Comprehensive GC System Based on Flow Modulation for the 7890A GC

Application Brief

Introduction

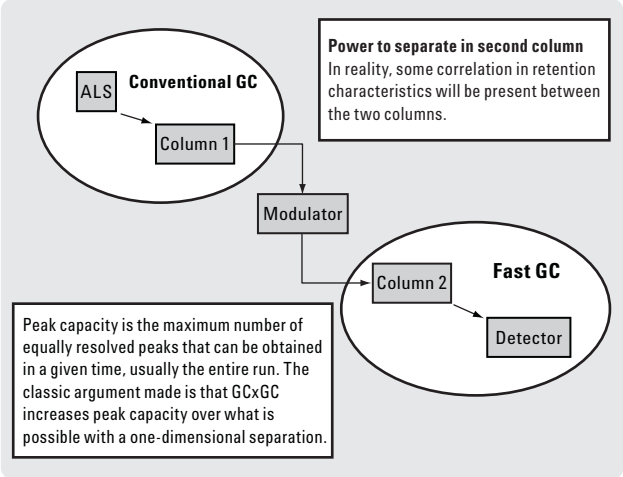
A hardware solution is available on the 7890A for the practice of comprehensive GC. The system uses a capillary flow modulator controlled by the 7890A GC. The system is offered with factory checkout using an FID detector. Other detectors, preferably those operating at 50 Hz or greater, can be used.

Comprehensive two-dimensional (2D) GC, or GCxGC, is a powerful technique that can be used to separate very complex mixtures, such as those found in the hydrocarbon processing, environmental, and food/fragrance industries.

The method uses two columns, typically of very different polarities, installed in series with a modulator in between. The second column is much shorter than the first column to effect a fast separation. The entire assembly is located inside the GC oven.

The modulator performs three functions:

1. It collects effluent from the first column for a fraction of the time equal to peak width. For example, if a peak from column one is six seconds wide, the modulator will accumulate material every two to three seconds, thereby dividing the peak from the first column into two or three "cuts."
2. It focuses the material collected from each cut into a very narrow band through flow compression.
3. It introduces the bands sequentially onto the second column, resulting in additional separation for each band injected onto the second column.



Comprehensive 2D GC uses a primary column (conventional separation), a flow modulator, a second column (very fast separation), and a fast detector.

This technique provides a second dimension of information that can increase the peak resolution and capacity.

A number of different modulator designs have been described in the literature, most relying on thermal cycling to focus the bands from the first column and release them into the second column. Some disadvantages to this approach are:

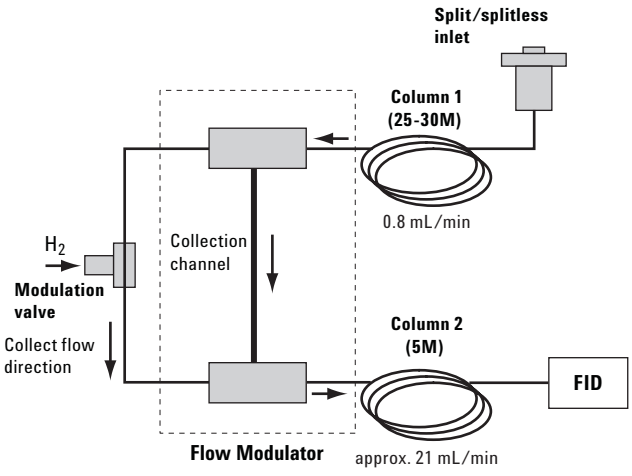
- Large usage of expensive cryogenic gases leading to a high cost of analysis
- Complexity of the hardware
- Longer analysis times

Agilent's proprietary Capillary Flow Technology and fourth-generation Electronic Pneumatics Control (EPC) enable the use of a differential flow modulator to conduct comprehensive 2D-GC without the use of cryogenic gases or complex hardware.

The key to operation is the flow differential (typically 20 to 1) between the second and first columns, respectively. This compresses and focuses the analytes present in any given modulation "inject" pulse into the second column. Precise timing of the modulator is made possible by installing a driver board in the Aux det 2 detector slot of the 7890A mainframe.

The Capillary Flow Technology modulator uses a deactivated, stainless steel structure with all flow splitters and the collector channel incorporated internally in the device. It has low thermal mass so it can track the oven temperature very closely, and its GC oven location allows precise temperature control without lag during programmed runs. All external connections are made using Agilent's Ultimate Union technology for leak-free operation and extremely small, well-swept volumes. A micro three-way solenoid valve, installed on the side of the gas chromatograph, connects to a pneumatics control module (PCM) to accurately and precisely control the flows through the modulator.

