Comprehensive Flow Modulated Two-Dimensional Gas Chromatography System

Application Brief

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Two-dimensional GC (GC x GC), a relatively new gas chromatographic technique, is being recognized for its powerful separation capabilities for the analysis of complex mixtures. The methodology involves the use of two capillary columns of usually very different polarities installed in series. Between the two columns a device known simply as a flow modulator is installed and interfaced to an auxillary programmable control module (PCM) on an Agilent 7890A gas chromatograph through a three-way solenoid valve. In the flow modulator, analyte bands from the first column are collected in a fixed volume channel and successively injected very quickly into the short second column in very narrow bands.[1] Any separation that occurs on the first column is preserved during transfer to the second column. In summary, GC x GC can greatly increase peak resolution and peak capacity.

The unique flow modulator used in this system is based on Agilent's Capillary Flow Technology hardware and does not require the use of cryogenics for focusing. The modulator consists of a planar structure where flow splitters and collector channel are all incorporated internally to the device. All external connections are made through Agilent CPM fittings (ultimate union technology) incorporated into the plate for zero unswept volumes and leak proof seals. A three-way solenoid valve is installed on top of the GC oven and is interfaced to a PCM module. Experimental conditions used are shown below.

Experimental

GC:	Agilent 7890A, FID at 200 Hz data collection rate, split/splitless inlet
Carrier:	Hydrogen
Column 1:	30 m x 0.25 mm x 0.25 µm HP-5ms, 19091S-433
Column 1 Pressure:	21.5 psig at 50 °C, constant flow mode
Column 2:	5 m x 0.25 mm x 0.15 µm HP-INNOWax
Column 2 Flow:	20 mL/min, constant flow mode
Oven Program:	50 °C (1.0 min) to 260 °C (4 min) @ 8 °C/min.
Modulator Period:	1.4 seconds collect, 0.12 seconds flush typical

GC x GC analysis software: GC Image[2]

An illustration of the modulator is given in Figure 1. The precisely timed and synchronized periodic switching between collect and flush states directs sample pulses continuously to the second column for additional separation during the

Highlights

- Flow modulation offers a viable alternative to thermal modulation without the burdens imposed by cryo requirements for comprehensive GC x GC.
- Modulation, timing (collect and inject), and synchronization are all integrated into the 7890A GC system for easy setup and operation.
- Agilent's fifth-generation electronic pneumatic control with setting to three decimal points combined with Capillary Flow Technology hardware forms the basis for an easy-to-use GC x GC system.

