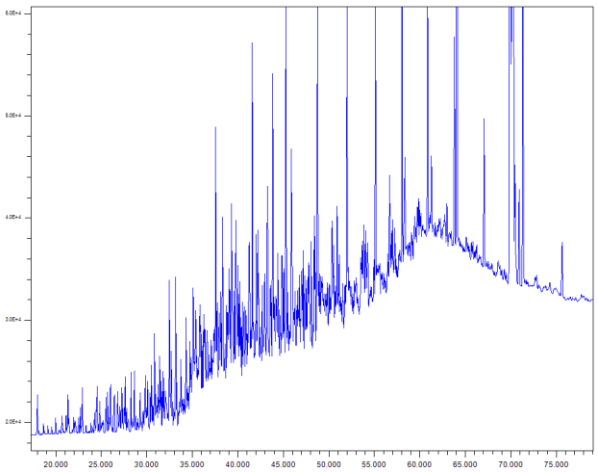

Figure 1: 1D Projection of Blended Biodiesel

This differential flow modulation technique, termed quasi-stop-flow modulation, was developed by Dr. Jim Luong and colleagues at Dow Canada (1). The two

columns are connected via a tee to an accumulation capillary which is in turn connected to a three-way solenoid valve. During a determined sample accumulation time the valve is vented to the atmosphere so the primary dimension column will flow to fill the accumulation capillary. After the accumulation capillary is filled during the sample accumulation time, the valve will switch to apply pressure to the accumulation capillary in fluidic communication with the second dimension column, effectively injecting onto the second dimension column while stopping flow in the first (Figure 2). This valve position will then be held for the determined modulation time before the process repeats. The total cycle time is the sample accumulation time + modulation time.

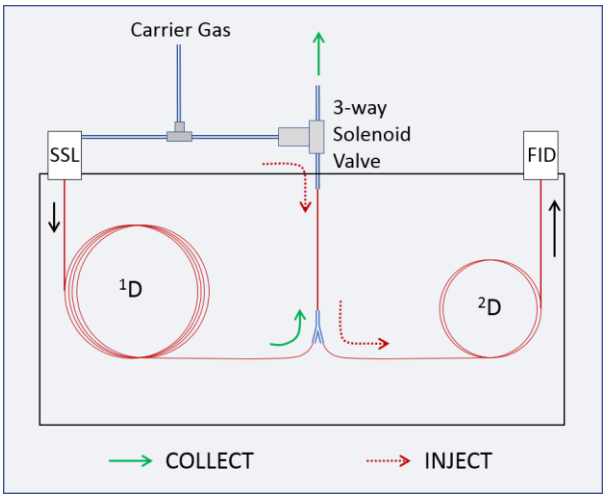

Figure 2: Quasi-Stop-Flow Modulation (1)

Experimental

A locally sourced sample of blended biodiesel was diluted into dichloromethane to a concentration of roughly 5,000 ppm biodiesel blend and analyzed using stop-flow modulated GCxGC-FID. An Agilent 7890 was used and the two columns were connected via a Restek deactivated press-fit tee (Restek, 20485). The resulting data was processed and analyzed using J&X Canvas software, version W1.8.0. The primary dimension flow was controlled in constant flow mode by the GC inlet, and the second dimension column flow was controlled in constant flow mode with an auxiliary EPC. The accumulation capillary was connected to the valve by adapting to 1/16" stainless steel tubing using a VICI Valco union (VICI Valco, ZU1C).

The valve on the modulator and its timing are controlled by a programmable logic controller and an Agilent event cable to enable modulation. The system can easily be run in 1D by keeping the valve on the GC method "on" and modifying the auxiliary EPC pressure controlling the modulator to match the flow rate of the first column. Because of this, the system can be run and modified simply by controlling the GC method remotely for unattended operation.

GC conditions

Back inlet	Multimode Inlet, split mode (Helium)
Injection volume	0.5 µL
Split ratio	200:1
Inlet temperature	250 °C
Inlet pressure	32.9 psi
Septum purge flow	0.5 sccm
Oven	40 °C (10 min), 4 °C/min to 240 °C (60 min)
^{1}D column	BP1 (60m x 0.25mm x 0.25µm)
^{2}D column	DB-WAX (3m x 0.25mm x 0.25 µL)

Modulator conditions

Modulation time	2 s
Injection time	0.1 s
Accumulation capillary	50 cm x 0.25 mm ID deactivated fused silica
Aux EPC pressure	21.6 psi, constant flow

FID conditions

Temperature	315 °C
H_2	35 sccm
Air	350 sccm
Makeup	20 sccm (He)
Sampling rate	200 Hz

Results and Discussion

The biodiesel blend sample 2D heatmap can be seen in Figure 3. Clear separation is observed between aliphatic hydrocarbons, aromatic hydrocarbons, FAMEs, and polycyclic aromatic hydrocarbons (PAHs). Measured ^{2}D peak widths range from 64 ms to 201 ms, allowing for distinct resolution of peaks on the second dimension during the 2 second modulation period. The multiplicative effect on peak capacity of GCxGC can be observed when comparing the number of peaks in the 1D projection (Figure 1) to Figure 3. There is a more than three-fold increase in peak capacity when comparing conventional gas chromatography to GCxGC.