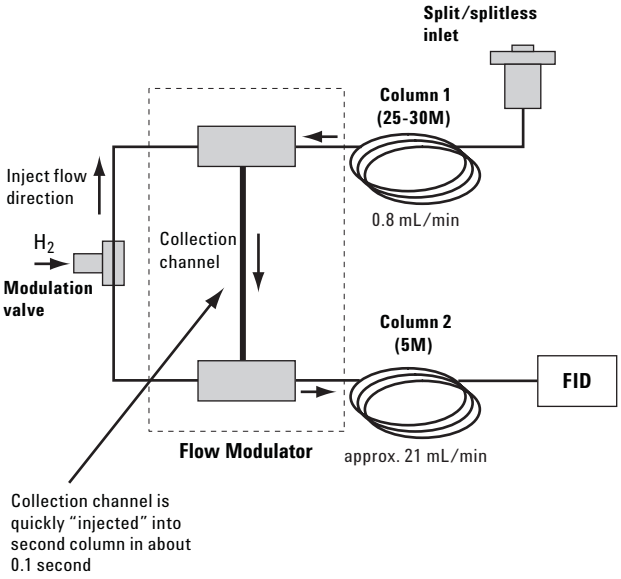
The figures below illustrate the modulator. A three-way solenoid valve receives a controlled supply of hydrogen gas from a PCM. The periodic switching of this three-way valve drives the modulator. The precisely timed and synchronized switching between the collect and inject states directs discrete sample pulses continuously to the second column for additional fast separation throughout the chromatographic run. Both columns are run in constant flow mode. For optimal performance, injection size and split ratio should be carefully adjusted to avoid overloading, which can lead to excessive peak tailing.



Flow rates and flow directions during the load or collect portion of the modulation cycle

Load or collect state (above): At the beginning of this state, the collection channel is filled with hydrogen gas from a previous injection cycle flush.

The primary column effluent enters the modulator's top tee connection and flows into the collection channel. The analytes from this column enter one end of the collection channel. Hydrogen flow from the PCM/three-way micro valve exits the modulator at the bottom tee and is sent to the second column.



Flow rates and flow directions during the transfer or inject portion of the modulation cycle

Inject or flush state (above): Hydrogen gas flow from the three-way solenoid valve is directed to the top tee. A high flow of typically 20 mL/min for about 0.1 second rapidly flushes the collection channel, transferring material in a very narrow band onto the second column where any analytes collected in the channel undergo rapid separation.

What is required:

- Agilent 7890A GC with firmware version A.04.06 or higher
- FID with 200 Hz data collection rate or other fast detector
- Split/splitless inlet
- Capillary Flow Technology modulator option or accessory
- Capillary Flow Technology modulator checkout kit
- Pneumatics control module (PCM)
- Agilent GC ChemStation B.03.02 or other data collection and analysis system that can control the flow modulator cycle
- 30-m × 0.25-mm × 0.25-µm DB-5ms column (included with option or accessory)
- 5-m × 0.25-mm × 0.15-µm INNOWax column (included with option or accessory)
- 2D data analysis software, GC Image recommended (not provided by Agilent)
- Internal column nuts and SilTite ferrules

Ordering Information

Description	Part number
7890A GC with Capillary Flow Technology Modulator (requires checkout kit)	G3440A Option 887 or accessory G3486A
7890A GC with 200 Hz FID	G3440A Option 211 or accessory G3462A
7890A GC with split/splitless inlet	G3440A Option 112 or accessory G3452A
Capillary Flow Technology modulator checkout kit	G3487A
PCM for 7890A GC	G3440A Option 309 or accessory G3471A
SilTite metal ferrules, 1/16-in × 0.4-mm id, 10/pk, includes 2 column nuts	5184-3569
Agilent 32-bit ChemStation for 1 GC	G2070BA
Agilent 32-bit ChemStation Bundle for 1 GC includes: – G2070BA 32-bit ChemStation software – Computer with monitor and Windows operating system – Printer	G1875BA
2D GC software Recommend GC Image software, which can be purchased from Zoex Corporation	www.zoex.com