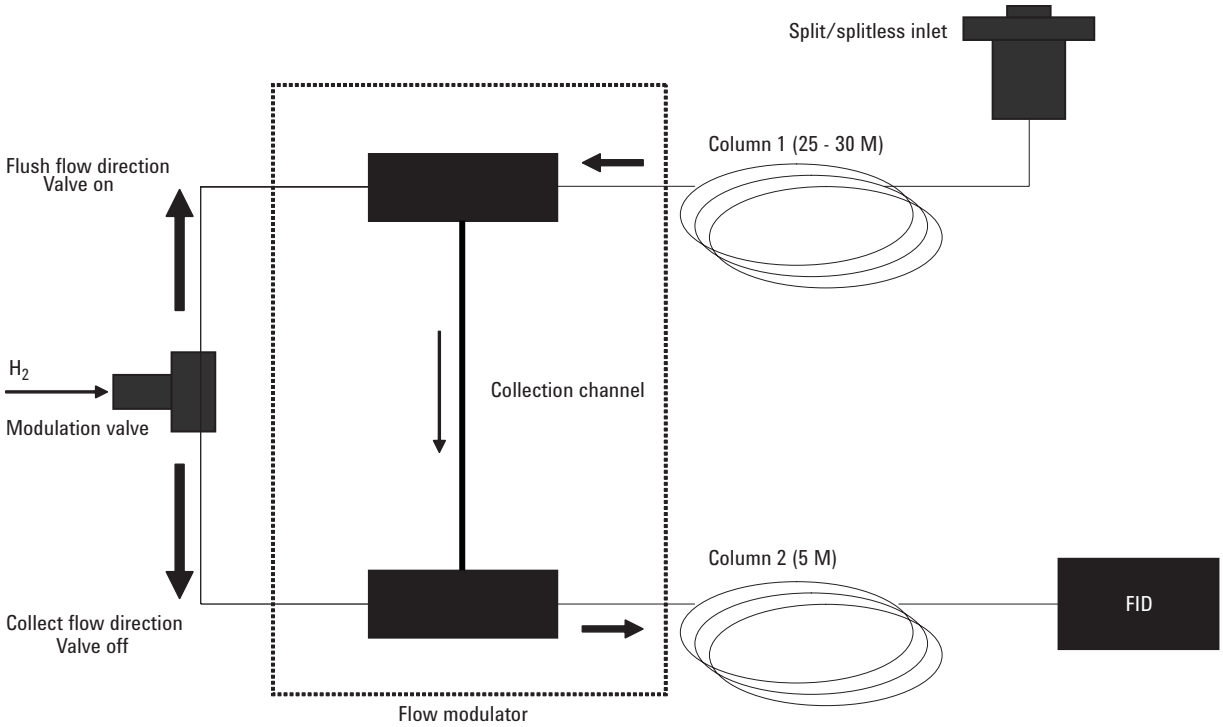

Figure 1. Flow modulator design – differential flow system.

length of the chromatographic run.

Discussion

Figures 2a and 2b show unmodulated and modulated peaks, respectively, of a pure analyte. In this example, n-butylbenzene is shown with approximately three modulations across the first-column peak. The areas of the modulated peaks should ideally equal the area of the un-modulated peak. In other words, no material should be lost in the transfer to the second column. Area agreement was within 3% for this test. Peak widths at half height for modulated butylbenzene are approximately 100 ms. Very narrow peaks as required for the technique are

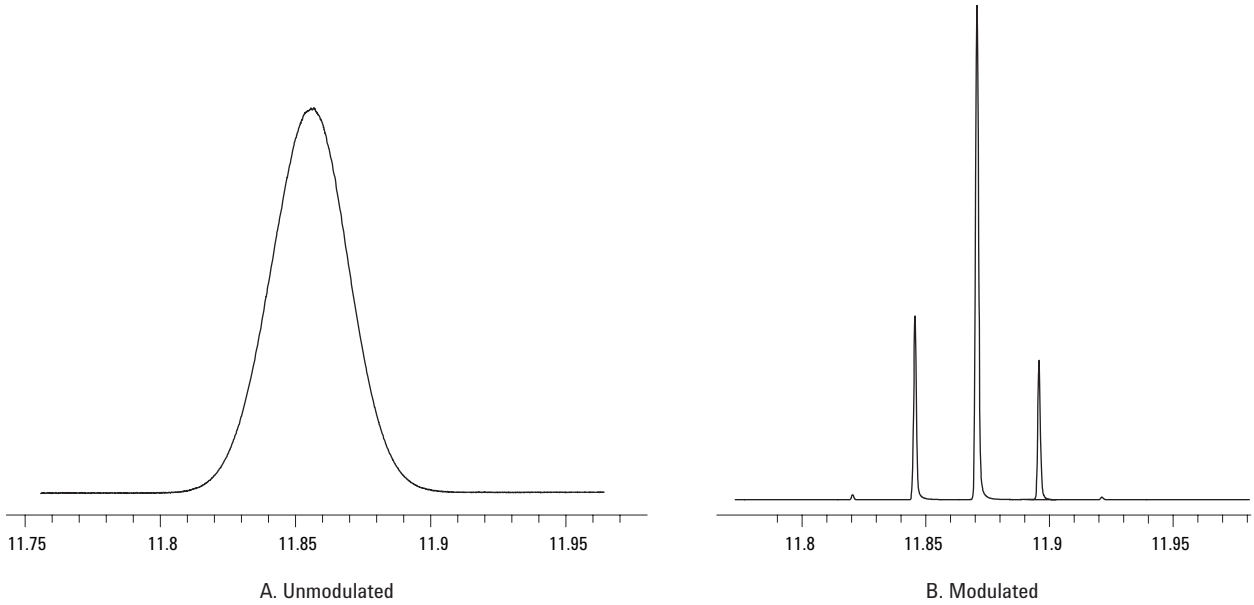

Figure 2. Modulated and unmodulated n-butylbenzene (not to same scale).