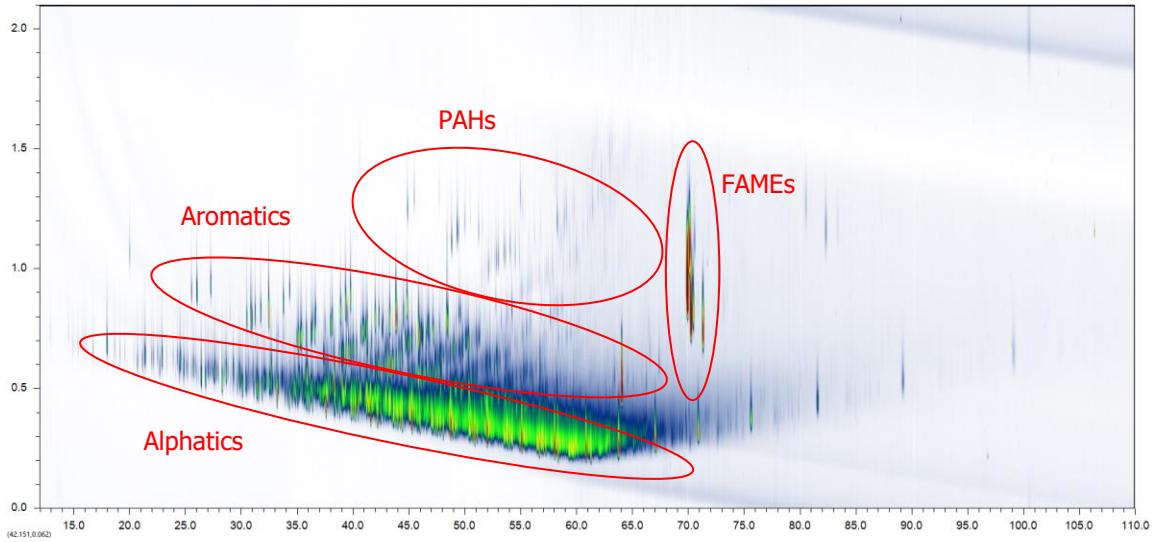

Figure 3 Heatmap projection of blended biodiesel (S/N = 7)

Separation in the second dimension can be seen in more detail in Figure 4 below. In multiple instances, more than one peak is eluting at the same 1D retention time, suggesting these peaks could not be fully resolved on a conventional 1D system.

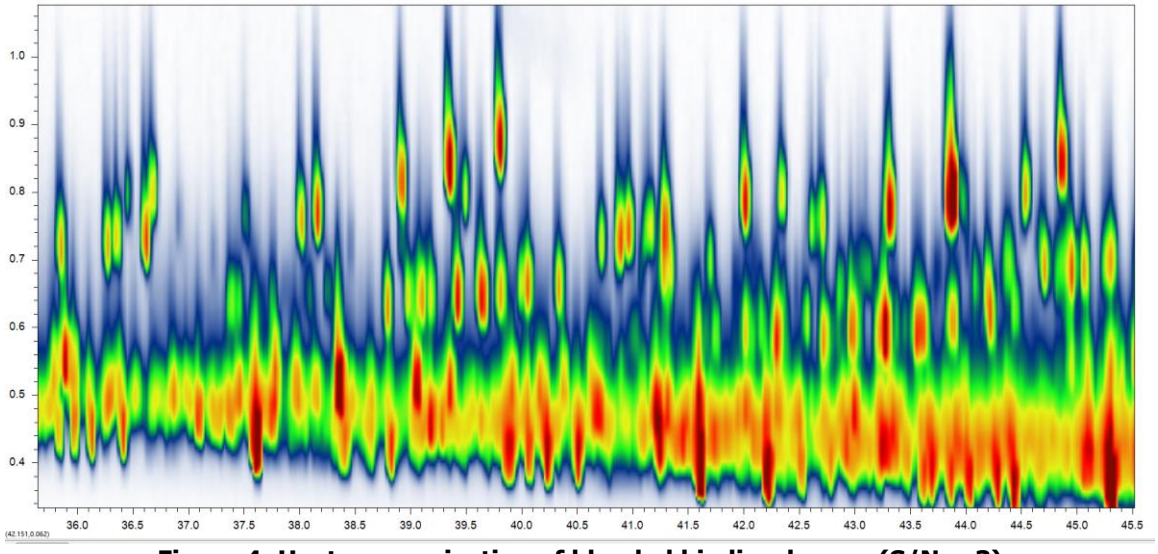

Figure 4: Heatmap projection of blended biodiesel zoom (S/N = 3)

Conclusions

Comprehensive multidimensional gas chromatography is a very powerful tool which enables analysts to multiply a GC system's peak capacity for resolution of hundreds of peaks in complex samples, but it is often cost prohibitive and too complex for widespread use. Here, we have implemented a comprehensive GCxGC system using stop-flow modulation effectively by achieving sufficiently narrow peaks for ^{2}D separation and complete analyte transfer through the modulator. This setup shows successful multidimensional separation of a biodiesel blend sample, with an effective peak capacity more than three times higher than the one-dimensional system.

References

[1]Quasi-Stop-Flow Modulation Strategy for Comprehensive Two-Dimensional Gas Chromatography
Xiaosheng Guan, Jim Luong, Ziwei Yu, and Hai Jiang
Analytical Chemistry 2020 *92* (9), 6251-6256
DOI: 10.1021/acs.analchem.0c00814

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For more information or to purchase an ARC Flow Modulated GC x GC system, please contact us at 612-787-2721 or contact@activatedresearch.com.

Please visit their website for details and additional technical literature.

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