Application Examples

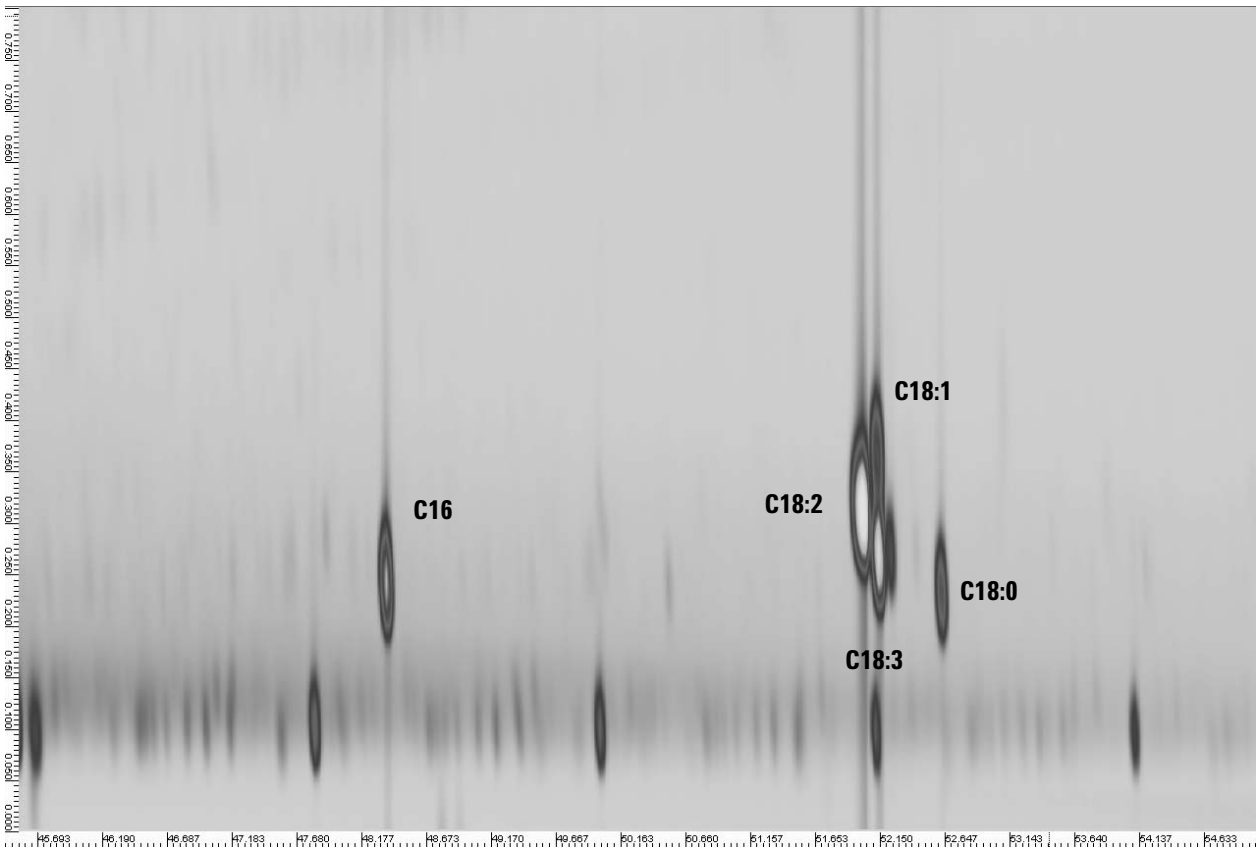
Several applications are shown. Note that primary column lengths have been chosen to give optimal results. While the 30M column that is shipped with the system is an excellent choice for a wide range of applications, other lengths can be used to optimize a given separation. Various columns have been used in these examples to illustrate some of the possibilities. The GC Image software package was used for processing the ChemStation data.