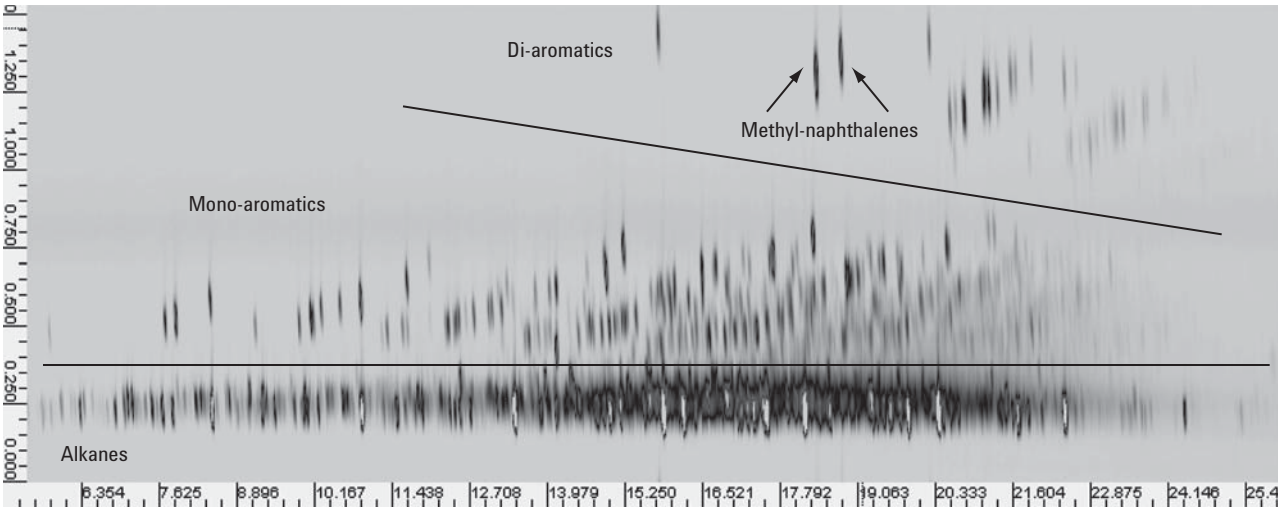

Figure 3. A 2D image of No. 2 kerosene.

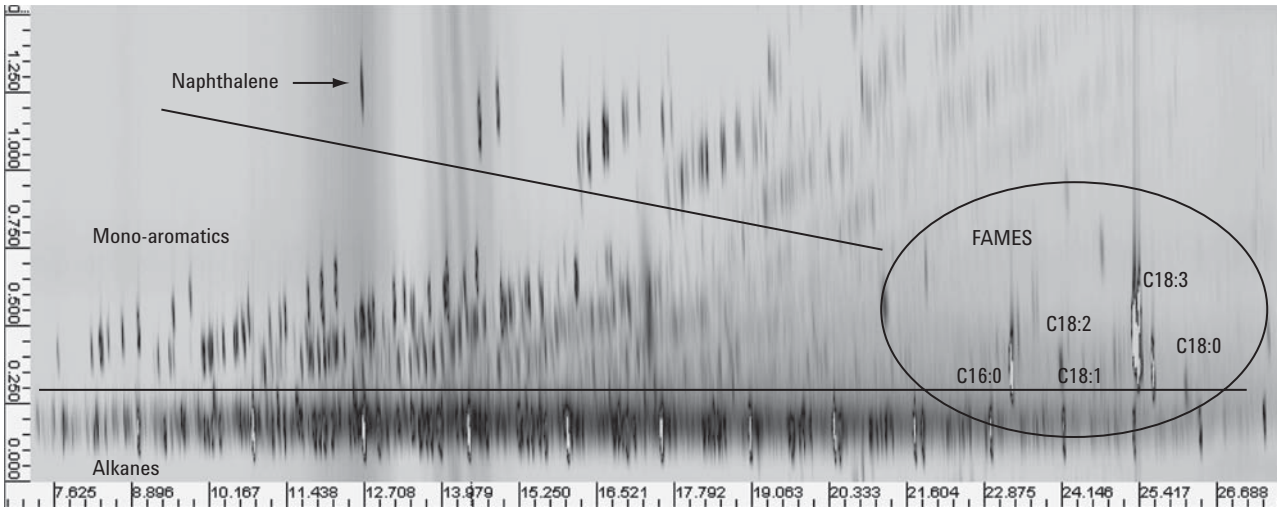

Figure 4. A B20 soy-based biodiesel (20% methyl ester, 80% diesel).

seen that approach the peak widths obtained by thermal modulation systems. Flow modulation has the distinct advantage of not requiring cryo fluid for focusing.

Use of a nonpolar column followed by a polar column produces hydrocarbon-type retention in the following order: alkanes, cyclic alkanes, olefins, single-ring aromatics, and multi-ring aromatics. An example of a 2D image of No. 2 kerosene is shown in Figure 3. Chemical classes are clearly discernable, with good resolution seen for the aromatics. Another example, B20 soy-based biodiesel (20% methyl ester, 80% diesel) is shown in Figure 4. Here the C16 and C18 fatty acid methyl esters are indicated. Data processing for all samples was performed using GC Image[2].

References

1. Pedro A. Bueno Jr., John V. Seeley, “Flow-switching device for comprehensive two-dimensional gas chromatography,” *Journal of Chromatography A*, 1027 (2004) 3-10.

2. Zoex Corporation, 5010 Sea Oak Court, Pasadena, TX 77505, and GC Image, LLC, PO Box 57403, Lincoln, NE 68505.

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