1. B20 biodiesel based on soy FAMES. Section of the 2D image showing the C16 and C18 FAMES is shown.

   Column 1: 60 m × 0.25 mm × 0.10 µm DB-5ms

   Column 2: 5 m × 0.25 mm × 0.15 µm INNOWax

   Modulation: 1.40 s load, 0.10 s inject

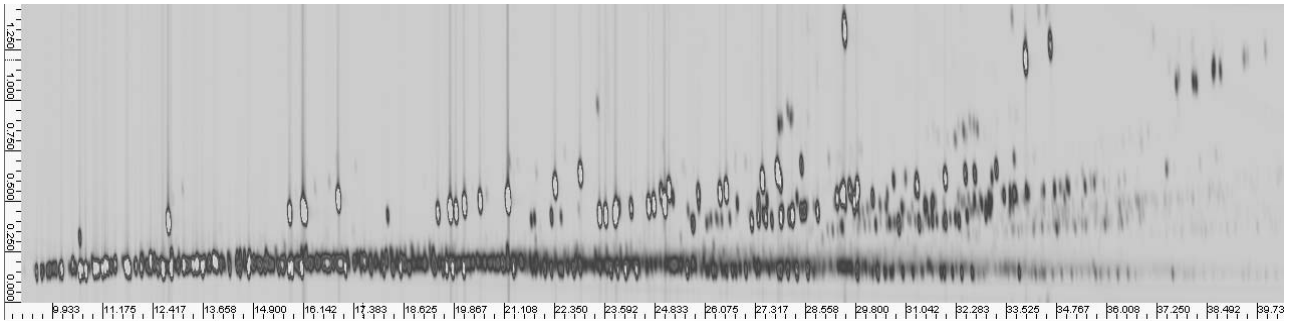


2. Complete 2D image of a sample of heavy gasoline. Each series of substituted 1-ring aromatics is well separated, making hydrocarbon class grouping possible.

   Column 1: 60 m × 0.25 mm × 0.10 µm DB-5ms

   Column 2: 5 m × 0.25 mm × 0.15 µm INNOWax

   Modulation: 1.40 s load, 0.10 s inject

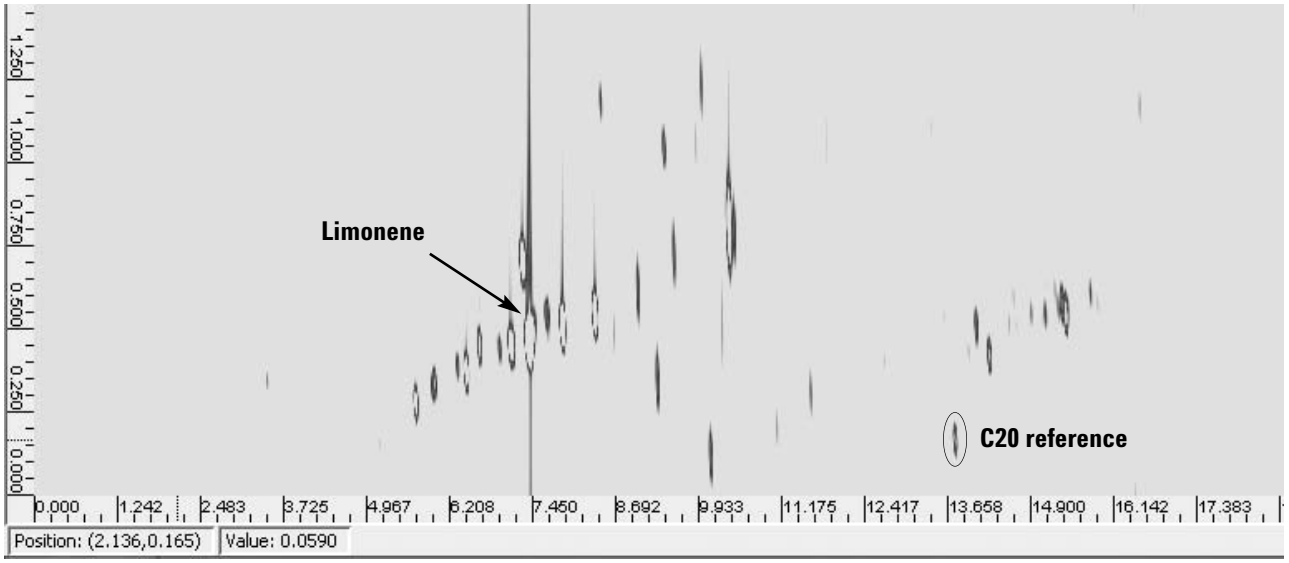


3. Lime oil 2D image.

   Column 1: 15 m × 0.25 m × 0.25 µm DB-5ms

   Column 2: 5 m × 0.25 mm × 0.15 µm DB-17HT

   Modulation: 1.40 s load, 0.10 s inject



Thermal vs. Flow Modulation

Since competitors offer only systems based on thermal modulation, the following table summarizes the key points about the respective approaches of thermal vs. flow modulation.

Thermal modulation	Differential Flow modulation
Cryo-focusing provides potentially narrower peaks in second dimension	Peak widths comparable to thermal. Usually no more than 20% wider. Many users want to sum regions of peaks where peak width is not as critical
Lower flows – Can be used with high-vacuum detectors (TOF)	MSD can be used with a splitter over limited scan range
Large consumption of cryogen	No cryogen required
Complex hardware design, set-up, and maintenance	Simple, reliable Capillary Flow Technology based hardware; small thermal foot print
Long chromatographic runs required for best performance	Run times comparable to a 1D separation
System price (estimate) $60 to $70K	Agilent system approximately $60K (list)

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